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Molecular weight distribution in living polymerization proceeding with reshuffling of polymer segments due to chain transfer to polymer with chain scission

Part IV. SYSTEMS WITH CYCLIZATION**)

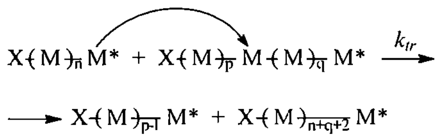
Summary — Continuing a series of modeling studies of the influence of reshuffling of polymer segments on the polydispersity index (*PDI*), the additional effect of cyclization was analyzed by means of Monte Carlo simulations. It was shown that the contribution of cyclization in overall reshuffling process can be important only in polymerization systems with high equilibrium concentrations of cyclic oligomers (*e.g.* polymerizations at low initial monomer concentration of ε-caprolactone or ε-caprolactone dimer). Cyclization contribution can easily be observed in ring opening polymerization of composite monomers (built of two or more repeating units), as for instance dilactide and dimer of ε-caprolactone. By comparing the observed frequency distributions of even and odd lactide oligomers in polymerization of dilactide with results of simulations it was possible to estimate the contribution of this type of reshuffling ($k_{c3}/k_{tr} = 1.07 \cdot 10^{-3}$ mol/L). However, if overall polydispersity index is concerned, this contribution is as small as in majority of polymerization systems. A phenomenon of kinetic enhancement of larger cycles, not described previously for systems without end-to-end intramacromolecular reaction, was observed in the simulations.

Key words: living polymerization, chain transfer, Monte Carlo simulation, cyclic ester, kinetics of polymerization.

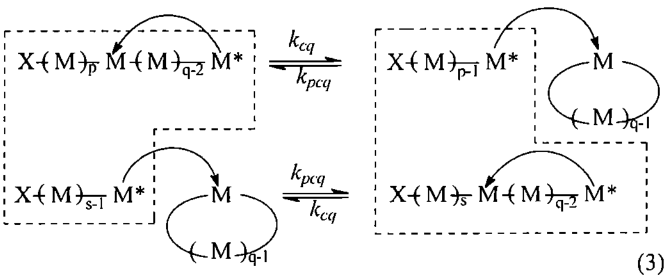
CHEMICAL INSPECTION OF THE PROBLEM

In ring opening polymerizations (*ROP*) cyclizations usually are not negligible. Consequently, a new route of interchain segmental exchange (reshuffling) accompanies the propagation and the direct exchange process:

$$X\text{-}(M)_{\overline{n}}M^* + M \xrightarrow{k_p} X\text{-}(M)_{\overline{n+1}}M^* \qquad (1)$$



$$X\text{-}(M)_{\overline{n}}M^* + X\text{-}(M)_{\overline{p}}M\text{-}(M)_{\overline{q}}M^* \xrightarrow{k_{tr}} X\text{-}(M)_{\overline{p-1}}M^* + X\text{-}(M)_{\overline{n+q+2}}M^* \qquad (2)$$



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In the previous papers [1—3] Monte Carlo simulations of reshuffling in polymerization systems were described and methods of estimation of k_p/k_{tr} on the basis of the observed dependences of the polydispersity indexes (*PDI*) on monomer conversion were proposed. The method described in the first of these papers (concerning the systems without disproportionation of chain functionalities) was successfully applied in analyses of real polymerizations [4, 5].

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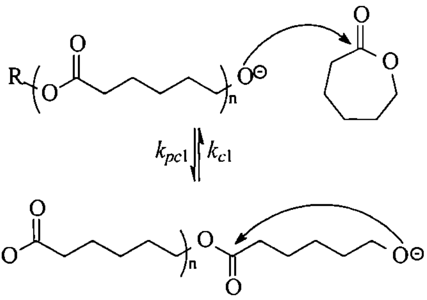
**) Part III see [3].

