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INTRA- AND INTERMOLECULAR CHAIN TRANSFER TO MACROMOLECULES WITH CHAIN SCISSION. THE CASE OF CYCLIC ESTERS

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Abstract: Chain transfer to macromolecules with chain scission is the most often observed "side" reaction in the polymerization of heterocyclics. In our previous works we analysed quantitatively the **intramolecular** chain transfer to the own macromolecule (back-biting). This paper gives a general treatment of the kinetics of polymerization with propagation and **intermolecular** chain transfer to macromolecules, accompanied with chain scission. The numerical solution developed allows determining the k_p/k_{tr} ratio from the dependence of $\overline{M}_w/\overline{M}_n$ on monomer conversion. This treatment was applied to the polymerization of L,L-lactide and k_p/k_{tr} ratios were measured for covalent alcoholate active species bearing Al, Fe, Ti, Sm, and La. In this way selectivities of active species (expressed with k_p/k_{tr}) were for the first time measured and finally correlated with the atomic number of the corresponding metal atoms, related to the strength of the bond involved in the monomer addition.

Introduction

Whenever the polymer repeating units contain the same heteroatoms as these present in monomers and reacting in the propagation step, chain transfer to polymer (macromolecules) with chain scission occurs. Either uni- or/and bimolecular reactions take place:

$$\cdots\!\left(m\right)_{n}m^{*} + M \underset{k_d}{\overset{k_p}{\rightleftharpoons}} \cdots\!\left(m\right)_{n+1}m^{*} \qquad \text{(propagation} \qquad (1a)$$

$$\cdots\!\left(m\right)_{n}m^{*} \underset{k_{p(x)}}{\overset{k_{tr(1)}}{\rightleftharpoons}} \cdots\!\left(m\right)_{n-x}m^{*} + \boxed{\left(m\right)_{x}} \qquad \text{(unimolecular chain transfer)} \qquad (1b)$$

$$\cdots\!\left(m\right)_{n}m^{*} + \cdots\!\left(m\right)_{p}m^{*} \overset{k_{tr(2)}}{\rightleftharpoons} \cdots\!\left(m\right)_{n+q}m^{*} + \cdots\!\left(m\right)_{p-q}m^{*} \qquad (1c)$$

(bimolecular chain transfer)

where m denotes the polymer repeating unit, m^* - the involved active species, M - the monomer molecule; $k_{tr(1)}$, $k_{tr(2)}$ - the rate constants of the uni- and bimolecular chain transfer,

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respectively; k_p and $k_{p(x)}$ - the rate constants of propagation of the monomer and the cyclic x-mer, respectively; k_d - the rate constant of depropagation.

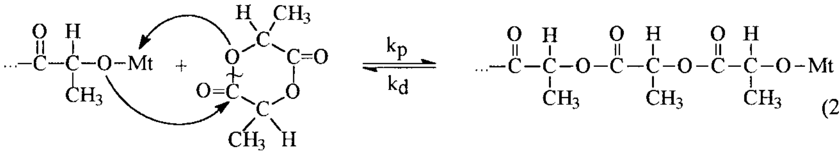
These reactions of transfer are of various intensities and have been observed in the polymerizations of cyclic ethers, acetals, esters, amides, and sulfides (see, e.g. Refs. 1-7). In our previous works we presented methods of measuring the $k_p/k_{tr(1)}$ ratio in the polymerization of ε-caprolactone and we correlated this ratio with k_p, determined from the polymerization kinetics. The $k_{tr(1)}$ was measured from the rates of appearance of cyclics (Refs. 8-10).

This paper summarizes our recent work on the bimolecular chain transfer in the polymerization of L,L-lactide and is based on the already published as well as submitted papers (Refs. 11-14).

