

**Polymerization of Oxetanes with Organoaluminium Catalysts.  
II. Analysis of Molecular-Weight Distributions in the  
Polymerization of 3-Methyl-3-chloromethyloxetane  
with the  $\text{Al}(i\text{-C}_4\text{H}_9)_3\text{-H}_2\text{O}$   
Catalyst System**

G. P. ALEKSIUK, V. V. SHAMANIN, A. F. PODOLSKY,  
L. V. ALFEROVA, and V. A. KROPACHEV

*Institute of Macromolecular Compounds, Academy of Sciences of the USSR,  
Bolshoj 31, Leningrad, 199004, USSR.*

(Received March 22, 1980)

**ABSTRACT:** Molecular-weight distributions and polydispersity parameters of the polymers formed in the polymerization of 3-methyl-3-chloromethyloxetane with the  $\text{Al}(i\text{-C}_4\text{H}_9)_3\text{-H}_2\text{O}$  catalyst system have been investigated. It was shown that the main feature of this process is the ability of macromolecules to regulate their own size in the formation of a polymer of high molecular weight ( $\sim 10^6$ ) and narrow molecular-weight distribution ( $M_w/M_n = 1.30 \pm 0.05$ ) without any dependence on conversion, and the initial monomer and catalyst concentrations. Proceeding from the suggestion that the ratio of the termination to propagation-rate constants ( $k_t/k_p$ ) depends on the size of the macromolecules, equations for the unnormalized weight molecular-weight distribution (MWD), and polydispersity parameters were derived. The experimental and calculated values of weight MWD and polydispersity parameters are in satisfactory agreement. On the basis of these data, a model for polymerization is proposed, assuming the formation of an active centre in the form of an ion-pair of the polymer zwitter-ion solvated by its own polymer chain. This model explains adequately the dependence of the  $k_t/k_p$  ratio on the degree of polymerization and the observed molecular-weight characteristics of the polymer.

**KEY WORDS** Molecular-Weight Distribution / Polydispersity Parameters /  
3-Methyl-3-chloromethyloxetane / Organoaluminium Catalyst / Zwitter-Ion  
Active Centres / Ring-Closure during Polymerization /

It was shown in the preceding paper<sup>1</sup> that the polymerization of 3-methyl-3-chloromethyloxetane (MCMO) with the  $\text{Al}(i\text{-C}_4\text{H}_9)_3\text{-H}_2\text{O}$  catalyst system involves not only the initiation and propagation reactions but also the termination of growing chains and the deactivation of the catalyst by the polymer. The propagation, termination, and initiation constants can be arranged in the following order:  $k_p \gg k_t \gg k_i$ . The lifetime of each macromolecule is much shorter than the time of the entire process and quasi-monomolecular reactions dominate the termination stage. After a relatively short induction period, a situation typical of the "equilibrium" polymerization could be observed:  $M_n$  and the width of the unimodal molecular-weight distribution (MWD) do not change with conversion (see Table I

in ref 1).

However, in this case the  $M_w/M_n$  and  $M_z/M_w$  ratios are much lower than the "most probable" ratio ( $M_w/M_n = 2.0$ ) or the "recombination" ratio ( $M_w/M_n = 1.5$ )<sup>2</sup> and are nearly equal to each other. The systematic increase in the  $M_w/M_n$  ratio as compared to the  $M_z/M_w$  ratio does not exceed 5.0%.

## EXPERIMENTAL

### *Procedures*

Polymerization was carried out by a previously described method.<sup>1</sup> The number-average molecular weight was determined by osmometry with a High-Speed Membrane Osmometer, Hewlett-Packard, model-502 automatic apparatus in toluene solution

at 37°C. MWD and polydispersity parameters were calculated with a Mir-2 computer (USSR) according to the data of high-speed sedimentation determined with the 3170 analytical centrifuge (MOM, Hungary). Sedimentation coefficients ( $S$ ) were determined in methyl ethyl ketone at 21°C and the rotor speed of 40 000 rev min<sup>-1</sup> and the distributions of shifts  $g(x)$  were established at different times and at four different concentrations. Diffusion coefficients were determined with a Tsvetkov polarizing diffractometer<sup>3</sup> and with an ultracentrifuge at a low rotor speed. Sedimentation coefficients were extrapolated to zero concentration, according to the equation  $1/s = (1/S_0)(1 + k_s c)$ , the value of  $k_s$  being 4.0 dl g<sup>-1</sup> at  $S_0 = 26$  Sv and 2.3 dl g<sup>-1</sup> at  $S_0 = 23$  Sv. Molecular weights were calculated according to Svedberg's equation from  $S_0$  and  $D$  and the value of partial specific volume ( $\bar{v}$ ) taken to be approximately equal to reciprocal density  $\bar{v} \approx 1.17$  cm<sup>3</sup> g<sup>-1</sup>.

