SZKOŁA DOKTORSKA
BioMedChem
Uniwersytetu Łódzkiego
i Instytutów Polskiej
Akademii Nauk w Łodzi

Karolina Cichoń

Praca doktorska:

Cykliczne acetale w syntezie (ko)polimerów o zwiększonej degradacji

Doctoral thesis:

Cyclic acetals in the synthesis of (co)polymers with enhanced degradability

- Promotor/Supervisor
  dr hab. Małgorzata Baśko
  Dział Funkcjonalnych Polimerów i Materiałów Polimerowych
  Centrum Badań Molekularnych i Makromolekularnych
  Polskiej Akademii Nauk
- Promotor pomocniczy/Assistant Supervisor
  dr Bartłomiej Kost
  Dział Funkcjonalnych Polimerów i Materiałów Polimerowych
  Centrum Badań Molekularnych i Makromolekularnych
  Polskiej Akademii Nauk

Łódź, 2026

Serdecznie dziękuję mojej Promotor, ***dr hab. Małgorzacie Baśko za*** *wyrozumiałość, opiekę naukową i nieocenione wsparcie merytoryczne. Dziękuję za poświęcony czas, cenne wskazówki oraz zaufanie, które pozwoliło mi rozwijać się i stawać coraz lepszym naukowcem.*

Dziękuję mojemu Promotorowi pomocniczemu, ***dr. Bartłomiejowi Kostowi****, za wsparcie merytoryczne i pomoc w pracy laboratoryjnej, cierpliwość, oraz inspirujące rozmowy, które pomogły mi spojrzeć na naukę z różnych perspektyw.*

Mojej Rodzinie i Przyjaciołom *dziękuję za obecność, wsparcie i wiarę we mnie. Dziękuję za otuchę i za to, że zawsze mogłam na Was liczyć.*



Praca doktorska pt. „Cykliczne acetale w syntezie (ko)polimerów o zwiększonej degradacji” wykonana w Centrum Badań Molekularnych i Makromolekularnych
Polskiej Akademii Nauk w Łodzi

Spis treści:

Przedmowa.....5
Streszczenie w języku polskim.....6
Streszczenie w języku angielskim.....8
Wstęp.....9
1.1. Przemysłowe metody recyklingu polimerów.....10
1.2. Sposoby chemicznego recyklingu polilaktydu.....14
1.3. Poliacetale - synteza łatwo recyklingowalnych polimerów na przykładzie poli(1,3-dioksolanu).....16
2. Opis badań własnych.....19
2.1. Synteza oraz charakterystyka bezładnych (ko)polimerów laktydu i cyklicznych acetali...20
2.2. Synteza i właściwości (ko)polimerów triblokowych typu ABA z zewnętrznymi blokami poliestrowymi A oraz łatwo degradowalnymi wewnętrznymi blokami poliacetalowymi B.....23
2.3. Chemicznie recyklingowalne folie z termoplastycznych (ko)polimerów triblokowych ABA zawierających bloki A z polilaktydu oraz łatwo degradowalne bloki B z polidoksolanu.....26
3. Literatura.....31
4. Spis wszystkich publikacji i osiągnięć naukowych.....36
4.1. Publikacje.....36
4.2. Postery.....36
4.3. Komunikaty ustne.....37
4.4. Zgłoszenia patentowe.....37
4.5. Wyróżnienia i nagrody.....38
4.6. Staże i szkolenia.....38
4.7. Działalność organizacyjna i popularyzatorska.....38
5. Oświadczenia współautorów i załączone publikacje.....39

Przedmowa

Przedstawiona rozprawa doktorska pt. „Cykliczne acetale w syntezie (ko)polimerów o zwiększonej degradacji" składa się z cyklu trzech oryginalnych, monotematycznych publikacji, które zostały opublikowane w czasopismach o zasięgu międzynarodowym, znajdujących się na tzw. Liście Filadelfijskiej. Dodatkowo, dysertacja zawiera jedną pracę przeglądową, będącą rozszerzeniem części literaturowej. Autoreferat, który jest komentarzem do załączonych publikacji, rozpoczynają streszczenia w języku polskim oraz angielskim.

W pierwszej części pracy przedstawiono motywację podjętej tematyki badawczej oraz omówiono zagadnienia dotyczące recyklingu i degradacji polimerów. Druga część zawiera skrócony opis przeprowadzonych badań, które zostały szczegółowo omówione w załączonych publikacjach. Część trzecia pracy obejmuje kopie trzech oryginalnych publikacji stanowiących podstawę rozprawy doktorskiej (wraz z opisami badań dodatkowych z sekcji „Supplementary Information") oraz jedną pracę przeglądową. Załączono również oświadczenia współautorów publikacji dotyczące ich wkładu w realizację poszczególnych etapów badań.

Cykl publikacji opisuje realizację podstawowych badań nad otrzymywaniem nowej klasy alifatycznych kopoliestrów zawierających bezładnie i blokowo rozmieszczone jednostki acetalowe, ich charakterystykę, a także wyniki wskazujące na ich potencjalne zastosowanie.

W zakres pracy doktorskiej wchodzą następujące publikacje:

P1. **Karolina Cichoń**, Bartłomiej Kost, Malgorzata Basko, Synthesis and properties of ABA-triblock copolymers from polyester A-blocks and easily degradable polyacetal B-blocks, Polymer Chemistry 2022,13, 5243-5255

P2. **Karolina Cichoń**, Irena I. Bak-Sypien, Malgorzata Basko, Bartłomiej Kost, Synthesis and characterization of functionalized polylactides containing acetal units**,** Macromolecules 2023, 56, 6951-6967

P3. **Karolina Cichoń**, Bartłomiej Kost, Marta Safandowska, Artur Różański, Malgorzata Basko, Chemically recyclable films from thermoplastic ABA-triblock copolymers containing polylactide A-blocks and easily degradable polydioxolane B-block - towards the novel type of sustainable plastics, Polymer 2026, 344, 129501

P4. **Karolina Cichoń**, Bartłomiej Kost, Malgorzata Basko, Przemysław Kubisa, Karin Odelius, Minna Hakkarainen, Polyethylene-like materials containing hydrolysable main-chain linkages: design, degradation and chemical recycling, European Polymer Journal, 2026, 255, 114929

Streszczenie w języku polskim

Nieustannie wzrastająca ilość produkowanych tworzyw sztucznych oraz ich nieefektywny recykling generują konieczność projektowania nowych materiałów polimerowych o zdolności do przyspieszonej degradacji lub chemicznego recyklingu. Jednym z obiecujących kierunków badań naukowych jest synteza polimerów zawierających w swoim łańcuchu labilne jednostki powtarzalne, które są podatne na selektywną degradację w łagodnych warunkach kwasowych. Celem przedstawionej dysertacji była modyfikacja właściwości fizykochemicznych oraz podatności na recykling chemiczny wybranych alifatycznych poliestrów poprzez wbudowanie do makrocząsteczek wiązań acetalowych.

Istotnym etapem pracy była synteza funkcyjnych, cyklicznych, pięcioczłonowych acetali a następnie zbadanie ich zdolności do kopolimeryzacji z cyklicznym estrem - laktydem. W efekcie, otrzymano (ko)polimery laktydu o masach molowych w zakresie 9 000 - 19 000 g/mol, zawierające bezładnie rozmieszczone jednostki acetalowe, wyposażone w grupy allilowe lub chlorometylowe. Wykazano, że obecność grup funkcyjnych w łańcuchu bocznym, pozwala na prostą modyfikację kopoliestrów i wytworzenie bardziej złożonych struktur polimerowych. Ponadto, udowodniono, że wprowadzenie do łańcucha jednostek acetalowych umożliwia kontrolowane rozszczepienie wiązań acetalo-estrowych, co ułatwia degradację polimeru na etapie zdefiniowanym przez użytkownika.

Zakres prac obejmował również syntezę (ko)polimerów blokowych typu ABA zawierających wewnętrzne, hydrofilowe bloki poliacetalu (poli(1,3-dioksolanu)) oraz zewnętrzne, hydrofobowe bloki poliestru (polilaktydu lub polikaprolaktonu). Otrzymano nowe (ko)polimery blokowe o masie molowej w zakresie 11 000 - 54 000 g/mol. Zaobserwowano, że zmiana stosunku molowego jednostek estrowych do acetalowych prowadzi do uzyskania materiałów o zróżnicowanych właściwościach fizykochemicznych, takich jak krystaliczność czy charakter hydrofilowo-hydrofobowy. Potwierdzono również możliwość selektywnej depolimeryzacji bloku poliacetalowego do monomerycznego 1,3-dioksolanu, w relatywnie łagodnych warunkach.

Integralną częścią badań było również otrzymanie folii polimerowych na bazie wcześniej zsyntezowanych (ko)polimerów blokowych typu ABA (PLA-PDXL-PLA), zawierających zewnętrzne bloki polilaktydowe i wewnętrzny blok poli(1,3-dioksolanu). Przeprowadzone analizy wykazały, że uzyskane folie charakteryzują się wysoką transparentnością, korzystnymi właściwościami mechanicznym i odpowiednim potencjałem do przeprowadzenia chemicznego recyklingu.

Rezultaty uzyskane w ramach pracy dowodzą, że modyfikacja struktury poliestrów poprzez wprowadzenie ugrupowania acetalowego jest skutecznym podejściem do otrzymywania polimerów o podwyższonej podatności na degradację, stanowiących wartościowe tworzywa w kontekście gospodarki o obiegu zamkniętym.

Streszczenie w języku angielskim

The continuously increasing amount of plastics produced, together with their inefficient recycling, necessitates the development of new polymeric materials capable of accelerated degradation or chemical recycling. One of the promising directions of scientific research is the synthesis of polymers containing labile repeating units within their chains, which are susceptible to selective degradation under mild acidic conditions. The aim of this dissertation was to modify the physicochemical properties and chemical recyclability of selected aliphatic polyesters by incorporating acetal linkages into their macromolecular structures.

An important stage of the work involved the synthesis of functional, cyclic, five-membered acetals and subsequently investigating their ability to copolymerize with the cyclic ester, lactide. As a result, lactide (co)polymers with molar masses ranging from 9 000 to 19 000 g/mol were obtained, containing randomly distributed acetal units bearing allyl or chloromethyl groups. It was demonstrated that the presence of functional groups in the side chains enables straightforward modification of the copolyesters and the formation of more complex polymeric structures. Furthermore, it was demonstrated that the incorporation of acetal units into the polymer chain enables the controlled cleavage of acetal–ester linkages, facilitating polymer degradation at a user-defined stage.

The scope of the work also included the synthesis of ABA-type block (co)polymers containing internal, hydrophilic polyacetal (poly(1,3-dioxolane)) blocks and external, hydrophobic polyester blocks (poly(lactide) or poly(caprolactone)). New block (co)polymers with molar masses ranging from 11 000 to 54 000 g/mol were obtained. It was observed that varying the molar ratio of ester to acetal units leads to materials with different physicochemical properties, such as crystallinity and hydrophilic–hydrophobic character. The possibility of selective depolymerization of the polyacetal block to the monomeric 1,3-dioxolane under relatively mild conditions was also confirmed.

An integral part of the research involved the preparation of polymer films based on the previously synthesized ABA-type block (co)polymers (PLA-PDXL-PLA), containing external poly(lactide) blocks and an internal poly(1,3-dioxolane) block. The analyses performed demonstrated that the obtained films are characterized by high transparency, favorable mechanical properties, and appropriate potential for chemical recycling.

The results obtained in this work demonstrate that modification of the polyester structure through the incorporation of acetal groups is an effective approach to obtaining polymers with enhanced susceptibility to degradation, representing valuable polymeric materials in the context of a circular economy.

Wstęp

Tworzywa sztuczne to materiały polimerowe, które szeroko stosowane są w różnych dziedzinach przemysłu i życia codziennego ze względu na swoje uniwersalne właściwości, umożliwiające przygotowanie szerokiej gamy produktów, w tym materiałów opakowaniowych, budowlanych, medycznych, elektronicznych, folii czy membran. Uniwersalny charakter tworzyw sztucznych wynika z ich lekkości, wysokiej wytrzymałości, stabilności termicznej oraz odporności chemicznej. O ich wszechstronności decydują również łatwość przetwórstwa, możliwość precyzyjnego dostosowania właściwości do konkretnych zastosowań oraz niskie koszty produkcji.[1][2] Ta charakterystyka przekłada się na ogromne ilości wytwarzanych materiałów prowadząc do rocznej globalnej produkcji osiągającej 430 milionów ton w 2024 roku a predykcja wskazuje na wzrost nawet do 1150 milionów ton w 2060 roku. Jednymi z najpowszechniej stosowanych polimerów na świecie są niebiodegradowlane polimery ropopochodne takie jak polietylen, polipropylen, polistyren, poli(tereftalanu etylenu), poli(chlorek winylu) czy poli(metakrylan metylu).[3] Konwencjonalne polimery pochodzenia petrochemicznego znane są jako związki odporne na hydrolizę oraz biodegradację, ze względu na występowanie trwałego wiązania węgiel-węgiel w łańcuchu głównym. Początkowo postrzegane zalety materiałów plastikowych takie jak ich wysoka trwałość, zmieniły się w powszechnie dostrzegany i rosnący problem powiązany z ciągłym zanieczyszczaniem środowiska naturalnego odpadami. Szybki wzrost produkcji polimerów nie wpisuje się w wymagania dotyczące zrównoważonego rozwoju, polegające między innymi na obniżeniu poziomu generowania odpadów. Jednym z proponowanych rozwiązań prowadzących do efektownego zagospodarowania odpadów polimerowych jest ich recykling. Należy jednak zwrócić uwagę, że jedynie 9% globalnej produkcji plastiku poddawana jest recyklingowi, a znaczna większość tj. 79% pozostaje na wysypiskach śmieci lub w środowisku naturalnym. Ponadto, jedynie 14% opakowań jest sortowanych, a zaledwie 2% poddaje się recyklingowi w obiegu zamkniętym w celu uzyskania materiału o tej samej jakości.[4] W obliczu gwałtownie pogłębiającego się kryzysu związanego z kumulowaniem tworzyw sztucznych w środowisku, coraz więcej ośrodków badawczych intensyfikuje wysiłki na rzecz opracowania materiałów w pełni recyklingowalnych lub ulegających biodegradacji.[5][6] Takie założenia potencjalnie ograniczają negatywne oddziaływanie w pełnym cyklu żywotności produktu poprzez zminimalizowanie ilości zanieczyszczeń niedegradowalnymi odpadami.

Szczególnie ciekawym podejściem do rozwiązania problemu degradowalności konwencjonalnych polimerów ropopochodnych okazało się wprowadzenie do ich

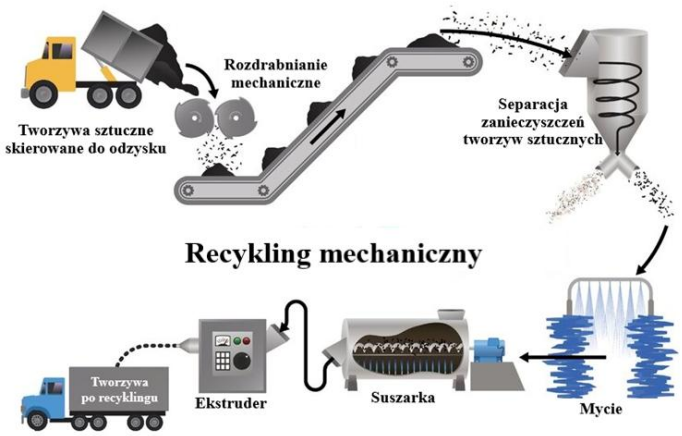
makrocząsteczek wiązań podatnych na hydrolizę takich jak wiązania estrowe, węglanowe, acetalowe, amidowe lub fosforanowe.[7][8] Polimery takie jak polilaktyd (PLA) lub polikaprolakton (PCL), coraz częściej stosowane są jako zamienniki ropopochodnych polimerów ze względu na nietoksyczność, biodegradowalność oraz odpowiednie właściwości fizykochemiczne. Choć materiały te, stanowią obiecującą alternatywę dla tworzyw konwencjonalnych, ich efektywna degradacja wymaga dalszych modyfikacji strukturalnych.[9] Dlatego pomimo wielu zalet zarówno PLA, jak i innych poliestrów, wciąż czas ich rozkładu jest zdecydowanie za długi w kontekście wydajnego recyklingu. W odpowiedzi na te wyzwania laboratoria badawcze intensywnie poszukują nowych materiałów polimerowych podatnych na recykling lub degradację, ponieważ ponowne przetwarzanie zużytych tworzyw sztucznych ma kluczowe znaczenie dla osiągnięcia zrównoważonej gospodarki o obiegu zamkniętym. Podejście to stanowi strategię ukierunkowaną na ograniczenie zużycia surowców pierwotnych, ochronę zasobów naturalnych oraz redukcję ilości odpadów trafiających do środowiska.[10]

1.1. Przemysłowe metody recyklingu polimerów

Recykling to proces przetwarzania odpadów, w wyniku którego powstają nowe produkty o właściwościach zbliżonych do materiałów wyjściowych. Jednym z surowców, które mogą podlegać recyklingowi są wyroby polimerowe. Proces ten polega na gromadzeniu, segregowaniu i przetwarzaniu zużytych tworzyw sztucznych oraz wprowadzeniu na rynek nowych materiałów. Recykling polimerów jest jednym ze sposobów na redukcję problemów środowiskowych wynikających z gromadzenia odpadów polimerowych na wysypiskach śmieci. Takie podejście dodatkowo pomaga zmniejszyć zużycie zasobów naturalnych takich jak ropa czy gaz, niezbędnych do syntezy konwencjonalnych polimerów syntetycznych.[11] Należy, jednak pamiętać, że proces recyklingu jest ekonomicznie wymagający, gdyż całkowity koszt surowców z odzysku w zestawieniu z surowcami pierwotnymi zazwyczaj nie stanowi konkurencji cenowej. Generuje to większą potrzebę poszukiwania nowych rozwiązań technologicznych, których wprowadzenie na skalę globalną będzie satysfakcjonującym kompromisem pomiędzy aspektem ekonomicznym, środowiskowym i technologicznym. Istnieją cztery główne typy recyklingu: mechaniczny (materiałowy), chemiczny, termiczny oraz organiczny (biodegradacja).

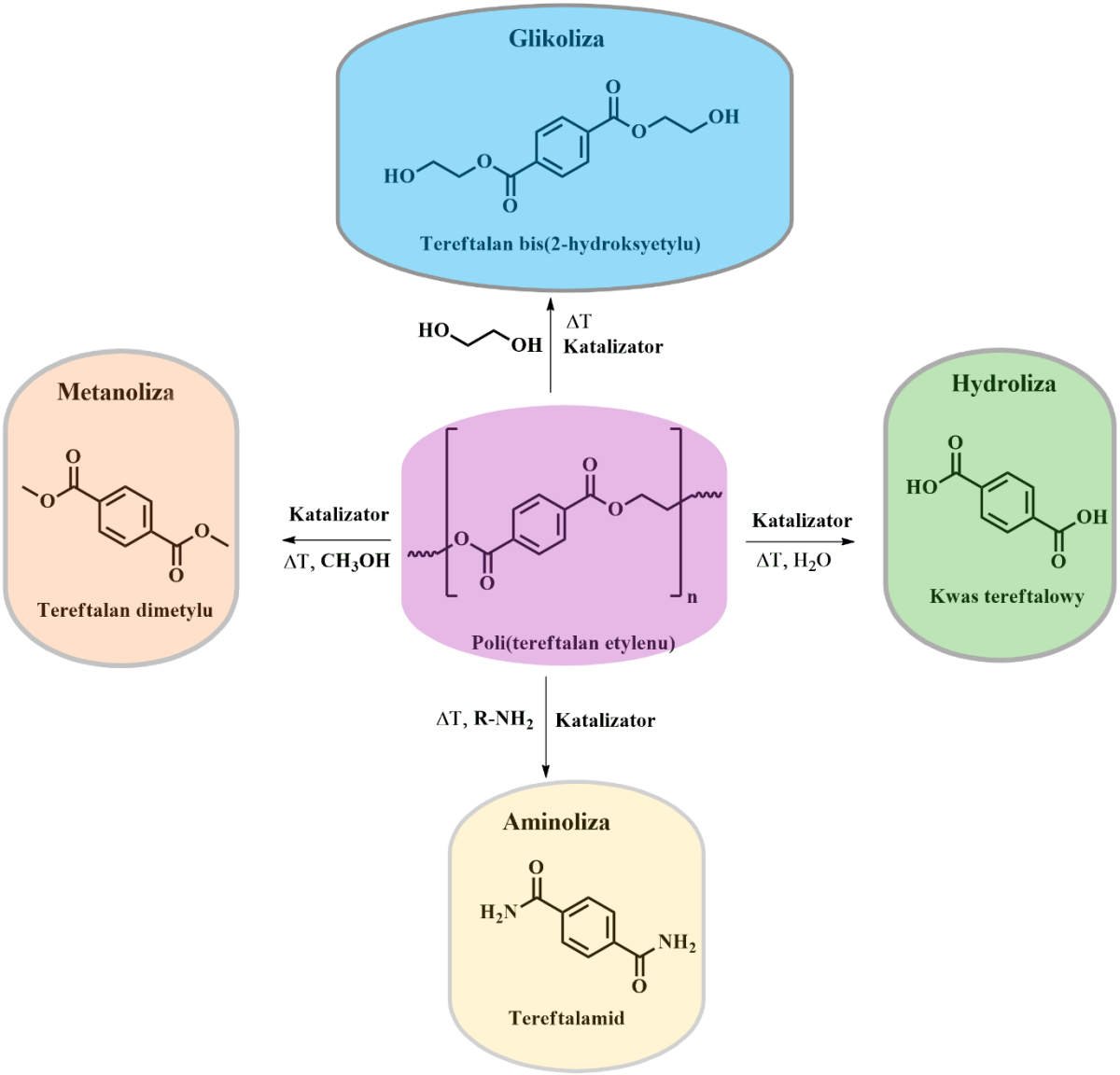
Recykling mechaniczny to powszechnie stosowana metoda zagospodarowania odpadów z tworzyw sztucznych, która uwzględnia sortowanie, mycie oraz rozdrabnianie odpadów polimerowych.[8][12] Uzyskane fragmenty poddawane są stopieniu oraz przetworzeniu na produkt w postaci płatków lub granulatu, stanowiąc surowiec do otrzymania nowych materiałów polimerowych.[10] Niewątpliwymi zaletami recyklingu mechanicznego jest zazwyczaj niskie zużycie energii oraz możliwość zastosowania w skali przemysłowej.[13] Nie jest to jednak

rozwiązanie bez wad. Znaczącym wyzwaniem tej metody jest selektywność wobec materiałów polimerowych nadających się do ponownego przetworzenia (poli(terftalen etylenu) (PET), polietylen wysokiej gęstości (HDPE), polietylen niskiej gęstości (LDPE), polipropylen (PP), polistyren (PS)), pogorszenie właściwości materiału po kilku cyklach recyklingu (downcycling) oraz konieczność dokładnego oczyszczania odpadów z zanieczyszczeń, przed poddaniem ich recyklingowi mechanicznemu.[14] Chociaż poli(tereftalanu etylenu), technicznie nadaje się do recyklingu mechanicznego, tylko niewielki odsetek materiałów otrzymanych z PET jest poddawana recyklingowi ze względu na obecność plastyfikatorów, barwników lub środków nukleujących, które powodują degradację makrocząsteczek podczas przetwarzania. W tym kontekście szacuje się, że globalne wskaźniki recyklingu PET-u wynoszą około 30%, co oznacza, że większość odpadów PET nadal trafia na wysypiska śmieci lub do środowiska. Ponadto, proces recyklingu mechanicznego można przeprowadzić tylko 3-5 razy bez pogorszenia właściwości fizykochemicznych polimeru.[15,16]



Rysunek 1.Etapy mechanicznego recyklingu [16]

Recykling chemiczny, określany także mianem depolimeryzacji, stanowi stosunkowo nową metodę odzysku tworzyw sztucznych. Umożliwia przekształcenie odpadów polimerowych ponownie do monomeru za pomocą reakcji chemicznych przy udziale ciepła i odpowiedniego ciśnienia.[17–19] Ta cecha recyklingu chemicznego fundamentalnie odróżnia i przewyższa metody degradacji termicznej, nie generując złożonych układów i mieszanin cieczy i gazów, wymagających dalszej separacji. Powszechnie stosowany PET (między innymi w butelkach na napoje), można poddać chemicznemu recyklingowi uzyskując w zależności od zastosowanych warunków (temperatura, katalizator, rozpuszczalnik) różne, wysokiej jakości produkty, które nadają się do zastosowań w recyklingu w obiegu zamkniętym (Rysunek 2).[20]



Rysunek 2. Przykład recyklingu chemicznego PET [20]

Niepodważalną zaletą zastosowania recyklingu chemicznego jest możliwość ponownej polimeryzacji odzyskanych monomerów w celu otrzymania nowych materiałów polimerowych, wykazujących zbliżone właściwości fizykochemiczne do pierwotnych produktów. Pomimo, że recykling chemiczny umożliwia przetwarzanie zarówno zanieczyszczonych oraz mieszanych tworzyw, to jego zastosowanie jest ograniczone. Dotychczas przeprowadzone badania wskazują, że tylko niektóre polimery takie jak poli(tereftalan etylenu), polipropylen czy polistyren można poddać procesowi chemicznego recyklingu.[21] Znaczący koszt materiałów, a szczególnie katalizatorów niezbędnych do prowadzenia odwracalnych reakcji chemicznych, często stosowanie wysokich temperatur i ciśnień, ograniczają szerokie wdrażanie tego procesu.[22]

W celu utylizacji odpadów polimerowych wykorzystuje się również metody termiczne takie jak piroliza czy gazyfikacja. Piroliza odpadów polimerowych polega na termicznym

rozkładzie długich łańcuchów polimerowych do mniej złożonych cząsteczek w wysokiej temperaturze (300–900°C) i warunkach beztlenowych, co umożliwia ich przetworzenie do postaci oleju pirolitycznego o dużej wartości dla przemysłu rafineryjnego. Niewątpliwą zaletą pirolizy jest możliwość manipulacji ciśnieniem i temperaturą co pozwala na optymalizację procesu spalania i otrzymanie produktów o oczekiwanym składzie.[23,24] W przeciwieństwie do recyklingu, piroliza uważana jest za zieloną technologię, gdyż nawet powstające gazowe produkty uboczne pirolizy można ponownie wykorzystać w celu zrekompensowania całkowitego zapotrzebowania energetycznego instalacji do pirolizy.[25] Piroliza stosowana jest do recyklingu mieszanych odpadów z tworzyw sztucznych (PS, PE oraz PP), bez konieczności ich wstępnego sortowania. Jednakże, ze względu na prowadzenie procesów w wysokich temperaturach, metoda jest wysoce energochłonna, wymaga zaawansowanego układu aparaturowego oraz dużych nakładów finansowych.[26]

Zgazowanie to proces termochemiczny polegający na przekształceniu m. in. tworzyw sztucznych w palny gaz syntetyczny poprzez ich ogrzewanie w wysokiej temperaturze, zwykle powyżej 700°C. Zgazowanie od pirolizy odróżnia zastosowanie kontrolowanej ilości tlenu celem niecałkowitego spalenia odpadów w wyniku czego jako główne produkty powstają: wodór i tlenek węgla (II) oraz produkty uboczne, takie jak tlenek węgla (IV), metan, woda, a także węgiel drzewny, smoła i popiół, które w kolejnych etapach znajdują zastosowanie do wywarzania energii elektrycznej czy paliwa.[27] Podobnie jak piroliza procesowi poddawane są odpady z mieszanych tworzyw, a także wielowarstwowe opakowania jednorazowe. Ze względu na konieczność zapewnienia wysokich temperatur proces ten jest równie energochłonny jak piroliza. Warto mieć na uwadze, że proces tym bardziej obciąża środowisko jeśli zapewnienie wysokiej temperatury jest generowane z wykorzystaniem nieodnawialnych źródeł energii.[28–30] Recykling biologiczny to proces, który stanowi innowacyjną metodę rozkładu materiałów polimerowych do prostych składników głównie woda i tlenek węgla (IV), z zastosowaniem enzymów oraz mikroorganizmów takich jak grzyby, bakterie czy algi.[31] Do najważniejszych typów biologicznego recyklingu zaliczamy enzymatyczną degradację, kompostowanie oraz degradację beztlenową.[32,33] W odróżnieniu od wyżej wspomnianych metod degradacji polimerów, recykling biologiczny nie wymaga istotnego nakładu energii. Należy jednak zwrócić uwagę, że zastosowanie tego rodzaju recyklingu wiąże się z ograniczeniami. Jedynie niektóre bioplastiki, zwłaszcza te zawierające wiązania estrowe (poliestry takie jak PLA, czy polihydroksyalkaniany) są podatne na rozkład enzymatyczny. Proces enzymatycznej degradacji (biodegradacja) przebiega zazwyczaj w temperaturze pokojowej, nie wywierając negatywnego

wpływu na środowisko, jednakże ze względu na wysoką masę cząsteczkową i hydrofobowy charakter polimerów czas tego procesu może wymagać nawet 60 lat.[7] Alternatywną drogą jest prowadzenie procesu kompostowania polimerów który, w odróżnieniu od biodegradacji, przeprowadzany jest w temperaturze 60°C, przy wysokiej wilgotności i wymaga zapewnienia specjalistycznych parametrów. W takich warunkach, 90% masy ulega rozkładowi w ciągu 12 tygodni do wody i tlenku węgla (IV).[34][35] Główną różnicą pomiędzy kompostowaniem a niekontrolowaną biodegradacją jest udział człowieka. Podczas gdy kompostowanie jest procesem prowadzonym w warunkach kontrolowanych, naturalna biodegradacja zachodzi samorzutnie w środowisku, bez bezpośredniej ingerencji ludzkiej. W perspektywie zwiększającego się nacisku na wykorzystywanie zielonych technologii oraz prowadzenia gospodarki o obiegu zamkniętym, wymagane warunki pozycjonują kompostowanie jako ekonomiczną alternatywę w przyszłości. Ponadto, mając na uwadze skalę wyzwań związanych ze składowaniem odpadów polimerowych, technologia ta wymaga dalszych badań i optymalizacji w celu zapewnienia jej skalowalności oraz zwiększenia wydajności procesowej.

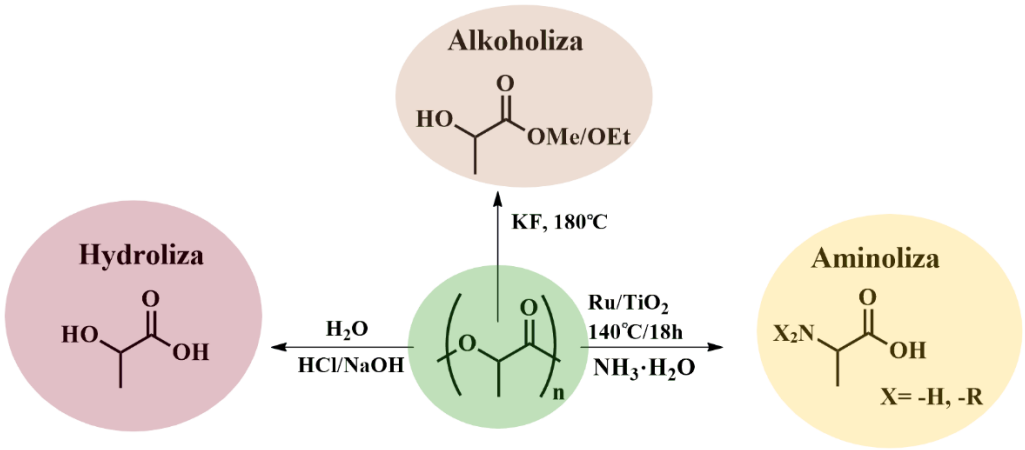
1.2. Sposoby chemicznego recyklingu polilaktydu

Poliestry alifatyczne stanowią niezwykle obiecującą klasę polimerów, które ze względu na obecność w łańcuchu głównym wiązań estrowych podatnych na hydrolizę mogą ulegać degradacji, co czyni je kluczowymi materiałami w kontekście ograniczania negatywnego wpływu tworzyw sztucznych na środowisko.[36] Zainteresowanie tą grupą polimerów wynika z dużej dostępności monomerów, możliwości kontrolowania procesu syntezy poliestrów oraz z potencjału jakie otwiera modyfikacja właściwości poprzez kopolimeryzację. W literaturze naukowej najczęściej opisywanym poliestrem alifatycznym o wszechstronnym zastosowaniu jest poli(kwas mlekowy) (PLA) oraz jego (ko)polimery . Materiał ten uznawany jest za niezwykle obiecujący polimer bioresorbowalny, który dzięki wysoki kompatybilności biologicznej, odnawialnemu pochodzeniu surowcowemu oraz dobrej przetwórczości znajduje szerokie zastosowanie zarówno w sektorze biomedycznym, jak i przemysłowym.[37] Równocześnie te same właściwości chemiczne i fizyczne, które determinują stabilność poliestrów (duża masa molowa, krystaliczność) drastycznie ograniczają podatność na szybką degradację, co komplikuje procesy recyklingu.

Istnieje kilka metod pozwalających na przeprowadzenie chemicznego recyklingu polilaktydu, które wykorzystują reakcje hydrolizy, alkoholizy lub aminolizy (Rysunek 3).

W roztworach wodnych degradacja hydrolityczna PLA przebiega poprzez losowe rozerwanie wiązania estrowego, które jest kontrolowane głównie przez szybkość penetracji wody wgłąb materiału polimerowego.[36] Wydajny proces hydrolizy PLA możliwy jest jedynie w warunkach

podwyższonej temperatury, w środowisku kwasowym lub zasadowym, co prowadzi do obniżenia masy molowej polimeru. Rozerwanie wiązania estrowego przebiega preferencyjnie w obszarach amorficznych początkowo prowadząc do wzrostu krystaliczności materiału.[38] Degradacja hydrolityczna stałych matryc polimerowych na bazie PLA może przebiegać według dwóch różnych mechanizmów: erozji objętościowej, podczas której woda dyfunduje w głąb polimeru, albo erozji powierzchniowej, która jest ograniczona jedynie do zewnętrznej warstwy materiału. Głównymi produktami hydrolitycznej degradacji PLA są kwas mlekowy (hydroliza kwasowa), mleczany (hydroliza zasadowa) oraz rozpuszczalne w wodzie oligomery, (takie jak dimery i trimery LA).[39] Alkoholiza jest powszechnie wykorzystywaną metodą depolimeryzacji PLA z wytworzeniem alkilomleczanów, które mogą służyć między innymi jako tzw. ekologiczne rozpuszczalniki. Do procesu alkoholizy wykorzystuje się najczęściej alkohol metylowy lub alkohol etylowy. W wyniku procesu metanolizy lub etanolizy powstają odpowiednio: mleczan metylu bądź mleczan etylu stosowany w przemyśle spożywczym i kosmetycznym jako rozpuszczalniki lub substancje zapachowe.[40] Otrzymane estry kwasu mlekowego można również efektywnie przekształcić w cykliczny dimer kwasu mlekowego (laktyd, (LA)), tym samym skutecznie zamykając „cykl życia" PLA. Głównymi katalizatorami tego procesu są kwasy, sole metali, kompleksy metaloorganiczne oraz organokatalizatory.[41] W procesie aminolizy rozerwanie łańcuchu PLA przebiega w wyniku reakcji amin z karobonylowym atomem węgla występującym w grupie estrowej polimeru, skutkując utworzeniem wiązania amidowego i równoległym rozerwaniem łańcucha makrocząsteczki. Głównymi produktami takich procesów są N-podstawione laktamidy, szeroko stosowane w przemyśle chemicznym. Zastosowanie roztworu amoniaku w procesie aminolizy PLA prowadzi do powstania aminokwasu alaniny z wysoką wydajnością.[42]

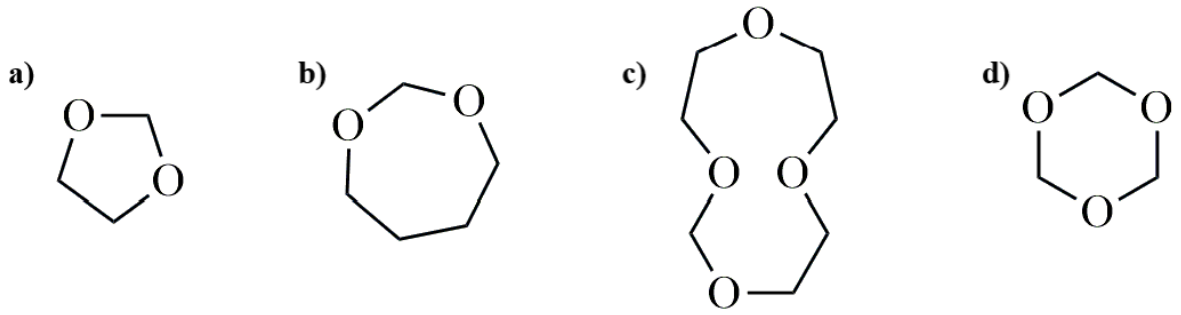


Rysunek 3. Degradacja PLA w wyniku hydrolizy, alkoholizy i aminolizy [43]

Mimo wielu dostępnych metod depolimeryzacji PLA, ich wdrożenie na skalę przemysłową pozostaje ograniczone, przede wszystkim z powodu koniecznego stosowania relatywnie wysokich temperatur, agresywnych odczynników oraz zbyt długiego czasu reakcji. Z tego powodu znaczną uwagę poświęca się modyfikacji chemicznej poliestrów, umożliwiająca ich wydajny recykling chemiczny w łagodniejszych warunkach procesowych.

1.3. Poliacetale - synteza łatwo recyklingowalnych polimerów na przykładzie poli(1,3-dioksolanu)

Cykliczne acetale to grupa monomerów zawierających w strukturze pierścienia wiązanie acetalowe (-O-CH_2-O-), w którym jeden atom węgla otoczony jest dwoma atomami tlenu. Przykładowe monomery należących do tej klasy związków przedstawiono na Rysunku 4.



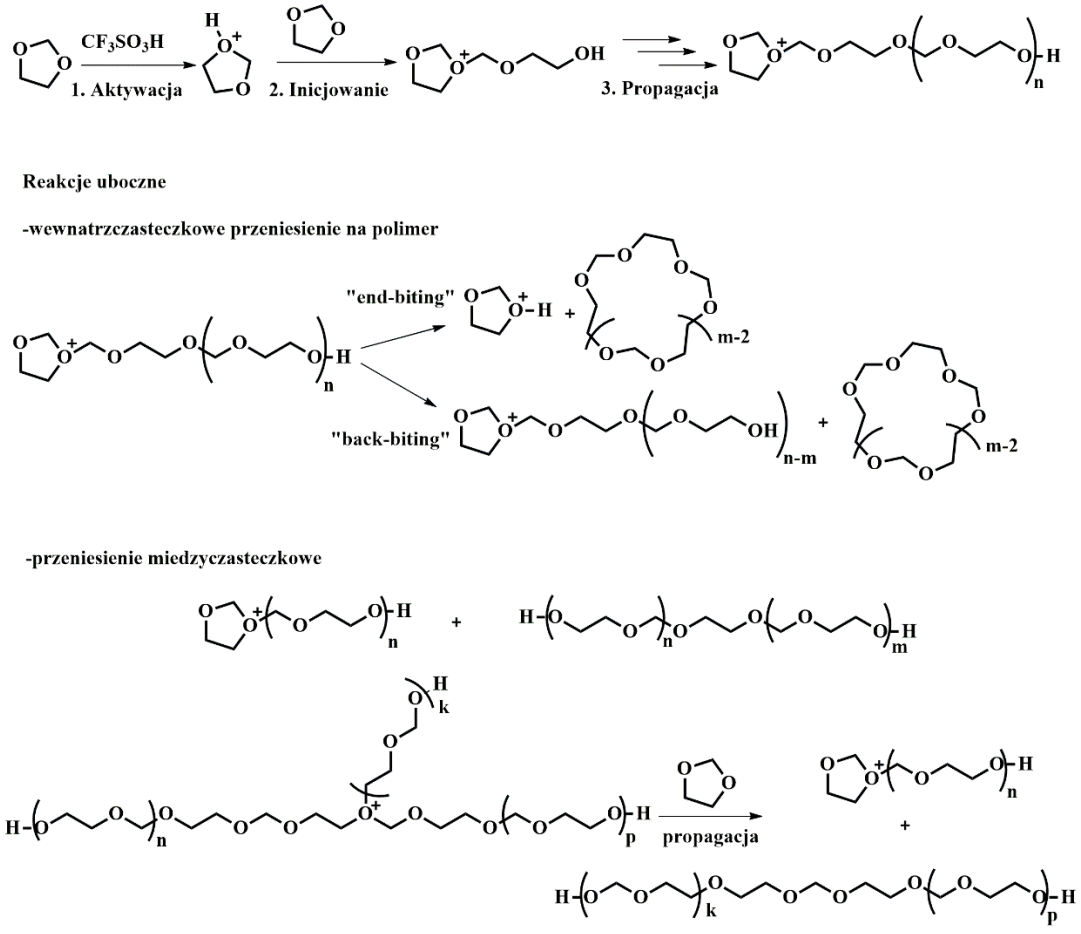
Rysunek 4. Przykłady cyklicznych acetali: a)1,3-dioksolan, b)1,3-dioksepan, c)1,3,6,9-tetraoksacykloundekan, d)1,3,5-trioksan

Takie heterocykliczne monomery o różnym rozmiarze pierścienia można otrzymać w wyniku kondensacji aldehydów lub ketonów z niższymi diolami (glikol etylenowy, glikol propylenowy, glikol butylenowy) prowadzonej w obecności 1–2% wag. kwasowego katalizatora (np. kwas p-toluenosulfonowy).[44] W przypadku zastosowania wyższych dioli, zawierających w cząsteczce ponad 9 atomów węgla, proces cyklizacji do acetali może być niemożliwy ze względów sterycznych i termodynamicznych. W takich warunkach zamiast struktur cyklicznych powstają liniowe oligomeryczne frakcje, które w wyniku depolimeryzacji prowadzonej w obecności kwasu i pod obniżonym ciśnieniem można przekształcić w makrocykliczne acetale. [45] Proces polimeryzacji cyklicznych monomerów jest możliwy gdy spełnione są dwa główne warunki: polimeryzacja jest termodynamicznie możliwa oraz istnieje mechanizm reakcji pozwalający na otwarcie pierścienia. Polimeryzacja z otwarciem pierścienia cyklicznych acetali, ze względu na niewielką ujemną wartość entalpii swobodnej ($\Delta G < 0$), jest procesem odwracalnym i prowadzi do ustalenia się równowagi pomiędzy monomerem a polimerem. Duża reaktywność wiązania acetalowego, ułatwia otwarcie pierścienia w obecności katalizatorów kwasowych, dzięki

czemu polimeryzacja kationowa stanowi właściwy mechanizm ich przekształcenia w liniowy polimer.[46]

Jednym z przedstawicieli poliacetali o interesujących właściwościach fizycznych i zdolności do degradacji jest poli(1,3-dioksolan) (PDXL)[47] Jest to hydrofilowy polimer o łańcuchu zbudowanym z naprzemiennie ułożonych jednostek oksymetylenowych i oksyetylenowych ($[-CH_2-O-CH_2-CH_2-O-]_n$, który może być rozpatrywany jako analog poli(glikolu etylenowego)).[48] Jest to polimer stabilny w środowisku obojętnym i zasadowym. W przypadku ogrzania powyżej temperatury sufitowej (T_c), w obecności aktywnego katalizatora kwasowego, PDXL szybko depolimeryzuje do monomeru.[49]

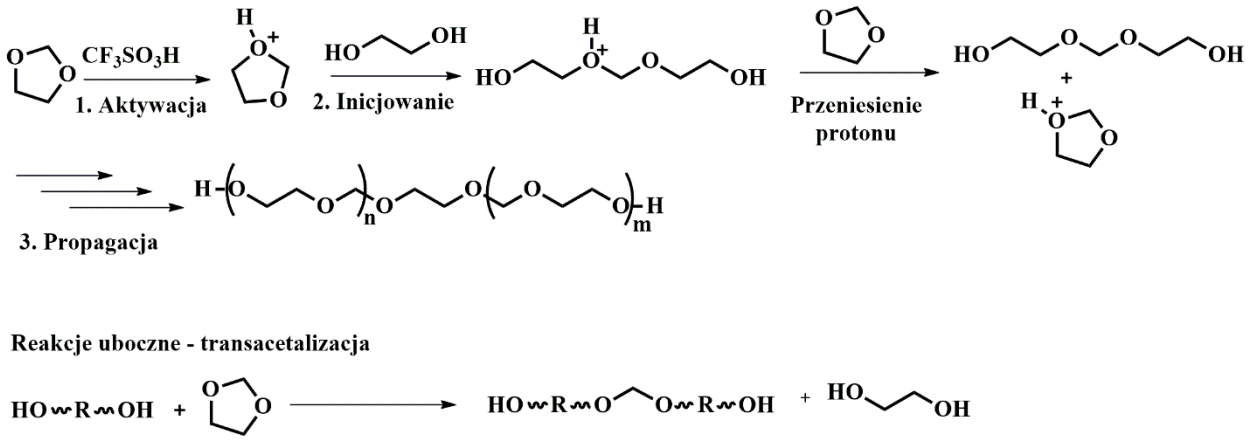
PDXL może być otrzymany w wyniku kationowej polimeryzacji z otwarciem pierścienia cyklicznego acetalu - 1,3-dioksolanu (DXL) - według mechanizmu aktywnego końca łańcucha (z języka angielskiego: Active Chain End (ACE)), jak pokazano na Rysunku 4. Typowymi katalizatorami w tym mechanizmie polimeryzacji są mocne kwasy protonowe, kwasy Lewisa i sole oksoniowe.[50] Schemat polimeryzacji DXL według mechanizmu ACE oraz reakcje uboczne zachodzące podczas polimeryzacji pokazano na Rysunku 5.



Rysunek 5. Kationowa polimeryzacja DXL wg mechanizmu ACE [51]

Należy pamiętać, że nieodłączną cechą kationowej polimeryzacji DXL wg mechanizmu ACE jest występowanie reakcji przeniesienia łańcucha na polimer, które mają miejsce ze względu na niższą nukleofilowość acetalu w monomerze w porównaniu z ugrupowaniami acetalowymi w łańcuchu polimeru.[51] W przypadku, gdy atom tlenu z łańcucha atakuje rosnący koniec własnego łańcucha następuje wewnątrzcząsteczkowe przeniesienie (z języka angielskiego „back-biting") prowadzące do powstania cyklicznego oligomeru. Wynikiem ataku tlenu na rosnący koniec innej makrocząsteczki jest międzycząsteczkowe przeniesienie na polimer (transacetalizacja), które skutkuje wymianą segmentalną i redystrybucją jednostek powtarzalnych.

Metodą pozwalającą na ograniczenie udziału cyklicznej frakcji w syntezie PDXL, jest polimeryzacja DXL z otwarciem pierścienia według mechanizmu Aktywowanego Monomeru (z języka angielskiego: Activated Monomer - AM). W mechanizmie tym, DXL polimeryzowany jest w obecności mocnych kwasów protonowych, które pełnią rolę katalizatora (np. kwas triflowy) oraz inicjatora zawierającego grupy hydroksylowe, którym może być np. glikol etylenowy, jak pokazano na Rysunku 6.



Rysunek 6. Kationowa polimeryzacja DXL wg mechanizmu AM [51]

Wzrost łańcucha w polimeryzacji według mechanizmu AM następuje w wyniku nukleofilowego ataku atomu tlenu grupy hydroksylowej na atom węgla w protonowanym (a więc aktywowanym) monomerze. Podczas propagacji według mechanizmu AM rosnący koniec łańcucha nie zawiera naładowanego centrum aktywnego, jak w mechanizmie ACE, lecz grupę hydroksylową o wyższej nukleofilowości w porównaniu z jednostkami acetalowymi w PDXL, co powoduje, że reakcje cyklizacji są silnie utrudnione.[52] Z drugiej strony, wiadomo, że mechanizm ACE może zachodzić równolegle z mechanizmem AM, dlatego proces polimeryzacji może prowadzić do powstania mieszaniny makrocząsteczek o różnej strukturze i topologii.[51] W celu zwiększenia udziału mechanizmu AM i uzyskania kontroli nad masą molową polimeru, proces należy prowadzić przy niskim chwilowym stężeniu DXL co można osiągnąć np. poprzez

dodawanie monomeru za pomocą pompy infuzyjnej. Zastosowanie mechanizmu AM umożliwia kontrolę masy molowej polimeru określonej na podstawie początkowego stosunku alkoholu do monomeru.

Ostatnio opracowano metodę umożliwiającą otrzymanie PDXL o masach zbliżonych do 1 000 kDa w układzie polimeryzacyjnym, który wykorzystuje niedrogie, niemetaliczne inicjatory (trietylowe sole oksoniowe) oraz gąbkę protonową. Otrzymano w ten sposób termoplastyczny, degradowalny materiał o bardzo dobrych właściwościach fizykochemicznych umożliwiających praktyczne zastosowania a zarazem wykazujący unikalną zdolność do recyklingu.[47,53]

2. Opis badań własnych

Cel pracy

Jak opisano we wstępie literaturowym, poszukiwane są nowe materiały polimerowe, które ulegałyby degradacji na zadanym etapie użytkowania, co pozwoliłoby na ich efektywny recykling chemiczny w łagodnych warunkach procesowych.

Celem pracy było zastosowanie cyklicznych acetali do syntezy kopoliestrów zawierających labilne jednostki powtarzalne. Założono, że wprowadzenie jednostek acetalowych w sposób bezładny do łańcucha poliestru doprowadzi do otrzymania kopoliestrów o przyspieszonej degradacji. Szczególnie ciekawym podejściem wydawało się połączenie bloków poliestrowych z blokami poliacetalowymi w celu otrzymania (ko)polimerów blokowych zdolnych do chemicznego recyklingu. Oczekiwano, że w warunkach kwasowych proces rozpadu makrocząsteczek przebiegać będzie w wyniku selektywnego rozerwania reaktywnego wiązania acetalowego, prowadząc do otrzymania bloków poliestrowych (ulegających biodegradacji w relatywnie krótkim czasie) oraz monomerycznego DXL. Integralną częścią badań była również ocena możliwości aplikacyjnych tak zaprojektowanych (ko)polimerów.

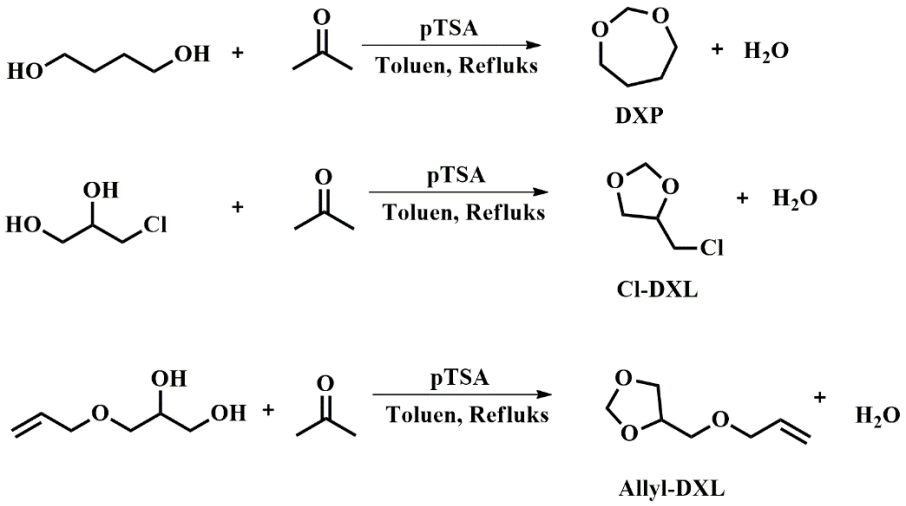
W ramach pracy doktorskiej zrealizowano trzy główne zadania badawcze, które obejmowały:

1. Syntezę i badanie właściwości fizyko-chemicznych (ko)polimerów laktydu i cyklicznych acetali. Modyfikację i hydrolizę otrzymanych materiałów polimerowych.
2. Otrzymanie (ko)polimerów blokowych typu ABA zawierających zewnętrzne bloki poliestrowe A oraz wewnętrzny blok poli(dioksolanu). Charakterystykę oraz chemiczny recykling otrzymanych (ko)polimerów blokowych.

3. Otrzymanie i charakterystykę folii polimerowych z (ko)polimerów blokowych typu ABA podatnych na recykling chemiczny i kwasową hydrolizę. Optymalizację warunków wytwarzania folii metodą prasowania na gorąco.

2.1. Synteza oraz charakterystyka bezładnych (ko)polimerów laktydu i cyklicznych acetali

Z punktu widzenia celu pracy kluczowe było zbadanie kationowej kopolimeryzacji laktydu z cyklicznymi acetalami zawierającymi boczne grupy funkcyjne, prowadzące do otrzymania sfunkcjonalizowanych kopoliestrów o podwyższonej podatności na degradację. Dwa, pięcioczłonowe cykliczne acetale wyposażone w grupy: allilową (Allyl-DXL) lub chlorometylową (Cl-DXL) zsyntetyzowano w wyniku reakcji 3-alliloksypropan-1,2-diolu oraz 3-chloropropan-1,2-diolu z paraformaldehydem. Dodatkowo, w celach porównawczych, w reakcji paraformaldehydu z butano-1,4-diolem otrzymano niesfunkcjonalizowany, siedmioczłonowy acetal: 1,3-dioksepan (DXP) (Rysunek 7).

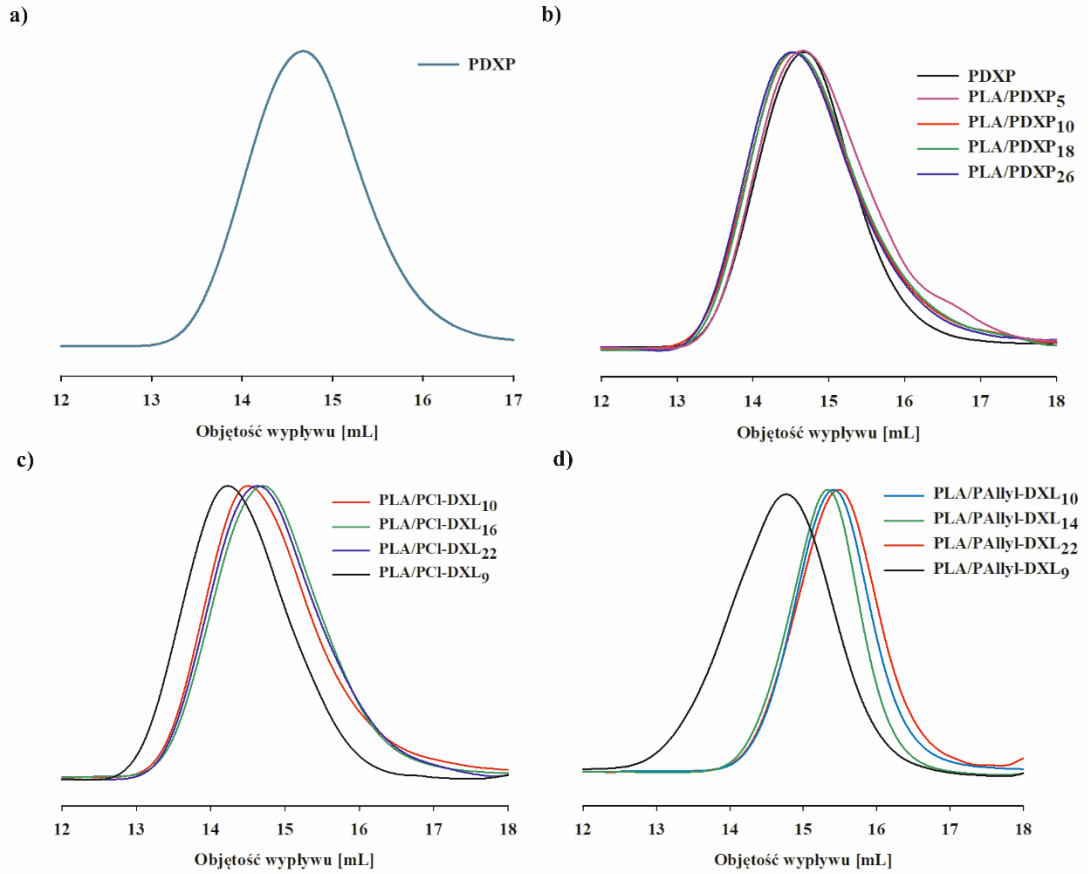


Rysunek 7. Synteza cyklicznych acetali

Kationową homopolimeryzację otrzymanych acetali prowadzono stosując butano-1,4-diol jako inicjator oraz kwas triflowy jako katalizator. W przypadku DXP, po 24 godzinach otrzymano homopolimer poli(1,3-dioksepanu) o masie cząsteczkowej M_n = 12 000 g/mol i rozkładzie masy M_w/M_n = 1,7. Jednak przy zastosowaniu tych samych warunków polimeryzacji dla Cl-DXL lub Allyl-DXL nie udało się uzyskać odpowiednich homopolimerów. Obserwacja ta jest zgodna z wcześniej opublikowanymi wynikami dotyczącymi homopolimeryzacji podstawionych cyklicznych acetali, w których podstawnik powoduje obniżenie wartości temperatury granicznej polimeryzacji[54]. W związku z tym, homopolimeryzację Allyl-DXL i Cl-DXL przeprowadzono również w temperaturze 2 °C i −15 °C. Jednakże, zarówno obniżenie temperatury układu

polimeryzacyjnego jak i wydłużenie czasu reakcji do 192 godzin nie pozwoliło na otrzymanie pożądanych produktów, homopolimerów Allyl-DXL lub Cl-DXL.

Niezdolność Cl-DXL i Allyl-DXL do tworzenia homopolimerów o dużej masie cząsteczkowej nie oznacza, że monomery te nie mogą być kopolimeryzowane z innymi komonomerami. Dlatego w kolejnym etapie pracy sprawdzono zdolność otrzymanych funkcyjnych acetali do kopolimeryzacji z wybranym cyklicznym estrem: laktydem. Zbadano wpływ temperatury (−15, 2 i 30 °C) i czasu kopolimeryzacji (24, 48, 72 i 192 h) na masę molową i skład (ko)polimerów (Rysunek 8).



Rysunek 8. Analiza chromatograficzna (ko)polimerów cyklicznych podstawionych acetali z laktydem

Analiza chromatograficzna z wykluczeniem objętości (SEC) produktów kopolimeryzacji potwierdziła otrzymanie polimerów laktydu zawierające jednostki acetalowe (DXP, Allyl-DXL lub Cl-DXL) o masach molowych w zakresie 9 000 - 19 000 g/mol. Strukturę otrzymanych (ko)polimerów zbadano stosując technikę ^{1}H i ^{13}C NMR. W widmach ^{1}H NMR oczyszczonego produktu, oprócz typowych sygnałów należących do sekwencji polilaktydu (5,17, 4,35 i 1,56 ppm), zidentyfikowano również piki należące do wbudowanych jednostek acetalowych. Obecność singletu przy przesunięciu chemicznym 4,80 ppm potwierdziła wbudowanie jednostek

acetalowych w strukturę (ko)polimeru i powstanie wiązań acetalo-estrowych. Kopolimeryzacja laktydu z Cl-DXL i Allyl-DXL w 30 °C prowadzona przez 24 godziny przebiegła z wysoką konwersją laktydu, jednak konwersja obu cyklicznych acetali była stosunkowo niska (około 20%), a po oczyszczeniu zawartość jednostek acetalowych w (ko)polimerze wynosiła około 12 mol %. Obniżenie temperatury do 2 °C spowolniło proces polimeryzacji i 90% konwersję laktydu osiągnięto dopiero po 48 godzinach. Jednocześnie konwersja acetali wzrosła jedynie nieznacznie, do 30% dla Cl-DXL i 32% dla Allyl-DXL. Przy temperaturze - 15 °C konwersja acetalu osiągnęła 40%, a ilość wbudowanych jednostek nie przekroczyła 22%. Jednak w tych warunkach polimeryzacji, konwersja laktydu osiągnęła jedynie 50% po 72 godzinach, dlatego kopolimeryzacji nie prowadzono poniżej tej temperatury. Analiza (ko)polimerów laktydu z Cl-DXL i Allyl-DXL wykazała bardziej skomplikowaną strukturę niż w przypadku (ko)polimerów laktydu z DXP, ponieważ podstawienie pozycji czwartej w cyklicznych acetalach pozwala na otwarcie pierścienia na dwa różne sposoby.

W kolejnym etapie prac, zbadano zdolność do modyfikacji otrzymanych kopoliestrów w reakcjach podstawienia nukleofilowego oraz reakcji „click". W tym celu grupy chlorometylowe zamienione na grupy azydkowe, a następnie w wyniku reakcji cykloaddycji azydkowo-alkinowej wprowadzano grupy hydroksylowe czy epoksydowe. (Ko)polimery zawierające grupy z wiązaniami podwójnymi poddano reakcji z kwasem tioglikolowym i merkaptoetanolem w wyniku reakcji tiol-en „click", co pozwoliło wprowadzić grupy hydroksylowe i karboksylowe. Reakcje te przebiegały w łagodnych warunkach, bez degradacji łańcucha polimerowego, co potwierdzono analizami NMR i SEC. Wykazanie możliwości efektywnej funkcjonalizacji kopoliestrów stwarza perspektywy ich wkoykorzystania jako uniwersalnych prekursorów do otrzymywania bardziej złożonych struktur polimerowych, co znacząco poszerza zakres ich potencjalnych zastosowań. W celu poznania wpływu jednostek acetalowych na właściwości termiczne i stabilność kopoliestrów przeprowadzono analizy TGA (termograwimetryczne) oraz DSC (różnicową kalorymetrię skaningową). Zaobserwowano, że wprowadzenie jednostek acetalowych do łańcucha PLA doprowadziło do zahamowania krystalizacji i otrzymania (ko)polimerów amorficznych o temperaturze zeszklenia w zakresie 6-40 ˚C. Zmodyfikowane kopoliestry z grupami funkcyjnymi wykazują podobne właściwości termiczne i stabilność, z wyjątkiem (ko)polimeru zmodyfikowanego kwasem tioglikolowym, którego maksymalna temperatura rozkładu jest nieco niższa ze względu na obecność bocznych grup karboksylowych podatnych na kondensację lub dekarboksylację.[55]

W celu wykazania możliwości przyspieszonej degradacji otrzymane polimery poddano działaniu roztworu kwasu solnego. Badania wykazały, że losowo rozmieszczone jednostki

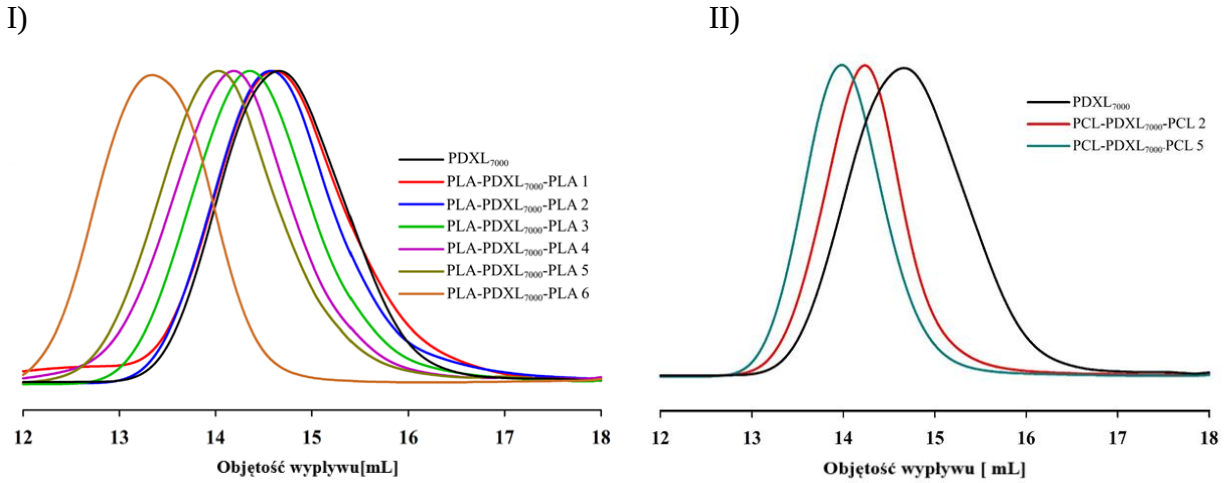
acetalowe w kopoliestrach PLA umożliwiają ich przyspieszoną degradację w środowisku kwaśnym, w odróżnieniu od homopolimerycznego PLA. Postęp rozszczepiania wiązań acetalo-estrowych śledzono metodą ^{1}H NMR w układzie wodnym HCl/deuterowany acetonitryl w 40 °C, co pozwoliło monitorować degradację w jednorodnym środowisku. Intensywność sygnału przypisanego protonom -OCH$_2$O- w wiązaniu acetalo-estrowym (4,78 ppm) stopniowo malała w czasie, co wskazuje na rozszczepienie wiązań w łańcuchu (ko)polimeru. Jednocześnie intensywność sygnałów w zakresie 5,03–5,20 nie zmieniała się, co pozwala stwierdzić, że nie zachodzi degradacja wiązań estrowych w homosekwencjach LA-LA. Dodatkowo, analiza chromatografii z wykluczeniem objętości wykazała spadek masy cząsteczkowej po degradacji w kwasie: z 10 000 do 3 000 g/mol dla (ko)polimerówPLA z PDXP i z 13 000 do 3 500 g/mol dla (ko)polimerów PLA z Cl-DXL w ciągu 24 h, co wynika z pękania wiązania acetalo-estrowego w głównym łańcuchu.

Podsumowując, na tym etapie prac otrzymano (ko)polimery polilaktydu, zawierające boczne grupy chlorometylowe i allilowe, przeprowadzono modyfikacje łańcucha kopoliestru za pomocą reakcji „click” oraz wykazano przyspieszoną degradację zmodyfikowanych kopoliestrów w warunkach kwasowych.

2.2. Synteza i właściwości (ko)polimerów triblokowych typu ABA z zewnętrznymi blokami poliestrowymi A oraz łatwo degradowalnymi wewnętrznymi blokami poliacetalowymi B

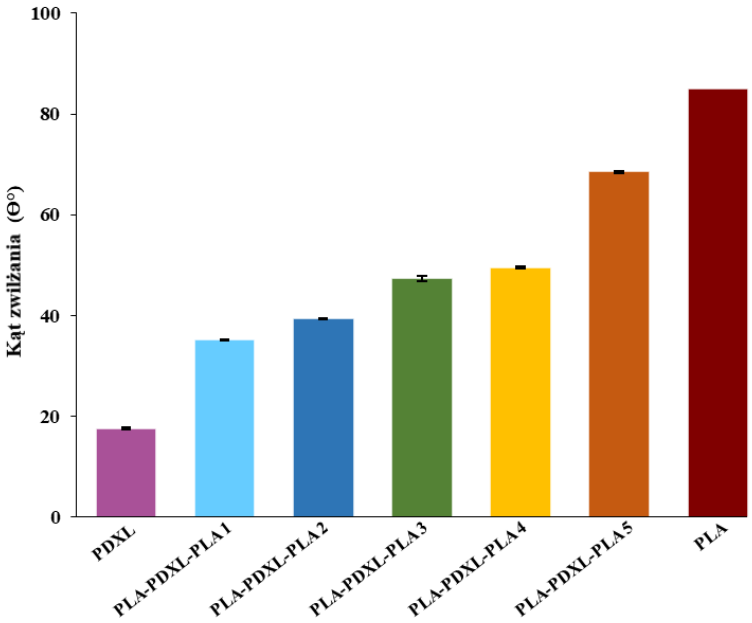
Rozwinięciem badań opisanych była synteza degradowalnych (ko)polimerów blokowych typu ABA, zawierających hydrofobowe poliestrowe bloki polilaktydu lub polikaprolaktonu oraz hydrofilowy blok poliacetalowy (poli(1,3-dioksolanu)) podatny na chemiczny recykling (PLA-PDXL-PLA). W pierwszym etapie badań, przygotowano α,ω-dihydroksylowe poliacetale (HO-PDXL-OH) w wyniku kationowej polimeryzacji z otwarciem pierścienia DXL. Proces prowadzono w obecności glikolu etylenowego pełniącego funkcję inicjatora oraz kwasu trifluorometanosulfonowego jako katalizatora. Zadane parametry syntezy umożliwiły przygotowanie dwóch dihydroksylowych poliacetali o średnich masach molowych 2 400 oraz 7 000 g/mol. Struktura i masa molowa otrzymanych poliacetali została scharakteryzowana za pomocą metod MALDI-TOF, SEC, ^{1}H NMR, ^{13}C NMR oraz HSQC NMR. Otrzymane dihydroksylowe poliacetale następnie wykorzystano jako makroinicjatory reakcji polimeryzacji z otwarciem pierścienia (ROP) L-laktydu lub kaprolaktonu, w której rolę katalizatora pełnił oktanian cyny (II). Polimeryzację przeprowadzono w masie, w podwyższonej temperaturze (105 °C dla laktydu oraz 80 °C dla kaprolaktonu). Wykazano, że zmieniając stosunek molowy

monomeru do makroinicjatora w mieszaninie reakcyjnej można uzyskać materiały o zróżnicowanej długości bloków poliestrowych oraz masach molowych w zakresie od 10 000 do 54 000 g/mol (Rysunek 9).



Rysunek 9. Analiza chromatograficzna GPC otrzymanych (ko)polimerów triblokowych (I) PLA-PDXL-PLA oraz (II) PCL-PDXL-PCL

Niezbędnym etapem pracy była weryfikacja blokowej struktury otrzymanych (ko)polimerów, do której wykorzystano analizę spektroskopową DOSY NMR. Współczynniki dyfuzji dla sygnałów pochodzących zarówno od segmentów poliestrowych, jak i poliacetalowych wykazywały niemal identyczne wartości co wskazuje, że sygnały należą do tej samej makrocząsteczki (ko)polimeru PLA-PDXL-PLA. Dodatkowym potwierdzeniem struktury (ko)polimerów była analiza ^{1}H i ^{13}C NMR, gdzie zaobserwowano przesunięcia chemiczne sygnałów, charakterystyczne dla homopolimerycznych bloków oraz wiązań pomiędzy blokami PDXL i PLA. Wykonane badania potwierdziły, że odpowiednio dobrane parametry składu mieszaniny reakcyjnej warunkują otrzymanie triblokowych (ko)polimerów o dobrze zdefiniowanej strukturze. Istotnym aspektem w badaniach była analiza wpływu segmentu poliacetalowego na charakter hydrofobowy materiałów. Pomiary kąta zwilżania wykazały, że wraz ze wzrostem udziału bloku poliacetalu w strukturze (ko)polimeru zwiększa się hydrofilowość materiału (Rysunek 10) co wskazuje na możliwość modulowania charakteru hydrofobowego materiału poprzez zmianę stosunku molowego poszczególnych bloków w (ko)polimerze.



Rysunek 10. Pomiar kąta zwilżania (ko)polimerów PLA-PDXL-PLA

Uzupełnieniem przedstawionych analiz było zbadanie właściwości termicznych otrzymanych polimerów metodami DSC i TGA. W przypadku omawianych (ko)polimerów zauważono, że przy relatywnie krótkich blokach polilaktydu, materiał jest amorficzny i charakteryzuje się niską temperaturę zeszklenia. Wraz ze wzrostem długości segmentów poliestrowych obserwowano pojawienie się piku topnienia charakterystycznego dla krystalitów PLA, jednakże obecność bloku poliacetalowego utrudniała proces krystalizacji co potwierdziło zauważalne obniżenie temperatur topnienia i entalpii topnienia względem niezmodyfikowanego PLA.

Kluczowym elementem badań było potwierdzenie zwiększonej podatności materiałów na proces degradacji. Założono, że obecność labilnych w środowisku kwaśnym wiązań acetalowych w wewnętrznym segmencie doprowadzi do przyspieszonej fragmentacji makrocząsteczki. Wykorzystanie metody spektroskopowej ^{1}H NMR umożliwiło obserwację stopniowego zaniku sygnałów o przesunięciach charakterystycznych dla PDXL przy równoległym braku zmian sygnałów pochodzących od PLA, dowodząc selektywnej degradacji segmentu poliacetalowgo. Wykazano, że szybkość hydrolizy bloku acetalowego można regulować poprzez zmianę stężenia kwasu. Mając na uwadze powyższe obserwacje, w ramach dalszej pracy badawczej oceniono również podatność syntezowanych (ko)polimerów PLA-PDXL-PLA na recykling chemiczny, ze szczególnym uwzględnieniem selektywnej depolimeryzacji bloku PDXL. Proces chemicznego recyklingu prowadzono w temperaturze 120 °C, pod ciśnieniem atmosferycznym, stosując kwas difenylofosforowy jako selektywny, kwasowy katalizator. Wykazano, że w warunkach podwyższonej temperatury selektywna degradacja bloku PDXL zachodzi w relatywnie łatwo,

osiągając pełną konwersję po 15 minutach. Głównym produktem rozkładu bloku PDXL był lotny 1,3-dioksolan, który sukcesywnie odprowadzano z układu reakcyjnego na drodze destylacji, uzyskując produkt o wysokiej czystości umożliwiającej jego zastosowanie w procesie powtórnej polimeryzacji. Analiza ^{1}H NMR oraz SEC nielotnej pozostałości poreakcyjnej wykazała obecność wyłącznie bloków PLA o niedużej masie molowej. Wnioski sformułowane na tym etapie pracy potwierdziły potencjał zsyntetyzowanych (ko)polimerów trójblokowych PLA-PDXL-PLA jako bazy do wytwarzania funkcjonalnych materiałów, wpisujących się w efektywniejszą gospodarkę odpadami polimerowymi.

2.3. Chemicznie recyklingowalne folie z termoplastycznych (ko)polimerów triblokowych ABA zawierających bloki A z polilaktydu oraz łatwo degradowalne bloki B z polidoksolanu

Zwieńczeniem badań było wykazanie, że wcześniej przygotowane (ko)polimery triblokowe typu ABA zawierające zewnętrzne bloki polilaktydowe A i wewnętrzne bloki poliacetalowe B ulegające degradacji w warunkach kwasowych mogą być wykorzystane do produkcji recyklingowalnych folii polimerowych. W tym celu, zsyntetyzowano (ko)polimery PLA-PDXL-PLA w skali kilkunastogramowej modyfikując procedurę opisaną w naszej wcześniejszej pracy.[56] Zgodnie z założeniem, iż poliestry są biodegradowalne jedynie przy masie molowej niższej niż 20 000 g/mol, masa molowa pojedynczego bloku PLA nie przekraczała tej wartości.[57] Otrzymano serię (ko)polimerów triblokowych PLA-PDXL$_{7000}$-PLA o masach molowych w zakresie 13 800 - 49 000 g/mol (SEC-MALLS) i różnej zawartości laktydu stosując w roli makroinicjatora PDXL o masie molowej 7 000 g/mol. (Tabela1)

Tabela 1. Charakterystyka (ko)polimerów PLA-PDXL$_{7000}$-PLA zastosowanych do otrzymywania folii

Skład (ko)polimeru	$M_{n\ PLA\ ramię,}$[a] (g mol^{-1})	$M_{n\ kop.}$[b] (g mol^{-1})	f_{LA}[c]
PLA$_{3400}$-PDXL$_{7000}$-PLA$_{3400}$	3 400	13 800	0,49
PLA$_{6900}$-PDXL$_{7000}$-PLA$_{6900}$	6 900	21 000	0,65
PLA$_{18500}$-PDXL$_{7000}$-PLA$_{18500}$	18 500	49 000	0,76

[a]obliczone na podstawie masy cząsteczkowej Mn wyznaczonej poprzez analizę chromatograficzna SEC-MALLS

[b] wyznaczona na podstawie analizy chromatograficznej SEC-MALLS

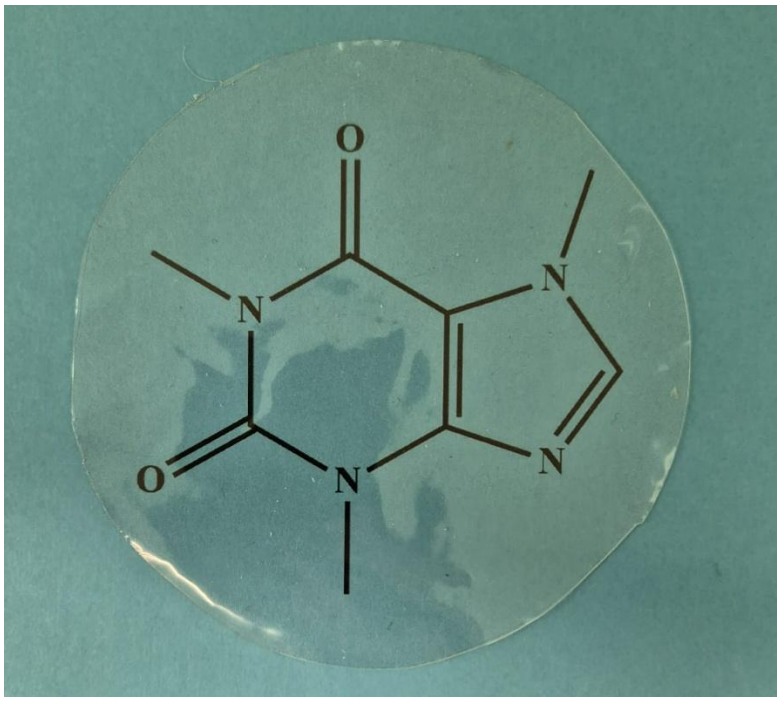
[c] obliczone na podstawie analizy ^{1}H NMR

W (ko)polimerach triblokowych uzyskanie właściwości elastomerów termoplastycznych wymaga rozdziału mikrofaz, w wyniku którego sztywne bloki tworzą domeny pełniące funkcję

fizycznych sieci, natomiast miękkie bloki stanowią ciągłą, elastyczną matrycę.[58] Mieszalność segmentów poliestrowych i poliacetalowych w otrzymanych (ko)polimerach oceniono na podstawie analizy DSC. Analiza DSC (ko)polimeru PLA_{3400}-$PDXL_{7000}$-PLA_{3400}, zawierającego 49 mol% estru, wykazała dwie temperatury przejścia szklistego (-51 °C i 48,9 °C), odpowiadające odpowiednio domenom bogatym w PDXL i PLA. W miarę wzrostu zawartości estru w (ko)polimerze obserwowano tylko jedną temperaturę przejścia szklistego zbliżoną do T_g PLA. Wszystkie analizowane próbki wykazały piki topnienia w zakresie 165-170 °C, charakterystyczne dla PLA. Niewielkie różnice w temperaturach topnienia oraz poszerzenie piku topnienia, szczególnie widoczne w (ko)polimerze PLA_{3400}-$PDXL_{7000}$-PLA_{3400}, mogą wskazywać na zaburzoną krystalizację PLA spowodowaną obecnością segmentów PDXL. Wprowadzenie segmentów PDXL zakłóca formowanie jednorodnych lameli PLA, prowadząc do bardziej heterogennej populacji kryształów, co skutkuje szerszym i mniej wyraźnym pikiem topnienia. Warto zauważyć, że wzrost zawartości jednostek estrowych w (ko)polimerze przyczynił się do zwiększenia stopnia krystaliczności z 10 % do 26 %.