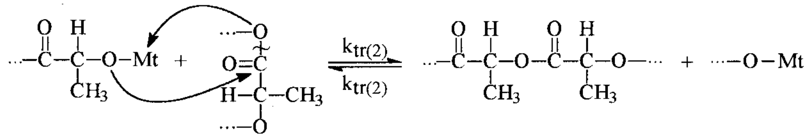
Molecular weight distribution (MWD) in polymerization with bimolecular transfer to macromolecules followed by chain scission

(a) formulation of the problem

When exclusively propagation and bimolecular chain transfer proceed (or when bimolecular transfer is more important, like it seems to take place in the polymerization of lactides):



(2a)



(2b)

the number of macromolecules remains constant and determination of $k_p/k_{tr(2)}$ is no more straightforward as for the $k_p/k_{tr(1)}$. There are then two distinctive situations:

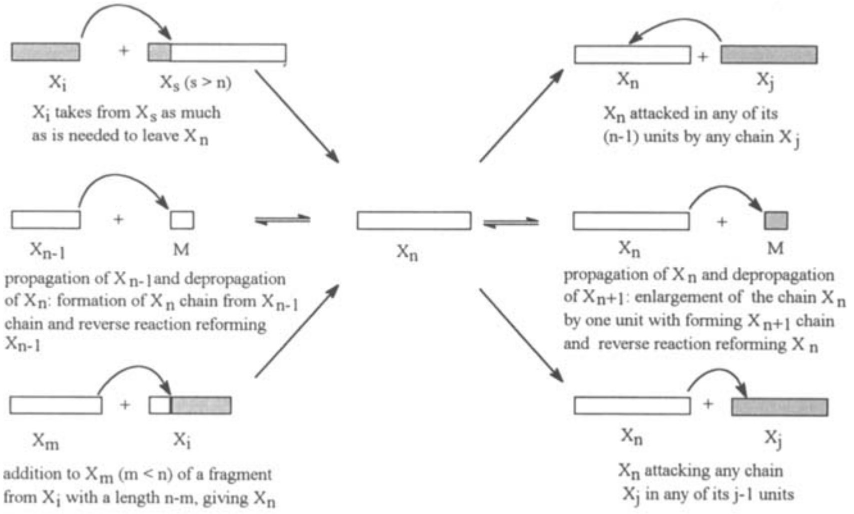
1°. Transfer is relatively slow ($k_{tr(2)} < k_p$). Poisson distribution is observed until a relatively high monomer conversion is reached. At certain conversion bimodal distribution can be observed. Deconvolution of the MWD curve gives a Poisson distribution (macromolecules that did not participate in transfer) superimposed on the second distribution, encompassing macromolecules that did already participate in transfer.

2°.Transfer is relatively fast (e.g. faster than propagation; $k_{tr(2)} >> k_p$). From the beginning of polymerization there is only one population of macromolecules and exclusively unimodal distribution is observed. All of the macromolecules participated at least ones in transfer at any monomer conversion. The MWD from the beginning of polymerization can then be close to the most probable one.

We aimed in our work to: (a) elaborate method relating the dependence of the polydispersity index ($\overline{M}_w/\overline{M}_n$) on degree of monomer conversion to $k_p/k_{tr(2)}$, (b) use this new dependence to determine $k_p/k_{tr(2)}$ for several initiators, and (c) correlate $k_p/k_{tr(2)}$ thus determined with a certain basic structural feature of the chain carrier.

(b) Kinetic scheme and its solution

Formulation of the kinetic equations is based on the following analysis of the chain transfer to polymer with chain scission for a given macromolecule with a chain length n (X_n).



Differential equations describing such a polymerization system (assuming instantaneous initiation) are as follows (Ref. 13):

$$\frac{d[X_1]}{dt} = -k_p[M][X_1] + k_d[X_2] - k_{tr(2)}\{[X_1]([X]-[I]_o) - [I]_o\sum_{i=2}^{\infty}[X_i]\} \tag{3a}$$

$$\frac{d[X_n]}{dt} = k_p[M]([X_{n-1}]-[X_n]) + k_d([X_{n+1}]-[X_n]) - k_{tr(2)}\{[X_n]([X]-[I]_o) + (n-1)[I]_o[X_n] -$$