In this paper the analysis of reshuffling systems with cyclizations was performed using Monte Carlo simulations. Only the systems with unidirectional chain scission (without chain functionality disproportionation), as for instance ε-caprolactone polymerization, were analyzed:



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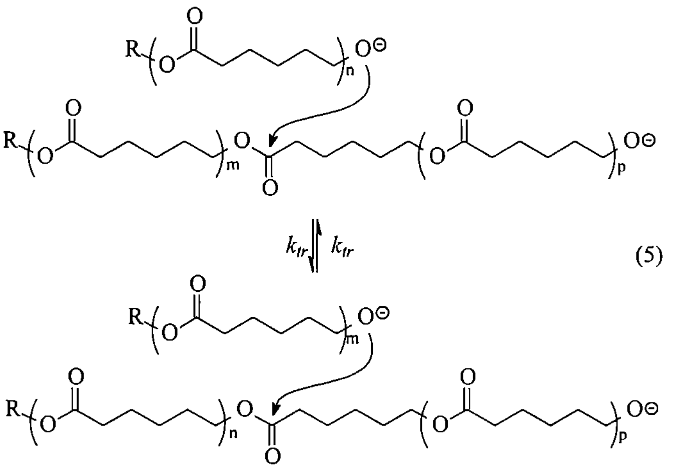

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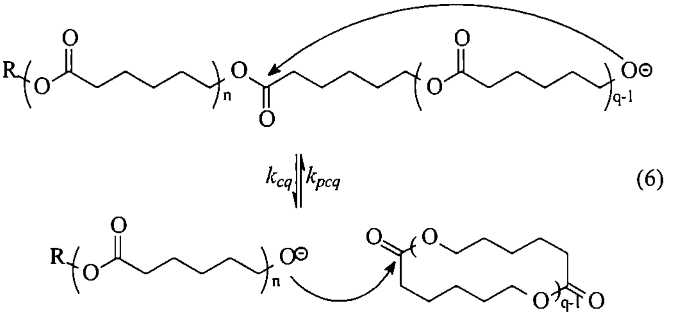

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The analysis of the systems with bidirectional chain scission [2] (resulting in disproportionation) has shown that overall molecular weight distribution (*MWD)* does not differ much from those predicted for analogous systems with unidirectional chain scission. Thus the majority of the results obtained in this work can be applied to the systems with disproportionation as well. Similarly, general conclusions are valid for polymerization systems initiated with multifunctional initiators too. Reshuffling in such systems without cyclization was analyzed in ref. [3].

Differential equations describing a polymerization system analyzed in the present work are as follows (assuming instantaneous irreversible initiation and no end-biting cyclization):

$$\frac{\mathrm{d}x_1}{\mathrm{d}t} = -\sum_{i=1}^{\infty} k_{pci} x_1 c_i + \sum_{i=1}^{\infty} k_{ci} x_{i+1} - k_{tr} \left[x_1 (P_x - x) - x \sum_{i=2}^{\infty} x_i \right] \qquad (7)$$

$$\frac{\mathrm{d}x_n}{\mathrm{d}t} = -\sum_{i=1}^{\infty} k_{pci} x_n c_i + \sum_{i=1}^{\infty} k_{ci} x_{i+n} + \sum_{i=1}^{n-1} k_{pci} x_{n-i} c_i + \qquad (8)$$

$$-\sum_{i=1}^{n-1} k_{ci} x_n - k_{tr} \left[x_n (P_x - x) + (n-1) x \cdot x_n - x \sum_{i=n+1}^{\infty} x_i - \sum_{m=1}^{n-1} \sum_{i=n-m+1}^{\infty} x_m x_i \right]$$

(n > 1)

where: x_i — *concentration of the growing i-mer* X_i *(*$x_i = [X_i]$*),* x — *total concentration of the growing species (*$x = \Sigma x_i$*),* P_x — *total concentration of monomer units in all polymer chains (*$P_x = \Sigma i \cdot x_i = \Sigma i \cdot [X_i]$*),* c_i — *concentration of cyclic oligomer composed of i repeating units (*$c_i = [C_i]$*),* k_{ci}*,* k_{pci}*, and* k_{tr} — *rate constants of cyclization and propagation of corresponding cyclic oligomer, and of direct reshuffling, respectively.*

Monomer is also one of cyclics, usually C_1, but in some systems (composite monomers) it can be any other cyclic oligomer (*e.g.* C_2 for dilactide or ε-caprolactone dimer polymerization).

Four general routes of consuming X_n and four of forming X_n were taken into account formulating the above equations. X_n can be consumed either by attacking cycles, other macromolecules, by cyclization and expelling a cycle of any possible size, or by being attacked by other macromolecules. X_n can be formed either in propagation (of various size cyclics), in expelling off surplus polymer segment from a longer chain in cyclization or direct reshuffling, or by linking a polymer segment to a shorter chain in direct exchange reaction.

