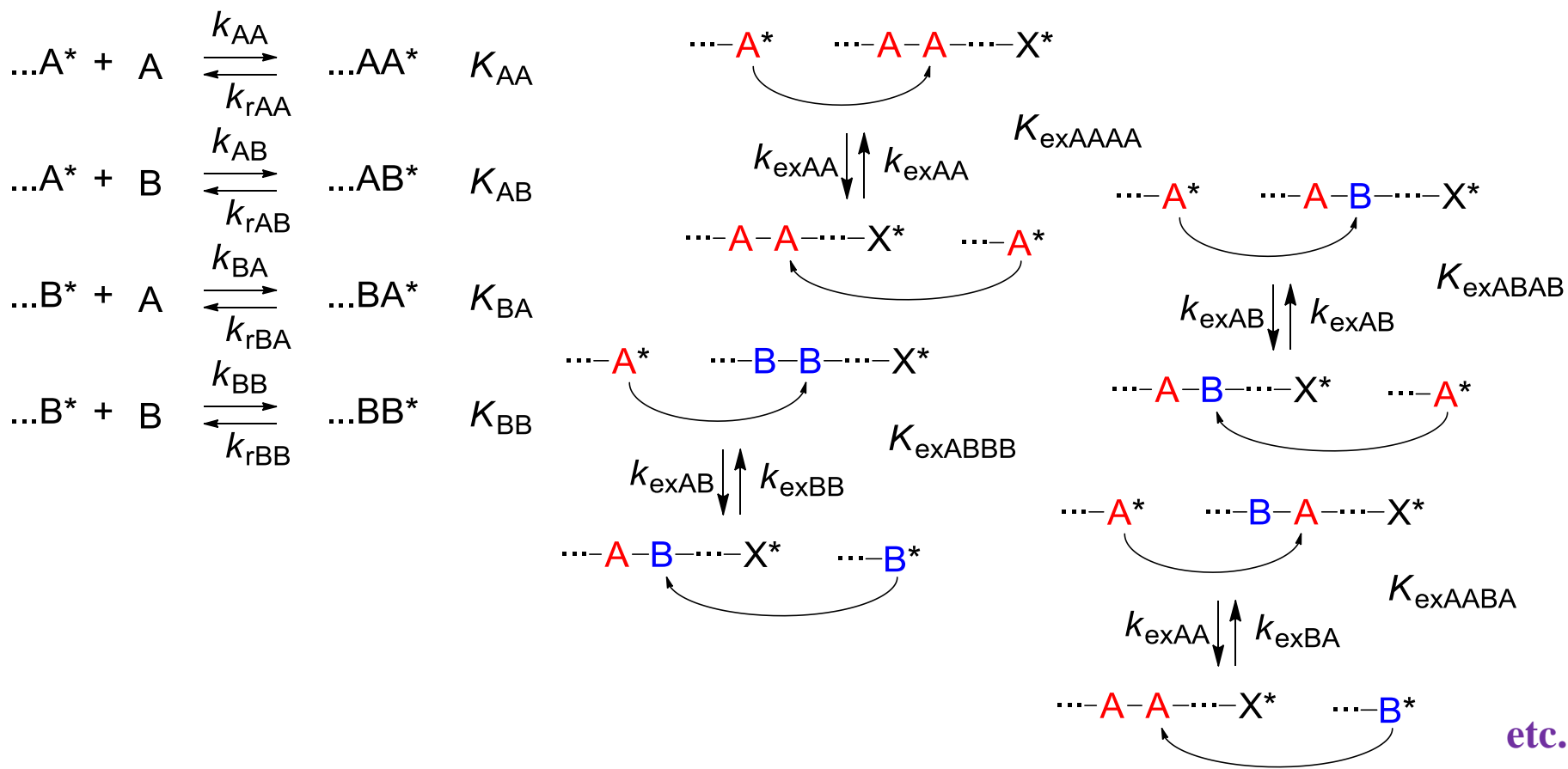


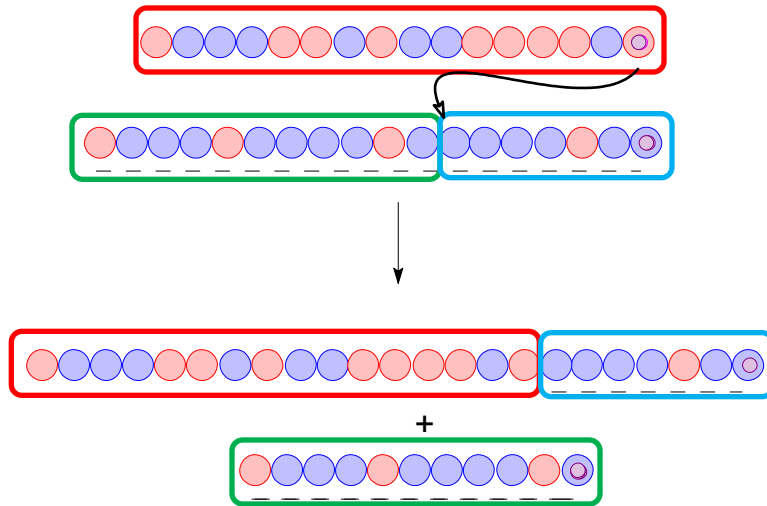
Kinetics of living reversible copolymerization with reshuffling of copolymer units (ROP). Monte Carlo and deterministic simulations

Ryszard Szymanski, Stanislaw Sosnowski

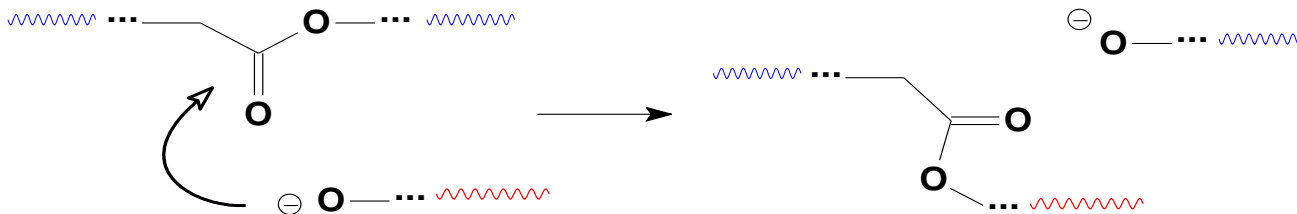
*Center of Molecular and Macromolecular Studies of Polish Academy of Sciences,
Sienkiewicza 112, 90-363 Lodz, Poland*



Segmental exchange (reshuffling) in copolymerization systems



It occurs when the active center of a polymer chain can attack a different chain, cutting it. Most often this process is observed in Ring Opening (co)Polymerizations.

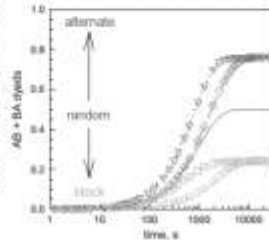


Main consequences: broadening of the chain length distribution (CLD) and changes of copolymer microstructure: its statistics becomes eventually identical at any position and in chains of any length.

Kinetic Monte Carlo Studies on the Importance of the Reaction Scheme in Segmental Exchange of Copolymer Chains^a

Ryszard Szymanski,* Stanislaw Sosnowski*

Kinetic Monte Carlo studies (confirmed by integration of the corresponding differential equations) are used to demonstrate the fundamental differences between the two most often accepted schemes of segmental exchange. Modeling of reshuffling systems, originally composed of homopolymers of various \overline{DP}_n , various mass distributions, and different compositions, is carried out until the equilibrium copolymers are obtained. It is shown that one of the schemes leads always to a random microstructure (Bernoulli statistics) whereas modeling of the other one indicates possibility of formation of all achievable distributions of comonomer units (from multiblock to nearly alternate). The concepts of the degrees of randomness and reshuffling are discussed and new definitions are proposed.

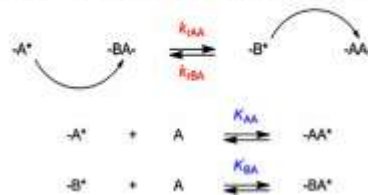


Macromol. Theory Simul. **2012**, *21*, 411–427

On the Importance of the Principle of Microscopic Reversibility in Copolymerization Systems

Ryszard Szymanski

The importance of taking into account the principle of microscopic reversibility in the analysis of complex copolymerization systems is demonstrated. The analysis of a reversible copolymerization system in which segmental exchange is possible from the point of view of the reaction microreversibility proves that hetero-reshuffling rate constants depend on homo-reshuffling rate constants and copolymerization thermodynamics.

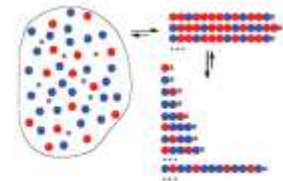


Macromol. Theory Simul. **2013**, *22*, 221–224

Evolution of Chain Microstructure and Kinetics of Reaching Equilibrium in Living Reversible Copolymerization

Ryszard Szymanski,* Stanislaw Sosnowski,* Marek Cypryk

Theoretical considerations and Monte Carlo simulations have proved that the microstructure of copolymer chains in living reversible copolymerization can be effectively described by the first-order Markov chain process only when the system space of this process reaches chain lengths above the number-average degree of polymerization (\overline{DP}_n). The time scale of equilibration depends mostly on \overline{DP}_n of the product, rate constants of depropagation, as well as on the equilibrium microstructure of copolymer. During the process, evolution encompasses, besides the chain-length distribution like in homopolymerization, also the chain microstructure. The kinetically determined microstructure (gradient, alternate, etc.) observed in the first stage of copolymerization is related to reactivity ratios. It evolves into the equilibrium microstructure, determined exclusively by the equilibrium constants and initial conditions. Discussion of this evolution together with the statistical description of the reversible binary copolymerization systems at various stages of equilibration is given.



