Anionic Polymerization of Acrylates. XI. Effect of Composition and Ageing of the Li Ester Enolate/*tert*-Butoxide Initiating Complex on the Anionic Polymerization of Methyl Methacrylate and 2-Ethylhexyl Acrylate

Petr Vlček*, Jaroslava Otoupalová, Jaroslav Kříž and Pavel Schmidt

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic,
162 06 Prague 6, Czech Republic

SUMMARY: The article presents the results of (meth)acrylate polymerization in THF initiated with various complexes of methyl 2-lithioisobutyrate (MIB-Li) and lithium *tert*-butoxide (*t*-BuOLi), prepared from the components in mole ratios 1:3, 1:6 and 1:10 in THF and aged for various time periods and at various temperatures. In dependence on the component ratio, temperature and storage time, the mixtures form cubic cross-aggregates with MIB-Li/*t*-BuOLi mole ratios 3:1, 2:2 and 1:3 which exhibit different behavior when used as initiators. It was found that the way of synthesis of the complex and its structure not only affect the kinetics of polymerization but also distinctly change the microstructure of the formed polymers.

Introduction

The ligated anionic polymerization (LAP) of (meth)acrylic esters is one of useful tools for tailoring (meth)acrylate polymers and copolymers[1]. General approach of the method consists in using appropriate additives which form complexes with initiators and/or growing chain-ends sterically hindering the enolate active centre of polymerization and lowering its basicity. This leads to lowering the extent of undesired side reactions in the initiation as well as in the propagation steps of the process, in particular the rate of self-termination by a "back-biting" reaction. Thus, LAP is the oldest successful method for tailoring poly(meth)acrylates and their block copolymers, e.g., with styrene. Various complexing additives (ligands) have been designed with different stabilizing effectivity as a consequence of forming different complexes with enolate centres. In this sense, LiCl described by Teyssie's group[2-5] in Liege, didentate alkoxides[6-8] of the $CH_3(OCH_2CH_2)_2OLi$ type (MEEOLi) of the same origin, alkali metal *tert*-alkoxides designed by the Prague group[9-12] and alkylaluminiums, described originally by Hatada[13,14] and recently by Haddleton et al[15-17] are the most important. Structure of complexes was recently studied by Wang et al[18-20] and by Kříž et al[21-23] by NMR using methyl 2-lithioisobutyrate (MIB-Li) as a model of active centre and LiCl or an alkoxide ligand. It was found that the structure and the number of complexes depend on the type of ligand, concentration of components, storage time, and temperature. LiCl completely destroys self-aggregates of MIB-Li and forms mixed complexes of various composition in dependence on the mole ratio of components. Nevertheless, only one type of the complex is formed with MIB-Li/LiCl mole ratios 3:1, 2:2 or 1:3 (depending on starting concentrations) having character of non-aggregated active species, which leads to one type of active species and preventing possible multiplicity of active centres[18]. However, the stabilizing efficiency of these complexes is rather moderate; they cannot be used for controlled polymerization of *n*-alkyl acrylates. Similarly, didentate alkoxides form one complex with MIB-Li, most probably with the mole ratio MIB-Li/MEEOLi 2:2; again, only one type of the complex is formed[20] with the same consequences as in the foregoing case. However, its stabilizing efficiency is much higher than that of LiCl, so that MEEOLi can be successfully used for controlled polymerization of *n*-alkyl acrylates provided the reaction temperature is sufficiently low[8].

In the presence of *tert*-alkoxides, specifically lithium *tert*-butoxide (*t*-BuOLi), formation of mixed complexes is more complicated. In a mixture of the components in THF, at least three types of mixed complexes are formed with MIB-Li/*t*-BuOLi mole ratios 3:1, 2:2, and 1:3 depending on concentration conditions, temperature and storage time[21]. *t*-BuOLi replaces molecules of MIB-Li in its tetramer, so that at room temperature, virtually immediately after mixing the components, the 3:1 complex is formed which is transformed during storage into the 2:2 complex. In this complex, the next molecule of the MIB-Li is replaced by the alkoxide forming the 1:3 MIB-Li/*t*-BuOLi complex which prevails in solutions aged for 24 h at –15 °C. In equilibrium, all the three complexes can be present in mixture, probably in different concentrations (Scheme 1).

