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Copolymerization of the Pair Maleic Anhydride-Dicyclopentadiene: II. Kinetics at Low Conversion

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Kinetic investigations regarding the copolymerization of the pair maleic anhydride (MA)–di-cyclo-pentadiene (DCPD) are presented. It has been shown that copolymerization takes place mainly by cross-propagation, implying both free monomers and charge transfer complexes (CTC) as well. In this case, homo-propagation of MA, even minor, can no longer be overlooked; termination is due to a degradative transfer. A suitable kinetic model has been devised, on this basis; the proposed model has been checked against experimental measurements.

Keywords maleic anhydride, dicyclopentadiene, copolymerization, kinetics, reaction mechanism

Introduction

We reported the behavior of the MA/DCPD in radical copolymerization system in a previous paper (1). Copolymerization of MA with DCPD represents a less studied process when compared with other co-polymerizations involving MA (i.e., with other linear, or cyclic olefins or diolefins (2a). The earlier two papers dedicated to this topic (3, 4) presented rather contradictory results; moreover, the conclusions regarding either the reaction mechanism, or the structure of the products obtained are completely different. Recent studies published by us (1, 5) have only partially confirmed Gaylord's or Rzaeva's reports. Even if cross propagation represents an important step, nevertheless, the classical models (with or without CTC) cannot satisfactorily describe the above-mentioned process. For instance, at high conversions, we have found (1) significant deviations from the Rzaeva (4) model. One of the reasons for the lack of agreement between theoretical premises and the experimental results probably lies in a powerful degradative transfer; this feature has been overlooked in earlier studies (4). The present paper recommends another, more detailed, kinetic model, which explains the behavior of the MA/DCPD system, both in its initial stage, as well as at high conversions.

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Experimental

MA, DCPD, as well as dioxane (D), used as solvent for the copolymer, have been purified as previously described (1, 4). Previously, azo-iso-butyro-di-nitrile (AIBN) and lauroyl peroxide (LP) have been purified by recrystallization. Tetrahydrofurane (THF), used in viscometric measurements, has been initially distilled from Cu_2Cl_2, dried on solid KOH, and finally redistilled from metallic Na.

Two distinct techniques (gravimetry and dilatometry) have been used to measure conversions, and reaction rates, respectively. The gravimetric method implies carrying out copolymerization in reactors and taking samples at pre-established times; the copolymer has been separated by precipitation and washing in ethyl ether. High conversions may be reached by gradually adding new amounts of AIBN; this technique has been previously described (1). For copolymerizations performed within a dilatometer, LP has been used as initiator; the reaction product was finally isolated as described above.

Structure of reaction products has been previously established by NMR analyses (1). In the present work, the composition was estimated by elemental analysis (C, H, and N). Viscometric measurements (THF, 30°C) proved to be beneficial in understanding molecular weights.

Results and Discussion

A first set of tests had the dependence of copolymer composition as a function of monomer feed composition in view. In this respect, the initial concentration of the two monomers has been kept constant (3.5 mole/l), while changing the molar fraction of MA (x_1) in the monomer feed. Reactions have been carried out in reactors equipped with stirring devices; AIBN has been chosen as initiator as it has similar activation energy with LP (6-a), used in subsequent dilatometric studies. On the other hand, the nitrogen content within the final product (copolymer) allows estimating the number of residual primary radicals corresponding to each copolymer molecule. For each monomer feed, at least six samples (at various conversions) have been separated. The results, selectively presented in Table 1, allow us to present the following remarks:

1. Initial copolymerization rate plotted against x_1 has the well-known shape displaying a maximum (4, 5). This feature has very often been considered as an unquestionable proof for alternating copolymerization.
2. Intrinsic viscosities measured for the reaction products are within the range $4 \div 8$ ml/g, regardless the composition and/or conversion. According to some previous studies (1, 5), these values would correspond to $\overline{M_n}$ being placed between $2*10^3$ and $3*10^3$. Consequently, measuring N percentage in copolymer gives quite accurately, its structure, written as $R_0(MA)_{n1}$ $(DCPD)_{n2}$. This statement implies, on one hand, that the contribution of termination involving two macro-radicals (or with the participation of primary radicals) recombination may be neglected; on the other hand, one may correctly calculate the copolymer composition $X_1/X_2 = n_1/n_2$, without being influenced by the errors introduced by the presence of residual fragments (R_0). It should be mentioned that numerical molecular weights obtained by GPC have the same order of magnitude with those calculated from the N content (elemental analysis).
3. We have found that regardless of monomer feed composition, the ratio X_1/X_2 is higher than 1.0. At the same time, we have shown (1) that the reaction product still keeps a residual unsaturation from DCPD, even at high conversions. These two divergent