The MWD curves were calculated from sedimentograms by a published method.<sup>4</sup> Distributions of shifts  $g(x)$  were converted into those of sedimentation coefficients  $g(S)$ . Several distributions  $g(S)$  obtained at different times were converted into a single distribution corresponding to infinite time. This prevented the diffusion spreading of the sedimentation boundary. As a result, the distributions of sedimentation coefficients  $g(S)$  were obtained at four concentrations for each sample. The exclusion of concentration dependence  $S(c)$  led to the distribution curve of sedimentation constant  $g(S_0)$  the relative width of which  $\sigma_s/S$  (see Table I in ref 1) is the experimental characteristics of polydispersity. If the dependence  $S_0 \sim M^{0.5}$  is assumed, parameters  $\sigma_s/S$  can be converted into the polydispersity characteristics  $M_z/M_w = \{[1/(1-b)](\sigma_s/S)\}^2$  and if the Schultz distribution is assumed, the parameters of inhomogeneity  $M_w/M_n$  can be evaluated (data reported in Table I in ref 1). The closeness of the values of molecular weights and polydispersity parameters is also retained if another limiting value of the exponent  $(1-b) = 0.4$  is incorporated into the equation  $S_0 = k_s M^{1-b}$ . This value could have been corrected to osmometric values of  $M_n$  but we did not do so, taking into consideration the agreement between the osmometric values of  $M_n$  and those obtained from sedimentation analysis.

Virtually the same polydispersity characteristic

values were obtained by treating the sedimentation curves in the Gaussian approximation according to a published method.<sup>4</sup> This also made possible avoiding the distorting effect of concentration and diffusion spreading of the concentration boundary on the  $g(S_0)$  shape.

## RESULTS AND DISCUSSION

It follows from the general principles of the statistic theory of polymerization<sup>2</sup> that when the statistical width of MWD and the absolute values of  $q$ -average molecular weights (MW) are independent of conversion and when recombination is impossible,<sup>1</sup> the distributions more narrow than the "most probable" distribution (and, even to a greater extent the "recombination" distribution) appear only if the propagation to termination-rate ratio ( $R_p/R_t$ ) decreases with a increase in the length of the growing chains. It is known that in the most general case when, in stationary processes, the probabilities of chains propagation or termination depend on chain length, the equilibrium distribution is determined by the equation,<sup>2</sup>

$$q_n(M) = \alpha(M) \exp - \int_0^M \alpha(M) dM \quad (1)$$

where  $\alpha(M) = R_t/R_p = F(k_t/k_p)$ .

In our case, the parameters of polydispersity do not change with conversion. This means that the distribution parameter  $\alpha$  depends on one parameter only, MW, but does not depend on conversion. The dependence of  $\alpha$  on MW can be brought about by a change in either  $k_p$  or  $k_t$  or both of these with increasing MW.

It may be expected that this dependence is continuous and that it can adequately be described by an approximation of the type,

$$\alpha(M) = \alpha_0 M^\beta \quad (2)$$

where  $\alpha_0$  and  $\beta$  are constants that should be determined.

In this approximation eq 1 becomes,

$$q(M) = \alpha_0 M^\beta \exp - \frac{\alpha_0}{\beta+1} M^{\beta+1}. \quad (3)$$

The distribution moment of the order  $\nu$  is given by,

$$\bar{M}^\nu = \int_0^\infty M^\nu q_n(M) dM = \left( \frac{\beta+1}{\alpha_0} \right)^{\nu/(\beta+1)} \frac{\nu}{\beta+1} \Gamma \left( \frac{\nu}{\beta+1} \right) \quad (4)$$

where  $\Gamma$  is the complete gamma-function.

It follows from the character of averaging that all moments  $\bar{M}^v$  are number-average values of  $M^v$ . The first  $v$ -average weight ( $M^1$ ) is the number-average molecular weight ( $M_n$ ).