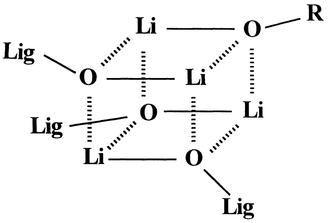
$$\text{MIB-Li]}_4 + 3\,[t\text{-BuOLi}]_4 \rightleftharpoons \underset{\mathbf{3:1}}{[(\text{MIB})_3\,\text{Li}_4\,(t\text{-BuO})]} \rightleftharpoons \underset{\mathbf{2:2}}{[(\text{MIB})_2\,\text{Li}_4\,(t\text{-BuO})_2]}$$

$$[(\text{MIB})_2\,\text{Li}_4\,(t\text{-BuO})_2] \rightleftharpoons \underset{\mathbf{1:3}}{[(\text{MIB})\,\text{Li}_4\,(t\text{-BuO})_3]}$$

Scheme 1

The core of cross-aggregates, as well as that of MIB-Li tetramer have cubic structure in which Li and O atoms alternate; the results of NMR studies were corroborated by theoretical calculations[24]. Thus, the complex with mole ratio MIB-Li/*t*-BuOLi 1:3 should have the structure given in Scheme 2 in which Lig represents an alkoxide unit and R ester enolate.

Similar structures may also form during propagation; here, R is the enolate growing chain end.



Scheme 2

In foregoing studies of acrylate polymerization initiated with the ester enolate/*t*-BuOLi complex, the initiating components were always mixed at room temperature and used without ageing[25-27]. Stability of active centres was high (at low temperatures) and the initiating efficiency of the enolate was about 50%. It can be reasonably assumed that the various ester enolate/*tert*-alkoxide complexes mentioned above can behave differently when used as initiators of (meth)acrylate polymerization and this is why this study was performed. Complexes of MIB-Li with *t*-BuOLi were prepared by mixing the components in ratios MIB-Li/*t*-BuOLi 1:3, 1:6 and 1:10 at room temperature or at –60 °C in THF and ageing for various time periods at room temperature, –15 or –60 °C; then they were used as initiators of MMA polymerization in THF.

Experimental

Preparation and purification of MIB-Li and *t*-BuOLi were described elsewhere[28,29]; MMA and THF were purified by usual methods. Polymerizations were performed in a glass reactor with a dosing cell, allowing to withdraw samples of the reaction mixture in various time intervals for determination of monomer conversion by gas chromatography. Polymers were analyzed by GPC, ^{1}H and ^{13}C NMR, and by infrared spectroscopy.

Results and Discussion

Complexes prepared at room temperature and aged for 24 h at –15 °C

In these experiments, a THF solution of *t*-BuOLi and a calculated amount of solid MIB-Li were mixed and than kept in a freezer at –15 °C for 24 h. Then the solutions were used as initiators of MMA polymerizations; the results are summarized in Table 1.

Table 1: Polymerization of MMA initiated with MIB-Li/*t*-BuOLi prepared at room temperature and aged at –15 °C for 24 h

Run	Z^a	Temperature	Time	X^b	SEC^c		φ^d	MWD
		°C	min	%	$10^{-3} M_n$	M_w/M_n	%	
1	1 : 3	-60	120	100	10.00	1.17	51	unimodal
2	1 : 3	-40	20	100	14.13	2.46	-	polymodal
3	1 : 6	-60	120	100	7.32	1.29	70	unimodal
4	1 : 10	-60	90	100	7.63	1.24	67	unimodal
5^e	1 : 10	-60	120	100	8.71	1.21	58	unimodal

Conditions: $[MMA]_0 = 0.468$ mol/l, $[MIB\text{-}Li]_0 = 0.0093$ mol/l, THF.
[a] MIB-Li/*t*-BuOLi mole ratio; [b] conversion of MMA; [c] measured in crude reaction mixtures; [d] efficiency of initiator; [e] the complex was aged for 24 h at room temperature.