Table 1
Copolymerization tests initiated by AIBN, for various monomer feeds
(AIBN $= 5 * 10^{-2}$ mole/l, $M_{01} + M_{02} = 3.5$ mole/l, t = 80°C)

x_1	Conv (%)	% C	% H	% N	X_1/X_2[a]	R_{po} (mole/l*s)
0.2	5.49	65.06	6.20	0.39	1.92	$6.10 * 10^{-5}$
	7.97	65.16	6.30	0.55		
	15.66	64.90	6.46	0.54		
0.25	9.86	64.64	6.02	0.34	2.05	$1.09 * 10^{-4}$
	25.53	64.77	6.08	0.47		
	44.74	64.51	5.65	0.64		
0.33	11.20	67.40	6.61	0.28	1.52	$1.18 * 10^{-4}$
	14.41	67.42	6.65	0.29		
	44.74	67.30	6.86	0.37		
0.5	15.63	65.40	5.80	0.32	1.92	$1.59 * 10^{-4}$
	22.10	65.25	6.07	0.36		
	58.44	65.36	6.17	0.41		
0.67	17.50	65.12	5.25	0.46	2.11	$1.69 * 10^{-4}$
	51.22	64.85	5.15	0.37		
	73.29	65.03	4.93	0.42		
0.75	17.35	64.15	5.68	0.46	2.20	$1.65 * 10^{-4}$
	35.58	63.85	5.68	0.37		
	56.60	64.00	5.72	0.42		
0.8	17.19	63.87	5.98	0.39	2.25	$1.62 * 10^{-4}$
	23.76	63.63	5.48	0.38		
	38.06	64.20	5.73	0.62		

[a] Mole ratio of MA/DCPD units in the copolymer.

findings might be accommodated only by accepting a minor homopropagation for radicals ending in MA. However, if that sounds very unusual, there are data reporting MA "homopolymerization" under similar conditions to those used by us (2-b) in the literature.

4. Copolymer composition slightly changes as a function of monomer feed composition; moreover, for a given monomer feed, copolymer composition remains constant, regardless of conversion reached. This last observation is important, as it allows the use of a dilatometric technique (far more advantageous) for kinetic studies. The data accumulated until now call for a kinetic model, and is able to adequately describe all experimental remarks.

In this respect, the following simplifying hypotheses are to be made:

1. Initiation takes place mainly by the addition of primary radicals to MA. When a primary radical meets a DCPD molecule, the result is their deactivation, as new inactive alyl radicals are formed;
2. Radicals ending in MA are able to participate to a limited homo-addition;
3. Cross propagation involves both free monomers, as well as CTC;

4. Termination by recombination (either of propagating or primary radicals) might be neglected. We think that termination takes place mainly by the degradative transfer with DCPD.

Making MA as monomer 1, and DCPD as monomer 2, the main elementary reactions, influencing both the process rate and product composition, are:

1. $I \xrightarrow{k_d} 2\overset{\bullet}{R}_o;\ R_d$
2. $\overset{\bullet}{R}_o + M_1 \xrightarrow{k_i} \overset{\bullet}{M}_1;\ R_i$
3. $\overset{\bullet}{M}_1 + M_1 \xrightarrow{k_{11}} \overset{\bullet}{M}_1;\ R_i$
4. $\overset{\bullet}{M}_1 + M_2 \xrightarrow{k_{12}} \overset{\bullet}{M}_2;\ R_{12}$
5. $\overset{\bullet}{M}_2 + M_1 \xrightarrow{k_{21}} \overset{\bullet}{M}_1;\ R_{21}$
6. $\overset{\bullet}{M}_1 + CTC \xrightarrow{k_{1c}} \overset{\bullet}{M}_1;\ R_{1c}$
7. $\overset{\bullet}{M}_2 + CTC \xrightarrow{k_{2c}} \overset{\bullet}{M}_2;\ R_{2c}$
8. $\overset{\bullet}{M}_1 + M_2 \xrightarrow{k_{lT}} P + \overset{\bullet}{A};\ R_{lT}$
9. $\overset{\bullet}{M}_2 + M_2 \xrightarrow{k_{2T}} P + \overset{\bullet}{A};\ R_{2T}$