Although an analytical solution to the presented differential equations is unknown, similarly as in the case of previously analyzed systems [1—3], Monte Carlo method was successfully applied to analyze the kinetics and *MWD* of polymers in the systems under consideration.

Monte Carlo simulations of the analyzed polymerization systems, presented in this paper allowed to estimate the evolution of distribution functions of polymer chains and cyclics and consequently to propose an approximate method of determination of the ratio k_p/k_{tr} from a set of experimental *MWD*. A method of estimation of the contribution of cyclization is proposed as well.

RELATIONSHIPS BETWEEN THE EQUILIBRIUM CONCENTRATIONS OF CYCLICS AND CONTRIBUTION OF CYCLIZATION IN RESHUFFLING

Equilibrium concentrations of cyclic oligomers depend on the rate constants of cyclizations and their propagations, as well as on DP_n of a linear polymer:

$$X_n^* + C_i \underset{k_{ci}}{\overset{k_{pci}}{\rightleftarrows}} X_{n+i}^* \quad (9)$$

$$[C_i]_e = \frac{k_{ci}}{k_{pci}}\left(1-\frac{1}{DP_n}\right)^i \quad (10)$$

For the nonstrained cycles propagation rate constant is related with the rate constant of reshuffling (equal reactivities of repeating units in polymer and large cycles):

$$k_{pci} = i \cdot k_{tr} \quad (11)$$

where: $i > i_{min}$ *(i_{min} depends on monomer structure).*

Assuming that $i_{min} = 3$ one gets:

$$\sum_{i=3}^{\infty} i \cdot [C_i]_{\infty} = \frac{\sum_{i=3}^{\infty} k_{ci}}{k_{tr}} \quad (12)$$

where: $[C_i]_{\infty}$ — *equilibrium concentration of a cycle at infinitely long linear chains.*

The sum at the left side of eq. (12) can be treated as limiting cyclic polymer concentration expressed in repeating unit moles per liter.

Consequently, the ratio of rates of cyclization and direct reshuffling is equal to the ratio of concentrations of cyclic (at equilibrium) and linear polymer:

$$\frac{R_{cycl(i>2)}}{R_{tr}} = \frac{\sum_{i=3}^{\infty} i \cdot [C_i]_{\infty}}{\sum_{i=1}^{\infty} (i-1) \cdot [X_i]} \approx \frac{P_{cycl(eq)}}{P_{linear}} \quad (13)$$

In majority of the systems the concentration of cyclic polymer is much lower than that of linear one and consequently cyclization does not influence much *MWD* of the linear polymer.

MONTE CARLO COMPUTATIONS

Monte Carlo simulations were performed using a method described in [1], modified by introducing a number vector corresponding to the concentrations of cyclics, including monomer, and procedures computing probabilities of all possible cyclizations of a chain of given length and probabilities of propagations of cyclics. Chain transformation procedures were modified correspondingly and the procedures computing the concentrations of cyclics were added. A set of six pairs of cyclization and propagation rate constants for cyclics — monomer to hexamer — were introduced as parameters; rate constants for larger macrocycles were computed on the basis of data for hexamer and assuming Jacobson—Stockmayer relationships [6]. Cycles containing more than 100 repeating units were neglected.

Moreover, similarly to the simulations of reshuffling with disproportionation [2], a procedure of checking of the internal consistency was introduced. During this test DP_n of a linear polymer computed on the basis of simulated chains was checked whether it had not differed more than 5% from that computed on the basis of cyclics concentration. After each computation step, reaching a new reaction time $t + \Delta t$, the internal consistency was checked and if failed the computation was repeated. The new Monte Carlo step started only after passing the internal consistency test.

Monte Carlo computations were repeated 10—10^4 times for any simulation in order to get relatively smooth *MWD* curves (number of simulated chains varied between 10^4 to 10^7).

In the simulations of the polymerization systems the starting species contained one repeating unit (or two units in M_2 composite monomer polymerizations) what corresponded to the assumption of fast (instantaneous) initiation. No end-to-end cyclization was allowed what was consistent with fast irreversible initiation.

RESULTS AND DISCUSSION

In this section the results of simulation of the evolution of *MWD* of polymer chains and cyclic oligomers are presented. Polymer reshuffling reactions both direct and *via* cyclization, led to redistribution of polymer segments. The first set of simulations was performed taking kinetic parameters for ε-caprolactone determined in our laboratory [7]. Keeping the ratio of initial concentrations of monomer and initiator constant but changing their values, the different contributions of cyclizations and different evolutions of *MWD* of linear and cyclic oligomers could be observed.