$$-[X]\sum_{i=n+1}^{\infty}[X_i] - \sum_{m=1}^{n-1}\sum_{i=n-m+1}^{\infty}[X_m][X_i]\} \qquad (n \geq 2) \tag{3b}$$

where $[X_i]$ is the concentration of the growing i-mer X_i, $[X]$ is the total concentration of the repeating units in the polymer formed $([X] = \Sigma i[X_i])$; $[M]$ is a monomer concentration, and $[I]_o$ is an initiator concentration in the feed (equal to the total concentration of the growing species. $([I]_o = \Sigma[X_i])$); k_p, k_d, and $k_{tr(2)}$ are the rate constants of propagation, depropagation, and reshuffling, respectively.

Four terms in the brackets following $k_{tr(2)}$ in eq. (3b) stem from two routes of consuming X_n in chain transfer reaction: X_n is considered as an "active molecule" attacking the other macromolecules, and as a "passive" one being attacked by active macromolecules. On the other hand, there are two routes of forming X_n in the chain transfer reaction, namely by removing of a polymer segment from a polymer chain longer than X_n or by linking a polymer segment shorter than X_n to the polymer chain.

This set of equations can be solved if chain lengths distribution is known. Therefore, we computed MWD's, using a simple Monte-Carlo method and without any simplifying assumptions. The corresponding computing has shown, that indeed in a certain range of conditions the bimodal distribution appears (cf. point 1° above). Below, in Fig. 1 a few of the Monte-Carlo generated MWD curves are given in the the GPC trace resembling coordinates, i.e. with the ordinate giving value $n_{DP}\, DP^2 / \Sigma(n_{DP}\, DP^2)$ and with the abscissa - $\log_{10} DP$, where DP and n_{DP} denote the degree of polymerization of macromolecules and the number of macromolecules of the given DP, respectively (Ref. 15).

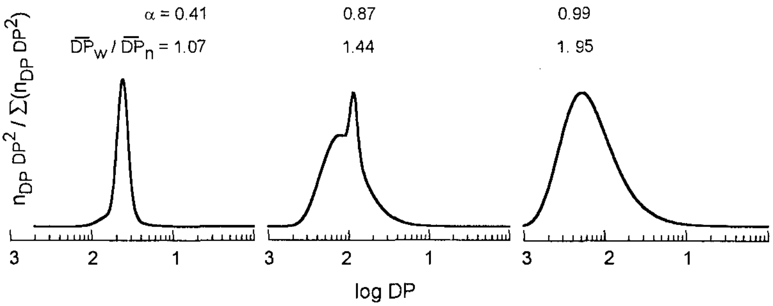


Fig. 1. Computed (Monte-Carlo method) chain length distribution ($\overline{DP}_w/\overline{DP}_n$) as a function of monomer conversion degree (α). Conditions: $[M]_o/[I]_o = 10^2$, $k_p/k_{tr(2)} = 10^2$, $k_p >> k_d$.

The appearance of the bimodal distribution takes place, when transfer is relatively slow (in comparison with propagation). First the Poisson distribution is observed until the fraction of macromolecules that were subjected to transfer becomes large enough. Then, there are two populations of macromolecules: those resulting from initiation and propagation and those suffering on the top of these two reactions an additional transfer. Both have the same $\overline{M}_n$, although differ in $\overline{M}_w$. Below, in Fig. 2 we give a superposition of MWD of these two populations, both having $\overline{DP}_n = 100$ and one of them Poisson distribution and the second one the most probable. Whether the bimodality is or is not observed depends, as we are showing in Fig. 2, on the way the distributions are presented, e.g. as frequency, weight or GPC trace resembling functions.