Using eq 4 it is easy to obtain the expressions for the corresponding average molecular weights and polydispersity parameters,

$$M_n = \bar{M}^1 = \left(\frac{\beta+1}{\alpha_0}\right)^{1/(\beta+1)} \frac{1}{\beta+1} \Gamma\left(\frac{1}{\beta+1}\right)$$

$$M_w = \frac{\bar{M}^2}{\bar{M}^1} = \left(\frac{\beta+1}{\alpha_0}\right)^{1/(\beta+1)} \frac{\Gamma\left(\frac{2}{\beta+1}\right)}{\Gamma\left(\frac{1}{\beta+1}\right)}$$

$$M_z = \frac{\bar{M}^3}{\bar{M}^2} = \left(\frac{\beta+1}{\alpha_0}\right)^{1/(\beta+1)} \frac{3}{2} \frac{\Gamma\left(\frac{3}{\beta+1}\right)}{\Gamma\left(\frac{2}{\beta+1}\right)}$$

$$\frac{M_w}{M_n} = 2(\beta+1) \frac{\Gamma\left(\frac{2}{\beta+1}\right)}{\left[\Gamma\left(\frac{1}{\beta+1}\right)\right]^2} \quad (5)$$

$$\frac{M_z}{M_w} = \frac{3}{4} \frac{\Gamma\left(\frac{3}{\beta+1}\right)\Gamma\left(\frac{1}{\beta+1}\right)}{\left[\Gamma\left(\frac{2}{\beta+1}\right)\right]^2} \quad (6)$$

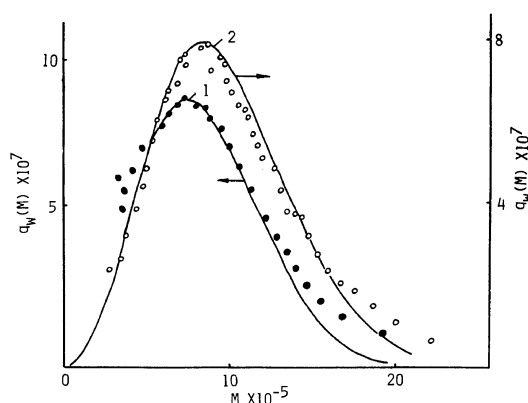
Equations 5 and 6 show that polydispersity parameters depend only on the  $\beta$  constant. Its numerical value can be determined by selection, comparing the experimental values of polydispersity parameters and their values calculated from eq 5 and 6 (Table I). The data in Table I shows that at  $\beta=0.9$ – $1.0$  the calculated values of  $M_w/M_n$  and  $M_z/M_w$  are closest to experimental values (see Table I in ref 1). The agreement between the calculated and experimental values of polydispersity parameters shows that the selected approximation (eq 2) is valid and actually means that the distribution parameter  $\alpha$  (or the  $k_t/k_p$  ratio) is proportional to MW.

Substituting the value of  $\beta=1.0$  into eq 3 and multiplying by  $\text{MW}(M)$ , we obtain the expression for the unnormalized weight MWD,

$$q_w = M^2 \exp\left(-\frac{\alpha_0}{2} M^2\right). \quad (7)$$

**Table I.** Parameters of polydispersity calculated according to eq 5 and 6 vs. value of the  $\beta$  coefficients

$\beta$	$M_w/M_n$	$M_z/M_w$
0.5	1.46	1.27
0.6	1.41	1.25
0.7	1.37	1.23
0.8	1.33	1.21
0.9	1.30	1.19
1.0	1.27	1.18
1.1	1.25	1.17
1.2	1.23	1.15
1.3	1.21	1.14
1.4	1.19	1.13
1.5	1.18	1.13



**Figure 1.** MWD curves of poly(MCMO) for conversions of (1) 4.6% and (2) 89.0%. Points represent the experimental values and lines represent the calculated values. Initial conditions:  $[\text{M}_0]$ ,  $0.55 \text{ mol l}^{-1}$ ;  $[\text{H}_2\text{O}]$ ,  $0.003 \text{ mol l}^{-1}$ ;  $[\text{i-Bu}_3\text{Al}]$ ,  $0.01 \text{ mol l}^{-1}$ ; a chlorobenzene solution,  $20^\circ\text{C}$ .