Figure 1 shows the simulated frequency distributions of linear chains obtained for the highest monomer concentration, hence the lowest contribution of cyclization. Evolution of the concentrations of cycles is given in Fig. 2.

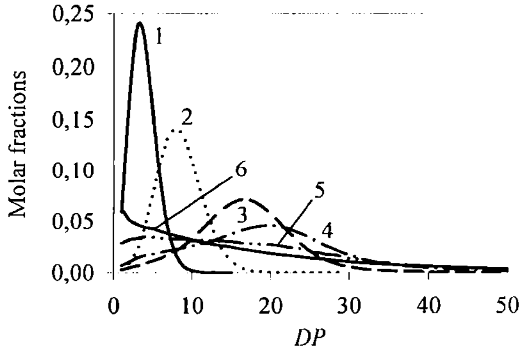

Fig. 1. Frequency distribution plots obtained by Monte Carlo simulations of reshuffling in ε-caprolactone polymerization computed for conditions: $[M]_0/[I]_0 = 22.7$, $[M]_0 = 2$ mol/L, rate constant determined by the authors of ref. [5] for 20 °C. Different curves correspond to different degrees of monomer conversion: 1 — 12.5%, 2 — 33.0%, 3 — 73.4%, 4 — 93.0%, 5 — 99.5%, 6 — 99.95% (close to the equilibrium value)

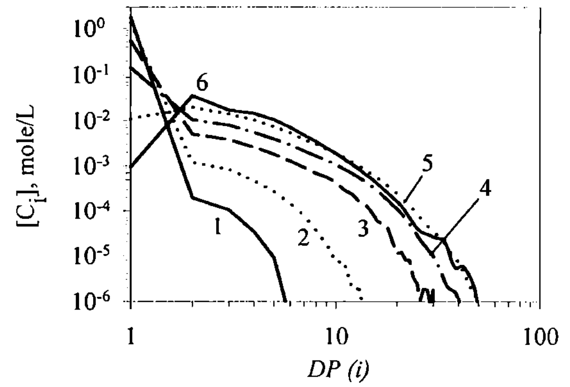

Fig. 2. Concentrations of cyclics ($[C_i]$) obtained by Monte Carlo simulations of reshuffling in ε-caprolactone polymerization computed for the same conditions as in Fig. 1. Different curves correspond to different degrees of monomer conversions — description as in Fig. 1

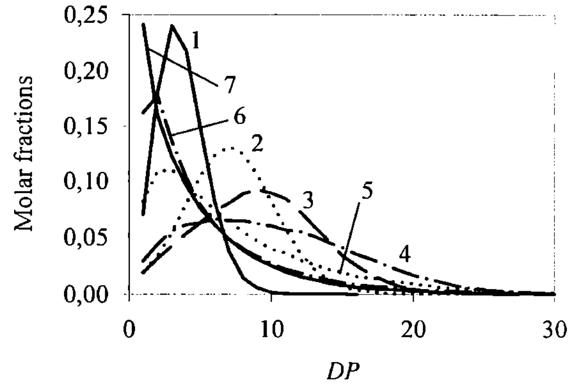

Fig. 3. Frequency distribution plots obtained by Monte Carlo simulations of reshuffling in ε-caprolactone polymerization computed for conditions similar to those in Fig. 1 but $[M]_0$ = 0.2 mol/L. Different curves correspond to different degrees of monomer conversions: 1 — 12.5%, 2 — 32.5%, 3— 48.3%, 4 — 73.1%, 5 — 92.5%, 6 — 97.8%, 7 — 99.7% (close to the equilibrium value)

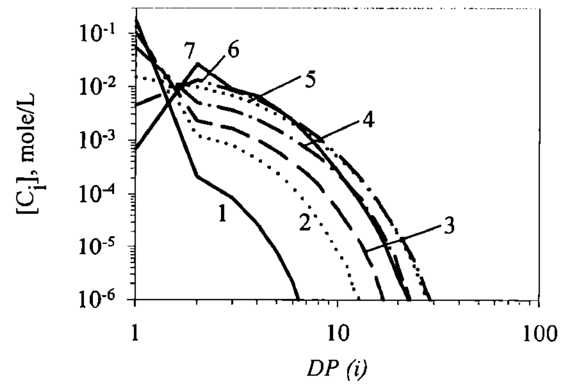

Fig. 4. Concentrations of cyclics ($[C_i]$) obtained by Monte Carlo simulations of reshuffling in ε-caprolactone polymerization computed for the same conditions as in Fig. 3. Different curves correspond to different degrees of monomer conversions — description as in Fig. 3