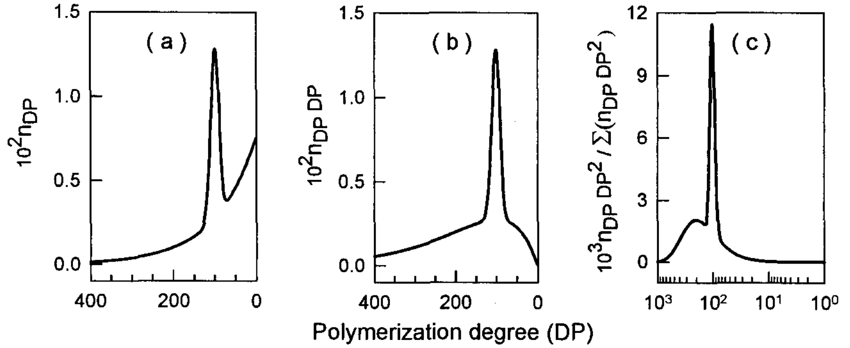


Fig. 2. Superposition of the Poisson distribution and of the most probable distribution functions for two sets of macromolecules, both with $\overline{DP}_n = 100$: (a) frequency distribution, (b) weight distribution, and (c) GPC resembling distribution. The masses of the sets related to Poisson and most probable distribution are in the 1/3 ratio.

In experimental GPC traces the bimodality is less apparent due to the additional instrumental broadening effect overshadowing the actual distribution. A few experimental GPC traces showing the evolution of the MWD with monomer conversion, are given in Fig. 3. The thin lines in Fig. 3 (a) illustrate a contribution of the poissonian population of macromolecules, as calculated on a basis of the kinetic equations (3).

Thus, now when the distributions are known the set of equations (3) could be and was solved taking into account the presence of two populations of polymer chains. The MWD of each of these was assumed to be described by the negative binomial Polya distribution (Ref. 13). Finally, a series of plots was generated numerically, giving access to the $k_p/k_{tr(2)}$ ratio from the dependencies of $\overline{M}_w/\overline{M}_n$ on monomer conversion degree ($\alpha = ([M]_o - [M])/[M]_o$). Several of these plots are given in Fig. 4.

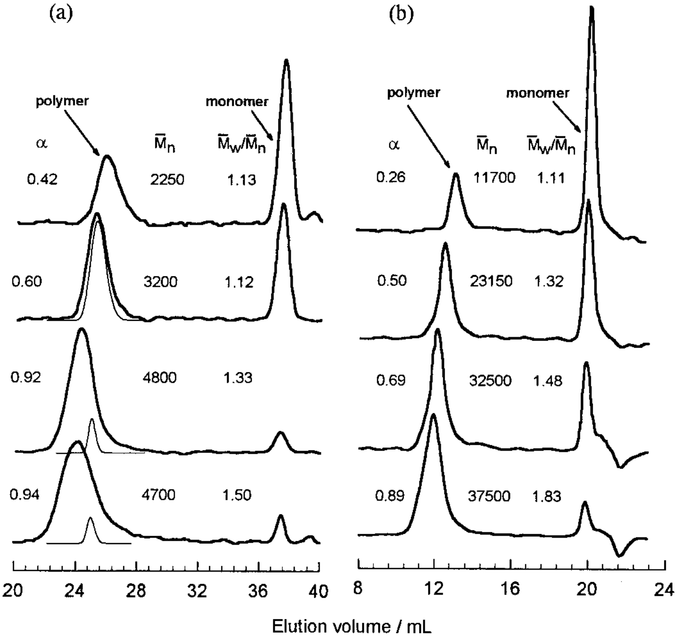


Fig. 3. GPC traces of the polymerizing mixtures recorded at various monomer conversion degrees (α). Polymerization of L,L-lactide (LA) initiated with: (a) $Al(O^iPr)_3$ trimer and (b) $Fe(OEt)_3$. Polymerization conditions: $[LA]_0 = 1$ mol·L^{-1}, $[Al(O^iPr)_3]_0 = 10^{-2}$ mol·L^{-1}, $[Fe(OEt)_3]_0 = 1.4 \cdot 10^{-3}$ mol·L^{-1}, THF, 80°C. Conditions of GPC measurements: (a) Waters ultrastyragel (10^3, $5 \cdot 10^2$, 10^2, and 10^2) columns, flow rate: 0.7mL·min^{-1}, (b) Toyo Soda (G4000 HXL and G2000 HXL) columns, flow rate: 0.8mL·min^{-1}, THF as eluent. $\overline{M}_n$ given in the figure are the absolute values determined as described in Ref. 11 and/or with multiangle laser light scattering (MALLS) detector. Surface areas under polymer and monomer signals are normalized according to the molar content of the repeating units and monomer molecules. (Ref. 14).