It is possible to determine  $\alpha_0$  from the condition of the coincidence of the maxima for calculated and experimental curves of weight MWD. Under this condition, we have

$$\frac{dq_w}{dM} = (2M_{\max} - \alpha_0 M_{\max}^3) \exp\left(-\frac{\alpha_0}{2} M_{\max}^2\right) = 0.$$

Hence,  $\alpha_0 = 2/M_{\max}^2$  where  $M_{\max}$  is the MW value corresponding to the maximum of the experimental curve of weight MWD.

Using eq 7, we obtain the final expression for the unnormalized weight MWD,

$$q_w = M^2 \exp\left(-\frac{M^2}{M_{\max}^2}\right). \quad (8)$$

The curves of weight MWD calculated according to eq 8 reproduce satisfactorily the experimental results (Figure 1). The curves are normalized to the maximum value of the ordinate of experimental curves of weight MWD. Satisfactory agreement between the experimental and calculated MWD curves and polydispersity parameters confirms the suggestion that the  $k_t/k_p$  ratio depends on the length of the growing chain.

In our kinetic analysis of the MCMO polymerization,<sup>1</sup> the dependence of propagation and termination constants on the length of the growing chain was not taken into account. Therefore it should be shown that this dependence does not contradict the assumed kinetic scheme of the process on the basis of which the main kinetic equations were derived and by which constants for the elementary reactions were calculated.

It has been shown previously<sup>5</sup> (see theorem (eq 1)) that the kinetic scheme of reactions of single-centre addition polymerization satisfies the condition of quasi-stationary propagation under which the ratio of the probability of propagation to that of termination is determined only by the length of the growing chain. This scheme does not depend on conversion, and both the MWD of "dead" chains (DC MWD) and that of the growing chains (GC MWD) depend on the relative values of propagation and termination constants rather than on their absolute values. The same values of DC MWD and GC MWD correspond to each number-average degree of polymerization ( $\bar{P}_n$ ) regardless of the ratio and absolute values of initial monomer and catalyst concentrations.

Since it was shown experimentally that in the case considered  $\bar{P}_n$  is independent of conversion, it follows that in accordance to ref 3 GC MWD also remains constant during polymerization. Thus, we have

$$-\frac{dm}{dt} = \sum_{j=0}^{\infty} k_{pj}'' n_j^* = n^* \sum_{j=0}^{\infty} k_{pj}'' \frac{n_j^*}{n^*} = k_p'' n^*,$$

where

$$n^* = \sum_{j=0}^{\infty} n_j^*$$

is the current concentration of growing chains and

$$k_p'' = \sum_{j=0}^{\infty} k_{pj}'' n_j^* / n^* = \text{const},$$

since  $n_j^*/n^* = \text{const}_j$  is the number-average normalized GC MWD.

In a similar manner, it is possible to determine

$$k_t'' = \sum_{j=0}^{\infty} k_{tj}'' \frac{n_j^*}{n^*}$$

so that the equation  $dn^*/dt = -k_t'' n^*$  should be satisfied.

Hence, the hypothesis that  $k_t$  and  $k_p$  depend on the length of the growing chain does not contradict the kinetic analysis carried out previously.<sup>1</sup> However, the rate constants for elementary reactions determined previously<sup>1</sup> should be considered as "average kinetic" constants obtained by averaging over the GC MWD, *i.e.*, by averaging over lengths. They cannot determine  $\bar{P}_n$  since this value is determined from the averaged  $\bar{k}_t/\bar{k}_p$  ratio rather than from the average values of  $\bar{k}_t$  and  $\bar{k}_p$  constants.

Hence, we established that in the MCMO polymerization with the *i*-Bu<sub>3</sub>Al-H<sub>2</sub>O catalyst system, a real mechanism of self-limitation of chain propagation exists and that the  $k_t/k_p$  ratio increases with the degree of polymerization. These facts show that the Flory principle, which states that the reactivity of an active centre of a linear macromolecule is independent of the length of the polymer chain, is not observed here. It is not observed if the free energy of the growing chain varies non-linearly with its length. In principle, this may be due to various structural or energetic factors.

Our analysis of this situation showed that the most satisfactory interpretation of experimental data is based on the concept of a "cyclic" propagation of the polymer chain. In accordance with this concept, the growing macromolecule is a zwitter-ion. Owing to electrostatic interaction, its charged ends do not become separated from each other during chain propagation but associate to form an ion-pair which is the active centre.