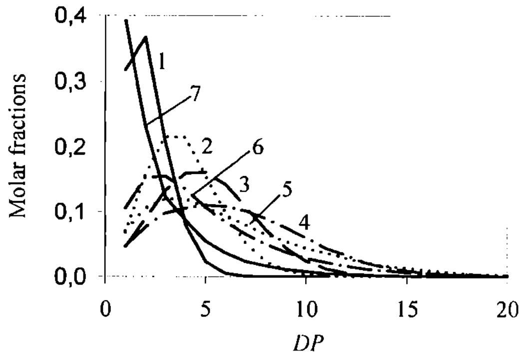

Fig. 5. Frequency distribution plots obtained by Monte Carlo simulations of reshuffling in ε-caprolactone polymerization computed for conditions similar to those in Fig. 1 but $[M]_0$ = 0.08 mol/L. Different curves correspond to different degrees of monomer conversions: 1 — 5.1%, 2 — 14.5%, 3 — 23.0%, 4 — 40.6%, 5 — 64.6%, 6 — 78.8%, 7 — 99.9% (close to the equilibrium value)

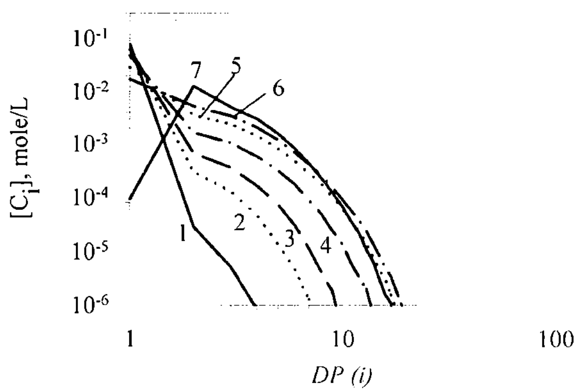

Fig. 6. Concentrations of cyclics ($[C_i]$) obtained by Monte Carlo simulations of reshuffling in ε-caprolactone polymerization computed for the same conditions as in Fig. 5. Different curves correspond to different degrees of monomer conversions — descriptions as in Fig. 5

Analogous results obtained for 10 times lower concentrations are given in Figs. 3 and 4, while Figs. 5 and 6 present the results obtained for 25 times lower concentrations.

As expected, the lower the initial concentration, the lower DP_n of the final linear polymer was observed. At lower monomer concentration much of monomer was consumed in formation of the macrocycles. Furthermore, the lower the monomer concentration, the higher *PDI* for a given monomer conversion. It proves that cyclization participates in reshuffling of the monomer units at least at lower initial monomer concentrations, because without cyclizations *MWD* dependences would be alike. Plotting the simulated *PDI* data beside a curve simulated for segmental exchange without participation of cyclization proves the above statement (see Fig. 7). Only for the highest initial monomer concentration the cyclization route of reshuffling can be neglected. One

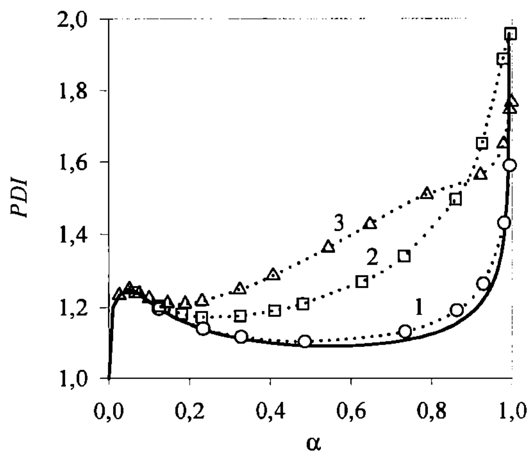

Fig. 7. Polydispersity index (PDI) versus monomer conversion (d) plotted for simulations presented in Figs. 1, 3, and 5 beside a curve (solid line) computed for the identical polymerization process with reshuffling but without cyclization (initial monomer concentrations do not matter); $[M]_0$ in mol/L: 1 — 2, 2 — 0.2, 3 — 0.08

could predict it when computing, according to eq. (13), the ratios of rates of cyclization and the rates of direct exchange at conversions corresponding to the highest DP_n. The computed ratios are 0.25, 1.6, and 3.2 for initial monomer conversions equal to 2, 0.2, and 0.08, respectively. Thus, the reshuffling *via* cyclization can be neglected only for the highest studied concentration.