Macromol. Theory Simul. **2016**, *25*, 196–214

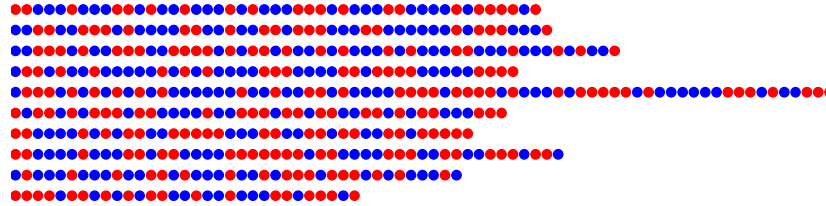
Kinetics of attaining equilibrium in reversible copolymerization (comonomer concentrations, CLD, microstructure)

Kinetics of reshuffling, giving the equilibrium copolymer (CLD, microstructure)

Relations between the rate constants of reshuffling and the equilibrium propagation constants

Copolymer microstructure

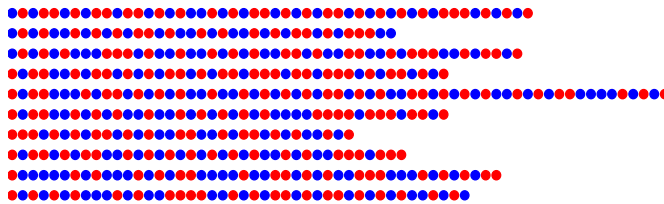
✓ Random



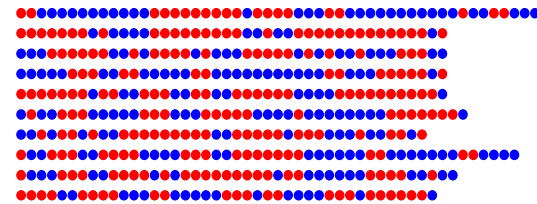
✓ Statistical

alternate

...



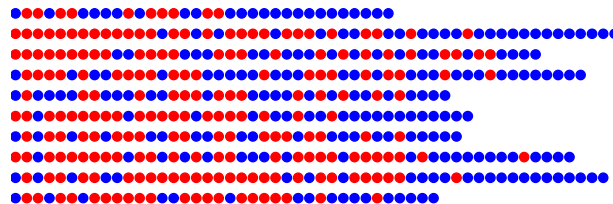
...



...

block

✓ Gradient



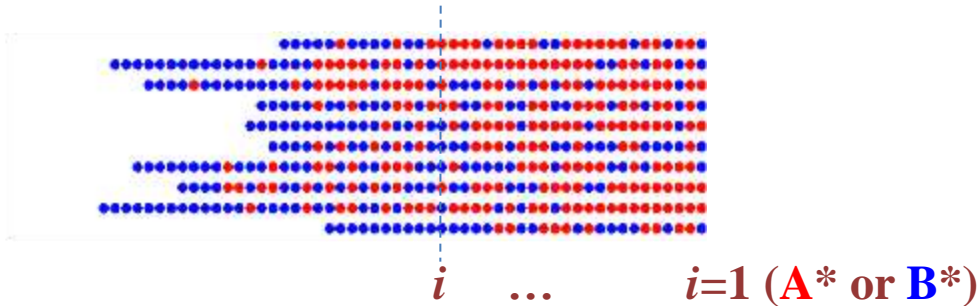
Various statistics

Simulations: Monte Carlo,
limited results by numerical integration

What we knew before simulations:

- Conditional probabilities in copolymerization $q_i(\mathbf{X}, \mathbf{Y}, \mathbf{W})$ depend on the position i of unit \mathbf{Y} in chain

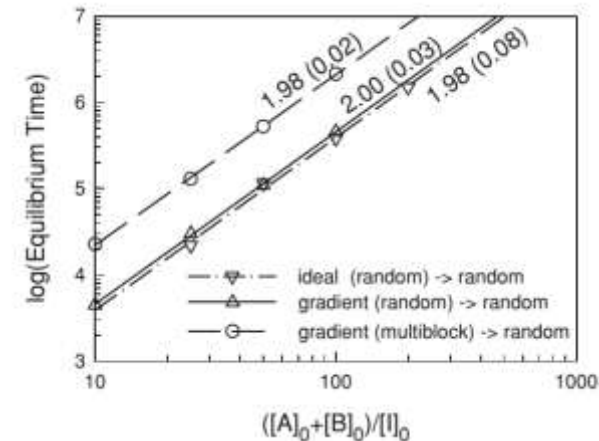
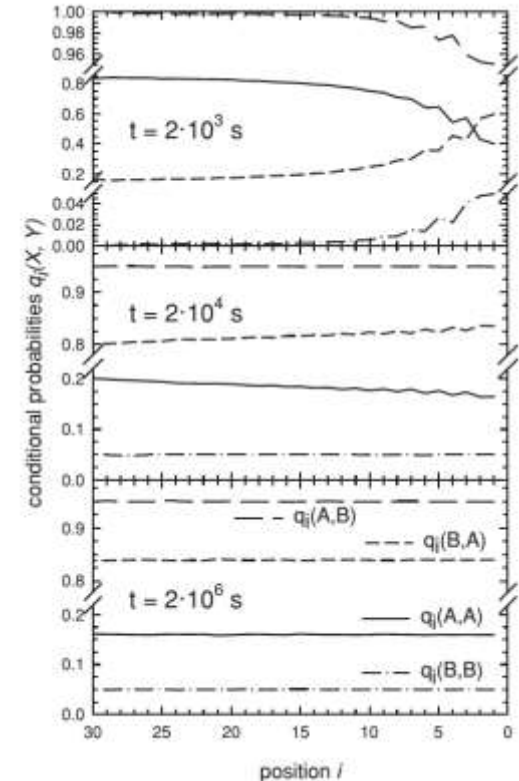
$$q_i(\mathbf{X}, \mathbf{Y}, \mathbf{W}) = \frac{[(\mathbf{XY})_i \mathbf{W}^*]}{[(\mathbf{Y})_i \mathbf{W}^*]}; \quad \mathbf{X}, \mathbf{Y}, \mathbf{W} = \mathbf{A} \text{ and/or } \mathbf{B}$$



and they change with conversion and reaction time

- Equilibration time depends on DP_n

Goal: determination of the effect of reshuffling on evolution of copolymerization (conversion, equilibration time, CLD, copolymer microstructure)

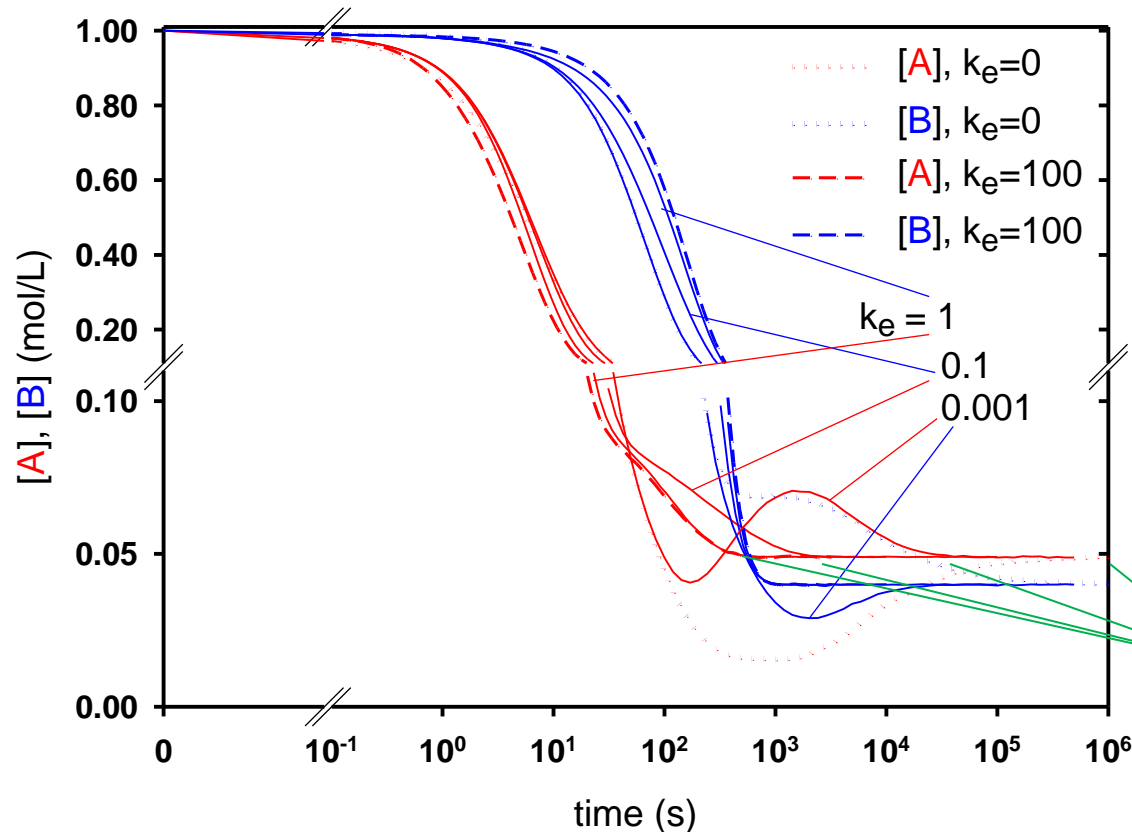


Main results of Monte Carlo simulations (to make a long story short)