The described above approach allows thus to measure $k_p/k_{tr(2)}$ ratio. It is sufficient to determine $\overline{M}_w/\overline{M}_n$ as a function of α for a known $[M]_0$ and $[I]_0$ (e.g. by GPC) and to compare the experimental dependence with the computed nomographs. This approach is based, however, on an assumption, that the $\overline{M}_w/\overline{M}_n$ ratio results almost exclusively from the bimolecular chain transfer and from reversibility of the propagation but only for α approaching very close the value of $\alpha_{eq} = ([M]_0 - [M]_{eq})/[M]_0$, for majority of monomers. The complete kinetic theory, encompassing both transfers (i.e. uni- and bimolecular) is still under study.

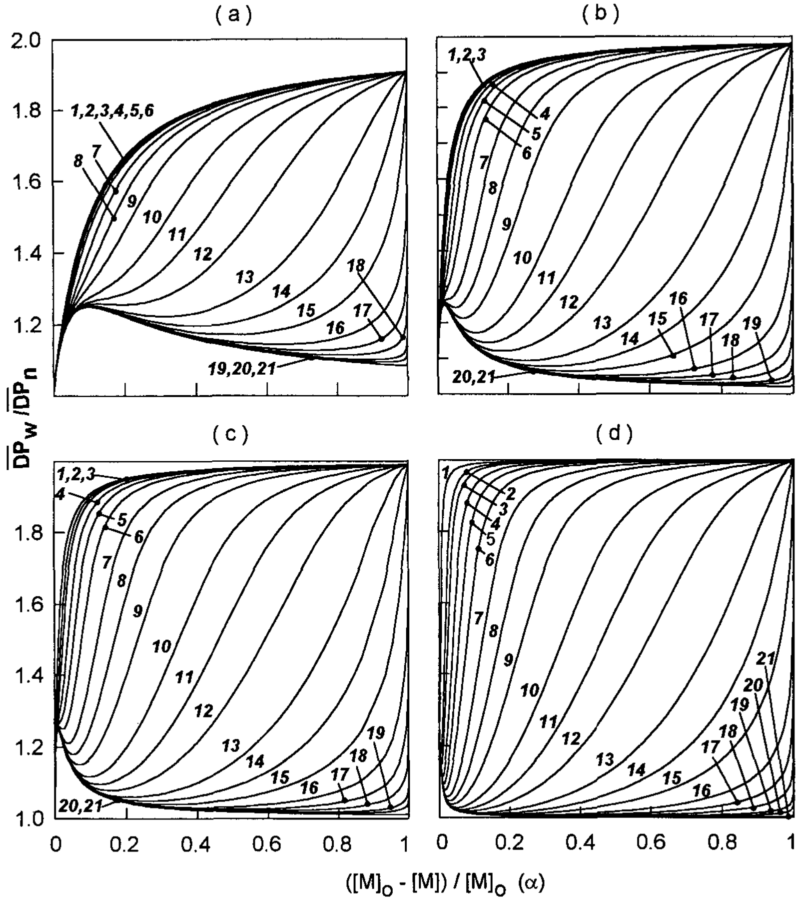


Fig. 4. Computed dependencies of $\overline{DP}_w/\overline{DP}_n$ on degree of monomer conversion (α). Conditions: $[M]_0/[I]_0 = 10^1$ (a), $5\cdot10^1$ (b), 10^2 (c), 10^3 (d); $k_p/k_{tr(2)} = z\cdot([M]_0/[I]_0)$, where $z = (k_p/k_{tr(2)})\cdot([I]_0/[M]_0) = 10^{-5}$ *(1)* , 10^{-4} *(2)*, $2\cdot10^{-4}$ *(3)*, $5\cdot10^{-4}$ *(4)*, 10^{-3} *(5)*, $2\cdot10^{-3}$ *(6)*, $5\cdot10^{-3}$ *(7)*, 10^{-2} *(8)*, $2\cdot10^{-2}$ *(9)*, $5\cdot10^{-2}$ *(10)*, 10^{-1} *(11)*, $2\cdot10^{-1}$ *(12)*, $5\cdot10^{-1}$ *(13)*, 10^0 *(14)*, $2\cdot10^0$ *(15)*, $5\cdot10^0$ *(16)*, 10^1 *(17)*, $2\cdot10^1$ *(18)*, $5\cdot10^1$ *(19)*, 10^2 *(20)*, 10^3 *(21)*; $k_p >> k_d$.