W kolejnym etapie, oceniono podatność (ko)polimerów PLA-$PDXL_{7000}$-PLA na degradację w obecności zewnętrznego katalizatora kwasowego, stosując analizę TGA. Oczyszczone (ko)polimery wykazały wartość $T_{d,5\%}$ na poziomie około 220 °C, natomiast dodatek kwasu difenylofosforowego do matrycy (ko)polimerów skutecznie katalizował degradację, obniżając ten parametr do 160 °C. W celu potwierdzenia termicznej stabilności (ko)polimerów podczas wytwarzania folii metodą prasowania na gorąco, przeprowadzono izotermiczną analizę TGA czystych (ko)polimerów w 180 °C, w trakcie której nie zaobserwowano istotnej utraty masy podczas 5-minutowego eksperymentu. W kolejnym etapie przygotowano folie polimerowe stosując metodę prasowania na gorąco w 180 °C w ciągu 3 min. Proces ten pozwolił na uzyskanie bezbarwnych, przezroczystych folii polimerowych jak pokazano na Rysunku 11.

Otrzymane folie z (ko)polimerów PLA-$PDXL_{7000}$-PLA, różniących się masą cząsteczkową zewnętrznych bloków scharakteryzowano za pomocą jednoosiowego rozciągania, oraz zbadano odporność na starzenie oraz transparentność. Dla porównania przeanalizowano również folię przygotowaną z granulatu PLA komercyjnie dostępnego.



Rysunek 11. Folia polimerowa otrzymana z przygotowanych (ko)polimerów PLA-PDXL$_{7000}$-PLA

Analiza krzywych naprężenie-odkształcenie wykazała istotne różnice między foliami przygotowanymi z (ko)polimerów triblokowych o różnej długości zewnętrznych bloków PLA. Próbka folii przygotowana z (ko)polimeru PLA$_{3400}$-PDXL$_{7000}$-PLA$_{3400}$ wykazała największe odkształcenie i znaczne wydłużenie przy zerwaniu, co wiąże się ze stosunkowo niską wytrzymałością na rozciąganie. Dodatkowo wartość wydłużenia przy zerwaniu przekracza 191%, wskazując na stosunkowo wysoką wytrzymałość na rozciąganie, porównywalną z typowymi elastomerami oraz poliolefinami stosowanymi do otrzymywania folii i opakowań. Zwiększenie molowej zawartości LA w ((f_{LA} = 0,65) doprowadziła do wzrostu wytrzymałości na rozciąganie folii, przy jednoczesnym zmniejszeniu wydłużenia przy zerwaniu. Dalsze zwiększenie udziału LA w (ko)polimerze (PLA$_{18500}$-PDXL$_{7000}$-PLA$_{18500}$) do zawartości molowej równiej 0,76 spowodowało wzrost kruchości otrzymanych folii. Analiza odporności folii na starzenie (40°C, wilgotność 50%) ujawniła brak istotnych statystycznie zmian masy folii przed i po kondycjonowaniu. Badanie przezroczystość folii polimerowych za pomocą metody UV/Vis wykazały transmitancję powyżej 90% w zakresie światła widzialnego dla wszystkich badanych folii, co klasyfikuje je jako materiały wysoce przezroczyste. W zakresie promieniowania UV (280–400 nm) zaobserwowano spadek transmisji światła do około 60% dla próbek zawierających 65% i 76% molowych laktydu, przy czym wyższy stopień krystaliczności korelował ze zwiększoną zdolnością blokowania promieniowania UV. Jedną z kluczowych właściwości folii

opakowaniowych jest przepuszczalność wobec gazów i pary wodnej. Spośród badanych materiałów najlepsze właściwości barierowe wykazała folia przygotowana z (ko)polimeru PLA_{6900}-$PDXL_{7000}$-PLA_{6900}, w której obecność faz krystalicznych znacząco zmniejszyła przepuszczalność tlenu. Natomiast w próbce folii przygotowanej z (ko)polimeru PLA_{3400}-$PDXL_{7000}$-PLA_{3400} separacja faz doprowadziła do pogorszenia właściwości barierowych. Folia PLA_{18500}-$PDXL_{7000}$-PLA_{18500} nie została poddana analogicznym badaniom właściwości, ze względu na jej wysoką kruchość i podatność na uszkodzenia podczas pomiarów. Należy zauważyć, że folia otrzymana z komercyjnego polilaktydu wykazywała charakter amorficzny, podczas gdy folie przygotowane z syntetyzowanych (ko)polimerów charakteryzowały się częściową krystalicznością.

Tak scharakteryzowane folie poddano chemicznemu recyklingowi w obecności kwasu difenylofosforowego, w kolbie destylacyjnej w temperaturze 150 °C, pod ciśnieniem atmosferycznym. W podwyższonej temperaturze materiał polimerowy uległ szybkiej degradacji, co umożliwiło efektywne odzyskanie monomeru - 1,3-dioksolanu. Co istotne, polilaktyd pozostały po destylacji, charakteryzował się masą molową poniżej 20 000 g/mol, co według literatury wskazuje, że może on łatwo ulegać procesowi biodegradacji.[59] Wyniki te potwierdziły, że folie polimerowe przygotowane z (ko)polimerów PLA-PDXL-PLA wykazują duży potencjał w zakresie efektywnego recyklingu chemicznego.

Podsumowanie

W niniejszej dysertacji opracowano metodę syntezy poliestrów zawierających w swojej strukturze jednostki acetalowe. Wykazano, że wprowadzenie wiązania acetalowego do makrocząsteczek wpływa na właściwości fizykochemiczne materiałów, zwiększa ich podatność na degradację, umożliwiając przeprowadzenie recyklingu chemicznego. Po raz pierwszy otrzymano (ko)polimery laktydu z funkcyjnymi cyklicznymi acetalami wyposażonymi w boczne grupy allilowe i chlorometylowe oraz potwierdzono ich zwiększoną degradowalność w wyniku selektywnego rozszczepienia wiązań w kwaśnym środowisku. Jednocześnie potwierdzono, że otrzymane kopoliestry można łatwo zmodyfikować przy użyciu reakcji typu „click", wprowadzając do łańcucha różne grupy funkcyjne, otwierające możliwości syntezy złożonych układów polimerowych.

Zbadano również możliwość otrzymywania trójblokowych (ko)polimerów typu ABA zawierających wewnętrzne hydrofilowe bloki poliacetalu oraz zewnętrzne hydrofobowe bloki poliestrowe. Wykorzystanie dihydroksylowego poliacetalu jako makroinicjatora kopolimeryzacji

z otwarciem pierścienia cyklicznych estrów umożliwiło przygotowanie (ko)polimerów o dobrze zdefiniowanej strukturze, modulowanych właściwościach fizykochemicznych oraz kontrolowanej masie molowej. Udowodniono, że zmiana stosunku jednostek estrowych do acetalowych w (ko)polimerze umożliwia kontrolowanie charakteru hydrofobowo-hydrofilowego oraz krystaliczności. Przeprowadzone badania potwierdziły, że segment poliacetalowy ulega selektywnej depolimeryzacji do monomerycznego 1,3-dioksolanu.

W ostatnim kroku opracowano folie polimerowe z wcześniej przygotowanych triblokowych (ko)polimerów PLA-PDXL-PLA oraz zbadano ich właściwości mechaniczne. Otrzymano transparentne w zakresie światła widzialnego, termoplastyczne folie wykazujące dobre właściwości barierowe oraz charakteryzujące się wysokimi wartościami wydłużenia przy zerwaniu. Udowodniono, że otrzymane folie są stabilne podczas przetwarzania oraz, że mogą zostać poddane recyklingowi chemicznemu poprzez selektywną depolimeryzację bloku poli(1,3-dioksolanu).

Program badań zrealizowany w ramach pracy doktorskiej przyczynił się do opracowania nowej strategii projektowania kopoliestrów z jednostkami acetalowymi i reprezentuje podejście umożliwiające wydajny recykling chemiczny oraz kontrolowaną degradację nowoczesnych materiałów funkcjonalnych.

3. Literatura

[1] B.A. Abel, G.W. Coates, Introduction: The Future of Plastics Sustainability, Chem. Rev. 125 (2025) 1255–1256. https://doi.org/10.1021/acs.chemrev.4c00958.

[2] M.R. Azani, A. Hassanpour, High-performance polymer nanocomposites: advanced fabrication methods and critical insights, Journal of Polymer Research 31 (2024). https://doi.org/10.1007/s10965-024-04025-0.

[3] M. Esterhuizen, Y.J. Kim, Effects of polypropylene, polyvinyl chloride, polyethylene terephthalate, polyurethane, high-density polyethylene, and polystyrene microplastic on Nelumbo nucifera (Lotus) in water and sediment, Environmental Science and Pollution Research 29 (2022) 17580–17590. https://doi.org/10.1007/s11356-021-17033-0.

[4] M.E. Kirby, A. Hornung, M. Ouadi, M.K. Theodorou, The role of thermo-catalytic reforming for energy recovery from food and drink supply chain wastes, in: Energy Procedia, Elsevier Ltd, 2017: pp. 15–21. https://doi.org/10.1016/j.egypro.2017.07.279.

[5] L. Cederholm, J. Wohlert, P. Olsén, M. Hakkarainen, K. Odelius, "Like Recycles Like": Selective Ring-Closing Depolymerization of Poly(L-Lactic Acid) to L-Lactide, Angew. Chem. Int. Ed. 61 (2022). https://doi.org/10.1002/anie.202204531.

[6] M. Häußler, M. Eck, D. Rothauer, S. Mecking, Closed-loop recycling of polyethylene-like materials, Nature 590 (2021) 423–427. https://doi.org/10.1038/s41586-020-03149-9.

[7] A. So, È. Êrd, M. Stolt, Properties of lactic acid based polymers and their correlation with composition, n.d. www.elsevier.com/locate/ppolysci.

[8] S. Momeni, K. Craplewe, M. Safder, S. Luz, D. Sauvageau, A. Elias, Accelerating the Biodegradation of Poly(lactic acid) through the Inclusion of Plant Fibers: A Review of Recent Advances, ACS Sustain. Chem. Eng. 11 (2023) 15146–15170. https://doi.org/10.1021/acssuschemeng.3c04240.

[9] K. Wang, Z. Sun, W. Guo, M. Chen, C. Zhu, J. Fei, Y. Liu, H. He, Y. Cao, X. Bao, Upgrading Waste Polylactide via Catalyst-Controlled Tandem Hydrolysis-Oxidation, ChemSusChem 16 (2023). https://doi.org/10.1002/cssc.202301128.

[10] K. Ragaert, L. Delva, K. Van Geem, Mechanical and chemical recycling of solid plastic waste, Waste Management 69 (2017) 24–58. https://doi.org/10.1016/j.wasman.2017.07.044.

[11] K. Hamad, M. Kaseem, F. Deri, Recycling of waste from polymer materials: An overview of the recent works, Polym. Degrad. Stab. 98 (2013) 2801–2812. https://doi.org/10.1016/j.polymdegradstab.2013.09.025.

[12] N. Von Thienen, T. Consulting, M. Patel, Recycling of Plastics in Germany, n.d.

[13] S.M. Aldosari, B.M. AlOtaibi, K.S. Alblalaihid, S.A. Aldoihi, K.A. AlOgab, S.S. Alsaleh, D.O. Alshamary, T.H. Alanazi, S.D. Aldrees, B.A. Alshammari, Mechanical Recycling of Carbon Fiber-Reinforced Polymer in a Circular Economy, Polymers (Basel). 16 (2024). https://doi.org/10.3390/polym16101363.

[14] A.E. Krauklis, C.W. Karl, A.I. Gagani, J.K. Jørgensen, Composite material recycling technology—state-of-the-art and sustainable development for the 2020s, Journal of Composites Science 5 (2021). https://doi.org/10.3390/jcs5010028.

[15] T. Muringayil Joseph, S. Azat, Z. Ahmadi, O. Moini Jazani, A. Esmaeili, E. Kianfar, J. Haponiuk, S. Thomas, Polyethylene terephthalate (PET) recycling: A review, Case Studies in Chemical and Environmental Engineering 9 (2024) 100673. https://doi.org/10.1016/j.cscee.2024.100673.

[16] K.A. Sarpong, F.A. Adesina, L.W. DeVetter, K. Zhang, K. DeWhitt, K.R. Englund, C. Miles, Recycling agricultural plastic mulch: limitations and opportunities in the United States, Circular Agricultural Systems 4 (2024) 0–0. https://doi.org/10.48130/cas-0024-0003.

[17] A.R. Rahimi, J.M. Garciá, Chemical recycling of waste plastics for new materials production, Nat. Rev. Chem. 1 (2017). https://doi.org/10.1038/s41570-017-0046.

[18] T. Thiounn, R.C. Smith, Advances and approaches for chemical recycling of plastic waste, Journal of Polymer Science 58 (2020) 1347–1364. https://doi.org/10.1002/pol.20190261.

[19] I. Vollmer, M.J.F. Jenks, M.C.P. Roelands, R.J. White, T. van Harmelen, P. de Wild, G.P. van der Laan, F. Meirer, J.T.F. Keurentjes, B.M. Weckhuysen, Beyond Mechanical Recycling: Giving New Life to Plastic Waste, Angew. Chem. Int. Ed. 59 (2020) 15402–15423. https://doi.org/10.1002/anie.201915651.

[20] M. Babaei, M. Jalilian, K. Shahbaz, Chemical recycling of Polyethylene terephthalate: A mini-review, J. Environ. Chem. Eng. 12 (2024) 112507. https://doi.org/10.1016/j.jece.2024.112507.

[21] T. Muringayil Joseph, S. Azat, Z. Ahmadi, O. Moini Jazani, A. Esmaeili, E. Kianfar, J. Haponiuk, S. Thomas, Polyethylene terephthalate (PET) recycling: A review, Case Studies in Chemical and Environmental Engineering 9 (2024) 100673. https://doi.org/10.1016/j.cscee.2024.100673.

[22] X. Jiang, M. Shao, B. Bateer, Economic and environmental analysis of composite recycling techniques for the design of future waste management supply chains, Clean Technol. Environ. Policy 25 (2023) 1659–1671. https://doi.org/10.1007/s10098-022-02462-3.

[23] S.D. Anuar Sharuddin, F. Abnisa, W.M.A. Wan Daud, M.K. Aroua, A review on pyrolysis of plastic wastes, Energy Convers. Manag. 115 (2016) 308–326. https://doi.org/10.1016/j.enconman.2016.02.037.

[24] M.S. Qureshi, A. Oasmaa, H. Pihkola, I. Deviatkin, A. Tenhunen, J. Mannila, H. Minkkinen, M. Pohjakallio, J. Laine-Ylijoki, Pyrolysis of plastic waste: Opportunities and challenges, J. Anal. Appl. Pyrolysis 152 (2020). https://doi.org/10.1016/j.jaap.2020.104804.

[25] F. Abnisa, W.M.A. Wan Daud, A review on co-pyrolysis of biomass: An optional technique to obtain a high-grade pyrolysis oil, Energy Convers. Manag. 87 (2014) 71–85. https://doi.org/10.1016/j.enconman.2014.07.007.

[26] G. Lopez, M. Artetxe, M. Amutio, J. Alvarez, J. Bilbao, M. Olazar, Recent advances in the gasification of waste plastics. A critical overview, Renewable and Sustainable Energy Reviews 82 (2018) 576–596. https://doi.org/10.1016/j.rser.2017.09.032.

[27] S.A. Salaudeen, P. Arku, A. Dutta, Gasification of plastic solid waste and competitive technologies, in: Plastics to Energy: Fuel, Chemicals, and Sustainability Implications, Elsevier, 2018: pp. 269–293. https://doi.org/10.1016/B978-0-12-813140-4.00010-8.

[28] E. Anastasiou, K.O. Lorentz, G.J. Stein, P.D. Mitchell, Prehistoric schistosomiasis parasite found in the Middle East, Lancet Infect. Dis. 14 (2014) 553–554. https://doi.org/10.1016/S1473-3099(14)70794-7.

[29] C. G&et, M. Daroux+, F. Billaudi, Methane pyrolysis: thermodynamics, 1997.

[30] G.R. Mong, C.T. Chong, W.W.F. Chong, J.-H. Ng, H.C. Ong, V. Ashokkumar, M.-V. Tran, S. Karmakar, B.H.H. Goh, M.F. Mohd Yasin, Progress and challenges in sustainable pyrolysis technology: Reactors, feedstocks and products, Fuel 324 (2022) 124777. https://doi.org/10.1016/j.fuel.2022.124777.

[31] L. Alaerts, M. Augustinus, K. Van Acker, Impact of bio-based plastics on current recycling of plastics, Sustainability (Switzerland) 10 (2018). https://doi.org/10.3390/su10051487.

[32] E. Rudnik, Composting methods and legislation, in: Compostable Polymer Materials, 2019: pp. 89–110.

[33] Biodegradability testing of compostable polymer materials 6.1. DEFINITIONS RELATED TO BIODEGRADATION TESTING Maximum level of biodegradation (ISO/DIS I4855 part 2), n.d.

[34] M. Fogašová, S. Figalla, L. Danišová, E. Medlenová, S. Hlaváčiková, Z. Vanovčanová, L. Omaníková, A. Baco, V. Horváth, M. Mikolajová, J. Feranc, J. Bočkaj, R. Plavec, P. Alexy, M. Repiská, R. Přikryl, S. Kontárová, A. Báreková, M. Sláviková, M. Koutný, A. Fayyazbakhsh, M. Kadlečková, PLA/PHB-Based Materials Fully Biodegradable under Both Industrial and Home-Composting Conditions, Polymers (Basel). 14 (2022). https://doi.org/10.3390/polym14194113.

[35] R. Mouhoubi, M. Lasschuijt, S. Ramon Carrasco, H. Gojzewski, F.R. Wurm, End-of-life biodegradation? how to assess the composting of polyesters in the lab and the field, Waste Management 154 (2022) 36–48. https://doi.org/10.1016/j.wasman.2022.09.025.

[36] M.A. Elsawy, K.H. Kim, J.W. Park, A. Deep, Hydrolytic degradation of polylactic acid (PLA) and its composites, Renewable and Sustainable Energy Reviews 79 (2017) 1346–1352. https://doi.org/10.1016/j.rser.2017.05.143.

[37] K.J. Jem, B. Tan, The development and challenges of poly (lactic acid) and poly (glycolic acid), Advanced Industrial and Engineering Polymer Research 3 (2020) 60–70. https://doi.org/10.1016/j.aiepr.2020.01.002.

[38] F. Von Burkersroda, L. Schedl, A.G. Opferich, Why degradable polymers undergo surface erosion or bulk erosion, 2002.

[39] D. da Silva, M. Kaduri, M. Poley, O. Adir, N. Krinsky, J. Shainsky-Roitman, A. Schroeder, Biocompatibility, biodegradation and excretion of polylactic acid (PLA) in medical

implants and theranostic systems, Chemical Engineering Journal 340 (2018) 9–14. https://doi.org/10.1016/j.cej.2018.01.010.

[40] F.M. Lamberti, L.A. Román-Ramírez, P. Mckeown, M.D. Jones, J. Wood, Kinetics of alkyl lactate formation from the alcoholysis of poly(lactic acid), Processes 8 (2020). https://doi.org/10.3390/PR8060738.

[41] A. Ramos, J. Berzosa, J. Espí, F. Clarens, A. Rouboa, Life cycle costing for plasma gasification of municipal solid waste: A socio-economic approach, Energy Convers. Manag. 209 (2020). https://doi.org/10.1016/j.enconman.2020.112508.

[42] G. Raia, S. Marullo, G. Lazzara, G. Cavallaro, S. Marino, P. Cancemi, F. D'Anna, Upcycling of Poly(lactic acid) Waste: A Valuable Strategy to Obtain Ionic Liquids, ACS Sustain. Chem. Eng. 11 (2023) 17870–17880. https://doi.org/10.1021/acssuschemeng.3c07024.

[43] F. Wu, Y. Wang, Y. Zhao, M. Tang, W. Zeng, Y. Wang, X. Chang, J. Xiang, B. Han, Z. Liu, Lactate anion catalyzes aminolysis of polyesters with anilines, 2023. https://www.science.org.

[44] K.C. Frish, Cyclic monomers, in: High Polymers, Wiley-Intersciences, 1973.

[45] K. Penczek, S.; Kubisa, P.; Matyjaszewski, Cationic Ring-Opening Polymerization of Heterocyclic Monomers,Part II: Synthetic Applications, Springer-Verlag, Berlin, Germany, 1985.

[46] R. Szymanski, P. Kubisa, S. Penczek, Mechanism of cyclic acetal polymerization. End of a controversy?, Macromolecules 16 (1983) 1000–1008. https://doi.org/10.1021/ma00240a034.

[47] H.G. Hester, B.A. Abel, G.W. Coates, Ultra-High-Molecular-Weight Poly(Dioxolane): Enhancing the Mechanical Performance of a Chemically Recyclable Polymer, J. Am. Chem. Soc. 145 (2023) 8800–8804. https://doi.org/10.1021/jacs.3c01901.

[48] A.M.J. Coenen, J.A.W. Harings, S. Ghazanfari, S. Jockenhoevel, K. V. Bernaerts, Formation of cyclic structures in the cationic ring-opening polymerization of 1,3-dioxolane, RSC Adv. 10 (2020) 9623–9632. https://doi.org/10.1039/d0ra00904k.

[49] B.A. Abel, R.L. Snyder, G.W. Coates, Chemically recyclable thermoplastics from reversible-deactivation polymerization of cyclic acetals, Science (1979). 373 (2021) 783–789. https://doi.org/10.1126/science.abh0626.

[50] S. Penczek, J. Pretula, Activated Monomer Mechanism (AMM) in Cationic Ring-Opening Polymerization. The Origin of the AMM and Further Development in Polymerization of Cyclic Esters, ACS Macro Lett. 10 (2021) 1377–1397. https://doi.org/10.1021/acsmacrolett.1c00509.

[51] A.M.J. Coenen, J.A.W. Harings, S. Ghazanfari, S. Jockenhoevel, K. V. Bernaerts, Formation of cyclic structures in the cationic ring-opening polymerization of 1,3-dioxolane, RSC Adv. 10 (2020) 9623–9632. https://doi.org/10.1039/d0ra00904k.

[52] P. Kubisa, S. Penczek, Cationic activated monomer polymerization of heterocyclic monomers, 1999.

[53] J.M. Williams, H.-R. Schulten, N.E. Vanderborgh, R.D. Walker, Polymerization-depolymerization of 1,3-dioxolane, 1992.

[54] P.Kubisa.K.M. S. Penczek, Cationic Ring-Opening Polymerization, Advances in Polymer Science 68/69 (1985) 91–135.

[55] F. Schmid, Understanding and Modeling Polymers: The Challenge of Multiple Scales, ACS Polymers Au 3 (2023) 28–58. https://doi.org/10.1021/acspolymersau.2c00049.

[56] K. Cichoń, B. Kost, M. Basko, Synthesis and properties of ABA-triblock copolymers from polyester A-blocks and easily degradable polyacetal B-blocks, Polym. Chem. 13 (2022) 5243–5255. https://doi.org/10.1039/d2py00620k.

[57] ChemSusChem - 2023 - Wang - Upgrading Waste Polylactide via Catalyst-Controlled Tandem Hydrolysis-Oxidation.pdf, (n.d.).

[58] A. Hotta, E. Cochran, J. Ruokolainen, V. Khanna, G.H. Fredrickson, E.J. Kramer, Y.-W. Shin, F. Shimizu, A.E. Cherian, P.D. Hustad, J.M. Rose, G.W. Coates, Semicrystalline thermoplastic elastomeric polyolefins: Advances through catalyst development and macromolecular design, 2006. www.pnas.orgcgidoi10.1073pnas.0602894103.

[59] T.F. Garrison, A. Murawski, R.L. Quirino, Bio-based polymers with potential for biodegradability, Polymers (Basel). 8 (2016). https://doi.org/10.3390/polym8070262.

4. Spis wszystkich publikacji i osiągnięć naukowych

4.1. Publikacje

1. **Karolina Cichoń**, Bartłomiej Kost*, Malgorzata Basko, *Synthesis and properties of ABA-triblock copolymers from polyester A-blocks and easily degradable polyacetal B-blocks*, Polymer Chemistry, 2022,13, 5243-5255
2. Agnieszka Kobylińska, Bartłomiej Kost*, **Karolina Cichoń**, Irena I Bąk-Sypień, Marek Brzeziński, *Stereocomplexed Microparticles as Quercetin Carriers for Improving Plant Growth During Salinity Stress*, 2023, Journal of Polymers and the Environment, 31, 1209–1220
3. **Karolina Cichoń**, Irena I. Bak-Sypien, Malgorzata Basko, Bartłomiej Kost*, *Synthesis and Characterization of Functionalized Polylactides Containing Acetal Units*, Macromolecules 2023, 56, 6951−6967
4. Bartłomiej Kost*, Marta Socka, **Karolina Cichoń**, Marek Brzeziński, Malgorzata Basko, Tadeusz Biela, *Molar mass determination via linear regression from SEC measurements: The case of polylactide, polycaprolactone and poly (2, 2-dimethylthrimethylene carbonate)*, Polymer Advanced Technologies, 2024, 35, e6296
5. **Karolina Cichoń**, Bartłomiej Kost*, Marta Safandowska, Artur Różański, Malgorzata Basko, *Chemically recyclable films from thermoplastic ABA-triblock copolymers containing polylactide A-blocks and easily degradable polydioxolane B-block - towards the novel type of sustainable plastics*, Polymer, 2026, 344**,**129501
6. **Karolina Cichoń**, Bartłomiej Kost*****, Malgorzata Basko, Przemysław Kubisa, Karin Odelius, Minna Hakkarainen, *Polyethylene-like materials containing hydrolysable main-chain linkages: design, degradation and chemical recycling*, European Polymer Journal, 2026, 255, 114929

4.2. Postery

1. **Karolina Cichoń**, Bartłomiej Kost, Malgorzata Basko**,** *Synteza i charakterystyka funkcjonalizowanego polilaktydu zawierającego jednostki acetalowe***,** X Łódzkie Sympozjum Doktorantów Łódź, 18-19.05. 2023
2. **Karolina Cichoń**, Bartłomiej Kost, Malgorzata Basko**,** *Poli(laktyd) w drodze do zrównoważonego rozwoju: wprowadzenie funkcyjnych acetali do łańcucha poliestru*, XIV Sesja Magistrantów i Doktorantów Łódzkiego Środowiska Chemików, Łódź, 13.06.2023

3. **Karolina Cichoń**, Bartłomiej Kost, Malgorzata Basko, *Synthesis of degradable ABA triblock copolymers with controlled block lengths,* XXIII Scientific Conference: Controlled Polymerization, Łódź, 03.06.2024
4. **Karolina Cichoń**, Bartłomiej Kost, Malgorzata Basko, *Polylactide modifications: Towards sustainability,* 85th Prague Meeting on Macromolecules 11th Conference on green chemistry and nanotechnologies in polymeric materials, Praga, 24-28.06.2024,
5. **Karolina Cichoń**, Bartłomiej Kost, Malgorzata Basko**,** *Poly(lactide) for sustainable development: Incorporation of functional acetals into the polyester backbone*, EPF European Polymer Congress, Groningen, 22-27.06.2026

4.3. Komunikaty ustne

1. **Karolina Cichoń**, Bartłomiej Kost, Malgorzata Basko**,** *Synteza i właściwości kopolimerów blokowych typu „ABA" zawierających poliestrowe bloki „A" oraz poliacetalowe bloki „B", 64 Zjazd Naukowego Polskiego Towarzystwa Chemicznego*, Lublin 11-16.09.2022
2. **Karolina Cichoń**, Bartłomiej Kost, Malgorzata Basko**,** *Synthesis and properties of ABA-triblock copolymers from polyester A-blocks and easily degradable polyacetal B-blocks,* Nordic Polymer Days, Kopenhaga, 8-10.05.2023
3. **Karolina Cichoń**, Bartłomiej Kost, Malgorzata Basko**,** *Poly(Lactide) on the path to sustainable development: introducing functional acetals into the polyester chain*, 7th Conference of doctoral students of the PAS, Wrocław, 13-15.10.2023
4. **Karolina Cichoń**, Bartłomiej Kost, Malgorzata Basko**,** *W drodze do zrównoważonego rozwoju. Modyfikacje łańcucha poli(laktydu) i jego kopolimery*, XI Łódzkie Sympozjum Doktorantów Łódź, 16-17.05. 2024
5. **Karolina Cichoń**, Bartłomiej Kost, Malgorzata Basko**,** *Kopolimery cyklicznych estrów i acetali: nowe perspektywy w dążeniu do zrównoważonego rozwoju*, XV Sesja Magistrantów i Doktorantów Łódzkiego Środowiska Chemików, Łódź, 12.06.2024
6. Bartłomiej Kost**, Karolina Cichoń**, Malgorzata Basko**,** *Synthesis and properties of ABA- triblock copolymers from polyester A-blocks and easily degradable polyacetal B-blocks,* European Polymer Federation Congress, Groningen, 22-27.06.2025

4.4. Zgłoszenia patentowe

1. Małgorzata Baśko, Bartłomiej Kost, **Karolina Cichoń**, Marta Safandowska, *Recykling materiałów polimerowych z kopolimerów blokowych typu ABA,*

zawierających zewnętrzne bloki poliestru (A) oraz wewnętrzny blok poliacetalu (B), 2025, P.452791

4.5. Wyróżnienia i nagrody

1. Nagroda za najlepsze wystąpienie ustne podczas konferencji XV Sesja Magistrantów i Doktorantów Łódzkiego Środowiska Chemików, Łódź, 12.06.2024
2. Wyróżnienie Dyrektora Szkoły Doktorskiej BioMedChem za interesujące wyniki przedstawione podczas konferencji XV Sesja Magistrantów i Doktorantów Łódzkiego Środowiska Chemików, Łódź, 12.06.2024
3. Nagroda za najlepsze wystąpienie dydaktyczne podczas konferencji XI Łódzkie Sympozjum Doktorantów Łódź, 16-17.05. 2024
4. Nagroda za 3-cie najlepsze wystąpienie ustne podczas 7th Conference of doctoral students of the PAS, Wrocław, 13-15.10.2023

4.6. Staże i szkolenia

1. Staż naukowy 11.2024-03.2025 - KTH Królewski Uniwersytet Technologiczny w Sztokholmie (3 miesiące)
2. Staż naukowy 07.2025 - Uniwersytet Jagielloński, Zespół Elektrochemii (2 tygodnie)
3. Staż naukowy 09.2025 - Instytut Agrofizyki im. Bohdana Dobrzańskiego PAN (2 tygodnie)

4.7. Działalność organizacyjna i popularyzatorska

1. Członkini Kolegium Nadzorczego Doktorantów UŁ oraz Samorządowej Komisji Rewizyjnej Doktorantów UŁ w latach 2022-2024
2. Członkini zespołu ds. organizacji VII edycji Konferencji Doktorantów Polskiej Akademii Nauk (KonDokPAN 2023), organizowanej przez Radę Samorządu Doktorantów PAN
3. Udział w XXII Festwialu Nauki, Techniki i Sztuki w Łodzi, 2023
4. Przewodnicząca komitetu organizacyjnego konferencji XXIII Scientific Conference: Controlled Polymerization, 2024
5. Udział w Łódzkiej Nocy Naukowców, 2024
6. Udział w XXIII Festwialu Nauki, Techniki i Sztuki w Łodzi, 2024
7. Członkini zespołu ds. organizacji XII Łódzkiego Sympozjum Doktorantów, 2025
8. Udział w Łódzkiej Nocy Naukowców, 2025
9. Przedstawicielka Doktorantów w Radzie Naukowej Centrum Badań Molekularnych i Makromolekularnych PAN w Łodzi w latach 2025-2026

10. Udział w Wielkim Pikniku Europejskim w Łodzi, 26.06.2026, Łódź
11. Udział w Pikniku Rodzinnym Łódzkiej Specjalnej Strefy Ekonomicznej, 12.07.2026, Łódź

5. Oświadczenia współautorów i załączone publikacje

P1. **Karolina Cichoń**, Bartłomiej Kost, Malgorzata Basko, Synthesis and properties of ABA-triblock copolymers from polyester A-blocks and easily degradable polyacetal B-blocks, Polymer Chemistry 2022,13, 5243-5255

P2. **Karolina Cichoń**, Irena I. Bak-Sypien, Malgorzata Basko, Bartłomiej Kost., Synthesis and characterization of functionalized polylactides containing acetal units**,** Macromolecules 2023, 56, 6951-6967

P3. **Karolina Cichoń**, Bartłomiej Kost, Marta Safandowska, Artur Różański, Małgorzata Basko, Chemically recyclable films from thermoplastic ABA-triblock copolymers containing polylactide A-blocks and easily degradable polydioxolane B-block - towards the novel type of sustainable plastics, Polymer 2026, 344, 129501

P4. **Karolina Cichoń**, Bartłomiej Kost, Malgorzata Basko, Przemysław Kubisa, Karin Odelius, Minna Hakkarainen, Polyethylene-like materials containing hydrolysable main-chain linkages: design, degradation and chemical recycling, European Polymer Journal, 2026, 255, 114929

Łódź 20.06.2026

mgr Karolina Cichoń

Centrum Badań Molekularnych

i Makromolekularnych Polskiej

Akademii Nauk

Oświadczenie o udziale oraz wykonanych zadaniach w ramach przygotowania artykułu naukowego

Oświadczam, że w ramach przygotowania następujących artykułów naukowych,

[P1] **Karolina Cichoń**, Bartłomiej Kost*, Malgorzata Basko, *Synthesis and properties of ABA-triblock copolymers from polyester A-blocks and easily degradable polyacetal B-blocks*, Polymer Chemistry, (2022),13, 5243-5255

[P2] **Karolina Cichoń**, Irena I. Bak-Sypien, Malgorzata Basko, Bartłomiej Kost*, *Synthesis and Characterization of Functionalized Polylactides Containing Acetal Units*, Macromolecules 2023, 56, 6951−6967

[P3] **Karolina Cichoń,** Bartłomiej Kost*, Marta Safandowska, Artur Różalski, Malgorzata Basko, *Chemically recyclable films from thermoplastic ABA-triblock copolymers containing polylactide A-blocks and easily degradable polydioxolane B-block - towards the novel type of sustainable plastics,* Polymer, 344 (2026), 129501

[P4] Karolina Cichoń, Bartłomiej Kost*,Małgorzata Basko, Przemysław Kubisa, Karin Odelius, Minna Hakkarainen, *Polyethylene-like materials containing hydrolysable main-chain linkages: design, degradation and chemical recycling,* European Polymer Journal, 2026, 255, 114929

Wykonałam następujące zadania badawcze:

[P1] Synteza telechelicznych poli(dioksolanów) użytych jako makroinicjatory polimeryzacji laktydu, synteza kopolimerów blokowych typu ABA zawierających zewnętrzne bloki polilaktydowe lub polikaprolaktonowe, wyznaczanie kąta zwilżania, przeprowadzenie hydrolizy oraz chemicznego recyklingu otrzymanych kopolimerów. Analiza otrzymanych wyników. Przygotowanie rysunków do manuskryptu

[P2] Synteza kopolimerów bezładnych laktydu z cyklicznymi podstawionymi acetalami, analiza otrzymanych wyników, przygotowanie rysunków do manuskryptu

[P3] Synteza kopolimerów blokowych, przygotowanie folii polimerowych metodą prasowania na gorąco, optymalizacja procesu przygotowania folii, badanie kąta zwilżania, przeprowadzenie badań związanych ze starzeniem otrzymanych folii oraz badań związanych z chemicznym recyklingiem, udział w przygotowaniu manuskryptu, przygotowanie rysunków do publikacji

[P4] Przygotowanie tekstu, edycja manuskryptu

Cichoń Karolina

mgr Karolina Cichoń

Łódź 12.06.2026

dr Bartłomiej Kost
Centrum Badań Molekularnych
i Makromolekularnych Polskiej
Akademii Nauk

Oświadczenie o udziale oraz wykonanych zadaniach w ramach przygotowania artykułu naukowego

Oświadczam, że w ramach przygotowania następujących artykułów naukowych,

[P1] Karolina Cichoń, Bartłomiej Kost*, Malgorzata Basko, *Synthesis and properties of ABA-triblock copolymers from polyester A-blocks and easily degradable polyacetal B-blocks*, Polymer Chemistry, (2022),13, 5243-5255

[P2] Karolina Cichoń, Irena I. Bak-Sypien, Malgorzata Basko, Bartłomiej Kost*, *Synthesis and Characterization of Functionalized Polylactides Containing Acetal Units*, Macromolecules 2023, 56, 6951−6967

[P3] Karolina Cichoń, Bartłomiej Kost*, Marta Safandowska, Artur Różański, Malgorzata Basko, *Chemically recyclable films from thermoplastic ABA-triblock copolymers containing polylactide A-blocks and easily degradable polydioxolane B-block - towards the novel type of sustainable plastics,* Polymer, 344 (2026), 129501

[P4] Karolina Cichoń, Bartłomiej Kost*,Małgorzata Basko, Przemysław Kubisa, Karin Odelius, Minna Hakkarainen, *Polyethylene-like materials containing hydrolysable main-chain linkages: design, degradation and chemical recycling,* European Polymer Journal, 2026, 255, 114929

Wykonałem następujące zadania badawcze:

[P1] Opracowanie metodologii syntezy polimerów, analiza i opracowanie danych do publikacji, korekta manuskryptu

[P2] Współautorstwo koncepcji pracy, nadzór nad prowadzonymi badaniami, przeprowadzenie badań wstępnych, opracowanie metodologii, analiza i opracowanie danych, korekta manuskryptu

[P3] Koncepcja pracy, opracowanie metodologii syntezy i chemicznego recyklingu, przygotowanie tekstu, nadzór na prowadzeniem badań, analiza otrzymanych wyników, przygotowanie manuskryptu

[P4] Koncpecja pracy, przygotowanie tekstu, korekta manuskryptu

Bartłomiej Kost

dr Bartłomiej Kost

Łódź 12.06.2026

dr hab. Małgorzata Baśko

Centrum Badań Molekularnych

i Makromolekularnych Polskiej

Akademii Nauk

Oświadczenie o udziale oraz wykonanych zadaniach w ramach przygotowania artykułu naukowego

Oświadczam, że w ramach przygotowania następujących artykułów naukowych,

.

[**P1**] Karolina Cichoń, Bartłomiej Kost*, Malgorzata Basko, *Synthesis and properties of ABA-triblock copolymers from polyester A-blocks and easily degradable polyacetal B-blocks*, Polymer Chemistry, (2022),13, 5243-5255

[**P2**] Karolina Cichoń, Irena I. Bak-Sypien, Malgorzata Basko, Bartłomiej Kost*, *Synthesis and Characterization of Functionalized Polylactides Containing Acetal Units*, Macromolecules 2023, 56, 6951−6967

[**P3**] Karolina Cichoń, Bartłomiej Kost*, Marta Safandowska, Artur Różański, Malgorzata Basko, *Chemically recyclable films from thermoplastic ABA-triblock copolymers containing polylactide A-blocks and easily degradable polydioxolane B-block - towards the novel type of sustainable plastics,* Polymer, 344 (2026), 129501

[P4] Karolina Cichoń, Bartłomiej Kost*,Małgorzata Basko, Przemysław Kubisa, Karin Odelius, Minna Hakkarainen, *Polyethylene-like materials containing hydrolysable main-chain linkages: design, degradation and chemical recycling,* European Polymer Journal, 2026, 255, 114929

Wykonałam następujące zadania badawcze:

[P1] Współautorstwo koncepcji pracy, nadzór nad wykonywanymi pracami, analiza wyników, przygotowanie manuskryptu oraz odpowiedzi na recenzje

[P2] Nadzór nad wykonywanymi pracami, analiza wyników, przygotowanie i korekta manuskryptu oraz przygotowanie odpowiedzi na recenzje

[P3] Współautorstwo koncepcji pracy, nadzór nad prowadzonymi badaniami, przygotowanie i korekta manuskryptu, analiza wyników

[P4] Przygotowanie tekstu manuskryptu

M Baśko

.....

dr hab. Małgorzata Baśko

Łódź 20.06.2026

dr inż. Irena Bąk-Sypień

Centrum Badań Molekularnych

i Makromolekularnych Polskiej

Akademii Nauk

Oświadczenie o udziale oraz wykonanych zadaniach w ramach przygotowania artykułu naukowego

Oświadczam, że w ramach przygotowania następujących artykułów naukowych,

[P1] Karolina Cichoń, Irena I. Bak-Sypien, Malgorzata Basko, Bartłomiej Kost*, *Synthesis and Characterization of Functionalized Polylactides Containing Acetal Units*, Macromolecules 2023, 56, 6951−6967

Wykonałam następujące zadania badawcze:

[P1] Wykonanie analizy GC-MS otrzymanych monomerów, przygotowanie fragmentu publikacji zawierającego opis otrzymanych wyników.

.....

dr inż. Irena Bąk-Sypień

Łódź, 19.06.2026

dr inż. Marta Safandowska

Centrum Badań Molekularnych i Makromolekularnych PAN
ul. Sienkiewicza 112, 90-363 Łódź

Oświadczenie o udziale oraz wykonanych zadaniach w ramach przygotowania artykułu naukowego

Oświadczam, że w publikacji:

[**P3**] Karolina Cichoń*, Bartłomiej Kost, Marta Safandowska, Artur Rozanski, Malgorzata Basko, *Chemically recyclable films from thermoplastic ABA-triblock copolymers containing polylactide A-blocks and easily degradable polydioxolane B-block - towards the novel type of sustainable plastics,* Polymer, 344 (2026), 129501.

mój wkład polegał na wykonaniu badań właściwości mechanicznych i barierowych folii polimerowych, wyznaczeniu indeksu płynięcia polimerów, analizie i interpretacji wyników, przygotowaniu tekstu publikacji oraz odpowiedzi dla recenzentów.

Marta Safandowska

dr inż. Marta Safandowska

Łódź 22.06.2026

dr hab. Artur Różański, prof. CBMiM

Centrum Badań Molekularnych

i Makromolekularnych Polskiej

Akademii Nauk

Oświadczenie o udziale oraz wykonanych zadaniach w ramach przygotowania artykułu naukowego

Oświadczam, że w ramach przygotowania następujących artykułów naukowych,

[P3] Karolina Cichoń*, Bartłomiej Kost, Marta Safandowska, Artur Różański, Malgorzata Basko, *Chemically recyclable films from thermoplastic ABA-triblock copolymers containing polylactide A-blocks and easily degradable polydioxolane B-block - towards the novel type of sustainable plastics,* Polymer, 344 (2026), 129501.

Wykonałem następujące zadania badawcze:

[P3] Nadzór nad badaniami związanymi z właściwościami barierowymi otrzymanych folii polimerowych, korekta tekstu publikacji.

Artur Różański

Elektronicznie podpisany przez Artur Różański
Data: 2026.06.22 20:02:09 +02'00'

…….

dr hab. Artur Różański

Łódź 20.08.2026

prof. dr hab. Przemysław Kubisa

Centrum Badań Molekularnych

i Makromolekularnych Polskiej

Akademii Nauk

Oświadczenie o udziale oraz wykonanych zadaniach w ramach przygotowania artykułu naukowego

Oświadczam, że w ramach przygotowania następujących artykułów naukowych,

[P1] Karolina Cichoń, Bartłomiej Kost*, Małgorzata Basko, Przemysław Kubisa, Karin Odelius, Minna Hakkarainen, *Polyethylene-like materials containing hydrolysable main-chain linkages: design, degradation and chemical recycling,* European Polymer Journal, 2026, 255, 114929,

Wykonałem następujące zadania badawcze:

[P1] Udział w przygotowaniu tekstu manuskryptu, edycja tekstu.

.....

Prof. dr hab. Przemysław Kubisa

Stockholm, 2026-08-17

Statement of Contribution and Tasks Performed in the Preparation of a Scientific Article

I hereby declare that, as part of the preparation of the following scientific article:

[**P1**] Karolina Cichoń, Bartłomiej Kost*, Małgorzata Basko, Przemysław Kubisa, Karin Odelius, Minna Hakkarainen, Polyethylene-like materials containing hydrolysable main-chain linkages: design, degradation and chemical recycling, European Polymer Journal, 2026, 255, 114929.

I performed the following research tasks:

[**P1**] Preparation of the initial manuscript draft, as well as proofreading, editing, and revision of the manuscript text.

Kind regards

Karin Odelius
Professor
Department of Fibre and Polymer Technology
Phone: 08 790 80 76
hoem@kth.se

Stockholm 14.08.2026

Professor Minna Hakkarainen,

KTH Royal Institute of Technology

in Sweden,

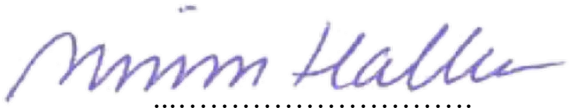
Statement of Contribution and Tasks Performed in the Preparation of a Scientific Article

I hereby declare that, as part of the preparation of the following scientific article:

[P1] Karolina Cichoń, Bartłomiej Kost*, Małgorzata Basko, Przemysław Kubisa, Karin Odelius, Minna Hakkarainen, *Polyethylene-like materials containing hydrolysable main-chain linkages: design, degradation and chemical recycling*, European Polymer Journal, 2026, 255, 114929.

I performed the following research tasks:

[P1] Preparation of the initial manuscript draft, as well as proofreading, editing, and revision of the manuscript text.



……

Prof. Minna Hakkarainen,

Publikacja 1:

Karolina Cichoń, Bartłomiej Kost, Malgorzata Basko, Synthesis and properties of ABA-triblock copolymers from polyester A-blocks and easily degradable polyacetal B-blocks, Polymer Chemistry 2022, 13, 5243-5255

Polymer Chemistry

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal

Published on 30 August 2022. Downloaded by Ghent University Library on 8/30/2022 10:31:30 AM.

Check for updates

Cite this: DOI: 10.1039/d2py00620k

Synthesis and properties of ABA-triblock copolymers from polyester A-blocks and easily degradable polyacetal B-blocks†

Karolina Cichoń, Bartłomiej Kost * and Malgorzata Basko *

Received 13th May 2022,
Accepted 21st August 2022

DOI: 10.1039/d2py00620k

rsc.li/polymers

Novel, degradable amphiphilic ABA triblock copolymers with a polyacetal chain as the hydrophilic internal block and polyesters as external hydrophobic segments were designed and prepared for the first time in a controlled manner. Initially, α,ω-hydroxy-terminated polyacetals were obtained *via* the cationic polymerization of dioxolane (DXL) conducted in the presence of ethylene glycol as an initiator and triflic acid as a catalyst. In the next step, the resulting polyacetals were used as efficient macroinitiators in the ring-opening polymerization (ROP) of selected cyclic esters catalysed by tin(II) octoate ($Sn(Oct)_2$). The length of the polyester blocks was varied by using different molar ratios of cyclic monomer (L-lactide or ε-caprolactone) to polyacetal macroinitiator (PDXL: $M_{n\ NMR}$ = 7000 g mol^{-1} or $M_{n\ NMR}$ = 2400 g mol^{-1}). High conversions of cyclic esters (>95%) afforded block copolymers with monomodal molar mass distributions and molar masses ranging from 10 000 g mol^{-1} to 56 000 g mol^{-1}. The formation of triblock block copolymers was proven by DOSY NMR. The resulting amphiphilic copolymers were characterized by ^{1}H NMR, ^{13}C NMR, SEC, DSC, and TGA. Additionally, the influence of the blocky copolymer structure on the degradability was investigated. Combining polyester blocks with polyacetal segments allowed the preparation of new materials with tuneable hydrophobic/hydrophilic balance and enhanced degradability.

Introduction

Currently, scientific research aimed at the design of materials that are easily recyclable or degraded constitutes an important direction in academia and industry.[1,2] The main reasons for this interest are mostly caused by the growing problems related to littering the natural environment with plastic waste.[3] At the same time, the biodegradability of polymers is a specific feature very often required for materials intended for biomedical applications.[4,5] For this purpose, continuous research is carried out on innovative synthetic materials that, after fulfilling their function, can undergo controlled degradation. As a result of extensive efforts, a wide variety of natural and synthetic degradable polymers have been investigated in search of the appropriate properties that can be matched to the intended function. The class of hydrolysable polymers includes high molecular weight compounds having ester, carbonate, anhydride, acetal, amide, or phosphate repeating units in the main chain that determine the temporary stability of the material.[6–8]

Due to their nontoxicity and appropriate mechanical properties, aliphatic polyesters and copolyesters are broadly exploited biodegradable materials.[9,10] This group of polymers plays a significant and continuously increasing role in the design of drug delivery formulations.[11] The most widely used polylactide, showing a favourable combination of many features, including the possibility of synthesis based on renewable sources, has been quite extensively tested in terms of its ability to replace traditional polymers obtained from fossil sources.[12,13] Undoubtedly, PLA has been increasingly used recently as "green" food packaging or disposable cutlery.[14]

To achieve fine-tuning of the physical properties to the intended function, cyclic esters are often copolymerized with properly selected comonomers.[15–17] Block copolymers containing degradable polyester segments represent a particularly interesting and useful class of materials.[18–21] Structural variations within building blocks, such as changes in the hydrophilicity or ability for crystallization, provide the possibility for tuning the thermal and degradation behaviour of the final block polymer. For the construction of block copolymers containing polyesters (polylactide or polycaprolactone) as external segments, nondegradable polymers such as poly(isobutylene), poly(dimethylsiloxane) or poly(thiophene) were used as

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland. E-mail: baskomeg@cbmm.lodz.pl, kost@cbmm.lodz.pl

† Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d2py00620k

Published on 30 August 2022. Downloaded by Ghent University Library on 8/30/2022 10:31:30 AM.

midblocks.[22–24] Additionally, block copolymers composed of degradable midblocks based on poly(3-hydroxybutyrate), poly(1,3-trimethylene carbonate), poly(1,5-dioxepan-2-one), and poly(menthide) or poly(lactide) have been reported.[15,25–27] By combining polyester segments with hydrophilic PEO segments, ABA block copolymers with improved hydrophilicity, swelling and crystallinity were obtained.[28,29] This type of copolymer is of great interest for applications in the field of sustained drug delivery when residual crystalline particles may be a potential source of inflammatory responses.[30] While there are examples of polyester ABA block copolymers in the literature, the goal of preparing this type of copolymer with enhanced degradability still represents a significant challenge.

Poly(1,3-dioxolane) (PDXL) is a water-soluble polyacetal that shows low T_g and sensitivity to pH.[31] As demonstrated, complex polymeric systems, including hydrogels and degradable networks, may be prepared using PDXL as a building block.[32,33] Importantly, it has recently been shown that in the presence of strong protic acids, PDXL can degrade into monomeric DXL in nearly quantitative yield, which enables the preparation of recyclable polymeric materials.[34] Additionally, we demonstrated that the introduction of acid-sensitive acetal units into the polyester chain had profound effects on the final copolymer properties, which manifested as changes in the crystallinity and degradation profile of the copolymers.[35] Since a significant acceleration of hydrolysis was observed for these copolymers, caused by the relatively small number of acetal units randomly distributed in the chain, it was justified to study the influence of the presence of the acetal block on the properties of the copolymers.

In the current study, directed toward developing polyester triblock copolymers with enhanced degradability, we attempted to apply di-hydroxy-functionalized PDXL as a macroinitiator for selected cyclic ester (lactide or caprolactone) ring-opening polymerization catalysed by $Sn(Oct)_2$. The present paper describes the first successful synthesis of copolymers consisting of polyester A-blocks linked to a hydrophilic, acid-sensitive polyacetal B-block. The obtained copolymers were characterized in terms of their structure, hydrophilicity, and thermal properties. The effect of the blocky structure on the susceptibility to degradation was investigated. From these studies, we concluded that the degradation rates of these triblock copolymers may be purposefully controlled, making them potentially useful recyclable materials.

Experimental part

Materials

L-LA acquired from Purac (99%, The Netherlands) was subjected to recrystallization from dry 2-propanol, sublimated and stored under reduced pressure. Anhydrous 1,3-dioxolane (DXL) (99.8%, BHT as an inhibitor) from Sigma Aldrich was distilled under reduced pressure directly before use. Anhydrous ethane-1,2-diol (EG) (99.8%), and diphenyl phosphate (DPP, 99%) were acquired from Sigma Aldrich and used as received. Tin(II) octoate ($Sn(Oct)_2$) was purchased from Sigma Aldrich, distilled under reduced pressure at 10^{-3} mbar at 140 °C, and stored over dried molecular sieves under vacuum. Methylene chloride (99.8%) from POCH was distilled over P_2O_5 and kept over the dried molecular sieves. Triflic acid (>99%) and CaO were purchased from Sigma Aldrich and used as received. Diethyl ether (99.5%), pentane, hexane (for analysis), and hydrochloric acid (36% water solution) were acquired from POCH and used without purification. Acetonitrile (containing approximately 0.6% mol of water) was purchased from Chem Solve and used as received.

Synthesis of polyacetal diol macroinitiators (HO-PDXL-OH)

Polymerization was carried out in a two-necked round bottom flask equipped with a magnetic stir bar. As an example, the synthesis of HO-$PDXL_{7000}$-OH ($M_{n\ NMR}$ = 7000 g mol^{-1}) is described. First, the vessel was degassed and filled with argon, and subsequently, methylene chloride was introduced (15 mL) through the rubber septum. Next, EG (56 μL, 0.9 mmol) and triflic acid (30 μL, 0.2 mmol) were added to the reaction mixture. Then, DXL (10 mL, 0.14 mol) was added dropwise to the solution by using an infusion pump at a rate of 0.59 mL per hour. After the instillation of the monomer, the mixture was additionally stirred for 2 hours; subsequently, CaO was added, and the reaction mixture was stirred for 24 hours. CaO was filtered off, and the polymer was precipitated into diethyl ether (yield = 65%). The homopolymer was characterized by ^{1}H NMR, ^{13}C NMR, SEC, TGA, and DSC. According to the above procedure, poly(dioxolane) with a lower molar mass ($M_{n\ NMR}$ = 2400 g mol^{-1}) was also prepared.

HO-$PDXL_{7000}$-OH. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 4.63 (s, 2H, –OCH_2O–), 3.60 (s, 4H, –OCH_2CH_2O–), 3.50 (br, 8 H,–OCH_2CH_2OH) ^{13}C NMR (400 MHz, DMSO-d_6): δ (ppm) = 95.4 (s, 1C, –OCH_2O–), 69.5 (s, 1C, OCH_2CH_2OH), 66.7 (s, 1C, –OCH_2CH_2O–), 60.5 (s, 1C, OCH_2CH_2OH).

HO-$PDXL_{7000}$-OH. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.76 (s, 2H, –OCH_2O–), 3.72 (s, 4H, –OCH_2CH_2O–), ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) = 92.9 (s, 1C, –OCH_2O–), 62.7 (s, 1C, –OCH_2CH_2O–).

Synthesis of PLA-PDXL-PLA copolymers

As an example, the synthesis of PLA_{2500}-$PDXL_{7000}$-PLA_{2500} is described. The copolymerization was performed using a high vacuum technique. Previously prepared HO-$PDXL_{7000}$-OH (M_n = 7000 g mol^{-1}, 0.5 g, 0.071 mmol) and the appropriate amount of L-LA (0.347 g, 2.4 mmol) were introduced into the glass ampoule. Next, a solution of tin(II) octoate in methylene chloride (0.1 mL, 0.15 mg $Sn(Oct)_2$ per mL CH_2Cl_2) was added to the reaction mixture. Then, the methylene chloride was removed under vacuum, the ampoule was sealed with a gas burner, and the polymerization was conducted in an oven at 105 °C within 16 hours. After cooling, a sample of the reaction mixture was withdrawn for SEC analysis. The remaining PLA-PDXL-PLA copolymers were dissolved in methylene chloride, precipitated in pentane or hexane, dried under vacuum, and analysed by ^{1}H NMR, ^{13}C NMR, SEC, TGA, and DSC.

This journal is © The Royal Society of Chemistry 2022

Published on 30 August 2022. Downloaded by Ghent University Library on 8/30/2022 10:31:30 AM.

PLA-PDXL$_{7000}$-PLA-1. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.19 (q, 1H, –C$\underline{H}$(CH)$_3$), 4.76 (s, 2H, –OC$\underline{H}_2$O–), 4.34 (m, overlapping, –C$\underline{H}$(OH)–, –(C═O)–OC$\underline{H}_2$CH$_2$O–) 3.72 (s, 4H, –OCH$_2$CH$_2$O–), 1.45–1.61 (d, overlapping-CH$_3$–), ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) = 175.21 (2C, –(C═O) end group), 172.58 (2C, –(C═O)–OCH$_2$CH$_2$O–), 169.7 (1C, –CH$_2$–(C═O)–O–), 95.63 (1C, –OCH$_2$O–), 94.75 (2C, –OCH$_2$O–, end group) 69.1 (1C, –C(CH)–), 68.59 (2C, –CH–(C═O)–OCH$_2$CH$_2$O–), 67.46 (2C, –C(CH)– end group), 66.92 (2C, –OCH$_2$CH$_2$O–), 65.4 (2C, –OCH$_2$CH$_2$O– end group), 64.5 (2C, –OCH$_2$CH$_2$O– end group), 20.63 (1C, –C(CH$_3$) end group), 18.61 (1C, –C(CH$_3$)–C(═O)–OCH$_2$CH$_2$O–), 16.74 (1C, –C(CH$_3$)–).

The triblock ABA copolymers were typically prepared on a 2 g scale. The isolated yield of the copolymers after precipitation was approximately 80%. Polymers prepared by bulk polymerization appeared as white powders.

Synthesis of PCL-PDXL-CL copolymers

A total of 0.5 g (0.071 mmol) of PDXL ($M_{n\ NMR}$ = 7000 g mol^{-1}) and an appropriate amount of CL (0.524 mL, 4.7 mmol) were placed in a glass ampoule. All other steps were performed analogously as described for PLA-PDXL$_{7000}$-PLA copolymers. The ampoule was placed in an oven at 80 °C for 16 hours. The obtained copolymer was dissolved in methylene chloride, precipitated in hexane, dried under reduced pressure, and analysed by ^{1}H NMR, ^{13}C NMR, SEC, TGA, and DSC.

PCL-PDXL$_{7000}$-PCL-2. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.76 (s, 2H, –O–CH$_2$–O–), 4.25 (m, 2H, –(C═O)–O–C$\underline{H}_2$–CH$_2$–O–), 4.05 (m, 2H, –O–C$\underline{H}_2$–CH$_2$–CH$_2$–CH$_2$–CH$_2$–(C═O)–), 3.77 (m, 2H, –(C═O)–O–CH$_2$–C$\underline{H}_2$–O–), 3.72 (s, 4H, –O–CH$_2$–CH$_2$–O–), 3.64 (m, 4H, HO–C$\underline{H}_2$–CH$_2$–CH$_2$–CH$_2$–CH$_2$–), 2.3 (m, 2H, –CH$_2$–CH$_2$–CH$_2$–CH$_2$–C$\underline{H}_2$–C═O), 1.64 (m, overlapping, OH–CH$_2$–CH$_2$–CH$_2$–C$\underline{H}_2$–CH$_2$–(C═O)–, –CH$_2$–C$\underline{H}_2$–CH$_2$–C$\underline{H}_2$–CH$_2$–(C═O)–), 1.37 (m, overlapping, OH–CH$_2$–C$\underline{H}_2$–C$\underline{H}_2$–CH$_2$–CH$_2$–(C═O)–, –CH$_2$–CH$_2$–C$\underline{H}_2$–CH$_2$–CH$_2$–(C═O)–), ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) = 173.55 (1C, –(C═O)–O–), 173.4 (2C, –(C═O)–O–CH$_2$–CH$_2$–O–), 95.55 (1C, –O–CH$_2$–), 66.87 (2C, –O–CH$_2$–CH$_2$–O–), 65.9 (2C, –(C═O)–O–CH$_2$–C$\underline{H}_2$–O–), 64.12 (1C, –(C═O)–O–C$\underline{H}_2$–CH$_2$–CH$_2$–CH$_2$–CH$_2$–), 63.42 (2C, –(C═O)–O–C$\underline{H}_2$–CH$_2$–O–), 62.49 (2C, OH–C$\underline{H}_2$–CH$_2$–CH$_2$–CH$_2$–CH$_2$–), 34.09 (1C, –CH$_2$–CH$_2$–CH$_2$–CH$_2$–C$\underline{H}_2$–(C═O)–), 32.32 (2C, HO–CH$_2$–C$\underline{H}_2$–CH$_2$–CH$_2$–CH$_2$–), 28.30 (1C, –CH$_2$–C$\underline{H}_2$–CH$_2$–CH$_2$–CH$_2$–(C═O)–), 25.49 (1C, –CH$_2$–CH$_2$–C$\underline{H}_2$–CH$_2$–CH$_2$–(C═O)–), 24.62 (1C, –CH$_2$–CH$_2$–CH$_2$–C$\underline{H}_2$–CH$_2$–(C═O)–).

The triblock ABA copolymers were typically prepared on a 2 g scale. The isolated yield of the copolymers after precipitation was approximately 80%. Polymers prepared by bulk polymerization appeared as white powders.

Contact angle measurement

Contact angles were measured at room temperature with the sessile drops method using a Phoenix-300 goniometer and software (SEO SurfaceElectro Optics, Korea). The measurements were performed using 5 μL drops of deionized water deposited on the polymer films. Polymer films were prepared by casting polymer solutions (5 mg of the copolymer dissolved in 2 mL of methylene chloride) on glass plates (drying at room temperature for 24 h). As confirmed by ^{1}H-NMR, such prepared films did not contain any residual solvent (Fig. S9 in the ESI†). Contact angle data were obtained by averaging ten measurements.

Degradation of triblock ABA copolymers

The degradation of the copolymers was studied for two acid concentrations that were chosen based on the expected molar ratio of added acid to the acetal units on the poly(dioxolane) chain. SEC and ^{1}H NMR analyses were performed according to the steps described below. For SEC analysis, 0.048 g of PLA-PDXL$_{7000}$-PLA-4 was placed into the vial and dissolved in methylene chloride (8 mL). Subsequently, a wet acetonitrile solution of hydrochloric acid (160 μL, 3.63 mg hydrochloric acid per mL acetonitrile) was added to the vials. After selected time intervals of 1 h, 5 h, 24 h, 48 h, 72 h, the samples were drawn and analysed by SEC. For ^{1}H NMR analysis, 10 mg of the copolymer PLA-PDXL$_{7000}$-PLA-4 was dissolved in wet deuterated solvent (0.68 mL of CD_3CN) in an NMR tube. After that, a wet nondeuterated acetonitrile solution of hydrochloric acid (20 μL, 0.073 mg hydrochloric acid per mL acetonitrile, 0.363 mg hydrochloric acid per mL acetonitrile, or 3.6 mg μg hydrochloric acid per acetonitrile) was added to the NMR tube to reach 0.7 mL. The ^{1}H NMR spectra were recorded at 25 °C after selected time intervals: 1 h, 5 h, 22 h, 55 h, 96 h, and 122 h.

Thermal degradation by depolymerisation of the polyacetal block

The degradation of the copolymer was performed by applying a procedure described by Coates and coworkers.[34] Briefly, 0.5 g of copolymer (PLA-PDXL-PLA-2) and 50 mg of diphenyl phosphate were dissolved in 5 mL of methylene chloride. The methylene chloride was evaporated on a rotary evaporator without heating. Subsequently, the distillation apparatus was assembled, and the flask was heated to 100 °C. The distilled 1,3-dioxolane was collected in a flask cooled with liquid nitrogen. The distillate and residue were analysed by ^{1}H NMR and SEC (Fig. 10 and 11).

Characterization and methods

^{1}H NMR and ^{13}C NMR and 2D HSQC NMR spectra were recorded on an Avance Neo 400 NMR spectrometer (400.15 MHz for ^{1}H and 100.63 MHz for ^{13}C, 9.4 T), whereas DOSY NMR analysis was performed on a Bruker DRX500 spectrometer operating at 500 MHz (11.7 T). The number-average molar masses of copolymers and polydispersity were determined by SEC using an Agilent Pump 1100 Series (preceded by an Agilent G1379A Degasser) equipped with a set of two PLGel 5 μm MIXED-C columns. A Wyatt Optilab Rex differential refractometer and a Dawn Eos8 (Wyatt Technology Corporation) laser photometer were used as detectors. Methylene chloride was used as an eluent at a flow rate of 0.8 mL min^{-1}. The measurements were registered at 25 °C. Premineralisation was carried out in an ultrasonic bath (Bandelin). Mineralization was performed using the UltraWave

Published on 30 August 2022. Downloaded by Ghent University Library on 8/30/2022 10:31:30 AM.

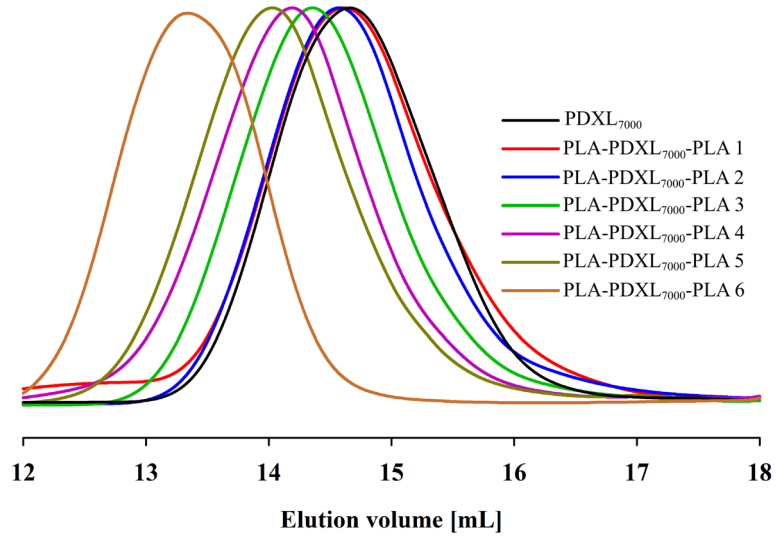


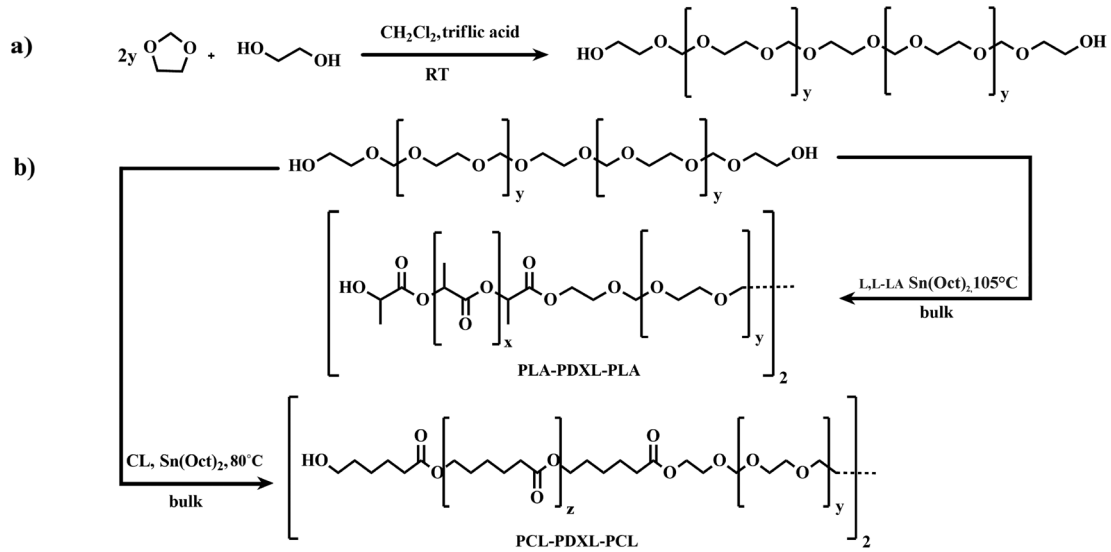
Fig. 1 SEC curves of the polyacetal macroinitiator HO-PDXL$_{7000}$-OH and the resulting purified PLA-PDXL$_{7000}$-PLA copolymers.

microwave system (Milestone). The ICP-OES technique (optical emission spectrometry with inductively coupled plasma) operating with the iCAP 7000 SERIES spectrometer (Thermo) was used for sulfur content determination (Table S1 in the ESI†). Differential scanning calorimetry (DSC) analysis was used to determine the thermal properties of the copolymers. Measurements were carried out at temperatures from −90 °C to 200 °C on a DSC 2500 (TA instruments, Discovery system). The analyses were carried out in a nitrogen stream at heating and cooling rates of 10 °C min^{-1}. Thermogravimetric analyses (TGA) were performed by placing approximately 5 mg of polymer sample in a measuring cell. Measurements were registered under nitrogen flow by heating the samples from ambient temperature to 600 °C at a heating rate of 20 °C min^{-1} on a Hi-Res TGA 2950 thermogravimetric analyser (TA Instruments). Contact angle measurements were carried out using a Phoenix-300 goniometer by SEO Surface Electro-Optics (Korea). The measurements were performed using deionized water.

Results and discussion

Synthesis of polyacetal diols HO-PDXL-OH as macroinitiators

To obtain well-defined di-hydroxy terminated polyacetals (HO-PDXL-OH), the cationic polymerization of dioxolane was performed under conditions suitable for the so-called activated monomer (AM) mechanism (step a in Scheme 1).[36,37] As shown earlier, applying ethylene glycol as an initiator and



Scheme 1 Synthesis of ABA triblock copolymers using HO-PDXL$_{7000}$-OH as a macroinitiator in the ROP polymerization of lactide or caprolactone.

This journal is © The Royal Society of Chemistry 2022

Published on 30 August 2022. Downloaded by Ghent University Library on 8/30/2022 10:31:30 AM.

triflic acid as a catalyst enables the formation of PDXL containing a hydroxyl HO–CH_2–CH_2– end-group at both chain ends, with a molar mass that can be controlled by the molar ratio of monomer to initiator.[32] In our work, to gain control over the molar mass of the homopolymer, the polymerization was carried out at a low instantaneous concentration of DXL in the reaction mixture, which was ensured by the slow addition of the monomer to the reaction mixture using an infusion pump. The syntheses were carried out under conditions that allowed the preparation of two polyacetals differing in molar mass.

However, it should be remembered that during DXL cationic ring-opening polymerization (CROP), the formation of cyclic structures as byproducts cannot be avoided, as it is an inherent feature of this polymerization system.[38] Thus, in our work, we followed the procedure recently reported by Bernaerts and coworkers to purify the obtained homopolymers from cyclic fractions and from traces of the acid.[39] It should be noted that the proper purification of PDXL from acidic impurities is essential for the successful synthesis carried out in the second step, namely, for the proper ROP of cyclic esters. Therefore, to check the level of acid traces in the prepared polymers, we performed analysis on the sulfur content (present in CF_3SO_3H molecules), which may indicate a triflic acid content. Although the presence of ~920 ppm sulfur was found in the purified polymers, there was no indication of a negative effect of these impurities on further cyclic ester ring-opening polymerization. The obtained, carefully purified homopolymers were characterized by SEC, MALDI (Fig. S1 in the ESI†), ^{1}H NMR, and ^{13}C NMR (Fig. S2 in the ESI†).

The expected structure of PDXL diols was confirmed on the basis of MALDI TOF analysis (Fig. S1 in the ESI†). To determine the actual degrees of polymerization and absolute molar masses of α,ω-hydroxy-terminated polyacetals, ^{1}H NMR spectra were recorded in deuterated DMSO, which enabled the observation of protons located near hydroxyl end-groups. The assignment of signals in the spectrum together with 2D HSQC NMR is provided in Fig. S3.† Based on the analysis of the NMR spectra (taking into account the signal intensities at 3.48 ppm and 3.59 ppm), the molar masses of the obtained homopolymers were determined to be 2400 g mol^{-1} and 7000 g mol^{-1}.

These polymers, containing acetal groups in the main chain and terminated by primary hydroxyl groups (denoted HO-PDXL$_{7000}$-OH and HO-PDXL$_{2400}$-OH), were used as macroinitiators for the synthesis of ABA copolymers, enabling the introduction of a polyacetal middle block into the polyester chain.

Synthesis of ABA-triblock copolymers containing polyester A-blocks and polyacetal B-blocks

To obtain triblock copolymers comprising a polyacetal middle (B) block and polyester (A) outer blocks, HO-PDXL-OH was used as a macroinitiator in the insertion ring-opening polymerization with L,L-lactide or ε-caprolactone. The strategy is illustrated in Scheme 1 (step b).

The synthesis of triblock copolymers was conducted in bulk (at 105 °C for LA and 80 °C for CL) in the presence of tin(II) octoate as a catalyst that is capable of inducing the efficient polymerization of cyclic esters in the melt.[12] To prepare a range of copolymers containing increasing contents of ester units in external segments, a series of experiments was performed with a given precursor using an increasing ratio of cyclic ester to macroinitiator in the reactive mixture. As observed in SEC, after 16 hours of the reaction, almost full conversion (~96%) of the cyclic esters was reached (Fig. S5 in the ESI†) regardless of the composition of the mixture. The SEC chromatograms of the starting HO-PDXL-OH and resulting ABA copolymers with different molar contents of the selected ester are shown in Fig. 1, Fig. S4, and S6.†

SEC traces for unpurified and purified copolymers (Fig. S4 and S5 in the ESI†) were similar, showing symmetric, monomodal molar mass distributions. The analysis of the chromatograms revealed a gradual increase in the molar masses of the synthesized copolymers with increasing molar ratio of the cyclic ester to macroinitiator in the reaction mixture, confirming the efficient initiation of the coordination polymerization by the –OH end-groups from the used polyacetal. The observed shift for each reaction mixture to higher molar masses relative to the HO-PDXL-OH homopolymer strongly indicates the formation of the copolymers and not the formation of a homopolymer blend. The results of the ring-opening polymerization of L-LA and CL performed in bulk using HO-PDXL$_{7000}$-OH and HO-PDXL$_{2400}$-OH as macroinitiators are listed in Table 1.