Reshuffling has important effect on:

- 1. Rates of comonomer conversions – due to changing proportions of A* and B***
- 2. CLD – due to statistical nature of redistribution of chain lengths after attack of one chain on another**
- 3. Microstructure – due to new routes of formation and consumption of AA, AB, BA, and BB dyads (and consequently of other sequences as well)**
- 4. Time of equilibration – due to new routes of achieving equilibrium CLD and equilibrium copolymer microstructure (including chain-ends)**

Effect of reshuffling on comonomer consumption



$$k_{eAB} = k_{eBB} \times \frac{K_{AB}}{K_{BB}}$$

$$k_{eBA} = k_{eAA} \times \frac{K_{BA}}{K_{AA}}$$

Shortening of equilibration time

Example systems: multi-block gradient copolymer - initially consumption of **A**, next **B**, homodyads preferred, equilibration gives random copolymer.

$$[A]_0 = [B]_0 = 1 \text{ mol/L}, [A_1^*]_0 = [B_1^*]_0 = 0.01 \text{ mol L}^{-1},$$

$$k_{AA} = 10, k_{AB} = 0.2, k_{BA} = 0.5, k_{BB} = 1 \text{ (mol}^{-1} \text{ L s}^{-1}\text{)}, \quad [(k_{AA} k_{BB}) / (k_{AB} k_{BA}) = 10]$$

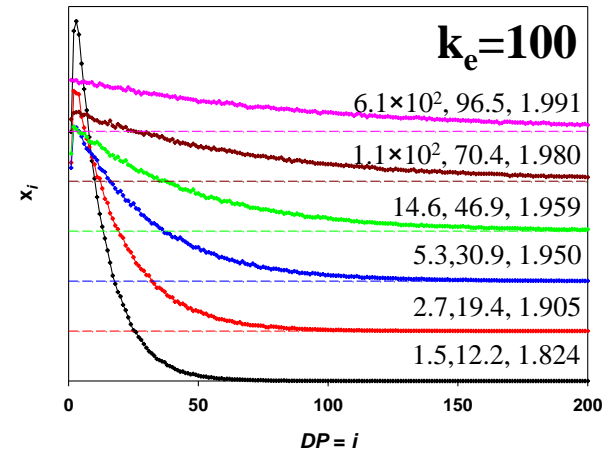
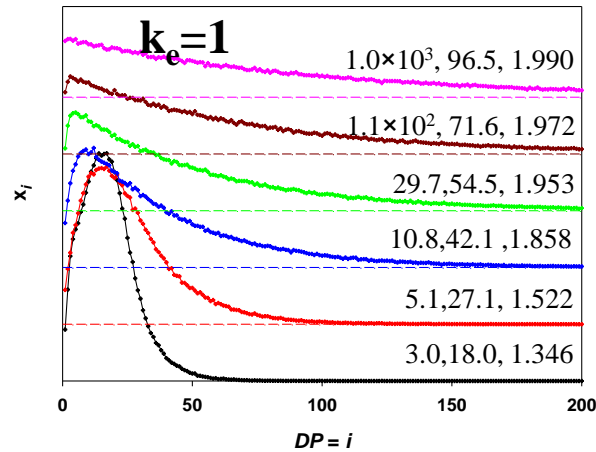
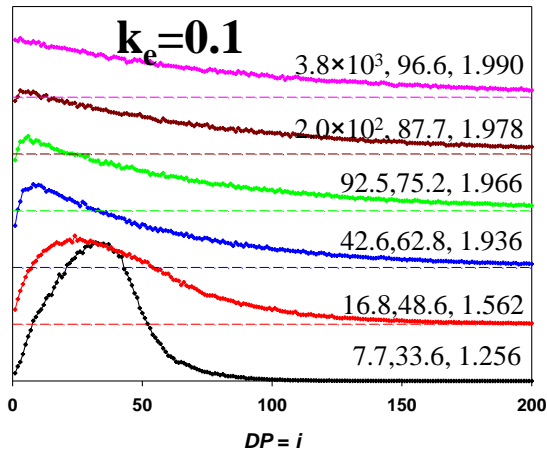
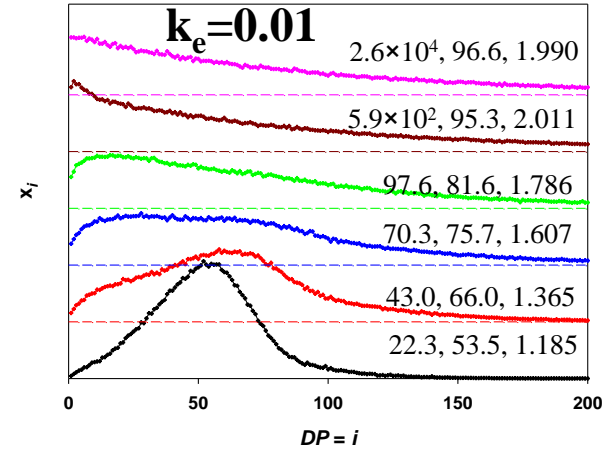
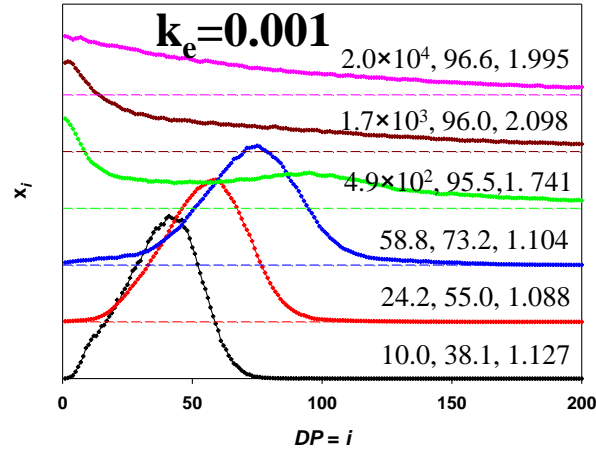
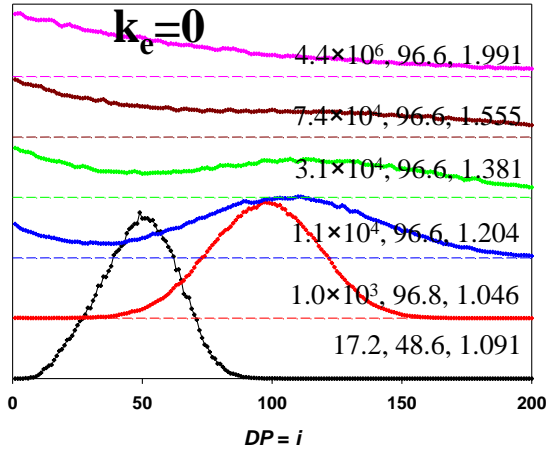
$$k_{AA} = 1, k_{AB} = 0.04, k_{BA} = 0.02, k_{BB} = 0.08 \text{ (s}^{-1}\text{)},$$

$$[K_{AA} = 10, K_{AB} = 5, K_{BA} = 25, K_{BB} = 12.5 \text{ (mol}^{-1} \text{ L}^1\text{)}; \quad (K_{AA} K_{BB}) / (K_{AB} K_{BA}) = 1]$$

$$\text{reshuffling: } k_e = k_{eAA} = k_{eBB} = 0; 0.001; 0.1; 1; 100 \text{ (mol}^{-1} \text{ L s}^{-1}\text{)}$$