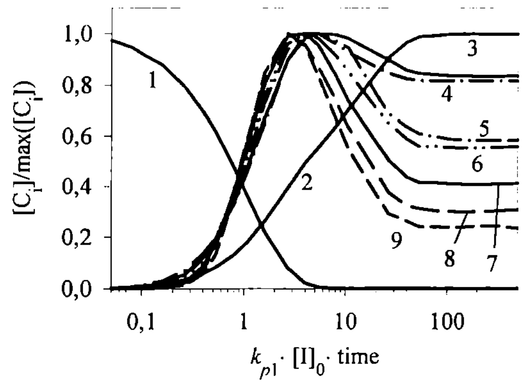

Fig. 8. Kinetics of monomer conversion and of formation of cyclic oligomers obtained by Monte Carlo simulations of reshuffling in ε-caprolactone polymerization ($[M]_0$ = 0.08 mol/L) computed for conditions described in Fig. 5. Maximal concentrations of cyclics in mol/L: 1 — 0.088, 2 — 0.0202, 3 — $5.29 \cdot 10^{-3}$, 4 — $3.05 \cdot 10^{-3}$, 5 — $1.65 \cdot 10^{-3}$, 6 — $9.15 \cdot 10^{-4}$, 7 — $5.21 \cdot 10^{-4}$, 8 — $3.12 \cdot 10^{-4}$, 9 — $1.88 \cdot 10^{-4}$

An interesting observation was made when analyzing the evolution of the concentration of macrocycles as a function of monomer conversion — namely the concentrations went through the maximum. The lower DP_n of linear polymer is this phenomenon, is the more significant. Figure 8 presents the observed kinetic curves plotted for $[M]_0$ = 0.08 mole/L system.

Kinetically controlled enhancement of macrocyclic oligomers was previously predicted by Slomkowski [8], but that phenomenon was based on end-biting cyclization being faster, than corresponding cyclization with participation of interchain units (back-biting cyclization). In the presented simulations end-biting reaction was forbidden (due to the assumption of instantaneous initiation with forming of unbreakable bond).