In Table 1, the theoretical number average molar mass of each polyester external block (A) and the number average molar mass of the PDXL midblock (B) introduced by the macroinintator used are shown. As presented, a range of ABA block copolymers with different compositions and different molar masses ($M_{n\ MALLS}$ in the range 10 000–54 000 g mol^{-1}) were successfully synthesized from a given PDXL precursor. The theoretical values of the molar masses calculated assuming molar masses of PDXL equal to 7000 g mol^{-1} (or 2400 g mol^{-1}) were in satisfactory agreement with the determined molar masses $M_{n\ MALLS}$, indicating the quantitative initiation of cyclic ester polymerization from the polyacetal precursor. The $M_{n\ RI}$ values based on the polystyrene calibration typically exceed the $M_{n\ MALLS}$ due to the difference in the hydrodynamic volume of the copolymers and that of polystyrene.

Inspection of the data in Table 1 confirmed a well-controlled synthesis of the triblock PLA-PDXL-PLA and PCL-PDXL-PCL copolymers under solvent-free conditions. Thus, the ring-opening polymerization of cyclic esters with α,ω-hydroxy-terminated polyacetals may be recognized as a suitable synthetic strategy allowing the production of block copolymers with segments defined by the composition of the reactive mixture.

The composition of the isolated block copolymers was examined by ^{1}H NMR spectral analysis. Fig. 2 shows a typical ^{1}H NMR spectrum of the block copolymer obtained in the ROP of L-LA initiated by HO-PDXL$_{7000}$-OH macromonomer (sample PLA-PDXL-PLA-4).

In the presented spectrum, in addition to signals characteristic of L-LA repeating units in the poly(L-LA) chain (signals a,

Published on 30 August 2022. Downloaded by Ghent University Library on 8/30/2022 10:31:30 AM.

Table 1 Results of $Sn(Oct)_2$-catalysed ring-opening polymerization of L-LA or CL in the presence of HO-PDXL-OH macroinitiators (polyacetal B-block)

Name	Theoretical composition of the ABA copolymer chain	Theoretical ester content mol%	Theoretical length of A block	$M_{n\ theor}$ [a] [g mol^{-1}]	$M_{n\ SEC}$ [b] [g mol^{-1}] RI	$M_{n\ SEC}$ [b] [g mol^{-1}] MALLS	$Đ$ [c]	Determined length of A block [d]	Determined ester content [e] mol %
PLA-PDXL-PLA-1	PLA_{2500}-$PDXL_{7000}$-PLA_{2500}	26	2500	12 000	12 000	11 000	1.8	2000	26
PLA-PDXL-PLA-2	PLA_{3750}-$PDXL_{7000}$-PLA_{3750}	35	3750	14 500	13 000	14 500	1.7	3750	35
PLA-PDXL-PLA-3	PLA_{5000}-$PDXL_{7000}$-PLA_{5000}	43	5000	17 000	17 000	15 000	1.5	4000	44
PLA-PDXL-PLA-4	PLA_{7500}-$PDXL_{7000}$-PLA_{7500}	52	7500	22 000	22 000	19 000	1.7	6000	53
PLA-PDXL-PLA-5	PLA_{10000}-$PDXL_{7000}$-PLA_{10000}	59	10 000	27 000	25 000	23 000	1.6	8000	60
PLA-PDXL-PLA-6	PLA_{25000}-$PDXL_{7000}$-PLA_{25000}	79	25 000	57 000	63 000	54 000	1.3	23 500	82
PLA-PDXL-PLA-7	PLA_{3750}-$PDXL_{2400}$-PLA_{3750}	62	3750	9900	17 000	10 000	2.2	3800	64
PLA-PDXL-PLA-8	PLA_{5000}-$PDXL_{2400}$-PLA_{5000}	68	5000	12 400	20 000	12 000	2.0	4800	68
PLA-PDXL-PLA-9	PLA_{7500}-$PDXL_{2400}$-PLA_{7500}	76	7500	17 400	26 500	16 000	1.7	6800	76
PLA-PDXL-PLA-10	PLA_{10000}-$PDXL_{2400}$-PLA_{10000}	81	10 000	22 400	34 000	27 000	1.8	12 000	80
PCL-PDXL-PCL-1	PCL_{3750}-$PDXL_{7000}$-PCL_{3750}	41	3750	14 500	25 000	13 000	1.4	3000	42
PCL-PDXL-PCL-2	PCL_{10000}-$PDXL_{7000}$-PCL_{10000}	65	10 000	27 000	36 000	18 000	1.3	5500	65

[a] $M_{n\ theoretical}$ calculated as a sum: $M_{n\ B\ block} + 2{\cdot}M_{n\ A\ block}$, where $M_{n\ B\ block}$ = 7000 g mol^{-1} or 2400 g mol^{-1}. [b] M_n determined by SEC with RI detection (polystyrene as a standard) and by MALLS (the value of the refractive index increment (d_n/d_c) was calculated by using Astra® software supporting the chromatographic devices). [c] The dispersity M_w/M_n estimated from SEC. [d] Length of block A calculated based on the copolymer molar masses determined by MALLS assuming $M_{n\ B\ block}$ = 7000 g mol^{-1} or $M_{n\ B\ block}$ = 2400 g mol^{-1}. [e] Ester content calculated on the basis of ^{1}H NMR spectra.

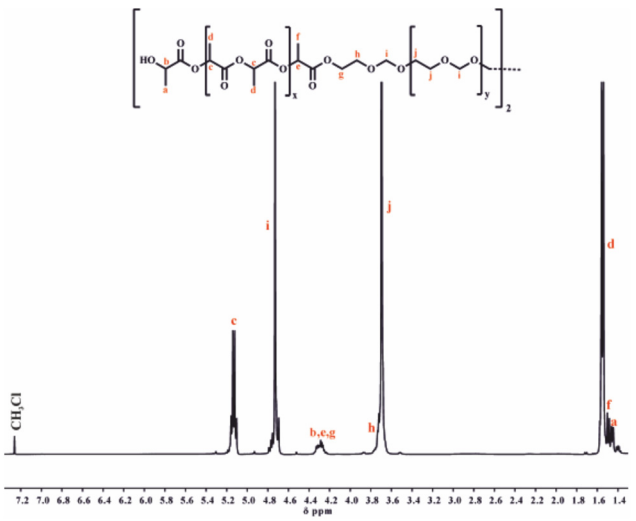


Fig. 2 A representative ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of a block copolymer obtained by copolymerization of HO-$PDXL_{7000}$-OH with L-lactide (after precipitation, sample PLA-PDXL-PLA-4, Table 1).

b, c, d, e, and f), signals from the PDXL macroinitiator are also observed with chemical shifts of 4.75 ppm (signal i) and 3.69 ppm (signal j).[35,40] The signal from PLA end-group –(CH_3)C<u>H</u>–OH typically observed at 4.35 ppm (signal b) partially overlaps with the signal from –(CH_3)C<u>H</u>–O– in the L-LA unit directly connected with a dioxolane unit (signal e) and the signal from the –OC<u>H_2</u>CH_2O– unit connected with the ester unit (signal g). Since well-separated signals are also observed in the spectrum, the composition of the PLA-PDXL-PLA copolymers was calculated by comparing the intensity of the peaks at 5.15 ppm and 4.75 ppm derived from the protons –(CH_3)C<u>H</u>–O– and –OC<u>H_2</u>O–, respectively. Analysis of the ^{1}H NMR spectra of the copolymers obtained by copolymerization of the HO-$PDXL_{7000}$-OH macroinitiator with ε-caprolactone (presented in Fig. S7a in the ESI†) also confirmed the presence of signals with chemical shifts typical for long CL sequences as well as signals from the PDXL block. As shown in Table 1, the compositions of the prepared ABA copolymers were close to the targeted values predicted based on the starting comonomer ratio in the feed. In this way, it was possible to change the content of ester units and, consequently, control the length of the polyester block in the copolymer.

To unequivocally confirm the formation of block copolymers rather than homopolymer mixtures, diffusion-ordered spectroscopy (DOSY) NMR was used. This relatively new analytical method allows studies on the structure, composition and molar mass of polymers.[41,42] An expanded view of the DOSY experiments for starting PDXL, PLA and the resulting PLA copolymer, with the related ^{1}H spectra projected on top, is shown in Fig. 3.

The diffusion coefficient of PDXL was found to be D = 1.26 × 10^{-6} cm^2 s^{-1}, whereas D = 1.34 × 10^{-6} cm^2 s^{-1} for PLA. As shown in the DOSY map ^{1}H NMR of copolymer PLA and PDXL, signals exhibited the same diffusion coefficient (data presented in Table S2 in the ESI†) as they are on the same horizontal line, indicating that the signals belong to the same PLA-PDXL-PLA copolymer macromolecule. Thus, the DOSY results confirmed the presence of PLA chains covalently bonded to the PDXL segment and excluded the presence of the individual homopolymers. Therefore, it can be concluded that no residual $PDXL_{7000}$ or PLA homopolymer was observed on the DOSY map of the copolymer, that all the $PDXL_{7000}$ macroinitiator was consumed during the initiation step and that no PLA homopolymer was formed during the ROP.

The triblock structure of the copolymers was further proven on the basis of the ^{13}C NMR spectrum, as shown in Fig. 4.

This journal is © The Royal Society of Chemistry 2022

Published on 30 August 2022. Downloaded by Ghent University Library on 8/30/2022 10:31:30 AM.

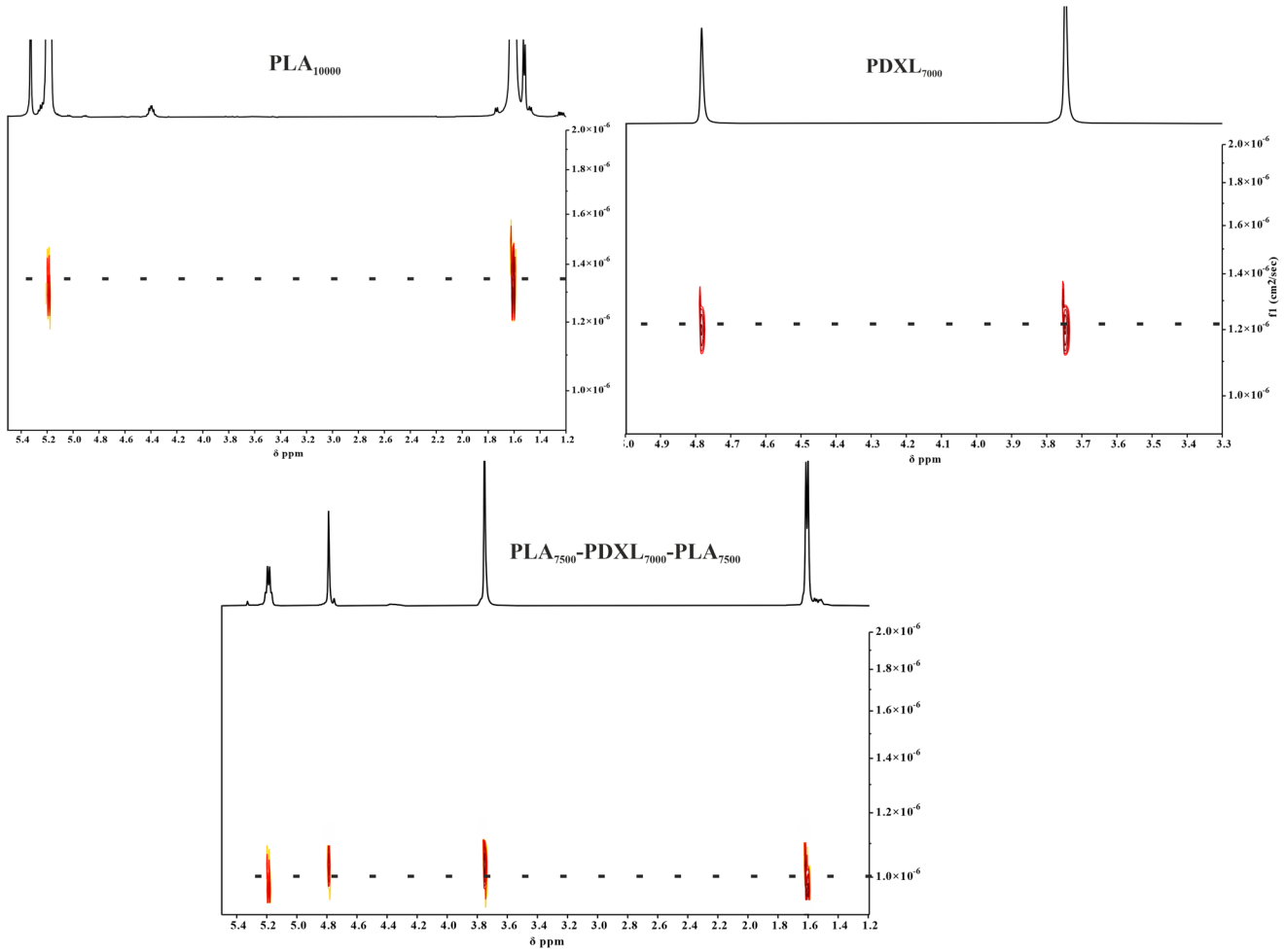


Fig. 3 500 MHz 2D DOSY NMR spectra obtained at 298 K in a $CDCl_3$ solution of PLA (M_n = 10 000 g mol^{-1}), PDXL (M_n = 7000 g mol^{-1}) and PLA_{7500}-$PDXL_{7000}$-PLA_{7500} copolymer ($M_{n\ MALLS}$ = 19 000 g mol^{-1}).

In the ^{13}C NMR spectrum, high-intensity sharp peaks (denoted as e, d, f and m, (n)), coming from long –$(LA)_x$- and –$(DXL)_y$-sequences, are observed. Additionally, much less intensive signals are also present. Signals denoted as a and b were assigned to –($\underline{C}H_3$)CH–OH and –(CH_3)$\underline{C}$H–OH carbons in PLA end-groups. Signals g, j, k, and l were attributed to carbons located in heterodyads formed at the junction of PDXL and PLA blocks. In the carbonyl region, signals from homodyads in the isotactic poly(L-LA) block, heterodyads and carbonyl groups in the terminal units were observed at 169.7 ppm and 172.6 ppm and 175.5 ppm, respectively, with intensities characteristic of the blocky structure of the copolymer.

For PCL-$PDXL_{7000}$-PCL copolymers, a complete peak assignment in the ^{13}C NMR spectrum (presented in Fig. S7b in the ESI†) also proved the presence of both polyester and polyacetal block sequences.

As demonstrated by NMR spectroscopy during the tin-catalysed polymerization of cyclic esters with the acetal macroinitiator, chain exchange reactions are negligible, resulting in the formation of a triblock copolymer chain. It may be speculated that using $Sn(Oct)_2$ as a catalyst is essential for the successful preparation of this type of block copolymer, applying the PDXL macroinitiator for coordination polymerization, because the polyacetal block is not involved in the intermolecular transacetalisation reaction (typical for cationic polymerization).

Hydrophilicity of ABA-triblock copolymers

As PDXL shows a hydrophilic character, one may expect that the attachment of the polyacetal block to the hydrophobic polyester segments will influence the hydrophilicity of the resulting ABA copolymer. To prove our hypothesis, we evaluated static contact angles measured on solvent-cast films.

The dependence of the static contact angle on the polylactide block length in PLA-$PDXL_{7000}$-PLA copolymers is presented in Fig. 5 and Fig. S8† for PCL.

Compared to pure PLLA, the synthesized copolymers show an altered hydrophilic character depending on the contents of both building blocks. Furthermore, it may be expected that the introduction of hydrophilic PDXL domains into hydrophobic polyesters should influence the hydrolytic degradation rate, which may be of particular interest in the context of material recyclability.

Published on 30 August 2022. Downloaded by Ghent University Library on 8/30/2022 10:31:30 AM.

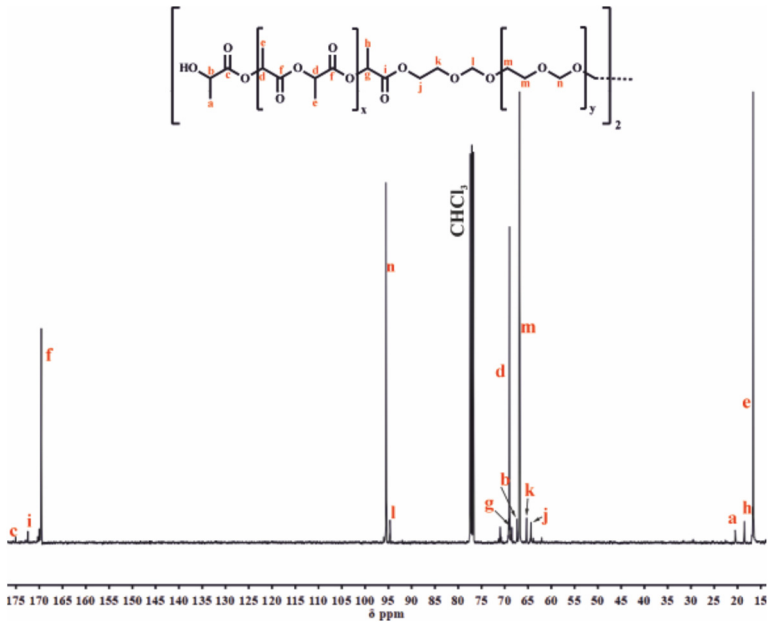


Fig. 4 A representative ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of purified block copolymer obtained by copolymerization of HO-PDXL$_{7000}$-OH with L-LA (PLA-PDXL$_{7000}$-PLA-4, Table 1).

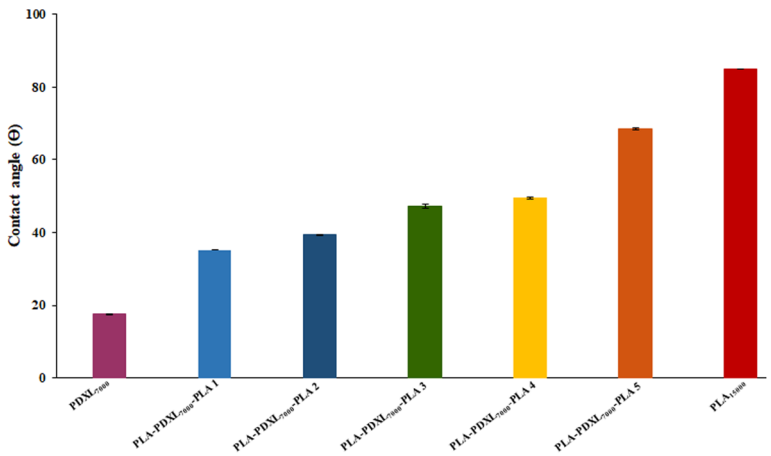


Fig. 5 Assessment of the mean static contact angles of PLA-PDXL$_{7000}$-PLA block copolymers in comparison to pure PDXL$_{7000}$ and PLA.

Thermal properties

To understand the structure–property relationships in the ABA copolymers, we studied the impact of the polyester content on the thermal properties. The thermal characteristics of ABA triblock copolymers with the polyacetal middle segment were investigated by differential scanning calorimetry (DSC). Thermograms recorded during the second scan for HO-PDXL$_{7000}$-OH diol, PLA$_{15000}$, and PLA-PDXL$_{7000}$-PLA are shown in Fig. 6a.

Neat PDXL exhibits a low glass temperature (T_g) below −50 °C and an endothermic melting peak at approximately 50 °C.[43] Poly(L-lactide) is a semicrystalline polymer with a T_g of approximately 60 °C and a peak melting temperature (T_m) of up to 180 °C.[44] For copolymers, the proportion of building blocks can be considered a key factor influencing the thermal properties. When the lactide content in the copolymer is below 50 mol%, melting endotherms corresponding to crystalline PLA or PDXL segments are not detected. Thus, PLA-PDXL$_{7000}$-PLA-1 and PLA-PDXL$_{7000}$-PLA-2 are essentially amorphous powders displaying a low glass transition temperature (−41 and −26 °C, respectively). The lack of any significant degree of crystallinity may be attributed to the short segmental length of PLA and the disrupted crystalline phase of PDXL. Copolymers containing 50%, 58% and 65% L-LA demonstrated some degree of crystallinity, indicating that the PLA blocks may be easily phase separated and form crystalline domains. However, the T_m and ΔH of copolymers having the highest L-LA contents

This journal is © The Royal Society of Chemistry 2022

Published on 30 August 2022. Downloaded by Ghent University Library on 8/30/2022 10:31:30 AM.

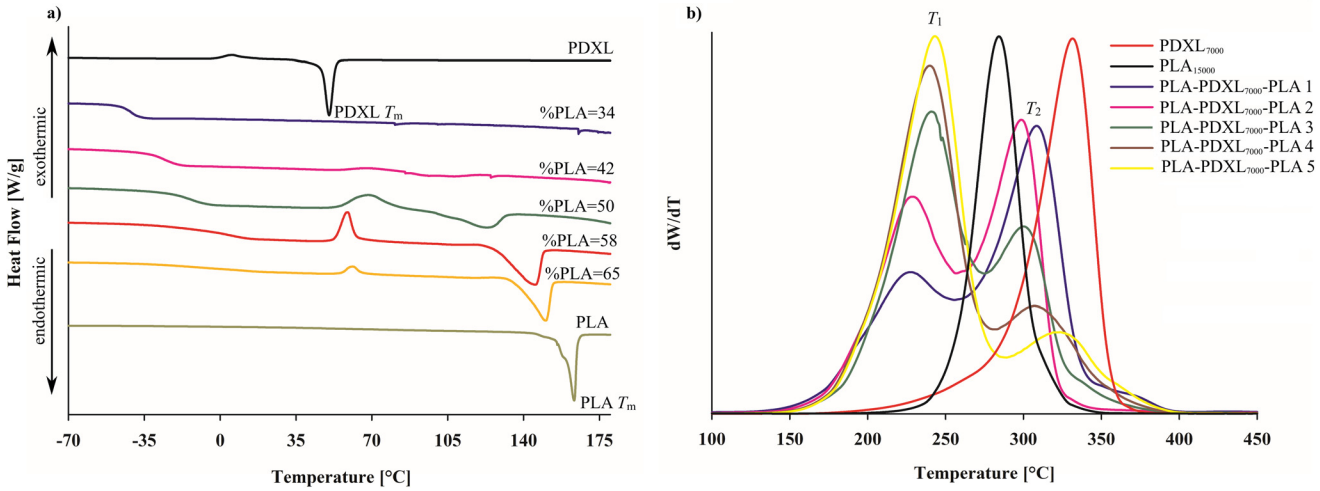


Fig. 6 (a) The DSC thermograms registered during the second scan and (b) TGA curves for starting HO-PDXL$_{7000}$-OH diol, PLA$_{15000}$, and PLA-PDXL$_{7000}$-PLA. For DSC analysis, samples were heated at 10 °C min^{-1} and cooled at 10 °C min^{-1}, whereas for TGA measurement, samples were heated at 20 °C min^{-1}.

(PLA-PDXL$_{7000}$-PLA-4, PLA-PDXL$_{7000}$-PLA-5) are still considerably lower than those of the PLA homopolymer (where the literature value for the melting enthalpy of the 100% crystalline PLLA homopolymer is ΔH_m = 106 J g^{-1}), indicating that the presence of a second PDXL phase influences the crystallization behaviour of polyester to a large extent.[45]

In the case of PCL-PDXL$_{7000}$-PCL copolymers, it should be noted that PCL building blocks, in contrast to PLA, display a low melting temperature (T_m = 59–64 °C) and low glass temperature (T_g = −60 °C).[46] The DSC curves of PCL triblock copolymers (shown in Fig. S10a in the ESI†) exhibited two endothermic peaks, indicating that phase separation took place in the block copolymer, enabling the formation of crystallisable domains. Thus, PCL-PDXL$_{7000}$-PCL copolymers are semicrystalline powders displaying a low glass transition temperature (∼−60 °C). Values of T_g, melting temperatures and melting enthalpies determined by differential scanning calorimetry for PLA-PDXL$_{7000}$-PLA and PCL-PDXL$_{7000}$-PCL are presented in Table S3 in ESI.†

The results of differential thermogravimetric (DTG) analysis for PLA-PDXL$_{7000}$-PLA copolymers composed of blocks of different relative lengths confirmed the blocky structure of the copolymer chain. Integral curves for copolymers clearly indicate that thermal decomposition occurs in two distinct stages at the temperature of maximum decomposition determined by the copolymer composition. Thermal decomposition profiles of selected PLA-PDXL$_{7000}$-PLA copolymers are shown in Fig. 6b, whereas the characteristic temperatures of decomposition are listed in Table S3 in the ESI.†

The onset decomposition temperatures (and temperatures of maximum decomposition) of PCL-PDXL$_{7000}$-PCL copolymers (Fig. S10b†) are much higher than those of PLA-PDXL$_{7000}$-PLA copolymers, indicating the better thermal stability of caprolactone triblock copolymers, which is in agreement with previous observations.[47] Thus, DSC analysis revealed that the thermal properties of ABA copolymers can be tuned by the selection of the cyclic ester-type and its ratio to macroinitiator.

In vitro degradation of PLA-PDXL-PLA copolymers

The hydrolytic degradation of PLA is determined by several factors, including the molar mass, structure, crystallinity, pH and temperature of the degradation medium.[48,49] Thus, bulk PLA degrades relatively slowly because of its hydrophobic nature and semicrystalline structure that does not allow fast water penetration, whereas amorphous PLA exhibits a higher susceptibility to degradation (<5 months) as a consequence of its enhanced permeability.[9,50] PDXL is sensitive to acidic media, and chain degradation may occur in two steps: primary chain scissions and depolymerization.[51] As reported, when the polyacetal in organic solvent is treated with a strong acid, the degradation starts immediately and continues until reaching the equilibrium monomer concentration that is dependent on the reaction temperature.[52,53] However, it was also observed that in the presence of alcohols and water, decrosslinking of the network can be prevented.[54] As presented in our previous work, in the case of lactide-dioxolane copolymers containing randomly distributed acetal units in the polyester chain, hydrolytic degradation in solution may be simply modulated by the content of acid-sensitive units in the copolymer chain.[35]

Presently studied ABA block copolymers contain polyacetal blocks; thus, three types of reactive sites may potentially be distinguished, namely, ester bonds within the (A) PLA blocks, acetal-ester bonds linking PLA to PDXL blocks, and acetal bonds in (B) PDXL blocks. However, it could be expected that the cleavage of acid-labile acetal bonds present in the middle segment should occur preferentially, leading to the scission of the block, which should be manifested by a significant reduction in the molar mass of the resulting copolymer. It can be assumed that in an acidic medium, depending on the con-

Published on 30 August 2022. Downloaded by Ghent University Library on 8/30/2022 10:31:30 AM.

ditions, the degradation of the copolymer chain may proceed by hydrolysis or depropagation reactions.

In our research, at the first step, the process of degradation was investigated with a focus on changes in the molar masses of triblock copolymers after incubation in a medium containing water, organic solvent and hydrochloric acid ([acetal units] : [H^+] = 10 : 1). The experiments were carried out at 25 °C in CH_2Cl_2 using PLA-PDXL$_{7000}$-PLA-4 copolymer. The acid-triggered degradation of the copolymer chain verified by SEC analysis is demonstrated in Fig. 7.

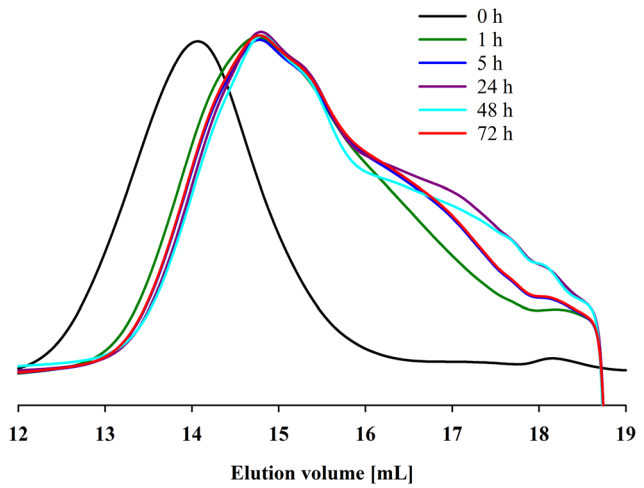


Fig. 7 CH_2Cl_2 SEC traces of PLA$_{7500}$-PDXL$_{7000}$-PLA$_{7500}$ copolymer before ($M_{n\ RI}$ = 22 000 g mol^{-1}) and after incubation ($M_{n\ RI}$ = 7000 g mol^{-1}, after 1 h) in organic medium containing hydrochloric acid ([acetal units] : [H^+] = 10 : 1).

As observed in SEC under the conditions used, the degradation of the copolymer proceeded relatively fast. SEC analysis revealed significant loss of the molar mass of the polymeric product from 22 000 g mol^{-1} to 7000 g mol^{-1} after 60 minutes. Additionally, the formation of low-molecular-weight products was observed on the basis of SEC traces at higher elution volumes (17.5–19 mL). With increasing time, the polymeric peak only slightly shifted towards higher elution times, whereas further disintegration of the low-molecular fraction was visible. As observed earlier in our studies, in acidic medium, PLA did not degrade appreciably (45 days of incubation), contrary to PDXL, which was significantly decomposed after 24 h of incubation.[35] The presented SEC profiles strongly support the assumption that under acidic treatment, the degradation of the copolymer chain occurs mainly in the middle hydrophilic segment of PDXL that is sensitive to acid and where the fast cleavage of the acetal bonds is highly possible. To evaluate this hypothesis, kinetic experiments were designed utilizing NMR spectroscopy to determine the type of groups that disappeared during copolymer degradation. As the degradation in CH_2Cl_2 at 25 °C was relatively fast for monitoring by the ^{1}H NMR technique, we studied the copolymer degradation with deuterated acetonitrile as a solvent. The ^{1}H NMR spectra obtained after incubation with an acetonitrile solution of hydrochloric acid are presented in Fig. 8 and Fig. S11.†

In the registered spectra for the PLA-PDXL$_{7000}$-PLA-4 system, the intensities of signals from the PDXL block (4.69 ppm in CD_3CN) gradually decreased over time, indicating

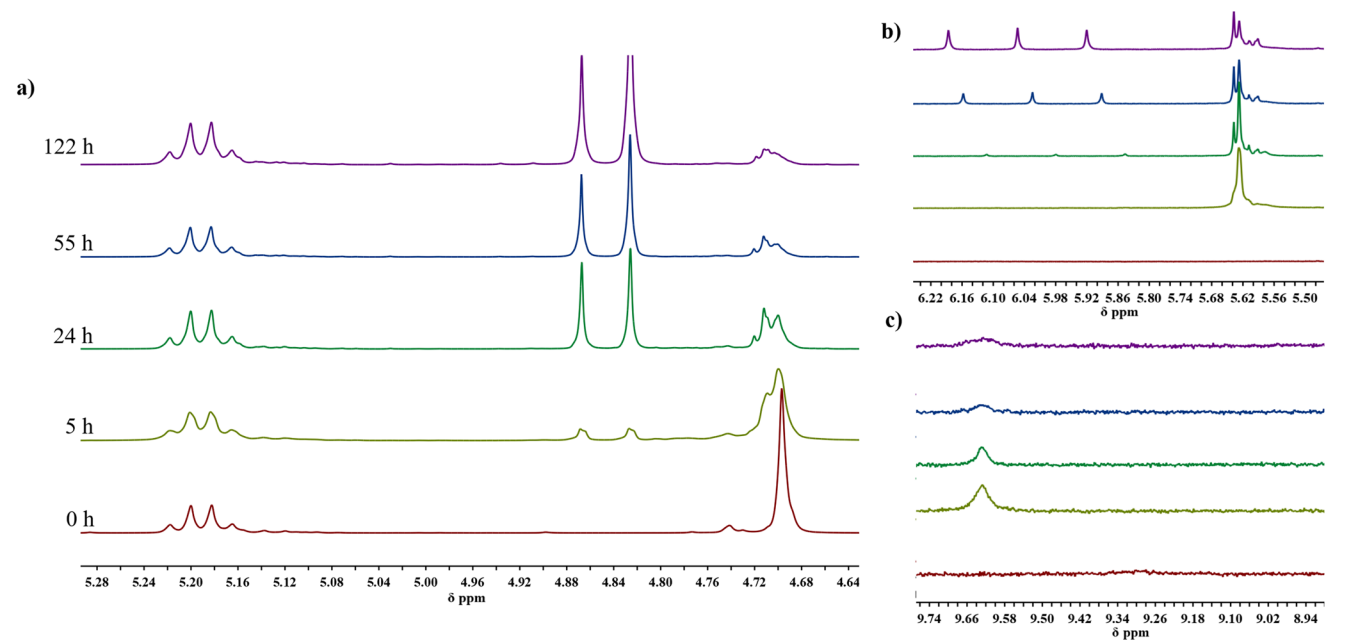


Fig. 8 Acid-induced degradation of PLA-PDXL$_{7000}$-PLA copolymer followed by ^{1}H NMR spectra ([acetal units] : [H^+] = 10 : 1), (CD_3CN, 400 MHz) observed at three different regions: (a) 4.6–5.3 ppm; (b) 5.5 ppm-6.2 ppm; (c) 8.9 ppm-9.7 ppm.

This journal is © The Royal Society of Chemistry 2022

Published on 30 August 2022. Downloaded by Ghent University Library on 8/30/2022 10:31:30 AM.

the degradation of the polyacetal segment. At the same time, the signals from PLA remained unchanged during the experiment, which strongly indicates that the hydrolysis of acetal bonds in triblock copolymer proceeds preferentially. This observation is in agreement with our earlier results reported for lactide-dioxolane copolymers obtained in the statistical copolymerization.[35] The appearance of new signals at 4.77 ppm and 4.83 ppm in the region from 4.5 ppm to 6.2 ppm and at 9.60 ppm was attributed to the formation of degradation products (Fig. 8a–c). After analysing the GC-MS spectrum (Fig. S12†) of the volatile components present in the hydrolysed mixture, the signal at 4.77 ppm was assigned to monomeric dioxolane, whereas the signal at 4.83 ppm was assigned to 1,3,5-trioxepane. A new signal at 9.60 ppm was attributed to formaldehyde, which is not observed in GC due to its high volatility. The ^{1}H NMR spectra revealed that the intensity of the trioxepane signal decreased over time, whereas the dioxolane signal increased. At the same time, the signal attributed to formaldehyde first grew, and then its intensity decreased. Thus, it may be speculated that under applied conditions, the decomposition of 1,3,5-trioxepane occurs, leading to formaldehyde and dioxolane formation. Furthermore, the released formaldehyde may be quickly converted into methylene glycol (5.60 ppm), which in turn becomes oligomerised, leading to the formation of the less harmful product poly(oxymethylene) glycol, which is observed at 6.17 ppm, 6.01 ppm, and 5.90 ppm (Fig. 8b).[55]

Therefore, combining evidence from SEC and NMR, it may be concluded that in an acidic medium containing water, the acetal bonds are easily broken, leading to copolymer disintegration. The rate of degradation may be regulated by the amount of acid introduced into the system, as presented for hydrochloric acid in Fig. 9.

In the case of a lower acid concentration, the decomposition of the copolymer proceeds much slower, which is reflected in the slower rate of acetal unit decay. As a result, the

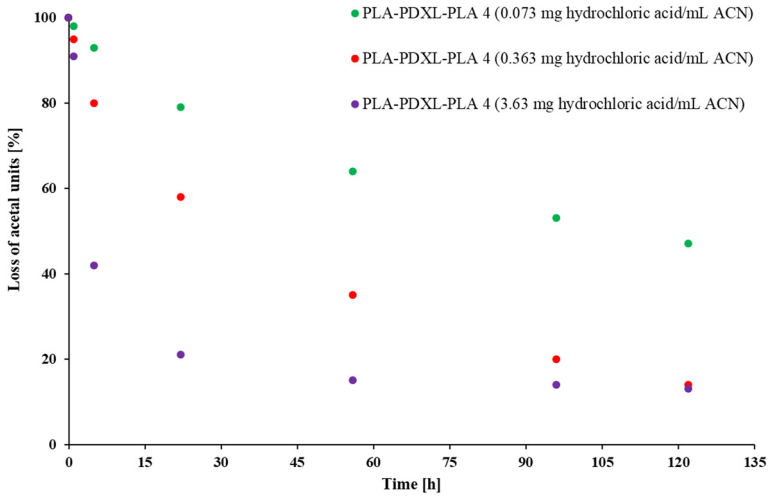


Fig. 9 Disappearance of the signal attributed to $-OCH_2O-$ groups in the PDXL block during acid-induced degradation of the PLA-PDXL$_{7000}$-PLA-4 copolymer, determined on the basis of the ^{1}H NMR spectra collected within 120 hours, (CD_3CN, 400 MHz).

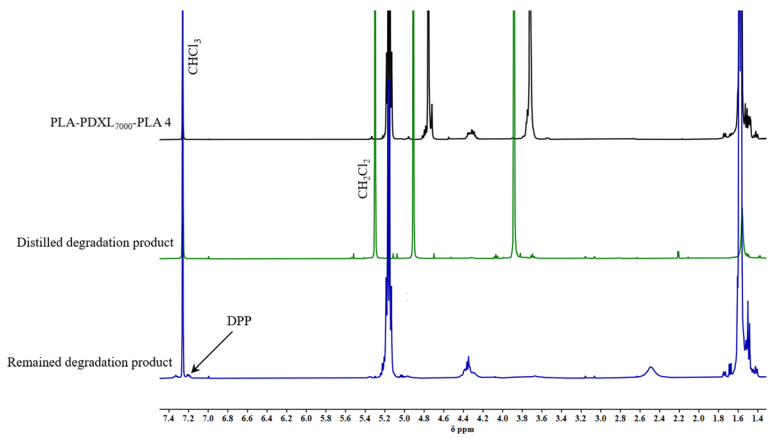


Fig. 10 ^{1}H NMR of the starting copolymer PLA-DXL$_{7000}$-PLA-4, distilled degradation product and remaining product.

Published on 30 August 2022. Downloaded by Ghent University Library on 8/30/2022 10:31:30 AM.

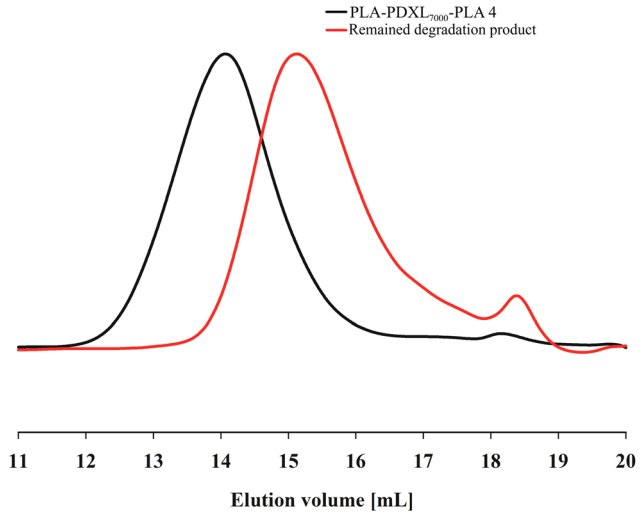


Fig. 11 SEC of the starting copolymer PLA-DXL$_{7000}$-PLA-4 and the remaining degradation product.

hydrolytic degradation process can be controlled and carried out on demand under the control of the environment's acidity.

Furthermore, we investigated the degradation of the ABA triblock copolymer by the selective depolymerisation of the PDXL block in the presence of a strong acid. The ability to decompose PDXL into a monomeric compound by depolymerisation, due to its relatively low ceiling temperature, has recently been demonstrated by Coates *et al.*[34] In our experiment, degradation was performed by heating (at 120 °C) a mixture of PLA-PDXL$_{7000}$-PLA copolymer with diphenyl phosphate, enabling distillation of the formed volatile degradation products under ambient pressure. As observed, at elevated temperatures, the degradation of the polydioxolane block occurred quite easily (for 15 minutes), resulting in the recovery of 1,3-dioxolane. The residue contained only short PLA blocks, as presented in Fig. 10 in the NMR spectra.

The decrease in the copolymer molar mass was demonstrated by SEC analysis, as shown in Fig. 11.

These results obtained during this stage of studies demonstrated the merits of combining the PDXL segment with selected polyester blocks to form copolymers with the readily acid-triggered degradable segment. As these types of polymers can be degraded under acidic conditions to monomeric DXL and degradable PLA, these materials may be of special interest in the context of recycling. Ongoing studies are focused on the mechanism of degradation and the identification of formed products.

Conclusions

In summary, we have developed the synthesis of novel ABA-triblock copolymers containing hydrophobic polyester A-blocks and hydrophilic, acid-labile, polyacetal middle-blocks. It was proven that α,ω-hydroxy-terminated polyacetals may be successfully used as macroinitiators for the ring-opening polymerization of cyclic esters catalysed by commercially available tin(II) octoate catalyst. The length of polyester blocks could be easily tailored by varying the cyclic ester ratio to hydroxyl groups in the starting polymerization mixture. The present study confirmed that combining polyester blocks with polyacetal segments allowed the preparation of new materials with tuneable hydrophobic/hydrophilic balance and enhanced degradability in relation to other types of ABA copolymers. This type of block copolymer with acetal groups confined in one block has shown promise in terms of an increased degradation rate that can be easily tuned to suit specific applications.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

We would like to thank Professor P. Kubisa for the helpful and inspiring discussion of the results. The purchase of the Avance Neo 400 NMR spectrometer, used to obtain results included in this publication, was supported by the findings from the EU Regional Operational Program of the Lodz Region, RPLD.01.01.00-10-0008/18. The upgrade of the Avance III 500 NMR spectrometer used to obtain the results included in this publication was supported by the funds from the EU Regional Operational Program of the Lodz Region, RPLD.01.01.00-10-0008/18. B. Kost thanks the National Science Centre, Poland, Miniatura 5 Grant No DEC-2021/05/X/ST5/00491. M. Basko acknowledges financial support from the National Science Centre, Poland, Grant No. 2020/37/B/ST5/03302.

References

1 T. P. Haider, C. Völker, J. Kramm, K. Landfester and F. R. Wurm, *Angew. Chem., Int. Ed.*, 2019, **58**, 50–62.
2 *Degradable Polymers*, ed. G. Scott, Springer Netherlands, Dordrecht, 2002.
3 C. Y. Barlow and D. C. Morgan, *Resour., Conserv. Recycl.*, 2013, **78**, 74–80.
4 B. D. Ulery, L. S. Nair and C. T. Laurencin, *J. Polym. Sci., Part B: Polym. Phys.*, 2011, **49**, 832–864.
5 L. S. Nair and C. T. Laurencin, *Prog. Polym. Sci.*, 2007, **32**, 762–798.
6 Y. Liao, X. Zhang, C. Li, Y. Huang, M. Lei, M. Yan, Y. Zhou and C. Zhao, *Carbohydr. Polym.*, 2016, **147**, 415–425.
7 J. Zhao, H. Wang, J. Liu, L. Deng, J. Liu, A. Dong and J. Zhang, *Biomacromolecules*, 2013, **14**, 3973–3984.
8 N. Andronova and A. C. Albertsson, *Biomacromolecules*, 2006, **7**, 1489–1495.
9 R. P. Brannigan and A. P. Dove, *Biomater. Sci.*, 2017, **5**, 9–21.
10 H. Ye, K. Zhang, D. Kai, Z. Li and X. J. Loh, *Chem. Soc. Rev.*, 2018, **47**, 4545–4580.

 This journal is © The Royal Society of Chemistry 2022

Published on 30 August 2022. Downloaded by Ghent University Library on 8/30/2022 10:31:30 AM.

11 U. Edlund and A. C. Albertsson, *Adv. Polym. Sci.*, 2002, **157**, 67–112.
12 S. Slomkowski, S. Penczek and A. Duda, *Polym. Adv. Technol.*, 2014, **25**, 436–447.
13 E. Rezvani Ghomi, F. Khosravi, A. Saedi Ardahaei, Y. Dai, R. E. Neisiany, F. Foroughi, M. Wu, O. Das and S. Ramakrishna, *Polymers*, 2021, **13**, 1–16.
14 J. Muller, C. González-Martínez and A. Chiralt, *Materials*, 2017, **10**, 1–22.
15 M. Socka, A. Duda, A. Adamus, R. A. Wach and P. Ulanski, *Polymer*, 2016, **87**, 50–63.
16 Y. Ramot, M. Haim-Zada, A. J. Domb and A. Nyska, *Adv. Drug Delivery Rev.*, 2016, **107**, 153–162.
17 J. K. Oh, *Soft Matter*, 2011, **7**, 5096–5108.
18 D. K. Schneiderman and M. A. Hillmyer, *Macromolecules*, 2016, **49**, 2419–2428.
19 M. A. Hillmyer and W. B. Tolman, *Acc. Chem. Res.*, 2014, **47**, 2390–2396.
20 A. J. Poudel, F. He, L. Huang, L. Xiao and G. Yang, *Carbohydr. Polym.*, 2018, **194**, 69–79.
21 C. Diaz and P. Mehrkhodavandi, *Polym. Chem.*, 2021, **12**, 783–806.
22 B. W. Boudouris, C. D. Frisbie and M. A. Hillmyer, *Macromolecules*, 2010, **43**, 3566–3569.
23 Q. Xu, Q. Zhou, K. Shen, D. Jiang and L. Ni, *J. Polym. Sci., Part B: Polym. Phys.*, 2016, **54**, 424–432.
24 N. Kayaman-Apohan, O. Karal-Yilmaz, K. Baysal and B. M. Baysal, *Polymer*, 2001, **42**, 4109–4116.
25 S. Ando, A. L. Grote and K. Koide, *J. Org. Chem.*, 2011, **76**, 1155–1158.
26 C. L. Wanamaker, W. B. Tolman and M. A. Hillmyer, *Biomacromolecules*, 2009, **10**, 443–448.
27 J. Shin, M. T. Martello, M. Shrestha, J. E. Wissinger, W. B. Tolman and M. A. Hillmyer, *Macromolecules*, 2011, **44**, 87–94.
28 T. Kissel, Y. Li and F. Unger, *Adv. Drug Delivery Rev.*, 2002, **54**, 99–134.
29 E. Khodaverdi, Z. Heidari, S. A. S. Tabassi, M. Tafaghodi, M. Alibolandi, F. S. M. Tekie, B. Khameneh and F. Hadizadeh, *AAPS PharmSciTech*, 2014, **16**, 140–149.
30 M. H. Huang, S. Li, J. Coudane and M. Vert, *Macromol. Chem. Phys.*, 2003, **204**, 1994–2001.
31 H. Qiu, Z. Yang, M. Köhler, J. Ling and F. H. Schacher, *Macromolecules*, 2019, **52**, 3359–3366.
32 K. Naraghi, N. Sahli, M. Belbachir, E. Franta and P. J. Lutz, *Polym. Int.*, 2002, **51**, 912–922.
33 N. Sahli, S. Ould Kada, M. Belbachir, E. Franta, P. Lutz and L. Reibel, *Macromol. Symp.*, 1994, **85**, 167–174.
34 B. A. Abel, R. L. Snyder and G. W. Coates, *Science*, 2021, **373**, 783–789.
35 B. Kost and M. Basko, *Polym. Chem.*, 2021, **12**, 2551–2562.
36 S. Penczek, P. Kubisa and K. Matyjaszewski, *Cationic Ring-Opening Polymerization of Heterocyclic Monomers*, Springer Berlin Heidelberg, Berlin, Heidelberg, 1980, vol. 37.
37 P. Kubisa and S. Penczek, *Prog. Polym. Sci.*, 1999, **24**, 1409–1437.
38 E. J. Goethals, *Pure Appl. Chem.*, 1976, **48**, 335–341.
39 A. M. J. Coenen, J. A. W. Harings, S. Ghazanfari, S. Jockenhoevel and K. V. Bernaerts, *RSC Adv.*, 2020, **10**, 9623–9632.
40 D. Bourissou, B. Martin-Vaca, A. Dumitrescu, M. Graullier and F. Lacombe, *Macromolecules*, 2005, **38**, 9993–9998.
41 Y. Bakkour, V. Darcos, S. Li and J. Coudane, *Polym. Chem.*, 2012, **3**, 2006–2010.
42 P. Lewinski, S. Sosnowski, S. Kazmierski and S. Penczek, *Polym. Chem.*, 2015, **6**, 4353–4357.
43 R. A. Silva, G. G. Silva, C. A. Furtado, R. L. Moreira and M. A. Pimenta, *Electrochim. Acta*, 2001, **46**, 1493–1498.
44 S. Saeidlou, M. A. Huneault, H. Li and C. B. Park, *Prog. Polym. Sci.*, 2012, **37**, 1657–1677.
45 J.-R. Sarasua, R. E. Prud'homme, M. Wisniewski, A. Le Borgne and N. Spassky, *Macromol.*, 1998, **31**, 3895–3905.
46 M. A. Woodruff and D. W. Hutmacher, *Prog. Polym. Sci.*, 2010, **35**, 1217–1256.
47 Y. Aoyagi, K. Yamashita and Y. Doi, *Polym. Degrad. Stab.*, 2002, **76**, 53–59.
48 M. H. Rahaman and H. Tsuji, *Polym. Degrad. Stab.*, 2013, **98**, 709–719.
49 L. N. Woodard and M. A. Grunlan, *ACS Macro Lett.*, 2018, **7**, 976–982.
50 G. Gorrasi and R. Pantani, *Adv. Polym. Sci.*, 2018, **279**, 119–152.
51 P. Kubisa and J. P. Vairon, in *Polymer Science: A Comprehensive Reference*, Elsevier, 2012, pp. 183–211.
52 E. J. Goethals, R. R. De Clercq and S. R. Walraedt, *J. Macromol. Sci., Part A: Pure Appl.Chem.*, 1993, **30**, 679–688.
53 J. M. Williams, *Polymer*, 1992, **33**, 4630–4634.
54 R. R. De Clercq and E. J. Goethals, *Macromolecules*, 1992, **25**, 1109–1113.
55 M. Ott, H. H. Fischer, M. Maiwald, K. Albert and H. Hasse, *Chem. Eng. Process. Process Intensif.*, 2005, **44**, 653–660.

Supporting for

Synthesis and properties of ABA-triblock copolymers from polyesters A-blocks and polyacetals B-blocks with enhanced ability to degradation

Karolina Cichoń, Bartłomiej Kost*, Malgorzata Basko*

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland

Mail: baskomeg@cbmm.lodz.pl, kost@cbmm.lodz.pl

Table of contents:

Molar weight calculation……3

Assay of Sulphur content……3

Table S1. Conditions of mineralization……...3

Table S2. The diffusion coefficient for signals belonging to the $PDXL_{7000}$ and PLA_{7500}-$PDXL_{7000}$-PLA_{7500} block copolymer……..……..3

Table S3. Thermal properties of selected ABA copolymers (the second heating cycle at a rate of 10 °C/min in a DSC analysis)……..4

Figure S1. MALDI TOF of purified $PDXL_{2400}$…..…….5

Figure S2. The ^{1}H and ^{13}C NMR spectra (400 MHz, $CDCl_3$) of purified $PDXL_{7000}$ …….6

Figure S3. ^{1}H NMR spectrum, and 2D HSQC NMR (400 MHz, DMSO-d_6) of $PDXL_{2400}$ diol

..……...7

Figure S4. SEC trace of polyacetal macroinitiator HO-$PDXL_{7000}$-OH and prepared purified PCL-$PDXL_{7000}$-PCL copolymers. …….……8

Figure S5. The SEC traces of crude and purified a) PLA-$PDXL_{7000}$-PLA copolymer and b) PCL-$PDXL_{7000}$-PCL copolymer....…….……9

Figure S6. SEC curves of polyacetal macroinitiator HO-$PDXL_{2400}$-OH and resulting purified PLA-$PDXL_{2400}$-PLA copolymers……..10

Figure S7. The ^{1}H and ^{13}C NMR spectra (400 MHz, $CDCl_3$) of purified PCL-$PDXL_{7000}$-PCL copolymer……..11

Figure S8. Assessment of mean static contact angles of PCL-$PDXL_{7000}$-PCL block copolymers in comparison to pure $PDXL_{7000}$ and PCL_{14000}……...……12

Figure S9. The ^{1}H NMR of the films for the WCA measurements ($CDCl_3$, 400 MHz) ……...…….……...13

Figure S10. a)The DSC thermograms registered during the second scan and b) TGA curves for starting HO-PDXL$_{7000}$-OH diol, PCL$_{14000}$, and PCL-PDXL$_{7000}$-PCL. For DSC analysis samples were heated at 10 $^{\circ}$C/min and cooled at 10 $^{\circ}$C/min, whereas for TGA measurement samples were heated at 20 $^{\circ}$C/min……...13

Figure S11. Acid induced degradation of PLA-PDXL$_{7000}$-PLA copolymer followed by ^{1}H NMR spectra([acetal units]:[H^{+}] = 10:1), (CD_3CN, 400 MHz)……...14

Figure S12. The GC spectra of acid induced degradation of PLA-PDXL$_{7000}$-PLA after 122h……...15

Molecular weight calculation

Assay of Sulphur content

0.2 g of copolymers were placed into glass vessels, then 65% nitric acid (3 mL) and 36% hydrochloric acid (1 mL) spectrally pure were added. Samples were pre-mineralized at 25 ˚C within 25 min. by using an ultrasonic bath. Then, the samples were mineralized in the UltraWave closed microwave system in two steps, as presented in the Table 1.

Table S1. Conditions of mineralization

Step	Time [min.]	T1 [^{0}C]	T2 [^{0}C]	Pressure [Ba]	Power [W]
1	25	240	70	110	1500
2	10	240	70	110	1500

After mineralization, the samples were transferred to 25 mL volumetric flasks and filled with deionized water and characterized. The Sulphur content was determined to be 932 ppm.

Table S2. The diffusion coefficient for signals belonging to the $PDXL_{7000}$ and PLA_{7500}-$PDXL_{7000}$-PLA_{7500} block copolymer

$PDXL_{7000}$	
Signal [ppm]	Difusion coefficiency
4.75	$1.26 \cdot 10^{-6}$
3.70	$1.26 \cdot 10^{-6}$
PLA_{10000}	
5.17	$1.32 \cdot 10^{-6}$
1.60	$1.34 \cdot 10^{-6}$
PLA_{7500}-$PDXL_{7000}$-PLA_{7500}	
5.12	$9.95 \cdot 10^{-7}$
4.75	$1.02 \cdot 10^{-6}$
4.40-4.28	$1.02 \cdot 10^{-6}$
3.70	$9.99 \cdot 10^{-7}$
1.60	$1.01 \cdot 10^{-6}$

Table S3. Thermal properties of selected ABA copolymers (the second heating cycle at a rate of 10 °C/min in a DSC analysis)

Copolymer	**Ester content mol %**	**DSC**				**TGA**	
		T_g [°C]	T_m PDXL [°C]	T_m polyester [°C]	ΔH_m [J/g]	T_1 [°C]	T_2 [°C]
PLA-PDXL$_{7000}$-PLA 1	26	-41	-----	-----	-----	227	308
PLA-PDXL$_{7000}$-PLA 2	35	-26	-----	-----	-----	229	299
PLA-PDXL$_{7000}$-PLA 3	44	-13	-----	123	12.78	239	298
PLA-PDXL$_{7000}$-PLA 4	53	3	-----	145	23.51	239	308
PLA-PDXL$_{7000}$-PLA 5	60	3	-----	150	27.24	243	324
PCL-PDXL$_{7000}$-PCL 1	42	-63	31	53	68.34	305	355
PCL-PDXL$_{7000}$-PCL 2	65	-65	24	51	62.74	302	371

T_g, T_m - temperature of glass transition and melting

ΔH_m - polyester enthalpy of melting

T_1, T_2 - temperature of the maximum decomposition

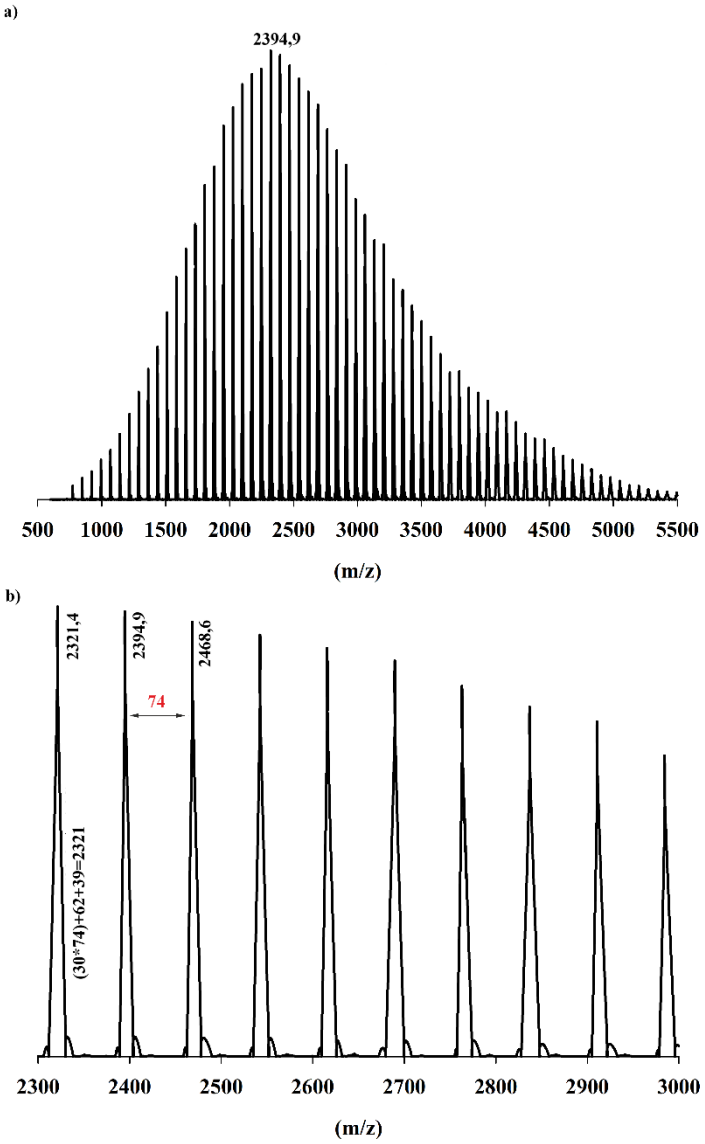


Figure S1. MALDI TOF of purified PDXL (M_{nNMR}= 2400 g/mol)

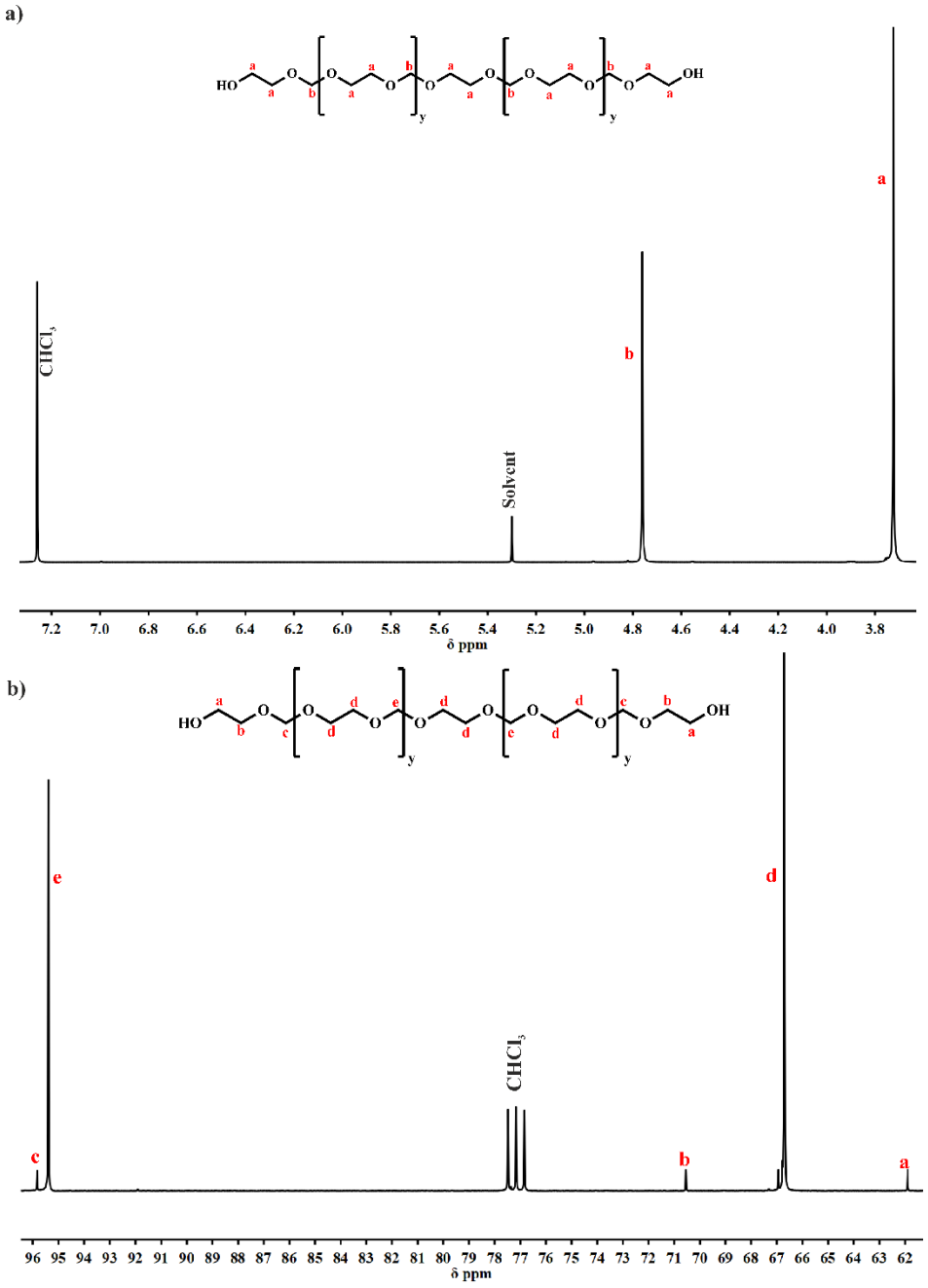


Figure S2. The ^{1}H and ^{13}C NMR spectra (400 MHz, $CDCl_3$) of purified $PDXL_{7000}$

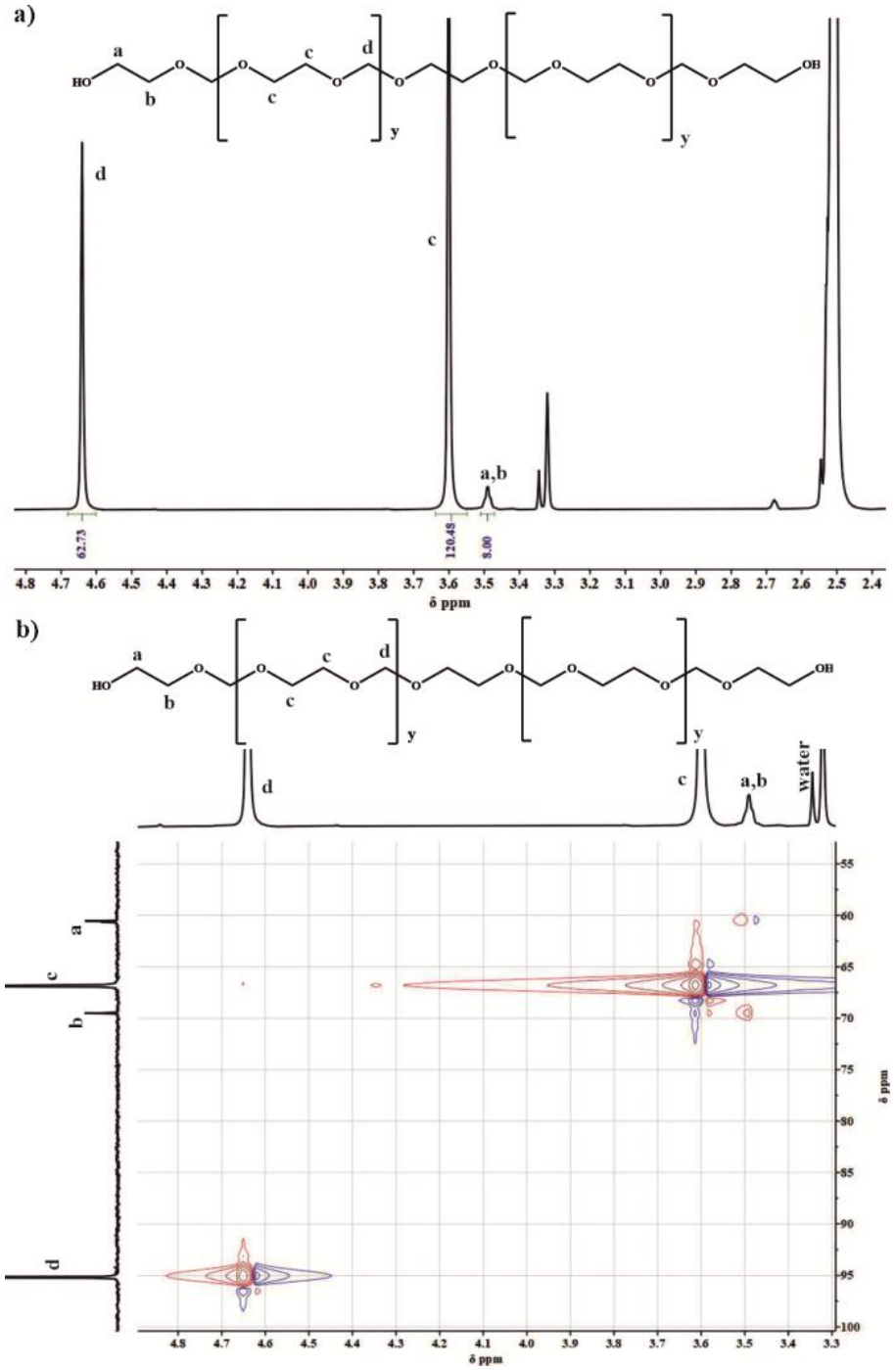


Figure S3. ^{1}H NMR spectrum, and 2D HSQC NMR (400 MHz, DMSO-d_6) of PDXL diol

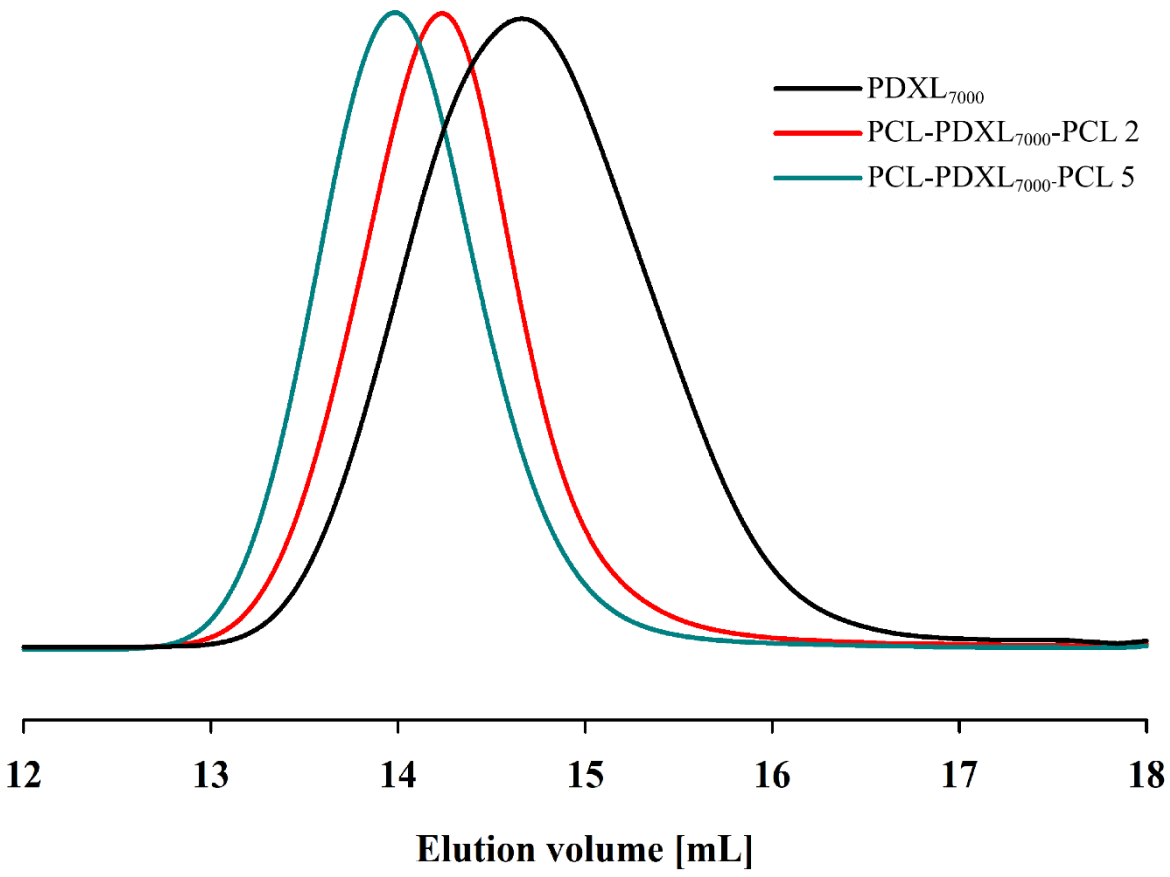


Figure S4. SEC trace of polyacetal macroinitiator HO-PDXL$_{7000}$-OH and prepared purified PCL-PDXL$_{7000}$-PCL copolymers

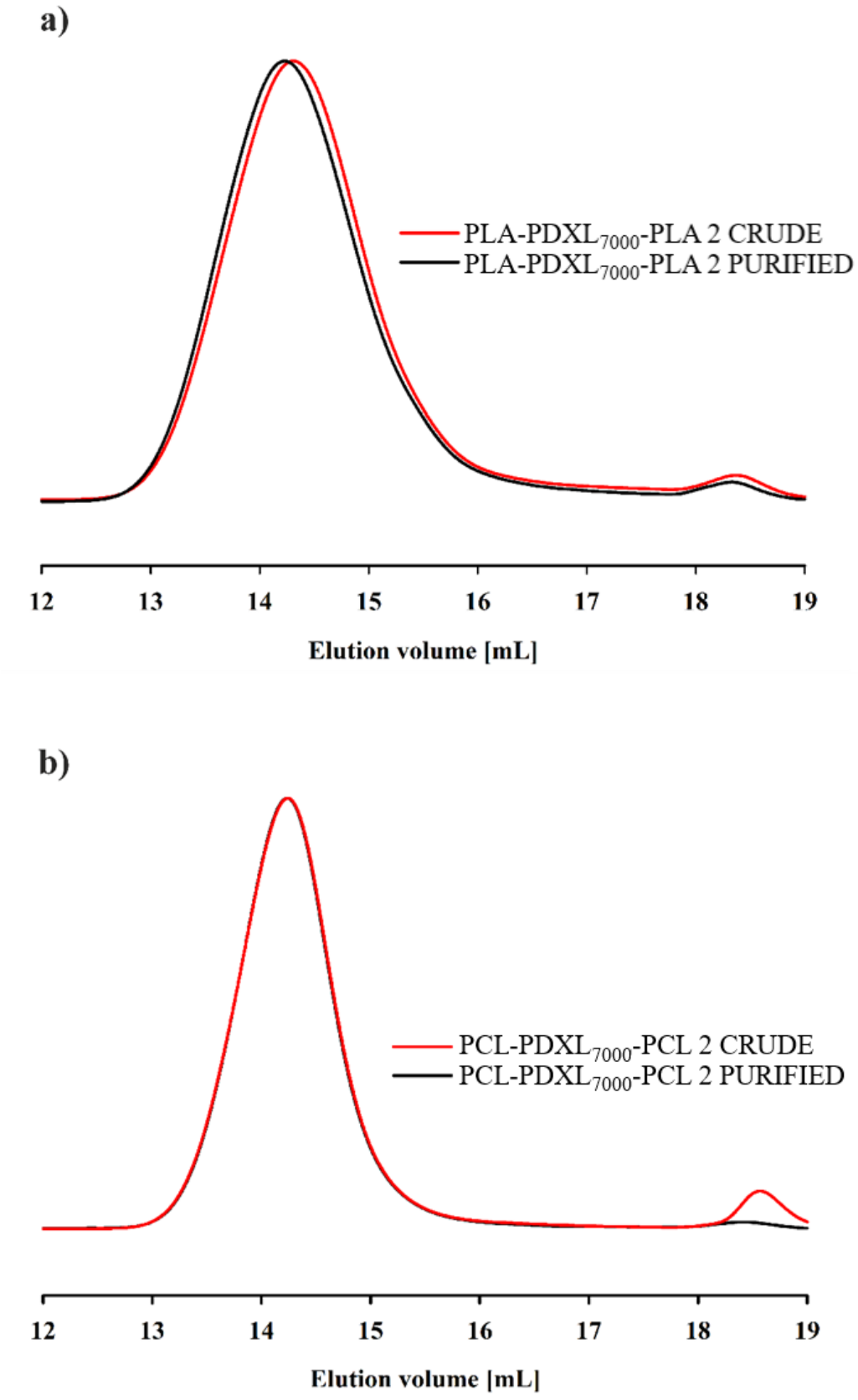


Figure S5. The SEC traces of crude and purified a) PLA-PDXL$_{7000}$-PLA copolymer and b) PCL-PDXL$_{7000}$-PCL copolymer

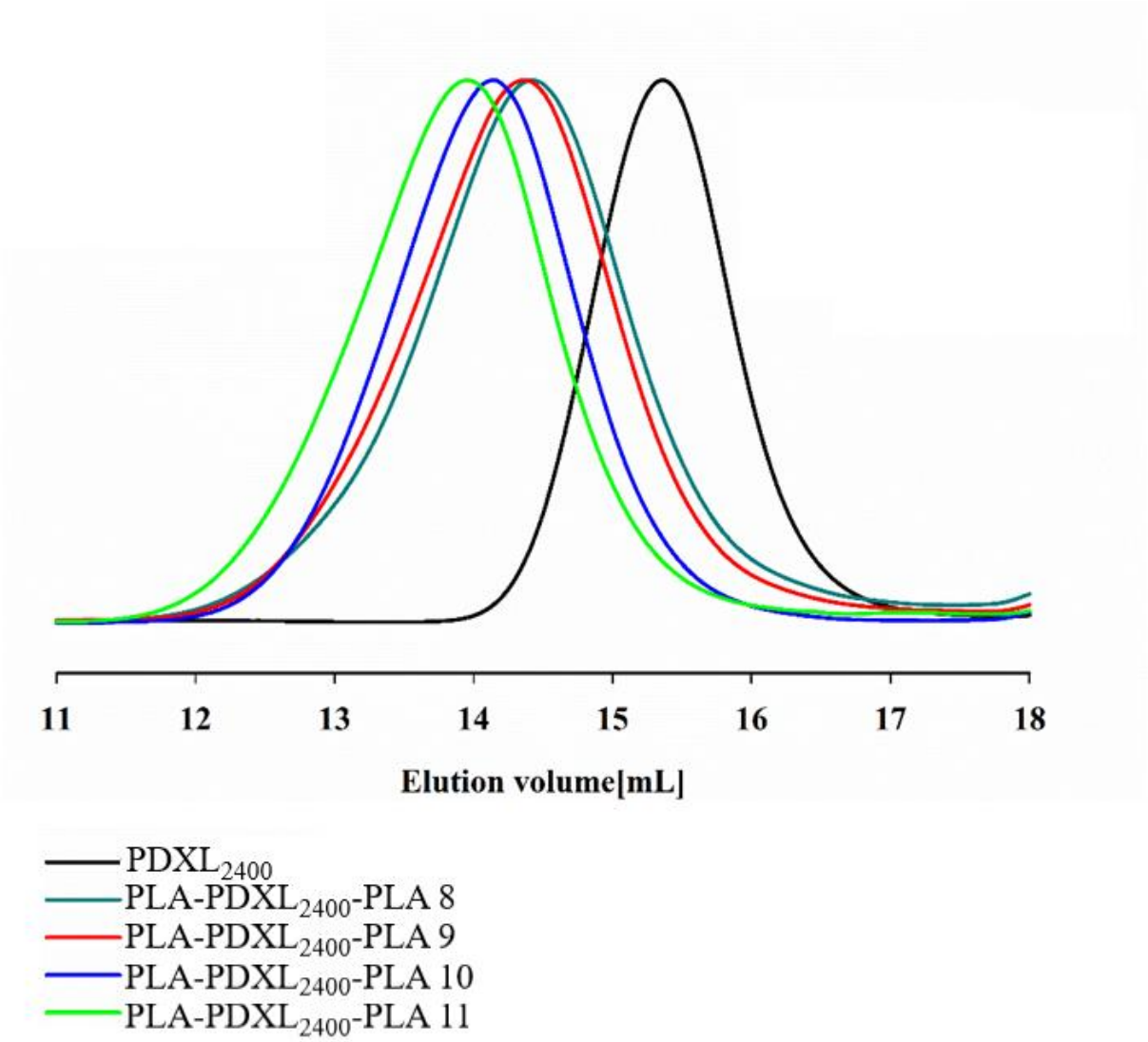


Figure S6. SEC curves of polyacetal macroinitiator HO-PDXL$_{2400}$-OH and resulting purified PLA-PDXL$_{2400}$-PLA copolymers.