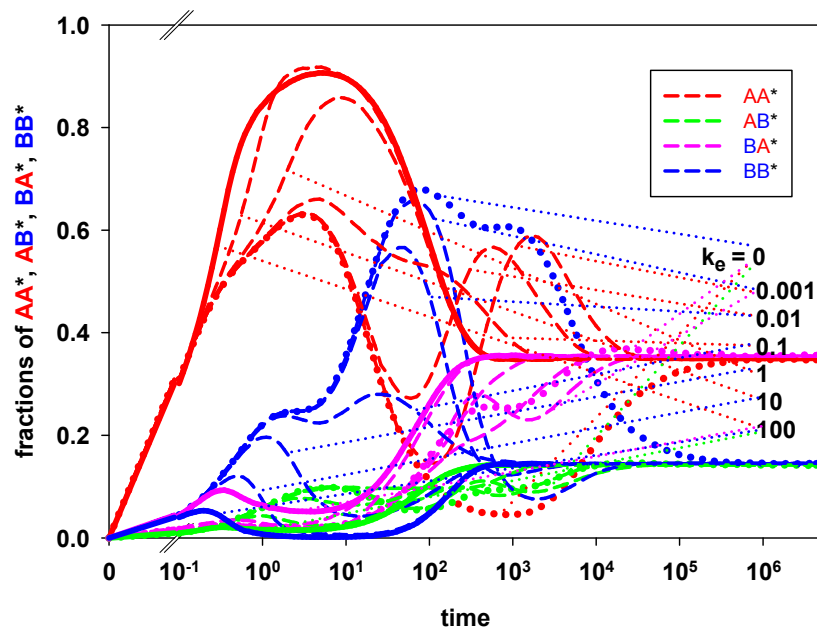
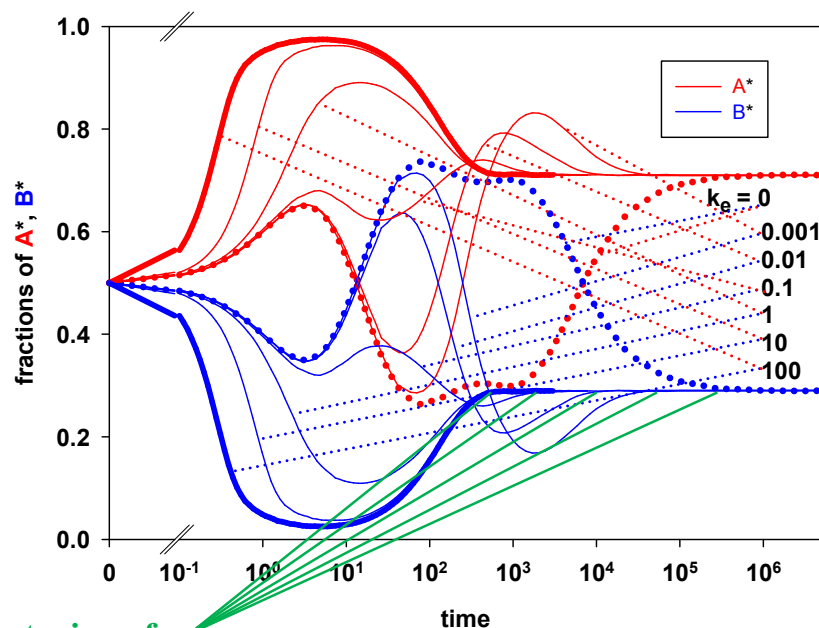
Effect of reshuffling on CLD

(t [s], DP_n , \bar{D})



The same multi-block gradient copolymerization systems - initially consumption of **A**, next **B**, homodyads preferred, equilibration gives random copolymer, $k_e=0 \dots 100$

Effect of reshuffling on active chain-ends



Shortening of equilibration time

$$\frac{d[A^*]}{dt} = -k_{AB}[A^*][B] + k_{rAB}[AB^*] + k_{BA}[B^*][A] - k_{rBA}[BA^*]$$

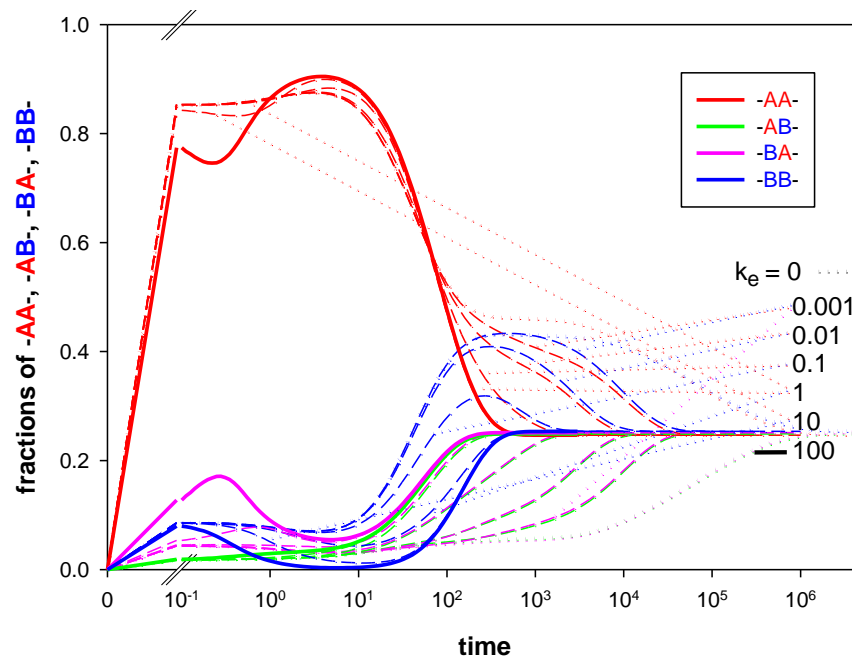
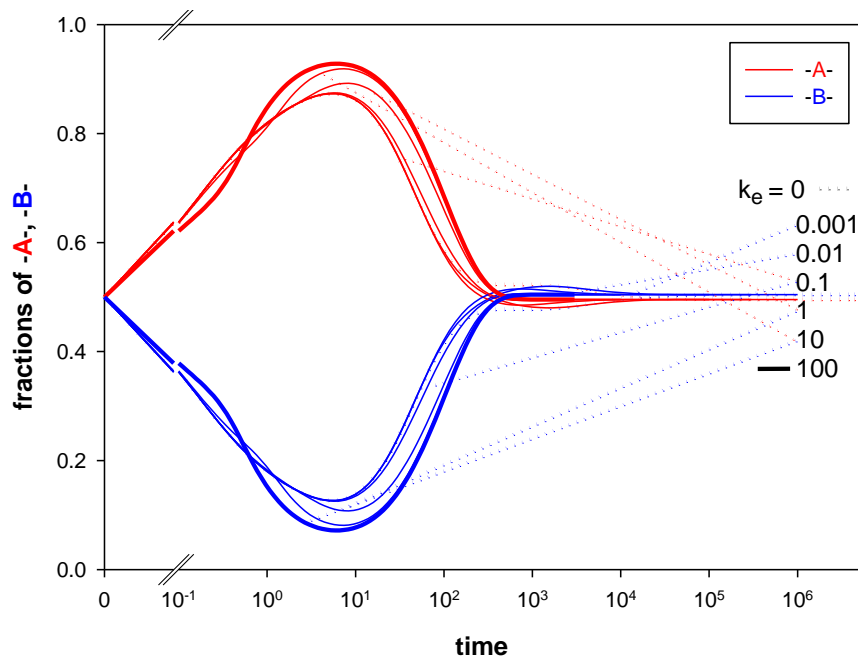
$$-k_{exBA}[B^*][-AA-] - k_{exBB}[B^*][-AB-] + k_{exAA}[A^*][-BA-] + k_{exAB}[A^*][-BB-]$$

$$\frac{d[B^*]}{dt} = -k_{BA}[B^*][A] + k_{rBA}[BA^*] + k_{AB}[A^*][B] - k_{rAB}[AB^*]$$

$$-k_{exAB}[A^*][-BB-] - k_{exAA}[A^*][-BA-] + k_{exBB}[B^*][-AB-] + k_{exBA}[B^*][-AA-]$$

$$\frac{d[dyad^*]}{dt} = f(\text{rate constants}, [A^*], [B^*], [dyads^*], [triads^*], [A], [B], [-dyads-], [-triads-])$$

Effect of reshuffling on microstructure



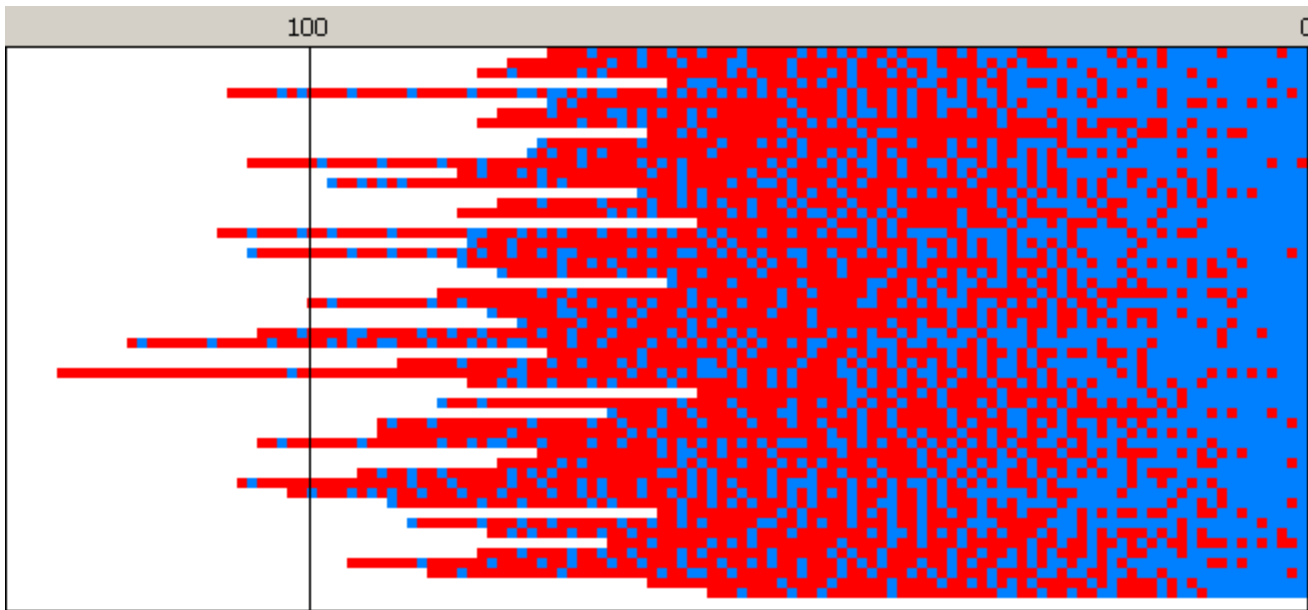
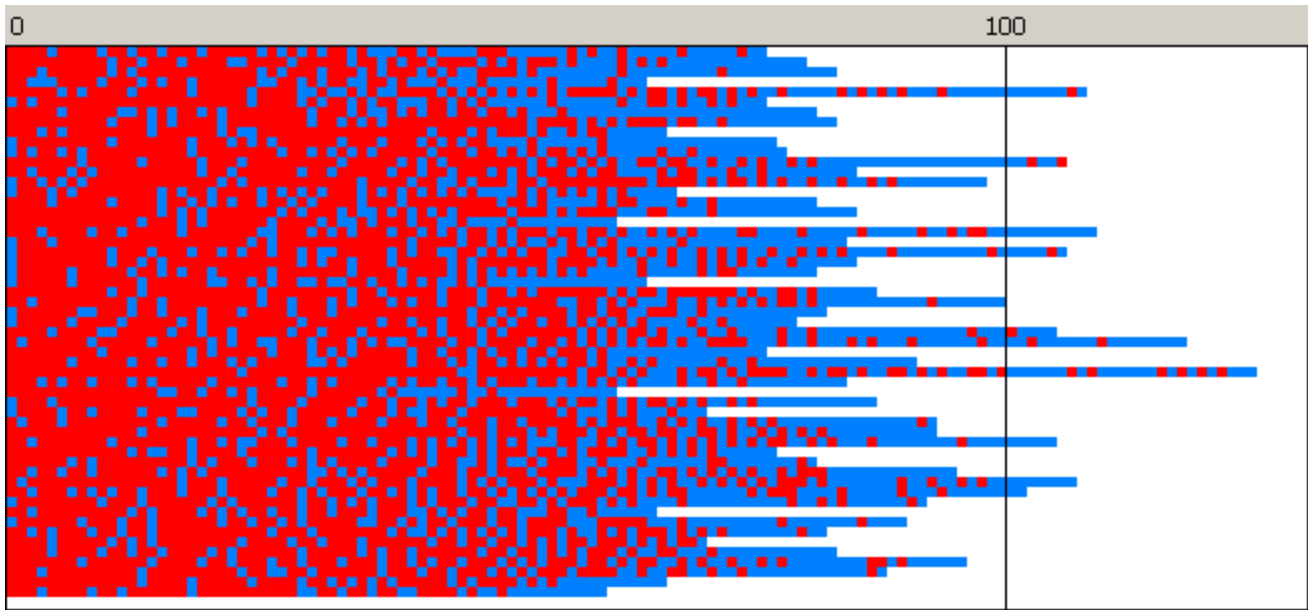
$$\frac{d[-AA-]}{dt} = k_{AA}[A^*][A] - k_{rAA}[AA^*] + k_{exAA}[A^*][-BA-] - k_{exBA}[B^*][-AA-]$$