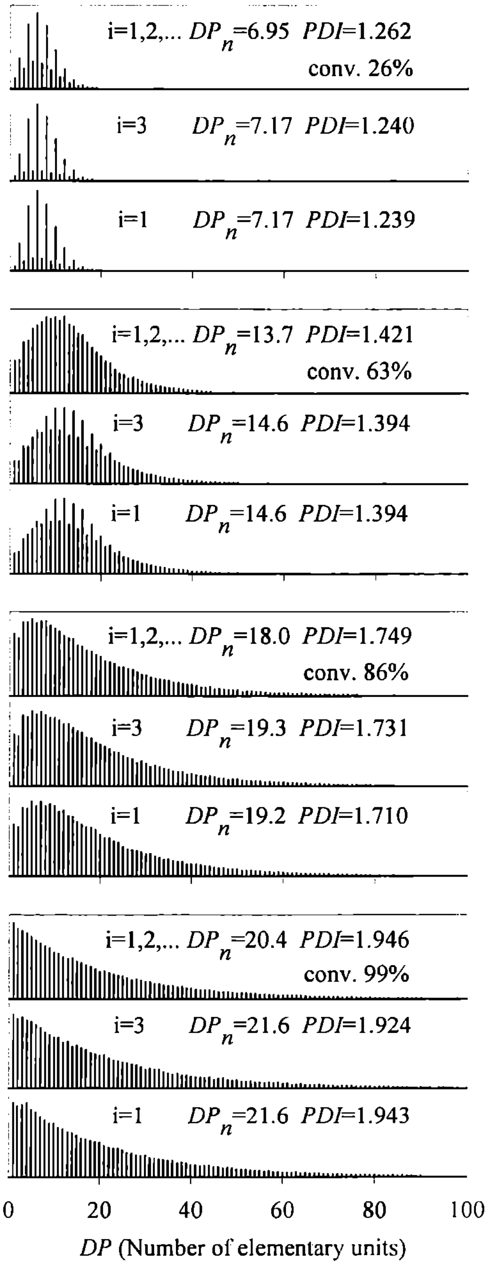

Fig. 9. MWD plots of the products of composite monomer (C_2) polymerizations proceeding with a reshuffling of segmental exchange and cyclization leading to C_i obtained by Monte Carlo simulations ($[C_2]_0$ = 1.0, $[I]_0$ = 0.1, $k_{p2}/k_{tr} = 10^1$, $k_{p2}[C_2]_0/\Sigma k_{ci} = 10^2$, $\Sigma[C_i]_e = 10^{-3}$)

Explanation is simple. Equilibrium of cyclic oligomers strongly depends on the average DP_n of linear polymer (eq. 10) and stems from the balancing of cyclization and propagation reactions. When *MWD* of a linear polymer is narrow, then the concentration of longer chains (not exceeding much DP_n) is relatively high and cyclization leading to larger cycles is faster than at equilibrium. At an equilibrium the linear chains are mostly short what makes the cyclization leading to longer chains relatively slow. Consequently, at intermediate monomer conversion the accumulation of larger cycles occurs, followed by a decrease in their concentrations leading to equilibrium *plateau*.

Participation of a cyclization in reshuffling can be observed in some cases even when the concentration of cyclic oligomers is negligible. The systems of polymerization of composite monomers, formed of two or more repeating units (capable to independent exchange when built in polymer chain) belong to this group of cases. The best example is the polymerization of dilactide, a monomer composed of two lactide units. MALDI-TOF studies have shown [9] indeed that even at low conversions, when a contribution of reshuffling reactions was low and *PDI* high, chains composed of "incorrect" odd number of lactide units had been formed.

Simulations showed that cyclization reaction manifested itself by formation of the chains composed of odd number of units even when no visible effect on *PDI* was observed. Some of the simulated *MWD* plots are shown on Fig. 9. If one assumes that equilibrium concentrations of cyclics are low, *i.e.* the corresponding propagation rate constants are fast, then almost no differences can be observed if a size of a cycle is 1, 3, or 5 (assuming only one type of cyclization). Contribution of cyclization depends, however, as it was discussed previously, on the initial monomer concentration.

An attempt was made to estimate the contribution of cyclization in dilactide polymerization. Estimation succeeded by fitting simulation results to the observed MALDI-TOF spectra. Figure 10 presents the relative concentrations of lactide oligomers, observed (MALDI-TOF) and simulated, with the assumption that the response coefficients in MALDI-TOF spectra for all oligomers are equal.

The result of simulations is additionally based on an arbitrary assumption that the formation of a cycle of one size, namely trilactide (9-membered cycle) dominates.

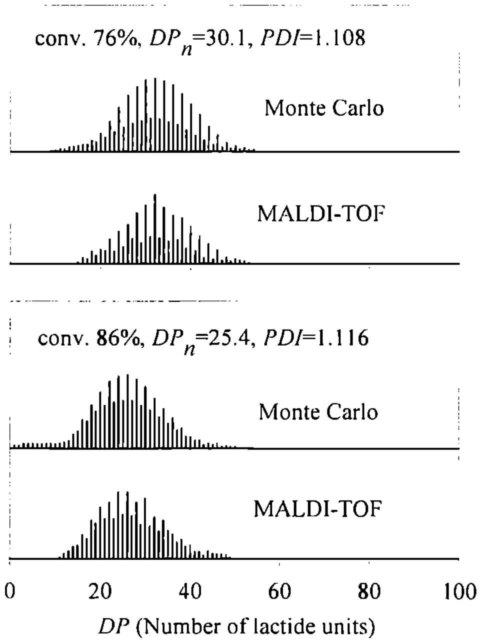

Fig. 10. MWD of the products of composite monomer (C_2) polymerizations (proceeding with a reshuffling of segmental exchange and cyclization leading to C_3 obtained by Monte Carlo simulations) fitted to the observed (MALDI-TOF) [9] relative concentrations of oligomers in L,L-dilactide polymerization (k_p/k_w = 83.3, k_{c3}/k_{tr} = 1.07 · 10^{-3} mol/L ≈ $[C_3]_e$)