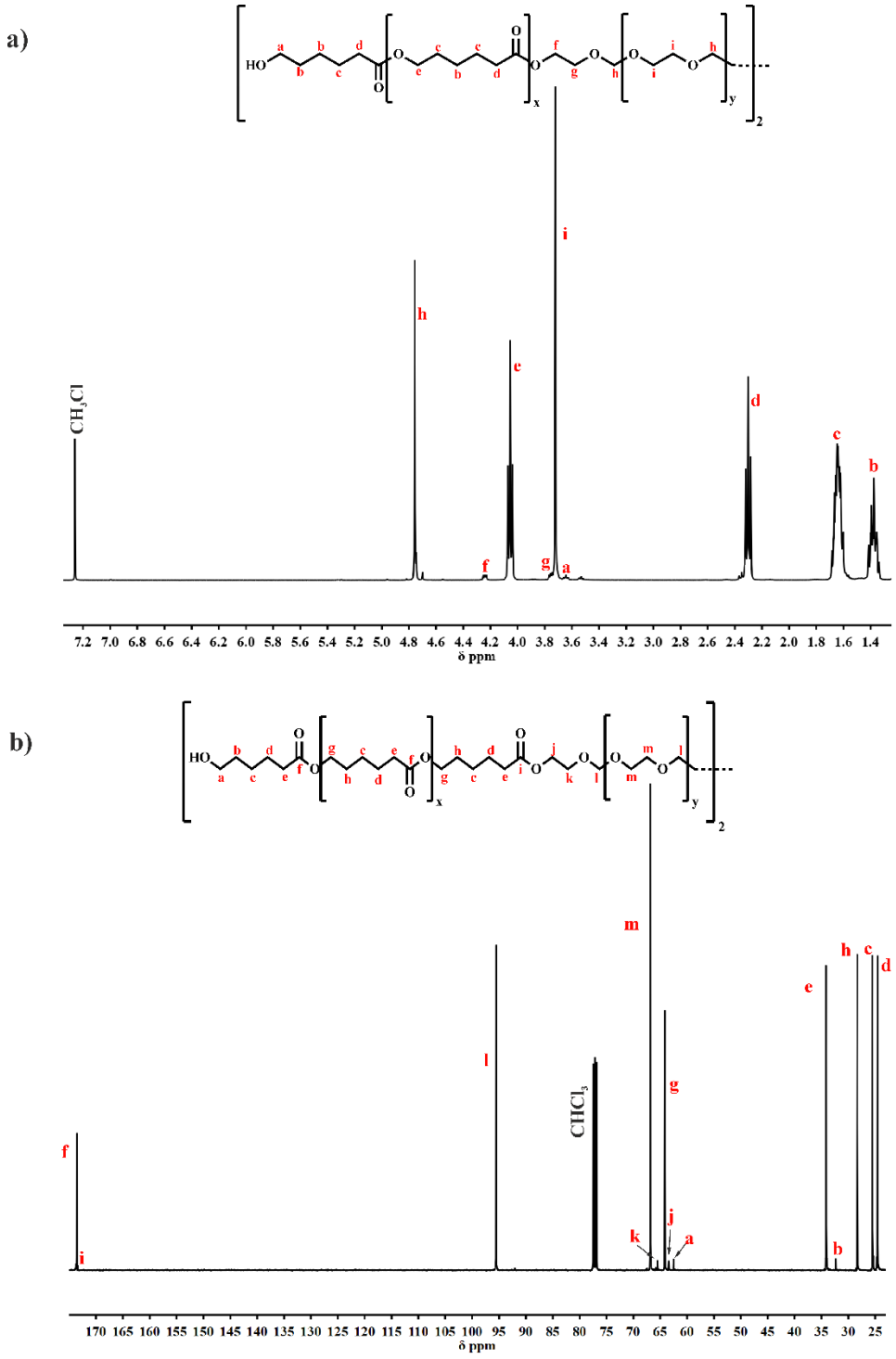


Figure S7. The ^{1}H and ^{13}C NMR spectra (400 MHz, $CDCl_3$) of purified PCL-PDXL$_{7000}$-PCL copolymer.

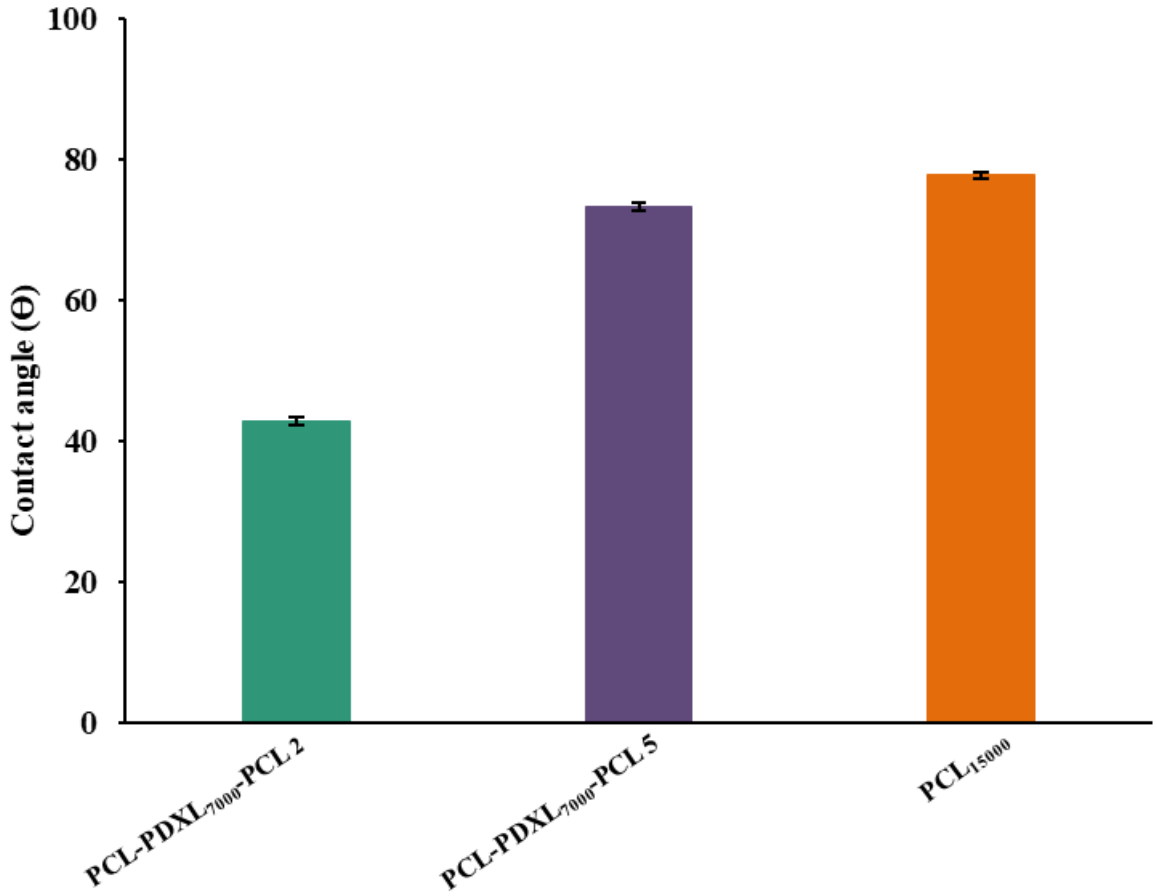


Figure S8. Assessment of mean static contact angles of PCL-PDXL$_{7000}$-PCL block copolymers in comparison to pure PDXL$_{7000}$ and PCL$_{14000}$.

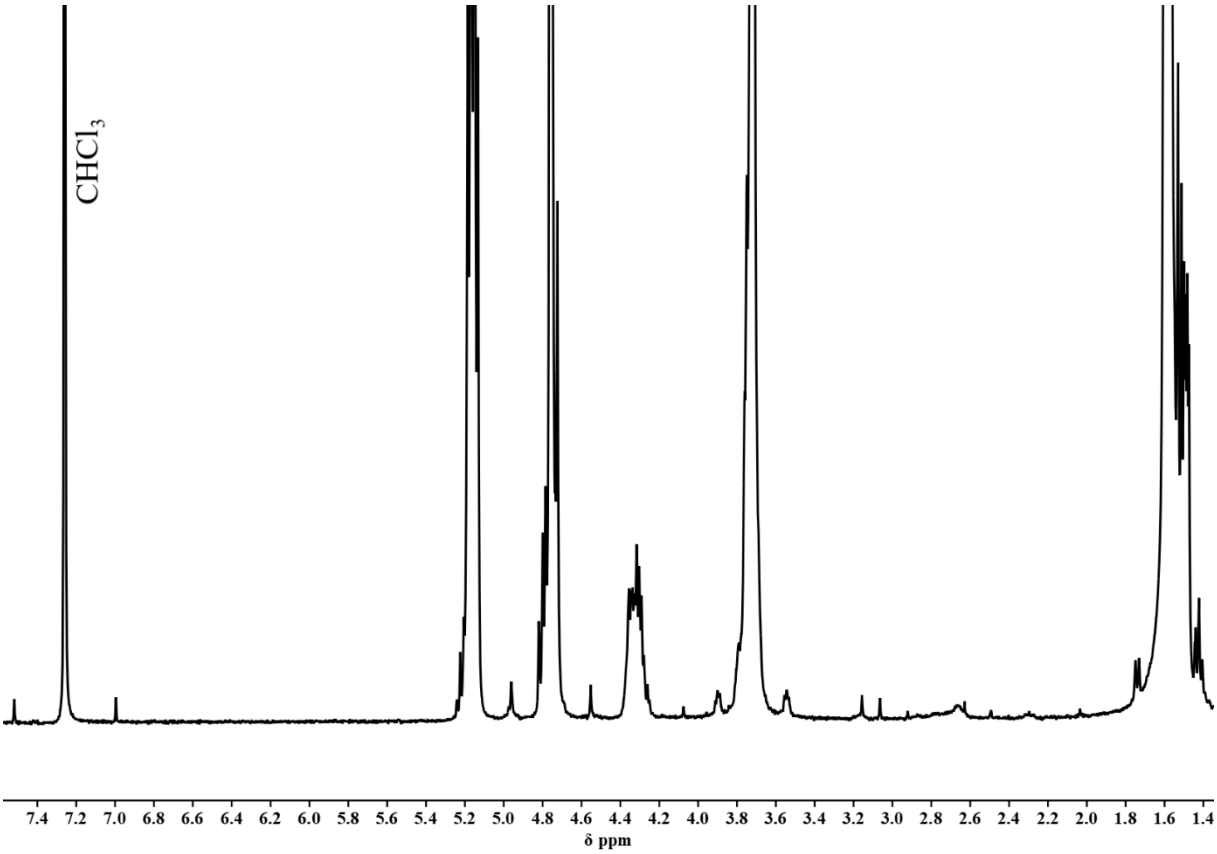


Figure S9. The ^{1}H NMR of the films for the WCA measurements ($CDCl_3$, 400 MHz)

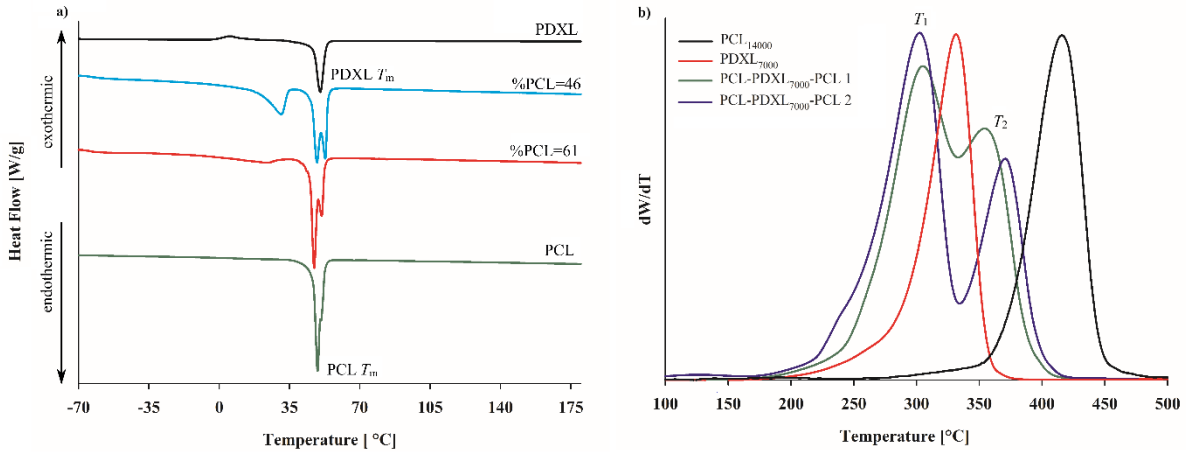


Figure S10. a)The DSC thermograms registered during the second scan and b) TGA curves for starting HO-PDXL$_{7000}$-OH diol, PCL$_{14000}$, and PCL-PDXL$_{7000}$-PCL. For DSC analysis samples were heated at 10 ˚C/min and cooled at 10 ˚C/min, whereas for TGA measurement samples were heated at 20 ˚C/min.

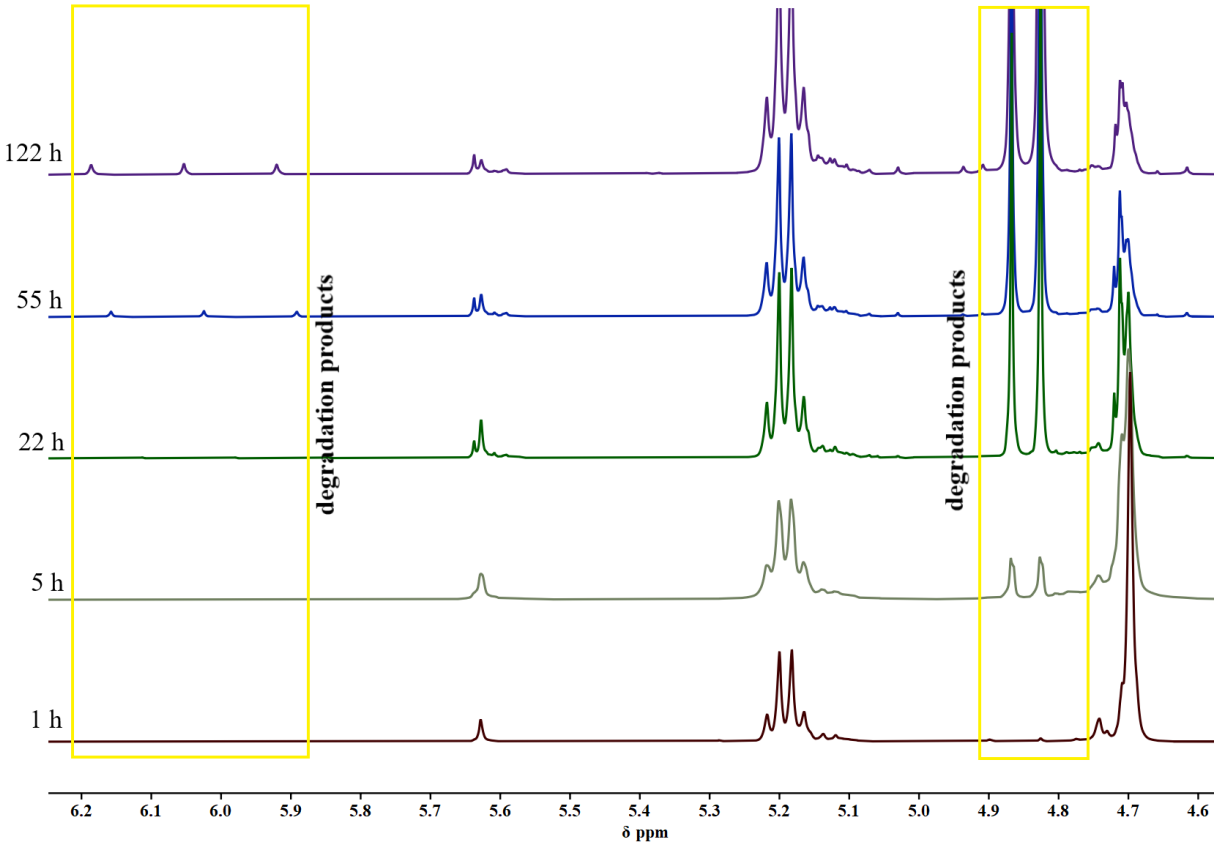


Figure S11. Acid induced degradation of PLA-PDXL$_{7000}$-PLA copolymer followed by ^{1}H NMR spectra([acetal units]:[H^{+}] = 10:1), (CD_3CN, 400 MHz).

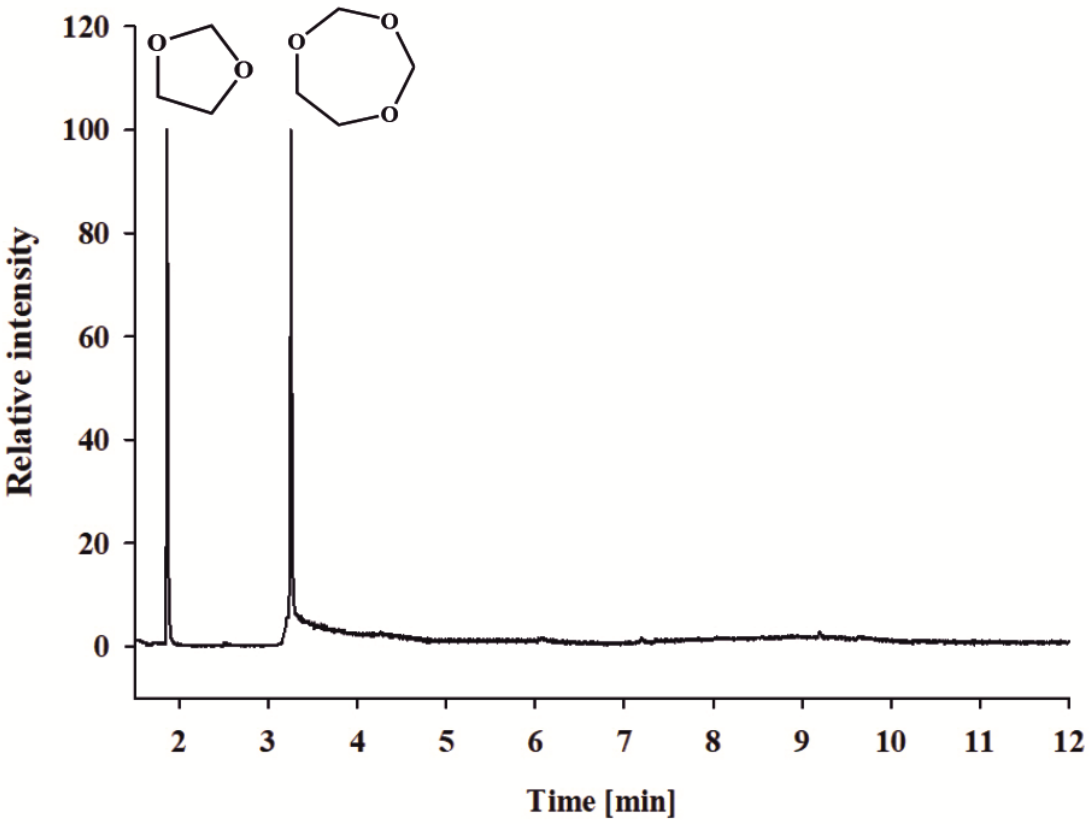


Figure S12. The GC spectra of acid induced degradation of PLA-PDXL$_{7000}$-PLA after 122h

Publikacja 2:

Karolina Cichoń, Irena I. Bak-Sypien, Malgorzata Basko, Bartłomiej Kost, Synthesis and characterization of functionalized polylactides containing acetal units, Macromolecules 2023, 56, 6951−6967

Macromolecules

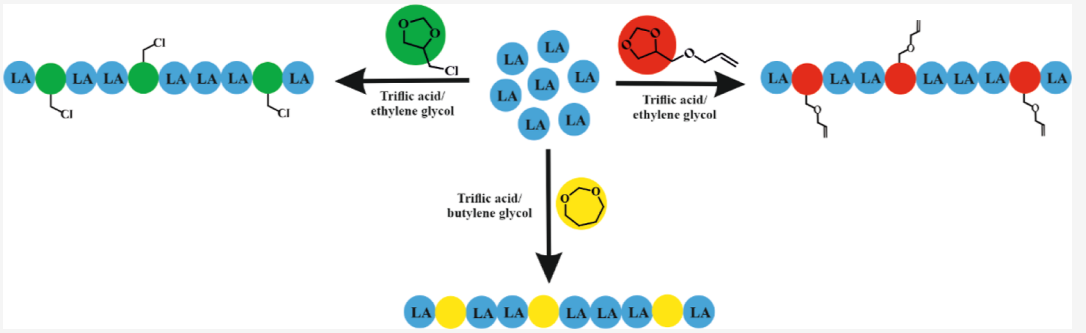
pubs.acs.org/Macromolecules Article

Synthesis and Characterization of Functionalized Polylactides Containing Acetal Units

Karolina Cichoń, Irena I. Bak-Sypien, Malgorzata Basko,* and Bartłomiej Kost*

Cite This: https://doi.org/10.1021/acs.macromol.3c01343 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information



ABSTRACT: New functionalized lactide copolymers containing acetal units were prepared for the first time in a controlled manner that enabled the regulation of the number of reactive groups introduced into the polyester chain. The presence of functional groups in the copolymer backbone provided chemical modification sites, and the nature of the acetal unit affected the material degradability. First, paraformaldehyde was reacted with selected diols containing reactive pendant groups (3-allyloxypropane-1,2-diol and 3-chloropropane-1,2-diol), which was catalyzed by *p*-toluenesulfonic acid, to synthesize new cyclic acetals with different functionalities (allyl- or chloro-). In addition, using butane-1,4-diol, a nonfunctionalized seven-membered cyclic acetal (dioxepane) was obtained for comparative studies. In the next step, the prepared cyclic acetals were used for cationic copolymerization with lactide in the presence of glycol as an initiator and triflic acid as a catalyst. Different temperatures (−15, 2, and 30 °C) and copolymerization times (24, 48, 72, and 192 h) were investigated to produce copolyesters with variable contents of acetal units in the range of 5−27%. The copolymers' structure and molar masses were carefully investigated using ^{1}H, ^{13}C NMR, 2D NMR, and size-exclusion chromatography. Moreover, the ability of functionalized copolymers to perform post modifications was also proven by the reaction with sodium azide and propanethiol. Finally, we speculate that structurally diverse groups can be attached to the copolyester chain, fine-tuning the on-demand properties, which could rapidly expand the library of polylactide-based materials.

INTRODUCTION

Research on the synthesis of biodegradable polymers used in various fields, such as medicine, health care, packaging, or environmental protection, is increasingly important in polymer science.[1] Currently, several different types of biodegradable polymers have been developed as potential "green materials" due to their specific properties, which can be adapted to the intended applications.[2,3] Among them, polyesters, such as polylactide, polycaprolactone, polyglycolide, or their copolymers, are the most promising candidates to replace non-degradable petroleum-based polymers. Due to its biocompatibility, biodegradability, and the possibility of obtaining raw materials for synthesis from renewable sources, polylactide (PLA) may be the most promising eco-friendly polymer with great potential for further development.[4] However, PLA also has numerous disadvantages that limit its application. For instance, to achieve sufficient degradation time, the molecular weight of PLA should be lower than 40 000 g/mol; otherwise, the polyester can degrade even for 60 years.[5] On the other hand, in the case of packaging applications, its relatively high crystallinity and brittleness may cause the material properties to deteriorate. The difficulty of modifying PLA is among the most important drawbacks as the linear aliphatic structure of the repeating unit does not contain any reactive groups in the polymer chain. The lack of functional side groups in polylactide strongly limits the possibility of subsequent post modification through further reactions with purposely selected compounds. Therefore, much scientific research has focused on finding new methods and approaches for the functionalization of polylactide.[6] A widely used way to modify the chemical properties of polylactide is the copolymerization of lactide with

Received: July 7, 2023
Revised: July 21, 2023

Downloaded via CTR MOLECULAR & MACROMOLECULAR STUD on August 24, 2023 at 06:44:53 (UTC).
See https://pubs.acs.org/sharingguidelines for options on how to legitimately share published articles.

© XXXX The Authors. Published by American Chemical Society

different monomers that may introduce degradable or nondegradable units into the polyester chain.

One of the first copolymers, which presented attractive mechanical and processing properties suitable for medical applications, was obtained in the copolymerization of lactide with glycolide.[7,8] Other cyclic monomers such as caprolactone,[9] valerolactone,[10] trimethylene carbonate,[11] or ethylene oxide[12] were also copolymerized with lactide to obtain a better balance of properties of the polymeric material. These comonomers enable the crystallinity, hydrophobicity, and mechanical properties of the material to be changed; however, they do not enable the functionalization of the polyester chain.[13] To obtain polyesters containing reactive groups in the side chains, functionalized comonomers were used in the copolymerization, which allowed polylactide with various groups, such as hydroxyl,[14] vinyl, allyl,[15] propargyl,[16] and chloromethylene[17] groups, to be synthesized. However, very often, introducing these pendant reactive groups into the polyester chain involves inserting repeating units (e.g., allyl and propargyl glycidyl ethers) that do not significantly improve the degradation rate of the final copolymer. Moreover, in some cases, only a few units of functional comonomer can be incorporated into the polymer chain (for example, in the copolymerization of lactide with substituted ethers, functional copolymers containing several functionalized units per chain were obtained).[16,18] When copolymerizing lactide with substituted lactides, multistage synthesis, which often proceeds with a low efficiency, must be considered.[17] Moreover, to incorporate the functionalities that can initiate polymerization (amine or hydroxyl groups), the lactide must first be blocked by a protecting group (e.g., benzyl group) in the monomer to prevent branched or cross-linked structures from forming. Thus, this process requires an additional step after polymerization to unblock the functionalities.[14] Due to these limitations, further studies on the functionalization of polyesters are justified.

Currently, one of the research directions in polymer chemistry is focused on the synthesis of polyesters containing unstable acetal repeating units in the main chain in order to obtain hydrolytically and thermally sensitive polymers. Various methods can achieve this effect. For example, cyclic hemiacetal esters, which are more hydrolytically and thermally labile than their acetal and ester counterparts, were used in cationic ring-opening polymerization enabling efficient synthesis of polymers with linkages that facilitated degradation.[19−21]

Our research group is performing extensive research to develop polyesters with modified properties by ring-opening copolymerization of lactide with cyclic acetals.[22,23] We determined that copolymerization with 1,3-dioxolane allowed for the crystallinity and degradation rate of the resulting polylactide to be modified. Labile acetal units in the polylactide copolymers cause material degradation in the presence of the acid for 72 h.[22] However, despite the accelerated degradation of the copolymer, 1,3-dioxolane does not introduce any additional functional groups that can create the possibility of further postmodification.

The aim of this work was to investigate the copolymerization of lactide with functionalized cyclic acetals to afford copolyesters in which different reactive pendant groups are distributed along the copolymer chain. To achieve this goal, cyclic acetals with allyl- or chloro-functional groups were copolymerized with lactide in the presence of diols (initiators) and strong protonic acid as a catalyst. Basic relationships between the reaction temperature, time, molar mass, and copolymer composition were established. The content of functional groups and acetal units and the structure of the copolymer chain were confirmed by ^{1}H, ^{13}C NMR, and 2D NMR. Moreover, the ability to functionalize copolymers was also proven by reaction with sodium azide, glycidyl propargyl ether, propargyl alcohol, mercaptoethanol, thioglycolic acid, and propanethiol. We anticipated that through our approach, functional copolyesters containing "clickable" pendant groups can be synthesized with an enhanced degradation ability.

EXPERIMENTAL SECTION

Materials. L,L-Lactide (LA) was purchased from Purac (99% Netherlands), crystallized from 2-propanol and stored under reduced pressure. Paraformaldehyde (99%), *p*-toluenesulfonic acid (pTSA, 98%), 3-allyloxypropane-1,2-diol (98%), 3-chloropropane-1,2-diol (98%), triflic acid (99%), phosphorus pentoxide (P_2O_5), propanethiol (99%), mercaptoethanol (95%), thioglycolic acid (98%), propargyl glycidyl ether (98%), propargyl alcohol (97%), copper (I) bromide, pentamethyldiethylenetriamine (95%, PMDTA), and sodium azide were purchased from Merck and used without further purification. Butan-1,4-diol (99%, Acros) was used as received. AIBN was purchased from Sigma-Aldrich and crystallized from ethanol at 40 °C. Methylene chloride from POCH was distilled over P_2O_5 and maintained under a vacuum. Toluene (95%), hexane (95%), diethyl ether (98%), and HCl (35%) were purchased from POCH (Gliwice, Poland) and used as received. Anhydrous ethylene glycol (ethane-1,2-diol) (<99.9%, Sigma-Aldrich) was used as received.

Synthesis of 1,3-Dioxepane (DXP). 50 g of butan-1,4-diol (0.55 mol), 20 g (0.71 mol) of paraformaldehyde, 94 mg (0,55 mmol) of pTSA, and 80 mL of toluene were placed in a round-bottomed flask. Then, the Dean−Stark apparatus and reflux condenser were placed in the flask, and the mixture was refluxed. The synthesis was performed until the appropriate amount of water was released (4 h). Subsequently, the obtained dioxepane was distilled (115−118 °C) under atmospheric pressure with a Vigreux column (40 cm) to well separate toluene (110 °C) from the product. The product with a purity of >99% (GC) was obtained with a yield of 90%. The product was kept over dried molecular sieves (4 Å) under an argon atmosphere.

^{1}H NMR, $CDCl_3$, 400 MHz, δ (ppm): 4.83 (2H, s, $-OC\underline{H}_2O-$), 3.75 (4H, s, $-CH_2OC\underline{H}_2C\underline{H}_2OCH_2-$), 1.73 (4H, s, $-C\underline{H}_2CH_2OCH_2C\underline{H}_2-$).

^{13}C NMR, $CDCl_3$, 100 MHz, δ (ppm): 94.48 (1C, s, $-O\underline{C}H_2O-$), 67.28 (2C, s, $-CH_2O\underline{C}H_2\underline{C}H_2OCH_2-$), 29.35 (2C, s, $-\underline{C}H_2CH_2OCH_2\underline{C}H_2-$).

MS: EI (70 eV), m/z (%): 102.00 $[M]^+$ (11), 71.15 (100), 55.20 (13), 42.25 (93); CI (CH_4), m/z calcd, 103.07; found, 103.05 $[MH]^+$.

Synthesis of 4-Chloromethyl-1,3-dioxolane (Cl-DXL). The synthesis of Cl-DXL was conducted as performed for DXP. Briefly, 50 g of 3-chloropropane-1,2-diol (0.45 mol), 15 g (0.54 mol) of paraformaldehyde, 77 mg (0,45 mmol) of pTSA, and 80 mL of toluene were placed in a round-bottomed flask. Then, the Dean−Stark apparatus and reflux condenser were placed in the flask, and the mixture was refluxed. Then, the toluene was removed from the product by using a rotary evaporator, and the crude Cl-DXL was distilled (146−150 °C) under atmospheric pressure. The product with a purity of >99% (GC) was obtained with a yield of 80%. The product was kept over dried molecular sieves (4 Å) under an argon atmosphere.

^{1}H NMR, $CDCl_3$, 400 MHz, δ (ppm): 5.07 and 4.90 (2H, s, $-OC\underline{H}_2O-$), 4.31−4.24 (1H, m, $-OCH_2O-C\underline{H}(CH_2Cl)CH_2$), 4.02−3.81 (2H, m, $-OCH_2O-CH(CH_2Cl)C\underline{H}_2$), 3.62−3.44 (2H, m, $-OCH_2O-CH(C\underline{H}_2Cl)CH_2$).

^{13}C NMR, $CDCl_3$, 100 MHz, δ (ppm): 95.62 (1C, s, $-O\underline{C}H_2O-$), 74.75 (1C, s, $-OCH_2O-\underline{C}H(CH_2Cl)CH_2$), 67.90 (1C, s, −

https://doi.org/10.1021/acs.macromol.3c01343
Macromolecules XXXX, XXX, XXX−XXX

$OCH_2O-CH(CH_2Cl)\underline{C}H_2$), 44.03 (1C, s, $-OCH_2O-CH(\underline{C}H_2Cl)-CH_2$).

MS: EI (70 eV), *m/z* (%): 121.00 $[M-H]^+$ (20), 73.05 (100), 57.00 (10), 45.05 (36); CI (CH_4), *m/z* calcd, 139.05; found, 138.95 $[MH]^+ + CH_4$.

Synthesis of 4-[(Allyloxy)methyl]-1,3-dioxolane (Allyl-DXL). 50 g of 3-propoxypropane-1,2-diol (0.39 mol), 15 g (0.53 mol) of paraformaldehyde, 68 mg (0,39 mmol) of pTSA, and 80 mL of toluene were placed in a round-bottomed flask. Then, the Dean–Stark apparatus and reflux condenser were placed in the flask. The synthesis was performed until an appropriate amount of water was released. Then, the toluene was removed from the product by using a rotary evaporator, and the crude Allyl-DXL was distilled (45–50 °C) under reduced pressure (1×10^{-1} mbar). The product with a purity of >99% (GC) was obtained with a yield of 85%. The product was kept over dried molecular sieves (4 Å) under an argon atmosphere at 4 °C.

^{1}H NMR, $CDCl_3$, 400 MHz, δ (ppm): 5.97–5.86 (1H, m, $CH_2=\underline{C}H-CH_2-O-$), 5.35–5.17 (2H, m $\underline{C}H_2=CH-CH_2-O-$), 5.07 and 4.90 (2H, s, $-OC\underline{H}_2O-$), 4.29–4.20 (1H, quin, $-OCH_2O-\underline{C}H(CH_2O-)CH_2$), 4.05 (2H, dd, $CH_2=CH-C\underline{H}_2-O-$), 3.98 and 3.72 (2H, m, $-OCH_2O-CH(CH_2O-)C\underline{H}_2$), 3.58–3.46 (2H, m, $CH_2=CH-CH_2-O-C\underline{H}_2-$).

^{13}C NMR, $CDCl_3$, 100 MHz, δ (ppm): 134.37 (1C, m, $CH_2=\underline{C}H-CH_2-O-$), 117.14 (1C, m $\underline{C}H_2=CH-CH_2-O-$), 95.16 (1C, s, $-O\underline{C}H_2O-$), 74.29 (1C, s, $-OCH_2O-\underline{C}H(CH_2O-)CH_2$), 72.36 (1C, dd, $CH_2=CH-\underline{C}H_2-O-$), 70.25 (1C, m, $-OCH_2O-CH-(CH_2O-)\underline{C}H_2$), 66.91 (1C, m, $CH_2=CH-CH_2-O-\underline{C}H_2-$).

MS: EI (70 eV), *m/z* (%): 143 $[M-H]^+$ (2), 113 (6), 103 (4), 86 (9), 73 (32), 57(39), 45(73), 41(100); CI (CH_4), *m/z* calcd, 145.09; found, 144.95 $[MH]^+$; APCI, HRMS *m/z*: calcd, 145.0865; found, 145.0863 $[M + H]^+$ for $C_7H_{13}O_3$.

Synthesis of Cyclic Acetal Homopolymers. Homopolymers of cyclic acetals were synthesized according to procedures described previously.[23] 10 mL of freshly distilled methylene chloride, 90 mg (1 mmol) of butane-1,4-diol (1 mmol of ethylene glycol was used instead of butane-1,4-diol in the case of Cl-DXL and Allyl-DXL), and 44 μL (0.5 mmol) of triflic acid were placed in a Schlenk flask filled with argon. Subsequently, 10 g (98 mmol) of DXP or Cl-DXL (82 mmol) or Allyl-DXL (69 mmol) was added dropwise to the reaction mixture within 8 h, and the polymerization was left for 24 h at room temperature. CaO was added to the reaction mixture to quench the polymerization. Next, the reaction mixture was diluted with 10 mL of dichloromethane, CaO was filtered off, and the polymer was precipitated with cold hexane. The obtained solid was dried under a vacuum until a constant weight was reached. In the case of Cl-DXL and Allyl-DXL, homopolymerization was also conducted at 2 and −15 °C within 192 h. The PDXP polymer was obtained with a yield of 60%.

PDXP. ^{1}H NMR, $CDCl_3$, 400 MHz, δ (ppm): 4.70 (2H, s, $HOCH_2CH_2CH_2CH_2OC\underline{H}_2O-$ end group), 4.68 (2H, s, $-OCH_2CH_2CH_2CH_2OC\underline{H}_2O-$), 3.68 (2H, q, $HOC\underline{H}_2CH_2CH_2CH_2OCH_2O-$ end group), 3.56 (4H, q, $-OC\underline{H}_2CH_2CH_2CH_2OC\underline{H}_2O-$), 1.68 (4H, m, $-OCH_2C\underline{H}_2C\underline{H}_2CH_2OCH_2O-$), 1.62 (2H, m, $HOCH_2C\underline{H}_2CH_2CH_2OCH_2O-$ end group)

^{13}C NMR, $CDCl_3$, 100 MHz, δ (ppm): 95.12 (1C, s, $-OCH_2CH_2CH_2CH_2O\underline{C}H_2O-$), 91.60 (1C, s, $HOCH_2CH_2CH_2CH_2O\underline{C}H_2O-$ end group), 67.30 (1C, s, $-O\underline{C}H_2CH_2CH_2\underline{C}H_2OCH_2O-$), 62.30 (1C, s, $HO\underline{C}H_2CH_2CH_2CH_2OCH_2O-$ end group), 29.70 (1C, s, $HOCH_2\underline{C}H_2CH_2CH_2OCH_2O-$ end group), 26.48 (1C, s, $-OCH_2\underline{C}H_2\underline{C}H_2CH_2OCH_2O-$).

Synthesis of Lactide/DXP Copolymers (PLA/PDXP). The synthesis of lactide/DXP copolymers was performed according to previously published procedures.[22] LA (4.5 g, 31.25 mmol) was placed in a Schlenk flask and dried under vacuum for 2 h. Subsequently, the flask was filled with argon and closed with a silicon septum. Ten mL of distilled methylene chloride, 39 μg (0.44 mmol) of butan-1,4-diol, and 38 μL (0.43 mmol) of triflic acid were introduced to the reaction vessel through the septum. To enhance the high contribution of the activated monomer (AM) mechanism and gain control over the copolymer molar mass, polymerization was carried out with a low instantaneous concentration of DXP in the reaction mixture. Thus, after 30 min of lactide polymerization, the appropriate amount of DXP (1.5 3.12, 5.6, and 12.12 mmol) was introduced to the reaction mixture within 8 h. Then, polymerization was performed for 24 or 48 h at 30 °C. Next, purification was performed as conducted for DXP homopolymerization. The polymers were obtained in a yield of 90%.

PLA/PDXP. ^{1}H NMR, $CDCl_3$, 400 MHz, δ (ppm): 5.17 (1H, q, $-C\underline{H}(CH_3)CO-$), 4.79 (2H, s, $-OCH_2CH_2CH_2CH_2OC\underline{H}_2O-CO-CH(CH_3)-$), 4.40 (1H, q, LA-C$\underline{H}$–OH end group), 4.13 (4H, br, $-OC\underline{H}_2CH_2CH_2C\underline{H}_2OCH_2O-CO-CH(CH_3)-$), 1.70 (4H, br, $-OCH_2C\underline{H}_2C\underline{H}_2CH_2OCH_2O-CO-CH(CH_3)-$), 1.54 (3H, d, $-CO-CH(C\underline{H}_3)-$), 1.50–1.43 (3H, m, $-CO-CH(C\underline{H}_3)-OH$).

^{13}C NMR, $CDCl_3$, 100 MHz, δ (ppm): 175.2 (1C, s, $\underline{C}$=O end group), 172.4 (1C, s, $-CH_2CH_2CH_2O\underline{C}(O)CH-$), 170.1–169.6 (1C, m, $-(CH_3)CH-\underline{C}(O)-$ homosequences), 92.8 (1C, s, $-OCH_2CH_2CH_2CH_2O\underline{C}H_2O-CH(CH_3)-$), 70.80 (1C, s, $-OCH_2CH_2CH_2CH_2OCH_2O-\underline{C}H(CH_3)-$), 69.4–68.7 (1C, m, $-\underline{C}H(CH_3)$-homosequences), 68.5 (1C, s, $-\underline{C}H(CH_3)-OH$ end group), 64.70 (1C, s, $-O\underline{C}H_2CH_2CH_2\underline{C}H_2OCH_2O-CH(CH_3)-$), 25.01 (1C, s, $-OCH_2\underline{C}H_2\underline{C}H_2CH_2OCH_2O-CH(CH_3)-$), 20.41 (1C, s, $-CH(\underline{C}H_3)-OH$ end group), 18.36 (1C, s, $-O\underline{C}H_2CH_2CH_2\underline{C}H_2OCH_2O-CH(\underline{C}H_3)-$), 17.01–16.03 (1C, m, $-CH(\underline{C}H_3)-$ homosequences).

Synthesis of Lactide/Cl-DXL (PLA/PCl-DXL) or Lactide/Allyl-DXL (PLA/PAllyl-DXL) Copolymers. The copolymerization of lactide with substituted cyclic acetals does not require the dropwise addition of acetals to the reaction mixture to avoid the cyclization reaction. To obtain a functionalized polyester, LA (4.5 g, 31.25 mmol) was placed in a Schlenk flask and dried under vacuum for 2 h. Subsequently, the flask was filled with argon and closed with a silicon septum. Ten mL of distilled methylene chloride, 25 μg (0.44 mmol) of ethylene glycol, and 38 μL (0.43 mmol) of triflic acid were introduced to the reaction vessel through the septum. After 30 min of lactide polymerization, the appropriate amount of Cl-DXL or Allyl-DXL (15.6 mmol) was introduced to the reaction mixture, and then, polymerization proceeded for 24 h at room temperature. Then, purification was performed, as in the case of DXP homopolymerization. Copolymerization was also performed at 2 °C (48 h) and −15 °C (72 h). In the case of Cl-DXL, the synthesis was additionally performed on a large scale (25 g of LA). PLA/Cl-DXL was afforded as a white powder, whereas PLA/Ally-DXL was a brownish powder (no possibility of determining the mass from the MALLS detector). The PLA/PCl-DXL copolymers were obtained with a yield of 85%, while PLA/PAllyl-DXL was obtained with a yield of 80%.

PLA/PCl-DXL. ^{1}H NMR, $CDCl_3$, 400 MHz, δ (ppm): 5.17 (1H, q, $-C\underline{H}(CH_3)CO-$), 4.82 (2H, s, $-CO-CH(CH_3)OC\underline{H}_2OCH_2CH-(CH_2Cl)O-$), 4.47–4.42 (3H, m, LA-C$\underline{H}$–OH end group, $-CO-CH(CH_3)OCH_2OCH_2C\underline{H}(CH_2Cl)O-$), $-C\underline{H}(CH_3)-OCH_2OCH_2C\underline{H}(CH_2Cl)O-$), 3.70–3.57 (4H, m, $-CH(CH_3)-OCH_2OC\underline{H}_2CH(C\underline{H}_2Cl)O-$), 1.76 (3H, d, $-CH(C\underline{H}_3)O-$), 1.54–1.44 (3H, m, $-CH(C\underline{H}_3)OH$, $-CH(C\underline{H}_3)OCH_2OCH_2CH-(CH_2Cl)O-$).

^{13}C NMR, $CDCl_3$, 100 MHz, δ (ppm): 175.2 (1C, s, $\underline{C}$=O end group), 172.1 (1C, s, $-\underline{C}OCH(CH_3)OCH_2OCH_2CH(CH_2Cl)O-$), 169.9–169.7 (1C, m, $-(CH_3)CH\underline{C}(O)-$ homosequences), 92.8 (1C, s, $-COCH(CH_3)O\underline{C}H_2OCH_2CH(CH_2Cl)O-$), 71.80 (1C, s, $COC\underline{H}(CH_3)OCH_2OCH_2CH(CH_2Cl)O-$), 69.4–68.7 (1C, m, $-\underline{C}H(CH_3)$-homosequences), 66.5 (1C, s, $-\underline{C}H(CH_3)-OH$ end group), 62.8 (1C, s, $-COCH(CH_3)OCH_2OCH_2C\underline{H}(CH_2Cl)O-$), 41.14 (1C, s, $-COCH(CH_3)OCH_2OCH_2CH(\underline{C}H_2Cl)O-$), 20.47 (1C, s, $-CH(\underline{C}H_3)-OH$ end group), 18.42 (1C, s, $-COCH(\underline{C}H_3)-OCH_2OCH_2CH(CH_2Cl)O-$), 16.08 (1C, s, $-CH(\underline{C}H_3)-$ homosequences).

PLA/PAllyl-DXL. ^{1}H NMR, $CDCl_3$, 400 MHz, δ (ppm): 5.90–5.73 (1H, m, $CH_2=C\underline{H}-CH_2-O-$), 5.30–5.10 (3H, m, $C\underline{H}_2=CH-CH_2-O-$, $-C\underline{H}(CH_3)CO-$), 4.81 (2H, s, $-COCH(CH_3)-$

https://doi.org/10.1021/acs.macromol.3c01343
Macromolecules XXXX, XXX, XXX–XXX

$OC\underline{H}_2OCH_2CH(CH_2O-)O-)$, 4.43 (1H, s, LA-C$\underline{H}$−OH end group), 4.34 (3H, overlapped $-COCH(CH_3)OCH_2OC\underline{H}_2C\underline{H}-(CH_2O-)O-)$ 3.99 (2H, m, $CH_2{=}CH-C\underline{H}_2-O-)$, 3.54 (2H, m, $-COCH(CH_3)OCH_2OCH_2CH(C\underline{H}_2O-)O-)$, 1.61 (3H, d, $-CH-(C\underline{H}_3)O-)$, 1.54−1.44 (6H, m, $-CH(C\underline{H}_3)OH$, $-COCH(C\underline{H}_3)-OCH_2OCH_2CH(CH_2O-)O-)$.

^{13}C NMR, $CDCl_3$, 100 MHz, δ (ppm): 175.2 (1C, s, C=O end group), 172.1 (1C, s, $-\underline{C}OCH(CH_3)OCH_2OCH_2CH(CH_2O-)-O-)$, 169.9−169.7 (1C, m, $-(CH_3)CH\underline{C}(O)-$ homosequences), 133.88 (1C, s, $CH_2{=}\underline{C}H-CH_2-O-)$, 117.52 (1C, s, $\underline{C}H_2{=}CH-CH_2-O-)$, 92.82 (1C, s, $-COCH(CH_3)O\underline{C}H_2OCH_2CH(CH_2O-)-O-)$, 72.27 (1C, d, $CH_2{=}CH-\underline{C}H_2-O-)$, 70.66 (1C, s, $-COCH(CH_3)OCH_2OCH_2\underline{C}H(CH_2O-)O-)$, 69.4−68.7 (1C, m, $-\underline{C}H(CH_3)$-homosequences), 67.80 (1C, d, $-COCH(CH_3)-OCH_2OCH_2CH(\underline{C}H_2O-)O-)$, 63.55 (1C, d, $-COCH(CH_3)-OCH_2O\underline{C}H_2CH(CH_2O-)O-)$, 20.39 (1C, s, $-CH(\underline{C}H_3)OH)$, 18.28 (1C, s, $-COCH(\underline{C}H_3)OCH_2OCH_2CH(CH_2O-)O-)$, 16.54 (1C, s, $-CH(\underline{C}H_3)O-)$.

Modification of PLA/PCl-DXL Copolymers by Azide and Alkyne Compounds. The reaction of PLA/PCl-DXL with sodium azide was performed to show the possibility of the copolymer being functionalized. Two g of PLA/PCl-DXL containing 13 mol % chloromethyl groups and 300 mg (4.28 mmol) of sodium azide were dissolved in 10 mL of distilled DMF. Then, the reaction was filled with argon and maintained at 55 °C for 24 h. After that, the solid was centrifuged, and DMF was evaporated with a rotary evaporator. Subsequently, the polymer was dissolved in methylene chloride and the rest of the organic salt was filtered off. The polymer was precipitated into diethyl ether. The conversion of the chloromethylene group to the azide group was checked by ^{13}C NMR. After successful conversion of the chloromethyl group into azide one, the copolymer was reacted with propargyl alcohol and propargyl glycidyl ether as follows: 200 mg of copolymers containing 13 mol % azide groups, 0.44 mmol alkyne compounds (propargyl alcohol or propargyl glycidyl ether), 0.24 mmol CuBr was dissolved in 2 mL of THF. After that, 0.24 mmol pentamethyldiethylenetriamine (PMDTA) was added to the reaction mixture and was stirred for 24 h at 40 °C. Then, the reaction was passed through the silica gel column and precipitated to the hexane/ether (1:1) solution. The obtained products were dried under vacuum to a constant weight. The PLA/PCl-DXL copolymers were obtained with a yield of 92%.

^{13}C NMR, $CDCl_3$, 100 MHz, δ (ppm): 175.2 (1C, s, C=O end group), 172.1 (1C, s, $-\underline{C}OCH(CH_3)OCH_2OCH_2CH(CH_2Cl)O-)$, 169.9−169.7 (1C, m, $-(CH_3)CH\underline{C}(O)-$ homosequences), 92.8 (1C, s, $COCH(CH_3)O\underline{C}H_2OCH_2CH(CH_2Cl)O-)$, 71.80 (1C, s, $CO\underline{C}H-(CH_3)OCH_2OCH_2CH(CH_2Cl)O-)$, 69.4−68.7 (1C, m, $-\underline{C}H-(CH_3)$-homosequences), 66.5 (1C, s, $-\underline{C}H(CH_3)-OH$ end group), 62.8 (1C, s, $COCH(CH_3)OCH_2O\underline{C}H_2CH(CH_2Cl)O-)$, 51.00 (1C, s, $COCH(CH_3)OCH_2OCH2CH(\underline{C}H_2N_3)O-)$, 20.47 (1C, s, $-CH(\underline{C}H_3)-OH$ end group), 18.42 (1C, s, $COCH(\underline{C}H_3)-OCH_2OCH_2CH(CH_2Cl)O-)$, 16.08 (1C, s, $-CH(\underline{C}H_3)-$ homosequences).

Modification of PLA/PAllyl-DXL Copolymers by Click Reaction. The reaction of PLA/PAllyl-DXL with propanethiol, mercaptoethanol, or thioglycolic acid was performed to show the possibility of the copolymer being functionalized. Briefly, 1 g of PLA/PAllyl-DXL containing 10 mol % of a double bond, 3.9 mmol of appropriate thiol, 20 mg (0.12 mmol) of AIBN, and 10 mL of THF was placed in a Schlenk tube. The reaction mixture was degassed in an ultrasound bath for 30 min. Then, the Schlenk tube was placed in an oil bath at 60 °C for 24 h. After that, the reaction mixture was cooled, precipitated to cold diethyl ether, and dried under a vacuum. The disappearance of the signal belonging to the double bond was checked by ^1H NMR. The PLA/PAllyl-DXLopolymers were obtained with a yield of 82%.

^1H NMR, $CDCl_3$, 400 MHz, δ (ppm): 5.15 (1H, q, $-C\underline{H}(CH_3)CO-)$, 4.81 (2H, s, $-COCH(CH_3)OC\underline{H}_2OCH_2CH-(CH_2O-)O-)$, 4.43 overlapped $-COCH(CH_3)OCH_2OC\underline{H}_2C\underline{H}-(CH_2O-)O-)$, 4.34 (1H, s, LA-C$\underline{H}$−OH end group), 3.54 (4H, m, $-COCH(CH_3)OCH_2OCH_2CH(C\underline{H}_2O-)O-$, $CH_3-CH_2-CH_2-S-CH_2-CH_2-C\underline{H}_2-O-)$, 2.55 (2H, m, $CH_3-CH_2-CH_2-S-C\underline{H}_2-CH_2-CH_2-O-)$, 2.49 (2H, m, $CH_3-CH_2-C\underline{H}_2-S-CH_2-CH_2-CH_2-O-)$, 1.61 (5H, d, $-CH(C\underline{H}_3)O-$, $CH_3-C\underline{H}_2-CH_2-S-CH_2-CH_2-CH_2-O-)$, 1.54−1.44 (6H, m, $-CH(C\underline{H}_3)-OH$, $-COCH(C\underline{H}_3)OCH_2OCH_2CH(CH_2O-)O-)$, 1.05 (3H, t, $C\underline{H}_3-CH_2-CH_2-S-CH_2-CH_2-CH_2-O-)$.

Acid Triggered Degradation of PLA/PDXP$_5$ and PLA/PCl-DXL Copolymers. The hydrolytic degradation assay of the purified copolymers was performed according to a previously published method.[22] For example, 10 mg of PLA/$PDXP_{10}$ or PLA/$PCl\text{-}DXL_{10}$ was placed in the NMR tube and dissolved in 680 μL of detreated acetonitrile (CD_3CN), 10 μL of concentrated HCl solution (35%) was added to the NMR tube, and the spectra were recorded after selected time interval within 15 h at 40 °C. For the analyzed copolymers, the molar ratio of acid to acetal groups was kept constant (1:1).

Characterization. ^1H NMR, ^{13}C NMR, and 2D HSQC NMR spectra were recorded on an Avance Neo 400 NMR spectrometer. ^1H DOSY NMR analysis and degradation assay were performed on a Bruker DRX500 spectrometer operating at 500 MHz (11.7 T). The molar masses (M_n) of copolymers and polydispersity were determined by size-exclusion chromatography using an Agilent Pump 1100 Series instrument equipped with two PLGel 5 μm MIXED-C columns. A Wyatt Optilab Rex differential refractometer (RI) and a Dawn Eos8 (Wyatt Technology Corporation) laser photometer were used as detectors. Dichloromethane was used as an eluent (0.8 mL/min, 25 °C). Gas chromatography was analyzed using a Shimadzu QP2010 Plus apparatus with a Zebron ZB-5MSi Capillary GC column (30 m × 0.25 mm × 0.25 μm) connected with the quadrupole mass spectrometer, Shimadzu QP2010 Ultra, with electron impact (EI, 70 eV) and chemical positive ionization (PCI, CH_4). The carrier gas was helium at 0.97 mL/min. The injector and ion source temperatures were set at 250 and 200 °C, respectively. The temperature program was as follows: hold at 35 °C for 5 min, heating to 240 °C at a rate of 10 °C/min, and hold at 240 °C for 5 min. The MS was scanned from 35 to 600 amu (atomic mass unit) by selecting full-scan mode. Additionally, Allyl-DXL mass spectrometry detection using an APCI source in positive high-resolution mode was performed. To ensure accurate mass measurements, the data were collected in centroid mode. Weight was corrected using leucine enkephalin solution as an external reference (Lock-SprayTM). The optimized source parameters included a corona voltage of 0.5 kV, probe temperature 400 °C, source temperature 80 °C, desolvation gas (nitrogen) flow rate 500 L/h, nebulizer gas pressure 6.5 bar. Mass spectra were recorded in the m/z range from 50 to 1200 Da. Differential scanning calorimetry (DSC) analyses were performed under a nitrogen atmosphere at heating and cooling rates of 10 °C min^{-1} on a DSC 2500 Discovery system (TA Instruments). The measurements were performed at temperatures ranging from −90 to 200 °C for homopolymers and copolymers. The temperature and heat flows were both calibrated with indium. Thermogravimetric analysis (TGA) was performed under nitrogen flow by heating the samples from ambient temperature to 500 °C at a heating rate of 20 °C min^{-1} on a Hi-Res TGA 2950 thermogravimetric analyzer (TA Instruments). The measurements were conducted by placing ∼5 mg of polymer samples in a measuring cell.

RESULTS AND DISCUSSION

Synthesis of the Functionalized Cyclic Acetals. In the strategy we proposed, it is essential to use appropriate comonomers that can introduce the necessary functional groups to the polyester chain and simultaneously influence or improve the material degradation properties. For this purpose, we designed two cyclic acetals that differ in their pendant functionality. Cyclic acetals may be prepared by condensation of formaldehyde or higher aldehydes with diols in the presence of an acid catalyst.[24] Thus, in our work, in the first step, 3-allyloxypropane-1,2-diol and 3-chloropropane-1,2-diol were

https://doi.org/10.1021/acs.macromol.3c01343
Macromolecules XXXX, XXX, XXX−XXX

Table 1. Cationic Ring-Opening Homopolymerization of Cyclic Acetals and Their Copolymerization with LA[a]

runs	sample	T (°C)	time [h]	reactive mixture composition [mol %]		theoretical molar mass [g/mol]	conversion [%][b]		M_nSEC[c] [g/mol]		$Đ$[c]	copolymer composition [mol %][d]		average number of repeating units[f]		homo LA block/acetal[g]
				LA	acetal		LA	acetal	RI	MALS		LA	acetal	LA	acetal	
1	PDXP	30	24	0	100	10 000	0	87	12 000	9000	1.7	0	100	0	83.0	
2	PLA/PDXP$_5$	30	24	97	4.5	10 500	95	98	9500	12 500	1.8	95	5	62.0	4.6	14
3	PLA/PDXP$_{10}$	30	48	93	9.0	11 000	94	95	10 000	12 500	2.2	89	10	62.0	10.0	6.4
4	PLA/PDXP$_{18}$	30	48	84	15.0	11 000	96	95	10 400	13 000	2.2	84	18	60.0	16.0	4.3
5	PLA/PDXP$_{26}$	30	48	72	27.0	11 000	98	94	11 000	9000	1.9	73	26	55.0	28.0	1.9
6	PLA/PDXP$_{11}$	30	48	91	9.1	25 000	99	98	16 000	17 000	1.7	88	11	98.0	17.0	6.3
7	PCl-DXL	30	192	0	100	11 800	100	0	0	0	0	0	0	0	0	
8	PCl-DXL	2	192	0	100	11 800	100	0	0	0	0	0	0	0	0	
9	PCl-DXL	−15	192	0	100	11 800	100	0	0	0	0	0	0	0	0	
10	PLA/PCl-DXL$_{10}$	30	24	67	33.3	11 000	97	20	13 000	14 000	1.9	90	10	81.0	13.0	8.0
11	PLA/PCl-DXL$_{16}$	2	48	67	33.3	11 000	90	30	11 000	13 000	1.9	82	16	65.0	17.0	4.5
12	PLA/PCl-DXL$_{22}$	−15	72	67	33.3	11 000	50	40	11 500	13 500	2.1	78	22	62.0	21.0	3.8
13	PLA/PCl-DXL$_9$	30	24	67	33.3	25 000	96	21	17 500	17 000	1.8	91	9	110.0	13.0	8.1
14	PAllyl-DXL	30	48	0	0	14 000	100	0	0	0	0	0	0	0	0	
15	PAllyl-DXL	2	192	0	0	14 000	100	0	0	0	0	0	0	0	0	
16	PAllyl-DXL	−15	192	0	0	14 000	100	0	0	0	0	0	0	0	0	
17	PLA/PAllyl-DXL$_{10}$	30	24	66.7	33.3	11 000	94	20	10 000	nd[e]	1.4	90	10	62.5	7.0	9.0
18	PLA/PAllyl-DXL$_{14}$	2	48	67	33.3	11 000	91	32	10 500	nd[e]	1.7	86	14	62.5	10.0	6.3
19	PLA/PAllyl-DXL$_{22}$	−15	72	67	33.3	11 000	55	40	9500	nd[e]	1.7	82	22	54.0	12.0	2.7
20	PLA/PAllyl-DXL$_9$	30	24	67	33.3	25 000	92	22	19 000	nd[e]	2.0	91	9	120.0	12.0	10.0

[a]Copolymerization conditions: for PDXP/PLA triflic acid (0.43 mmol) as catalyst, butylene glycol (0.44 mmol) as initiator; for PLA/PCl-DXL and PLA/PAllyl-DXL triflic acid (0.43 mmol) and ethylene glycol (0.44 mmol) as initiator. [b]Comonomer conversion determined from the NMR spectra. [c]The number-average molar masses were estimated for purified homo or copolymers by size-exclusion chromatography (SEC) with a MALLS detector (d_n/d_{cDXP} = 0.030, d_n/d_{cCDXL} = 0.044) or an RI detector calibrated with polystyrene standards. $Đ = M_w/M_n$ was measured by SEC with an RI detector. [d]The composition of the copolymer was calculated from the ^{1}H NMR spectra. [e]In the case of the PLA/Allyl-DXL copolymers, the molar mass was only estimated from the RI detector (polystyrene calibration). The molar mass from the MALLS detector was not measured because of the brownish color of the purified copolymers. [f]The average number of repeating units in the copolymer was calculated taking into account its molar mass (RI detection), composition (molar content of the given comonomer), and molar mass of the repeating unit according to the following formula: $M_{ncopolymer} \times$ [comonomer mol %]$/M_{comonomer}$. [g]Calculated from ^{1}H NMR spectra taking into account the signal from the −CH− group (LA−LA) and signal belonging to the −OCH$_2$O− acetal group.

https://doi.org/10.1021/acs.macromol.3c01343
Macromolecules XXXX, XXX, XXX−XXX

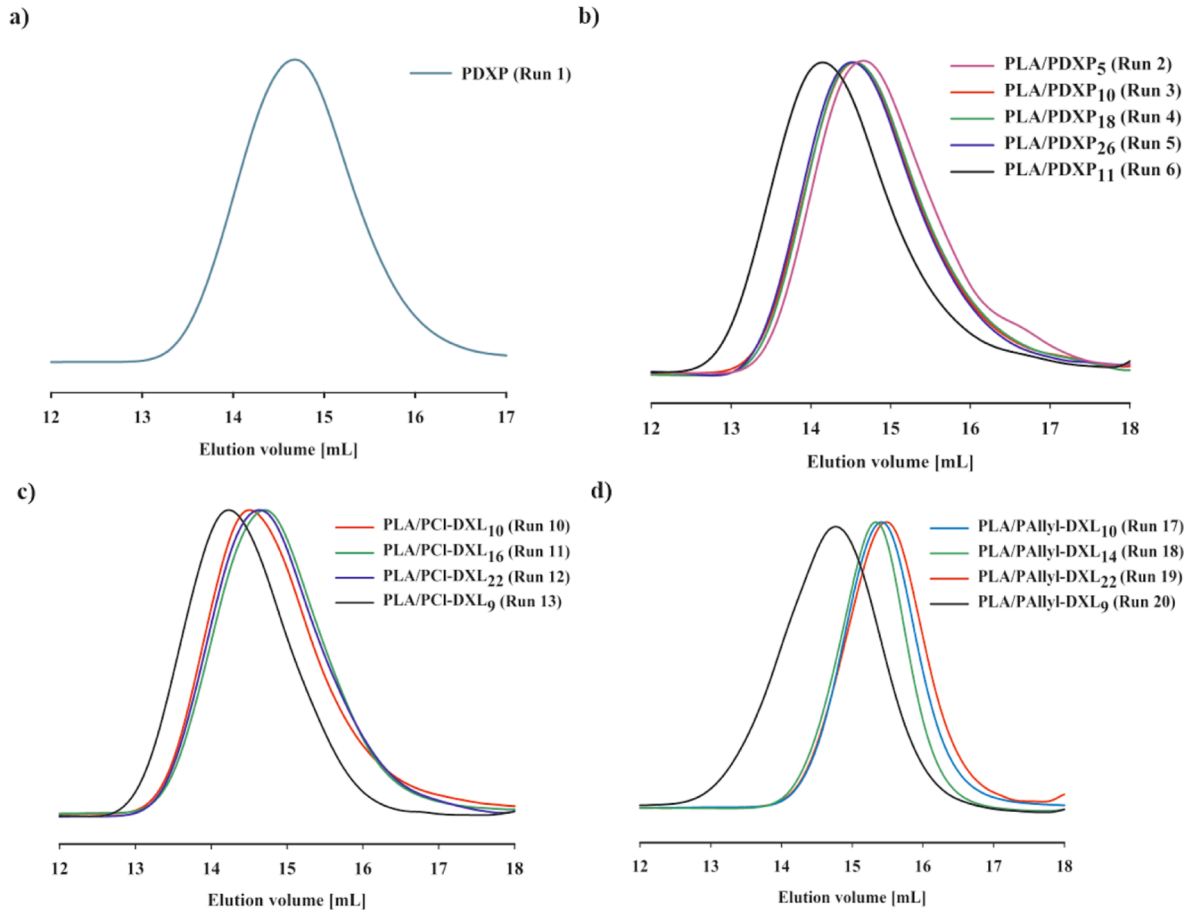


Figure 1. GPC traces of prepared (a) PDXP homopolymer, (b) PLA/PDXP, (c) PLA/PCl-DXL, and (d) PLA/PAllyl-DXL copolymers.

selected for the reaction with paraformaldehyde to afford the formation of five-membered cyclic acetals fitted with allyl- or chloro-functional groups (structures shown in Scheme S1). Additionally, for comparative studies, a nonfunctionalized seven-membered acetal was prepared using butane-1,4-diol. We observed that reactions leading to the formation of substituted cyclic acetals proceeded with high yields (80 and 85%) and were close to the reaction yield for the unsubstituted acetal, which was almost 90%. Notably, the synthesis methodology allowed for the reaction with diols having a chlorine substituent as well as an unsaturated moiety, and the applied conditions (110 °C, toluene, pTSA) prevented functional group side reactions during acetal formation.

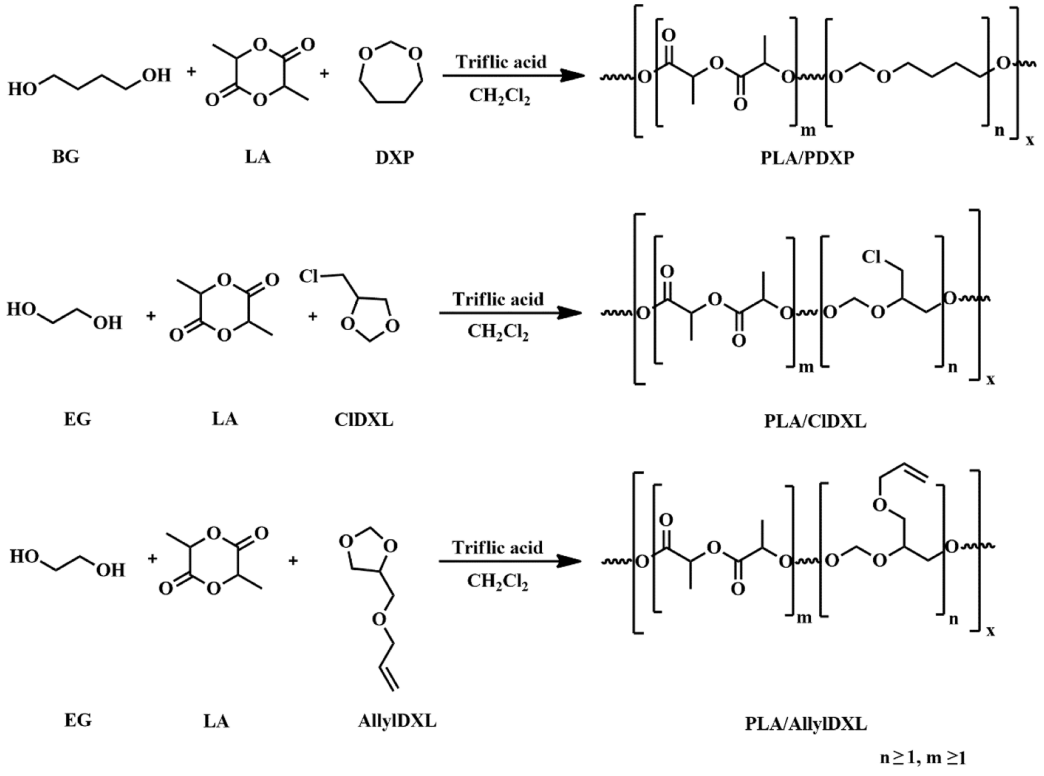
The required structures of the prepared monomers were confirmed based on the ^{1}H and ^{13}C NMR spectra (Figures S1 and S2). The characteristic signals belonging to the acetal bond (−OC$\underline{H}_2$O−) are observed in the range of 4.80−5.00 ppm and 95.60−94.35 for the proton and carbon, respectively. Additionally, the ^{1}H NMR spectra demonstrated a lack of a free aldehyde peak at 9.60 ppm or free alcohols.

Functionalized and nonfunctionalized cyclic acetals were purified by distillation to remove the acidic catalyst, unreacted diols, toluene, or other side products. The high purity of the synthesized cyclic monomers was confirmed by GC/MS analysis. In all cases, only one well-defined peak belonging to the particular cyclic acetal was observed in the GC chromatogram (Figure S3a). No additional peaks from volatile compounds, such as diols or acyclic acetals, were detected. In the MS spectra (EI ionization), weak molecular peaks at 121, 102, and 143 m/z were detected for Cl-DXL, DXP, and Allyl-DXL, respectively (Figure S3b−d). The mass spectrum of DXP shows a weak ion peak at the parent mass-to-charge ratio, m/z 102, of $C_5H_{10}O_2^+$ (Figure S3c). Fragment peaks clustered at m/z 71 and 42 are characteristic of ions $C_4H_7O^+$ and $C_3H_6^+$, respectively. The primary process is the loss of CH_2O.[25] In the mass spectra of 4-substituted 1,3-dioxolanes, the characteristic feature is the loss of H;[26] therefore, for Cl-DXL and Allyl-DXL, we observed weak parent ion signals with m/z 121 and 142, respectively (Figure S3b, d). Additionally, for Cl-DXL, a typical chlorine isotope distribution in the molecular peak was observed (Figure S3b) in the spectrum.[27] GC/MS and ^{1}H NMR spectra showed that two functional five-membered acetals and one nonfunctional seven-membered acetal were successfully synthesized. These results demonstrated that the reaction with paraformaldehyde with a proper diol is a simple and straightforward way to achieve functionalized cyclic acetals.

Synthesis of Functionalized Polylactides via Copolymerization with Cyclic Acetals. The main goal of this work was to develop functional, degradable lactide copolymers that can be prepared under metal-free conditions. In accordance with the above assumption, we designed the cationic copolymerization of lactide (LA) with functionalized cyclic acetals under conditions that had been successfully applied previously for the copolymerization of lactide with 1,3-dioxolane.[22] Before investigating the copolymerization, we tested the homopolymerization abilities of Allyl-DXL and Cl-DXL (Table 1). The homopolymerization of DXP was already

https://doi.org/10.1021/acs.macromol.3c01343
Macromolecules XXXX, XXX, XXX−XXX

Scheme 1. Synthesis of Lactide/Cyclic Acetal Copolymers [Copolymerization Conditions: For PDXP/PLA Triflic Acid (0.55 mmol) as the Catalyst, Butylene Glycol (1 mmol) as the Initiator; for PLA/PCl-DXL and PLA/PAllyl-DXL Triflic Acid (0.43 mmol) and Ethylene Glycol (0.44 mmol) as the Initiator]



reported by Pan et al.[28] It was shown that the cationic polymerization of DXP initiated by triflic acid in the presence of diols proceeded according to the Activated Monomer (AM) mechanism, at a high mole ratio of diol/initiator in which monomer was slowly added into the polymerization system.

Thus, for DXP applying butane-1,4-diol as an initiator and triflic acid as a catalyst after 24 h at 30 °C, we easily obtained a homopolymer (PDXP) with M_n = 12 000 g/mol and M_w/M_n = 1.7 (Figure 1 and Table 1, run 1). The ^{1}H NMR showed typical chemical shifts at 4.68, 3.56, and 1.68 ppm for $-OCH_2CH_2CH_2CH_2CH_2O-$, $-OCH_2CH_2CH_2CH_2O-$, and $-OCH_2OCH_2CH_2CH_2CH_2O-$, respectively. The ^{1}H, ^{13}C, and the structure of PDXP are shown in Figure S4a,b, whereas the SEC chromatogram is presented in Figure 1a.

However, using the same conditions for Cl-DXL or Allyl-DXL polymerization, we did not obtain the corresponding homopolymers (Table 1, runs 7 and 14 for PCl-DXL and PAllyl-DXL, respectively). This observation correlates with previously reported results regarding the homopolymerization of substituted acetals in which substitution causes lower negative enthalpy.[29] To undergo a significant extent of ring-opening polymerization, cyclic monomers must exhibit a negative free energy of polymerization under given conditions. In general, substituents invariably make ΔG less negative and are liable to change the sign of ΔG from negative to positive when five-, six-, and seven-membered rings are substituted.[30]

It is well-known that the polymerization of cyclic acetals characterizes the low ceiling temperature;[31] therefore, typically decreasing the temperature (thus decreasing the $-T\Delta S$ factor) should influence the thermodynamics of the polymerization process and contribute to the formation of the polymer. For example, it was reported that to prepare poly(4-ethyl-1,3-dioxolane), the temperature must be decreased to −20 °C to synthesize oligomers with a molecular weight of approximately 400 g/mol.[32] Therefore, we examined the effect of the temperature on the course of Allyl-DXL and Cl-DXL homopolymerization carrying out the reactions at 2 and −15 °C (Table 1, runs 8, 9 and 15, 16 for PCl-DXL and PAllyl-DXL, respectively). Nevertheless, neither lowering the temperature nor increasing the reaction time to 192 h enabled the formation of Allyl-DXL or Cl-DXL homopolymers.

The inability of Cl-DXL and Allyl-DXL to form high molar mass homopolymers does not imply that these monomers could not be copolymerized with other suitable comonomers. In principle, copolymerization of nonpolymerizable monomer M_2 with polymerizable monomer M_1 may occur up to a maxim um possible incorporation of 50% M_2 units, corresponding to an alternating copolymer.[30] For example, γ-butyrolactone, which is often considered "hardly homopolymerizable" at standard temperature and pressure,[33,34] was successfully copolymerized with some other lactones under these conditions.[35] Also, Okada et al. showed that Cl-DXL did not form homopolymers but it can be introduced to the polymer chain by copolymerization with 1,3-dioxolane.[36]

Therefore, we tested the ability of the obtained functional acetals to copolymerize with lactide to obtain copolyesters containing functional acetal units. The synthesis is illustrated in Scheme 1.

Nonfunctionalized seven-membered 1,3-dioxepane was also used for the copolymerization, which made it possible to study the effect of the substituent on the cyclic acetal reactivity (Table 1, runs 2−6). As DXP is known to undergo side reactions during homopolymerization that lead to cyclic

https://doi.org/10.1021/acs.macromol.3c01343
Macromolecules XXXX, XXX, XXX−XXX

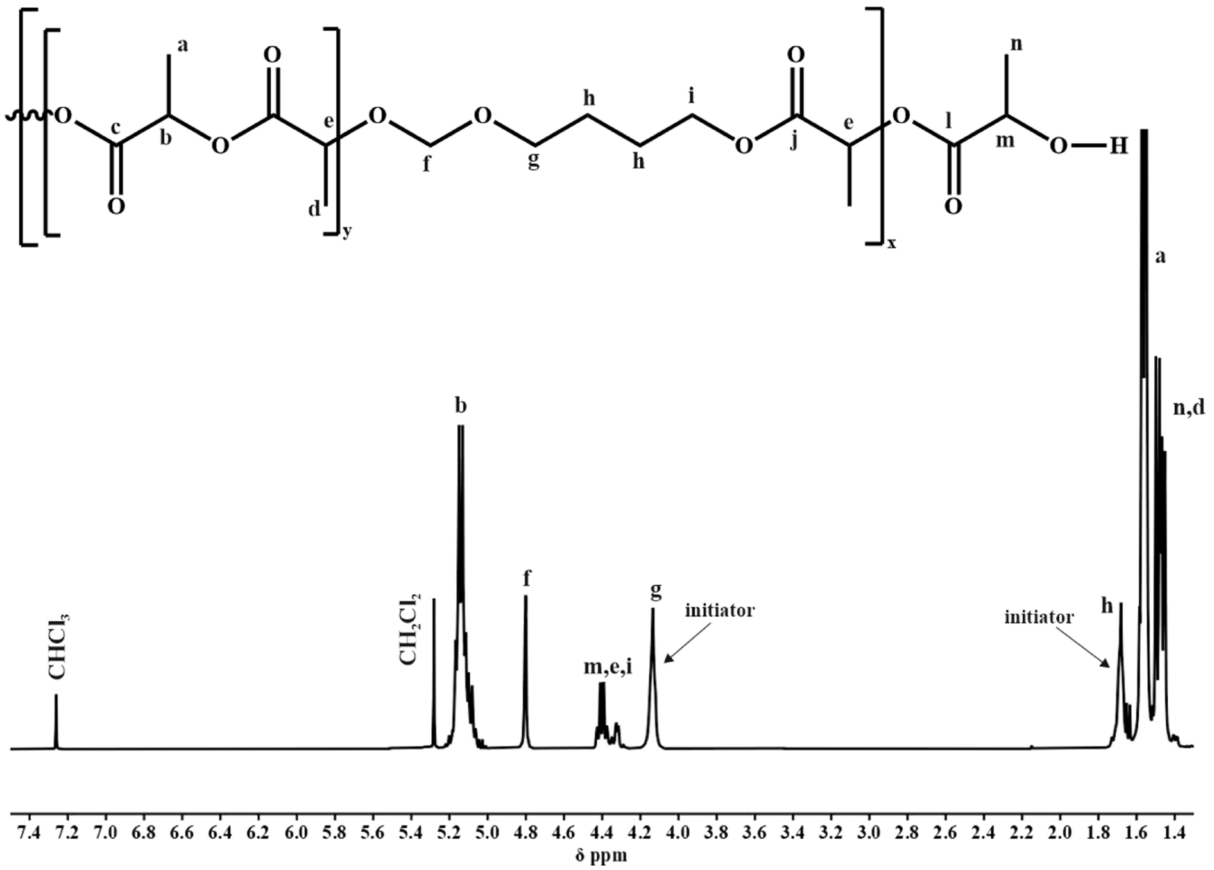


Figure 2. ^{1}H spectra of PLA/PDXP$_5$ ($CDCl_3$, 400 MHz).

structure formation,[37] to shift the mechanism of propagation toward the activated monomer[22] mechanism and prevent the presence of cycles, the monomer was manually added dropwise within 8 h to the reaction mixture containing lactide, butane-1,4-diol, and triflic acid. As presented in Table 1, high conversion of both comonomers (95−97%) was observed under the applied conditions, and using different contents of DXP in the feed (from 5 to 26 mol %) enabled the preparation of lactide copolymers comprising various acetal units per chain with high yields. The percentage of DXP units incorporated in the copolymer increased with the increase in the content of this comonomer in the polymerization feed. In our work, we used relatively small amounts of functional acetal to largely retain the properties of the unmodified LA homopolymer. SEC chromatograms showed for PLA/PDXP copolymers the unimodal molar masses distribution in the range of 9 000 to 17 000 g/mol (Figure 1b). The copolymers were purified as described in the Experimental Section, and the composition was carefully determined using ^{1}H and ^{13}C NMR. As we showed previously[22] for the unsubstituted 1,3-dioxolane, the units are incorporated into the copolymer as −O$\underline{C}$H$_2$OCH$_2$CH$_2$CH$_2$CH$_2$O− not as −OCH$_2$CH$_2$CH$_2$CH$_2$O$\underline{C}$H$_2$O−. In the NMR spectra of the purified product, in addition to the typical polylactide signals (5.17, 4.35, and 1.56 ppm), peaks belonging to the incorporated DXP units were identified. The presence of the acetal−ester structure was confirmed by the peaks described for DXP shifting toward higher frequencies to 4.80, 4.13, and 1.70 ppm (signals f, g, and h in Figure 2, respectively) compared to the chemical shifts observed for the homopolymer.