In reactions 8 and 9, A represents all alyl radicals produced by transfer with DCPD. Consequently, copolymerization rate may be written as:

$$R_p = R_i + R_{11} + R_{12} + R_{21} + R_{1c} + R_{2c}$$

By using the pseudo-stationary conditions, namely $\frac{dM_1}{dt} = 0$ and $\frac{dM_2}{dt} = 0$, the copolymerization rate becomes:

$$R_p = R_i(1 + T_1 + T_2 + T_3 + T_4 + T_5) \tag{1}$$

$$T_1 = \frac{C_1C_2M_1^2 + C_2M_1M_2}{C_2M_1M_2 + M_2^2 + C_3M_2^2}; \quad T_2 = \frac{C_2C_3M_1}{C_2M_1 + M_2 + C_3M_2}$$

$$T_3 = \frac{C_2C_3M_1M_2 + C_3M_2^2}{C_2M_1M_2 + M_2^2 + C_3M_2^2}; \quad T_4 = \frac{C_2C_4M_1^2M_2 + C_4M_1M_2^2}{C_2M_1M_2 + M_2^2 + C_3M_2^2}$$

$$T_5 = \frac{C_3C_5M_1M_2}{C_2M_1 + M_2 + C_3M_2}$$

where:

$$R_d = -\frac{dI}{dt}$$

$$R_i = 2 * f * R_d$$

$$C_1 = \frac{k_{11}}{k_{1T}};\ C_2 = \frac{k_{21}}{k_{2T}};\ C_3 = \frac{k_{12}}{k_{1T}};\ C_4 = \frac{k'_{1c}}{k_{1T}};\ C_5 = \frac{k'_{2c}}{k_{2T}}$$

As $k'_{1c} = k_{1c} * K$ and $k'_{2c} = k_{2c} * K \mathrm{k}'_{2c} = \mathrm{k}_{2c} * \mathrm{K}$, (K represents the equilibrium constant for the formation of CTS[4]), it proves that only the first three parameters get the physical meaning of being the reciprocal values of transfer constants. Accordingly, the equivalent form of Equation (1), as adapted for the independent variable x_1, when $M_0 = M_{01} + M_{02}$ = constant, is better describer by the relationship (1′).

$$R_p = R_i(1 + T'_1 + T'_2 + T'_3 + T'_4 + T'_5) \qquad (1')$$

where:

$$T'_1 = \frac{C_1C_2x_1^2 + C_1x_1(1 - x_1)}{C_2x_1(1 - x_1) + (C_3 + 1)(1 - x_1)^2}; \quad T'_2 = \frac{C_2C_3x_1}{C_2x_1 + (C_3 + 1)(1 - x_1)}$$

$$T'_3 = \frac{C_2C_3x_1 + C_3(1 - x_1)}{C_2x_1 + (C_3 + 1)(1 - x_1)}; \quad T_4 = \frac{C_2C_4x_1^2 + C_4x_1(1 - x_1)}{C_2x_1 + (C_3 + 1)(1 - x_1)} * M_o$$

$$T'_5 = \frac{C_3C_5x_1(1 - x_1)}{C_2x_1 + (C_3 + 1)(1 - x_1)} * M_o$$

Even if the proportionality $R_p \sim R_I$ seems surprising enough, we should consider that in chain polymerizations where termination reactions are first order (with respect to propagating radicals), this fact corresponds to a normal feature.