Conversion of the monomer was quantitative, whatever ratio of the initiating components was used. Semilogarithmic conversion curves (Fig. 1) indicate a virtually constant concentration of active centres during the polymerization up to the conversion over 95%. Molecular weights of the formed polymers also increase linearly with increasing conversion and polydispersities of the products prepared under comparable conditions are almost the same (Fig. 2), whatever was the starting MIB-Li/*t*-BuOLi ratio; hence, the polymerizations initiated by the 24-h-aged solutions of MIB-Li/*t*-BuOLi behave as virtually living processes. The initiator efficiency of MIB-Li clearly increases from 50 to 70 % with increasing excess of the alkoxide. As the results of the discussed polymerizations are very similar, it can be reasonably assumed that they are controlled by similar complexes (or mixtures of complexes), most probably with the

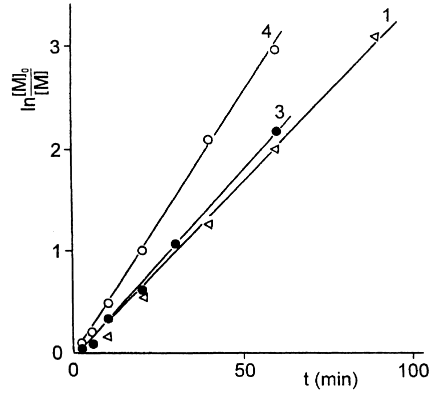


Fig. 1. Semilogarithmic conversion plots of methyl methacrylate polymerizations initiated with MIB-Li/*t*-BuOLi mixtures aged for 24 h at –15 °C. (The line numbers correspond to the runs in Table 1.)

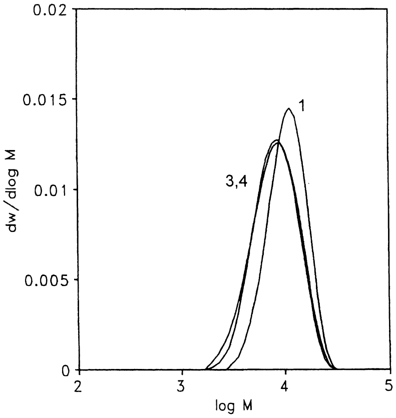


Fig. 2. MWD curves of poly(methyl methacrylate)s prepared with MIB-Li/*t*-BuOLi mixtures aged for 24 h at -15 °C. (The curve numbers correspond to the runs in Table 1.)

MIB-Li/*t*-BuOLi ratio predominantly 1:3 which is in accordance with the results of model studies of active centres. Further investigation is needed to understand the effect of an alkoxide excess; one can only preliminarily speculate on the rearrangement equilibria of individual complexes which can be affected by an alkoxide excess. Based on the results of model studies after ageing at –15 °C for 24 h, the equilibrium concentration of the complex MIB-Li/*t*-BuOLi 1:3 is reached, which means that the other complexes, 2:2 and perhaps also 3:1, can be present in the system, probably in low concentrations (Scheme 1). Clearly, a higher excess of *t*-BuOLi shifts the equilibria, in particular that between complexes 2:2 and 1:3, to the right-hand side and, assuming that the initiator efficiency of the 1:3 complex is higher than that of the 2:2 complex, the total initiator efficiency also increases. Consequently, also the reaction rate is higher and molecular weight of the product is lower in the polymerization in the presence of a higher concentration of the alkoxide. If the complex is aged at room temperature (Table 1, run 5), a certain extent of self-condensation of MIB-Li cannot be excluded, decreasing thus its concentration. The product, prepared in the polymerization at –40 °C with the aged complex 1:3 (Table 1, run 2), has clearly bimodal MWD, even though with a hint of polymodality, indicating multiplicity of active species and, perhaps, a certain extent of self-termination in this special system.