In the ^{13}C NMR spectra, apart from signals typical for lactide sequences, signals from the DXP units were also present with chemical shifts that were different from the signals observed in the homopolymer. Additionally, in the carbonyl region, we observed a characteristic signal (172.40, signal j) belonging to LA units directly connected to the DXP moieties in the formed acetal ester unit (Figure 3). To support the observation obtained from ^{1}H and ^{13}C NMR, 2D HSQC NMR was employed to estimate the correlation between carbon and the directly attached protons (Figure S5). All these analyses proved that the PLA/PDXP copolymer was formed successfully.

The copolymerization of lactide with Cl-DXL and Allyl-DXL does not require the dropwise addition of substituted acetals to the reaction mixture to avoid the cyclization reaction. Due to the inability of these monomers to homopropagation, the formation of longer homosequences is hindered, which limits the formation of undesirable cyclic products. Therefore, for both comonomers, the constant content of cyclic acetal (33 mol %) in the feed was kept during copolymerization with lactide (see Table 1, runs 10−13 and runs 17−20 for PLA/PCl-DXL and PLA/PAllyl-DXL, respectively). Different temperatures ranging from −15 to 30 °C were applied to study their effect on the copolymer composition and number of acetal units incorporated into the copolymer chain.

The copolymerization performed at 30 °C within 24 h proceeded with a high lactide conversion (runs 10 and 17); however, the conversion of both cyclic acetals was rather low (approaching 20%), and after purification, the content of acetal units in the copolymer (calculated from ^{1}H NMR spectra) was approximately 12 mol %. Decreasing the temperature to 2 °C

https://doi.org/10.1021/acs.macromol.3c01343
Macromolecules XXXX, XXX, XXX−XXX

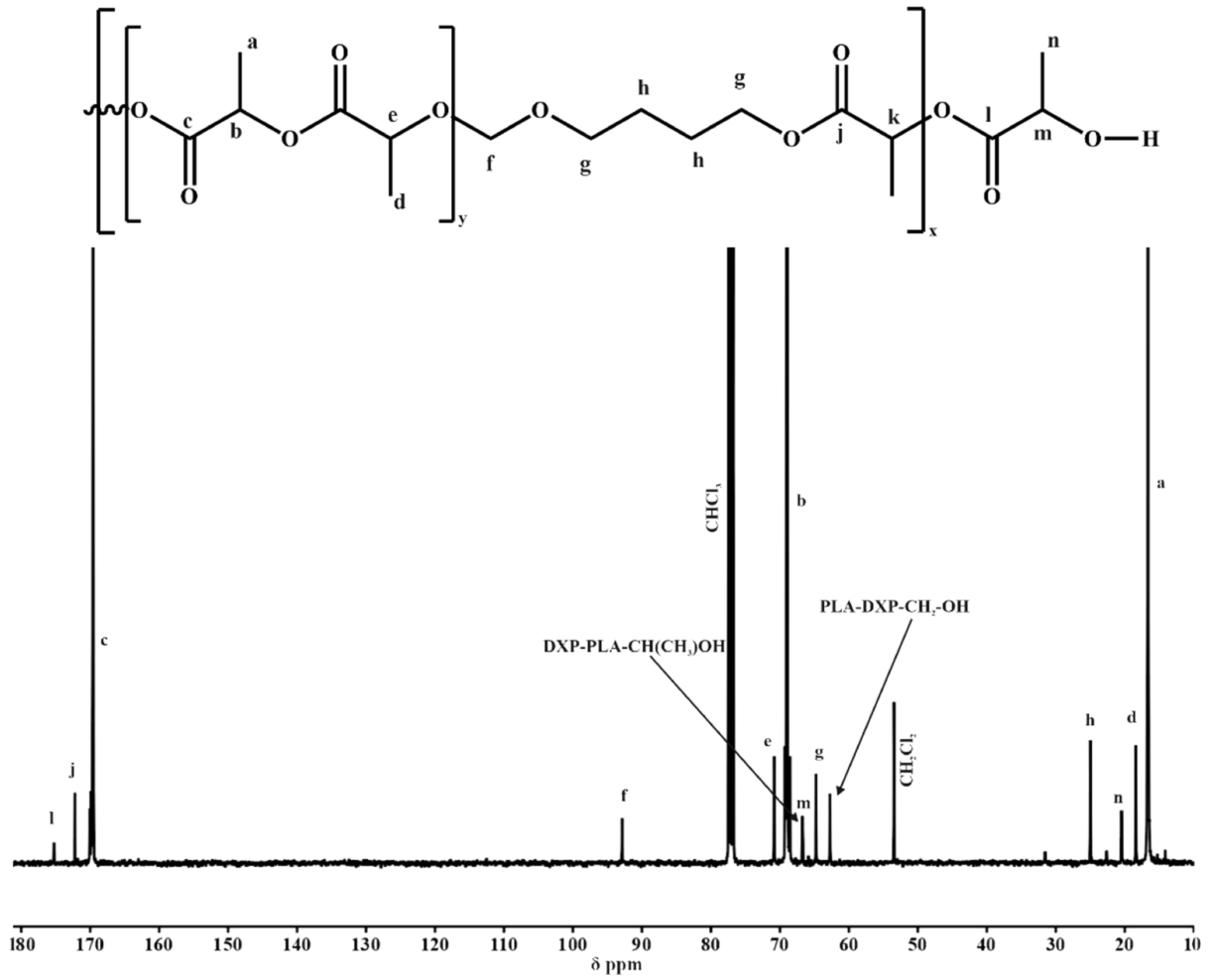


Figure 3. ^{13}C NMR spectra of the PLA/PDXP$_5$ copolymer ($CDCl_3$, 100 MHz).

slowed the reaction (runs 11 and 18), and a 90% conversion of lactide was reached after 48 h. Additionally, only a small increase in the conversion of cyclic acetals to 30 and 32% was observed for Cl-DXL and Allyl-DXL, respectively. For −15 °C, the acetal conversion reached 40%, and the amount of acetal incorporated did not exceed 22% (runs 12 and 19). However, under this condition, the polymerization of lactide significantly slowed down, and after 72 h, the conversion reached only 50%. Therefore, copolymerization with acetals was not performed below −15 °C because of a low cyclic ester conversion.

Size-exclusion chromatography showed that the elution peaks of the obtained copolymers were symmetrical and uniform ($Đ$ = 1.4−2.1), supporting the formation of the desired copolymers (Figure 1c,d). As presented in Table 1, the molar masses of the synthesized functional copolyesters after purification are in the range from 10 000 to 19 000 g/mol. Runs 6, 13, and 20 represent copolymers with the highest molecular weight achievable by using the current experimental procedures. Further attempts to obtain copolymers with M_n = 50 000 g/mol, by increasing the ratio of comonomers to the initiator, did not lead to the intended goal.

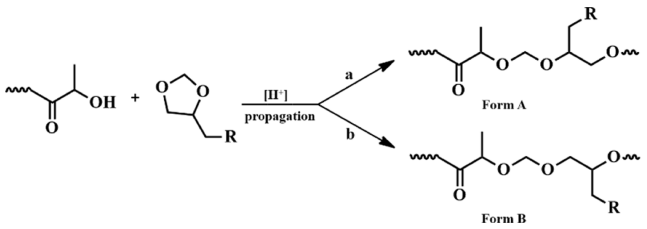
The conversion of comonomers over time in the cationic copolymerization of lactides with Cl-DXL was investigated. The resulting plots are presented in Figure S6. As described in the Experimental Section, a cyclic acetal was introduced into the polymerization mixture after 30 min of lactide homopolymerization, when the conversion of cyclic ester reached 10%. The measurements confirmed a significantly faster polymerization rate for lactide compared to Cl-DXL. After 550 min, almost complete conversion of lactide (90%) was achieved, while the conversion of Cl-DXL reached 33% at the final stage of polymerization. Judging from the plot, during incorporation into the polymer chain, both comonomers are consumed uniformly which should lead to the formation of copolyesters with a relatively homogeneous structure. Since the substituted acetal in this copolymerization system does not have the ability to propagate, no Cl-DXL/Cl-DXL homodiads will be present in the copolymer. Detailed investigations aimed at determining the microstructure of the copolymer (i.e., the distribution of repeating comonomer units in the chain) are planned as an independent aspect of future research. These studies will aim to elucidate the impact of microstructure on the susceptibility to degradation.

The composition of isolated copolyesters containing units introduced by functionalized cyclic acetals was estimated by ^1H NMR. The structure analysis is more complicated for PLA/PCl-DXL and PLA/PAllyl-DXL copolymers than for PLA/PDXP copolymers because there are two possible ways of ring opening in the cyclic acetal substituted at the fourth position. This effect was also reported previously by Okada[32] for unsymmetrical 4-ethyl-1,3-dioxolane and 4-chloromethyl-1,3-dioxolane,[36] in which the presence of asymmetric carbons led to the formation of a nonregular structure of the polymer chain. Similarly, in our work, functionalized acetals can be

https://doi.org/10.1021/acs.macromol.3c01343
Macromolecules XXXX, XXX, XXX−XXX

introduced into the copolyester chain in two different ways, as shown in Scheme 2.

Scheme 2. Possible Way of Opening the Acetal Ring during Copolymerization (R−Cl or $-OCH_2CH{=}CH_2$)



In the typical spectrum of the PLA/PCl-DXL copolymer, major peaks from the polyester backbone are observed, together with signals typical for the introduced acetal units. Thus, oxymethylene protons at the acetal-ester unit were identified at 4.80 ppm (signal f). The peaks with chemical shifts in the range from 3.70 to 3.50 ppm (signal g) and 5.20 ppm (signal h) were assigned to the acetal units only if the opening of the acetal ring occurred according to Scheme 2a. The second direction of the acetal ring opening introduces signal "o" and signal "p" in the range 4.47−4.22 ppm. The signals belonging to the ester −CH− groups located at the neighbor of acetal units are observed with a chemical shift of 4.47−4.22 (signal d, k) together with signal "m" from the $-C\underline{H}(CH_3)-OH$ end group, as shown in Figure 4.

^{13}C NMR (Figure 5) and HSQC NMR (Figure S7) were also used to confirm the presence of both opened acetal units and prove that the protons' signal was correctly assigned. Two different carbon peaks ($-CH_2Cl$, signal (i) at 41.80 and 41.20 ppm) were visible, which correlated with both opened forms of the cyclic acetal in the polymer structure. Additionally, the carbons "g" and "r" or "h" and "o" (−CH− group in the acetal moiety) differ depending on the opening mode of the acetal ring due to the different chemical neighbors, as shown in Figure 5. Moreover, the copolymer structure proved the presence of three different carbon signals at 20.46, 18.40, and 16.62 ppm, corresponding to the $-CH_3$ end group, $-CH_3$ in heterosequences, and $-CH_3$ homosequences, respectively.

In the ^1H NMR spectrum of the PLA/PAllyl-DXL copolymers (Figure 6), except for the signals corresponding to the polylactide units, the signals belonging to the oxymethylene and acetal moieties were also visible at 4.81, 3.99, and 3.54 ppm. Signals characteristic of protons located at double bonds were observed at 5.90 and 5.30 ppm. Thus, the ^1H NMR spectra also revealed that the unsaturated pendant group remained intact under the reaction conditions used, which is vital for further copolymer functionalization.

Similarly as for the PLA/PCl-DXL copolymer, the signals belonging to acetal-ester moieties at 172.18 (carbonyl) and 18.32 ppm (CH_3- group) appeared in the ^{13}C NMR (Figure 7) and 2D HSQC spectra (Figure S8). The $-CH_2-$ signals corresponding to the acetal moieties occurred in duplicate with a slight difference in chemical shift, which can be attributed to two open ring forms (Scheme 2).

For PLA/PCl-DXL copolymers, the contribution of form "A" or "B" at the polyester chain can be estimated based on the ^1H NMR spectrum due to the separation of signal "h" from the $-CH(CH_2Cl)-$ group in the "B" form. The results are summarized in Table S1. The NMR analyses revealed that at

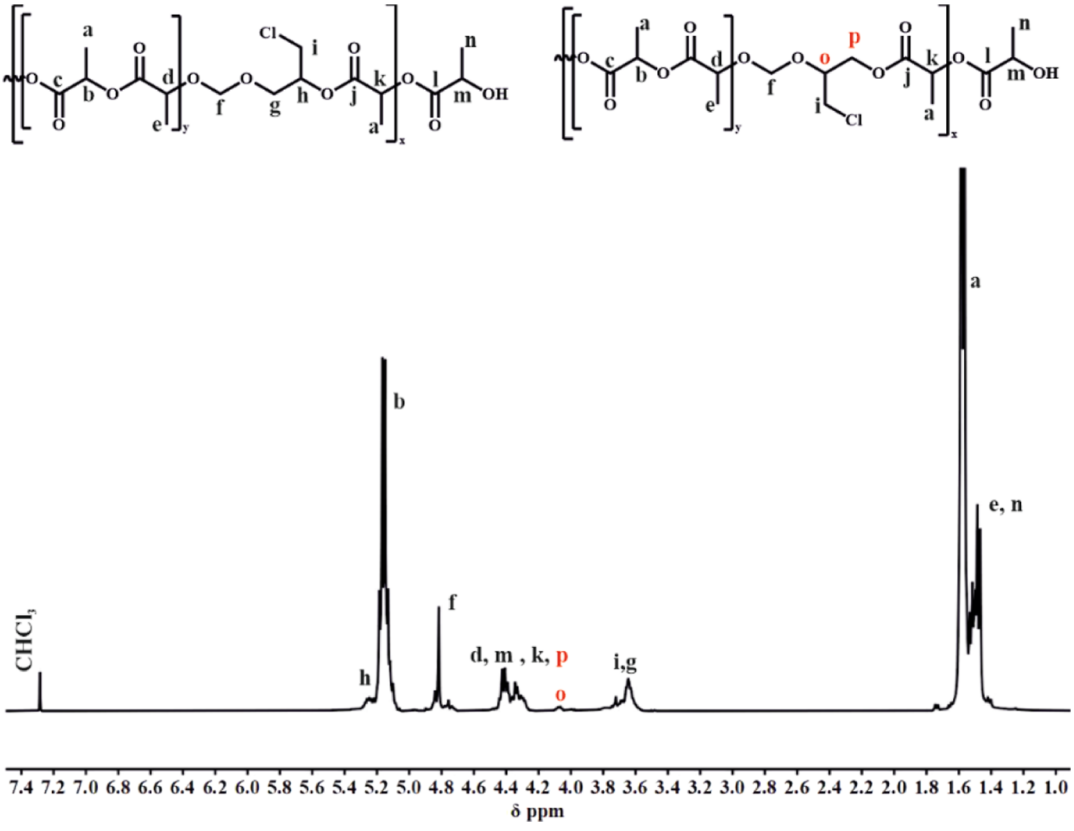


Figure 4. ^1H spectra of the PLA/PCl-DXL copolymer with 12 mol % of Cl-DXL ($CDCl_3$, 400 MHz).

https://doi.org/10.1021/acs.macromol.3c01343
Macromolecules XXXX, XXX, XXX−XXX

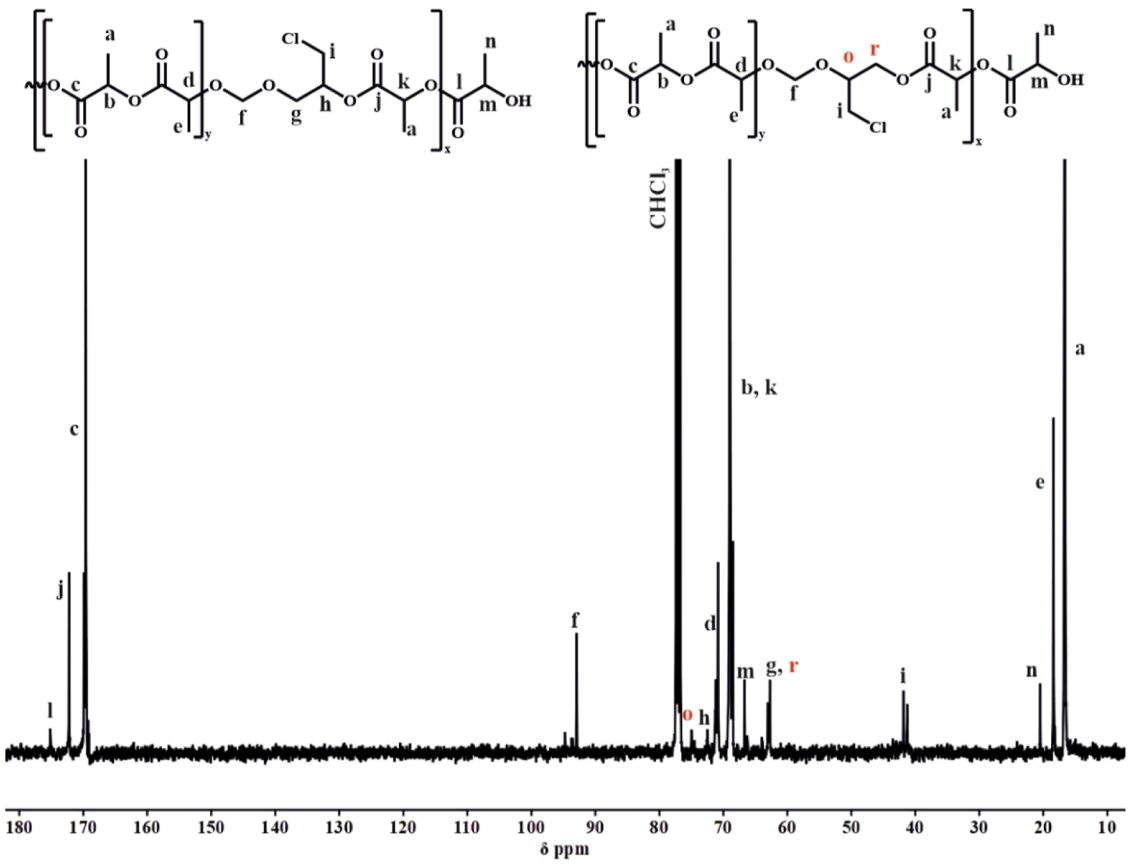


Figure 5. ^{13}C NMR spectra of PLA/PCl-DXL copolymer with 12 mol % of Cl-DXL ($CDCl_3$, 100 MHz).

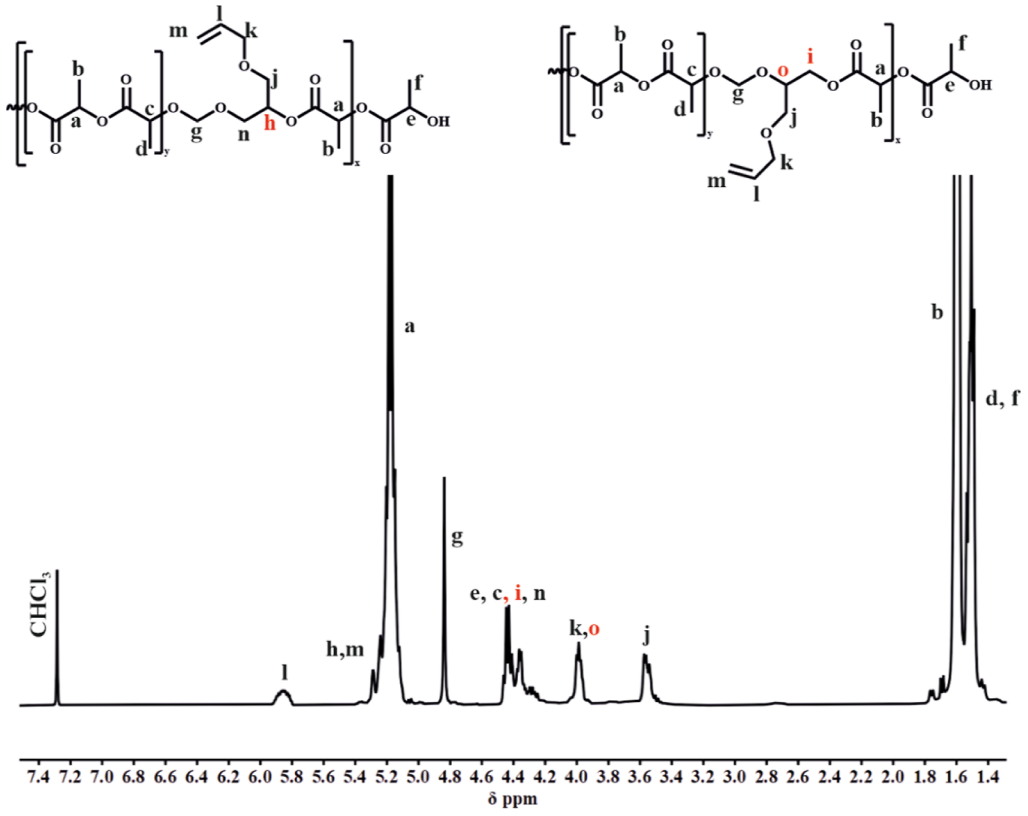


Figure 6. ^{1}H spectra of PLA/PAllyl-DXL copolymer with 10 mol % Allyl-DXL ($CDCl_3$, 400 MHz).

https://doi.org/10.1021/acs.macromol.3c01343
Macromolecules XXXX, XXX, XXX−XXX

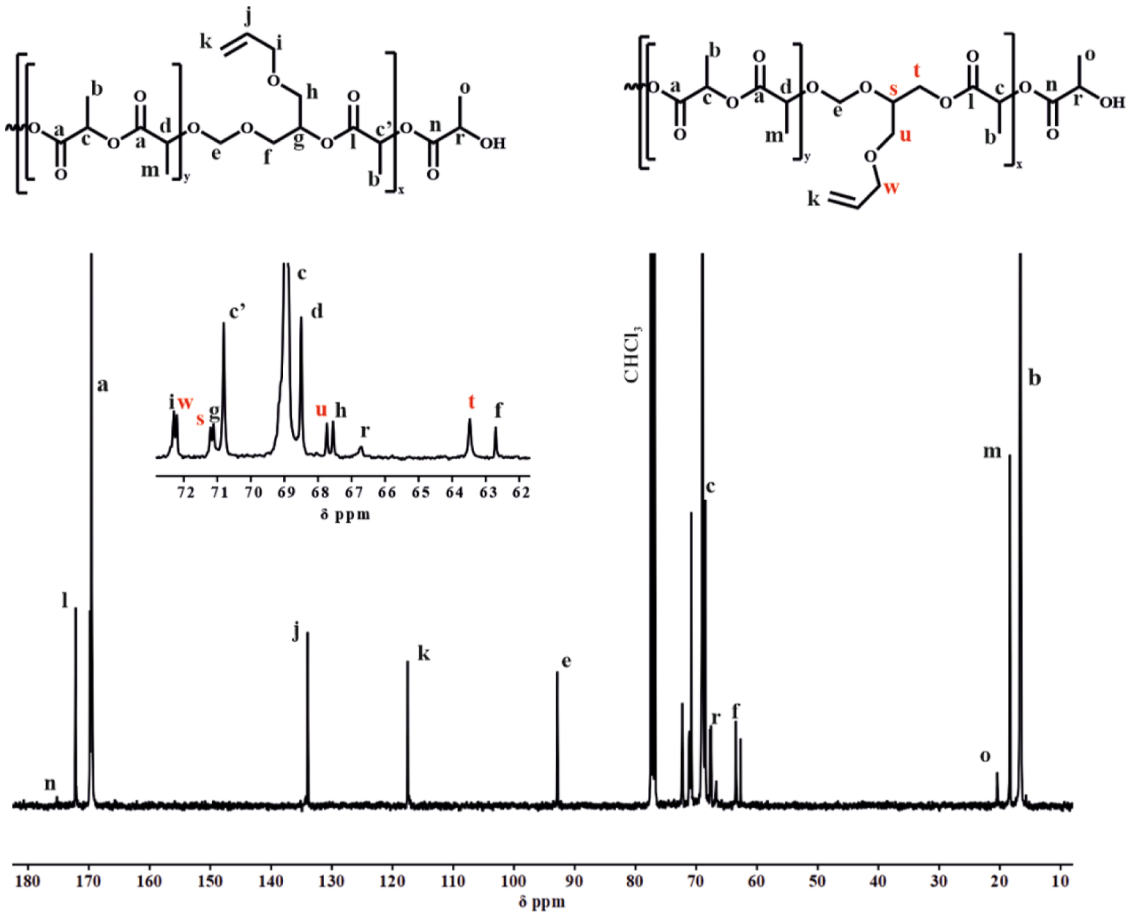


Figure 7. ^{13}C NMR spectra of the PLA/PAllyl-DXL copolymer with 10 mol % Allyl-DXL ($CDCl_3$, 100 MHz).

30 °C, the ratio of forms A (52%) and B (48%) in the copolymer chain was comparable. By decreasing the copolymerization temperature from 30 to 2 °C, the content of "A" form decreases from 52 to 43%. In addition, further lowering the temperature to −15 °C did not significantly decrease the content of acetal "A" units (40%) in the copolymer. However, for the PLA/PAllyl-DXL copolymers, these calculations are impossible due to the overlapping of the signals ("m", "a", and "o").

In the case of PLA/PCl-DXL and PLA/PAllyl-DXL copolymers with acetal-ester bonds (due to the inability to homopropagation and formation of acetal−acetal bonds), the sequence length of LA units can be determined taking into account the ratio of the average number of repeating units of the given comonomer (LA /acetal). The obtained values presented in Table 1 indicate that the presence of acetal units significantly disturbed the regularity of the ester sequence and shortened the average length of the PLA block. By changing the polymerization temperature from 30 to −15 °C, the length of the polyester block in the copolyester decreased almost twice.

For further characterization, diffusion-ordered spectroscopy (DOSY) NMR was employed. This relatively new method enables the structure, composition, molar mass, and diffusion coefficient of analyzed macromolecules to be estimated.[38,39] The 2D DOSY maps of PLA/PDXP, PLA/PCl-DXL, and PLA/PAllyl-DXL copolymers are shown in Figure 8. The signals belonging to the acetal and ester units in the copolymers exhibited the same diffusion coefficient, which clearly indicates that these moieties are covalently bonded in one macromolecule. The diffusion coefficients were as follows: $D_{PLA/PDXP} = -10.15$, $D_{PLA/PCl\text{-}DXL} = -9.98$, and $D_{PLA/PAllyl\text{-}DXL} = -10.28$ $\log(m^2/s)$. The other diffusion coefficients of polylactide [M_n = 10 000 D = −9.87 $\log(m^2/s)$][40] or low molar mass compounds were not observed. The DOSY analysis clearly demonstrated that copolyesters containing acetal units were successfully obtained in the cationic copolymerization of lactide with synthesized cyclic acetals.

The presented results confirmed that copolyesters comprising acetal units, which were fitted with reactive functionalities distributed along the copolymer chain, were successfully synthesized. The loading of alkyne and chloride pendant groups may be tuned by the ratio of the comonomers used in the cationic copolymerization. This proves the potential of the presented method as a tool for the effective synthesis of functionalized copolyesters terminated with hydroxyl end-groups under metal-free conditions.

Modification of the Prepared Polylactides Containing Acetal Functional Units. The pendant reactive groups in the polyester chain provide the opportunity for modification in nucleophilic substitution, azide−alkyne cycloaddition click, or thiol−ene click reactions, as shown in Scheme S2a,b. As a proof of concept, the PLA/PCl-DXL copolymers were reacted with sodium azide to replace the halide group with an azide group.[41,42] The reaction was performed in DMF or acetonitrile, solvents that are suitable for the S_N2 mechanism. The modification of copolymers was verified in the ^{13}C NMR spectra because of the overlapping proton signal in the ^1H

https://doi.org/10.1021/acs.macromol.3c01343
Macromolecules XXXX, XXX, XXX−XXX

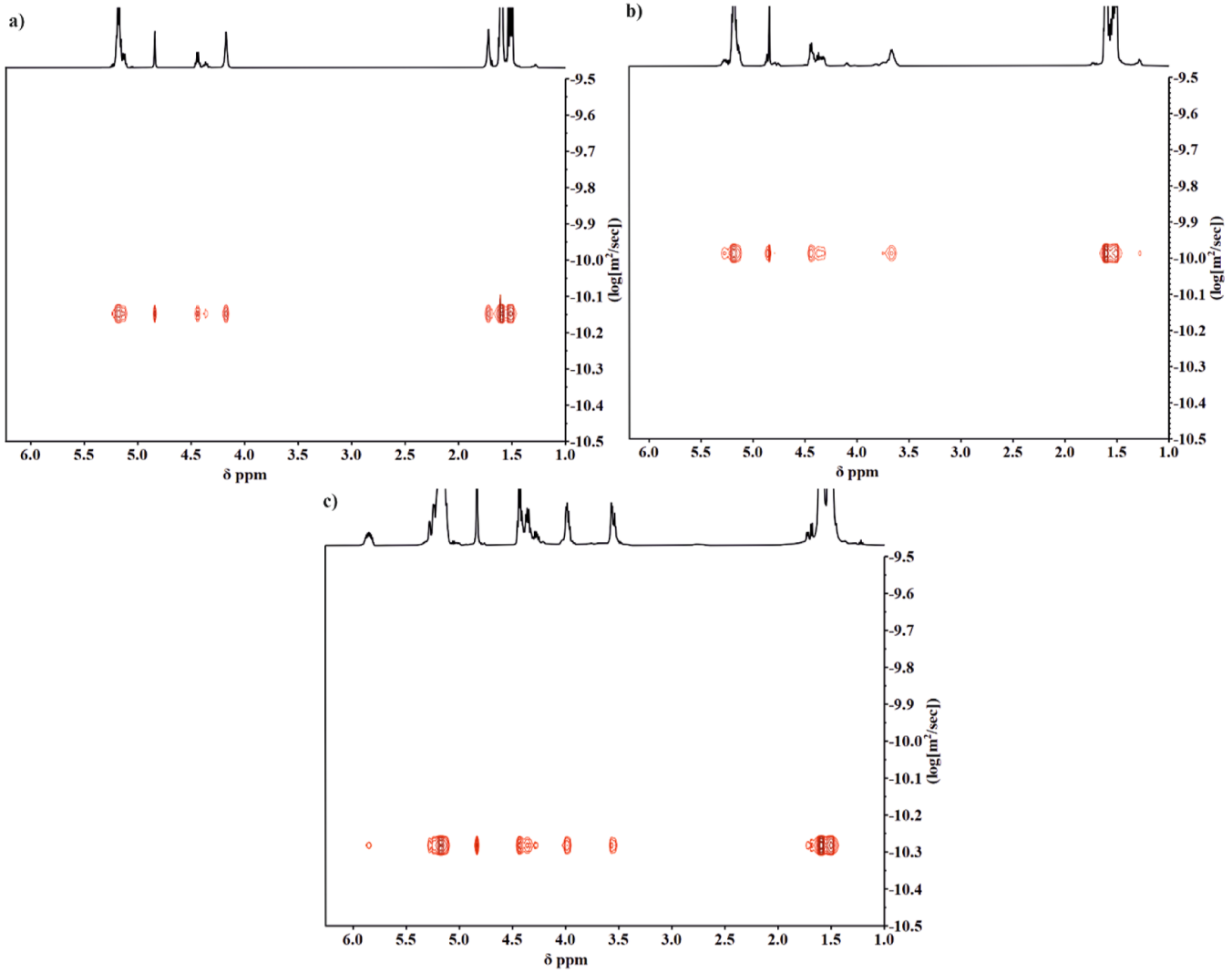


Figure 8. 2D DOSY NMR of purified (a) PLA/PDXP$_5$, (b) PLA/PCl-DXL, and (c) PLA/PAllyl-DXL copolymers ($CDCl_3$, 500 MHz).

NMR spectrum. As shown in Figure S9, the signal corresponding to the carbon directly connected to the chlorine ions at 41 ppm disappeared as a new signal from the carbon attached to the $-N_3$ at 51 ppm simultaneously appeared. This signal shifted toward a higher frequency due to the deshielding of the carbon by the electronegative azide function.[43] The SEC analysis (Figure S10a) showed unimodal molar mass distribution and only a slight peak shift toward the lower elution volume due to the small differences between the molar mass of −Cl (35.5 g/mol) and N_3 (42 g/mol) atoms. We also observed a decrease in the dispersity of azide-functionalized copolymers, which can be correlated with the successive precipitation of the copolymers. The introduction of an azide group to the polymer chain allows for further modification by compounds containing triple bonds.[44] For this purpose, we used propargyl glycidyl ether or propargyl alcohol to demonstrate that different functional groups may be introduced into copolyesters containing azide functionality through azide−alkyne cycloaddition reactions. The ^{13}C NMR showed that after modification, two new characteristic peaks belonging to the triazole ring at 144 and 125 ppm appeared, indicating that the click reaction was successful. Moreover, the spectra in Figure S8 show the presence of new peaks corresponding to the clicked compounds. However, modification of the copolymers with alkyne compounds led to a drastic change in the solubility of the polymers, making GPC analysis in dichloromethane unfeasible.

The presence in the polylactide chain pendant groups with double bonds enables further post modification by thiol−ene "click" chemistry with compounds containing the −SH group.[45] Compared to internal bonds, external double bonds cause faster and more efficient reactions. A wide range of compounds contain −SH groups, allowing for the introduction of various functionalities, such as carboxylic acid[15] and hydroxyls. To show the possibility of the copolymer for modification, we used mercaptopropane as a simple nonfunctional thiol to perform a model "click" reaction. As shown in the ^1H NMR (Figure S11), the conversion of double bonds was complete, as proven by the disappearance of the signal corresponding to the double bond at 5.80 and 5.30 ppm and the appearance of signals at 2.54 and 2.45 ppm, characteristic of $-O-CH_2-CH_2-C\underline{H}_2-S-$ and $-S-C\underline{H}_2-CH_2CH_3$, respectively. Thus, the ^1H NMR spectra clearly indicated the quantitative yields of the "click" reaction achieved on the copolyester chain. Additionally, to introduce functional groups into the copolymer chain, we reacted mercaptoethanol and thioglycolic acid with a pendant double bond. The representative ^1H NMR spectra of copolymers before and

https://doi.org/10.1021/acs.macromol.3c01343
Macromolecules XXXX, XXX, XXX−XXX

after the thiol−ene reaction are shown in Figure S11. For all of the reactions performed, the ^{1}H NMR results confirmed the addition of thiol molecules to the alkyne groups distributed along the polyester chain. These reactions resulted in the preparation of copolyesters with hydroxyl and carboxyl pendant groups. GPC analysis of "clicked" copolymers is in accordance with ^{1}H NMR, as the trace of the product almost exhibited the same shape as the trace of PLA/PAllyl-DXL before the modification but slightly shifted to lower elution volume values (higher molar mass), as shown in Figure S10b. The GPC analysis of the copolymers modified by thioglycolic acid was not possible due to the strong interaction of the carboxylic group with the PLGel chromatography column.

Most importantly, the applied modification conditions did not cause the copolymer chain containing acetal−ester bonds to degrade, which was proven by ^{1}H NMR analysis. Thus, this wide variety of functionalization reactions demonstrated that the synthesized copolyesters could be easily modified under mild conditions with a high yield by various functional and nonfunctional compounds.

Thermal Properties of Prepared Copolymers. The PLA/PDXP, PLA/PCl-DXL, and PLA/PAllyl-DXL represent a novel category of polymers distinguished from unmodified PLA due to the incorporation of diverse acetal units. In order to gain insights into the influence of these acetal units on the thermal properties and stability of the copolyesters, we conducted TGA (thermogravimetric analysis) and DSC (differential scanning calorimetry) analyses. Initially, we investigated the crystallization behavior of both the initial copolymers and their modified counterparts during the second DSC heating cycle. The DSC and TGA outcomes of the unmodified copolymers are summarized in Table 2 and Figures S12a−c and S13a−c.

Table 2. Thermal Properties of the Starting, Purified Copolymers Determined from TGA and DSC

		DSC		TGA
run	sample	T_g (°C)	T_m (°C)	T_{max} (°C)
	PLA[22]	60	160	300
1	PDXP	−78	16	350
2	PLA/PDXP$_5$	30		351
3	PLA/PDXP$_{10}$	22		318
4	PLA/PDXP$_{18}$	17		330
5	PLA/PDXP$_{26}$	6		357
10	PLA/PCl-DXL$_{10}$	40		320
11	PLA/PCl-DXL$_{16}$	35		350
12	PLA/PCl-DXL$_{22}$	25		355
17	PLA/PAllyl-DXL$_{10}$	38		340
18	PLA/PAllyl-DXL$_{14}$	27		310
19	PLA/PAllyl-DXL$_{22}$	14		327

Neat PDXP exhibited a glass transition (T_g) below −78 °C and the melting temperature (T_m) at 16 °C. The semicrystalline PLA exhibits a T_g of approximately 60 °C and a T_m up to 180 °C, depending on the molar masses.[46] As shown in Table 2, T_g and the crystallization capability were affected by the introduction of acetal units in all of the analyzed copolymers, regardless of their type. In all instances, the observation of the melting temperature peak was absent, suggesting that the copolyesters prepared are highly amorphous. This observation is in agreement with our previous studies,[22] that revealed that the incorporation of dioxolane units into the polylactide chain completely eliminated the crystallization of copolymer.

For copolymers of lactide with dioxepane and functionalized acetals, it is also noticeable that the increase in the number of acetal units in the polyester chain leads to a gradual decrease in T_g. The obtained copolymers exhibit T_g values ranging from 40 to 6 °C, depending on their structure and acetal content. The PLA/PDXP copolymer with 26% acetal content displays the lowest T_g, which could potentially be attributed to the presence of homopolydioxepane sequences.[22]

The thermal stability of the resulting copolymers was studied using thermogravimetric analysis with a heating rate of 20 °C/min from 30 to 650 °C. The results in Table 2 show that the temperature of the maximum rate of decomposition value increased by 50° in comparison to PLA, and it is close to the T_{max} of neat PDXP. The TGA results clearly indicate that the introduction of acetal units contributes to the modification of the thermal stability of polylactide.

The results of the modified copolyesters thermal analysis are summarized in Table 3. A comparison of the DSC scans for the starting and the corresponding modified copolymers showed that the incorporation of various functional groups to the copolymer chain did not affect the thermal properties and stability significantly. The modification only resulted in a slight decrease in the T_g value compared to the nonmodified copolymers, from 38 to 30 °C. The TGA results showed that only the copolymer modified with thioglycolic acid had a lower T_{max} compared to the nonmodified one. This effect can be correlated with the presence of the pendant carboxylic acid groups that can undergo condensation or decarboxylation upon thermal heating.[47]

Table 3. Characteristic Temperatures Determined from TGA and DSC of the Modified Copolymers in Comparison to the Starting Copolyester

		DSC		TGA
sample	modifying agent	T_g (°C)	T_m (°C)	T_{max} (°C)
PLA/PAllyl-DXL$_{10}$		38		340
PLA/PAllyl-DXL$_{10}$	propanethiol	35		324
PLA/PAllyl-DXL$_{10}$	thioglycolic acid	31		302
PLA/PAllyl-DXL$_{10}$	mercaptoethanol	30		324
PLA/PCl-DXL$_{10}$		40		320
PLA/PCl-DXL$_{10}$	sodium azide	34		350
PLA/PCl-DXL$_{10}$	sodium azide/propargyl glycidyl ether	32		300

Acid-Triggered Degradation of Functionalized Polylactides Containing Acetal Units. In our previously published work,[22] we proved that the random distribution of acetal units (27 mol %) in the polylactide chain enabled the degradation of copolymers within 72 h.

In the present paper, to show the possibility of the copolymer degradation in acidic medium, we selected for experiments nonfunctionalized (PLA/PDXP) and chlorofunctionalized (PLA/PCl-DXL) copolyesters. The progress of the copolymer chain cleavage was studied using ^{1}H NMR spectra (Figure 9). As we showed for the lactide copolymers with 1,3-dioxolane,[22] the presence of the acetal-ester bond requires harsher conditions to initiate the hydrolysis than a typical acetal bond.[23] For this purpose, we applied a hydrolytic system composed of a water solution of HCl (35%) and

https://doi.org/10.1021/acs.macromol.3c01343
Macromolecules XXXX, XXX, XXX−XXX

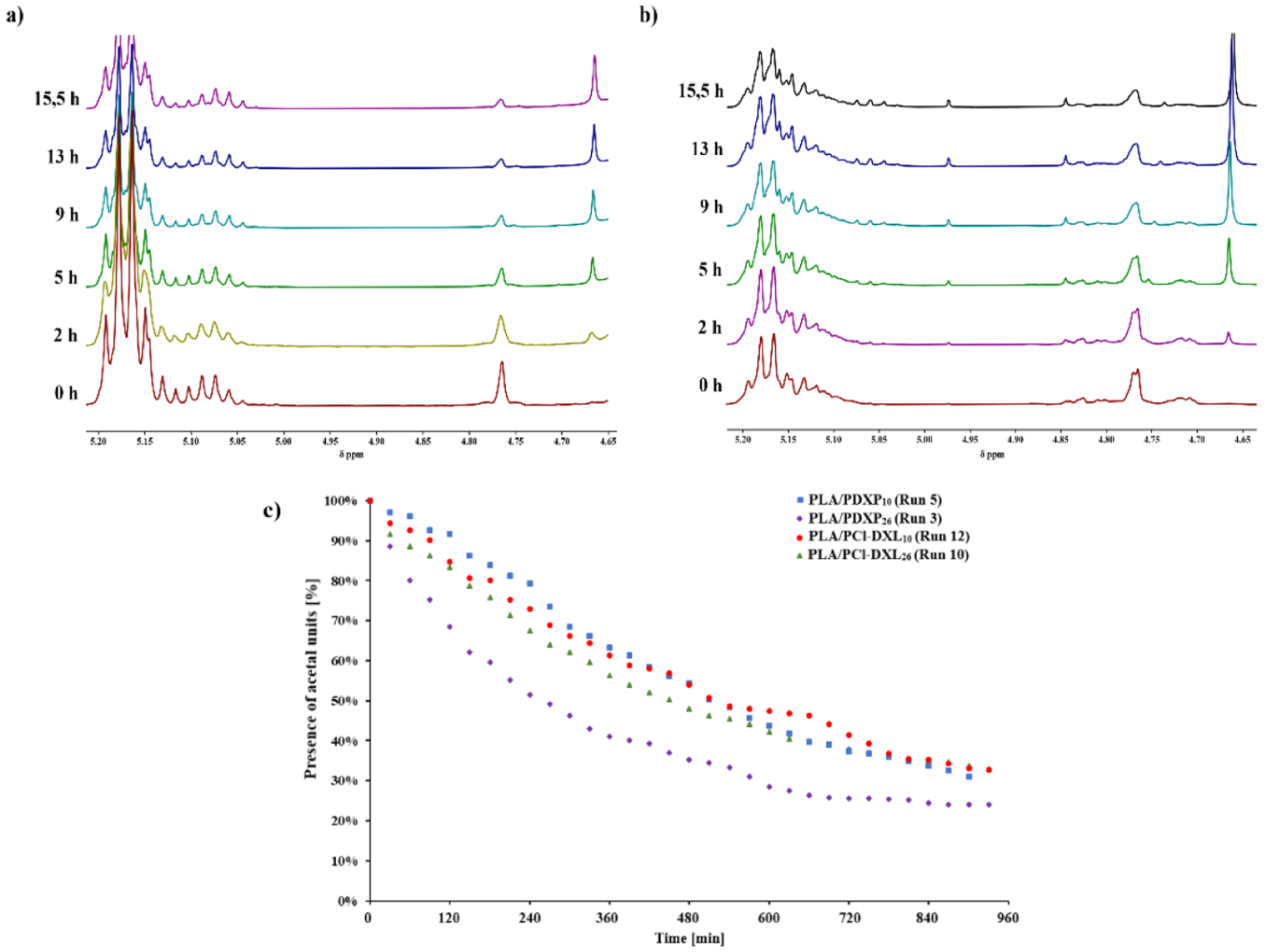


Figure 9. Acid-triggered degradation of (a) PLA/PDXP$_{10}$, (b) PLA/PCl-DXL$_{10}$ copolymers, and (c) disappearance of the signal attributed to $-OCH_2O-$ units in the copolymer chains (500 MHz, CD_3CN, solution of HCl in CD_3CN, see experimental part).

deuterated acetonitrile at 40 °C. This solvent combination allows to study degradation of copolymers in a homogeneous system, whereby the cleavage of acetal-ester bonds can be traced in the ^{1}H NMR spectra due to the good separation of signals. For the analyzed copolymers, the initial ^{1}H NMR spectra were recorded immediately after acid was added to the NMR tube and after a selected time interval.

First, we monitored changes in the spectra of lactide copolymers containing 10 mol % of acetal units. As shown in Figure 9a (PLA/PDXP$_{10}$) and Figure 9b (PLA/PCl-DXL$_{10}$) the intensity of the signal attributed to the $-OCH_2O-$ protons in an acetal−ester bond (4.78 ppm) gradually decreased over time, indicating the bond cleavage in the copolymer chain. At the same time, the intensity of signals in the region of spectra 5.03−5.20 did not change significantly, which allows us to conclude that there was no degradation of ester bonds in the LA−LA homosequences. Such an observation was also reported earlier for copolymers of lactide with 1,3-dioxolane under the conditions used [10 μL HCl (35%) in 690 μL CD_3CN].[22] At the same time, a new signal in the spectra appeared at 4.67 ppm, and its intensity grew with time. It can therefore be assumed that the presence of this signal may be related to the formation of population polymer chains with new end-groups or byproducts in the system. Identifying all the degradation products in the studied system is cumbersome due to the presence of substitution on the cyclic acetal (two ways of opening the acetal ring) and nonclassical acetal bonds (acetal−ester bond) in the copolymer chain. However, our group is currently conducting a more complex investigation to elucidate the mechanism of acid-triggered degradation of copolyesters containing various types of acetal units.

For copolymers differing in composition, we determined the rate of disappearance of signal located at 4.78 ppm, by analyzing its intensity (I) in time, expressed as the I_t/I_0 ratio (Figure 9c). The provided graph clearly demonstrates that, under the specified conditions, the 50% reduction in signal intensity was achieved after 270 min (4.5 h) for PLA/PDXP$_{26}$ (run 5), and about 510 min (8 h) for PLA/PDXP$_{10}$ (run 3), PLA/PCl-DXL$_{22}$ (run 12), and PLA/PCl-DXL$_{10}$ (run 10). Thus, the fastest degradation was observed for the copolymer containing the highest content of DXP−DXP sequences in the copolymer chain (run 5), which are more sensitive to pH than the acetal−ester bonds present in the other analyzed copolymers.

No significant difference in the rate of acetal unit loss was observed between chloro-functionalized PLA containing 10 and 20 mol % of acetal (runs 10 and 12). The increased content of Cl-DXL units within the polyester chains did not result in faster degradation since only acetal-ester bonds were present in this copolymer type. The slight differences in the

https://doi.org/10.1021/acs.macromol.3c01343
Macromolecules XXXX, XXX, XXX−XXX

degradation times between PLA/PDXL and PLA/PCl-DXL could be associated with the different hydrophobicities of the prepared materials. This effect was investigated by comparing the contact angle measured for PLA and selected copolymers, as shown in Figure S14. The introduction of various acetal units to the polyester chain caused a reduction in the contact angle from 85° (PLA) to 76° (PLA/PDXP) and 62° (PLA/PCl-DXL). These results are consistent with the degradation experiments, which indicated that PLA/PCl-DXL degrades slightly faster than PLA/PDXP, likely due to its higher hydrophilicity.

Additionally, to demonstrate the loss of copolymers' molar mass after acid-triggered degradation under the applied conditions, we performed SEC analysis. As shown in Figure S15 for PLA/PDXP$_{10}$ and PLA/PCl-DXL$_{10}$, the SEC traces showed a decrease in molar masses from 10 000 to 3 000 and from 13 000 to 3 500 g/mol, respectively, within 24 h. The decrease in molar masses of the copolymers was attributed to the cleavage of the labile acetal−ester bonds in the main chain.

CONCLUSIONS

In this work, we have successfully synthesized functionalized polylactides bearing chloride and allyl functions as side groups via cationic ring-opening copolymerization of lactide with the appropriate cyclic acetals. The strategy allowed a high content of functional pendant groups to be incorporated along the copolymer backbone during the polymerization process. The copolymer composition was controlled by changes in the copolymerization parameters or the feed ratio, and the final amount of cyclic acetals in the polylactide chain ranged from 5 to 27 mol %. Subsequently, nucleophilic substitution, thiol−ene, and azide−alkyne click reactions have been applied to modify the copolyester chain by reacting the pendant groups with sodium azide, propargyl alcohol, mercaptopropane, mercaptoethanol, or thioglycolic acid. The results obtained from the hydrolysis studies showed that the introduction of acetal units into the macromolecules led to the cleavage of the copolymer chain under relatively mild acid conditions. In summary, the described procedure allowed for the synthesis of functionalized polylactides with a controlled number of side functional groups, thanks to which it is possible further to construct more complex, polyester-based degradable structures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.3c01343.

^{1}H, ^{13}C NMR, and GC/MS spectra of comonomers; ^{1}H, ^{13}C, 2D HSQC NMR spectra of copolymers; SEC traces of starting and modified copolymers; contact angles of copolymers; scheme of synthesis of comonomers; and modification of the copolymers (PDF)

AUTHOR INFORMATION

Corresponding Authors

Malgorzata Basko − *Centre of Molecular and Macromolecular Studies Polish Academy of Sciences, 90-363 Lodz, Poland;* orcid.org/0000-0001-9495-6262; Email: malgorzata.basko@cbmm.lodz.pl

Bartłomiej Kost − *Centre of Molecular and Macromolecular Studies Polish Academy of Sciences, 90-363 Lodz, Poland;* orcid.org/0000-0002-7654-3162; Email: bartlomiej.kost@cbmm.lodz.pl

Authors

Karolina Cichoń − *Centre of Molecular and Macromolecular Studies Polish Academy of Sciences, 90-363 Lodz, Poland;* orcid.org/0000-0003-2509-2063

Irena I. Bak-Sypien − *Centre of Molecular and Macromolecular Studies Polish Academy of Sciences, 90-363 Lodz, Poland;* orcid.org/0000-0002-6070-2309

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.macromol.3c01343

Author Contributions

B.K.: conceptualization, methodology, synthesis of the copolymers, writing, editing, and supervising; M.B.: writing and supervising; K.C.: synthesis of the copolymers, analysis of the copolymers, editing, and preparation of figures; and I.I.B.-S.: GC/MS analysis.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Professor P. Kubisa is acknowledged for the helpful discussion (Centre of Molecular and Macromolecular Studies). B.K. acknowledges financial support from the National Science Centre, Poland, grant no. DEC-2021/05/X/ST5/00491. The Avance Neo 400 NMR spectrometer purchase, used to obtain results included in this publication, was supported by funds from the EU Regional Operational Program of the Lodz Region, RPLD.01.01.00-10-0008/18. Upgrade of the Avance III 500 NMR spectrometer used to obtain results included in this publication was supported by funds from the EU Regional Operational Program of the Lodz Region, RPLD.01.01.00-10-0008/18. Bio-Med-Chem Doctoral School of the University of Lodz and Lodz Institutes of the Polish Academy of Sciences are acknowledged for the support of this study by Karolina Cichoń.

REFERENCES

(1) Luckachan, G. E.; Pillai, C. K. S. Biodegradable Polymers- A Review on Recent Trends and Emerging Perspectives. *J. Polym. Environ.* **2011**, *19* (3), 637−676.

(2) Samir, A.; Ashour, F. H.; Hakim, A. A. A.; Bassyouni, M. Recent Advances in Biodegradable Polymers for Sustainable Applications. *Mater. Degrad.* **2022**, *6* (1), 68.

(3) Okada, M. Chemical Syntheses of Biodegradable Polymers. *Prog. Polym. Sci.* **2002**, *27* (1), 87−133.

(4) Slomkowski, S.; Penczek, S.; Duda, A. Polylactides-an Overview. *Polym. Adv. Technol.* **2014**, *25* (5), 436−447.

(5) Cong, S. Properties of Polylactic Acid Fiber Based Polymers and Their Correlation with Composition. *Proceedings of 2007 International Conference on Advanced Fibers and Polymer Materials, ICAFPM 2007*, 2007; Vol. *1*, pp 8−11.

(6) Williams, C. K. Synthesis of Functionalized Biodegradable Polyesters. *Chem. Soc. Rev.* **2007**, *36* (10), 1573−1580.

(7) Kricheldorf, H. R.; Jonté, J. M.; Berl, M. Polylactones 3. Copolymerization of Glycolide with L, L-Lactide and Other Lactones. *Die Makromol. Chemie* **1985**, *12* (S19851), 25−38.

(8) Martins, C.; Sousa, F.; Araújo, F.; Sarmento, B. Functionalizing PLGA and PLGA Derivatives for Drug Delivery and Tissue Regeneration Applications. *Adv. Healthcare Mater.* **2018**, *7* (1), 1701035.

(9) Fukuzaki, H.; Yoshida, M.; Asano, M.; Kumakura, M.; Mashimo, T.; Yuasa, H.; Imai, K.; Hidetoshi, Y. Synthesis of Low-Molecular-

Weight Copoly(l-Lactic Acid/ε-Caprolactone) by Direct Copolycondensation in the Absence of Catalysts, and Enzymatic Degradation of the Polymers. *Polymer* **1990**, *31* (10), 2006−2014.
(10) MacDonald, J. P.; Parker, M. P.; Greenland, B. W.; Hermida-Merino, D.; Hamley, I. W.; Shaver, M. P. Tuning Thermal Properties and Microphase Separation in Aliphatic Polyester ABA Copolymers. *Polym. Chem.* **2015**, *6* (9), 1445−1453.
(11) Darensbourg, D. J.; Choi, W.; Karroonnirun, O.; Bhuvanesh, N. Ring-Opening Polymerization of Cyclic Monomers by Complexes Derived from Biocompatible Metals. Production of Poly(Lactide), Poly(Trimethylene Carbonate), and Their Copolymers. *Macromolecules* **2008**, *41* (10), 3493−3502.
(12) Shin, D.; Shin, K.; Aamer, K. A.; Tew, G. N.; Russell, T. P.; Lee, J. H.; Jho, J. Y. A Morphological Study of a Semicrystalline Poly(l -Lactic Acid-b-Ethylene Oxide- b - l-Lactic Acid) Triblock Copolymer. *Macromolecules* **2005**, *38* (1), 104−109.
(13) Puthumana, M.; Santhana Gopala Krishnan, P.; Nayak, S. K. Chemical Modifications of PLA through Copolymerization. *Int. J. Polym. Anal. Charact.* **2020**, *25* (8), 634−648.
(14) Zhang, X.; Dai, Y. A Functionalized Cyclic Lactide Monomer for Synthesis of Water-Soluble Poly(Lactic Acid) and Amphiphilic Diblock Poly(Lactic Acid). *Macromol. Rapid Commun.* **2017**, *38* (2), 1600593.
(15) Kost, B.; Gonciarz, W.; Krupa, A.; Socka, M.; Rogala, M.; Biela, T.; Brzeziński, M. PH-Tunable Nanoparticles Composed of Copolymers of Lactide and Allyl-Glycidyl Ether with Various Functionalities for the Efficient Delivery of Anti-Cancer Drugs. *Colloids Surf., B* **2021**, *204*, 111801.
(16) Bednarek, M.; Basko, M.; Kubisa, P. Functional Polylactide by Cationic Ring-Opening Copolymerization of Lactide with Epoxides. *React. Funct. Polym.* **2017**, *119*, 9−19.
(17) Kalelkar, P. P.; Alas, G. R.; Collard, D. M. Synthesis of an Alkene-Containing Copolylactide and Its Facile Modification by the Addition of Thiols. *Macromolecules* **2016**, *49* (7), 2609−2617.
(18) Pound-Lana, G.; Rabanel, J.-M.; Hildgen, P.; Mosqueira, V. C. F. Functional Polylactide via Ring-Opening Copolymerisation with Allyl, Benzyl and Propargyl Glycidyl Ethers. *Eur. Polym. J.* **2017**, *90*, 344−353.
(19) Neitzel, A. E.; Petersen, M. A.; Kokkoli, E.; Hillmyer, M. A. Divergent Mechanistic Avenues to an Aliphatic Polyesteracetal or Polyester from a Single Cyclic Esteracetal. *ACS Macro Lett.* **2014**, *3* (11), 1156−1160.
(20) Neitzel, A. E.; Haversang, T. J.; Hillmyer, M. A. Organocatalytic Cationic Ring-Opening Polymerization of a Cyclic Hemiacetal Ester. *Ind. Eng. Chem. Res.* **2016**, *55* (45), 11747−11755.
(21) Neitzel, A. E.; Barreda, L.; Trotta, J. T.; Fahnhorst, G. W.; Haversang, T. J.; Hoye, T. R.; Fors, B. P.; Hillmyer, M. A. Hydrolytically-Degradable Homo- and Copolymers of a Strained Exocyclic Hemiacetal Ester. *Polym. Chem.* **2019**, *10* (33), 4573−4583.
(22) Kost, B.; Basko, M. Synthesis and Properties of L-Lactide/1,3-Dioxolane Copolymers: Preparation of Polyesters with Enhanced Acid Sensitivity. *Polym. Chem.* **2021**, *12* (17), 2551−2562.
(23) Cichoń, K.; Kost, B.; Basko, M. Synthesis and Properties of ABA-Triblock Copolymers from Polyester A-Blocks and Easily Degradable Polyacetal B-Blocks. *Polym. Chem.* **2022**, *13* (36), 5243−5255.
(24) Goodman, I. Cyclic Monomers. Edited by K. C. Frisch. Wiley-Interscience, New York. 1972. Pp. Ix + 782. £12.60. *Br. Polym. J.* **1973**, *5* (5), 413−414.
(25) Collin, J. E.; Conde-Caprace, G. Ionization and Dissociation of Cyclic Ethers by Electron Impact. *Int. J. Mass Spectrom. Ion Phys.* **1968**, *1* (3), 213−225.
(26) Lang, S. A.; Lin, Y.-I. Isoxazoles and Their Benzo Derivatives. *Comprehensive Heterocyclic Chemistry*; Elsevier, 1984; pp 1−130.
(27) Gross, R. A. A Mass Spectral Chlorine Rule for Use in Structure Determinations in Sophomore Organic Chemistry. *J. Chem. Educ.* **2004**, *81* (8), 1161.
(28) Liu, Y.; Wang, H.; Pan, C. Study on the Cationic Polymerization Mechanism of 1,3-Dioxepane in the Presence of Ethylene Glycol. *Macromol. Chem. Phys.* **1997**, *198* (8), 2613−2622.
(29) Penczek, S.; Kubisa, P. Cyclic Acetals. *Advance Polymer Science*; Springer: Berlin Heidelberg, 1985; pp 91−138.
(30) Ivin, K. J. Thermodynamics of Addition Polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38* (12), 2137−2146.
(31) Abel, B. A.; Snyder, R. L.; Coates, G. W. Chemically Recyclable Thermoplastics from Reversible-Deactivation Polymerization of Cyclic Acetals. *Science* **2021**, *373* (6556), 783−789.
(32) Okada, M.; Mita, K.; Sumitomo, H. Cationic Polymerization of 4-Ethyl-l,3-Dioxolane. *Die Makromol. Chemie* **1976**, *177*, 895−906.
(33) Bernat, R.; Maksym, P.; Tarnacka, M.; Koperwas, K.; Knapik-Kowalczuk, J.; Malarz, K.; Mrozek-Wilczkiewicz, A.; Dzienia, A.; Biela, T.; Turczyn, R.; Orszulak, L.; Hachuła, B.; Paluch, M.; Kamiński, K. The Effect of High-Pressure on Organocatalyzed ROP of γ-Butyrolactone. *Polymer* **2021**, *233*, 124166.
(34) Danko, M.; Mosnacek, J. Ring-Opening Polymerization of γ-Butyrolactone and Its Derivatives: A Review. *Polimery* **2017**, *62* (04), 272−282.
(35) Duda, A.; Penczek, S.; Dubois, P.; Mecerreyes, D.; Jérôme, R. Oligomerization and copolymerization of γ-butyrolactone — a monomer known as unable to homopolymerize, 1. Copolymerization with ε-caprolactone. *Macromol. Chem. Phys.* **1996**, *197*, 1273−1283.
(36) Okada, M. Polymerization of 1, 3-Dioxolane. *Makromol. Chem.* **1962**, *65* (5), 691−695.
(37) Reibel, L. C.; Durand, C. P.; Franta, E. Cationic Polymerization of 1,3-Dioxolane and 1,3-Dioxepane. Application to Graft and Block Copolymer Synthesis. *Can. J. Chem.* **1985**, *63* (1), 264−269.
(38) Lewinski, P.; Sosnowski, S.; Kazmierski, S.; Penczek, S. L-Lactide Polymerization Studied by 1H NMR with Diffusion-Ordered Spectroscopy (DOSY): A "One NMR Tube Experiment" Providing Data on Monomer Conversion, Polymer Structure, Mn and Mw. *Polym. Chem.* **2015**, *6* (24), 4353−4357.
(39) Bakkour, Y.; Darcos, V.; Li, S.; Coudane, J. Diffusion Ordered Spectroscopy (DOSY) as a Powerful Tool for Amphiphilic Block Copolymer Characterization and for Critical Micelle Concentration (CMC) Determination. *Polym. Chem.* **2012**, *3* (8), 2006−2010.
(40) Cichoń, K.; Kost, B.; Basko, M. Synthesis and Properties of ABA-Triblock Copolymers from Polyester A-Blocks and Easily Degradable Polyacetal B-Blocks. *Polym. Chem.* **2022**, *13* (36), 5243−5255.
(41) Huang, Y.; Gao, J.; Gao, H.; Chen, Y.; Zang, Y.; Sun, J.; Zhang, C. Azide Polyether with a Highly Flexible Main Chain as Energetic Materials. *ACS Appl. Polym. Mater.* **2023**, *5* (4), 3096−3103.
(42) Huang, Y.; Gao, J.; Gao, H.; Chen, Y.; Zang, Y.; Sun, J.; Zhang, C. Azide Polyether with a Highly Flexible Main Chain as Energetic Materials. *ACS Appl. Polym. Mater.* **2023**, *5* (4), 3096−3103.
(43) Gacal, B. N.; Filiz, V.; Shishatskiy, S.; Neumann, S.; Wind, J.; Abetz, V. Effect of Azidation and UV Cross-Linking of Poly(Epichlorohydrin) and Poly[(Ethylene Oxide)-Ran-(Epichlorohydrin)] on Gas Transport Properties. *J. Membr. Sci.* **2014**, *467*, 126−135.
(44) Bräse, S.; Gil, C.; Knepper, K.; Zimmermann, V. Organic Azides: An Exploding Diversity of a Unique Class of Compounds. *Angew. Chem., Int. Ed.* **2005**, *44* (33), 5188−5240.
(45) Debsharma, T.; Yagci, Y.; Schlaad, H. Cellulose-Derived Functional Polyacetal by Cationic Ring-Opening Polymerization of Levoglucosenyl Methyl Ether. *Angew. Chem.* **2019**, *131* (51), 18663−18666.
(46) Saeidlou, S.; Huneault, M. A.; Li, H.; Park, C. B. Poly(Lactic Acid) Crystallization. *Prog. Polym. Sci.* **2012**, *37* (12), 1657−1677.
(47) Mountaki, S. A.; Kaliva, M.; Loukelis, K.; Chatzinikolaidou, M.; Vamvakaki, M. Responsive Polyesters with Alkene and Carboxylic Acid Side-Groups for Tissue Engineering Applications. *Polymers* **2021**, *13* (10), 1636−1718.

https://doi.org/10.1021/acs.macromol.3c01343
Macromolecules XXXX, XXX, XXX−XXX

Supporting information for

Synthesis and characterization of functionalized polylactides containing acetal units

Karolina Cichoń, Irena I. Bak-Sypien, Malgorzata Basko*, Bartłomiej Kost*

Centre of Molecular and Macromolecular Studies Polish Academy of Sciences

Sienkiewicza 112, 90-363 Lodz, Poland

Emails: bartlomiej.kost@cbmm.lodz.pl, malgorzata.basko@cbmm.lodz.pl

Table of contents:

Table S1. The molar content of two different types of acetal repeating units in PLA/PCl-DXL$_{12}$ copolymer chain calculated from the ^{1}H NMR spectra, taking into account the intensity of signal "h" and "f"……..……..……... 3

Scheme S1. The synthesis of cyclic acetals via a dehydration reaction ……. 3

Figure S1. The ^{1}H NMR spectra of a) 1,3-dioxepane, b) 4-chloromethyl-1,-3-dioxolane, c) 4-[(allyloxy)methyl]-1,3-dioxolane ……. 4

Figure S2. The ^{13}C NMR spectra of a) 1,3-dioxepane, b) 4-chloromethyl-1,-3-dioxolane, c) 4-[(allyloxy)methyl]-1,3-dioxolane ……...…….. 4

Figure S3. a) the GC chromatogram of obtained cyclic acetals and b) 4- chloromethyl-1,3-dioxolane c) 1,4-dioxepane, and d) 4-[(allyloxy)methyl]-1,3-dioxolane MS spectra …… 5

Figure S4. a) ^{1}H NMR spectra and b) ^{13}C NMR spectra of poly(1,3-dioxepane) homopolymer ……. 6

Figure S5. a) 2D NMR HSQC spectra of PLA/PDXP$_5$ copolymer ($CDCl_3$, 400 MHz) ……. 6

Figure S6. Conversion vs time curves for cationic copolymerization of lactide with Cl-DXL……..…...……... 7

Figure S7. a) 2D NMR HSQC spectra of PLA/PCl-DXL copolymer ($CDCl_3$, 400 MHz) ….. 8

Figure S8. a) 2D NMR HSQC spectra of PLA/PAllyl-DXL copolymer ($CDCl_3$, 400 MHz)... 8

Scheme S2. Functionalization of a) PLA/PCl-DXL copolymer with sodium azide, propargyl alcohol or propargyl glycidyl ether and b) PLA/PAllyl-DXL copolymer with propanethiol, glycolic acid or ethanethiol……...…….. 9

Figure S9. Figure S8. The ^{13}C NMR spectra before and after modification of PLA/PCl-DXL (DMSO-d6, 100 MHz) …….…… 10

Figure S10. The SEC trace of PLA/PCl-DXL and PLA/PAllyl-DXL before and after modification…….. 11

Figure S11. The ^{1}H NMR spectra before and after modification of PLA/PAllyl-DXL (CDCl3, 400 MHz) ……..……..……... 12

Figure S12. The DSC traces of a) PLA/PDXP, b) PLA/PCl-DXL or PLA/Pallyl-DXL copolymers, and c) DSC traces of copolymers after modification…… 12

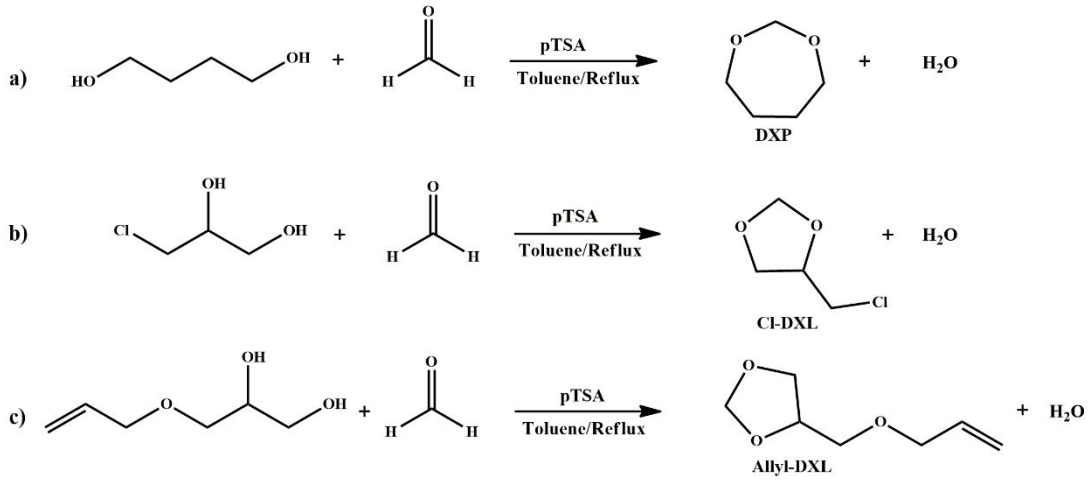
Figure S13. The TGA traces of a) PLA/PDXP, b) PLA/PCl-DXL or PLA/Pallyl-DXL copolymers, and c) DSC traces of copolymers after modification…… 13

Figure S14. Contact angles measured for neat PLA and PLA/PDXL and PLA/PCl-DXL copolymers (films on a glass plate with water as a reference liquid)…….. 13

Figure S15. The GPC traces of a) PLA/PDXP and b) PLA/PCl-DXL copolymers before and after hydrolysis……..... 14

Table S1. The molar content of two different types of acetal repeating units in PLA/PCl-DXL$_{12}$ copolymer chain calculated from the ^{1}H-NMR spectra taking into account the intensity of signal "h" and "f"

Sample	Temperature	„A" form [mol%]	„B" form [mol%]
PLA/PCl-DXL$_{12}$	30	52	48
PLA/PCl-DXL$_{18}$	2	43	57
PLA/PCl-DXL$_{22}$	-15	40	60



Scheme S1. The synthesis of cyclic acetals a) 1,3-dioxpeane (DXP), b) 4-chloromethyl-1,3-dioxolane, c) 4-[(allyloxy)methyl]-1,3-dioxolane

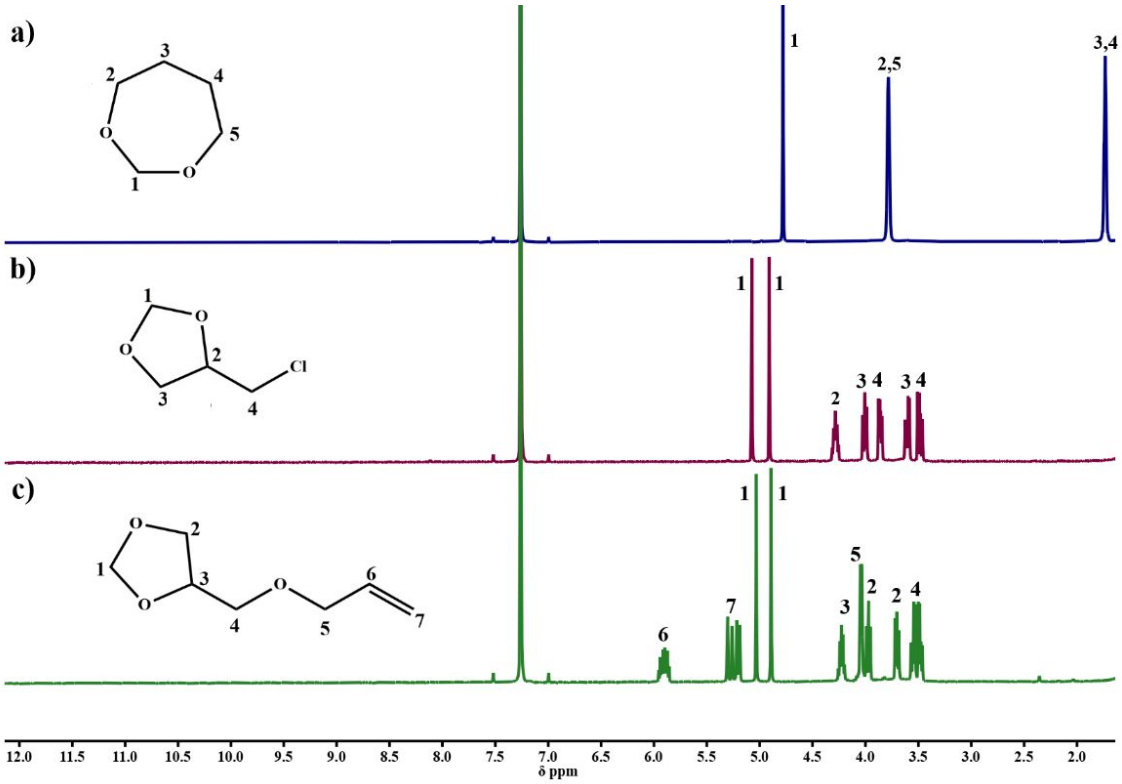


Figure S1. The ^{1}H NMR spectra of a) 1,3-dioxepane, b) 4-chloromethyl-1,3-dioxolane, c) 4-[(allyloxy)methyl]-1,3-dioxolane

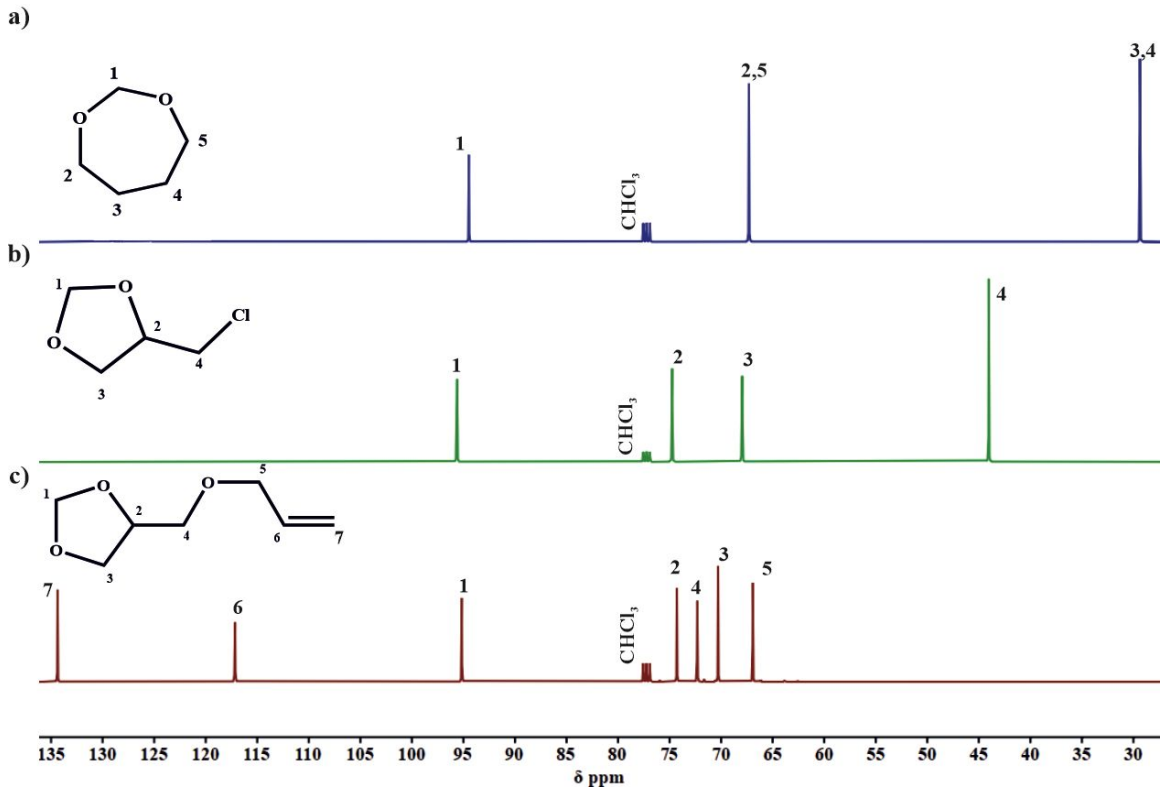


Figure S2. The ^{13}C NMR spectra of a) 1,3-dioxepane, b) 4-chloromethyl-1,3-dioxolane, c) 4-[(allyloxy)methyl]-1,3-dioxolane