$$\frac{d[-AB-]}{dt} = k_{AB}[A^*][B] - k_{rAB}[AB^*] + k_{exAB}[A^*][-BB-] - k_{exBB}[B^*][-AB-]$$

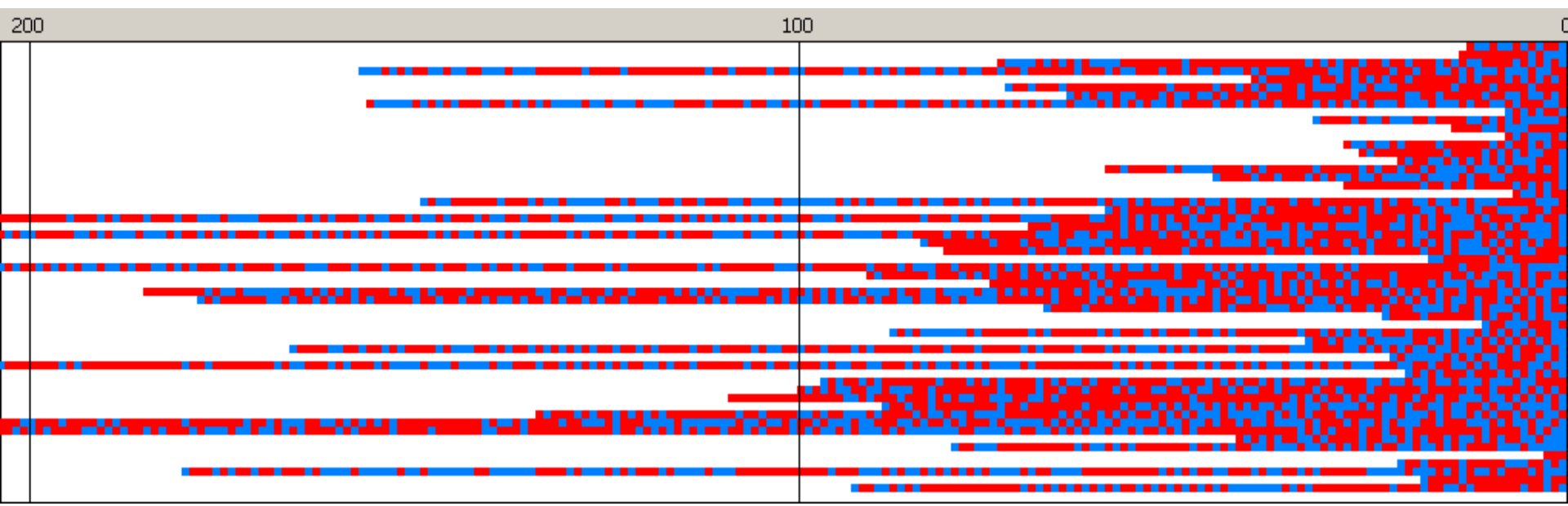
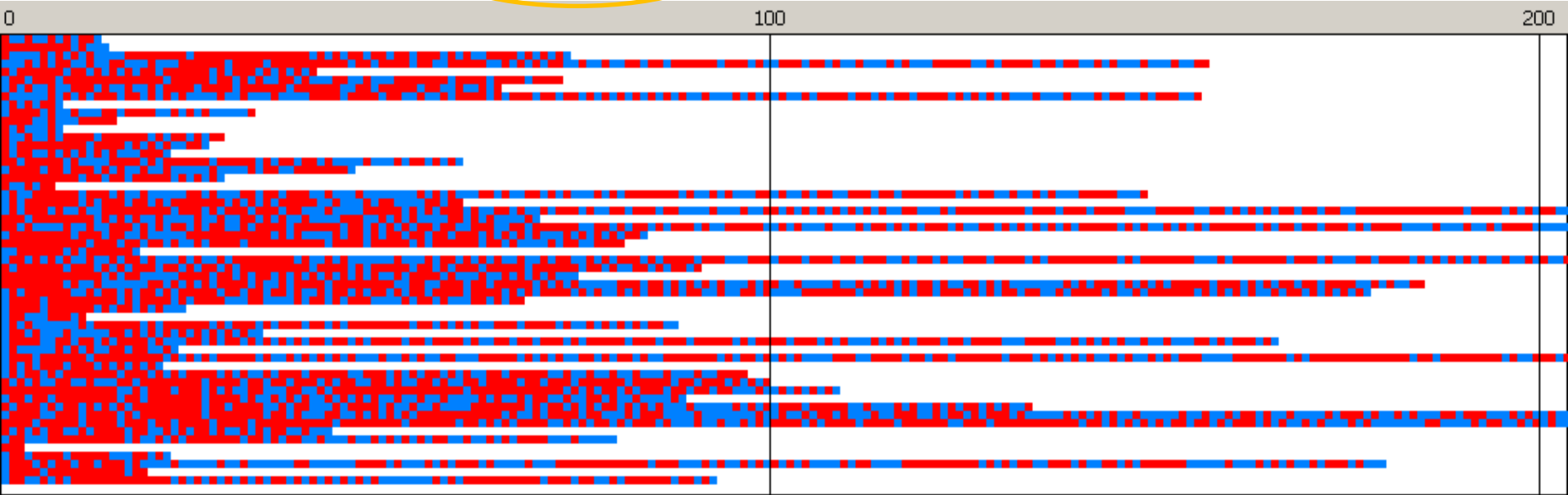
$$\frac{d[-BA-]}{dt} = k_{BA}[B^*][A] - k_{rBA}[BA^*] + k_{exBA}[B^*][-AA-] - k_{exAA}[A^*][-BA-]$$

$$\frac{d[-BB-]}{dt} = k_{BB}[B^*][B] - k_{rBB}[BB^*] + k_{exBB}[B^*][-AB-] - k_{exAB}[A^*][-BB-]$$