Using the same premises and the same notes, the composition equation with the general form $\frac{dM_1}{dM_2} = \frac{X_1}{1 - X_1} = f(x_1)$ becomes:

$$\frac{X_1}{1 - X_1} = \frac{Y}{Z} \qquad (2)$$

where:

$$\begin{aligned} Y &= 1 + C_1C_2x_1^2 + (C_1 + C_2C_3 + M_oC_2C_4x_1)x_1(1 - x_1) \\ &\quad + M_o(C_4 + C_3C_5x_1)(1 - x_1)^2 \\ Z &= C_1C_2x_1^2 + [C_1 + 2C_2C_3 + 2C_2C_4M_ox_1 + (C_3 + 2C_4M_o + 2C_3C_5M_o) \\ &\quad \times (1 - x_1)]x_1(1 - x_1) \end{aligned}$$

It may be said that both Equations (1) and (2) are valid, provided that $M_o = M_{o1} + M_{o2}$ = constant, x_1 being the only variable. These equations contain a high number of kinetic parameters, difficult to be obtained by experiment. This is the reason why our first attempt (Figures 1 and 2) was the graphical simulation of Equations (2) and (1′). To plot the theoretical curves, we have arbitrarily chosen the C_i parameters; the selection criteria were dictated by the analogy between the system studied and date in the literature (6b–d). On these graphs, our experimental points are in agreement with the data from Table 1.

The similarity between one of the theoretically simulated curves and the sets of experimental points might be, of course, only circumstantial; even so, we must make the following statements:

- The graphical shape suggested by the position of experimental points is similar to these plotted according to the kinetic model. The values for reaction rates (Figure 2) are more sensitive to the change in C_i parameters, than copolymer composition (Figure 1).

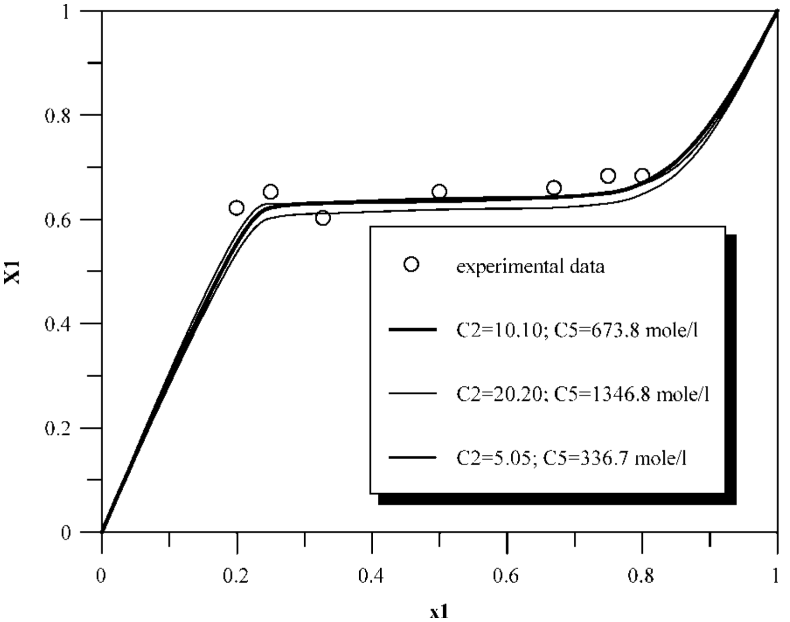

Figure 1. Copolymer composition vs. monomer feed composition ($M_{01} + M_{02} = 3.5$ mole/l, $C_1 = 1.43$; $C_3 = 14.29$; $C_4 = 23.81$ mole/l).

- The two monomers exhibit a quite different contribution in the main reactions, determining reaction rates and composition; this fact is revealed by the asymmetry of curves.

The kinetic scheme proposed implies checking the reaction kinetics. This request has been fulfilled by carrying out dilatometric studies (LP as initiator). Establishing the dependence of the copolymerization rate on the main process parameters has been the main target to accomplish, for instance, the reaction order with respect to initiator (Figure 3) has been found as being 1.32. At first glance, the fact seems surprising enough, however, this parameter is consistent with Equations (1) and (1′) as they explicitly contain the term R_i. On the other hand, kinetic studies regarding the decomposition of LP in D at 80°C (in the range of 10^{-2} mole/l) have revealed a dependence of the type:

$$-\frac{d(LP)}{dt} = k'_d(LP)^{1.4}$$

Obviously, as $R_d \sim I^{1.4}$ and since $R_i = 2 * f * R_d$, one gets $R_p \sim I^{1.4}$. The small difference among the two exponents (1.32 and 1.4, respectively) is easily explained by the contribution of both monomers in this minor change regarding the reaction order. Moreover, when measuring the total apparent activation energy (Figure 4) we have found 120 kJ/mole. This value is just a bit higher than that corresponding to the decomposition of LP (6-a). It is also reasonable to recognize that $\sum_{i=1}^{5} T_i$ from Equations (1) and (1′) is less influenced by temperature. This piece of evidence is probably due to the fact that many parameters exhibit similar activation energies.