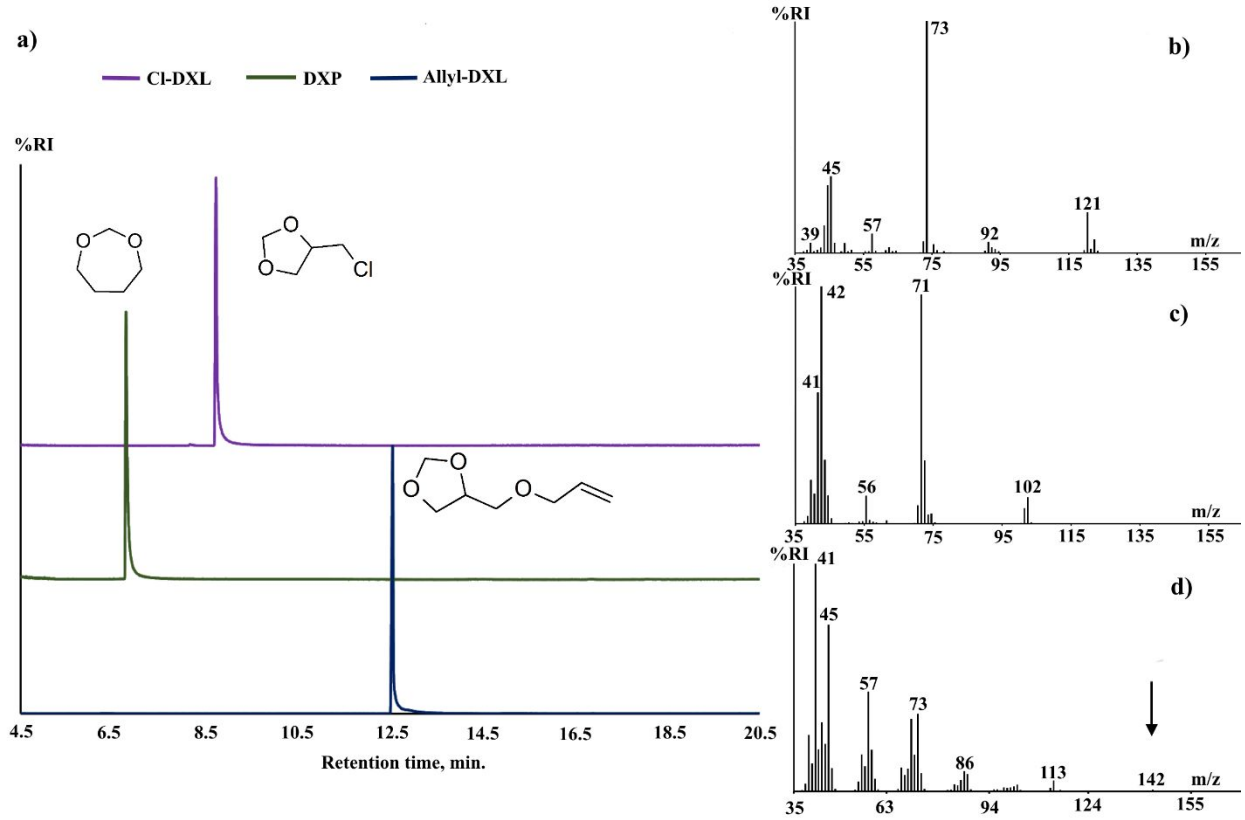


Figure S3. a) the GC chromatogram of obtained cyclic acetals and b) 4 -chloromethyl-1,3-dioxolane (Cl-DXL), c) 1,3-dioxepane (DXP), and d) 4-[(allyloxy)methyl]-1,3-dioxolane (Allyl-DXL) MS spectra

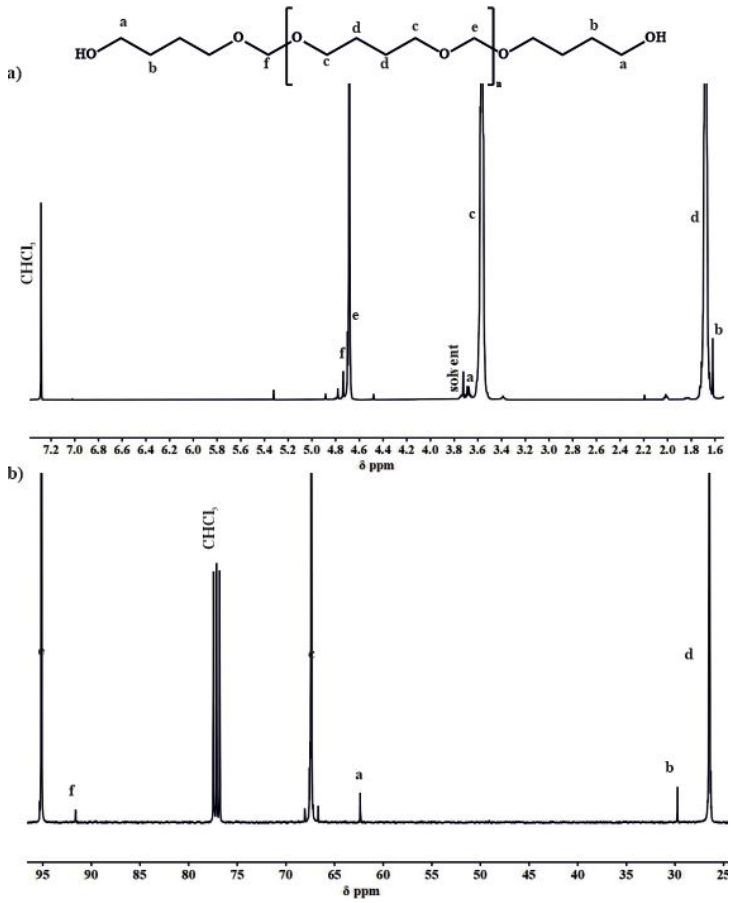


Figure S4. a) ^{1}H NMR spectra and b) ^{13}C NMR spectra of poly(1,3-dioxepane) homopolymer

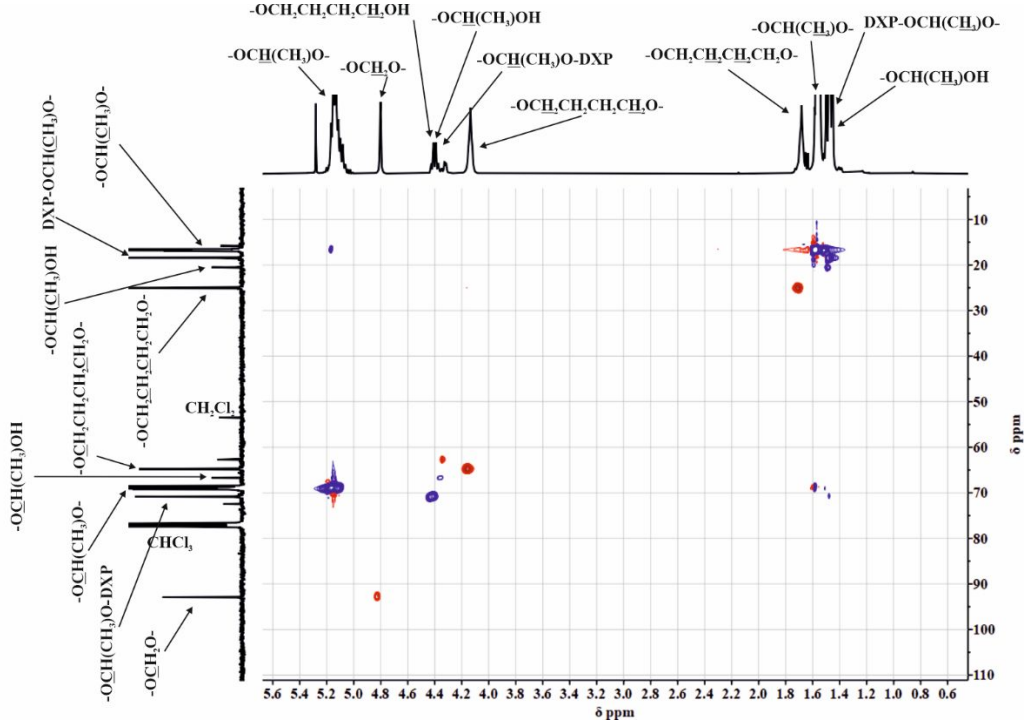


Figure S5. a) 2D NMR HSQC spectra of PLA/PDXP$_5$ copolymer ($CDCl_3$, 400 MHz)

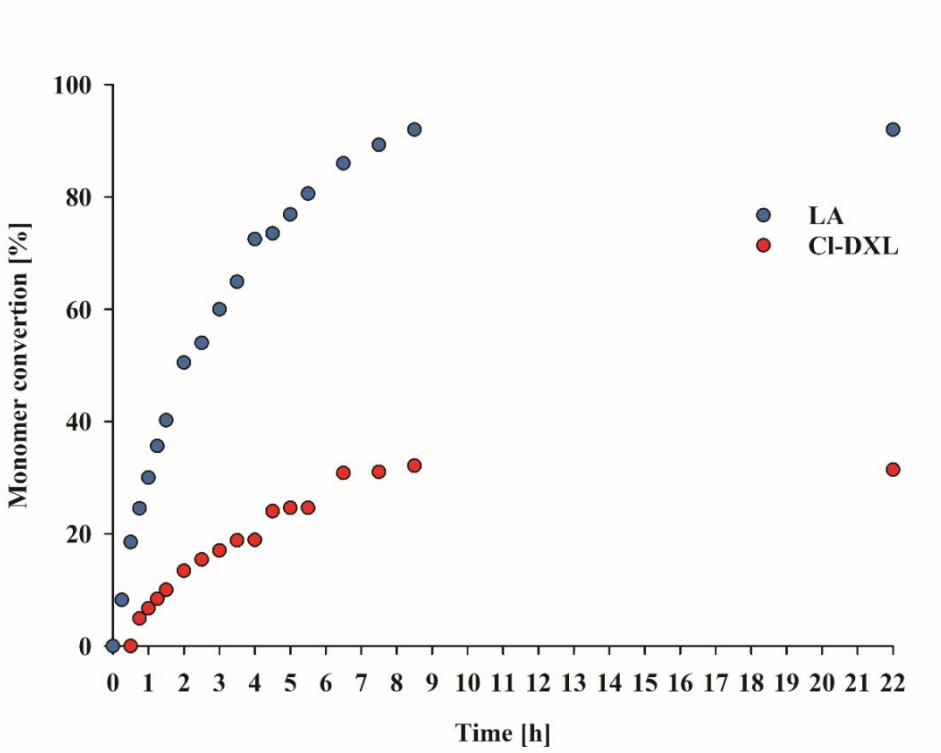


Figure S6. Conversion vs time curves for cationic copolymerization of lactide with Cl-DXL. Conditions: (LA/ Cl-DXL =67/33 mol%, ethylene glycol as an initiator, triflic acid as a catalyst, T= 2 ^{o}C, run 11 at Table 1).

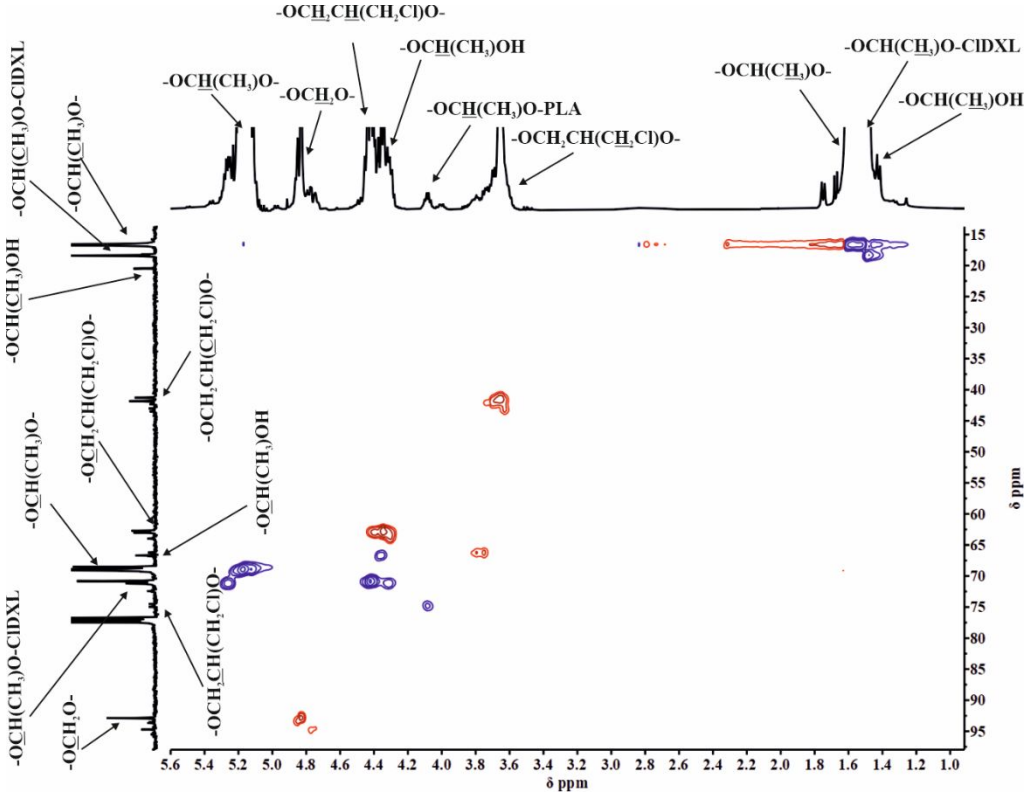


Figure S7. a) 2D NMR HSQC spectra of PLA/PCl-DXL copolymer ($CDCl_3$, 400 MHz)

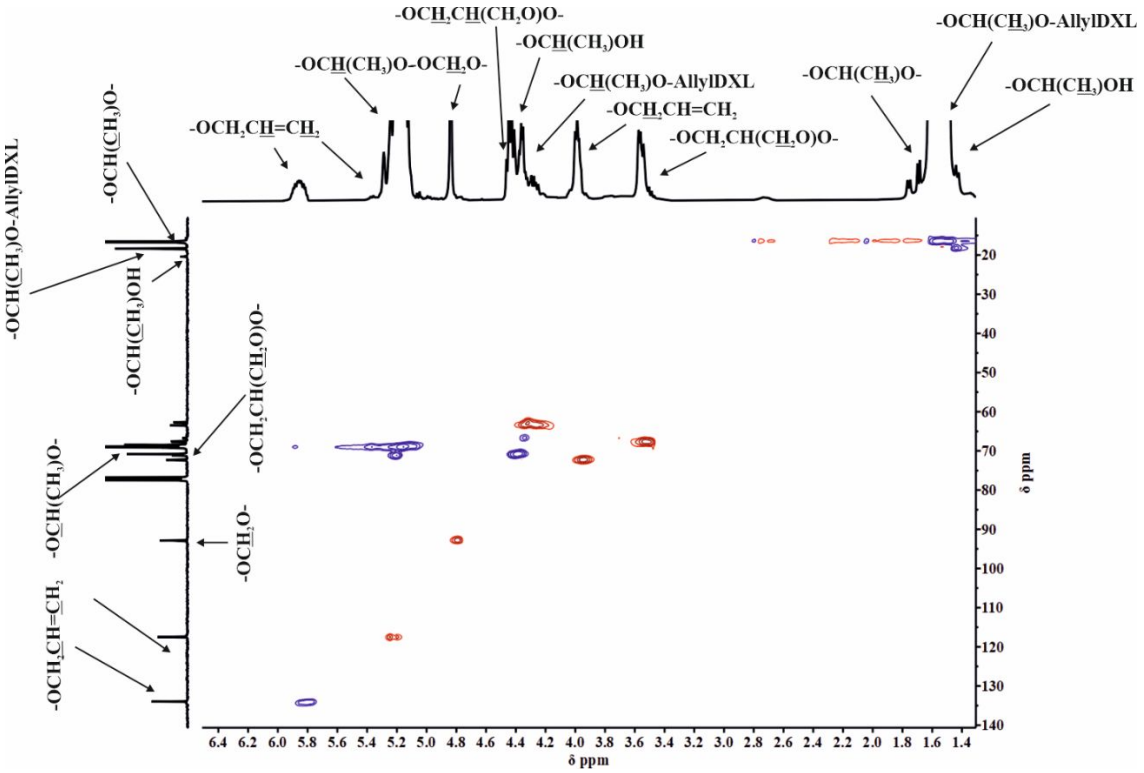
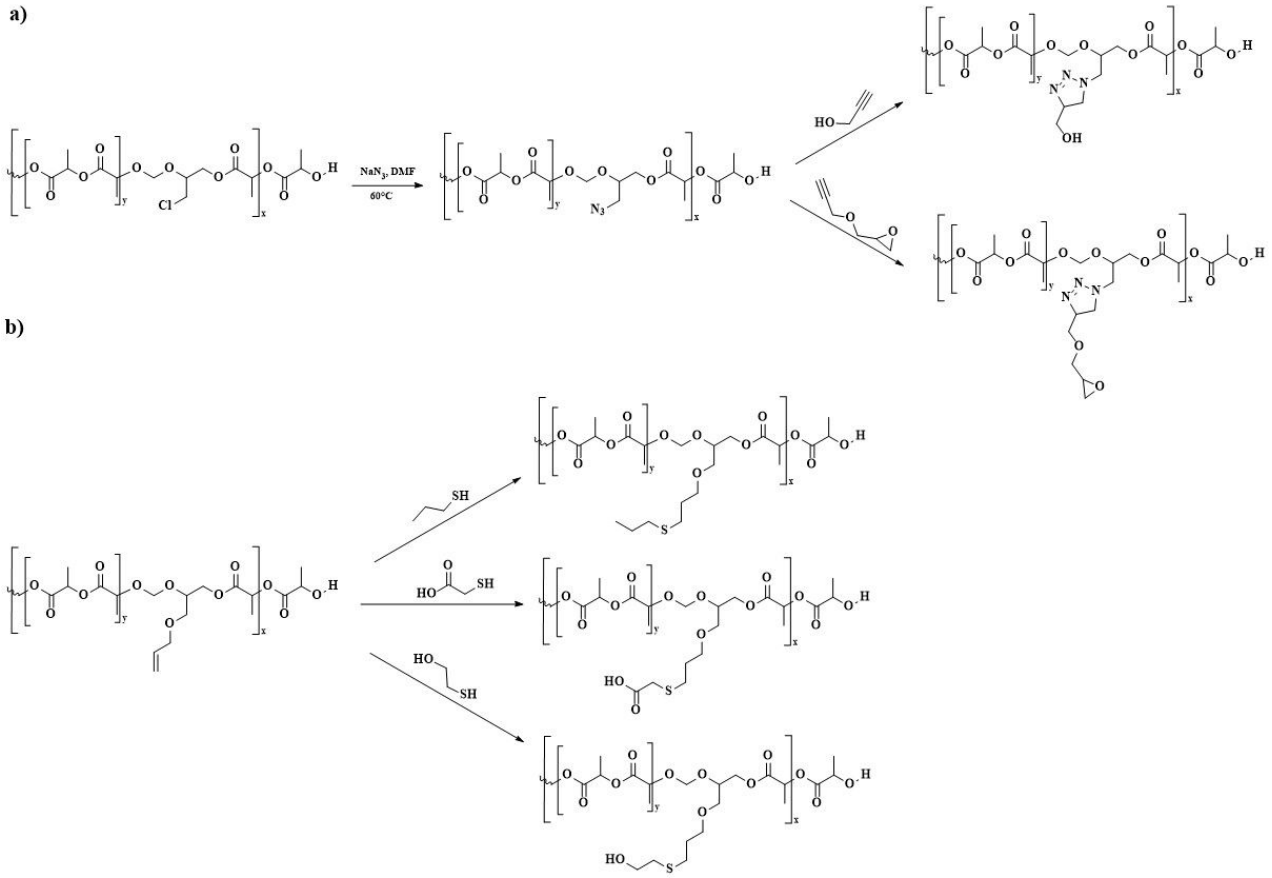


Figure S8. a) 2D NMR HSQC spectra of PLA/PAllyl-DXL copolymer ($CDCl_3$, 400 MHz)



Scheme S2. Functionalization of a) PLA/PCl-DXL with sodium azide, propargyl alcohol or propargyl glycidyl ether and b) PLA/PAllyl-DXL with propanethiol, glycolic acid or ethanethiol

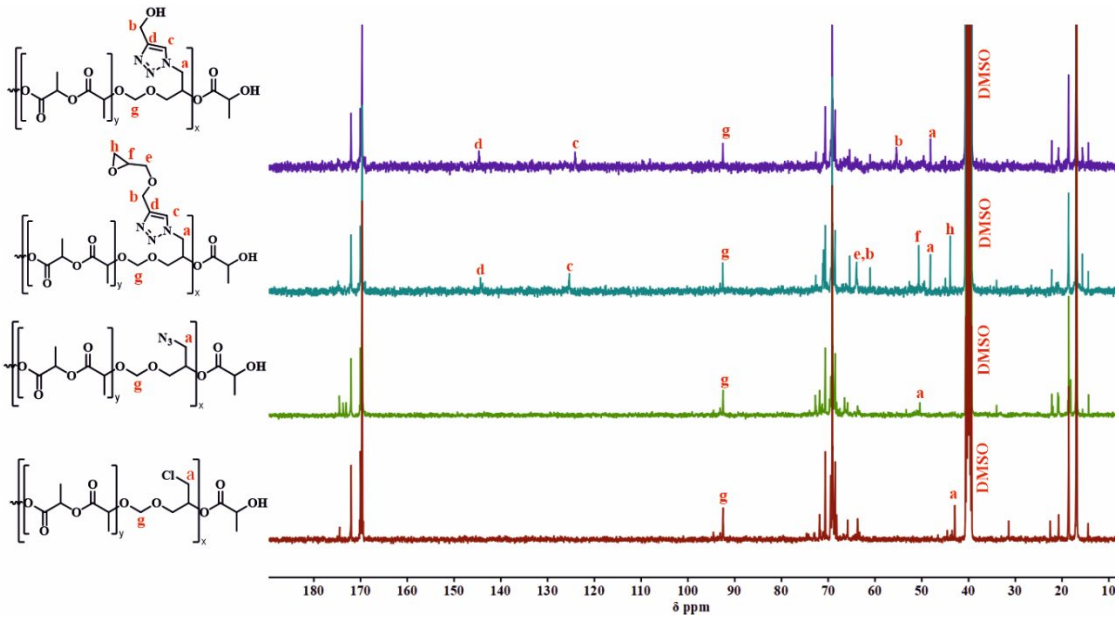


Figure S9. The ^{13}C NMR spectra before and after modification of PLA/PCl-DXL (DMSO-d_6, 100 MHz)

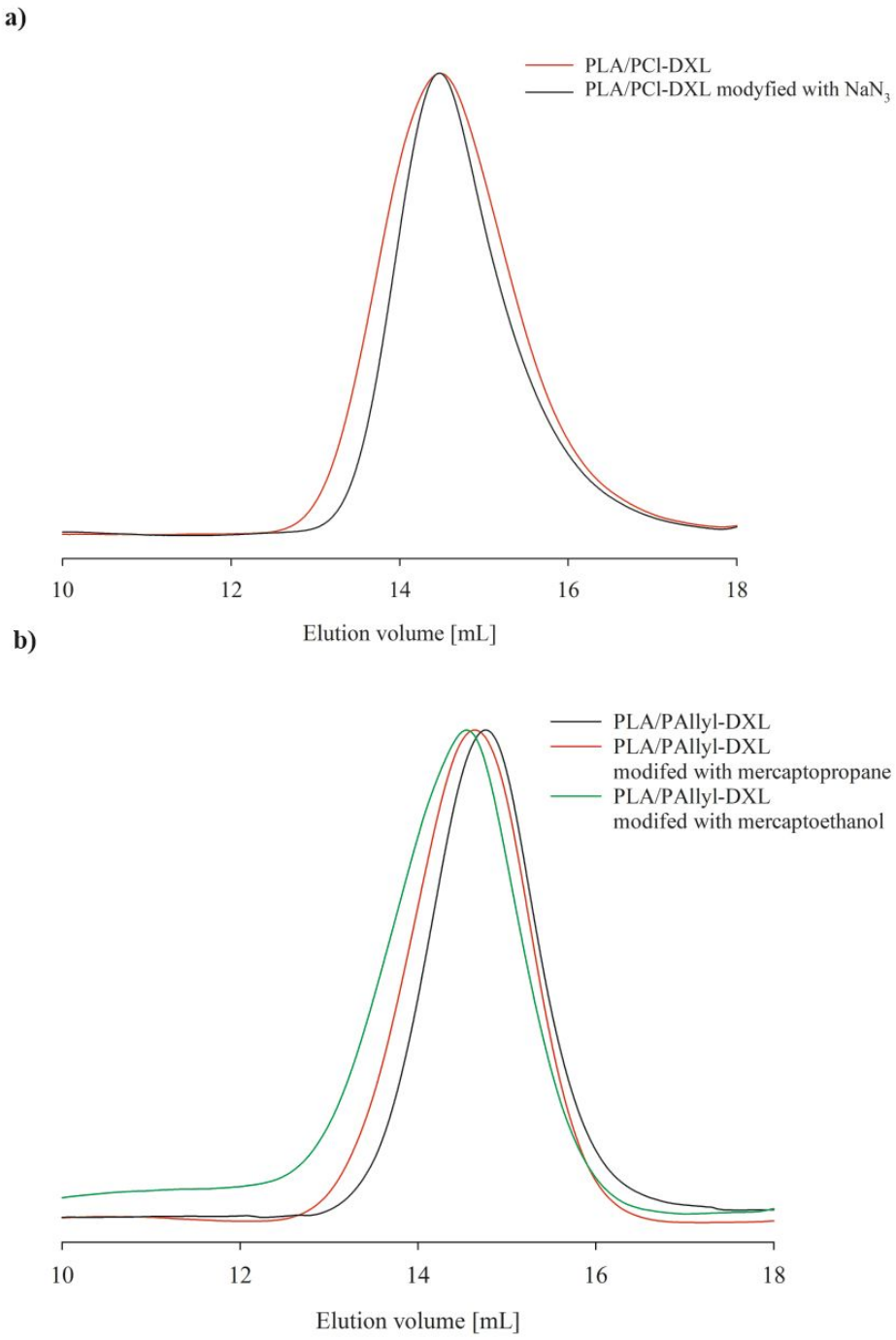


Figure S10. The SEC trace of PLA/PCl-DXL and PLA/PAllyl-DXL before and after modification

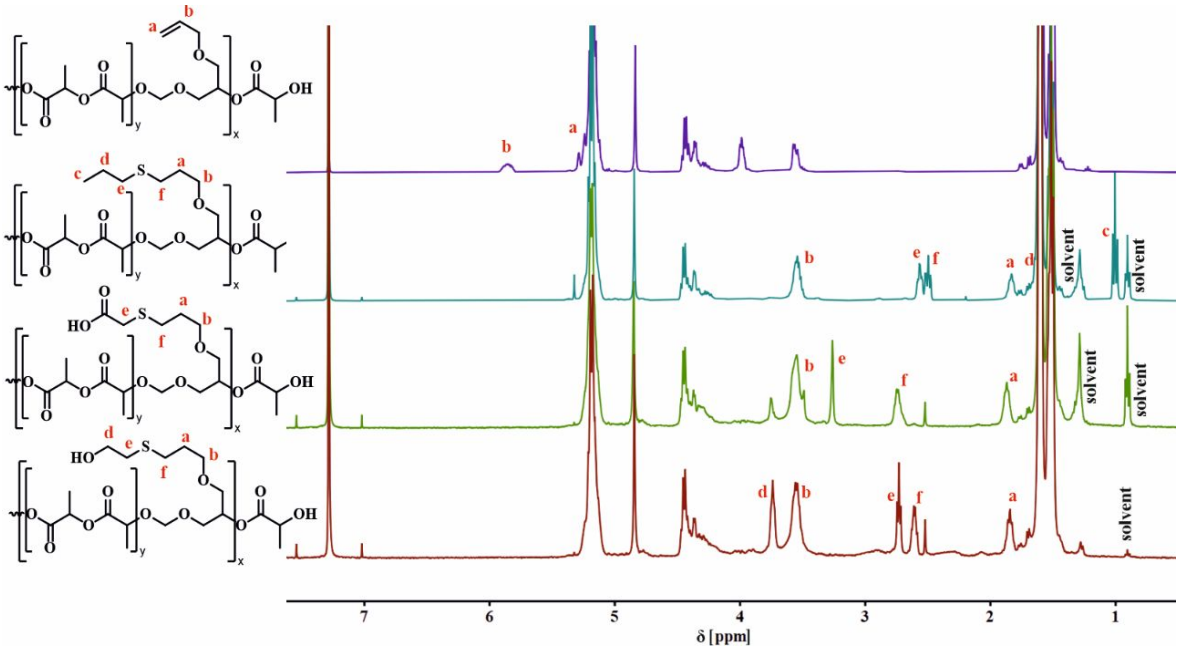


Figure S11. The ^{1}H NMR spectra before and after modification of PLA/PAllyl-DXL ($CDCl_3$, 400 MHz)

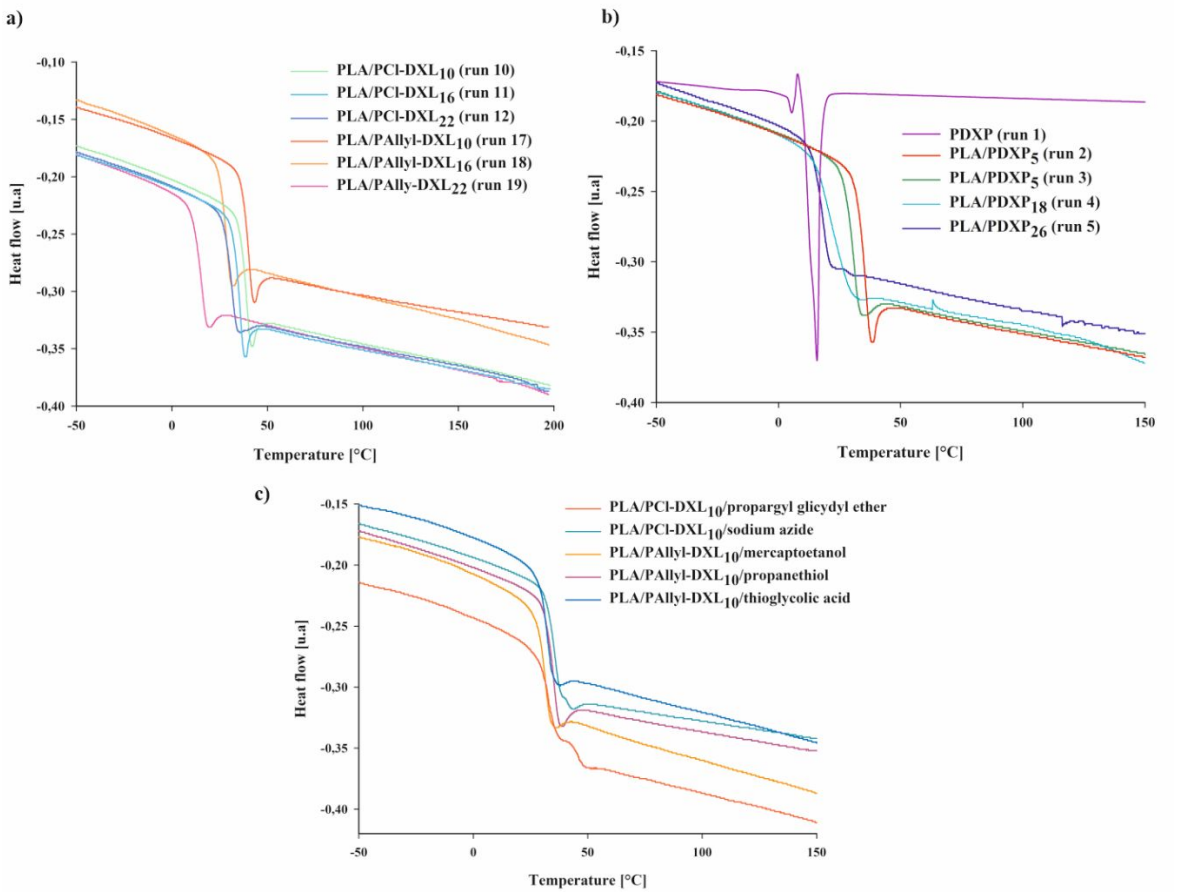


Figure S12. The DSC traces of a) PLA/PDXP, b) PLA/PCl-DXL or PLA/Pallyl-DXL copolymers, and c) DSC traces of copolymers after modification

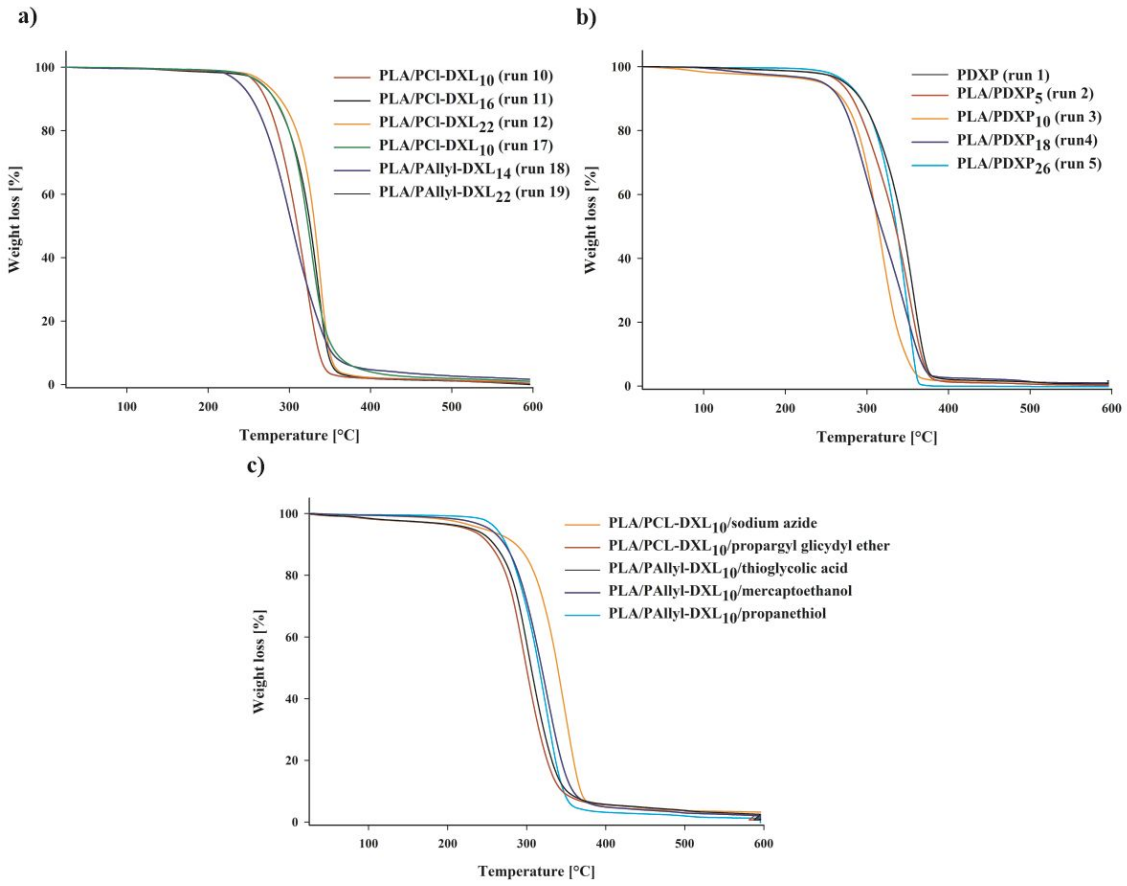


Figure S13. The TGA traces of a) PLA/PDXP, b) PLA/PCl-DXL or PLA/Pallyl-DXL copolymers, and c) DSC traces of copolymers after modification

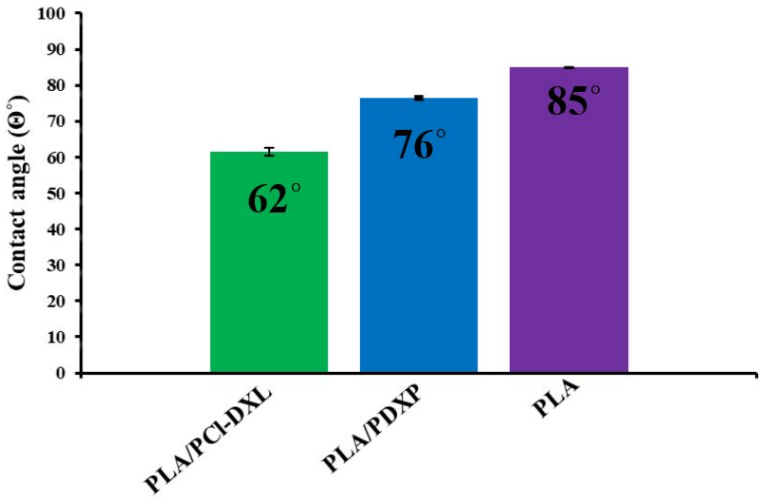


Figure S14. Contact angles measured for neat PLA and PLA/PDXL and PLA/PCl-DXL copolymers (films on a glass plate with water as a reference liquid)

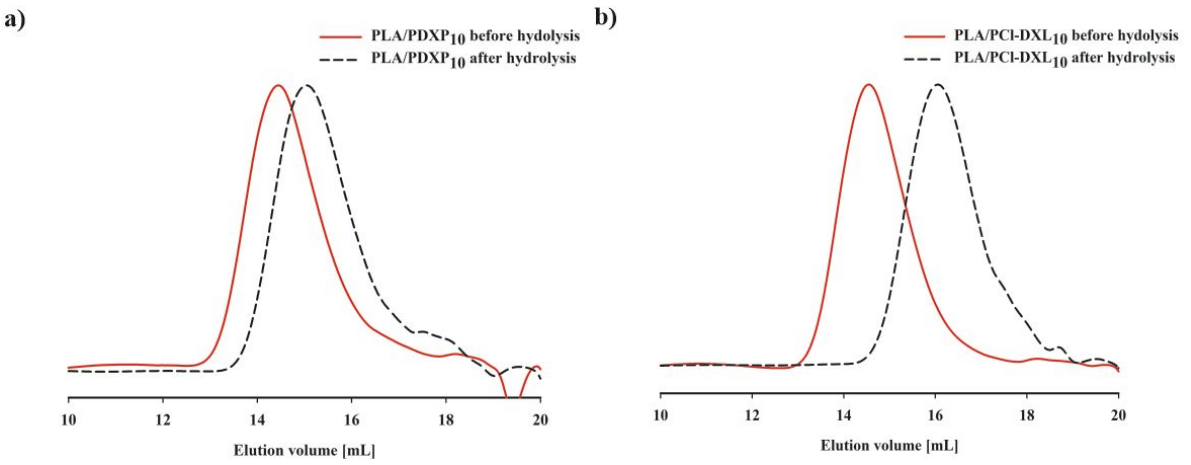


Figure S15. The GPC traces of a) PLA/PDXP and b) PLA/PCl-DXL copolymers before and after hydrolysis

Publikacja 3:

Karolina Cichoń, Bartłomiej Kost, Marta Safandowska, Artur Różański, Małgorzata Basko, Chemically recyclable films from thermoplastic ABA-triblock copolymers containing polylactide A-blocks and easily degradable polydioxolane B-block - towards the novel type of sustainable plastics, Polymer 2026, 344, 129501

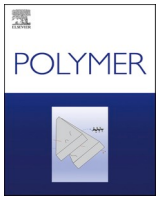
Polymer 344 (2026) 129501



Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



Chemically recyclable films from thermoplastic ABA-triblock copolymers containing polylactide A-blocks and easily degradable polydioxolane B-block - towards the novel type of sustainable plastics

Karolina Cichoń [a,b], Bartłomiej Kost [a,*], Marta Safandowska [a], Artur Rozanski [a], Malgorzata Basko [a,**]

[a] Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363, Lodz, Poland
[b] BioMedChem Doctoral School of the University of Lodz and Lodz Institutes of the Polish Academy of Sciences, Matejki 21/23, 90-237, Lodz, Poland

ARTICLE INFO

Keywords:
Recyclability
Triblock copolymers
Polyester
Polyacetal
Polymeric films

ABSTRACT

Research on the degradability of polymeric materials and their facilitated decomposition after use may significantly contribute to addressing the problem of increasing environmental pollution. In this work, recyclable films based on ABA triblock copolymers containing polylactide A-blocks and easily degradable polydioxolane B-blocks were prepared and investigated. To obtain copolymers suitable for commercial applications, a large-scale synthesis procedure was developed, and the process capacity was scaled up to hundreds of grams per batch. The results show that, under the conditions used, the molar mass and composition of the copolymers can be readily controlled by adjusting the ratio of cyclic ester to the α,ω-hydroxy-terminated polyacetal macroinitiator in the ring-opening polymerisation (ROP) catalyzed by tin(II) octoate ($Sn(Oct)_2$). To create copolymers with high potential for recovering recyclable compounds, a polyacetal block (7,000 g/mol) was combined with polyester blocks of varying lengths, whose molecular weights did not exceed 20,000 g/mol. Films formed from the studied copolymers were produced by compression moulding in a hot press and subsequently evaluated in detail for their thermal, barrier, and mechanical properties. Chemical recycling of the polymeric materials via depolymerization was examined using an acid catalyst at temperatures between 150 °C and 200 °C. We hypothesise that these novel films have strong potential to serve as next-generation recyclable materials, enabling the recovery of both the cyclic monomer and polylactide.

1. Introduction

To reduce the negative impact of plastic waste on the environment, research on polymer sustainability and chemical recycling has become increasingly important to both academia and industry [1–3]. One strategy for eliminating plastic at the end of its service life is the use of degradable polymers, which can be decomposed into simpler, nontoxic substances at a user-defined stage [4,5]. Chemical recycling, which involves depolymerization and the reuse of the resulting products, aligns with the principles of the circular economy by partially or completely breaking down waste into its monomers and oligomers [6–8].This approach, based on closed-loop recyclable polymers, requires the design of structures containing selectively activatable group [9]. Therefore, polymers capable of undergoing chain-cleavage reactions under specific conditions are seen as a promising alternative to commodity plastics, which are typically derived from chemically inert and hardly degradable chains [10]. Following this concept, hydrolytically unstable ester bonds have been introduced into selected commodity polymers with carbon–carbon backbones to increase their susceptibility to chain degradation. It has been shown that the appropriate placement of such single cleavable groups along the main chain does not deteriorate the mechanical properties of the material but enables chemical recycling [11,12]. This approach has been successfully implemented in the synthesis of polyethylene-like materials from long-chain C_{18} dimethyl ester and C_{18} diol [11]. Ester-linked polypropylene has also been obtained from isotactic propylene copolymer with main-chain unsaturation and subsequently depolymerized to a telechelic macromonomer using an olefin metathesis catalyst and 2-hydroxyethyl acrylate. The resulting polymers

* Corresponding author.
** Corresponding author.
E-mail addresses: bartlomiej.kost@cbmm.lodz.pl (B. Kost), malgorzata.basko@cbmm.lodz.pl (M. Basko).

https://doi.org/10.1016/j.polymer.2025.129501
Received 4 November 2025; Received in revised form 16 December 2025; Accepted 17 December 2025
Available online 19 December 2025
0032-3861/© 2025 Elsevier Ltd. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

exhibited thermal and mechanical properties comparable to polyethylene while being chemically recyclable, allowing recovery of the starting reagents [12].

Aliphatic polyesters, being sustainable and degradable under appropriate conditions, are increasingly studied as alternatives to petroleum-based plastics [13]. Research on these materials is particularly intensive in the field of packaging applications [14–16]. Among them, polylactide (PLA), which can be produced from renewable feedstocks and safely decomposed, has attracted growing attention as an environmentally friendly and sustainable polymer with significant potential for further development [4,17,18]. Notably, recent studies have reported the efficient depolymerization of PLA into its cyclic monomer, offering the potential to close the recycling loop for PLA-based materials [19].

However, to compete with industrially produced plastics, certain properties of polylactide-based materials must be modified and improved. Therefore, depending on the intended application, lactide (LA) has often been copolymerized with other appropriately selected comonomers to obtain statistical or block copolymers with tailored stiffness, brittleness, moisture sorption, or mechanical strength. ABA-type triblock copolymers containing polyester blocks represent a particularly attractive architecture, as they can exhibit thermoplastic elastomer behavior while remaining degradable. To achieve suitable elastomeric properties in linear ABA triblock copolymers, the A end blocks typically consist of a hard polymer with a high glass transition temperature (T_g) or high melting temperature (T_m), whereas the B midblock is a soft, rubbery polymer with a low T_g. In this configuration, the hard segments form physical cross-linking domains, while the soft segments act as flexible chains that provide elasticity. As reported in the literature, various polymers have been used as midblocks in block copolymer elastomers containing polylactide as the outer segments, including poly(β-methyl-δ-valerolactone), poly(ε-caprolactone-co-δ-valerolactone), poly(1,5-dioxepan-2-one), poly(γ-methyl-ε-caprolactone), poly(menthide), poly(thiophene), and poly(ε-caprolactone-co-ε-decalactone) [13,20–24]. In addition, other polyesters, such as polycaprolactone, poly(ε-decalactone), poly(2,2-diethyltrimethylene carbonate), trimethylene carbonate, and poly[(R,S)-3-hydroxybutyrate], have been combined with PLA to form triblock or multiblock degradable thermoplastic elastomers [16,25,26].

However, although the described triblock copolymers containing polyester blocks are degradable, only a limited number of systems have been designed to enable chemical recycling to the monomer level [26]. Consequently, the chemical recycling of PLA-based thermoplastics remains a scientific and technological challenge, providing strong motivation for further research.

Over the past few years, our group has been developing simple synthetic routes for the production of aliphatic copolyesters with modified degradability [27,28]. We proposed the introduction of acid-sensitive acetal units into the polyester chain to enhance material degradation. To this end, we initially employed the cationic copolymerization of 1,3-dioxolane (DXL) and lactide, which enabled the synthesis of statistical copolymers. Subsequently, ABA triblock copolymers featuring a polyacetal chain as the soft (hydrophilic) internal block and polyester chains as the hard (hydrophobic) external segments were prepared. The structure and thermal properties of these copolymers were then investigated [29]. The aim of this study was to demonstrate that these previously prepared copolymers can be used to produce recyclable polymeric films. To achieve this goal, polymer films were developed from thermoplastic ABA triblock copolymers containing polyester A-blocks and polyacetal B-blocks, which preferentially degrade under acidic conditions. First, the synthesis of the triblock copolymers was successfully scaled up to hundreds of grams per batch. Next, the feasibility of forming polymer films by compression moulding in a hot press was examined. The mechanical properties of the resulting films were analyzed and correlated with the molar mass and composition of the triblock copolymers. In addition, the oxygen transmission rate of the polymer films was evaluated. Finally, it was demonstrated that acid-triggered depolymerization of the poly(1,3-dioxolane) (PDXL) segments enables efficient chemical recycling of the polymer films, allowing recovery of the cyclic monomer (DXL) in high yields of up to 95 %, as well as PLA blocks that can be reused.

2. Materials

L-LA obtained from Purac (99 %, The Netherlands) underwent a recrystallisation process utilising dry 2-propanol, followed by sublimation and subsequent storage under reduced pressure. 2-propanol was dried by distillation over sodium and used directly for the crystalization of L-LA. Anhydrous 1,3-dioxolane (DXL) (99.8 % with BHT as an inhibitor) purchased from Sigma Aldrich was distilled under reduced pressure immediately before use. Anhydrous ethane-1,2-diol (EG) (99.8 %) and diphenyl phosphate (>99 %) obtained from Sigma Aldrich were used as received. Tin (II) octoate ($Sn(Oct)_2$) obtained from Sigma Aldrich underwent distillation under reduced pressure at 10^{-2} mbar at 140 °C and was subsequently stored over dried molecular sieves (4 Å) under vacuum conditions. Methylene chloride (99.8 %) acquired from POCH was distilled over P_2O_5 and was kept over dried molecular sieves (4 Å). Triflic acid (>99 %) was acquired from Sigma Aldrich and used without further purification. PLA granulate (4032D) was supplied by NatureWorks LLC (MN, USA) and has an average weight molecular mass (M_w) of 105,000 g/mol and a polydispersity index (M_w /M_n) of 1.35. Diethyl ether, pentane and hexane (analytical grade) were obtained from POCH without further purification.

2.1. Scale-up synthesis of HO-PDXL-OH

To obtain a well-defined di-hydroxy terminated polyacetal, the cationic homopolymerization of DXL was conducted in a round-bottom flask equipped with a magnetic stirrer. Initially, the vessel was filled with argon. Subsequently, methylene chloride (100 mL) was introduced through the rubber septum, and then 494 μL of ethylene glycol (9 mmol, equiv. 1) and 400 μL of triflic acid (4 mmol, equiv. 0.44) were added. After that, 100 mL of DXL (1.43 mol, equiv. 159) was introduced into the reaction mixture using an infusion pump. Firstly, 10 mL of DXL was introduced at a rate of 4 mL/h; the rest of the DXL was added dropwise at a rate of 0.85 mL/h, then the flask was left on the stirrer for 2 h, and placed at −20 °C for 12 h. Following this, triethylamine (1.26 mL, 17.18 mmol, equiv. 1.9) was added to the flask to neutralise the acid, the polymer was precipitated into diethyl ether (1000 mL), and dried under vacuum. The homopolymer was obtained as a white powder with a yield = 75 %. ($M_{n\ MALLS}$ = 7,000 g/mol, M_{nRI} = 13,000 $M_w/M_{n\ RI}$ = 1.6).

2.2. Scale-up synthesis of PLA-PDXL-PLA copolymers

The synthesis was performed according to the protocol described in our previous publication [29]. Polymerisation was conducted using a high-vacuum technique. In the first step, poly(1,3-dioxolane) (M_n = 7000 g/mol, 20 g, 2.9 mmol, equiv. 1) and LA (19.3 g, 134 mmol, equiv. 46.2) were accurately weighed and transferred into a glass ampoule. Subsequently, 2 mL of a methylene chloride solution of tin (II) octoate (6 mg/mL, 12 mg, 0.03 mmol, equiv. 0.003) was added as a catalyst. After the addition of the catalyst solution, methylene chloride was removed by vacuum evaporation to achieve a solvent-free environment. The ampoule was then sealed using a gas burner and placed in an oven preheated to 110 °C. Once the reagents began to melt, the ampoule was manually agitated to ensure uniform mixing of the reaction components. The reaction mixture was maintained at 110 °C for 24 h. Following the reaction, the resulting copolymer was dissolved in methylene chloride and subsequently precipitated in pentane to purify the product. The purified copolymer was then dried under vacuum to remove residual solvents. Characterisation of the copolymer was performed using ^1H and ^{13}C NMR spectroscopy, Size Exclusion Chromatography (SEC),

Thermogravimetric Analysis (TGA), and Differential Scanning Calorimetry (DSC).

PLA-PDXL$_{7000}$-PLA-1. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.19 (q, 1H, -C<u>H</u>(CH)$_3$), 4.76 (s, 2H, -OC<u>H</u>$_2$O-), 4.34 (m, overlapping, -C<u>H</u>(OH)-, -(C=O)-OC<u>H</u>$_2$CH$_2$O-) 3.72 (s, 4H, -OCH$_2$C<u>H</u>$_2$O-), 1.45-1.61 (d, overlapping-C<u>H</u>$_3$-),

^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) = 175.21 (2C, -(C=O) end group), 172.58 (2C, -(<u>C</u>=<u>O</u>)-OCH$_2$CH$_2$O-), 169.7 (1C, -CH$_2$-(<u>C</u>=<u>O</u>)-O-), 95.63 (1C, -OCH$_2$O-), 94.75 (2C, -OCH$_2$O-, end group) 69.1 (1C, -C(<u>CH</u>)-), 68.59 (2C, -<u>CH</u>-(C=O)-OCH$_2$CH$_2$O-), 67.46 (2C, -C(<u>CH</u>)- end group), 66.92 (2C, -OCH$_2$CH$_2$O-), 65.4 (2C, -OCH$_2$<u>CH$_2$</u>O- end group), 64.5 (2C, -O<u>CH$_2$</u>CH$_2$O- end group), 20.63 (1C, -C(<u>CH$_3$</u>) end group), 18.61 (1C, -C(<u>CH$_3$</u>)-C(=O)-OCH$_2$CH$_2$O-), 16.74 (1C, -C(CH$_3$-).

2.3. Polymer film preparation

Polymer films were prepared from triblock copolymers with an ABA structure, featuring external polylactide blocks and a central polydioxolane block (PLA-PDXL-PLA). First, the copolymer was thoroughly dried under a vacuum, then 0.1 mm thick polymer films were prepared by the compression moulding method. Typically, about 2 g of PLA-PDXL-PLA was put between a metal frame, and after that, the frame was placed in a hydraulic press heated to 180 °C for 3 min. Next, the polymer film was cooled by placing it between liquid nitrogen-cooled metal blocks for 3 min. All prepared films were stored in the presence of a desiccant at 4 °C for 24 h. A series of polymeric films (F1, F2 and F3) with a differential ratio of lactide to acetal units in copolymer chain was prepared (see Table 1). Polylactide granulate (4032D) was also processed under the same conditions to obtain an amorphous film (PLA).

2.4. Chemical recycling (thermal depolymerization) of polymer film

The degradation of the polymeric film was conducted according to the method described by Coates and coworkers, introducing slight modifications [30]. The procedure was described for a film prepared from the PLA$_{3400}$-PDXL$_{7000}$-PLA$_{3400}$ copolymer. 0.5 g of prepared film (containing 0.035 mmol of PDXL, equiv. 4.375) and 5 mg (0.008 mmol, equiv. 1) of diphenyl phosphate (DPP) were placed in a round-bottom flask equipped with a distillation apparatus and heated. The distillation was conducted within 30 min, at 150 °C and the volatile product was collected in a receiving flask cooled by liquid nitrogen. The distillate and the residue were analyzed using ^{1}H NMR spectroscopy and SEC.

2.5. Characterization methods

The Avance Neo 400 NMR spectrometer (400.15 MHz for 1H and 100.63 MHz for 13C, 9.4 T) recorded the ^{1}H NMR and ^{13}C NMR spectra. $CDCl_3$ was used as a deuterated solvent. To determine number-average molar masses and dispersity, Size Exclusion Chromatography equipped with an Agilent Pump 1100 Series with two PLGel 5 μm MIXED-C columns and detectors Wyatt Optilab Rex differential refractometer and a Dawn Eos8 laser photometer was used. Methylene chloride at a flow rate of 0.8 mL min^{-1}, with measurements taken at 25 °C, was used as an eluent. Differential scanning calorimetry (DSC) was employed to determine thermal properties across temperatures from −90 °C to 200 °C on a Discovery DSC 2500 (TA Instruments) under a nitrogen atmosphere, using heating and cooling rates of 10 °C min^{-1}. The instrument was calibrated with temperature and heat flow using indium as a standard. The degree of crystallinity (χ_c) was determined according to the formula [31]:

$$\chi_c \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0} \times 100\%$$

where:

ΔH_m – *the measured melting enthalpy of the sample* (J/g)

ΔH_{cc} – *the measured cold crystallization enthalpy of the sample* (J/g)

ΔH_m^0 – *the melting enthalpy of* 100% *crystalline PLA, taken as* 143 J/g [31].

Thermogravimetric analyses (TGA) involved placing approximately 5 mg of the polymer sample in a measuring cell and registering measurements under nitrogen flow, heating the samples from ambient temperature to 600 °C at a rate of 20 °C min^{-1} on a Hi-Res TGA 2950 thermogravimetric analyser (TA Instruments).

2.6. Contact angle measurement

Contact angles were measured at room temperature with the sessile drops method using a Phoenix-300 goniometer and software (SEO SurfaceElectro Optics, Korea). The measurements were performed using 5 μL drops of deionised water deposited on the polymer films. Polymer films were prepared by casting polymer solutions (5 mg of the copolymer dissolved in 2 mL of methylene chloride) on glass plates (drying at room temperature for 24 h). As confirmed by ^{1}H NMR, such prepared films did not contain any residual solvent. Contact angle data were obtained by averaging ten measurements.

2.7. Mechanical testing

Mechanical properties of the materials examined in the work were assessed using a tensile testing machine (Instron 5582) of load range 0–2 kN. The shape of the samples was according to the ISO 527-2 standard, with a 5 mm width. The gauge length was 25 mm. Tests were performed at room temperature at a rate of 3.3 × 10^{-3} s^{-1} (the crosshead speed of 5 mm/min).

2.8. Characterisation of the melt flow index

The melt flow index (MFI) was measured in accordance with ISO 1133 1:2022 standard method using a plastometer [32]. A 1 mm diameter nozzle was employed at a temperature of 170 °C and a mass of 2.16 kg. The elapsed time between two consecutive measurements was 15 s.

2.9. Oxygen permeability

The oxygen transmission rate (OTR) of the investigated polymer films was evaluated using a TotalPerm gas permeability analyser (ExtraSolution, Italy), following the standard ASTM D3985 [33]. Measurements were conducted at a temperature of 23 °C and 0 % relative humidity. To reset any influence arising from different film thicknesses,

Table 1
Characterisation of the precipitated PLA-PDXL$_{7000}$-PLA copolymers by SEC and ^{1}H NMR spectroscopy.

Copolymer code	$M_{n\ PLA\ arm,}$[a] (g mol^{-1})	$M_{n\ cop.}$[b] (g mol^{-1})	Đ	f_{LA}[c]
PLA$_{3400}$-PDXL$_{7000}$-PLA$_{3400}$	3,400	13,800	1.78	0.49
PLA$_{6900}$-PDXL$_{7000}$-PLA$_{6900}$	6,900	21,000	1.51	0.65
PLA$_{18500}$-PDXL$_{7000}$-PLA$_{18500}$	18,500	49,000	1.55	0.76

[a] Length of PLA segment calculated from M_n of copolymer and ester content.
[b] Determined from SEC-MALLS.
[c] LA mol fraction at the copolymer estimated from ^{1}H NMR.

OTR values were converted to permeability ([$cm^3 \times cm/(m^2 \times 24\ h)$]).

3. Results and discussion

The properties of ABA block copolymers can be tailored by adjusting the structure and length of the individual segments, enabling the design of materials for specific end-use applications. In the present work, the potential of PLA-PDXL-PLA copolymers, containing polydioxolane as an easily degradable internal block and polylactide as the outer segments, to form polymeric films was investigated. We assumed that this type of polymeric foil would ultimately be suitable for chemical recycling after fulfilling its intended function.

To enable the synthesis of PLA-PDXL-PLA copolymers on the scale of hundreds of grams per batch, the procedure described previously in our work was modified [29]. As intended, the length of the PLA arms did not exceed 20,000 g/mol in order to introduce biodegradable polyester chains into the block copolymers (Table 1).

The results presented in Table 1 confirm that a series of PLA-$PDXL_{7000}$-PLA triblock copolymers with molecular weights ranging from 13,800 to 49,000 g/mol (SEC-MALLS) was successfully obtained through large-scale synthesis. This successful scale-up suggests that film production from the studied copolymers may be feasible. Representative NMR spectra confirming the composition and block structure of the of PLA-$PDXL_{7000}$-PLA copolymers are shown in Figs. S1 and S2.

Microphase separation in triblock copolymers is essential for achieving the physical properties characteristic of thermoplastic elastomers, as it creates a structure in which the hard blocks aggregate to form rigid domains that act as physical crosslinks, while the soft blocks form a continuous, rubbery matrix that provides elasticity [34]. To assess the immiscibility of the polyester and polyacetal segments in the obtained copolymers, DSC analysis was performed. The results are summarized in Table 2, and representative thermograms are shown in Fig. 1.

DSC analysis of the PLA_{3400}-$PDXL_{7000}$-PLA_{3400} copolymer, which contained 49 mol% ester, revealed two glass transition temperatures (−51 °C and 48.9 °C), corresponding to the PDXL- and PLA-rich domains, respectively. These values are consistent with the previously reported T_g values of the respective homopolymer [35,36]. As the ester content in the copolymer increased, only a single glass transition temperature near that of PLA was observed. As shown in Fig. 1, all analyzed samples exhibit melting peaks in the range of 165–170 °C, characteristic of PLA. The slight differences in melting temperatures and the broadening of the melting peak, particularly evident in copolymer F1, may indicate disrupted PLA crystallization due to the presence of PDXL segments.

Consequently, the incorporation of PDXL segments disrupts the formation of homogeneous, well-defined PLA lamellae, resulting in a more heterogeneous crystal population with varying thicknesses and degrees of order, which produces a broader and less pronounced melting peak. This altered morphology can influence barrier properties, as reduced and less regular PLA crystallinity may diminish gas barrier performance. Notably, an increasing content of ester units in the copolymer contributed to a rise in the degree of crystallinity from 10 % to 26 % (see Table 2) and a narrowing of the melting transition (Fig. 1), which may, in turn, enhance barrier properties.

To demonstrate that PLA-$PDXL_{7000}$-PLA films can be efficiently

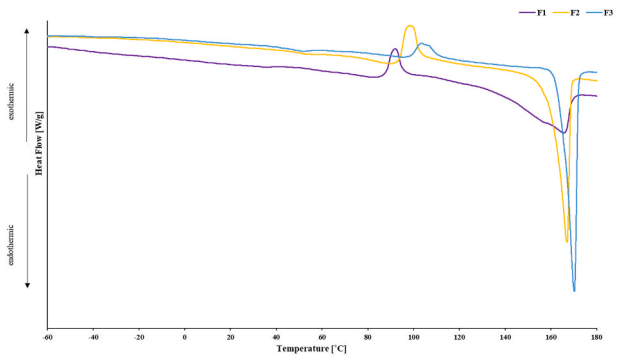


Fig. 1. DSC analysis of PLA-PDXL-PLA copolymers.

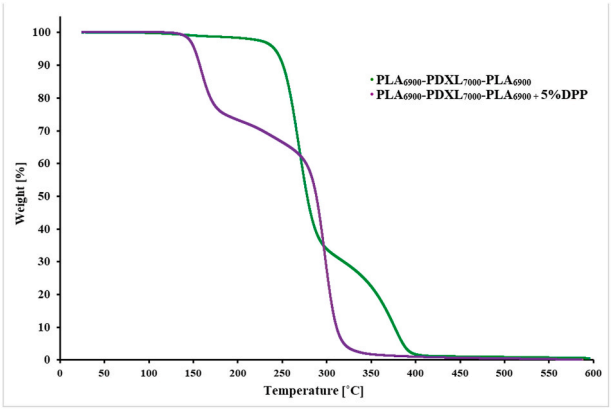


Fig. 2. Comparison of the thermal stability of PLA_{6900}-$PDXL_{7000}$-PLA_{6900} copolymer, highlighting the effect of diphenyl phosphate as an additive.

recycled via depolymerization, their susceptibility to degradation in the presence of an external acid catalyst was initially assessed using TGA analysis with diphenyl phosphate. A comparison of the TGA curves is shown in Fig. 2.

The thermal stability of the copolymers was quantified by determining the degradation temperature at which 5 % of the sample mass is lost (T_d,5 %). The pure PLA_{6900}-$PDXL_{7000}$-PLA_{6900} copolymer exhibited a T_d,5 % value of approximately 220 °C, whereas the presence of DPP efficiently catalyzed degradation, resulting in a reduced T_d,5 % of 160 °C. On the one hand, these results indicate that the copolymers are thermally stable at temperatures below 220 °C, enabling their processing at 180 °C. On the other hand, they confirm that the introduction of an acid catalyst accelerates copolymer decomposition via depolymerization. In addition, isothermal TGA analysis of the neat copolymers was performed at 180 °C (Fig. S3 in the Supporting Information). No significant weight loss was observed during the 5-min experiment. Therefore, the combined DSC and TGA results justify the use of melt pressing at 180 °C for foil preparation. This process, which involved melt-pressing and cooling the powdered copolymers, successfully produced colourless, transparent films (Fig. 3a).

Uniaxial tensile elongation tests were performed on films (F1, F2, and F3) prepared from PLA-$PDXL_{7000}$-PLA copolymers differing in the

Table 2
Thermal properties of PLA-$PDXL_{7000}$-PLA triblock copolymers.

Copolymer code	$T_{g\ (PDXL)}$ (°C)	$T_{g\ (PLA)}$ (°C)	$T_{m\ (PLA)}$ (°C)	$\Delta H_{m(PLA)}$ (J/g)	$\Delta H_{cc(PLA)}$ (J/g)	χ_{cPLA} (%)
PLA_{3400}-$PDXL_{7000}$-PLA_{3400}	−51	48.9	165	31.69	17.39	10
PLA_{6900}-$PDXL_{7000}$-PLA_{6900}	–	47.9	167	39.33	15.73	16.5
PLA_{18500}-$PDXL_{7000}$-PLA_{18500}	–	45.9	170	43.39	6.21	26
PLA 4032D	–	62.1	166	32.1	29.9	1.5

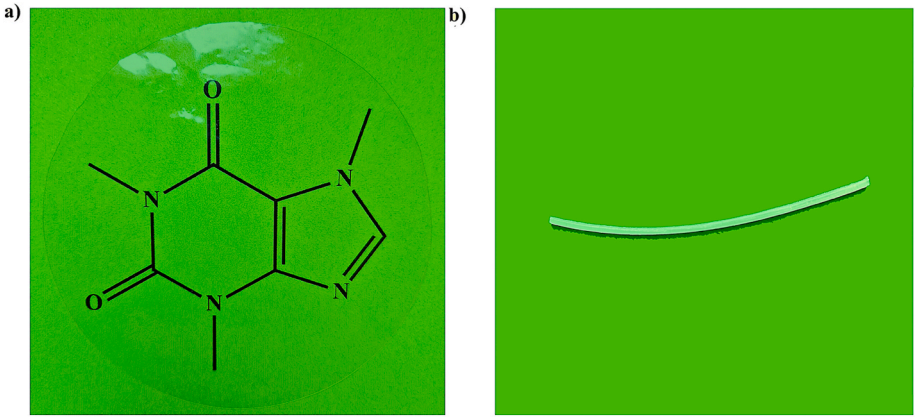


Fig. 3. a) Images of colourless, transparent films from PLA_{6900}-$PDXL_{7000}$-PLA_{6900} and b) extrudate obtained from PLA_{18500}-$PDXL_{7000}$-PLA_{18500} copolymer.

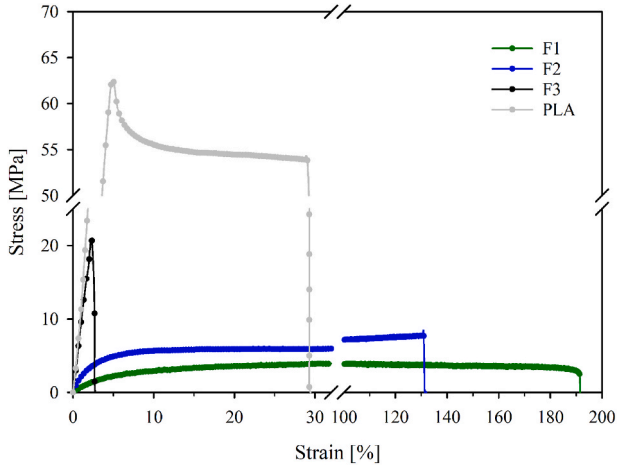


Fig. 4. Stress-strain response for films prepared from PLA-$PDXL_{7000}$-PLA copolymers and PLA granulate.

molecular weight of the outer PLA blocks (M_n = 3,400, 6,900, and 18,500 g/mol, respectively) to gain insight into their mechanical properties. For comparison, a film prepared from PLA granulate was also analyzed. Representative tensile stress–strain curves of the analyzed samples are shown Fig. 4.

Strength and toughness are two key mechanical properties of plastic films. The mechanical properties of all films, including tensile strength (σ_m) and elongation at break (ε_β), are summarized in Table 3. Typically, σ_m is used to assess tensile resistance and rigidity, whereas ε_β reflects the toughness of packaging materials.

Analysis of the tensile stress-strain curves and the data in Table 3 reveals significant differences among the triblock copolymers with varying lengths of the PLA hard blocks. Sample F1 exhibits the highest deformation and substantial elongation prior to fracture, which is associated with a relatively low tensile strength (σ_m). The σ_m value for PLA_{3400}-$PDXL_{7000}$-PLA_{3400} is 2.8 MPa. In addition, the elongation at break exceeds 191 %, indicating relatively high toughness, comparable to that of common elastomers and film or packaging polyolefins, whereas rigid plastics typically exhibit elongation values below 5 %. Increasing the molar content of LA in the copolymer results in higher tensile strength but reduced elongation at break. As shown in Table 3, increasing the ester content from 49 % to 76 % leads to an increase in tensile strength from approximately 3 MPa to 19 MPa, while the elongation at break decreases sharply from 191 % to 2.7 %. According to previous studies [37–39], such increases in tensile strength are largely attributed to greater crystal thickness or a higher degree of crystallinity. Consistent with this interpretation, Table 2 shows that the degree of crystallinity of PLA_{18500}-$PDXL_{7000}$-PLA_{18500} is approximately twice that of PLA_{3400}-$PDXL_{7000}$-PLA_{3400}. This observation is consistent with earlier reports demonstrating that crystallization-driven microstructure development strongly influences the mechanical performance of triblock copolymers. Ding et al. showed that the tensile strength of polylactide-*b*-polyisoprene-b-polylactide triblock copolymers increases upon crystallization of the PLA end blocks, while the elongation at break slightly decreases as a consequence of this crystallization [40,41]. A higher degree of crystallinity, in turn, renders films prepared from PLA_{18500}-$PDXL_{7000}$-PLA_{18500} copolymers more brittle. For comparison, pure PDXL with a molecular weight of 37,900 g/mol exhibits rather poor mechanical properties, with an elongation at break of approximately 5 %, and significant improvement in this parameter is observed only at higher molecular weights (Mn $\geq$ 60,000 g/mol) [30]. Similarly, PLA, as a glassy polymer, also displays low elongation at break. Combining PDXL blocks with PLA blocks - particularly when the ester content in the copolymer does not exceed 65 % - substantially increases elongation at break, thereby improving the ductility of the resulting materials. The results indicate that the mechanical properties of films from the triblock copolymers vary systematically with the length of the PLA blocks, and consequently with the overall ester content and crystallinity. Films containing shorter PLA blocks (e.g., PLA_{3400}-$PDXL_{7000}$-PLA_{3400}) exhibit high deformability, making them suitable for flexible films or soft packaging materials that require a high tolerance for deformation. In contrast, films with longer PLA blocks (e.g., PLA_{18500}-$PDXL_{7000}$-PLA_{18500}) display significantly higher tensile strength and stiffness due

Table 3
Mechanical properties for films (F1–F3) obtained from PLA-$PDXL_{7000}$-PLA copolymers in comparison with neat PLA.

Code	Copolymer	Ester content	ε_b [%]	σ_m [MPa]
F1	PLA_{3400}-$PDXL_{7000}$-PLA_{3400}	0.49	191.7 ± 18.3	2.8 ± 0.3
F2	PLA_{6900}-$PDXL_{7000}$-PLA_{6900}	0.65	131.4 ± 12.2	7.7 ± 0.5
F3	PLA_{18500}-$PDXL_{7000}$-PLA_{18500}	0.76	2.7 ± 0.3	19.6 ± 1.1
PLA	PLA 4032D	1	27.8 ± 2.1	53.8 ± 0.4

Note: Codes F1–F3 designate polymeric films derived from copolymers (composition detailed in the next column). Conversely, the symbol PLA designates the comparative lactide homopolymer.

to their increased crystallinity, which is advantageous for applications demanding rigidity or dimensional stability. This variability does not limit the usefulness of the materials; rather, it demonstrates that the triblock architecture allows for fine-tuning of mechanical properties, enabling the copolymers to be tailored for a wide range of applications.

From the perspective of future applications, another important parameter for evaluating processability is the melt flow index (MFI). MFI indicates the flowability of thermoplastic materials, measuring their ability to flow in the molten state under applied pressure, and reflects how easily a polymer can be processed using various techniques. For the copolymer F3, the MFI was determined to be 10.8 $g{\cdot}10^{-1}$ min^{-1} at 170 °C under a 2.13 kg load. This value suggests that the synthesized triblock copolymer is suitable for processing via extrusion as well as injection moulding. To further evaluate processability, the F3 copolymer was subjected to compounding using an extruder. Under the same conditions as the compression method (T = 180 °C, t = 3 min), a uniform extrudate was successfully produced (Fig. 2b). NMR analysis (Fig. S4 and SI) confirmed that the copolymer's structure remained intact during this process. These results indicate that the synthesized copolymers could be applied on a larger scale in the packaging industry using various processing techniques, including extrusion. The copolymer blending process was carried out using a conical co-rotating twin-screw mini-extruder, the EHP-5CS (Zamak-Mercator). This extruder enabled processing of small amounts of material (~5 cm^3), which was crucial for this study. Its plasticizing system included a bypass valve, allowing the copolymer to pass through the extruder multiple times to ensure uniform blending. The ability of a material to attract or repel water is an important property, depending on its intended application. To evaluate the hydrophilic character of the obtained polymer films, static contact angles were measured at room temperature using the sessile drop method. The relationship between the contact angle and the ester content in PLA-$PDXL_{7000}$-PLA films is shown in Fig. 5. Compared to films prepared from neat PLA, the PLA-$PDXL_{7000}$-PLA films exhibit modified hydrophilic behavior that depends on the molecular weight of the polylactide blocks. Increasing the length of the PLA blocks leads to higher contact angles, reaching a maximum of 74° for the F3 sample, which has the highest ester content.

To assess the effect of hydrophilicity on film stability, the resistance of the prepared films to aging under humid conditions at elevated temperatures was tested. F1–F3 films were cut into small pieces weighing 20.0 mg ± 0.1 mg and placed in glass vials within a humidity chamber set at 50 % relative humidity and 40 °C. After conditioning for selected time intervals (1, 2, 4, and 8 weeks), the films were removed, dried, and weighed. No significant changes in film mass were observed before or after conditioning, as shown in Fig. S5 in SI.

The transparency of polymer films is an important property, allowing consumers to evaluate the appearance and freshness of food before purchase [42]. Conversely, opaque packaging, which blocks light, protects food from UV/Vis radiation [43]. Transparency was measured according to the Standard Method for Transparency of Plastic Sheeting [44] with the most common parameter being transmittance in the visible light range (400–800 nm). Foils F1, F2, and F3, prepared from PLA-PDXL-PLA copolymers, exhibited transmittance above 90 % in the visible light region, classifying them as highly transparent, glass-like materials (Fig. 6) [45,46]. These values are comparable to those of poly(methyl methacrylate), polystyrene, and polycarbonate, which show transmittance above 92 % [46]. In the UV region (280–400 nm), a reduction in light transmission to approximately 60 % was observed for F2 and F3, with higher crystallinity correlating with increased UV-blocking ability.

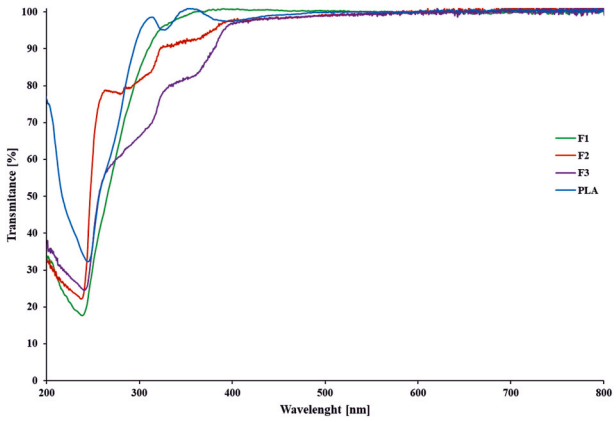


Fig. 6. Visible and UV light barrier properties of films produced with different molar ratios of LA to acetal units (F1, F2, F3) and PLA.