Complexes prepared and aged at room temperature

The behavior of polymerizations initiated with complexes prepared at room temperature and aged at the same temperature in THF for 2-60 min is different depending on the starting ratio of the initiator components. It has to be noted that the time period of 2 min is necessary for preparation and dosing of a mixed MIB-Li/*t*-BuOLi solution so that the prepared complex was used virtually without ageing in these experiments. The results are summarized in Table 2. If the starting mole ratio MIB-Li/*t*-BuOLi was 1:6 or 1:10 (runs 5-9) and the solutions are used for initiation without ageing, the polymerizations proceed quantitatively and products have narrow and unimodal MWDs, similar to those in which initiating solutions with the same mole ratios of the components were aged for 24 h at –15 °C (see the foregoing paragraph). Time plots of $\ln[M]_0/[M]$ for polymerizations initiated with the solutions having MIB-Li/*t*-BuOLi mole ratio 1:6 or 1:10 are linear and very similar (Fig. 3); again this indicates sufficient stability of active species. Nevertheless, polymerization initiated with the solution with the component ratio 1:10 seems to be slightly faster, which can be caused by a higher concentration of polymerization centres; this is corroborated by a lower M_n value of the product and, thus, a higher initiator efficiency in comparison with that of the polymer prepared with a solution of the MIB-Li/*t*-BuOLi mole ratio 1:6 (see Table 2, runs 5 and 7).

Table 2: Polymerization of methyl methacrylate initiated with MIB-Li/*t*-BuOLi solutions prepared and aged at room temperature[a]

Run	Z^b	$[MMA]_0$	$[MIB\text{-}Li]_0$	Time	X^c	SEC		φ^d
		mol/l	mol/l	min	%	$10^{-3}\,M_n$	M_w/M_n	%
1	1:3	0.468	0.0093	90	100	8.72	2.19^e	-
2	1:3	0.468	0.0093	90	100	12.21	2.34^e	-
3	1:3	0.468	0.0093	90	95	12.11	1.64^e	-
4	1:4	0.468	0.0093	90	95	11.03	1.18^f	44
5	1:6	0.468	0.0093	120	>95	9.24	1.24^f	55
6	1:6	0.936	0.0187	40	100	6.70	1.25^f	76
7	1:10	0.468	0.0093	100	100	7.46	1.22^f	68
8	1:10	0.936	0.0187	50	>95	6.73	1.23^f	72
9	1:10	0.936	0.0093	90	100	15.81	1.12^f	64

[a] Solutions aged for 2 min (runs 1, 5–9), for 5 min (run 2), for 60 min (runs 3 and 4); [b] mole ratio MIB-Li/*t*-BuOLi; [c] monomer conversion; [d] initiator efficiency of MIB-Li; [e] bimodal MWD; [f] unimodal MWD

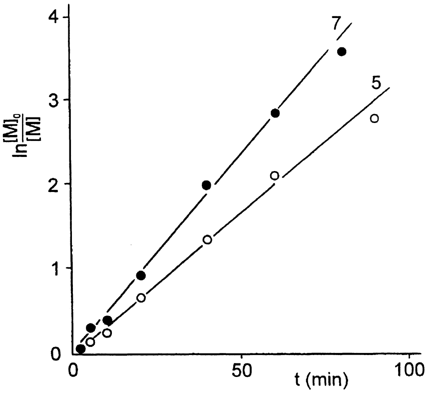


Fig 3. Plots of ln $[M_0]/[M]$ versus time for MMA polymerizations initiated with MIB-Li/*t*-BuOLi mixtures 1:6 and 1:10 prepared and aged at room temperature. (The line numbers correspond to the runs in Table 2.)

