

Abstract

A new method of the controlled copolymerization of lactides with the six-membered cyclic aliphatic carbonates, that enables synthesis of cyclic carbonate / lactide copolymers with the designed microstructure and the predicted molar mass has been elaborated. Thus, a synthetic pathway has been paved giving an access to a broad spectrum of the biodegradable and biocompatible materials with diversified thermo-mechanical properties.

First of all, it has been shown that homopolymerization of trimethylene carbonate (TMC) initiated with $\text{Al}(\text{O}i\text{Pr})_3$ – a typical anionic-coordination derivative is inevitably accompanied by chain-transfer reactions on the growing macromolecule, leading to molar mass distribution broadening of the resultant poly(TMC), disproportionation of the poly(TMC) end-groups and formation of an undesired fraction of the cyclic oligomers. Substitution of two isopropoxy groups in the initiator molecule for the bidentate chiral ligand [(*S*)-(+)- or (*R*)-(-)-2,2'-[1,1'-binaphthyl-2,2'-diylbis-(nitrylomethylidene)]-diphenolate] (SBO_2) resulted in practically quantitative elimination of the transesterification side-reaction in the polymerization of TMC initiated with $\text{SBO}_2\text{Al-O}i\text{Pr}$.

With regard to a lack of the reliable temperature dependencies of the equilibrium temperature in polymerizations of TMC and 2,2-dimethyltrimethylene carbonate (DTC) the standard enthalpies and entropies of polymerization of these monomers has been determined. Besides, kinetics of TMC and DTC homopolymerization initiated with $\text{SBO}_2\text{Al-O}i\text{Pr}$ was studied and the corresponding rate constants of the elementary propagation reaction have been determined.

Elimination of the transesterification side-reaction from copolymerizations of cyclic aliphatic carbonates with lactide (LA) opened a way for the controlled synthesis of the block copolymers of TMC or DTC with LA. Di- and triblock copolymers have been obtained for the first time in a sequential copolymerization employing the living polylactide (PLA*) as the macroinitiator of cyclic carbonate polymerization. Besides, it has been shown that PLA and polycarbonate blocks are connected by a short fragment of the gradient copolymer. Formation of the latter resulted from a presence of the unreacted comonomer being in equilibrium with its living homopolymer. This is in contrast to a widespread opinion, that PLA* is not able to initiate polymerization of the cyclic carbonates at all or that copolymerization (if any) is extremely slow and results in copolymers of the statistical or random structure.

Studies of the simultaneous polymerization of L,L-LA and TMC pointed out for the first time to a direct influence of a configuration of the chiral initiator in the copolymerization of the achiral carbonate with the otherwise chiral L,L-LA on the resulting copolymer microstructure. Copolymer block lengths analysis in a function of comonomers conversion and ^{13}C -NMR spectra in the carbonyl carbons absorption range revealed that copolymers are formed having poly(L,L-LA-*stat*-TMC) and poly(TMC-*grad*-L,L-LA)-*b*-poly(L,L-LA) microstructures in copolymerizations initiated with (*S*)-(+)- $\text{SBO}_2\text{Al-O}i\text{Pr}$ and (*R*)-(-)- $\text{SBO}_2\text{Al-O}i\text{Pr}$, respectively.

Concluding, results reported in the present doctoral thesis show that application of the initiator, that bears a sterically hindered chiral ligand provides a method of the precision, controlled synthesis of a wide spectrum of cyclic aliphatic carbonate / lactide copolymer structures - from blocky to almost random ones.