$k_{exAA}=k_{exBB}=0, t=1400 \text{ s}, DP_n=85.1, \bar{D}=1.043$

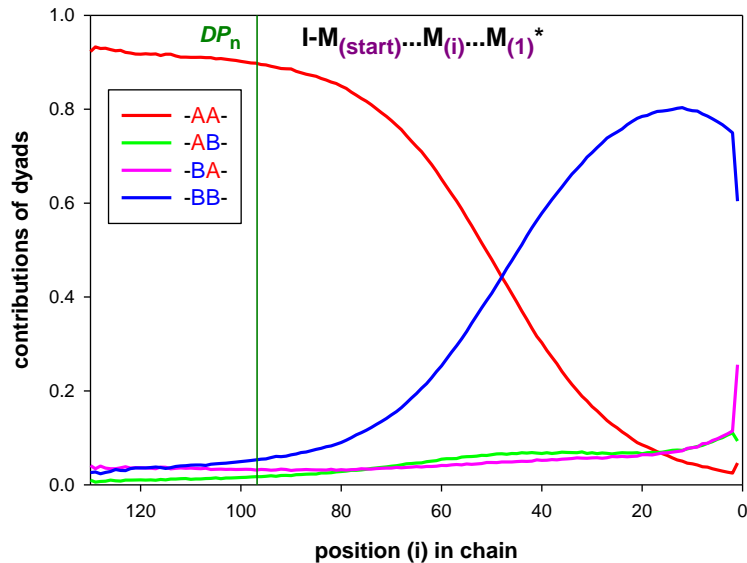


$k_{exAA}=k_{exBB}=0.01, t=596 \text{ s}, DP_n=80.0, \bar{D}=1.933$

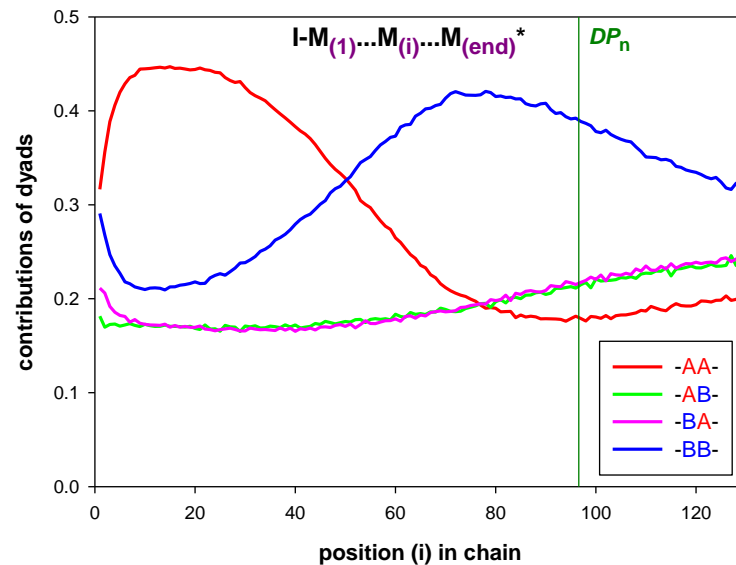
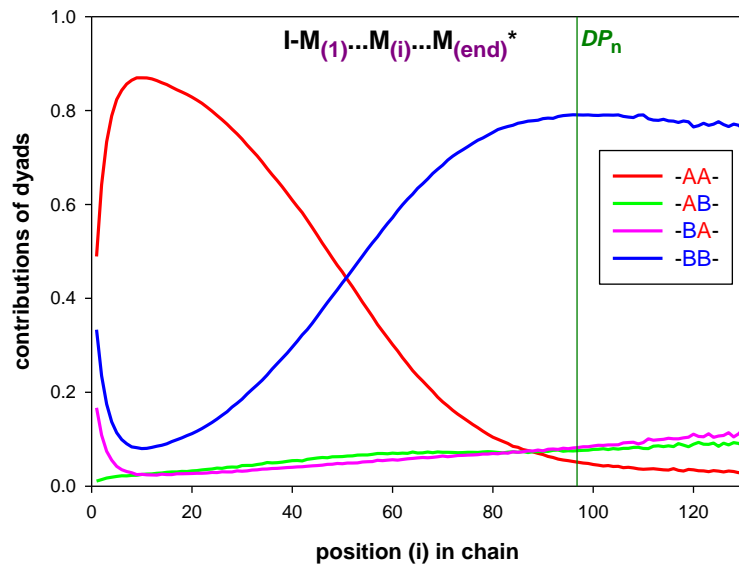
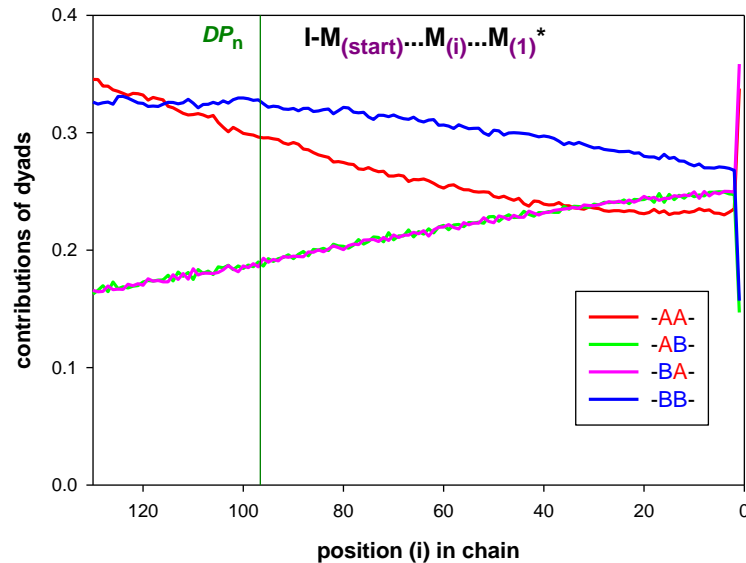


Effect of reshuffling on microstructure (sequences along chain length) $k_e=0$

$t=5.3 \times 10^2$, $DP_n=96.8$, $D=1.039$

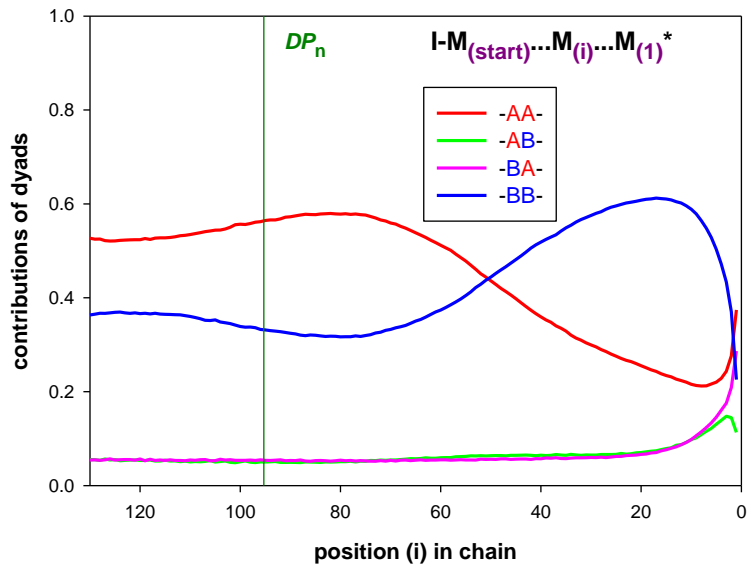


$t=1.7 \times 10^5$, $DP_n=96.7$, $D=1.729$

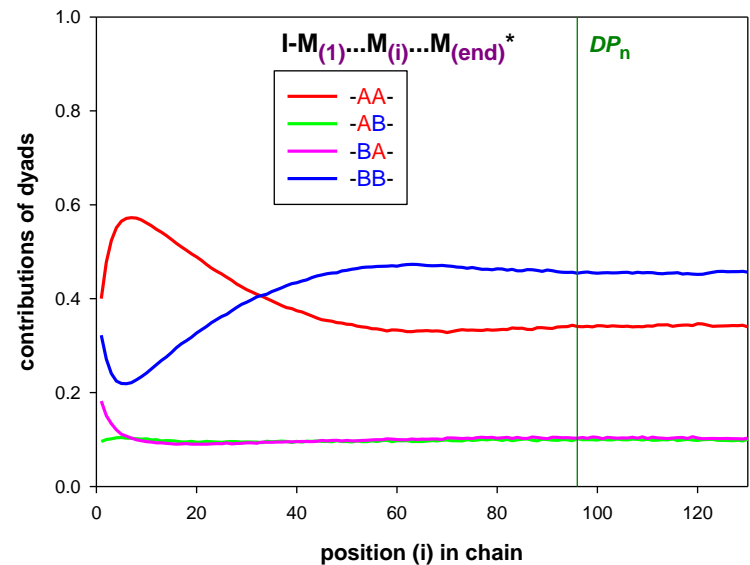
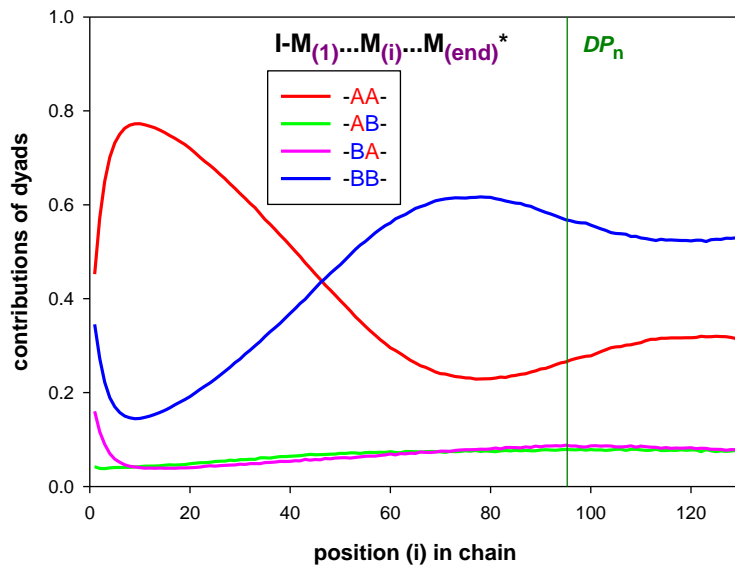
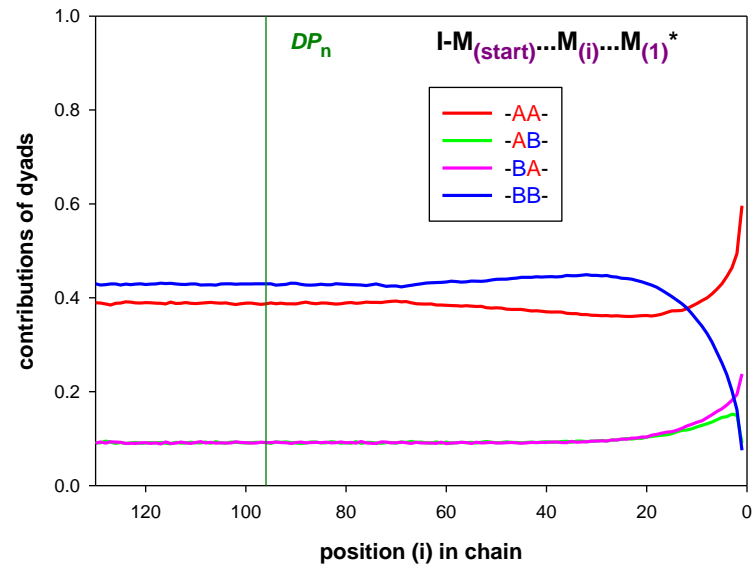