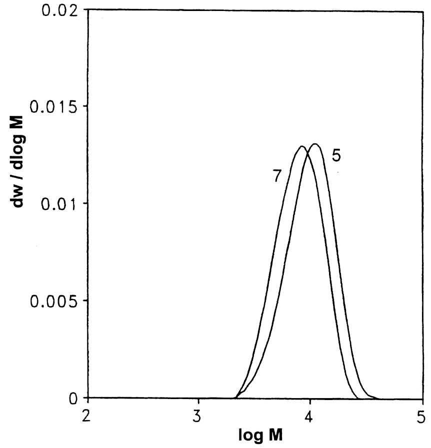


Fig. 4. MWD curves of PMMAs prepared with the complexes formed from MIB-Li/*t*-BuOLi mixtures 1:6 and 1:10 prepared and aged at room temperature. (The curve numbers correspond to the runs in Table 2.)

Also, molecular weights of polymers formed in these two systems increase linearly with increasing conversions and MWD curves are comparable (Fig. 4). It can be assumed that these two systems are controlled by the same complexes or, rather, by the same mixture of the complexes in which, however, equilibrium populations of the complex types are more or less different in dependence on the excess of *t*-BuOLi. If the starting concentrations of MMA, MIB-Li and *t*-BuOLi are twice higher (Table 2, runs 6 and 8), the reaction rates are expectedly higher. However, initiator efficiencies also slightly increase, in particular in run 6 in which a 1:6 MIB-Li/*t*-BuOLi mixture was used as an initiator. Formation and rearrangement of complexes probably also depend at least to certain extent on concentrations of the components, proceeding faster if the concentrations are higher.

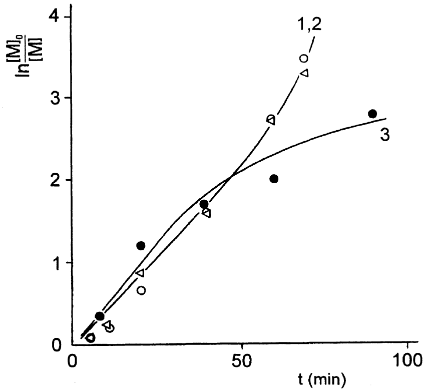


Fig. 5. Plots ln $[M]_0/[M]$ versus time for methyl methacrylate polymerizations initiated with MIB-Li/*t*-BuOLi mixtures 1:3 aged at room temperature. (The curve numbers correspond to the runs in Table 2.)

If the excess of *t*-BuOLi over MIB-Li is only 3 and the mixed initiator solution is aged at room temperature for 2-60 min, the polymerizations proceed differently in dependence on the ageing time (Table 2, runs 1-3). Monomer conversions are quantitative or almost quantitative whatever was the ageing time, and the semilogarithmic conversion plots for polymerizations initiated with complexes aged for 2 or 5 min (runs 1 and 2) are the same and almost linear (Fig. 5). The plot ln $[M]_0/[M]$ versus time for the process initiated with the 1:3 MIB-Li/*t*-BuOLi system aged for 60 min is clearly non-linear but curved downward. All the polymers prepared under these conditions have perceptibly bimodal MWDs regardless of the ageing time. In all cases, higher-molecular-weight peaks appear at higher monomer conversions; as can be seen in Fig. 6. Molecular weights follow the increasing conversion linearly up to a value of 50-60 % and then increase more steeply with increasing conversion (Fig. 7). In the same region, also MWD becomes broader and increases with increasing conversion. The mentioned changes correspond to appearance of a high-molecular-weight peak in the MWD curve of the formed polymer and, at least to a certain extent, to kinks on the corresponding semilogarithmic conversion curves (Fig. 5). It is worth noting that nothing like this was found if polymerization is initiated with the 1:4 MIB-Li/*t*-BuOLi system (Table 2, run 4). To explain the formation of polymers with bimodal MWDs under these conditions, a possibility of coupling of the chains via condensation reaction of the living chain-end and a carbonyl group of another chain leading to an increase in total molecular weight was also taken into account, regardless of the fact that in the presence of *tert*-alkoxides, condensation reactions are distinctly suppressed[30]. Moreover, no self-condensation products were observed in model studies with MIB-Li/*t*-BuOLi complexes[21].