A similar mechanism of chain propagation was observed in the anionic polymerization of acrylonitrile, formaldehyde, and  $\beta$ -propiolactone with triethylphosphine<sup>6</sup> and in the polymerization of  $\alpha$ -oxides with cationic catalysts.<sup>7</sup>

Evidently, if chain propagation occurs *via* a ring closed with an ionic-pair, the thermodynamic disadvantage of this stage increases with the chain length as a result of a decrease in cyclization entropy, and the probability of dissociation of

charged-chain ends increases. The "breaking" of the ring *via* the ion-pair leads to a sharp gain in configurational entropy. The higher the degree of polymerization of the "living" macroring, the greater is this gain. Model calculations taking into account the entropy contribution to the free energy of the chain that grows *via* the ring<sup>8,9</sup> have shown that the dissociation constant of the ion-pair of a polymer zwitter-ion is a function of the degree of polymerization of the growing chain and increases with ring size.

The energetic barrier, at which the ring "breaks," occurs at the moment when the forces of electrostatic interaction can no longer compensate for the increasing thermodynamic disadvantage of the propagation "via ring formation." In the approximation used (eq 2), the  $\beta$  parameter takes into account the effect of all possible factors (thermal or entropy factors), limiting and determining the size of the growing macroring.

In the case being investigated here, the dissociation moment of charged ends of the polymer chain should be considered similar to the irreversible "decay" of the active centre as a result of its interaction with a fragment of its own chain. The fact that  $M_n$ , MWD, and the polydispersity parameters are independent of conversion shows that reactions of intermolecular termination or reinitiation do not occur.

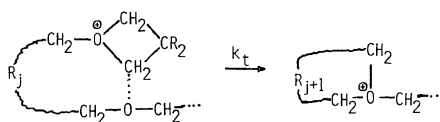
The autosolvation of the active centre by its own polymer chain, and the polydentate character and thermodynamic flexibility of the polymer chain favour the preferred intramolecular termination. The autosolvation effect, in turn, is due to the presence in the chain of a donor heteroatom capable of strong interactions with the cation. Hence, the polymer can successfully compete with the monomer for the formation of the solvent layer of the active centre.

It should be borne in mind that the longer the chain, the higher is the probability of the location of the active centre inside the polymer coil. In this case, the coefficient of the monomer diffusion to the active centre should decrease with the degree of polymerization, leading to a limitation of propagation rate. Diffusion effects cannot be the major factor in the mechanism of self-regulation of the size of the macromolecules itself since, close to the active centre, the dependence of the solvent layer on the chain length is weak and the density of the entire

coil should decrease with chain length.<sup>10</sup>

Hence, this model of polymerization "via ring formation" adequately accounts for the increase in the  $k_t/k_p$  ratio with the degree of polymerization (owing to increasing  $k_t$  and decreasing  $k_p$ ) and agrees with the experimental data.

When the polymer chain grows "via ring formation," the size of the macromolecule is determined primarily by the tendency of the ion-pair of the polymer zwitter-ion to undergo dissociation and this tendency increases with the degree of polymerization. The oxonium ion in the ion-pair is shielded by the counter-ion and this prevents its interaction with the polymer chain. At the moment of dissociation, unoccupied vacancies appear in the solvent layer of the oxonium ion. In consideration the difficulty of the monomer diffusion to the active centre, it may be assumed that the probability of occupying these vacancies by the polymer is very great. The preferred interaction of the cyclic oxonium ion with a fragment of its own chain leads to the formation of a monomacroring and to the decay of the active centre as shown by the following.



Since the probability of intramolecular termination by the proposed mechanism does not depend on the monomer and polymer concentrations, it becomes clear as to why the molecular-weight characteristics of the polymer do not depend on the initial concentrations of the monomer and the catalyst, and conversion. Evidently, if chain propagation and termination occur by this mechanism, the values of  $M_n$ , MWD, and parameters of polydispersity are determined only by the ratio of the  $k_t/k_p$  constants which depends on the size of the macromolecules and the polymerization temperature.