3.1. Oxygen permeability

From the point of view of the use of polymer materials in packaging, the key properties are the barrier properties for gases and water vapour. In the literature, it is assumed that the permeability of gases or water vapour through polymer layers is closely related to chain mobility and molecular packing within the amorphous regions [47–49]. In contrast, lamellar crystals are considered impermeable to penetrating substances [50,51]. Fig. 7 presents the results of oxygen permeability tests for films prepared from ABA triblock copolymers, as well as for a PLA film prepared under similar conditions using commercially available polylactide 4032D (NatureWorks). The F3 film was not tested for barrier properties due to its high brittleness and fragility during measurement.

It is important to note that the film prepared from commercially

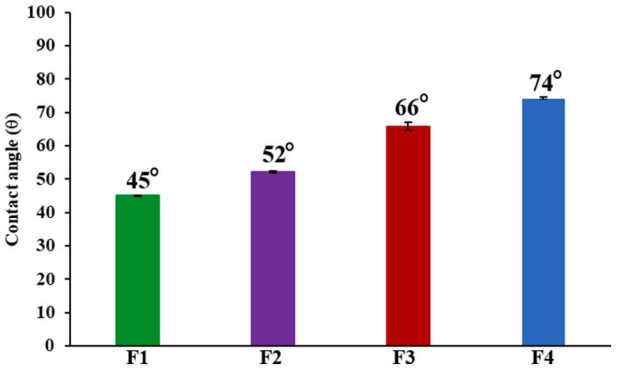


Fig. 5. Contact angle measurement of polymer films obtained from PLA-$PDXL_{7000}$-PLA copolymers with different molar ratios of lactide to acetal units in the polymer chain.

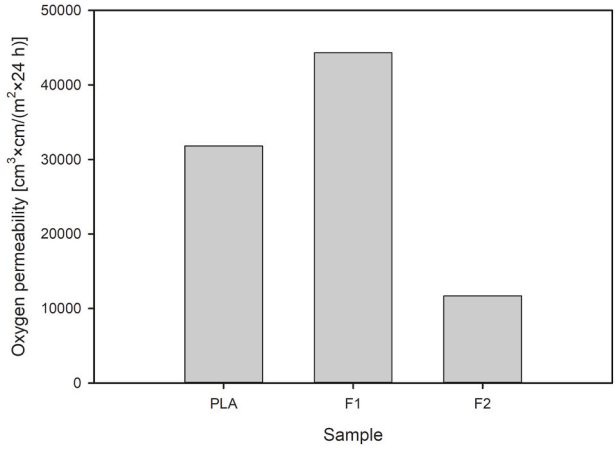


Fig. 7. Oxygen permeability through films from ABA-triblock copolymers (PLA-PDXL-PLA) and for commercially available polylactide NW 4032D.

available polylactide is amorphous, whereas films obtained from the synthesized copolymers are semicrystalline, with degrees of crystallinity ranging from 10 % to 26 %. The oxygen permeability of the amorphous PLA film was measured at 31,814 [$cm^3 \cdot cm/(m^2 \cdot 24\ h)$].

For film F2, prepared from the ABA triblock copolymer PLA_{6900}-$PDXL_{7000}$-PLA_{6900} containing 65 mol% ester groups, the presence of crystalline regions significantly improved oxygen barrier properties, resulting in a 63.3 % reduction in oxygen permeability compared to the amorphous reference. In contrast, film F1, produced from an ABA triblock copolymer with 49 mol% ester groups (PLA_{3400}-$PDXL_{7000}$-PLA_{3400}), exhibited inferior barrier performance relative to the commercial PLA film. In F1, the PDXL-rich and PLA-rich domains appear to be spatially isolated, which may explain the reduced barrier properties. Such phase separation likely limits interfacial interactions and facilitates oxygen diffusion through the film. In this case, the modest increase in crystallinity to 10 % is insufficient to offset the decline in barrier performance.

The literature reports contradictory findings regarding the relationship between PLA crystallinity and permeability. Colomines et al. [52]. ound no clear correlation between oxygen permeability and crystallinity, whereas Drieskens et al. [53] observed that increased crystallinity reduces permeability, though the relationship is non-linear. A comprehensive explanation of these phenomena falls beyond the scope of the present study. Based on our results, the PLA_{6900}-$PDXL_{7000}$-PLA_{6900} copolymer film demonstrates the most promising potential for applications requiring both high barrier performance and biodegradability.

Having demonstrated that the studied films exhibit good stability and promising elongation at break, we next investigated whether the polymeric foils could be efficiently chemically recycled. Since both homopolymers in the block copolymer are degradable, we hypothesized that the copolymer, composed of these two segments, should also be efficiently recyclable via acid-catalyzed processes. To test this, a film sample was melted in the presence of 5 wt% DPP using a simple distillation apparatus at 150 °C under ambient atmosphere (Fig. 8).

Under elevated temperature conditions (~60 min), the polymeric material underwent rapid degradation, resulting in the efficient recovery of 1,3-dioxolane (nearly quantitative yield, 95 % purity) in the distillate (Fig. 8b, blue line) and PLA in the distillation residue (Fig. 8b, green line). Notably, the polylactide remaining after distillation has a molar mass below 10,000 g/mol, which, according to the literature, is effectively biodegradable [54]. The selective degradation of the acetal block in PLA-PDXL-PLA copolymers under acidic conditions occurs relatively quickly, and the rate of degradation can be controlled by adjusting the amount of acid in the system, as previously observed with hydrochloric acid [29]. These results indicate that polymer films based on PLA-PDXL-PLA copolymers containing polyacetal blocks hold significant promise for efficient chemical recycling.

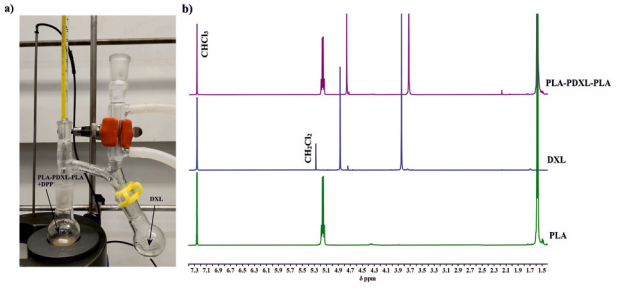


Fig. 8. a) Chemical recycling of polymer films prepared from ABA block copolymer, and b) ^{1}H NMR identification of products formed after chemical recycling of the foil: starting polymeric foil F1 (violet line), distillate (blue line) and distillation residue (green line).

4. Conclusion

In conclusion, we have developed novel thermoplastic films based on ABA-triblock copolymers composed of PLA outer blocks and a degradable PDXL inner block. A scalable synthetic protocol was established to produce PLA-PDXL-PLA copolymers with molar masses ranging from 13,800 to 49,000 g/mol and varied block lengths. We further demonstrated the advantage of directly forming polymer films via a solvent-free compression-moulding process, eliminating the need for solvents or plasticizing additives, which is important for sustainable processing. Mechanical analysis showed that the properties of the films depend strongly on copolymer composition. As the ester content in the copolymer increased from 49 % to 76 %, tensile strength increased from approximately 3 MPa to 19 MPa, while elongation at break decreased sharply from 191 % to 2.7 %. The films exhibited transmittance above 90 % in the visible light range, classifying them as highly transparent, glass-like materials. The chemical recyclability of the films was also demonstrated. A straightforward depolymerization process using diphenyl phosphate at 150 °C effectively degraded the PDXL middle block, yielding 1,3-dioxolane monomer with 95 % recovery. These results collectively demonstrate that the synthesized PLA-PDXL-PLA triblock copolymers function as thermoplastic elastomers with selective degradability under mild acidic conditions, providing a clear advantage for end-of-life management. The successful development of these films, together with their facile chemical recyclability, represents a significant advance in sustainable polymer design and has the potential to substantially reduce environmental impact. The unique combination of desirable mechanical properties, exceptional transparency, and inherent chemical recyclability positions these PLA-PDXL-PLA films for a wide range of high-value, sustainable applications, including packaging materials and transparent protective layers. Furthermore, the developed process offers a notable commercial advantage, allowing the films to be chemically broken down into high-purity raw materials for subsequent re-polymerisation, thereby minimizing reliance on virgin resources and supporting the principles of a circular economy.

CRediT authorship contribution statement

Karolina Cichoń: Visualization, Methodology, Investigation, Formal analysis, Data curation. **Bartłomiej Kost:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Formal analysis, Conceptualization. **Marta Safandowska:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Artur Rozanski:** Writing – review & editing, Resources. **Malgorzata Basko:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Purchase of the Avance Neo 400 NMR spectrometer and upgrade of the Avance III 500 NMR spectrometer, used to obtain results included in this publication, were supported by the funds from the EU Regional Operational Program of the Lodz Region, Poland, RPLD.01.01.00-10-0008/18.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2025.129501.

Data availability

Data will be made available on request.

References

[1] L. Filiciotto, G. Rothenberg, Biodegradable plastics: standards, policies, and impacts, ChemSusChem 14 (2021) 56–72, https://doi.org/10.1002/cssc.202002044.

[2] A.J. Ragauskas, G.W. Huber, J. Wang, A. Guss, H.M. O'Neill, C.S.K. Lin, Y. Wang, F. R. Wurm, X. Meng, New technologies are needed to improve the recycling and upcycling of waste plastics, ChemSusChem 14 (2021) 3982–3984, https://doi.org/10.1002/cssc.202101872.

[3] F.M. Haque, J.S.A. Ishibashi, C.A.L. Lidston, H. Shao, F.S. Bates, A.B. Chang, G. W. Coates, C.J. Cramer, P.J. Dauenhauer, W.R. Dichtel, C.J. Ellison, E.A. Gormong, L.S. Hamachi, T.R. Hoye, M. Jin, J.A. Kalow, H.J. Kim, G. Kumar, C.J. Lasalle, S. Liffland, B.M. Lipinski, Y. Pang, R. Parveen, X. Peng, Y. Popowski, E. A. Prebihalo, Y. Reddi, T.M. Reineke, D.T. Sheppard, J.L. Swartz, W.B. Tolman, B. Vlaisavljevich, J. Wissinger, S. Xu, M.A. Hillmyer, Defining the macromolecules of tomorrow through synergistic sustainable polymer research, Chem. Rev. 122 (2022) 6322–6373, https://doi.org/10.1021/acs.chemrev.1c00173.

[4] T.P. Haider, C. Völker, J. Kramm, K. Landfester, F.R. Wurm, Plastics of the future? The impact of biodegradable polymers on the environment and on Society, Angew. Chem., Int. Ed. 58 (2019) 50–62, https://doi.org/10.1002/anie.201805766.

[5] G.E. Luckachan, C.K.S. Pillai, Biodegradable Polymers- A review on recent trends and emerging perspectives, J. Polym. Environ. 19 (2011) 637–676, https://doi.org/10.1007/s10924-011-0317-1.

[6] I. Vollmer, M.J.F. Jenks, M.C.P. Roelands, R.J. White, T. van Harmelen, P. de Wild, G.P. van der Laan, F. Meirer, J.T.F. Keurentjes, B.M. Weckhuysen, Beyond mechanical recycling: giving new life to plastic waste, Angew. Chem. Int. Ed. 59 (2020) 15402–15423, https://doi.org/10.1002/anie.201915651.

[7] N. Singh, T.R. Walker, Plastic recycling: a panacea or environmental pollution problem, Npj Materials Sustainability 2 (2024) 17, https://doi.org/10.1038/s44296-024-00024-w.

[8] P. Sinha, S. Paul, S. Maity, S. Banerjee, Selective depolymerization of Poly(ethylene terephthalate) in mixed plastic waste using magnetically recoverable nZVI catalyst, Environ. Sci. Technol. 59 (2025) 15766–15776, https://doi.org/10.1021/acs.est.5c06820.

[9] S. Yang, S. Du, J. Zhu, S. Ma, Closed-loop recyclable polymers: from monomer and polymer design to the polymerization–depolymerization cycle, Chem. Soc. Rev. 53 (2024) 9609–9651, https://doi.org/10.1039/D4CS00663A.

[10] C. Jehanno, J.W. Alty, M. Roosen, S. De Meester, A.P. Dove, E.Y.X. Chen, F. A. Leibfarth, H. Sardon, Critical advances and future opportunities in upcycling commodity polymers, Nature 603 (2022) 803–814, https://doi.org/10.1038/s41586-021-04350-0.

[11] M. Häußler, M. Eck, D. Rothauer, S. Mecking, Closed-loop recycling of polyethylene-like materials, Nature 590 (2021) 423–427, https://doi.org/10.1038/s41586-020-03149-9.

[12] A.L. Kocen, S. Cui, T.-W. Lin, A.M. LaPointe, G.W. Coates, Chemically recyclable ester-linked polypropylene, J. Am. Chem. Soc. 144 (2022) 12613–12618, https://doi.org/10.1021/jacs.2c04499.

[13] M.A. Hillmyer, W.B. Tolman, Aliphatic polyester block polymers: renewable, degradable, and sustainable, Acc. Chem. Res. 47 (2014) 2390–2396, https://doi.org/10.1021/ar500121d.

[14] A.Z. Naser, I. Deiab, B.M. Darras, Poly(lactic acid) (PLA) and polyhydroxyalkanoates (PHAs), green alternatives to petroleum-based plastics: a review, RSC Adv. 11 (2021) 17151–17196, https://doi.org/10.1039/d1ra02390j.

[15] M. Holler, J. Alberdi-Cedeño, A. Auñon-Lopez, T. Pointner, A. Martínez-Yusta, J. König, M. Pignitter, Polylactic acid as a promising sustainable plastic packaging for edible oils, Food Packag. Shelf Life 36 (2023), https://doi.org/10.1016/j.fpsl.2023.101051.

[16] M. Musioł, W. Sikorska, G. Adamus, H. Janeczek, M. Kowalczuk, J. Rydz, (Bio) degradable polymers as a potential material for food packaging: studies on the (bio)degradation process of PLA/(R,S)-PHB rigid foils under industrial composting conditions, Eur. Food Res. Technol. 242 (2016) 815–823, https://doi.org/10.1007/s00217-015-2611-y.

[17] S. Slomkowski, S. Penczek, A. Duda, Polylactides-an overview, Polym. Adv. Technol. 25 (2014) 436–447, https://doi.org/10.1002/pat.3281.

[18] D.K. Schneiderman, M.A. Hillmyer, 50th anniversary perspective : there Is a great future in sustainable polymers, Macromolecules 50 (2017) 3733–3749, https://doi.org/10.1021/acs.macromol.7b00293.

[19] L. Cederholm, J. Wohlert, P. Olsén, M. Hakkarainen, K. Odelius, "Like recycles like": Selective ring-closing depolymerization of Poly(L-Lactic acid) to l-lactide, Angew. Chem. 134 (2022), https://doi.org/10.1002/ange.202204531.

[20] M. Ryner, A.C. Albertsson, Resorbable and highly elastic block copolymers from 1,5-dioxepan-2-one and L-lactide with controlled tensile properties and hydrophilicity, Biomacromolecules 3 (2002) 601–608, https://doi.org/10.1021/bm015658z.

[21] Y. Huang, R. Chang, L. Han, G. Shan, Y. Bao, P. Pan, ABA-Type thermoplastic elastomers composed of Poly(ε-caprolactone-co-δ-valerolactone) soft midblock and polymorphic poly(lactic acid) hard end blocks, ACS Sustain. Chem. Eng. 4 (2016) 121–128, https://doi.org/10.1021/acssuschemeng.5b00855.

[22] C.L. Wanamaker, L.E. O'Leary, N.A. Lynd, M.A. Hillmeyer, W.B. Tolman, Renewable-resource thermoplastic elastomers based on polylactide and polymenthide, Biomacromolecules 8 (2007) 3634–3640, https://doi.org/10.1021/bm700699g.

[23] B.W. Boudouris, C.D. Frisbie, M.A. Hillmyer, Polylactide-polythiophene-polylactide triblock copolymers, Macromolecules 43 (2010) 3566–3569, https://doi.org/10.1021/ma1002134.

[24] D.K. Schneiderman, E.M. Hill, M.T. Martello, M.A. Hillmyer, Poly(lactide)-block-poly(ε-caprolactone-co-ε-decalactone)-block-poly(lactide) copolymer elastomers, Polym. Chem. 6 (2015) 3641–3651, https://doi.org/10.1039/c5py00202h.

[25] D. Cohn, A. Hotovely Salomon, Designing biodegradable multiblock PCL/PLA thermoplastic elastomers, Biomaterials 26 (2005) 2297–2305, https://doi.org/10.1016/j.biomaterials.2004.07.052.

[26] L. Cederholm, P. Olsén, M. Hakkarainen, K. Odelius, Design for recycling: Polyester- and polycarbonate-based A-B-A block copolymers and their recyclability back to monomers, Macromolecules 56 (2023) 3641–3649, https://doi.org/10.1021/acs.macromol.3c00274.

[27] B. Kost, M. Basko, Synthesis and properties of l-lactide/1,3-dioxolane copolymers: preparation of polyesters with enhanced acid sensitivity, Polym. Chem. 12 (2021) 2551–2562, https://doi.org/10.1039/d1py00358e.

[28] K. Cichoń, I.I. Bak-Sypien, M. Basko, B. Kost, Synthesis and characterization of functionalized polylactides containing acetal units, Macromolecules 56 (2023) 6951–6967, https://doi.org/10.1021/acs.macromol.3c01343.

[29] K. Cichoń, B. Kost, M. Basko, Synthesis and properties of ABA-triblock copolymers from polyester A-blocks and easily degradable polyacetal B-blocks, Polym. Chem. 13 (2022) 5243–5255, https://doi.org/10.1039/d2py00620k.

[30] B.A. Abel, R.L. Snyder, G.W. Coates, Chemically recyclable thermoplastics from reversible-deactivation polymerization of cyclic acetals, Science 373 (1979) 783–789, https://doi.org/10.1126/science.abh0626, 2021.

[31] M.C. Righetti, M. Gazzano, M.L. Di Lorenzo, R. Androsch, Enthalpy of melting of α′- and α-crystals of poly(l-lactic acid), Eur. Polym. J. 70 (2015) 215–220, https://doi.org/10.1016/j.eurpolymj.2015.07.024.

[32] ISO 1133-1:2022, Plastics — Determination of the Melt mass-flow Rate (MFR) and Melt volume-flow Rate (MVR) of Thermoplastics, n.d. https://doi.org/ISO1133-1:2022.

[33] Test method for oxygen gas transmission rate through plastic film and sheeting using a coulometric sensor. https://doi.org/10.1520/D3985-17, 2017.

[34] G. Holden, Thermoplastic elastomers, in: Applied Plastics Engineering Handbook, Elsevier, 2011, pp. 77–91, https://doi.org/10.1016/B978-1-4377-3514-7.10006-6.

[35] S. Saeidlou, M.A. Huneault, H. Li, C.B. Park, Poly(lactic acid) crystallization, Prog. Polym. Sci. 37 (2012) 1657–1677, https://doi.org/10.1016/j.progpolymsci.2012.07.005.

[36] R.A. Silva, G.G. Silva, C.A. Furtado, R.L. Moreira, M.A. Pimenta, Structure and Conductivity in Polydioxolane/Licf 3 SO 3 Electrolytes, vol. 46, 2001, pp. 1493–1498.

[37] N. Brooks, Temperature and stem length dependence of the yield stress of polyethylene, Polymer (Guildf.) 41 (2000) 1475–1480, https://doi.org/10.1016/S0032-3861(99)00362-6.

[38] T. Kazmierczak, A. Galeski, A.S. Argon, Plastic deformation of polyethylene crystals as a function of crystal thickness and compression rate, Polymer (Guildf.) 46 (2005) 8926–8936, https://doi.org/10.1016/j.polymer.2005.06.073.

[39] M.A. Kennedy, A.J. Peacock, L. Mandelkern, Tensile properties of crystalline polymers: Linear polyethylene, Macromolecules 27 (1994) 5297–5310, https://doi.org/10.1021/ma00097a009.

[40] S. Ding, C. Fang, X. Wang, Z. Wang, Crystallization-driven microstructure changes during microphase separation for environment-friendly thermoplastic triblock copolymer elastomers, Polymer (Guildf.) 186 (2020) 121993, https://doi.org/10.1016/j.polymer.2019.121993.

[41] S. Ding, C. Fang, J. Zhang, X. Wang, Z. Wang, Effect of crystallization on enhancement of mechanical property for polylactide-b-polyisoprene-b-polylactide triblock copolymers, Polymer (Guildf.) 202 (2020) 122724, https://doi.org/10.1016/j.polymer.2020.122724.

[42] G. Simmonds, A.T. Woods, C. Spence, 'Show me the goods': assessing the effectiveness of transparent packaging vs. product imagery on product evaluation, Food Qual. Prefer. 63 (2018) 18–27, https://doi.org/10.1016/j.foodqual.2017.07.015.

[43] J. Shojaeiarani, D.S. Bajwa, C. Ryan, S. Kane, Enhancing UV-shielding and mechanical properties of polylactic acid nanocomposites by adding lignin coated cellulose nanocrystals, Ind. Crops Prod. 183 (2022) 114904, https://doi.org/10.1016/j.indcrop.2022.114904.

[44] M. Sulfate, iTeh standards iTeh standards, Design: E 778 – 787 (Reapproved 2004) (2018) 3–787, https://doi.org/10.1520/D1746-23.2.

[45] Y. Lin, R. Patel, J. Cao, W. Tu, H. Zhang, E. Bilotti, C.W.M. Bastiaansen, T. Peijs, Glass-like transparent high strength polyethylene films by tuning drawing temperature, Polymer (Guildf.) 171 (2019) 180–191, https://doi.org/10.1016/j.polymer.2019.03.036.

[46] S. Guzman-Puyol, J.J. Benítez, J.A. Heredia-Guerrero, Transparency of polymeric food packaging materials, Food Res. Int. 161 (2022) 111792, https://doi.org/10.1016/j.foodres.2022.111792.

[47] M. Safandowska, C. Makarewicz, A. Rozanski, R. Idczak, Diminishment the gas permeability of polyethylene by "densification" of the amorphous regions, Sci. Rep. 13 (2023) 19838, https://doi.org/10.1038/s41598-023-46276-9.

[48] M. Safandowska, C. Makarewicz, A. Rozanski, R. Idczak, Barrier properties of semicrystalline polylactide: the role of the density of the amorphous regions, Macromolecules 55 (2022) 10077–10089, https://doi.org/10.1021/acs.macromol.2c01490.

[49] M. Safandowska, C. Makarewicz, A. Rozanski, Tuning barrier properties of low-density polyethylene: impact of amorphous Region nanostructure on gas

transmission rate, Molecules 29 (2024) 4950, https://doi.org/10.3390/molecules29204950.
[50] S. Kanehashi, A. Kusakabe, S. Sato, K. Nagai, Analysis of permeability; solubility and diffusivity of carbon dioxide; oxygen; and nitrogen in crystalline and liquid crystalline polymers, J. Membr. Sci. 365 (2010) 40–51, https://doi.org/10.1016/j.memsci.2010.08.035.
[51] S. Kanehashi, K. Nagai, Analysis of dual-mode model parameters for gas sorption in glassy polymers, J. Membr. Sci. 253 (2005) 117–138, https://doi.org/10.1016/j.memsci.2005.01.003.
[52] G. Colomines, V. Ducruet, Ć. Courgneau, A. Guinault, S. Domenek, Barrier properties of poly(lactic acid) and its morphological changes induced by aroma compound sorption, Polym. Int. 59 (2010) 818–826, https://doi.org/10.1002/pi.2793.
[53] M. Drieskens, R. Peeters, J. Mullens, D. Franco, P.J. Lemstra, D.G. Hristova-Bogaerds, Structure versus properties relationship of poly(lactic acid). I. Effect of crystallinity on barrier properties, J. Polym. Sci. B Polym. Phys. 47 (2009) 2247–2258, https://doi.org/10.1002/polb.21822.
[54] K. Wang, Z. Sun, W. Guo, M. Chen, C. Zhu, J. Fei, Y. Liu, H. He, Y. Cao, X. Bao, Upgrading waste polylactide via catalyst-controlled Tandem Hydrolysis-Oxidation, ChemSusChem 16 (2023), https://doi.org/10.1002/cssc.202301128.

Supporting Information for

Chemically recyclable films from thermoplastic ABA-triblock copolymers containing polylactide A-blocks and easily degradable polydioxolane B-block - towards the novel type of sustainable plastics

Karolina Cichoń[a,b], Bartłomiej Kosta[*], Marta Safandowska[a], Artur Rozanski[a], Malgorzata Basko[a*]

[a] Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland

[b] BioMedChem Doctoral School of the University of Lodz and Lodz Institutes of the Polish Academy of Sciences, Matejki 21/23, 90-237 Lodz, Poland

emails: malgorzata.basko@cbmm.lodz.pl, bartlomiej.kost@cbmm.lodz.pl

Table of contents:

Figure S1. ^{1}H NMR analysis of PLA_{6900}-$PDXL_{7000}$-PLA_{6900} copolymer. 2
Figure S2. ^{13}C NMR analysis of PLA_{6900}-$PDXL_{7000}$-PLA_{6900} copolymer. 2
Figure S3. Isothermal TGA analysis of PLA_{6900}-$PDXL_{7000}$-PLA_{6900} copolymer. 3
Figure S4. ^{1}H NMR analysis of copolymer after extrusion. 3
Figure S5. Humidity resistance testing of polymer films. 4
UV VIS 4

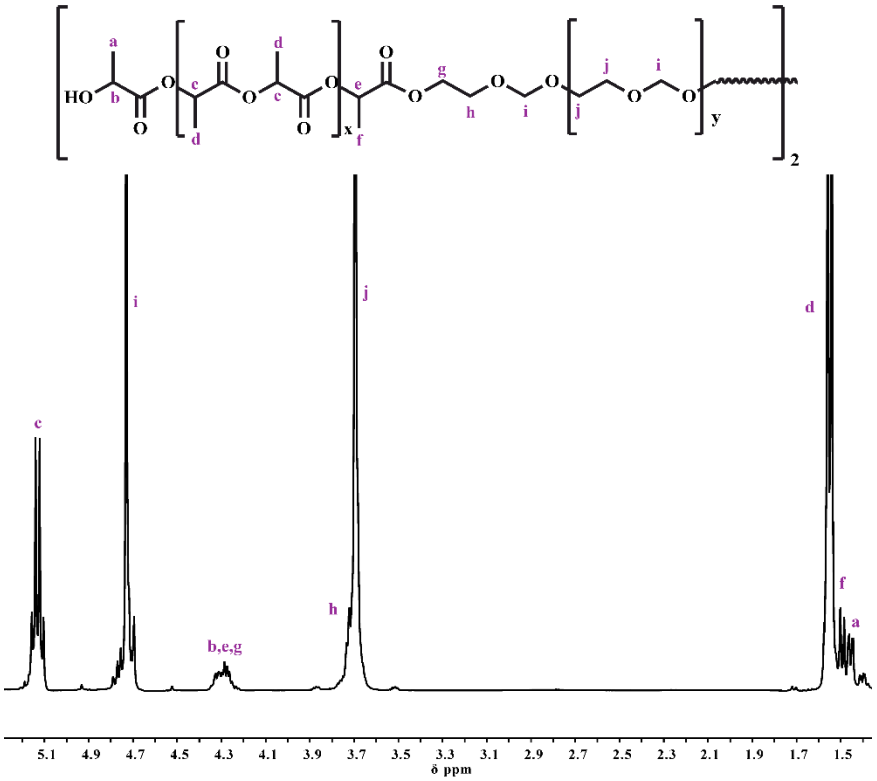


Figure S1. ^{1}H NMR analysis of PLA_{6900}-$PDXL_{7000}$-PLA_{6900} copolymer.

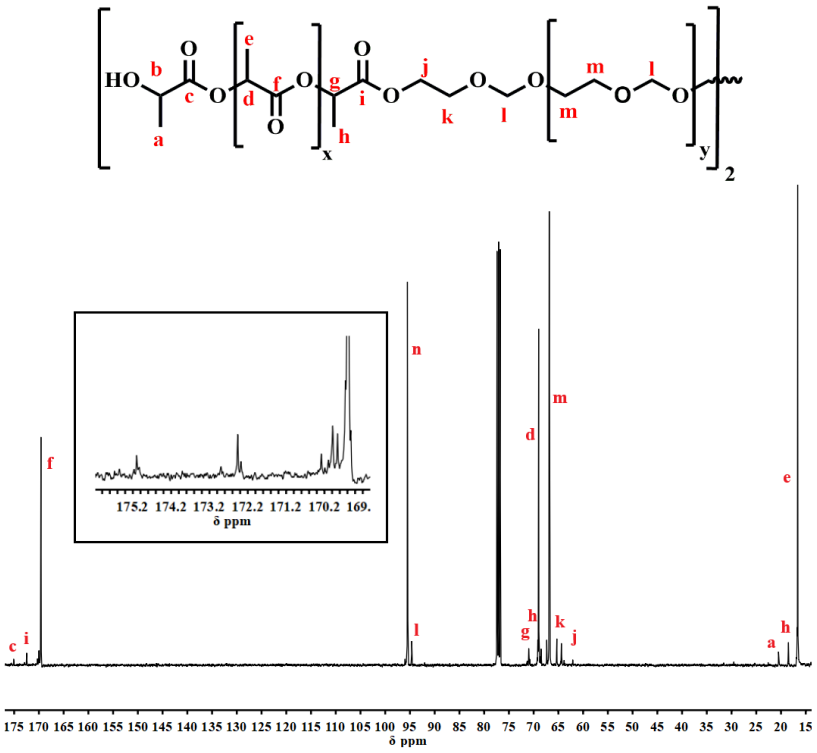


Figure S2. ^{13}C NMR analysis of PLA_{6900}-$PDXL_{7000}$-PLA_{6900} copolymer.

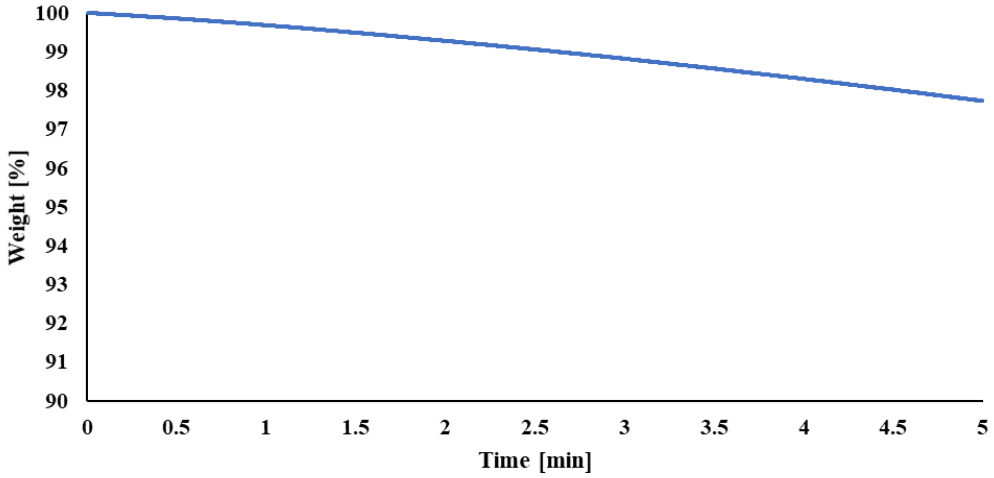


Figure S3. Isothermal TGA analysis of PLA_{6900}-$PDXL_{7000}$-PLA_{6900} copolymer.

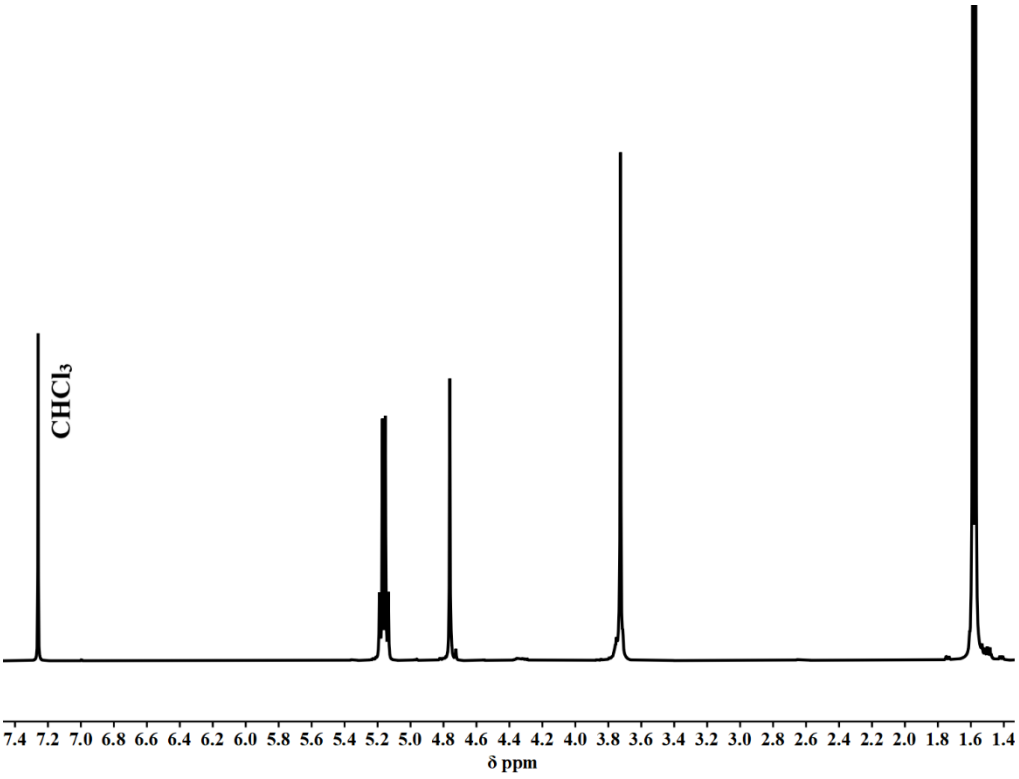


Figure S4. ^{1}H NMR analysis of copolymer after extrusion.

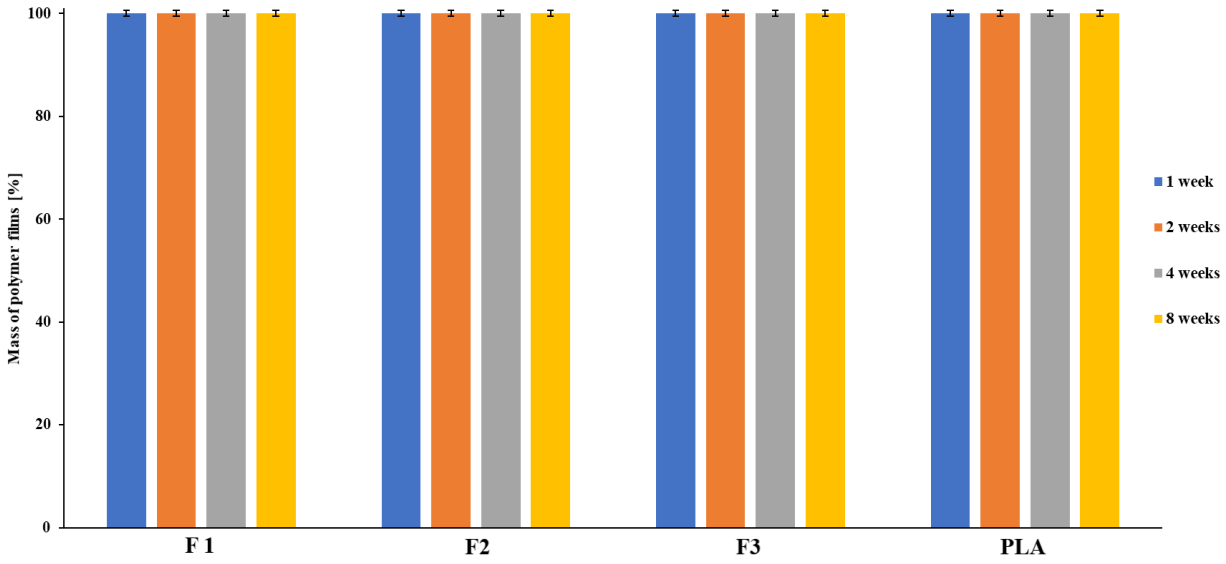


Figure S5. Humidity resistance testing of polymer films.

UV VIS

Four circular polymer film samples with a thickness of 0.1 mm and a diameter of 1,5 cm were prepared for the study. Before measurement, the samples were conditioned for 24 hours at room temperature in the presence of a desiccant to eliminate the effect of moisture on their optical properties. Transmittance was measured using a UV/Vis spectrophotometer (Double Beam Spectrophotometer UV/Vis Evolution 220, Thermo Scientific, USA) equipped with an integrating sphere. To ensure measurement accuracy, a blank test was performed by recording the background signal of the empty measurement chamber. The samples were placed in the integrating sphere holder, and the transmittance spectrum was recorded in the 200-800 nm range. The measurements were normalized to the transmittance value at 600 nm, identified as the midpoint of the visible range. Three independent measurements were taken for each sample, and the obtained values were averaged.

Publikacja 4:

Karolina Cichoń, Bartłomiej Kost, Malgorzata Basko, Przemysław Kubisa, Karin Odelius, Minna Hakkarainen, Polyethylene-like materials containing hydrolysable main-chain linkages: design, degradation and chemical recycling, European Polymer Journal 2026, 255, 114929

European Polymer Journal 255 (2026) 114929

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Review

Polyethylene-like materials containing hydrolysable main-chain linkages: design, degradation and chemical recycling

Karolina Cichoń [a,b], Malgorzata Basko [a], Przemysław Kubisa [a], Karin Odelius [c], Minna Hakkarainen [c], Bartłomiej Kost [a,*]

[a] Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland
[b] BioMedChem Doctoral School of University of Lodz and Lodz Institutes of the Polish Academy of Sciences, Matejki 21/23, 90-237 Lodz, Poland
[c] KTH Royal Institute of Technology, Department of Fiber and Polymer Technology, Teknikringen 56-58, 100 44, Stockholm, Sweden

ARTICLE INFO

Keywords:
Closed-loop chemical recyclability
Polyethylene
Hydrolytically labile groups

ABSTRACT

Polyethylene (PE), the plastic with the largest production volume globally (>110 million tons per year), is mainly used in short term applications. A high molecular weight PE with a carbon main chain is not biodegradable; however, its lower molecular weight oligomers (M~500−1,000 g/mol) are reported to undergo microbial degradation. Therefore, there is an increasing interest in PE-like materials that can be degraded into shorter chain segments to augment the materials susceptible to biodegradation. This review highlights research concerning the introduction of hydrolysable repeating units, such as carboxylic esters, carbonates, phosphate esters, or acetal groups, into the PE main-chain. The strategy offers new opportunities in the design of PE-like materials with an enhanced ability to undergo controlled degradation, which can take place at the stage defined by the user and enables closed-loop chemical recyclability. This mini-review highlights typical examples of PE-like materials with hydrolytically labile groups in the main-chain and discusses the influence of such groups on the degradability of resulting polymers.

1. Introduction

Polyethylene (PE) is the most widely produced synthetic polymer worldwide, with a global production exceeding 110 million tonnes annually [1,2]. Owing to its excellent mechanical properties, chemical resistance, thermal stability, low density, and low production cost, PE is used in numerous applications ranging from packaging materials and consumer products to engineering components. [1,3]. However, the same chemical inertness and durability that make PE highly attractive in use also contribute to its persistence in the environment after disposal. For example, PE samples exposed to soil environments have been reported to undergo negligible degradation even after several decades [4].

To address this challenge, significant efforts have been devoted to developing polyethylene-like materials that retain the desirable properties of PE while exhibiting improved end-of-life characteristics. One commonly explored strategy involves introducing hydrolytically labile linkages, such as ester, carbonate, acetal, or phosphate ester groups, into predominantly methylene-based polymer backbones. These materials typically contain long polyethylene-like segments separated by bonds that may undergo hydrolysis or other cleavage reactions under appropriate conditions. As a result, the polymers can either be depolymerized into recoverable monomers suitable for chemical recycling or degraded into lower molecular weight oligomers that may subsequently undergo biodegradation [5–14].

Chemical recycling is particularly attractive when degradation leads to a well-defined set of monomers or oligomers that can be efficiently recovered, purified, and reused for polymer synthesis. In many of the systems discussed in this review, medium-length oligoethylene building blocks bearing reactive end groups, typically hydroxyl or carboxylic acid functionalities, are connected through hydrolysable linkages. Cleavage of these bonds regenerates the original building blocks, enabling closed-loop recycling pathways. Alternatively, degradation can reduce the molecular weight of polyethylene-like materials to oligomeric species that become susceptible to microbial utilization. Studies have shown that low-molecular-weight linear hydrocarbons and polyethylene oligomers can be metabolized by microorganisms, whereas high-molecular-weight polyethylene remains essentially non-biodegradable [15–20]. Consequently, the introduction of strategically placed cleavable bonds

* Corresponding author.
E-mail address: bartlomiej.kost@cbmm.lodz.pl (B. Kost).

https://doi.org/10.1016/j.eurpolymj.2026.114929
Received 25 May 2026; Received in revised form 25 June 2026; Accepted 1 July 2026
Available online 3 July 2026
0014-3057/© 2026 Elsevier Ltd. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

represents a promising approach toward reducing the environmental persistence of polyethylene-derived materials. Several classes of polyethylene-like polymers containing hydrolysable linkages have been reported, including polyesters, polycarbonates, polyacetals, and polyphosphates components. Although a number of reviews have summarized the synthesis, crystallization behaviour, and physical properties of long-chain aliphatic polymers, the influence of different hydrolysable linkages on degradation pathways and chemical recyclability has received comparatively less attention. Therefore, the objective of this review is to provide a focused overview of polyethylene-like materials containing ester, carbonate, acetal, and phosphate-based bonds, with particular emphasis on their degradation mechanisms, degradation behaviour, and potential for closed-loop chemical recycling. The susceptibility of these materials toward degradation is largely determined by the chemical nature of the incorporated linkage. Although direct comparison of degradation studies is often difficult because of differences in experimental conditions and polymer morphology, model compound studies provide useful insight. Ester, carbonate, and acetal bonds exhibit hydrolysis rate constants that are several orders of magnitude higher than those of ether bonds under acidic conditions [21–23]. Consequently, these functionalities may serve as strategically placed weak points within polyethylene backbones, enabling controlled degradation and facilitating chemical recycling. Recently, a comprehensive review of PE-like materials covering a broad range of synthetic methodologies and polymer architectures designed to mimic the structural and mechanical characteristics of polyethylene was published [24–26]. In the present work, we adopted the classification according to the nature of the hydrolysable linkage because the chemical nature of the cleavable bond is the primary factor controlling degradation pathways, hydrolytic stability, degradation products, and chemical recyclability. Since identical functional groups may be introduced by different polymerization techniques, organizing the review according to bond type facilitates direct comparison of degradation behavior among polyethylene-like materials. While presented review provides an overview of synthetic strategies and structure − property relationships, degradability and chemical recyclability are discussed only as one of several emerging design aspects. In contrast, the present review specifically focuses on polyethylene-like materials containing hydrolysable main-chain linkages and examines these systems from an end-of-life perspective. Particular emphasis is placed on the relationship between bond chemistry (ester, carbonate, phosphate ester, and acetal groups), degradation mechanisms, degradation conditions, degradation products, and opportunities for closed-loop chemical recycling. By organizing the discussion according to the nature of the hydrolysable linkage, this review aims to provide design guidelines for the development of future polyethylene-like materials that combine polyethylene-like properties with controlled degradability and circularity.

2. Polyethylene containing ketone bonds

Ketone-containing polyethylene-like materials represent a distinct class of degradable polyolefin analogues in which isolated carbonyl groups are incorporated into otherwise polyethylene backbones. Unlike hydrolysable polyethylene mimics containing ester, carbonate, or acetal linkages, these materials generally retain a carbon–carbon backbone and therefore do not undergo conventional hydrolytic degradation. Instead, the incorporated ketone functionalities act as photolabile defects that promote chain scission upon exposure to ultraviolet radiation. Among the various approaches developed to introduce degradable functionalities into polyethylene chains, the copolymerization of ethylene with carbon monoxide has attracted particular attention because isolated ketone groups can act as photolabile defects while preserving polyethylene-like properties. A major breakthrough was reported by Mecking and co-workers, who demonstrated nonalternating ethylene/CO copolymerization using phosphinophenolate Ni(II) catalysts. High-molecular-weight polyethylene materials containing isolated in-chain ketones were obtained with molecular weights reaching M_n = 200,000 g/mol while retaining the crystallinity, processability, and mechanical properties characteristic of PE. The degradability of these materials originates from the incorporated ketone groups, which undergo Norrish type I and II photochemical reactions upon exposure to UV light. Photodegradation experiments on injection-molded specimens demonstrated efficient chain scission initiated at the isolated carbonyl sites, resulting in progressive molecular-weight reduction while maintaining satisfactory mechanical performance prior to irradiation. The homogeneous distribution of ketone functionalities throughout the polyethylene backbone was proposed to promote more uniform fragmentation compared with conventional polyethylene materials containing only adventitious carbonyl defects [27]. A complementary free-radical approach was reported by Morgen et al., who synthesized branched keto-functionalized polyethylenes containing approximately 1 mol% carbonyl groups under comparatively mild conditions (<350 atm). The resulting materials could be processed into thin films and molded specimens. Photodegradation studies were performed using simulated sunlight under marine-like conditions, including exposure of polymer films in artificial seawater environments. Under irradiation, the incorporated ketone groups promoted Norrish type I and II reactions, leading to photooxidative chain cleavage, substantial molecular-weight reduction, and progressive deterioration of the polymer materials. These results demonstrated that even relatively low carbonyl contents are sufficient to trigger efficient degradation while preserving polyethylene-like properties before exposure [28]. Subsequent mechanistic studies by Voccia et al. were focused on elucidating the origin of nonalternating ketone incorporation and identifying the elementary steps governing catalyst selectivity. However, no degradation experiments were reported [29]. The scope of the methodology was further expanded through catalytic terpolymerization of ethylene, carbon monoxide, and methyl acrylate, yielding linear polyethylene materials containing both isolated in-chain ketone groups and side-chain ester functionalities. The obtained terpolymers had molecular weights around M_n = 20,000 g/mol while retaining polyethylene-like crystallinity. Although both ketone and ester groups may potentially facilitate degradation, no such studies or recycling efforts were reported [30]. An alternative strategy developed by Nozaki and co-workers employed palladium-catalyzed copolymerization of ethylene with metal carbonyl complexes as carbon monoxide sources. High-density polyethylene (HDPE) materials bearing isolated in-chain carbonyl groups were obtained, with no loss of PE-like thermal and mechanical properties. Accelerated degradation was observed upon UV irradiation, where the isolated ketone groups acted as photochemical weak points that initiated Norrish-type chain scission reactions. Compared with conventional polyethylene, the carbonyl-containing materials exhibited faster molecular-weight reduction and fragmentation [31]. Similarly, Yonezaki et al. utilized $Fe_2(CO)_9$ as an external carbonyl source in nickel-catalyzed polymerization, achieving highly selective incorporation of isolated ketone groups into polyethylene chains with photodegradability properties [32]. More recently, Song et al. reported hydrogen-controlled nonalternating ethylene/CO copolymerization, enabling simultaneous regulation of molecular weight and chain-end functionality. Linear ketone-polyethylenes containing 1.0–9.3 mol% ketone groups and molecular weights ranging from 43,000 to 195,000 g/mol were obtained. Their photodegradability was evaluated under UV irradiation, which induced substantial molecular-weight reduction and generated lower-molecular-weight oligomers bearing vinyl and acetyl end groups [33,34]. The degradation studies reported for ethylene/CO-derived polyethylene materials are almost exclusively based on photochemical degradation initiated by ketone functionalities under UV or simulated sunlight irradiation. In contrast, systematic investigations of hydrolytic degradation, chemical depolymerization, monomer recovery, and closed-loop chemical recycling remain largely underexplored for this family of materials.

3. Polyethylene containing ester bonds

Several routes to prepare polymers containing longer segments of methylene units connected by ester bonds have been undertaken and different methods to introduce this type of chemical connection into polyethylene chains have been developed including polycondensation, ring-opening polymerization and addition polymerization of ketene acetals. As it was mentioned, copolymerization of ethylene with CO resulted in polyethylenes with in-chain ketone contents as high as 15 mol% [27]. The keto group might not bring immediate hydrolytic degradability, but this effect could be introduced by ester groups from copolymerization with CO_2. Copolymerization of CO_2 with ethylene has long been recognized as a significant, but highly challenging transformation, because most frequently it leads to ethylene homopolymerization [35].

Utilizing free radical polymerization, copolymers containing ester groups in the carbon backbone were obtained by copolymerization of ethylene and the ketene acetal (2-methylene-1,3-dioxepane) at 120°C in the presence of di−tertbutyl peroxide (Fig. 1) [36].

To achieve uniform composition, reaction conversion was kept low as the comonomers exhibit different reactivities. A series of copolymers containing from 2.1 to 10.4 mol% of the ester units was prepared. Average molecular weights of around 5,000 g/mol were achieved, making these polymers a good model system to study. The produced copolymers biodegraded in the presence of the soil microflora, where the rate of biodegradability was followed by determining the amount of carbon dioxide produced by the microbial metabolism of the polymer samples [36]. It is noteworthy that so few studies have followed this work, likely due to the challenge in achieving high molecular weight polymers.

Another method for the synthesis of polyethylene containing ester bonds is the polycondensation of relatively long-chain olefin acids and diols [37–43]. All-aliphatic polyesters with melting and crystallisation transitions similar to polyethylene may be achieved when longer-chain aliphatic repeating units crystallise via van der Waals interactions between the hydrocarbon segments. However, classical organic syntheses of long-chain PE-like monomers (diacids or diols) by polycondensation remains tedious and inefficient. Alternative approaches have been developed by e.g., utilising plant-oil-derived fatty acids [40]. Long-chain monomers, both diacids and diols, may be obtained by catalytic conversion of plant oils, via biotechnological and purely chemical approaches, whereas availability of long-chain monomers in the required purity is a key prerequisite for possible industrial applications, and currently, the production of these PE diacids and diols remains relatively costly [44]. Chain-transfer ring-opening metathesis polymerization (CT-ROMP) provides a route to telechelic polyethylene containing carboxyl or hydroxyl end-groups [45]. Carboxytelechelic polyethylene of controlled molecular weight was prepared by this approach. Solvent-free melt polycondensation of such telechelics with neopentyl glycol and adipic acid yields segmented copolyesters [41]. More representative examples of incorporating ester groups into PE-like structures via polycondensation are presented below. Diethyl triacontanedioate ($CH_3CH_2O_2C(CH_2)_{28}CO_2CH_2CH_3$) and triacontane-1,30-diol ($HO(CH_2)_{30}OH$) were prepared and condensed to synthesize poly(triacontamethylene triacontanedioate) [39]. The resulting polymer was semicrystalline with molecular weight characterized by viscosity measurements (n_{inh} up to 0.76), and melting temperature in the range 106–113°C. In addition, it exhibited a higher stiffness modulus, comparable tensile strength and much lower elongation at break as compared to low density polyethlene (LDPE). Biodegradation of the synthesized polymer under the action of enzymes (lipase) was not efficient due to the high crystallinity and hydrophobic character of the long chains of methylene units [39]. Another synthetic route to ester-containing polyethylene involves the self-metathesis of erucic acid [(Z)-docos-13-enoic acid], followed by hydrogenation of the remaining double bond to yield 1,26-hexacosanedioic acid (AA). Polycondensation of this biobased long-chain α,ω-dicarboxylic acid with hexacosane-1,26-diol (BB), generated from the former by reduction, yielded the polyester 26,26. Molecular weight of the polymer was rather high (M_w = 33,840 g/mol, M_n = 14,100 g/mol), its melting temperature was equal to 104°C, but unfortunately, no information on the degradation of this product was provided [40].

Polycondensation of carboxytelechelic PE-segments with adipic acid and neopentyl glycol provided segmented copolyesters with 48, 75, and 95 wt% PE depending on the ratio of the comonomers. Copolymer with the structure poly(ethylene 95-co-neopentyl adipate 5) was semi-crystalline (53% degree crystallinity) and had a melting point equal to 123°C. Strain at break, Young's modulus , maximum stress , and stress at break were roughly half compared to the tested commercial HDPE sample. Obviously, the balance between alcohol and carboxylic acid groups is crucial for achieving high-molar-mass polymers. This may be the reason why the ultimate strain for PE-esters was lower than that of HDPE, especially for the materials synthesized from low-molar-mass macromonomers [41].

An interesting strategy to synthesis high molar mass linear PE-esters from stoichiometrically self-balanced telechelic polyethylene macromonomer was also recently reported [42].

In this approach, first a chain-transfer agent (CTA) containing an alcohol and an ester group at each end was synthesized (Fig. 2). Ring-opening of oxacycloheptadec-10-en-2-one, known as isoambrettolide, under reflux conditions in methanol gave quantitative conversions (>99%) of CTA [42].

After ring-opening metathesis polymerisation (ROMP) and hydrogenation, this chain-transfer agent generated telechelic polyethylene macromonomers which had stoichiometrically balanced hydroxy and ester end groups; thus, step-growth polymerisation of the macromonomers produced high molar mass PE-ester with molar masses up to $M_{n,SEC}$, = 111,000 g/mol. Melting temperatures of the resulting polymers ranged from 131 to 135°C, which is comparable to that of commercial HDPE (T_m = 132°C). Mechanical properties of the polymers were also competitive with HDPE. Telechelic polyethylene macromonomers were regenerated by the depolymerisation of the PE-like polyester ester under methanolysis conditions.

It was shown that properly designed polyesters with a low density of in-chain functional groups-acting as break points in a polyethylene chain can be recycled chemically by solvolysis. At the same time, the break points do not disturb the crystalline structure of polyethylene, and the desirable materials properties (like those of high-density polyethylene) are fully retained upon recycling [37,46]. A schematic presentation of the discussed procedure for manufacturing such polyethylene-like polymers is shown in Fig. 3.

Included in the investigation were polyester-18,18 (PE-18,18) and polycarbonate-18 (PC-18) leading to polymers with properties similar to those of commercially relevant high-density polyethylene (HDPE). High

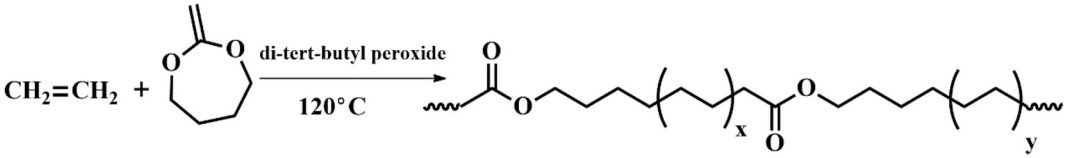


Fig. 1. Synthesis of polyethylene containing ester units by radical copolymerization of ethylene and the ketene acetal.[36]

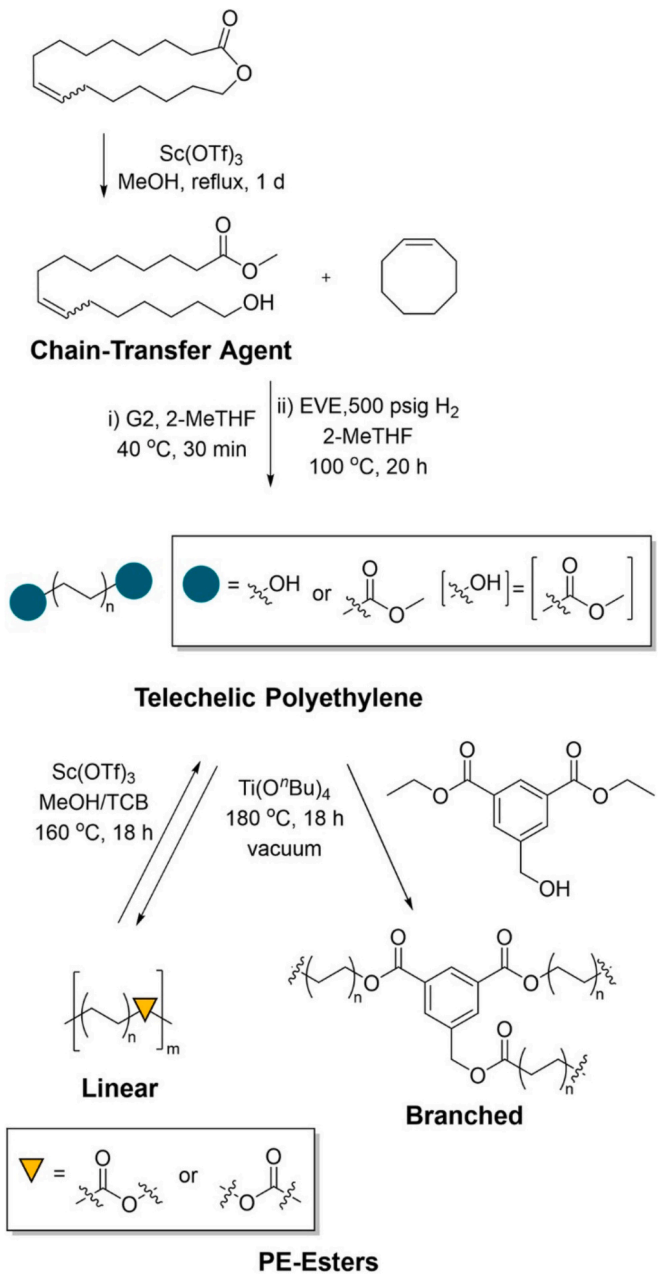


Fig. 2. Approaches to synthesize chemically recyclable polyethylene-like materials [42] (ACS, copyright 2024).

molecular weight polymers were obtained with M_w = 300,000 g/mol and M_n = 90,000 g/mol for polycarbonate and M_w = 80,000 g/mol, M_n = 50,000 g/mol for polyester. It should be pointed out that polyethylene-like hydrocarbon segments connected by ester or carbonate bonds accounted for ~85% of the total mass of the polymer.

PE18,18 was, however, resistant to degradation; it was found to be inert in aqueous acid over an extended period of one year [37]. To increase the susceptibility to hydrolysis and (bio)degradation, an approach combining long and short monomers was investigated. A library of "short–long" diol–diacid polyesters containing polyethylene segments was synthesized [47], and it was shown that the degradation deepens on the length of oligoethylene diacid and decreased when the length of the this component increased from C_{10} to C_{14}, while the short diol (C_2) benefited the degradation rate. That was confirmed by degradation studies of polymer of 1,18-dimethyl octadecanedioate and ethylene glycol (abbreviated as PE-2,18), which is readily hydrolyzable by natural enzymes and biodegraded completely under industrial composting conditions. The degradability of PE-2,18 by microorganisms was assessed by a controlled laboratory composting test, monitoring the evolution of carbon dioxide formed by mineralization of the polyester according to ISO standard 14855–1. Remarkably, PE-2,18 mineralization reached 96 ± 2 % within only two months at 58 °C. By comparison, PE-18,18 exhibited only partial biodegradation in industrial composting, with around 30 % mineralization after two months under the same conditions [48]. More recently, it was reported that when a high molecular weight polymer formed by polycondensation of oligoethylene diol (C12) with oligoethylene diacid (C_{18}) was subjected to depolymerisation in methanol, dimer (~2 repeat units with M_n = 950 g/mol) was recovered, instead of a mixture of C_{18}-diester and C_{12}-diol. The recovered dimer was further used for a polycondensation reaction. The molecular weight of repolymerized polyester was comparatively lower (M_n = 25,000 g/mol) with respect to the virgin polymer, possibly due to the stoichiometric imbalance of the monomers after depolymerisation and workup [49].

Although the commercial availability of C_{18} diacid and C_{18} diol was announced in 2013, both are still rather expensive substrates [50]. Therefore, alternative ways to incorporate ester bonds in polyethylene-like structures are being developed. The most frequently used methods for synthesising polyethylene-like polymers containing ester bonds are based on the ring-opening polymerisation of macrocyclic lactones. Among the macrocyclic lactones, the most commonly used are pentadecalactone (PDL) [51], globalide (GL) hexadecalactone (HDL) [51], ambrettolide (Am) [52], butylene adipate [52], nondecanolate and tricosalactone [53].

The ring-opening polymerisation of these monomers enables the synthesis of long-chain aliphatic polyester that can match the properties of polyethylene. Different polymerisation methods, such as anionic, coordination or enzymatic polymerisation, were developed to achieve a polymer with a high molecular weight. The enzymatic polymerisation of PDL, in the presence of Novozyme-435, resulted in a polymer with a high molecular weight (65,000 g/mol) and dispersity close to the

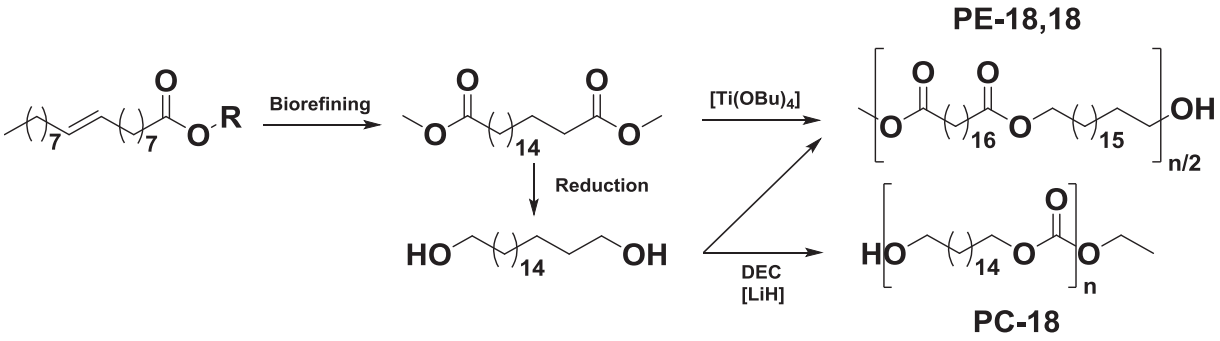


Fig. 3. Monomers synthesis starting from biorefining of plant or microalgae oils (examples shown: sunflowers, oil palms, microalgae Phaeodactylum tricornutum) for producing polyesters with a low density of in-chain functional groups as break points in a polyethylene chain [37].

theoretical value [54]. The same catalyst is also effective for the synthesis of polymer from HDL, GL or Am [55]. The degradation of polyglobalide (PGL) and polyambrettolide (PAm) was performed in the solution of PBS with and without the addition of *Pseudomonas cepacia* lipase. Hydrolytic or enzymatic degradation of PPDL in phosphate-buffered saline showed no mass loss, molar mass reduction, or change in crystallinity over 100 days, indicating high degradation resistance. Similar results were obtained for PGL and PAm. After 100 days of degradation in a 0.1 M solution of phosphate-buffered saline (pH = 7.4) containing 1 mg of *Pseudomonas cepacia* lipase, no changes in mass loss, crystallinity, or molecular masses were observed. The high hydrolytic stability of PPDL, PGL, and PAm results from their hydrophobic nature and low concentration of hydrolysable groups, which prevents the water penetration necessary to start the hydrolysis process [55]. Comparing degradability data across different studies is rather challenging due to the variations in experimental conditions. Depolymerisation of long-chain polycarbonates (PC-18) and long-chain polyesters (PE-18,18) prepared by polycondensation was conducted at 120°C in EtOH or MeOH, yielding highly pure monomers after recrystallisation. As break points in the chain, carbonate groups are particularly attractive as they yield crystallizable, long-chain diols and volatile dialkyl carbonates that can be easily separated. It was concluded that the approach outlined in Fig. 4 provides fully recyclable polyethylene-like materials suitable for high quality applications [37,56–59].

An alternative strategy to enhance the sustainability of polyethylene-like materials was reported by Buchard and co-workers through the incorporation of renewable xylose-derived building blocks into long-chain α,ω-unsaturated aliphatic polyesters and polyethers which were polymerized via acyclic diene metathesis (ADMET) polymerization. The resulting polymers combined bio-based carbohydrate-derived units with long methylene sequences, yielding polyethylene-like materials with molecular weights up to 71,000 g/mol after hydrogenation. Hydrolytic stability was evaluated under strongly acidic and alkaline conditions using 1 M HCl or 1 M NaOH aqueous solutions at room temperature for up to seven days. The study demonstrated that the incorporation of rigid xylose-derived units provides an additional structural handle to tune polymer properties and hydrolytic behaviour while maintaining the polyethylene-like character of the materials. These results demonstrate that incorporation of ester linkages provides selectively cleavable sites enabling chemical degradation while maintaining polyethylene-like properties during use. Furthermore, alkaline hydrolysis was proposed to generate the original carbohydrate-derived core together with 1,20-eicosanedioic acid, both of which could potentially be recovered and reused as feedstocks for subsequent polymer syntheses, highlighting a viable chemical recycling route [60]. Xia et al. developed a series of chemically recyclable polyethylene-like sulfur-containing polymers through the polymerization of carbonyl sulfide (COS), water, and long-chain α,ω-aliphatic diacrylates, including 1,9-nonamethylene glycol diacrylate, 1,12-dodecamethylene glycol diacrylate, 1,14-tetradecamethylene glycol diacrylate and 1,16-hexadecamethylene glycol diacrylate. Polymerization was carried out in a sealed autoclave using methyl-TBD (2 mol%) as an organocatalyst and a slight excess of COS (1.1 equiv.) relative to the diacrylate and water. Depending on the monomer structure, reactions were performed at 60–80°C for 4 h, affording high-molecular-weight polymers with M_n values up to 176,000 g/mol. Importantly, the authors demonstrated closed-loop chemical recycling of representative polymer. Alkaline hydrolysis was performed in water containing 50 wt% KOH relative to the polymer at 120°C for 48h, resulting in complete depolymerization and recovery of 1,9-nonanediol and 3,3′-thiodipropionic acid in 98% and 90% yields, respectively. Furthermore, representative polyethylene-like poly(monothiocarbonates) containing long hexadecamethylene segments underwent efficient methanolysis in the presence of $Ti(OBu)_4$ (0.042 mol%) at 120°C for 24h. This treatment afforded a repolymerizable, stoichiometric 1:1 mixture of dimethyl 3,3′-thiodipropanoate and 1,16-hexadecanediol in 99% yield. Subsequent repolymerization of the recovered monomers demonstrated the feasibility of a closed-loop chemical recycling process [61]. Li et al. reported an alternative approach toward degradable polyethylene mimics through ROMP copolymerization of 3,4-dehydro-ε-lactone and *cis*-cyclooctene followed by hydrogenation. By incorporating only a very low concentration of ester groups (ester: methylene units = 1:413), the resulting polyester retained PE-like properties. The degradability and circularity of the ester-containing PE mimics were demonstrated through base-catalyzed methanolysis of the PE-like materials. Depolymerization was carried out in a mixture of toluene, methanol, and sodium methoxide solution at 130°C, resulting in cleavage of ester bonds along the polymer backbone. The process converted the high-molecular-weight polymer into lower-molecular-weight oligomeric diols, diesters and hydroxy-esters. Subsequently, the recovered degradation products were repolymerized via melt polycondensation in the presence of 1,18-dimethyl octadecanedioate, 1,5-pentanediol and dibutyltin oxide (DBTO) catalyst, affording a recycled polyester with mechanical properties comparable to those of the original material [62]. Recently, Jian and co-workers reported PE-like materials containing sparsely distributed ester linkages prepared via ROMP copolymerization of cyclooctene with a tailored 16-membered unsaturated lactone, followed by exhaustive hydrogenation. Depending on the comonomer feed ratio, high-molecular-weight semicrystalline materials (M_n = 36,000 – 140,000 g/mol) containing 1.0–7.1 mol% ester groups were obtained. Importantly, the ester functionalities enabled complete depolymerization through methanolysis in the presence of MeOH and KOH, affording well-defined AB-type telechelic polyethylene macromonomers in 91–98% isolated yields. For example, a polymer with M_n = 140,000 g/mol was converted into a telechelic polyethylene macromonomer with M_n = 5,800 g/mol, while a material with M_n = 55,000 g/mol yielded a macromonomer with M_n = 12,000 g/mol. The recovered

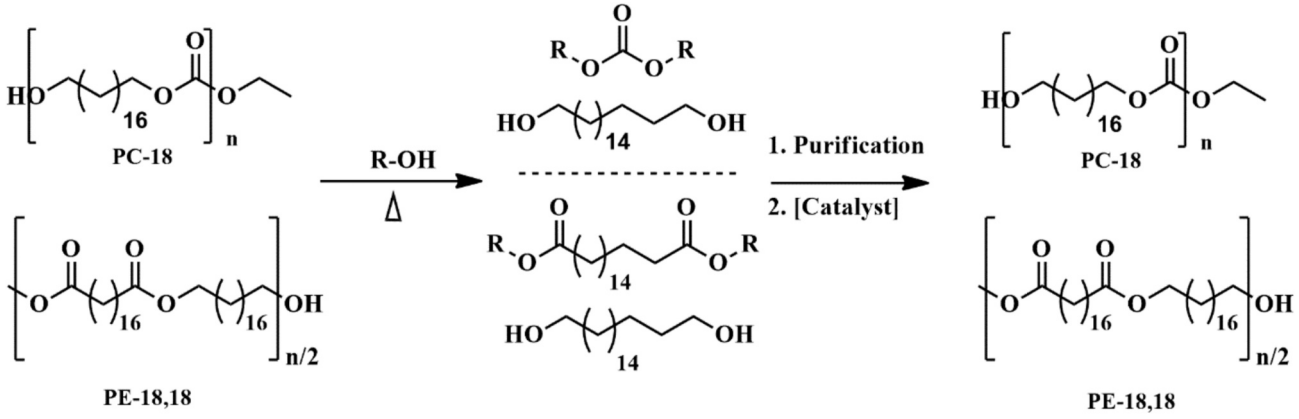


Fig. 4. Schematic overview of the chemical recycling of PC-18 and PE-18,18 via solvolysis and repolymerization [37].

macromonomers were subsequently repolymerized via $Ti(OBu)_4$catalyzed polycondensation at 180°C to regenerate high-molecular-weight PE-like materials in quantitative yield, establishing a closed-loop recycling process. Notably, the recycling cycle could be repeated multiple times without significant deterioration of thermal or mechanical properties, highlighting the potential of sparsely ester-functionalized polyethylene-like materials for circular polymer design [63]. Xu et al. introduced a mechanochemically triggered approach toward chemically recyclable polyethylene-like materials. Polar PE-like copolymers were synthesized via palladium-catalyzed coordination copolymerization of ethylene with a cyclobutene-fused ester (CBE) comonomer, yielding materials with tuneable thermomechanical properties while maintaining high crystallinity. Mechanical activation by ball milling (30 Hz, 60 min, 10 wt% BHT) induced cyclobutane ring opening and converted the pendant ester-containing units into in-chain ester functionalities. The resulting ester-containing polyethylene-like copolymers were subjected to ethanolysis. Degradation was performed using mechanically activated polymer, 1,5,7-Triazabicyclodec-5-ene (TBD) as an organocatalyst, ethanol, and xylene. The reaction mixture was degassed with argon for 15 min and subsequently heated in a sealed pressure tube at 120°C for 12h. Under these conditions, selective cleavage of the newly generated ester bonds occurred, leading to a substantial reduction in molecular weight and formation of multifunctional oligomers suitable for subsequent recycling and repolymerization [64]. Li et al. reported synthesis of polyethylene-like materials prepared via cyclic-acyclic monomer metathesis polymerization (CAMMP) of cyclooctene (COE) with diene comonomers containing photolabile *ortho*-nitrobenzyl (o-NB) units. Following hydrogenation, the resulting polymers exhibited thermal properties comparable to conventional polyethylene-like materials, and were efficiently photodegraded upon exposure to 365 nm UV irradiation (80 W). Cleavage of the incorporated *ortho*-nitrobenzyl groups induced backbone fragmentation, resulting in substantial reductions in molecular weight by nearly half within 96h of irradiation. Depending on polymer structure, the number-average molecular weight decreased from 10,000–12,400 g/mol before irradiation to 4,300 – 6,300 g/mol after 96h of UV exposure. These results demonstrate that incorporation of photolabile o-NB groups enables controlled light-triggered degradation of polyethylene-like materials without the need for additional chemical reagents. In addition to polyethylene-like thermoplastics, the authors also prepared photodegradable thermosets via cyclic-acyclic monomer metathesis polymerization using diene comonomers containing o-NB functionalities. Exposure to a 365 nm LED source (80 W) under ambient conditions induced cleavage of the o-NB groups, resulting in significant deterioration of the mechanical properties of the thermosets, while the corresponding non-degradable materials remained unaffected [65]. Data on the synthesis methods of polyethylene-like materials containing hydrolysable ketone, ester, carbonate, phosphate bonds, acetal are summarized in Table 1.

4. Polyethylene-like polymers containing carbonate bonds

Carbonate groups are another functional group enabling increased degradability and chemical recyclability of polyethylene-like materials. Currently, the most popular method for synthesising polycarbonates is based on transesterification reaction [68], metathesis polymerization [37,69] and ring-opening polymerisation of macrocyclic carbonates [70].

The first two methods were used by Mecking and co-workers to prepare polyethylene-like materials based on carbonate and acetal linkages (Fig. 5).

The synthesis of long-chain polycarbonate was carried out in a one-pot process, which included the transformation of longer diols (octadecan-1,18-diol, nonadecane-1,19-diol, and tricosane-1,23-diol) in reaction with dimethyl carbonate, in the presence of a catalytic amount of potassium bicarbonate [68]. Subsequently, the *in situ* prepared carbonates were condensed under reduced pressure to form the desired polymers. Nuclear Magnetic Resonans (NMR) and Size Exclusion Chromatography (SEC) analysis conducted in trichlorobenzene revealed that the molecular weight of the polymers ranged from 15,000 to 28,000 g/mol, with relatively high dispersity values for the polymers prepared from tricosane-1,23-diol, reaching up to 7.5. Hydrolysis studies were conducted using three different degradation media: a 20 wt% NaOH solution, a 2 wt% NaOH solution, and concentrated HCl. Applying a 2wt % NaOH solution did not lead to any significant changes in the weight and appearance of the pellets after 4 weeks at 40°C. The increase of NaOH concentration from 2 wt% to 20 wt% caused only 2.3 wt% mass loss of pellets in the case of the polymer prepared from octadecane-1,18-diol. The experiments performed in concentrated HCl solution gave similar results to those obtained with 20 wt% NaOH. The weight loss of the pellets was not significant and varied from 0.5 to 2.5% depending on chain length as shown in Fig. 6 E, F, G, H. Moreover, in another work it was shown, the polycarbonates containing segments of 12 to 15 carbon atoms in the main chain did not degrade in aqueous solutions with HCl (pH = 1) or NaOH (pH = 14), regardless of the carbon chain length [79].

The degradation of PE-like polycarbonates increased when they were place in high concentration of NaOH in methanol (10 M) at 40°C. After 15h, the pellets illustrated a weight reduction of 20% for polymers prepared from octadecane-1,18-diol and nonadecane-1,19-diol. This accelerated degradation was attributed to the more favorable interaction of polymers with a methanolic solution of NaOH. In parallel, Vanderhenst and co-workers carried out work related to PE-like polycarbonate from renewable sources [69]. They applied the same procedures as Mecking; however, by testing different compounds as catalysts for carbonate metathesis polymerisation, polymers with higher molar masses, up to 50,000 g/mol were obtained. The paper presented only the synthesis procedures and thermal properties; no information regarding the degradation of the polymers was provided. In the case of octadecane-1,18-diol, changing the catalyst from potassium bicarbonate to titanium (IV) butoxide ($Ti(BuO)_4$) allowed the synthesis of PE-like polycarbonate with a molar mass of 90,000 g/mol [37]. The high molar mass of the polymer ensures appropriate entanglement of the chains, enabling fabrication into filaments for 3D printing. Chemical recycling of the prepared filament was carried out in an ethanolic solution of KOH at 120°C, resulting in the formation of octadeca-1,18-diol and diethyl carbonate in stoichiometric amounts. The applied method did not require prior grinding of the filaments or mixing, and already after 1h, 99% of the starting materials were recovered. Moreover, the studies showed that increasing the temperature to 150°C results in depolymerisation of the materials after 24h using only ethanol, without the addition of KOH. The long-chain diol was crystallised from the reaction mixture, while diethyl carbonate, due to its volatility, was recovered through distillation. These straightforward procedures yielded octadeca-1,18-diol of high purity (>99%) and nearly quantitative amounts. The authors demonstrated that the reaction of these two recovered monomers leads to PE-like polycarbonate with a molar mass of 70,000 g/mol, which is slightly lower than the product derived from commercially available components. Further experiments proved that, using previously established conditions, allows for the selective degradation of PE-containing polycarbonate bond from a mixture of other polymers, such as native polyethylene and poly(ethylene terephthalate). In this process, octadeca-1,18-diol and diethyl carbonate are recovered, while polyethylene and poly(ethylene terephthalate) remain unaffected. It is worth noting that depolymerisation for chemical recycling can also be easily achieved through hydrolysis using water as the reaction medium, despite the heterogeneous nature of the aqueous mixtures containing both the hydrophobic polymer and monomer [37]. Furthermore, the recyclability of PE-like polycarbonate prepared by condensation of dodecane-1,12-diol with diphenyl carbonate was investigated. An ethanol solution where KOH was replaced with NaOH at a temperature of 150°C extended the degradation time necessary to recover 95% of high-purity dodecane-1,12-diol to 5h. In this case, instead of diphenyl carbamate, dimethyl carbonate was recovered and needed to be

Table 1
Representative polyethylene-like materials containing hydrolysable linkages: synthesis methods, molecular characteristics, and thermal properties.