Effect of reshuffling on microstructure (sequences along chain length) $k_e=0.001$

$t=4.1 \times 10^2$, $DP_n=95.3$, $\bar{D}=1.657$

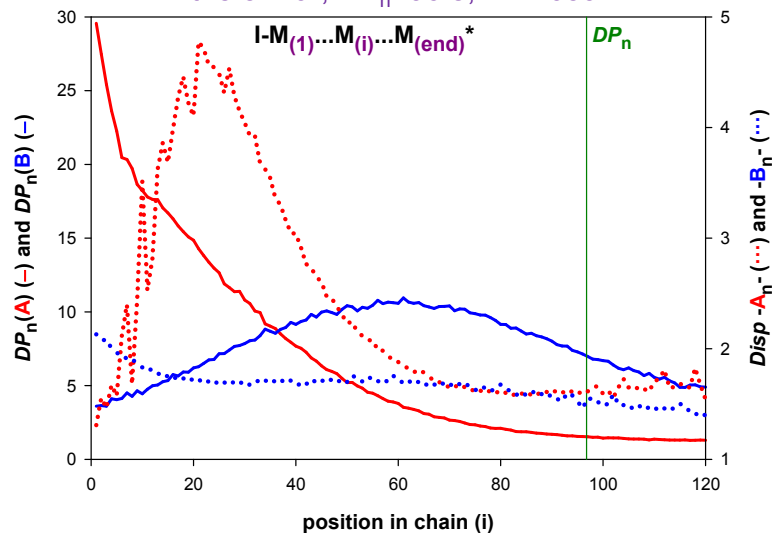


$t=2.0 \times 10^3$, $DP_n=96.0$, $\bar{D}=2.096$

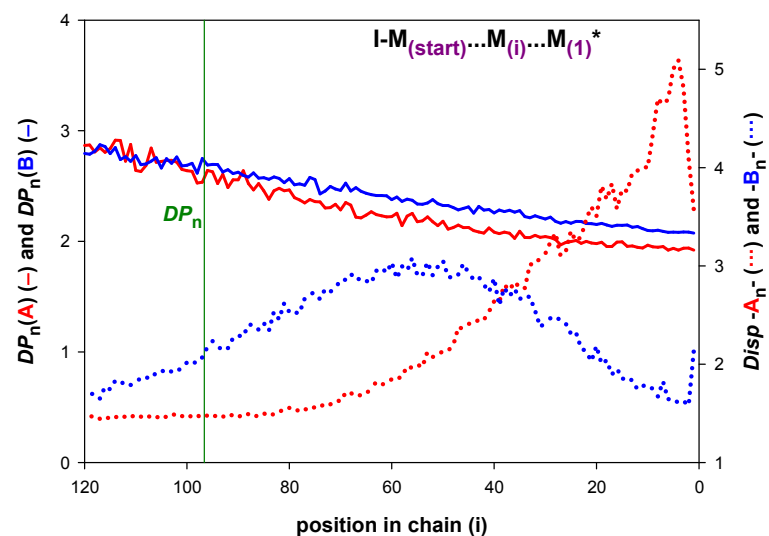
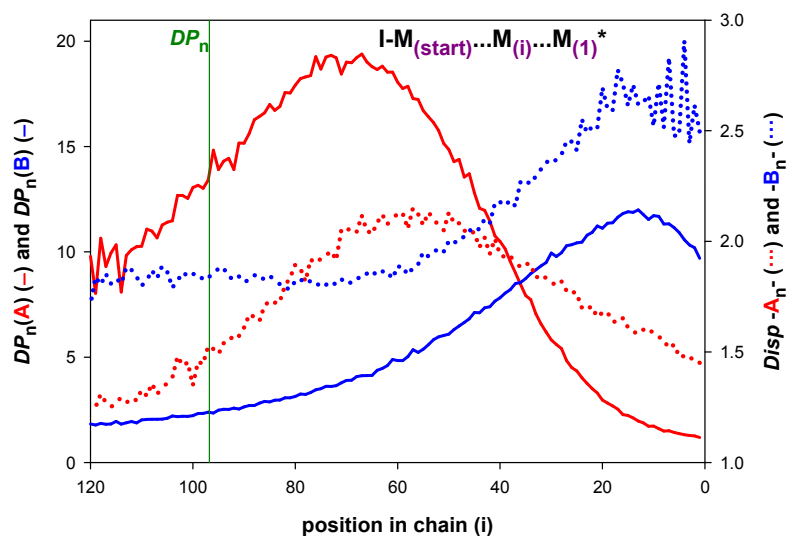
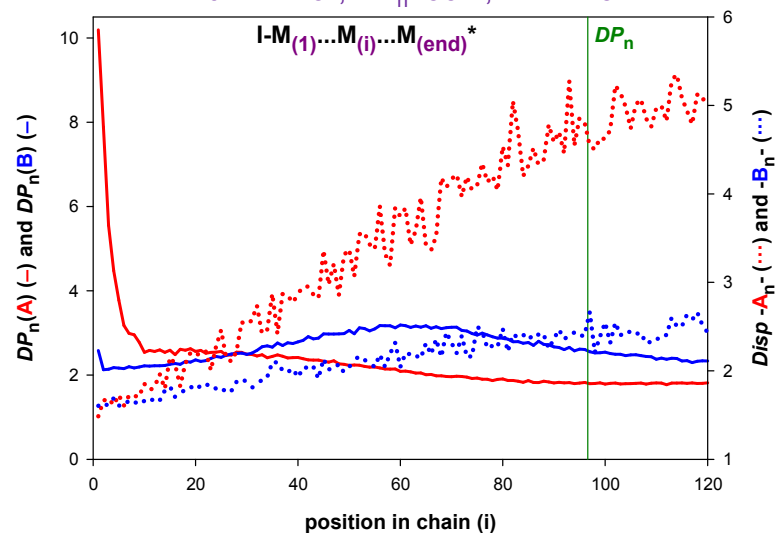