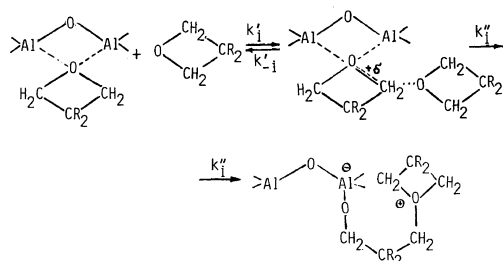
Our results do not permit a strict formulation of the chemistry of the elementary reactions in the polymerization of MCMO with the  $i\text{-Bu}_3\text{Al-H}_2\text{O}$  catalyst system. However, by taking into account the literature data available, the polymerization scheme may be represented as follows.

The mechanism of the formation of active centres comprises two stages:

1. The addition of the monomer to the alumoxane solution leads to the rapid formation of stable complexes with the (1 : 1) composition.

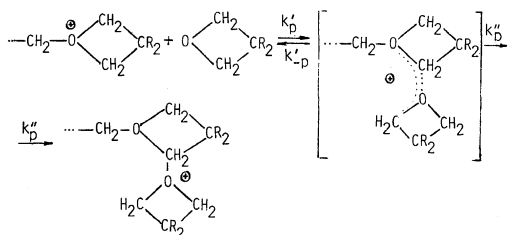
2. The initiation stage consists in the transformation of this complex into the active centre by a ring opening in the complexed monomer and the formation of a cyclic oxonium ion capable of initiating chain-propagation.

The second stage consists of two elementary reactions: the nucleophilic coordination of a monomer molecule with the  $\alpha$ -carbon atom of the monomer molecule complexed with alumoxane and the ionic-ring opening with the addition of this molecule to the broken bond. The first reaction is reversible and, as quantitative analysis of kinetic data shows, the equilibrium shifts to the left and  $k'_i$  is much less than  $k_{-i}$ . The second reaction is irreversible and leads to the formation of a zwitterion whose positive charge is borne by the cyclic oxonium ion.



The suggested mechanism of the formation of active centres is approximate and requires further specification. For example, the part played by the second aluminium atom in the alumoxane molecule is not clear.

The propagation also consists of two stages:

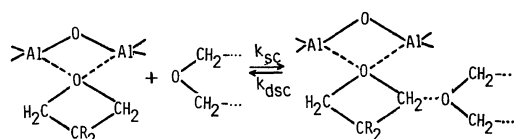


The first stage is the nucleophilic coordination of the monomer molecule to the  $\alpha$ -carbon atom of the cyclic oxonium ion. This is a reversible reaction but the equilibrium strongly shifts to the right,  $k'_p$  is much greater than  $k'_{-p}$ , and the active centre is

always complexed with the monomer. In the second stage, the monomer molecule is attached to the broken bond of the oxonium ion with the formation of a new cyclic-oxonium ion. This is an irreversible reaction and proceeds more slowly, its rate determining the propagation rate.

For simplicity of the scheme, the counter-ion has been omitted but it should be remembered that propagation occurs by the ion-pair of the polymer zwitter-ion and the polymer chain solvates its own active centre.

The deactivation of the catalyst by the polymer is brought about by the coordination of the polymer with the  $\alpha$ -carbon of the monomer complexed with alumoxane. This prevents an attack of the catalyst centre by the monomer and thus prevents initiation,



The mathematical treatment of the kinetic data showed that the equilibrium of this reaction shifts to the right and  $k_{sc}$  is greater than  $k_{dsc}$ . The displacement of the monomer by the polymer from the complex with alumoxane seems very doubtful since these complexes are known to be very stable and resistant to heat up to 100°C. Our data confirm this. The inability of the alumoxane·(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O system to initiate the polymerization of MCMO shows that the monomer is unable to displace diethyl ether from the complex with alumoxane.<sup>11</sup>

## CONCLUSIONS

The results of the present work show that the polymer is an active component of the polymerization system and can profoundly affect both the kinetics of the process and the molecular-weight characteristics of the product. Hence, for a thorough understanding of the mechanism for the formation of hetero-chain polymers, it is necessary to analyse in detail the possible participation of the macromolecules in all elementary reactions of polymerization. Otherwise serious errors can arise in the interpretation of experimental results and in the elucidation of the mechanisms for these reactions.

*Acknowledgement.* The authors should like to express their appreciation to P. N. Lavrenko and O. V. Okatova for making the experimental determination of MWD and polydispersity parameters by high-speed sedimentation.

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