Synthetic approach	Conditions	Molecular weight (M_n, g/mol)	Thermal properties	Ref.
Copolymerization of Etylene with CO	TBPO T = 135°C	2,00–4,300	T_m 70–117°C	[66]
Copolymerization of Etylene with CO	Ni (II) catalyst	54,000–216,000	T_m 133–134°C % cryst. 60 – 71 %	[27]
Copolymerization of Etylene with CO	TBPO 300 bar and 100–160°C	nd	T_m 99–114°C % cryst. 30–55%	[28]
Copolymerization of Etylene with CO	Ni (II) catalyst 10 bar 100°C	13,000–140,000	T_m 117–136°C	[30,31]
Copolymerization of Etylene and 3-ethylidene-6-vinyltetrahydro-2H-pyran-2-one with CO_2	DBU or BuLi or $BnNH_2$ or AIBN T = 100°C	5,000–19,000	T_m 100–102°C	[35]
Polycondensation of C_{26}–C_4 diol with C_{26}–C_{12} diacid	$(Bi(OTf)_3$ 90°C	8,000–14,000	T_m 74–104°C	[40]
Polycondensation of neopentyl glyco and adipic acid with carboxytelechelic PE	$Ti(iPrO)_4$ 220°C 2 mmHg	nd	T_m 120–130°C	[41]
	500 PSI 100°C, 30 min Grubbs 2nd generation	16,000–111,000	T_m 95–135°C	[42]
Polycondensation of C_{18} diester with C_{18} diol and branched monomer	180°C $Ti(OBu)_4$	36,000–50,000	T_m 74–99°C % cryst. 45–70%	[43]
Ring-opening metathesis polymerization of maleic acid and *cis*-cyclooctene	40°C Grubbs 2nd generation	52,000–688,000	T_m 129°C	[45]
Fluoride-Promoted Carbonylation Polymerization of Long-Chain Aliphatic Polycarbonates	CsF 110°C	24,000–42,000	T_m 70–79°C	[48]
Polycondensation of C_2-C_{10} diols with diphenyl carbamate	$NaOH/PPh_4OPh$	92,000–12,000	T_m 17–84°C	[48]
Polycondensation of C_{18} dimetyl ester and C_3-C_{12} diols	DBTO 150°C 7 torr	42,000–66,000	T_m 82–127°C	[49]
ROP of renewable macrolactones (pentadecalactone, 13-tetradecen-15-olide, globalide)	aluminum–selen complex	24,000–155,000	nd	[51]
	Novosyme-435	24,000–54,000	T_m 46–92°C	[55]
Acyclic diene metathesis of ω-unsaturated diester and dirthers of xylose	Grubbs 2nd generation RT	1,700–71,000	T_m 4–50°C	[60]
Polymerization of H_2O, COS, and diacrylates	DBU/TBD/MTBD 60 °C	27,000–176,000	T_m 35–44°C	[61]
Ring-opening metathesis polymerization of 3,4-dehydro-lactone with *cis*-cyclooctene	Hoveyda-Grubbs II catalyst RT	11,000–635,000	T_m 146–149°C	[62]
		36,000 – 140,000	T_m 109–136°C	[63]
Cyclic-acyclic monomers metathesis polymerization of *cis*-cyclooctene and diene	Ruthenium-catalyst 365 nm	43,000 – 123,000	T_m 101–128°C	[65]
Polycondensation C_{18} dimethylester with C_{18} diol	$Ti(OBu)_4$ or LiH RT	Up to 80,000	T_m 88°C	[37]
Dehydrogenation polymerization	ruthenium-catalyst	62,000 – 92,000	T_m 128°C	[38]
Polycondensation of diethyl triacontanedioate and triacontane-1,30- diol	$Ti(OiPr)_4/Sn(Bu)_4$ 185°C	nd	T_m 106–113°C	[39]
Polycondensation of $C_{2-4,6}$ diols, and C_{10-16} diacids	$Ti(OBu)_4$ 170°C	nd	T_m 57–94°C	[47]
Polycondensation of C_{18} dimetyl ester and ethylene glycol	DBTO 180°C 0.02 mbar	48,000	T_m 75°C	[67]
Polycondensation of diethoxymethane with C_{19}- and C_{23}-diol	pTSA 150°C	14,000–16,000	T_m 82–87°C	[68]
Polycondensation of dimethyl carbamate with C_{19}- and C_{23}-diol	K_2CO_3 110-200°C	15,000–28,000	T_m 89–97°C	
Carbonate metathesis polymerization of decane-1,10-diyl dimethyl dicarbonate	Na_2CO_3 100–200 °C	7,800–49,000	T_m 52–60°C	[69]

(*continued on next page*)

Table 1 (*continued*)

Synthetic approach	Conditions	Molecular weight (M_n, g/mol)	Thermal properties	Ref.
Ring-opening polymerization of Macrocyclic Carbonates	*t*-Bu-P_4 *t*-BuOK *t*-BuONa	9,800–52,000	nd	[70]
Acyclic diene metathesis of phosphate monomer	Grubbs castalyst generation	7,700–45,000	T_m −7–86°C % cryst. 0–35%	[71–75]
Esterification of nonadecane-1,19-diol and tricosane-1,23-diol with methylphosphonic dichloride or phenyl dichlorophosphate	Pyridine 60°C	110,000–200,000	T_m 13–87°C	[76]
Polycondensation of linear long-chain α,ω-diacetals	pTSA 80 °C	10,000–38,000	T_m 68–88°C	[77]
Acetal metathesis polymerization of linear and branched renewable polyacetals	pTSA 80 – 200 °C	8,800–27,500	T_m 10–67°C	[78]

nd – not determined.

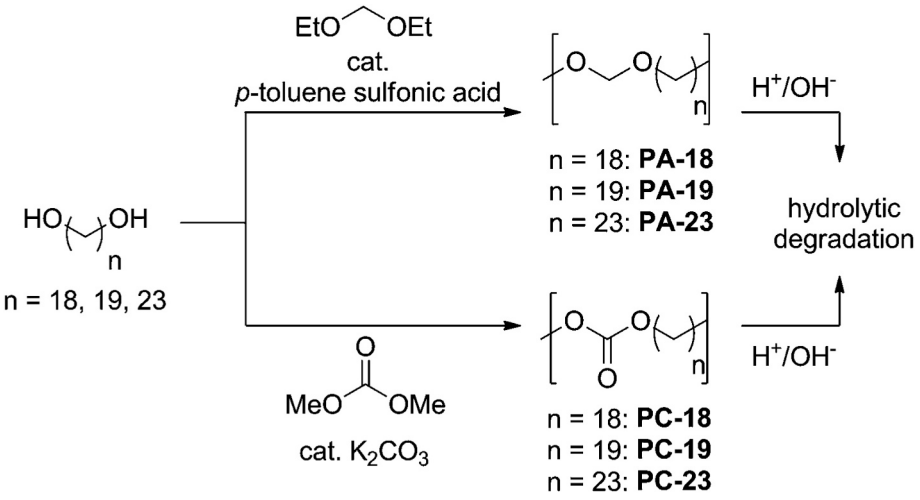


Fig. 5. Synthesis of polyethylene-like polycarbonate and polyacetal [68].

converted to the starting compound, which generates an additional step during the closed-loop recycling [48]. As expected, the decrease of the temperature of the concentrated NaOH solution to 120°C also extended the degradation time up to 36h, while retaining the high recovery of the diols, for the polycarbonates containing 13–15 carbon atoms in the main chain [79].

Odelius et al. [70] applied a different approach to synthesizing PE-like polycarbonates with chemical recyclability properties. In this work, the polycondensation between the diols composed of 4 to 10 carbons and dimethyl carbonate in the presence of sodium hydride as a catalyst leads to the formation of polycarbonates with molar masses up to 73,000 g/mol. The polymers obtained were subjected to polymerisation tests at elevated temperatures and high pressure. The optimization of the depolymerization procedures enabled the preparation of a library of macrocyclic carbonates, as illustrated in Fig. 7.

The highest yield was obtained for carbonates with the smallest rings (up to 10-membered rings), with yields decreasing as the ring size increased. For medium-sized rings (12- to 13-membered rings), the depolymerisation yield was moderate and resulted in the formation of a mixture of monomeric (9MC) and dimeric ($(9MC)_2$) carbonates. The study also demonstrated that the molar mass of the depolymerised polymers significantly influences the formation cyclic carbonate. Furthermore, increasing the depolymerisation temperature from 240°C to 280°C did not reduce the depolymerisation time but shifted the equilibrium toward the formation of 9MC. Under the applied conditions, the formation of macrocyclic carbonates occurred via transesterification depolymerisation rather than chain-end depolymerisation [70].

In conclusion, it is important to recognise that factors such as the size, shape, crystal morphology, and molecular weight of a given polycarbonate sample can significantly impact its degradation profile.

5. Polyethylene containing phosphate bonds

The introduction of phosphate ester bonds to polymers is of great interest in polymer chemistry due to their susceptibility to hydrolytic degradation. The incorporation of phosphate ester bonds enables the design of functional materials with tuneable architectures, offering a wide range of applications in drug delivery, gene therapy, thermoresponsive materials, and tissue engineering. One of the most common ways to introduce the phosphate bond to the macromolecules is the condensation of diols with phosphonic dichlorides. This method is a sustainable approach for preparing PE-like polyphosphates from long-chain dodecan-1,12-diol, nonadecane-1,19-diol, tricosane-1,23-diol, methylphosphonic dichloride, and phenyl dichlorophosphate. In a one-step reaction, with pyridine as a catalyst, polymers with a molar mass of up to 31,000 g/mol can be synthesised within 24h. Wurm et al. [71] applied another method for introducing phosphate ester bonds into the polymer chain, utilising acyclic diene metathesis polymerisation as shown in Fig. 8.

The monomer used in this study was synthesised through a straightforward esterification of commercially available phenyl dichlorophosphate with an alcohol containing 3 to 11 carbon atoms and a terminal double bond. The polymerisation of the prepared monomer was studied in bulk employing different generations of Grubbs catalyst. The process of optimising polymerisation conditions led to the synthesis of polymers with molar masses in the range of 7,200 to 57,000 g/mol. The highest molar masses were achieved with the monomer containing the longest carbon chain, as this eliminated the “negative neighbouring

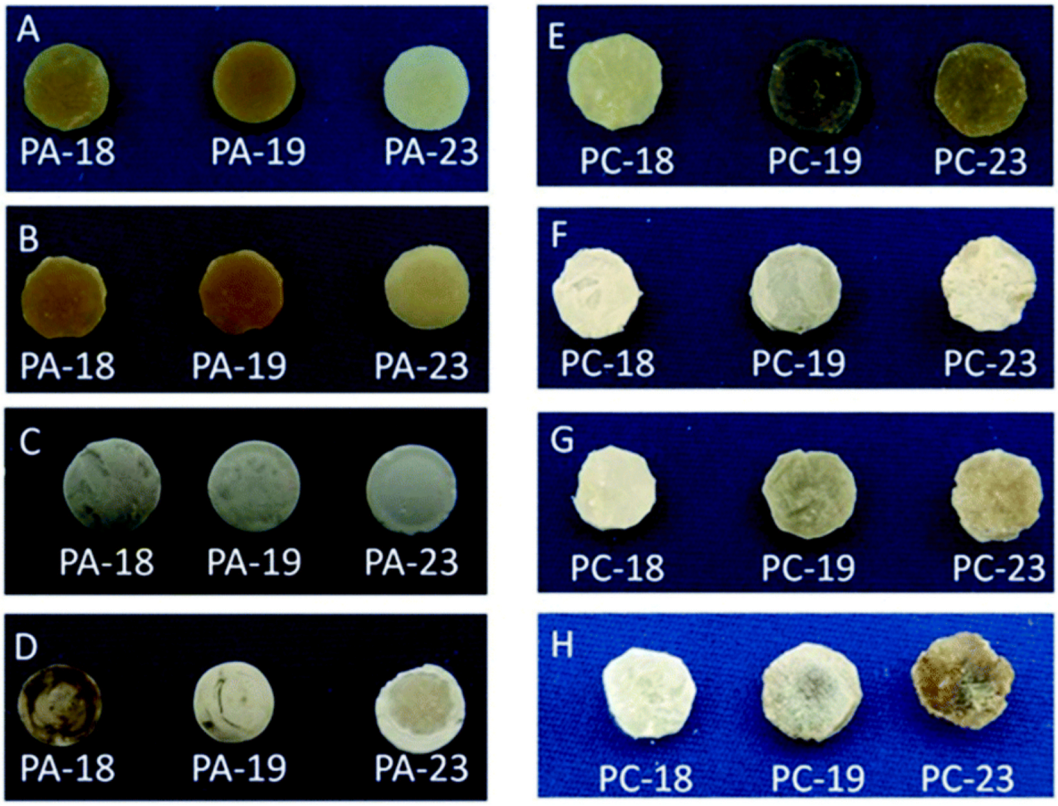


Fig. 6. Pellets of polyacetals PA-18, PA-19 and PA-23 before (A) and after hydrolytic degradation in 20 wt% aq. NaOH (B), 3 M aq. HCl (C), and concentrated aq. HCl (D). Pellets of polycarbonates PC-18, PC-19 and PC-23 before (E) and after hydrolytic degradation in 20 wt% aq. NaOH (F), 2 wt% aq. NaOH (G), and concentrated aq. HCl (H) [68].

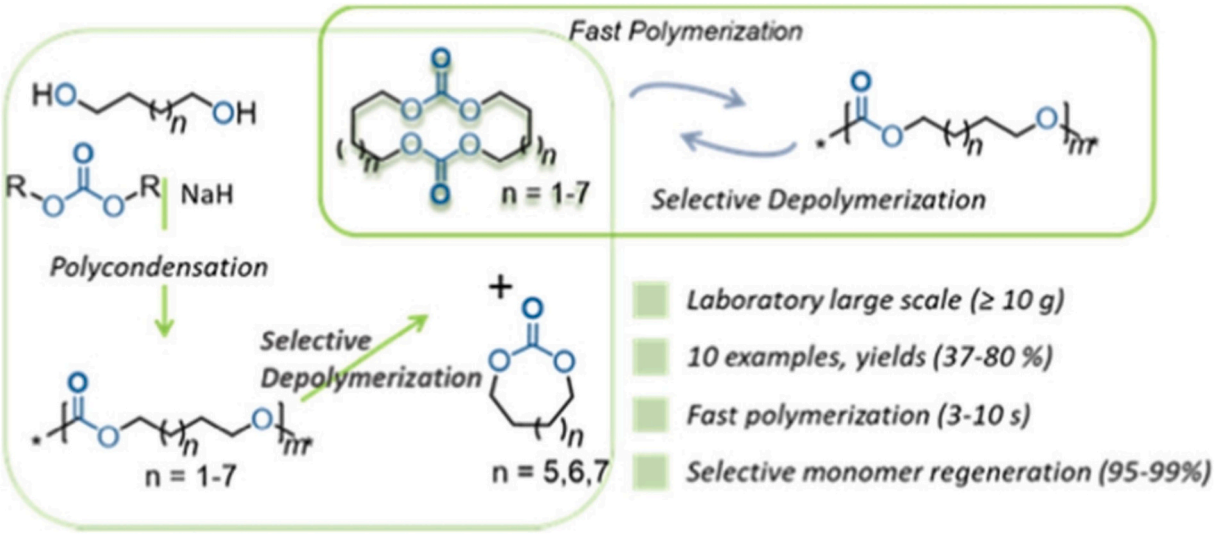


Fig. 7. Synthesis of PE-like polycarbonates with chemical recyclability based on macrocyclic carbonates [70].

group effect". Taking this effect into account, no polymer was obtained from the monomer synthesised from allyl alcohol. ^{31}P NMR showed only one signal at −7 ppm, corresponding to the isolated phosphate group [73]. By utilising ADMET, the authors overcame the limitations of the polycondensation reaction between diols and dichlorides, which is associated with the formation of P-O-P anhydride units, potentially affecting the hydrolytic degradation.

The hydrolysis process for the prepared PE-like polyphosphates was monitored over several months at constant temperatures to assess the mechanism of degradation. NMR spectra showed no changes in the signals corresponding to the P-OMe and alkyl chloride end groups, indicating that these groups do not degrade preferentially. However, in the corresponding ^{31}P NMR spectrum, the disappearance of the signal corresponding to the anhydride group (−0.29 ppm) was observed, suggesting that the hydrolysis proceeds through the cleavage of −P-O-P- units, instead of the P-O-C bond [73,76]. Based on the observation related to the faster hydrolysis of −P-O-P bonds, PE-like phosphate esters containing only anhydride-like bonds were prepared by Wurm et al.

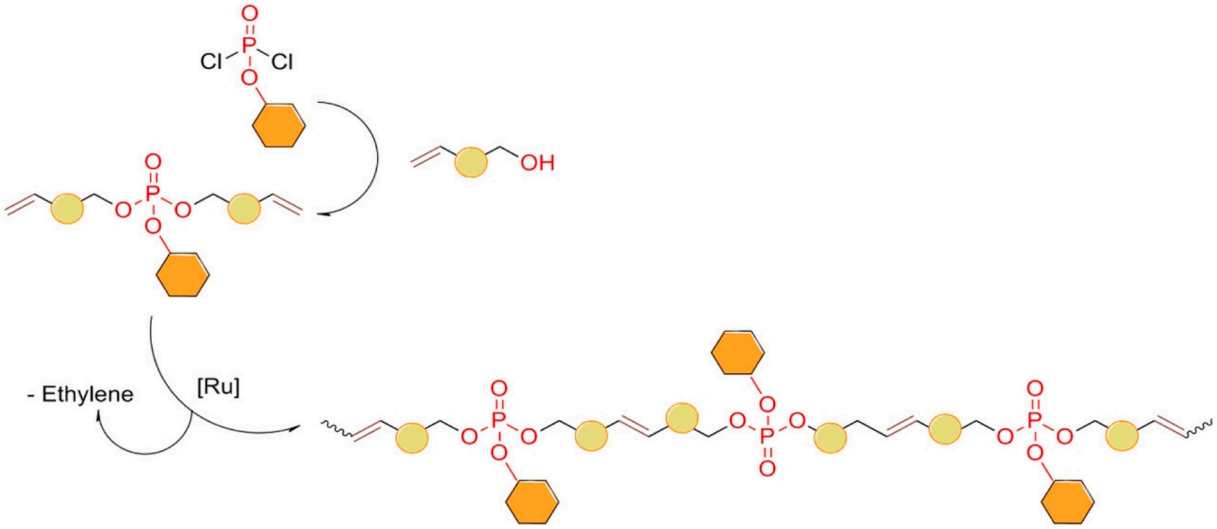


Fig. 8. Synthesis of unsaturated polyphosphoesters based on acyclic diene metathesis polymerization is described [71] (ACS, copyright 2012).

The novel pyrophosphate monomer was synthesised through a three-step reaction involving the esterification of dichlorophosphate with 10-undecen-1-ol, followed by hydrolysis of the intermediate and the coupling of two hydrolysed molecules using dicyclohexylcarbodiimide as shown in Fig. 9.

The previously established conditions for ADMET allowed the preparation of polymers with a molar mass of 13,000 g/mol and a dispersity of 1.9. ^{31}P NMR showed a single peak at −12.95 ppm, corresponding to pyrophosphate units. To evaluate the hydrolysis mechanism, films made from polymers with anhydride bonds (P1-H) and phosphate ester bonds (P2-H) were immersed in water solutions with different pH values, ranging from 0 to 13, at 37°C. The degradation process was monitored by ^{31}P NMR after dissolving the dried films at selected time intervals. The fastest hydrolysis of the P1-H film was

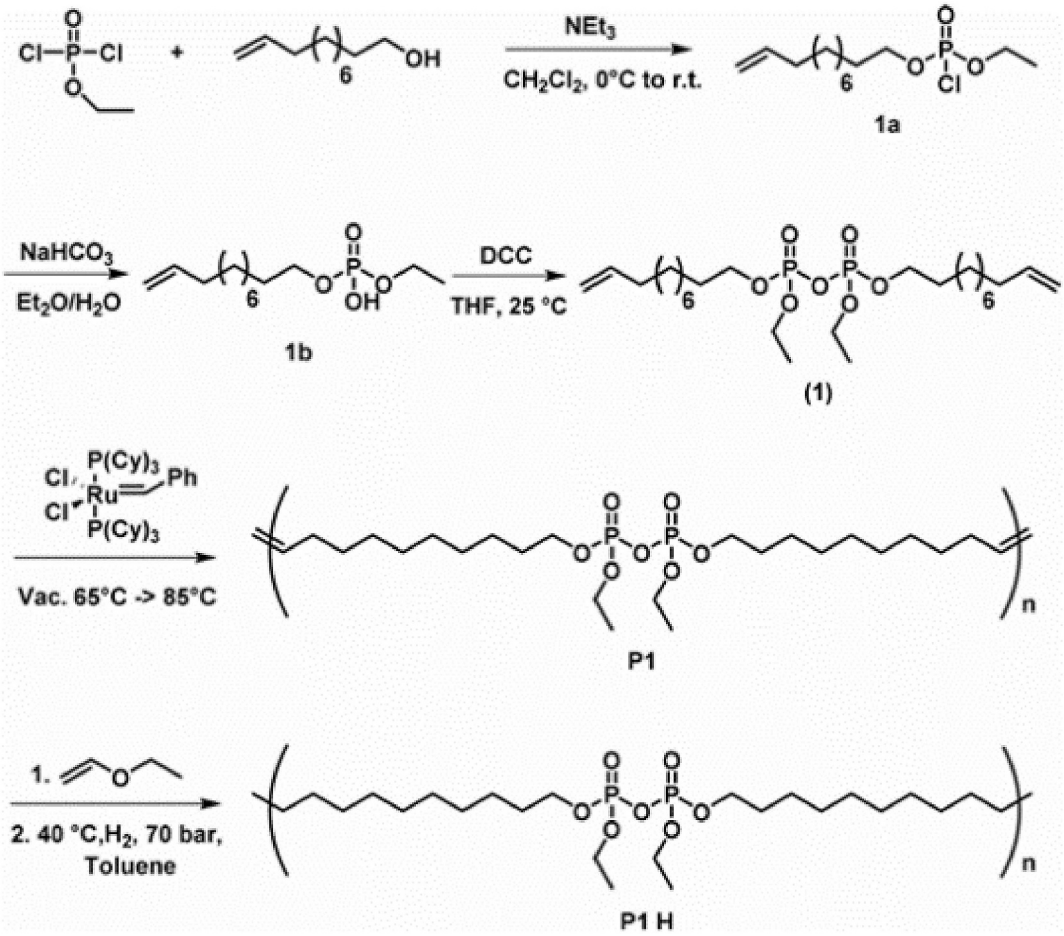


Fig. 9. Synthesis of Monomer 1 and Its Subsequent Polymerization by Acyclic Diene Metathesis (to P1) and Hydrogenation (to P1-H) [74].

observed at pH 13, with complete dissolution occurring after 2h. Reducing the pH from 13 to 7 led to rapid swelling and weight loss of the P1-H film after 7h. ^{31}P NMR of the dried film confirmed full hydrolysis of the anhydride bonds. Further reducing the pH to 0 showed no significant changes in sample weight, but ^{31}P NMR indicated a decrease in the signal corresponding to anhydride units and the appearance of a new signal corresponding to phosphoric acid. Interestingly, in a mixture of organic solvent (THF-d_8/D_2O, 5:1), the degradation of P1-H was significantly slower than in water. Under acidic conditions (in the presence of trifluoroacetic acid), the polymer completely degraded after two months, whereas in the presence of diisopropylethylamine, the degradation time was twice as long as in the acidic medium. In the case of the polymer film prepared from P2-H, no degradation was observed at neutral pH and 37°C. However, at pH 13, 70% of the diester underwent hydrolysis at the same temperature. Given the results of hydrolysis obtained for P1-H and P2-H films, the biodegradation process was also carried out in an aqueous environment with activated sludge from the local sewage plant. After 28 days, P1-H degradation reached a value comparable to starch (73%), which is considered an easily biodegradable polymer. At the same time, the P2-H showed legible biodegradation (3%), which is attributed to the phosphate ester bond, which does not degrade under neutral pH within 30 days [74]. The effect of substituting phosphorus with an ethoxy hydroxyl group on the degradation rate was also examined. The presence of a free hydroxyl group in the backbone allows hydrolysis to proceed via a different pathway, as shown in Fig. 10. In the presence of a strong base such as diazabicycloundecene, the new signal at 17.5, associated with the cyclic intermediate, appears in the ^{31}P NMR spectrum, suggesting that the degradation of the polymers occurred through an intermolecular nucleophilic attack. As the hydroxyl group was blocked, the peak at 17.5 ppm was not observed, excluding hydrolysis via an intermolecular nucleophilic attack. Additionally, the SEC measurement showed selective and faster degradation of a polymer with a hydroxyl pendant group in the blend with the polymer containing the benzyl group [72].

The effect of polyphosphates composed of long-chain diols on the hydrolytic degradation of a polymeric blend was investigated. The blends, consisting of polyphosphate-like PE and polyester-like PE (a copolymer of 1,18-octadecanoic acid and octadeca-1,18-diol), were

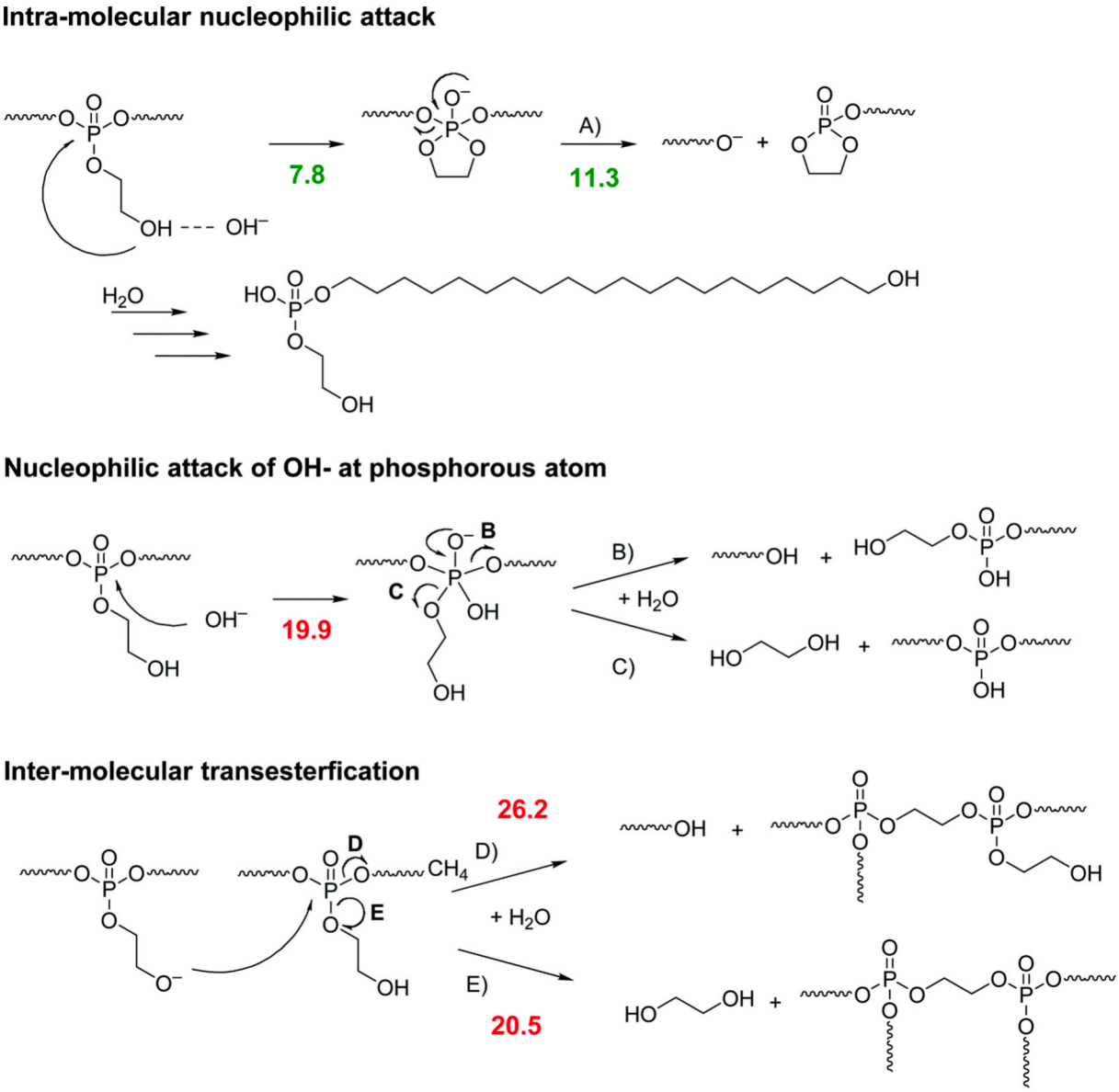


Fig. 10. Potential hydrolysis pathways for poly-1H either by intra or inter-molecular transesterification (the numbers indicate the Gibbs free energies for the rate-determining steps in kcal mol^{-1} for the respective pathway) [72].

exposed to pure water and phosphate buffer. ^{1}H and ^{31}P NMR analysis revealed that the materials hydrolysed into the corresponding long-chain diols and phosphoric acid after 4 months. The released phosphoric acid further accelerated the degradation of the polyester component of the blend, causing the molar mass to decrease from 50,000 g/mol to 7,000 g/mol. It was observed that the release of phosphoric acid from the polyphosphate part occurred within the first 4 months, and extending the time to 12 months did not significantly increase the degree of degradation. Moreover, no significant effect of varying the amount of polyphosphate polymer on the degradation rate of the blend was demonstrated [75].

6. Polyethylene containing acetal bonds

Recently, increasing attention has been devoted to sustainable polymers containing acetal functionalities due to their susceptibility to controlled depolymerization and chemical recycling. Reversible acetal chemistry has been successfully utilized for the preparation of chemically recyclable thermoplastics, where depolymerization enables efficient monomer recovery and closed-loop recycling. Furthermore, sustainable and bio-based polyacetals have emerged as an important class of polymers combining renewable feedstocks with tunable degradation behavior. Consequently, acetal-containing polymer systems represent a highly promising class of materials to replace conventional, non-degradable plastic [24,80]. Their inherent susceptibility to acid hydrolysis makes these linkages excellent candidates for driving controlled polymer degradation [81]. In recent years, researchers have focused on the introduction of these bonds to polyesters [82,83], or polyolefins [68] to enhance their degradability and recyclability. For the first time, the polyolefins containing acetal bonds in the main chain were prepared by Carothers et al. in 1935. Their approach utilized higher glycols, from hexamethylene to octadecamethylene, dibutyl acetals, and ferric chloride to prepare polyformals with long carbon sequences of up to 18 carbon atoms. The applied polycondensation conditions allow for the synthesis of the polymers with a molar mass of 2,500 g/mol. The authors claimed that these types of polymers can be difficult to depolymerise; however, no further details about depolymerisation conditions and characterisation of degradation products were provided by the authors [84]. Several researchers extended Carothers's concept. In this context, vegetable oils become an attractive source for preparing PE-like polymers due to the high content of long-chain α,ω-difunctional compounds C_{18} to C_{23}. The conversion of an internal double bond in the fatty acid by alkoxycarbonylation, followed by catalytic reduction of resulting diesters leads to the formation of a wide range of diols (mainly dodecane-1,12-diol (poly-1), nonadecane-1,19-diol (poly-2) and, tricosane-1,23-diol (poly-3)), which can be employed to the preparation of PE-like polymers with enhanced degradability. The two-step polycondensation involves the formation of diacetals from long-chain α,ω-diols, and further self-condensation polymerisation gives the polymers with molar masses up to 10^4 g/mol. Compact pellets with an average thickness of 1.1 mm and a diameter of 7.8 mm were prepared from polymers poly-1, poly-2, and poly-3, and subsequently exposed to aqueous solutions containing varying concentrations of hydrochloric acid. Under slightly acidic conditions (pH 6.9), no changes in the weight of the pellets were observed after 1 week of exposition. Applying a 3 M solution of HCl significantly accelerated the degradation of prepared material. Over periods of 92h and 116h, the polymeric pellets reduced their weight to 65% for the poly-2 and poly-3, respectively. In the case of poly-1, the applied conditions cause degradation of the major part of the material. The differences in the degradation rate are associated with the different hydrophobicity of the materials, which increases with the increase of carbon atoms in the polymeric chain. To better understand the degradation process, the hydrolysis of poly-1 was monitored by ^{1}H NMR in a mixture of deuterated HCl and THF-d_8. The signal belonging to the oxymethylene proton (4.65 ppm) gradually decreased while the multiples in the range of 4.7 to 4.5 ppm belonging to the diol appeared with time. However, the authors do not discuss in more detail the remaining degradation products [77].

Octadecan-1,18-diol, nonadecane-1,19-diol and tricosane-1,23-diol were also converted to the corresponding polyacetals by Mecking et al. [44,68]. One-pot synthesis based on the reaction of diols with diethoxy methane and further polycondensation under high vacuum led to the preparation of polyacetals with molar masses ranging from 16,000 to 28,000 g/mol. The prepared round-shaped pellets were subjected to three different water solutions: 20% NaOH, 3 M HCl, and concentrated HCl. In comparison to the previously published papers, the authors obtained different results from degradation measurement by applying the same degradation conditions. The experiments performed in the solution of 20 wt% NaOH showed no changes in the weight of the tested pellets after 16 days, proving the high stability of polyacetals in the employed environment. Unexpectedly, the changes in the weight of pellets exposed to 3 M HCl were not satisfactory and were in the range of 0.6–0.8%. The best result was observed for concentrated HCl, and observable changes in the materials up to 5.1% were observed for the polyacetals prepared from octadecane-1,18-diol. The increase in methylene units in the main chain to C_{23} resulted in a two-fold reduction in the degradation rate. The changes in the surface appearance were caused only by acidic conditions, which indicates that the prepared materials are not stable in the solution of HCl. The appearance of the tested materials before and after degradation tests is shown in Fig. 6A, B, C, D.

The linear and branched diols containing additional sulphur atoms in the main chain were designed to prepare polyethylene-like polyacetals [78]. The linear diol was synthesised in three steps: (1) reduction of 10-undecenoic acid to 10-undecen-1-ol by lithium aluminium hydride, (2) click reaction between the double bond of 10-undecen-1-ol and 2-mercaptoethanol and (3) oxidation of sulphide moieties to sulphone using m-chloroperbenzoic acid. The synthesis of linear and diols is presented in Fig. 11.

A highly effective Horner-Wadsworth-Emmons (modification of Wittig reaction) (HWE) reaction was used as a first step to obtain the branched diols with a sulphur atom in the main chain. Heptanal was converted to the α,β-unsaturated ester using the HWE reaction and then further modified by Michael addition or dimerised to reach unsaturated branched esters. After the reduction of diester, the desired branched diols were achieved in 80% yield. The structure of prepared polyacetals from biobased diols are presented in Fig. 12.

The synthesised diols were subjected to acid-catalysed acetal interchange polymerisation or acetal metathesis polymerisation. These types of step-growth polymerisations are driven by the removal of low molecular weight compounds, ensuring a high degree of polymerisation. This approach requires the transformation of diols into acetals and then condensation to polyacetals, removing the released dimethoxymethane in the process. The structures of all prepared polyacetals are presented in Fig. 12.

As in the previously described paper, the authors obtained the polyacetals with molar masses ranging from 8,000 to 27,000 g/mol. The lowest number of methylene units in the main chain of branched diols favours the formation of the cyclic structure, resulting in the synthesis of the polymers with the lowest molecular weight. However, the presence of sulfur in the main chain causes the formation of insoluble fractions (up to 30%) due to the cross-linking of macromolecules via bridges between the sulfur atoms. The degradation studies of the copolymers were performed in a mixture of chloroform and chloric acid at 25°C. The first part of the investigation assessed the effect of chloric acid concentration on the degradation rate. The changes in the molar mass were monitored by SEC measurement after one, two and four hours. The lowest acid concentration (0.02 mol/dm^3) caused a 60% reduction in the polymer molar mass, while a threefold increase in the concentration of chloric acid (0.06 mol/dm^3) led to an almost complete degradation (reduction up to 90%) as shown in Fig. 13.

The hydrolysis process was also monitored by ^{1}H NMR spectroscopy.

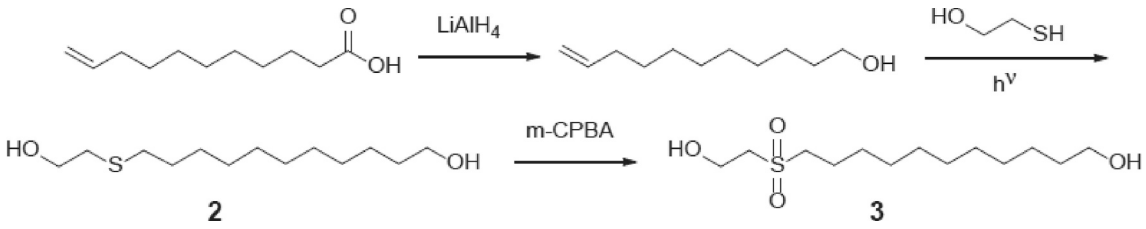


Fig. 11. Synthesis of diols from renewable 10-undecenoic acid [78].

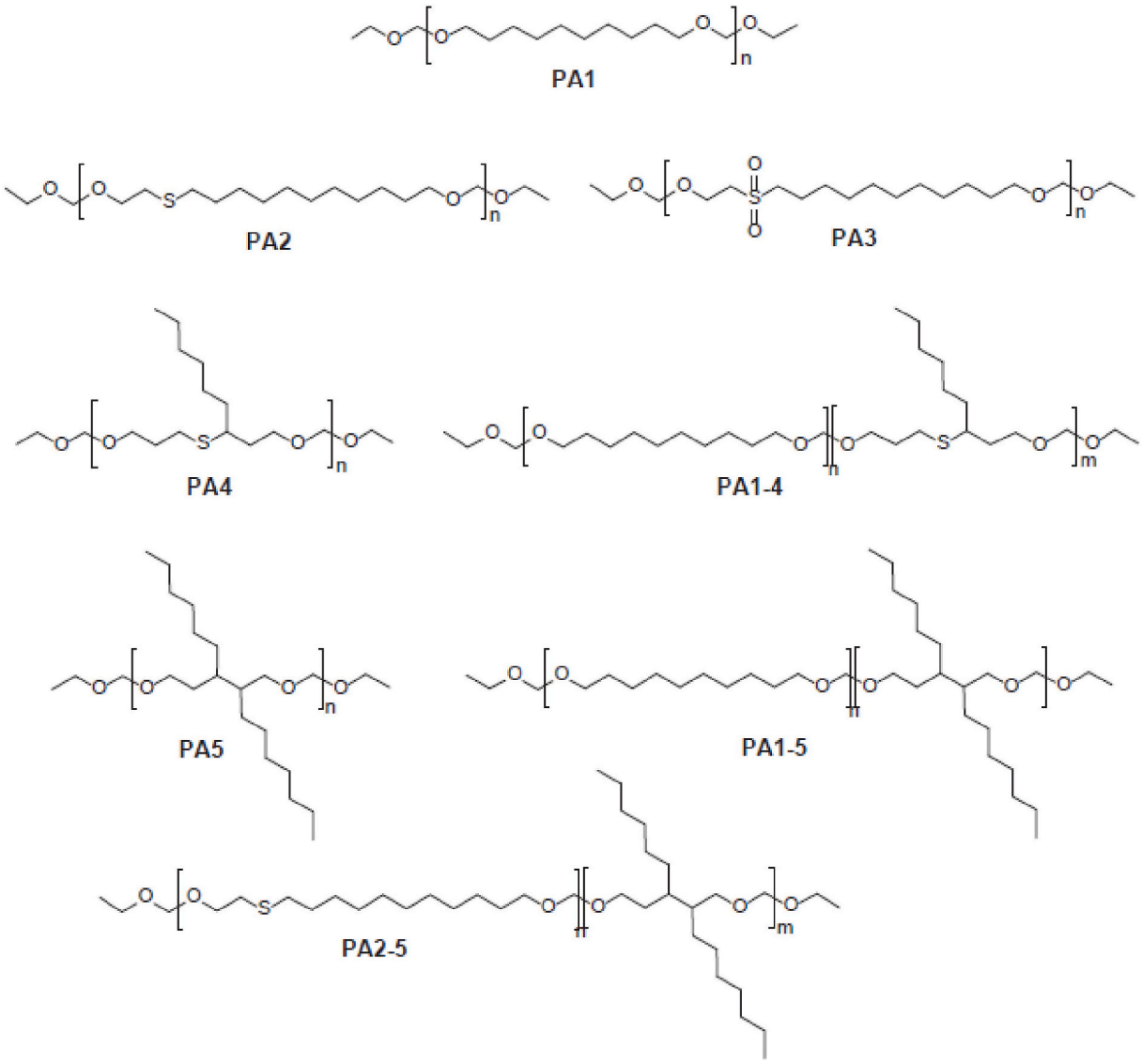


Fig. 12. Structure of linear brunched polyacetal from renewable biobased diols [78] (Elsevier, copyright 2018).

After 4h, in addition to the signal at 4.67 ppm belonging to oxymethylene units, new peaks were observed that could be attributed to free diols. The analyses showed no relationship between the degradation rate and the structure of the obtained polyacetals. All prepared polyacetals in the applied conditions (4h, 0.04 mol/dm^3) showed almost the same degradation pattern, reaching molar mass reduction values of approximately 80% [78].

7. Summary and outlook

Several laboratory-scale methods have been developed to introduce hydrolyzable groups into polyethylene chains to evaluate their degradation under various environmental conditions (Table 2). Some of these materials resemble polyethylene concerning thermal and mechanical properties, at the same time showing potential for enhanced degradability and/or chemical closed-loop recyclability. Aliphatic ester bonds are typically more easily biodegraded than C–C bonds therefore incorporation of these bonds into polyethylene chain should favor biodegradation. But the systematic knowledge in this area and especially the relationship between COOH/CH_2 ratio and (bio)degradability of long-chain polyester materials is limited and the search for suitable enzymatic systems is desirable. Described methods involve application of

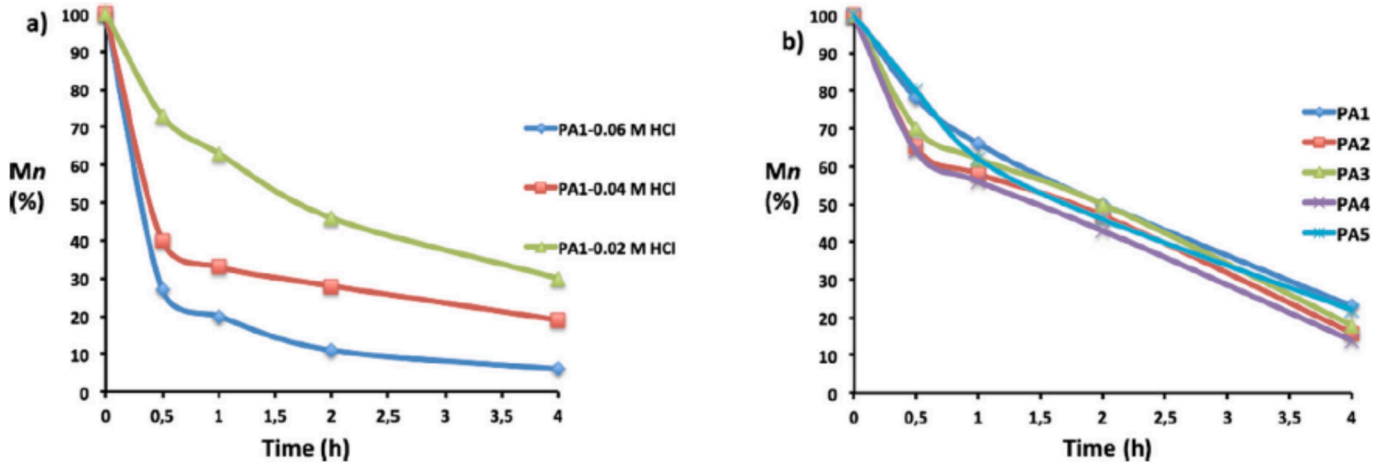


Fig. 13. Hydrolysis studies measured by (M_n/M_n initial) × 100 (a) of PA1 for different acid media concentrations (b) for the different polyacetals (PA1-PA5) in 0.04 M HCl [78] (Elsevier, copyright 2018).

Table 2
Representative polyethylene-like materials containing hydrolysable linkages: degradation methods, conditions, and products.

Cleavable group	Degradation method	Conditions	Products recovered	Yield	Reference
Ester	Biodegradation (industrial composting)	58°C, 2 months (ISO 14855–1)	CO_2 (mineralization)	96 ± 2%	[67]
	Methanolysis	MeOH/KOH	Telechelic PE macromonomers	91–98%	[63]
Monothiocarbonate	Alkaline hydrolysis	50 wt% KOH, 120°C, 48h	1,9-Nonanediol + 3,3′-thiodipropionic acid	98% / 90%	[61]
	Methanolysis	MeOH, $Ti(OBu)_4$ (0.042 mol%), 120°C, 24h	Dimethyl 3,3′-thiodipropanoate + 1,16-hexadecanediol	99%	[61]
Carbonate	Chemical recycling (ethanolysis)	EtOH/KOH, 120°C, 1h	Octadecane-1,18-diol + diethyl carbonate	99%	[37]
	Alcoholysis	EtOH, 150°C, 24h	Octadecane-1,18-diol + diethyl carbonate	Near-quantitative recovery	[37]
	Ethanolysis	NaOH/EtOH, 150°C, 5h	Dodecane-1,12-diol + dimethyl carbonate	95%	[48]
	Thermal depolymerization	240–280°C	Macrocyclic carbonates (monomeric and dimeric species)	Ring-size dependent	[48]
Pyrophosphate	Hydrolysis	Water, pH 13, 37°C	Phosphate-containing hydrolysis products	Complete dissolution after 2h	[74]
Phosphate ester	Biodegradation	Activated sludge, 28d	Biodegradation products	73% biodegradation	
	Hydrolysis	pH 13, 37°C	Hydrolyzed phosphate species	70% hydrolysis	
	Hydrolysis in blends	Water or phosphate buffer, 4 months	Long-chain diols + phosphoric acid	nd	[75]
Acetal	Acid hydrolysis	3 M HCl, 92–116h	Long-chain diols (confirmed by ^{1}H NMR)	Extensive degradation; polymer mass reduced to ~65% (poly-2/poly-3), major degradation for poly-1	[77]
	Acid hydrolysis	Concentrated HCl	Partial hydrolysis and surface erosion	Up to 5.1 wt% mass loss	[68]
	Acid hydrolysis	$CHCl_3$/HCl, 25°C, 0.06 M HCl, 4h	Free diols	~90% M_n reduction	[78]

medium-length methylene chains containing carboxylate or hydroxyl groups (diacids and/or diols). Long-chain monomers, both diacids and diols, may be obtained by catalytic conversion of plant oils, via biotechnological and purely chemical approaches. Classical organic syntheses of those long-chain PE monomers (diacids or diols) for polycondensation remain tedious and inefficient. Alternative approaches have been developed utilizing plant-oil-derived fatty acids. Several such straight-chain compounds occur naturally. Their purity, however, is low, and the removal of contaminants is difficult. The availability of long-chain monomers in the required purity is a key prerequisite for possible industrial applications. Independent of the method applied (classical organic synthesis or biotechnological approach) crucial issue is obtaining the long-chain products with a purity that meets the requirements of polycondensation reactions. Additional purification steps will obviously add to the overall effort and cost. Therefore, replacing existing polyethylene grades by long-chain polycondensates in the predictable future requires, first of all, developing cost-effective methods of large-scale production of long-chain polyethylene monomers (diacids or diols) of sufficient purity. Polyethylene-like polyester has limited degradation rates and an environmentally unfriendly chemical recycling pathway. Despite the in-chain ester groups, its high crystallinity and hydrophobicity reduce a tendency toward hydrolysis. A green enzymatic recycling process is also often constrained by the crystalline structures and the limited hydrolytic activity of the enzyme. At the same time, PE-like polycarbonates have emerged as particularly attractive candidates for circular materials design. Although their hydrolytic degradation under ambient conditions is limited by high crystallinity and hydrophobicity, they can undergo efficient depolymerization under relatively mild solvolytic conditions, enabling recovery of high-purity monomers and repeated polymer synthesis. These features make polycarbonates

especially promising for closed-loop recycling schemes. PE-like polyacetals provide a different route toward degradability. Their acid-labile acetal linkages enable selective degradation under acidic conditions while maintaining satisfactory stability in neutral and alkaline environments. Such stimuli-responsive behaviour may be advantageous for applications requiring degradation only under predefined conditions. However, a deeper understanding of the relationship between polymer microstructure, crystallinity, and degradation kinetics is still needed. PE-like polyphosphates appear particularly interesting from the perspective of environmental degradability. The presence of phosphate and pyrophosphate groups significantly increases hydrolytic susceptibility and may promote biodegradation. Furthermore, the release of phosphorus-containing degradation products may influence the degradation of other polymeric components in blends. Nevertheless, systematic studies addressing their long-term stability, degradation mechanisms, and recycling pathways remain limited. Overall, the examples discussed in this review demonstrate that the incorporation of ester, carbonate, acetal, phosphate, and other cleavable functionalities into predominantly methylene-based polymer backbones provides a powerful strategy for designing next-generation polyethylene-like materials. Future developments will likely focus on achieving a more precise balance between durability during service life and efficient degradation or chemical recycling at the end-of-life. In this context, controlling the density and distribution of cleavable groups, understanding the role of crystallinity and morphology in degradation processes, and developing scalable recycling technologies will be essential. Furthermore, recently emerging concepts based on dynamic covalent chemistry, mechanochemically activated degradation, sulfur-containing linkages, and side-chain polyethylene-like materials indicate that the field is rapidly expanding beyond conventional long-chain polycondensates. These advances are expected to broaden the range of sustainable polyethylene-like materials and contribute to the transition from linear plastics use toward a circular polymer economy.

Very recently, the concept of polyethylene-like materials has been expanded beyond polymers containing polyethylene-like main chains to include side-chain crystalline polymers bearing long linear alkyl pendants. In these systems, polyethylene-like properties originate primarily from the crystallization of densely packed alkyl side chains rather than from the polymer backbone itself. Particularly noteworthy are recyclable polypentenamers containing long crystalline side chains and depolymerizable polycyclopentene backbones. Owing to the low ceiling temperature of the cyclopentene-derived repeat units, these materials can undergo efficient chemical recycling through catalytic depolymerization to regenerate the corresponding monomers, which can subsequently be repolymerized, enabling full closed-loop recycling. Biomass-derived analogues containing up to 83 wt% renewable content have further demonstrated that polyethylene-like mechanical performance can be combined with both sustainable feedstocks and monomer recovery. In addition, comb-like polymers with long alkyl pendants have emerged as promising PE-like materials for advanced applications such as phase-change materials and hot-melt adhesives. Although these side-chain crystalline polymers fall outside the primary scope of the present review, they illustrate how future polyethylene-like materials may integrate polyethylene-like performance with chemical recyclability, renewable feedstocks, and circular material design principles [85–87].

CRediT authorship contribution statement

Karolina Cichoń: Writing – original draft, Visualization. **Malgorzata Basko:** Writing – original draft. **Przemysław Kubisa:** Writing – review & editing, Writing – original draft, Supervision. **Karin Odelius:** Writing – review & editing, Writing – original draft. **Minna Hakkarainen:** Writing – review & editing, Writing – original draft. **Bartłomiej Kost:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

B Kost thanks the National Science Centre, Poland, Miniatura 5 Grant No DEC-2021/05/X/ST5/00491.

Data availability

No data was used for the research described in the article.

References

[1] S.T. Schwab, M. Baur, T.F. Nelson, S. Mecking, Synthesis and deconstruction of polyethylene-type materials, Chem. Rev. 124 (2024) 2327–2351, https://doi.org/10.1021/acs.chemrev.3c00587.
[2] PET recycling: Review of the current available technologies and industrial perspectives, in: 2022: pp. 215–267. Doi: 10.1016/bs.ache.2022.09.003.
[3] Y. Wang, G. Feng, N. Lin, H. Lan, Q. Li, D. Yao, J. Tang, A review of degradation and life prediction of polyethylene, Appl. Sci. 13 (2023) 3045, https://doi.org/10.3390/app13053045.
[4] Y. Otake, T. Kobayashi, H. Asabe, N. Murakami, K. Ono, Biodegradation of low-density polyethylene, polystyrene, polyvinyl chloride, and urea formaldehyde resin buried under soil for over 32 years, J. Appl. Polym. Sci. 56 (1995) 1789–1796, https://doi.org/10.1002/app.1995.070561309.
[5] R. Ilianu, M. Hayashi, K. Lawrence, Z. Fedoruk, A. Ta, J.C. Thacker, V.C. Deroche, J. Greig, B.C. MacGillivray, The role of PETase in breaking down polyethylene plastics, FASEB J. 36 (2022), https://doi.org/10.1096/fasebj.2022.36.S1.R3666.
[6] K. Espinoza-García, A. Marcos-Fernández, R. Navarro, A. Ramírez-Hernández, J. E. Báez-García, G. Rangel-Porras, Polymerization of ε-caprolactone with degraded PET for its functionalization, J. Polym. Res. 26 (2019), https://doi.org/10.1007/s10965-019-1821-6.
[7] L. Umdagas, R. Orozco, K. Heeley, W. Thom, B. Al-Duri, Advances in chemical recycling of polyethylene terephthalate (PET) via hydrolysis: a comprehensive review, Polym. Degrad. Stab. 234 (2025) 111246, https://doi.org/10.1016/j.polymdegradstab.2025.111246.
[8] C.S. Marcelino, V.E. de S. Gomes, L. Marangoni Júnior, Post-consumer recycled PET: a comprehensive review of food and beverage packaging safety in Brazil, Polymers (Basel) 17 (2025) 594, https://doi.org/10.3390/polym17050594.
[9] J. Han, J. Zuo, G. Zillante, R. Chang, L. Du, A systematic review of PET circularity technologies and management strategies: challenges and future directions, Resour. Conserv. Recycl. 219 (2025) 108280, https://doi.org/10.1016/j.resconrec.2025.108280.
[10] V. Sinha, M.R. Patel, J.V. Patel, Pet waste management by chemical recycling: a review, J. Polym. Environ. 18 (2010) 8–25, https://doi.org/10.1007/s10924-008-0106-7.
[11] Y.-H.-V. Soong, M.J. Sobkowicz, D. Xie, Recent advances in biological recycling of polyethylene terephthalate (PET) plastic wastes, Bioengineering 9 (2022) 98, https://doi.org/10.3390/bioengineering9030098.
[12] H. Abedsoltan, A focused review on recycling and hydrolysis techniques of polyethylene terephthalate, Polym. Eng. Sci. 63 (2023) 2651–2674, https://doi.org/10.1002/pen.26406.
[13] R.R.A. Silva, C.S. Marques, T.R. Arruda, S.C. Teixeira, T.V. de Oliveira, Biodegradation of polymers: stages, measurement, standards and prospects, Macromol 3 (2023) 371–399, https://doi.org/10.3390/macromol3020023.
[14] A. Bher, Y. Cho, R. Auras, Boosting degradation of biodegradable polymers, Macromol. Rapid Commun. 44 (2023), https://doi.org/10.1002/marc.202200769.
[15] P.K. Barua, S.D. Bhagat, K.R. Pillai, H.D. Singh, J.N. Baruah, M.S. Iyengar, Comparative utilization of paraffins by a trichosporon species, Appl. Microbiol. 20 (1970) 657–661, https://doi.org/10.1128/am.20.5.657-661.1970.
[16] J.E. Potts, R.A. Clendinning, W.B. Ackart, W.D. Niegisch, The Biodegradability of Synthetic Polymers, in: Polymers and Ecological Problems, Springer US, Boston, MA, 1973: pp. 61–79. Doi: 10.1007/978-1-4684-0871-3_4.
[17] J.R. Haines, M. Alexander, Microbial degradation of high-molecular-weight alkanes, Appl. Microbiol. 28 (1974) 1084–1085, https://doi.org/10.1128/am.28.6.1084-1085.1974.
[18] T.L. Miller, M.J. Johnson, Utilization of normal alkanes by yeasts, Biotechnol. Bioeng. 8 (1966) 549–565, https://doi.org/10.1002/bit.260080408.
[19] A.-C. Albertsson, Z.G. Bánhidi, Microbial and oxidative effects in degradation of polyethene, J. Appl. Polym. Sci. 25 (1980) 1655–1671, https://doi.org/10.1002/app.1980.070250813.
[20] E. Byrne, L.G. Schaerer, D.G. Kulas, S.K. Ankathi, L.I. Putman, K.R. Codere, S. K. Schum, D.R. Shonnard, S.M. Techtmann, Pyrolysis-aided microbial biodegradation of high-density polyethylene plastic by environmental inocula enrichment cultures, ACS Sustain. Chem. Eng. 10 (2022) 2022–2033, https://doi.org/10.1021/acssuschemeng.1c05318.

[21] Y.-H. Hsieh, N. Weinberg, S. Wolfe, The neutral hydrolysis of methyl acetate — part 1. Kinetic experiments, Can. J. Chem. 87 (2009) 539–543, https://doi.org/10.1139/v09-003.

[22] D. McIntyre, F.A. Long, Acid-catalyzed hydrolysis of methylal. I. Influence of strong acids and correlation with hammett acidity function, J. Am. Chem. Soc. 76 (1954) 3240–3242, https://doi.org/10.1021/ja01641a050.

[23] C.A. Lewis, R. Wolfenden, Ether hydrolysis, ether thiolysis, and the catalytic power of etherases in the disassembly of lignin, Biochemistry 58 (2019) 5381–5385, https://doi.org/10.1021/acs.biochem.9b00698.

[24] M. Eck, S. Mecking, Closed-loop recyclable and nonpersistent polyethylene-like polyesters, Acc. Chem. Res. 57 (2024) 971–980, https://doi.org/10.1021/acs.accounts.3c00811.

[25] X. Li, N.A. Mahadas, M. Zhang, J. DePodesta, M. Stefik, C. Tang, Sustainable high-density polyethylene via chemical recycling: from modification to polymerization methods, Polymer (Guildf) 295 (2024) 126698, https://doi.org/10.1016/j.polymer.2024.126698.

[26] L.-H. Zeng, Z. Deng, L. Shiyong, Precision oligomeric building blocks toward chemically recyclable polyolefin-like materials, Precision Chem. 4 (2026) 92–106, https://doi.org/10.1021/prechem.5c00068.

[27] M. Baur, F. Lin, T.O. Morgen, L. Odenwald, S. Mecking, Polyethylene materials with in-chain ketones from nonalternating catalytic copolymerization, Science 374 (2021) (1979) 604–607, https://doi.org/10.1126/science.abi8183.

[28] T.O. Morgen, M. Baur, I. Göttker-Schnetmann, S. Mecking, Photodegradable branched polyethylenes from carbon monoxide copolymerization under benign conditions, Nat. Commun. 11 (2020) 3693, https://doi.org/10.1038/s41467-020-17542-5.

[29] M. Voccia, L. Odenwald, M. Baur, F. Lin, L. Falivene, S. Mecking, L. Caporaso, Mechanistic insights into Ni(II)-catalyzed nonalternating ethylene–carbon monoxide copolymerization, J. Am. Chem. Soc. 144 (2022) 15111–15117, https://doi.org/10.1021/jacs.2c04563.

[30] M. Baur, S. Mecking, Polyethylenes with combined in-chain and side-chain functional groups from catalytic terpolymerization of carbon monoxide and acrylate, ACS Macro Lett. 11 (2022) 1207–1211, https://doi.org/10.1021/acsmacrolett.2c00459.

[31] S. Tang, F.W. Seidel, K. Nozaki, High density polyethylenes bearing isolated in-chain carbonyls**, Angew. Chem. 133 (2021) 26710–26714, https://doi.org/10.1002/ange.202110957.

[32] G. Yonezaki, F.W. Seidel, K. Takahashi, K. Nozaki, Nickel-catalyzed selective incorporation of isolated in-chain carbonyls into ethylene/carbon monoxide copolymer using metal carbonyls as a carbonyl source, Bull. Chem. Soc. Jpn 96 (2023) 545–549, https://doi.org/10.1246/bcsj.20230073.

[33] M. Chen, S. Tang, Accessing degradable polyethylenes via catalytic ethylene copolymerization, Chem. – A Eur. J. (2026), https://doi.org/10.1002/chem.71033.

[34] C. Song, D. Yang, C. Wang, Z. Tang, Y. Long, Y. Zhang, Z. Jian, Aldehyde End-Capped Degradable Polyethylenes From Hydrogen-Controlled Ethylene/CO Copolymerization, Angew. Chem. Int. Ed. 63 (2024), https://doi.org/10.1002/anie.202410885.

[35] S. Tang, K. Nozaki, Advances in the synthesis of copolymers from carbon dioxide, dienes, and olefins, Acc. Chem. Res. 55 (2022) 1524–1532, https://doi.org/10.1021/acs.accounts.2c00162.

[36] W.J. Bailey, B. Gapud, Synthesis of Biodegradable Polyethylene, in: 1985: pp. 423–431. Doi: 10.1021/bk-1985-0280.ch029.

[37] M. Häußler, M. Eck, D. Rothauer, S. Mecking, Closed-loop recycling of polyethylene-like materials, Nature 590 (2021) 423–427, https://doi.org/10.1038/s41586-020-03149-9.

[38] Y. Zhao, E.M. Rettner, K.L. Harry, Z. Hu, J. Miscall, N.A. Rorrer, G.M. Miyake, Chemically recyclable polyolefin-like multiblock polymers, Science 382 (2023) (1979) 310–314, https://doi.org/10.1126/science.adh3353.

[39] I. Cho, K. Lee, Poly(triacontamethylene triacontanedioate) as polyethylene analogue: properties and enzymatic degradation, Macromol. Chem. Phys. 198 (1997) 861–869, https://doi.org/10.1002/macp.1997.021980316.

[40] C. Vilela, A.J.D. Silvestre, M.A.R. Meier, Plant oil-based long-chain C 26 monomers and their polymers, Macromol. Chem. Phys. 213 (2012) 2220–2227, https://doi.org/10.1002/macp.201200332.

[41] A.S. Arrington, J.R. Brown, M.S. Win, K.I. Winey, T.E. Long, Melt polycondensation of carboxytelechelic polyethylene for the design of degradable segmented copolyester polyolefins, Polym. Chem. 13 (2022) 3116–3125, https://doi.org/10.1039/D2PY00394E.

[42] Y.-J. Jang, S. Nguyen, M.A. Hillmyer, Chemically recyclable linear and branched polyethylenes synthesized from stoichiometrically self-balanced telechelic polyethylenes, J. Am. Chem. Soc. 146 (2024) 4771–4782, https://doi.org/10.1021/jacs.3c12660.

[43] S.T. Schwab, L.Y. Bühler, D. Schleheck, T.F. Nelson, S. Mecking, Correlation of enzymatic depolymerization rates with the structure of polyethylene-like long-chain aliphatic polyesters, ACS Macro Lett. 13 (2024) 1245–1250, https://doi.org/10.1021/acsmacrolett.4c00463.

[44] F. Stempfle, P. Ortmann, S. Mecking, Long-chain aliphatic polymers to bridge the gap between semicrystalline polyolefins and traditional polycondensates, Chem. Rev. 116 (2016) 4597–4641, https://doi.org/10.1021/acs.chemrev.5b00705.

[45] L.M. Pitet, M.A. Hillmyer, Carboxy-telechelic polyolefins by ROMP using maleic acid as a chain transfer agent, Macromolecules 44 (2011) 2378–2381, https://doi.org/10.1021/ma102975r.

[46] R.A. Pérez-Camargo, L. Meabe, G. Liu, H. Sardon, Y. Zhao, D. Wang, A.J. Müller, Even–odd effect in aliphatic polycarbonates with different chain lengths: from poly (hexamethylene carbonate) to poly (dodecamethylene carbonate), Macromolecules 54 (2021) 259–271, https://doi.org/10.1021/acs.macromol.0c02374.

[47] L. Zhou, P. Qin, L. Wu, B.G. Li, P. Dubois, Potentially biodegradable "short-long" type diol-diacid polyesters with superior crystallizability, tensile modulus, and water vapor barrier, ACS Sustain. Chem. Eng. 9 (2021) 17362–17370, https://doi.org/10.1021/acssuschemeng.1c06752.

[48] M. Zheng, W. Peng, Y.Y. Zhang, X. Zhang, W. Chen, Synthesis, characterization, and application of high-molecular-weight polyethylene-like polycarbonates: toward sustainable and recyclable fibers, Macromolecules 57 (2024) 7020–7030, https://doi.org/10.1021/acs.macromol.4c00933.

[49] N.A. Mahadas, A. Suhail, M.T. Sobczak, X. Li, K. Chen, K. Song, G. Dong, O. Kuksenok, C. Tang, High molecular weight biobased long-chain aliphatic polyesters with degradability: insights into mimicking polyethylene, Macromolecules 58 (2025) 4070–4081, https://doi.org/10.1021/acs.macromol.5c00176.

[50] Inc. Elevance Renewable Sciences, Elevance Announces Commercial Availability of Bio-Based Inherent^{TM} C18 Diacid, (2013).

[51] I. Van Der Meulen, E. Gubbels, S. Huijser, R. Sablong, C.E. Koning, A. Heise, R. Duchateau, Catalytic ring-opening polymerization of renewable macrolactones to high molecular weight polyethylene-like polymers, Macromolecules 44 (2011) 4301–4305, https://doi.org/10.1021/ma200685u.

[52] M.P.F. Pepels, M. Bouyahyi, A. Heise, R. Duchateau, Kinetic investigation on the catalytic ring-opening (co)polymerization of (macro)lactones using aluminum salen catalysts, Macromolecules 46 (2013) 4324–4334, https://doi.org/10.1021/ma400731c.

[53] D. Myers, T. Witt, A. Cyriac, M. Bown, S. Mecking, C.K. Williams, Ring opening polymerization of macrolactones: high conversions and activities using an yttrium catalyst, Polym. Chem. 8 (2017) 5780–5785, https://doi.org/10.1039/C7PY00985B.

[54] M.L. Focarete, M. Scandola, A. Kumar, R.A. Gross, Physical characterization of poly (ω-pentadecalactone) synthesized by lipase-catalyzed ring-opening polymerization, J. Polym. Sci. B Polym. Phys. 39 (2001) 1721–1729, https://doi.org/10.1002/polb.1145.

[55] I. Van Der Meulen, M. De Geus, H. Antheunis, R. Deumens, E.A.J. Joosten, C. E. Koning, A. Heise, Polymers from functional macrolactones as potential biomaterials: enzymatic ring opening polymerization, biodegradation, and biocompatibility, Biomacromolecules 9 (2008) 3404–3410, https://doi.org/10.1021/bm800898c.

[56] J. Fernández, A. Etxeberria, A.L. Varga, J.-R. Sarasua, Synthesis and characterization of ω-pentadecalactone-co-ε-decalactone copolymers: evaluation of thermal, mechanical and biodegradation properties, Polymer (Guildf) 81 (2015) 12–22, https://doi.org/10.1016/j.polymer.2015.11.001.

[57] J. Liu, Z. Jiang, S. Zhang, C. Liu, R.A. Gross, T.R. Kyriakides, W.M. Saltzman, Biodegradation, biocompatibility, and drug delivery in poly(ω-pentadecalactone-co-p-dioxanone) copolyesters, Biomaterials 32 (2011) 6646–6654, https://doi.org/10.1016/j.biomaterials.2011.05.046.

[58] K. Czifrák, C. Lakatos, M. Árpád Kordován, L. Nagy, L. Daróczi, M. Zsuga, S. Kéki, Block copolymers of poly(ω-pentadecalactone) in segmented polyurethanes: novel biodegradable shape memory polyurethanes, Polymers (Basel) 12 (2020) 1928, https://doi.org/10.3390/polym12091928.

[59] J. Fernández, A. Etxeberria, J.-R. Sarasua, Synthesis and properties of ω-pentadecalactone-co-δ-hexalactone copolymers: a biodegradable thermoplastic elastomer as an alternative to poly(ε-caprolactone), RSC Adv. 6 (2016) 3137–3149, https://doi.org/10.1039/C5RA23404B.

[60] M. Piccini, J. Lightfoot, B.C. Dominguez, A. Buchard, Xylose-based polyethers and polyesters via ADMET polymerization toward polyethylene-like materials, ACS Appl. Polym. Mater. 3 (2021) 5870–5881, https://doi.org/10.1021/acsapm.1c01095.

[61] Y. Xia, X. Yue, Y. Sun, C. Zhang, X. Zhang, Chemically recyclable polyethylene-like sulfur-containing plastics from sustainable feedstocks, Angew. Chem. Int. Ed. 62 (2023), https://doi.org/10.1002/anie.202219251.

[62] X. Li, A. Suhail, N.A. Mahadas, M. Zhang, Z. Hu, M. Stefik, O. Kuksenok, C. Tang, Modulating polyethylene mimics with degradability via synthesis and modeling, Macromolecules 58 (2025) 2094–2105, https://doi.org/10.1021/acs.macromol.5c00039.

[63] P.-A. Chen, X. Kang, K. Li, Z. Jian, Tailored synthesis of circular polyolefins, Nat. Sustain. 8 (2025) 422–431, https://doi.org/10.1038/s41893-025-01524-w.

[64] M. Xu, P. Liu, C. Chen, T. Choi, Mechanically triggered chemical recyclable polyethylene-like materials, Angew. Chem. Int. Ed. 65 (2026), https://doi.org/10.1002/anie.202522618.

[65] W. Li, D. Liao, Y. Li, G. Si, C. Chen, Cyclic-acyclic monomers metathesis polymerization to access photodegradable polydicyclopentadiene and polyethylene-like materials, Sci. China Chem. 67 (2024) 1311–1315, https://doi.org/10.1007/s11426-023-1883-4.

[66] M.M. Brubaker, D.D. Coffman, H.H. Hoehn, Synthesis and characterization of ethylene/carbon monoxide copolymers, a new class of polyketones [1], J. Am. Chem. Soc. 74 (1952) 1509–1515, https://doi.org/10.1021/ja01126a047.

[67] M. Eck, S.T. Schwab, T.F. Nelson, K. Wurst, S. Iberl, D. Schleheck, C. Link, G. Battagliarin, S. Mecking, Biodegradable high-density polyethylene-like material, Angew. Chem. 135 (2023) 1–4, https://doi.org/10.1002/ange.202213438.

[68] P. Ortmann, I. Heckler, S. Mecking, Physical properties and hydrolytic degradability of polyethylene-like polyacetals and polycarbonates, Green Chem. 16 (2014) 1816–1827, https://doi.org/10.1039/c3gc42592d.

[69] R. Vanderhenst, S.A. Miller, Polycarbonates from biorenewable diols via carbonate metathesis polymerization, Green Mater. 1 (2013) 64–78, https://doi.org/10.1680/gmat.12.00022.

[70] J. Huang, P. Olsén, E. Svensson Grape, A.K. Inge, K. Odelius, Simple approach to macrocyclic carbonates with fast polymerization rates and their polymer-to-monomer regeneration, Macromolecules 55 (2022) 608–614, https://doi.org/10.1021/acs.macromol.1c02225.
[71] F. Marsico, M. Wagner, K. Landfester, F.R. Wurm, Unsaturated polyphosphoesters via acyclic diene metathesis polymerization, Macromolecules 45 (2012) 8511–8518, https://doi.org/10.1021/ma301508s.
[72] T.P. Haider, O. Suraeva, I. Lieberwirth, P. Paneth, F.R. Wurm, RNA-inspired intramolecular transesterification accelerates the hydrolysis of polyethylene-like polyphosphoesters, Chem. Sci. 12 (2021) 16054–16064, https://doi.org/10.1039/d1sc05509g.
[73] E.M. Alexandrino, S. Ritz, F. Marsico, G. Baier, V. Mailänder, K. Landfester, F. R. Wurm, Paclitaxel-loaded polyphosphate nanoparticles: a potential strategy for bone cancer treatment, J. Mater. Chem. B 2 (2014) 1298, https://doi.org/10.1039/c3tb21295e.
[74] H.T. Tee, I. Lieberwirth, F.R. Wurm, Aliphatic long-chain polypyrophosphates as biodegradable polyethylene mimics, Macromolecules 52 (2019) 1166–1172, https://doi.org/10.1021/acs.macromol.8b02474.
[75] M. Eck, L. Bernabeu, S. Mecking, Polyethylene-like blends amenable to abiotic hydrolytic degradation, ACS Sustain. Chem. Eng. 11 (2023) 4523–4530, https://doi.org/10.1021/acssuschemeng.2c07537.
[76] H. Busch, S. Majumder, G. Reiter, S. Mecking, Semicrystalline long-chain polyphosphoesters from polyesterification, Macromolecules 50 (2017) 2706–2713, https://doi.org/10.1021/acs.macromol.7b00243.
[77] S. Chikkali, F. Stempfle, S. Mecking, Long-chain polyacetals from plant oils, Macromol. Rapid Commun. 33 (2012) 1126–1129, https://doi.org/10.1002/marc.201200226.
[78] A. Moreno, G. Lligadas, J.C. Ronda, M. Galià, V. Cádiz, Linear and branched acetal polymers from castor oil via acetal metathesis polymerization, Eur. Polym. J. 108 (2018) 348–356, https://doi.org/10.1016/j.eurpolymj.2018.09.013.
[79] Z.W. Xu, J.L. Pan, J. Xu, W.M. Cheng, Z.L. Li, C. Cheng, Recyclable, reprocessable, anticorrosive, and hydrolysis-resistant long-chain aliphatic polycarbonates as polyethylene-like materials, ACS Appl. Polym. Mater. 6 (2024) 1551–1562, https://doi.org/10.1021/acsapm.3c02804.
[80] A.C. Renner, S.S. Thorat, M.P. Sibi, Synthesis of biobased polyacetals: a review, RSC Sustain. 2 (2024) 3669–3703, https://doi.org/10.1039/D4SU00488D.
[81] B.A. Abel, R.L. Snyder, G.W. Coates, Chemically recyclable thermoplastics from reversible-deactivation polymerization of cyclic acetals, Science 373 (2021) (1979) 783–789, https://doi.org/10.1126/science.abh0626.
[82] B. Kost, M. Basko, Synthesis and properties of l-lactide/1,3-dioxolane copolymers: preparation of polyesters with enhanced acid sensitivity, Polym. Chem. 12 (2021) 2551–2562, https://doi.org/10.1039/d1py00358e.
[83] L. Aristizábal-Lanza, S.V. Mankar, C. Tullberg, B. Zhang, J.A. Linares-Pastén, Comparison of the enzymatic depolymerization of polyethylene terephthalate and AkestraTM using Humicola insolens cutinase, Front. Chem. Eng. 4 (2022) 1–13, https://doi.org/10.3389/fceng.2022.1048744.
[84] J.W. Hill, W.H. Carothers, Cyclic and polymeric formals 1, J. Am. Chem. Soc. 57 (1935) 925–928, https://doi.org/10.1021/ja01308a045.
[85] X.-L. Chen, S.-S. Li, Q. Wu, B. Sun, J. Xu, Z.-L. Li, C. Cheng, Ring-opening metathesis polymerization of tricyclic oxanorbornene derivatives enables partially renewable comb-like polymers as phase change materials and hot-melt adhesives, ACS Appl. Polym. Mater. 7 (2025) 4329–4339, https://doi.org/10.1021/acsapm.5c00038.
[86] L. Chen, Z. Wang, E. Fang, Y. Guo, Z. Liu, W. Song, H. Li, J. Xu, Z. Fan, M. A. Winnik, S. Song, Recyclable polypentenamers with precise crystallization and versatile functionalization, Macromolecules 58 (2025) 1048–1059, https://doi.org/10.1021/acs.macromol.4c02655.
[87] Z. Wang, E. Fang, L. Chen, Y. Guo, Z. Fan, S. Song, Recyclable biomass-derived polyethylene-like plastics, Macromolecules 58 (2025) 9712–9723, https://doi.org/10.1021/acs.macromol.5c01976.