Effect of reshuffling on microstructure (homoblocks along chain length) $k_e=0$

$t=5.3 \times 10^2$, $DP_n=96.8$, $\mathcal{D}=1.039$

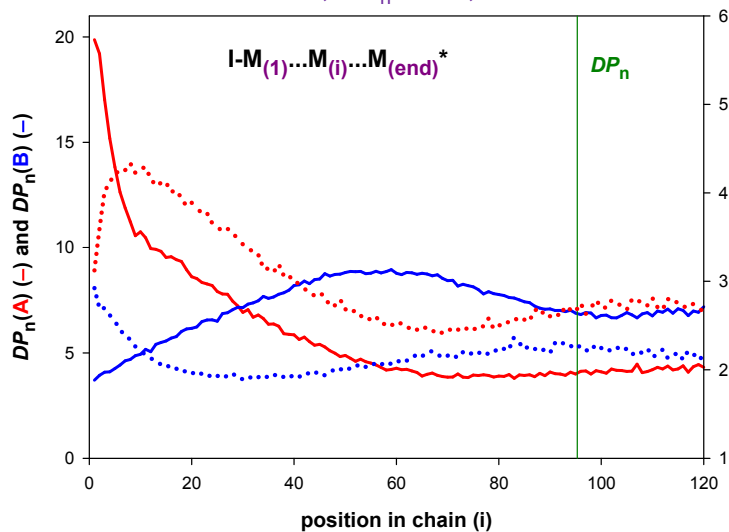


$t=1.7 \times 10^5$, $DP_n=96.7$, $\mathcal{D}=1.729$

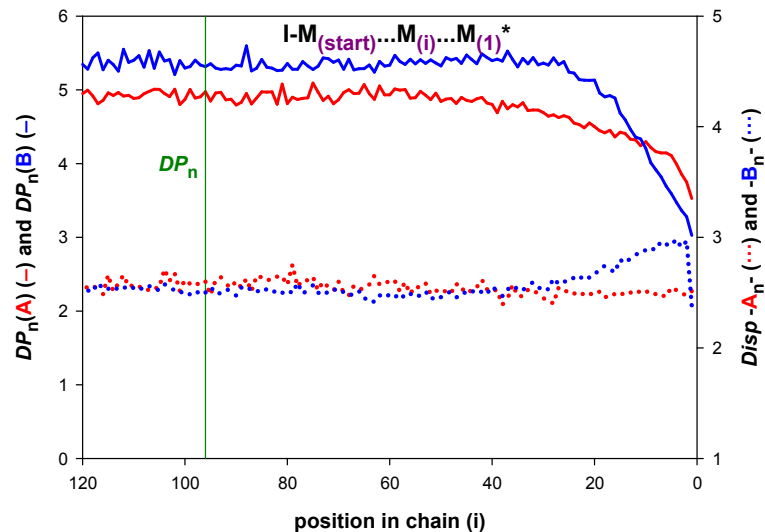
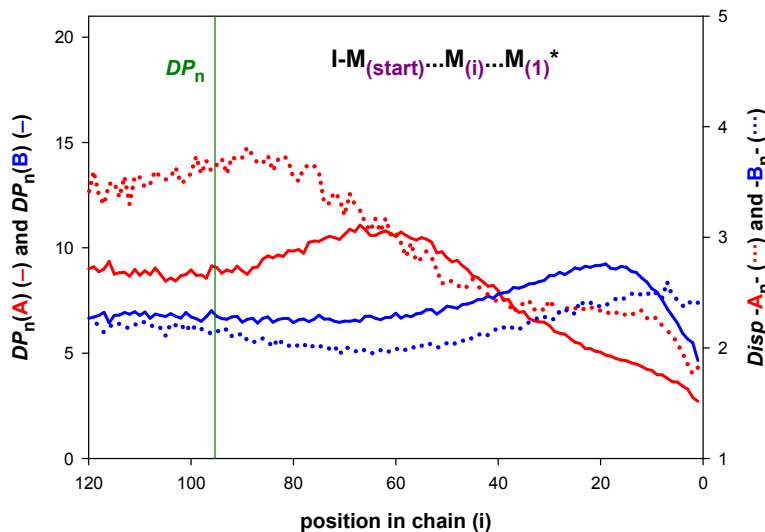
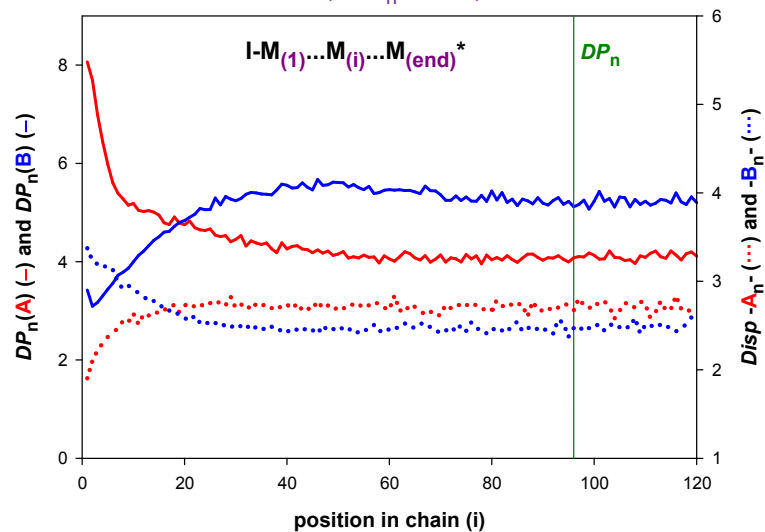


Effect of reshuffling on microstructure (homoblocks along chain length) $k_e=0.001$

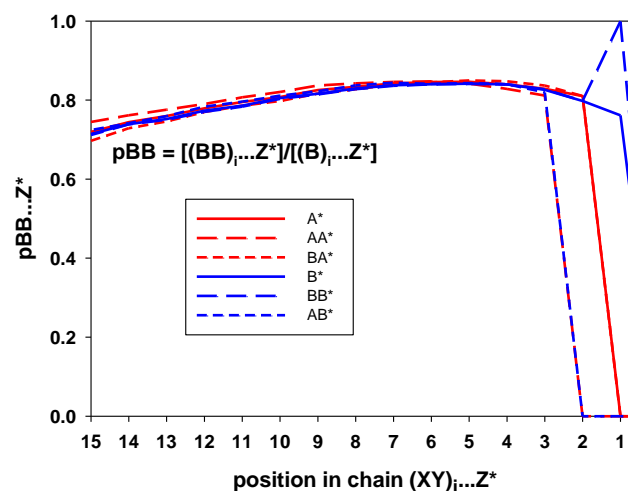
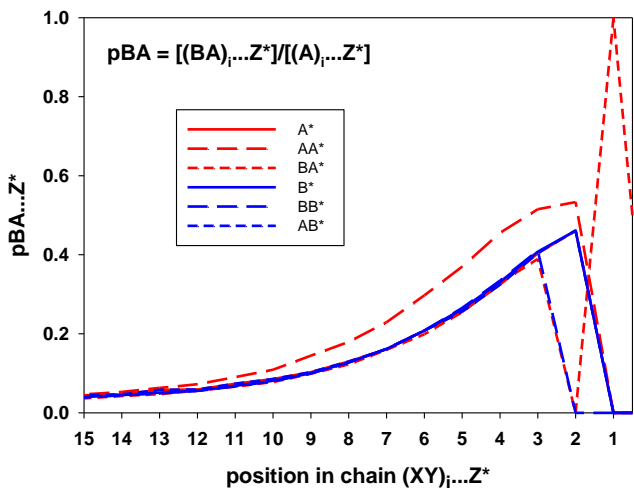
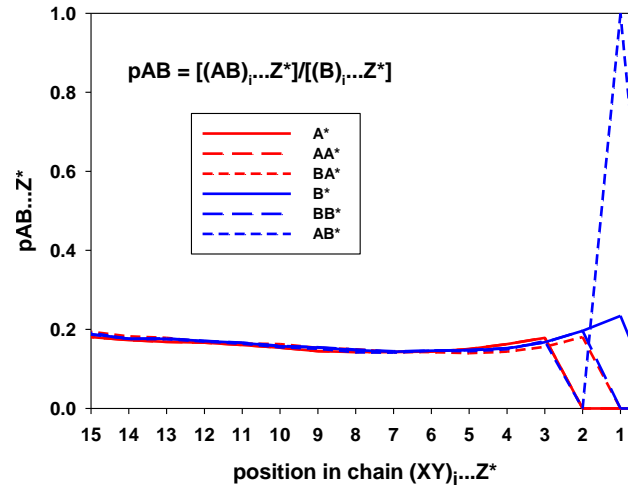
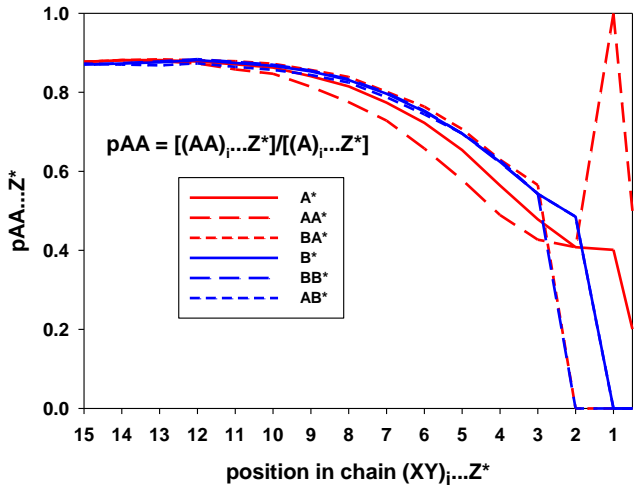
$t=4.1 \times 10^2$, $DP_n=95.3$, $\bar{D}=1.657$



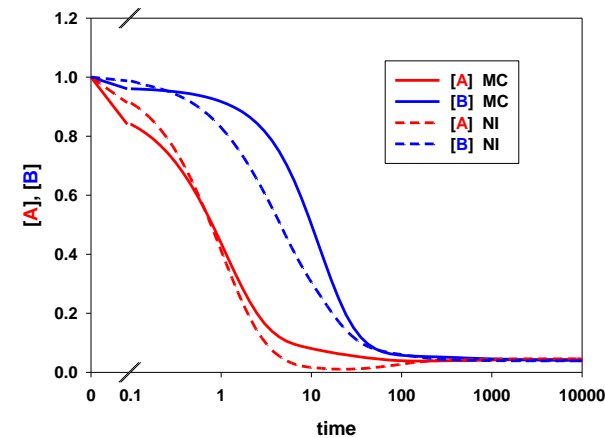
$t=2.0 \times 10^3$, $DP_n=96.0$, $\bar{D}=2.096$



Deterministic simulations: problem of conditional probabilities (MC results)



Numerical integration gives erroneous results when long homoblocks are formed and differences of conditional probabilities in respect to active centers are neglected



(the same multi-block gradient copolymerization system, $k_e=0$, but $\max DP_n = 20$)

Conclusions

- 1) **Reshuffling** changes proportions of active species AA^* , AB^* , BA^* and BB^*
- 2) Consequently, it changes also the rates of comonomer conversions and microstructure of kinetically formed product
- 3) **Reshuffling** shortens the time of reaching copolymerization equilibrium
- 4) **Reshuffling** makes that evolution of comonomer concentrations can be non-monotonous (possible minima and maxima)

Conditional probabilities of copolymer units to be preceded by units of the given kind **depend** not only on the types of units and unit position in chain but **also on the type of active species**. It makes **simulation of the copolymerization process by deterministic methods more difficult, in many cases ineffective**.