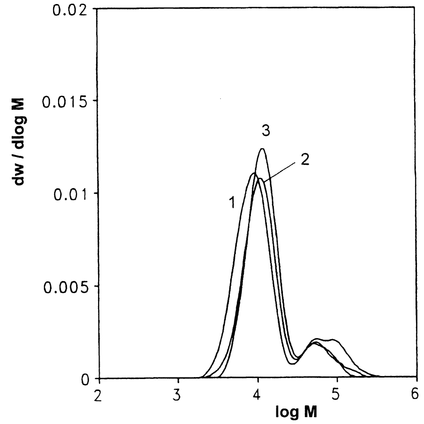


Fig. 6. MWD curves of PMMAs prepared with the 1:3 mixtures MIB-Li/*t*-BuOLi aged at room temperature. (The curve numbers correspond to the runs in Table 2.)

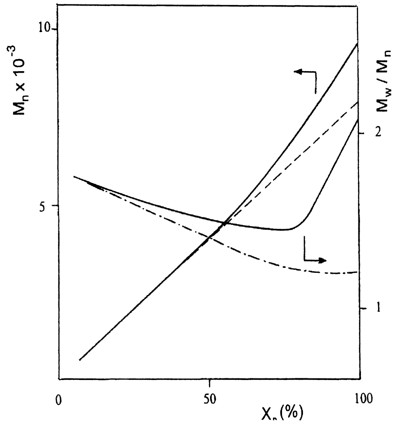
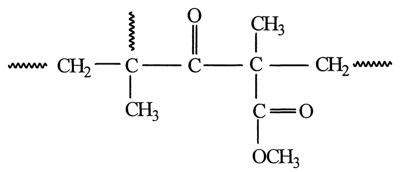


Fig. 7. Dependences of M_n and M_w/M_n on monomer conversion for MMA polymerization initiated with the 1:3 MIB-Li/*t*-BuOLi system without ageing (Table 2, run 1).

If such a condensation proceeded, long chains would be formed (probably more or less branched) containing two types of carbonyl groups (Scheme 3).



$$\sim CH_2-\overset{\wr}{\underset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\underset{\underset{OCH_3}{C=O}}{C}}-CH_2\sim$$

Scheme 3

To check this, one of the polymers with bimodal MWD was fractionated; then, low-molecular-weight and high-molecular weight portions were analyzed separately by NMR and IR spectroscopy. However, the results did not corroborate the idea of chain extension via condensation reactions so that the formation of high-molecular-weight fractions in the presence of three-fold excess of the alkoxide has probably another origin. A possible reason can be transformation of complexed growing centres into another type of different activity leading to faster polymerization. Such transformation of the centres probably does not proceed in the presence of a higher excess of *t*-BuOLi, i.e., if the MIB-Li/*t*-BuOLi ratio is higher than 3. Nevertheless, to get more insight into the problem, further investigation is needed.

Complexes prepared and aged at –60 °C

In this case, THF solutions of the initiator complex components were mixed in various ratios in the polymerization reactor at –60 °C and, after ageing for a chosen time period, the monomer solution was quickly added. The polymerization systems initiated with the complexes prepared at the low temperature behave in very different ways in dependence on the mole ratio of MIB-Li/*t*-BuOLi and storage time; the results of the experiments are summarized in Table 3. It can hardly be assumed that under these conditions, i.e., at a low temperature, complexes with higher contents of the alkoxide are formed; hence, the polymerizations in this special case are probably initiated by the 3:1 MIB-Li/*t*-BuOLi complex. Moreover, its formation can also be affected by the starting ratio of the components.