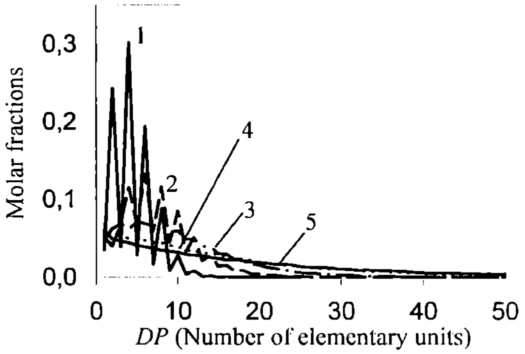

Fig. 11. Frequency distribution plots obtained by Monte Carlo simulations of reshuffling in ε-caprolactone dimer polymerization computed for conditions similar to those in Fig. 1 but $[C_2]_0$ = 1 mol/L ($2[C_2]_0/[I]_0$ = 22.7 and rate constant the same as in Fig. 1). Different plots correspond to different degrees of C_2 conversion: 1 — 12%, 2 — 28%, 3 — 46%, 4 — 78%, 5 — 95% (equilibrium value)

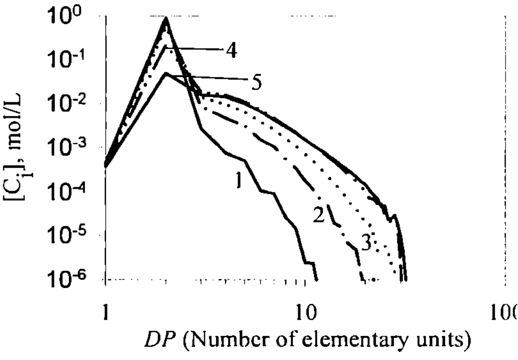

Fig. 12. Concentrations of cyclics ([Ci]) obtained by Monte Carlo simulations of reshuffling in ε-caprolactone dimer polymerization computed for the same conditions as in Fig. 11. Different plots correspond to different degrees of C_2 conversion — descriptions as in Fig. 11

Equally good fitting could be obtained, however, assuming the formation (as an intermediate) of monolactide (3-membered cycle) or pentalactide (15-membered cycle). The idea of monolactide was rejected because of its high ring-strain, while pentalactide, on the basis of entropic considerations favoring the smaller rings, was considered not likely. Consequently, one can assume that in the studied conditions mostly trilactides are formed with $k_{c3}/k_{tr} \approx 1.07 \cdot 10^{-3}$ mol/L $\approx [C_3]_e$.

Dimer of ε-caprolactone was chosen as another example of a composite monomer. Kinetic parameters of the polymerization of this compound can be taken from ε-caprolactone system studied previously [7]. Polymerization of this compound differs from polymerization of dilactide by an evident participation of cyclization. Simulations have confirmed this assumption. Results of the simulations are given in Figs. 11 and 12.

Although some experimental data were available, including MALDI-TOF spectra, attempts to get qualitative agreement with simulations failed. It was caused by the problems in determining of the correct response coefficients for cyclic and linear oligomers in MALDI-TOF spectra.

CONCLUSIONS

Monte Carlo simulations appeared to be a good tool for analysis of reshuffling process in the polymerization systems in which the cyclization reactions accompany the propagation and direct interchain segmental exchange. It was thus possible to determine the contribution of cyclizations in a broadening of *MWD* of linear polymer. Modeling of polymerization of ε-caprolactone has proved that this participation strongly depends on the monomer concentration.

When initial monomer concentration is sufficiently higher than the equilibrium concentration of cyclics (expressed in monomer units), then the participation of a cyclization in a reshuffling of polymer segments is insignificant. It becomes, however, important, when initial monomer concentration is comparable with the equilibrium concentration of cyclic fraction, even if polymerization is stopped when majority of a polymer is linear.

Modeling has shown that in the polymerization systems under consideration a phenomenon of kinetic enhancement of cyclics can be expected. This phenomenon is more significant, when the $[M]_0/[I]_0$ ratio is lower.

In the polymerizations of composite monomers the participation of cyclization in the segmental interchain exchange is often manifested by the formation of the chains composed of "incorrect" number of units. Simulations have proved that this effect could be observed even when no broadening of *MWD* was observed.

Fitting of the simulation results to the experimental data can give access to determination of the rate constant of cyclization. Using this method k_{c3}/k_{tr} was determined for dilactide polymerization.

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