In Fig. 5 two experimentally determined dependencies of $\overline{M}_w/\overline{M}_n$ on α are given. Points are experimental and lines are calculated for the $k_p/k_{tr(2)}$ giving the best fit (lines were generated assuming $\overline{DP}_n = ([M]_0-[M]_{eq})/[I]_0$, i.e. omitting the fact that in the particular case of polylactide the repeating unit derived from one molecule of monomer contains two ester groups). In calculations the value of $[M]_{eq} = 5.5\cdot10^{-2}$ mol·L^{-1} (Ref. 16) was used.

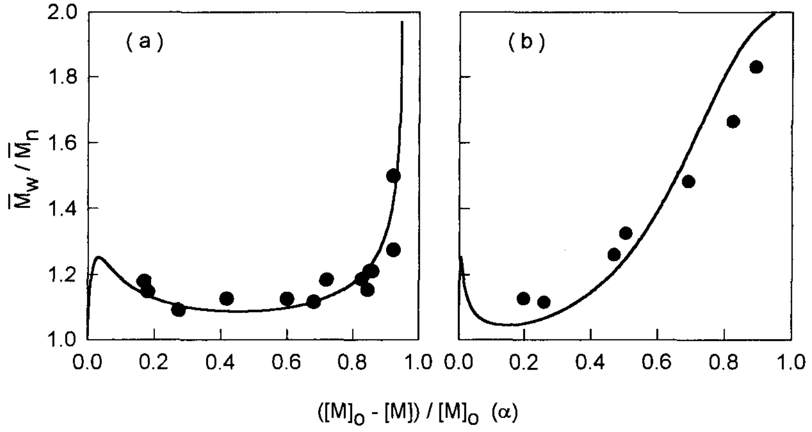


Fig. 5. Dependencies of $\overline{M}_w/\overline{M}_n$ on degree of monomer conversion (α) determined for L,L-lactide (LA) polymerization initiated with: (a) $Al(O^iPr)_3$ trimer and (b) $Fe(OEt)_3$. Conditions: $[LA]_o = 1.0$ mol·L^{-1}, $[Al(O^iPr)_3]_o = 10^{-2}$ mol·L^{-1}, $[Fe(OEt)_3]_o = 1.4 \cdot 10^{-3}$ mol·L^{-1}, THF solvent, 80°C ($[LA]_{eq} = 5.5 \cdot 10^{-2}$ mol·L^{-1} (Ref. 16)). Points experimental, lines computed assuming $k_p/k_{tr(2)} = 100$ (a) and 60 (b) (Refs. 11 and 14, respectively).