Table 3: Polymerization of methyl methacrylate initiated with MIB-Li/*t*-BuOLi complexes prepared and aged at –60 °C

Run	Z^a	Time (min)		X	SEC		φ^b	Note
		ageing	polym.	%	$10^{-3} M_n$	M_w/M_n	%	
1	1:3	2	60	>99	13.22	6.63	-	polymodal
2	1:3	60	90	96	10.25	2.89	-	polymodal
3	1:6	2	60	95	18.74	4.43	-	bimodal
4	1:10	2	120	90	18.45	1.11	25	unimodal
5	1:10	1440	120	90	15.75	1.14	30	unimodal

[a] MIB-Li/*t*-BuOLi mole ratio; [b] initiating efficiency of MIB-Li

The polymerization initiated with a 1:3 MIB-Li/*t*-BuOLi mixture prepared at –60 °C and used virtually without ageing (ageing time approx. 2 min; Table 3, run 1) starts very quickly, reaching 80% monomer conversion within 5 min; its ln $[M]_0/[M]$ - time plot (Fig. 8, curve 1) is almost linear in this part. After that, the plot curves and the polymerization rate distinctly decrease; nevertheless, also this part is virtually linear without additional kinks and polymerization proceeds up to quantitative monomer conversion. The product has very broad polymodal MWD (Fig. 9, curve 1) composed of a rather narrow main central peak and broad low- and high-molecular-weight parts. A similar product with a broad polymodal MWD is obtained when the polymerization is initiated with the same MIB-Li/*t*-BuOLi mixture which was, however, left aging at –60 °C for 1 h (Table 3, run 2). The semilogarithmic conversion plot of this process is different: the polymerization starts slowly, the rate seems to increase (Fig. 8, curve 2) and the MWD of the product is broad and polymodal (Fig. 9, curve 2). If MIB-Li is mixed with a six-fold excess of *t*-BuOLi at the same temperature and used as initiator without ageing (Table 3, run 3), polymerization starts again with a relatively high rate, but the slope and the time period of this rapid part are distinctly lower in comparison with the polymerization performed in the presence of three-fold excess of the alkoxide under otherwise identical conditions (Fig. 8). The product has a broad MWD again but bimodal in this case with two clearly separated peaks. On the basis of the present results, it is not possible to explain the behavior of the system. Nevertheless, it can be reasonably assumed that the very rapid polymerization induced by a 1:3 MIB-Li/*t*-BuOLi mixture prepared at low temperature and used without ageing is probably initiated with neat MIB-Li, i.e., its aggregates. Cross-aggregates with *t*-BuOLi, having probably the 3:1 MIB-Li/*t*-BuOLi ratio can be, to a certain extent, formed during polymerization which is indicated by a change in the polymerization rate (Fig. 8). Hence, the formation of mixed complexes is responsible for the kink on the semilogarithmic conversion curve. This is corroborated by a polymodal MWD of the product which clearly indicates multiplicity of active species. The processes of formation and transformation of mixed complexes are probably very slow under the given conditions, especially at a low reaction temperature and at a low excess of the alkoxide. Hence, they proceed also in systems in which either a 1:3 mixture of MIB-Li/*t*-BuOLi was left aging for 1 h or a mixture with a six-fold excess of *t*-BuOLi was used for initiation.