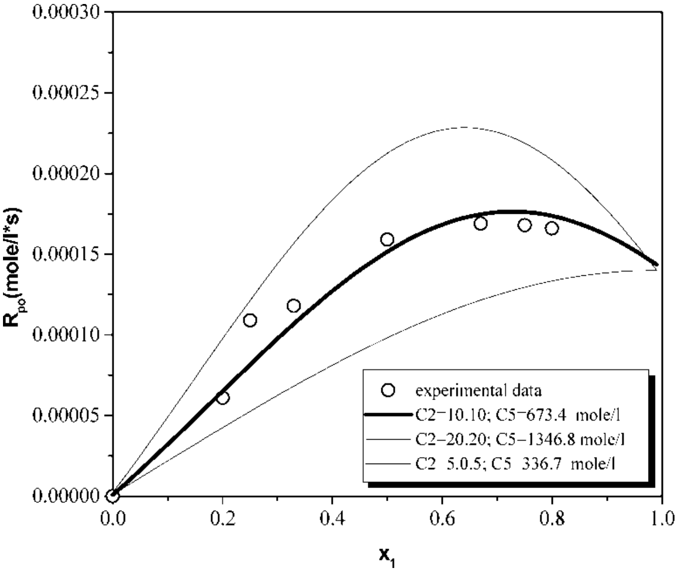

Figure 2. Initial polymerization rate against monomer feed composition ($M_{01} + M_{02} = 3.5$ mole/l; $C_1 = 1.43$; $C_3 = 14.29$; $C_4 = 23.81$ mole/l).

At any rate, this value is far higher than those usually common in radical polymerizations or copolymerizations where $R_p \sim R_i^{0.5}$. Therefore, the value obtained for the total activation energy represents a supplementary proof for the connection $R_p \sim R_i$.

Obviously, the relationship (1) is asymmetrical with respect to the two variables M_1 and M_2, respectively. Indeed, graphical simulation of Equation (1) for different C_i values, leads to quite distinct shapes when using the monomer concentrations as variables. For

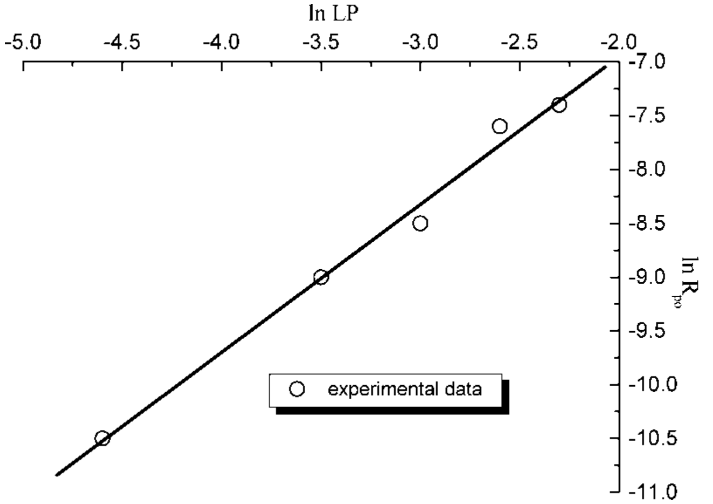

Figure 3. Computation of the partial reaction order with respect to LP ($M_{01} + M_{02} = 3.5$ mole/l, T = 80°C, LP: 10^{-2}, $3 * 10^{-2}$, $5 * 10^{-2}$, $8 * 10^{-2}$, 10^{-1} mole/l).