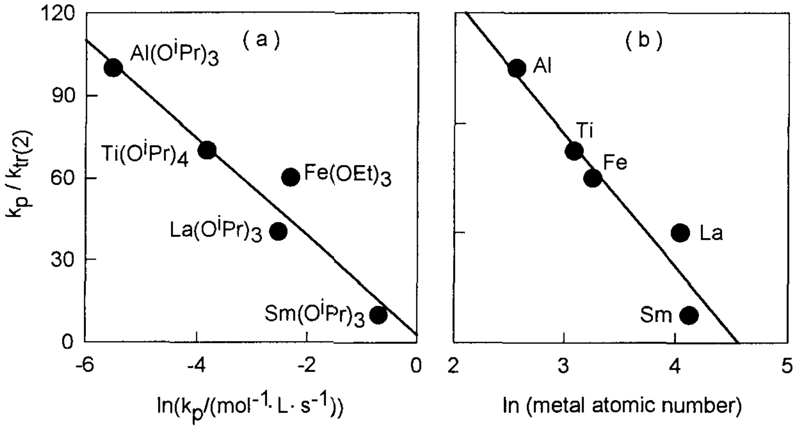


Fig. 6. Dependencies of $k_p/k_{tr(2)}$ on ln k_p (a) and on the atomic number of the metal atoms involved in active species (b), determined in polymerizations of L,L-lactide initiated by the covalent metal alkoxides (THF, 80°C) (Ref. 4).

Finally, in Fig. 6 the tentatively determined dependence of thus obtained $k_p/k_{tr(2)}$ on k_p and on the atomic number of metal atoms involved in active species is given. It is remarkable, that for a series of similar alcoholates as growing centres this dependence conforms to the rules of the Reactivity-Selectivity Principle, that also governs $k_p/k_{tr(1)}$ in the polymerization of ϵ-caprolactone, proceeding mostly with the intramolecular chain transfer (Refs. 9-11). Moreover, the larger the size of the metal atom in the growing species the higher the rate constant of propagation, as it could be expected for the lower bond energy for larger atomic radius.

The observed dependencies rise an important question: would it be possible to get for a polymerization initiated with $Al(OR)_3$ at a given temperature T_2 the rate similar as (e.g.) with $Sm(OR)_3$ at T_1 ($T_2 > T_1$)? Would then polymerization with $Al(OR)_3$ at this temperature T_2 have the selectivity higher, lower, or the same, as for $Sm(OR)_3$ at the temperature T_1?

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References

(1) B.A. Rozenberg, V.I. Irzhak, N.S. Enikolopyan, *"Interchain Exchange in Polymers"* (in Russian), Khimiya, Moscow 1975.

(2) S. Penczek, P. Kubisa, K. Matyjaszewski, *Adv.Polym.Sci.* **68/69**, 1(1985).

(3) G. Pruckmayr, T.K. Wu, *Macromolecules* **11**, 265(1978).

(4) W. Chwialkowska, P. Kubisa, S. Penczek, *Makromol.Chem.* **183**, 753(1982).

(5) K. Ito, Y. Yamashita, *Macromolecules* **11**, 68(1978).

(6) O. Wichterle, *Makromol.Chem.* **35**, 127(1960).

(7) E.J. Goethals, R. Simonds, N. Spassky, A. Momtaz, *Makromol.Chem.* **181**, 2481(1980).

(8) A. Hofman, S. Slomkowski, S. Penczek, *Makromol.Chem., Rapid Commun.* **8**, 387(1987).

(9) S. Penczek, A. Duda, S. Slomkowski, *Makromol.Chem., Macromol.Symp.* **54/55**, 31(1992).

(10) S. Penczek, A. Duda, *Macromol.Symp.* **107**, 1(1996).

(11) J. Baran, A. Duda, A. Kowalski, R. Szymanski, S. Penczek, *Macromol.Rapid Commun.* **18**, 325(1997).

(12) J.Baran, A.Duda, A.Kowalski, R.Szymanski, S.Penczek, *Macromol.Symp.* **123**, 93(1997).

(13) R.Szymanski, *Macromol.Theory Simul.* **7**, 27(1998).

(14) J.Baran, A.Duda, S.Penczek, in preparation.

(15) K. Matyjaszewski, R. Szymanski, M. Teodorescu, *Macromolecules* **27**, 7565(1994).

(16) A.Duda, S.Penczek, *Macromolecules* **23**, 1636(1990).