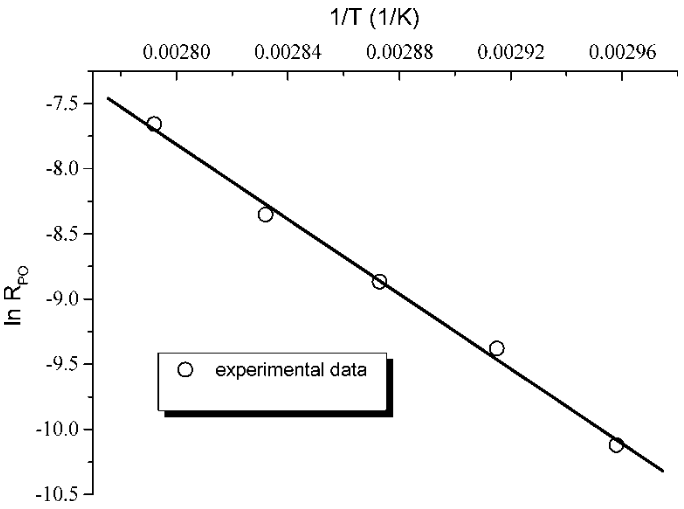

Figure 4. Measuring of activation energy ($M_{01} + M_{02} = 3.5$ mole/l; LP $= 5 * 10^{-2}$ mole/l, T: 65, 70, 75, 80, 85°C).

instance, for M_2 = constant, a group of curves (almost without intercept) would result in $R_p = f(M_1)$. However, for some C_i values, one gets linear dependence. On the contrary, when M_1 = constant, the function $R_p = f(M_2)$ is also represented by a group of curves, this time showing an significant value for the intercept; this is to be explained by the initial presumption saying that M_1 might homo-propagate, while M_2 could not. Based on these findings, a formal reaction order for M_1 (but not for M_2) seems reasonable. The partial reaction order with respect to M_1 (for M_2 = constant) found by us is 0.93, close to the anticipated value (see also Figure 5).

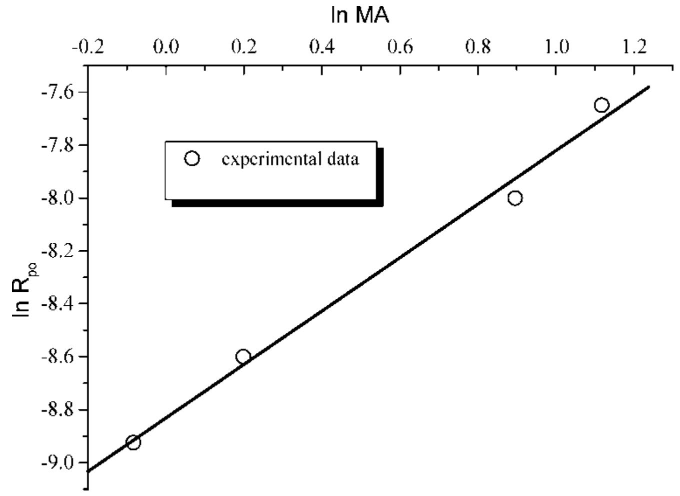

Figure 5. Calculation of the partial reaction order with respect to MA ($M_{02} = 2.14$ mole/l; T = 80°C, LP $= 10^{-2}$ mole/l, M_{01}: 0.92, 1.22, 2.45, 3.06 mole/l).

Conclusions

Copolymerization of the MA-DCPD pair, reported by us, presents a large number of specific features. They might be satisfactorily explained only by taking into account all the elementary reactions, strongly influencing both the rate and the composition

As predicted (1), both initiation and termination cannot be ignored in this process that may be named co-oligomerization, rather than copolymerization.

The kinetic model proposed by us accounts for experimental observations and is sufficiently well verified by the kinetic measurements carried out for this purpose. In anycase, the model based on "ideal" alternating copolymerization (4), based only on cross-propagation seems to be inadequate for describing the behavior of the system.

For binary systems involving only hetero-propagations in long chains, the general expression for the copolymerization rate (7), may be written as $R_p = kI^{\alpha}M_1^{\beta}M_2^{\gamma}$. For an ideal situation, $\alpha = \beta = \gamma = 0.5$; however, in practice these coefficients are found in the 0.4–0.6 range, depending on the degree of CTC participation in propagation. It must be underlined that such dependence has not been noticed for the system currently under scrutiny; the differences easily overcome any experimental errors.

By simply admitting the homo-addition of MA, we may reasonably explain the excess of MA units in "copolymer", as noticed also by Gaylord (3), but not by Rzaeva (4); this account does not imply exotic structural structures as proposed by the former one.

It has also to be noted that the presented hypotheses regarding the development of the process at low conversions do not disagree with our previous observations and explanations (1) regarding the phenomena taking place at high conversions (post-copolymerization).

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