Ten-fold excess of *t*-BuOLi likely increases rates of formation of various types of MIB-Li/*t*-BuOLi complexes (cross-aggregates). If a 1:10 mixture of the components is prepared at -60 °C and used without ageing, it initiates MMA polymerization with a low reaction rate (Table 3, run 4), the ln $[M]_0/[M]$ versus time plot being linear up to the MMA conversion

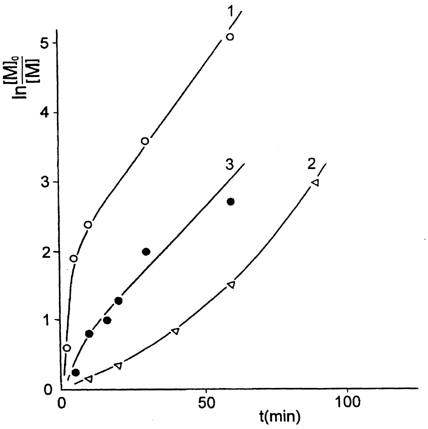


Fig. 8. Plots ln $[M]_0/[M]$ versus time for MMA polymerizations initiated with MIB-Li/*t*-BuOLi mixtures 1:3 prepared and aged at –60 °C. (The curve numbers correspond to the runs in Table 3.)

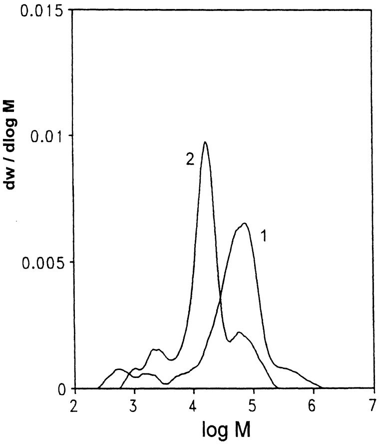


Fig. 9. MWD curves of poly(methyl methacrylate)s prepared with the 1:3 mixtures MIB-Li/*t*-BuOLi aged at –60 °C. (The curve numbers correspond to the runs in Table 3.)

about 90 % (Fig. 10). MWD of the product is significantly unimodal and narrow indicating the existence of only one type of active species during the whole process. However, if compared with the polymerization initiated with the same mixture but prepared at room temperature and used without ageing (Table 2, run 7) or after ageing at –15 °C (Table 1, run 4), the initiating efficiency of MIB-Li is distinctly lower for the non-aged complex prepared at –60 °C. If the same 1:10 MIB-Li/*t*-BuOLi mixture is left aging for 24 h at –60 °C and then used for initiation (Table 3, run 5), the polymerization in this case proceeds in a very similar manner to the last case (Fig. 10) and the product has again a slightly lower molecular weight with a narrow unimodal distribution. It seems probable that both the polymerizations initiated with1:10 MIB-Li/*t*-BuOLi mixtures are initiated with the same type of complex; clearly, it cannot be excluded that the complexes have different composition in dependence on ageing. However, both of them have very similar initiating behavior.

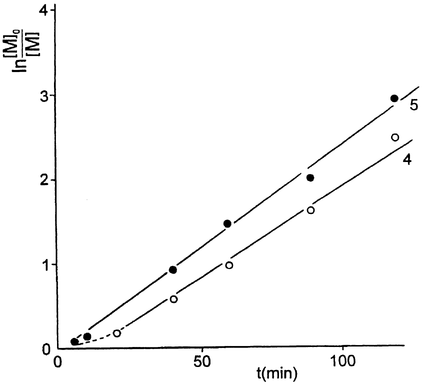


Fig. 10. Plots ln $[M]_0/[M]$ versus time of methyl methacrylate polymerizations initiated with the 1:10 MIB-Li/*t*-BuOLi mixtures prepared and aged at –60 °C. (The line numbers correspond to the runs in Table 3.)

Microstructures of PMMAs

Microstructures of polymers prepared with various MIB-Li/*t*-BuOLi mixtures and, consequently, probably with various initiating complexes were determined by ^{1}H NMR spectroscopy; the results are summarized in Table 4. Surprisingly, the polymers prepared in neat THF in the presence of three-fold or higher excess of the alkoxide have distinctly enhanced contents of isotactic triads, which is in contrast with the results of polymerizations initiated with Li initiators in THF published earlier[31,32]. The only exception is the polymer prepared with the complex the components of which were premixed in the 1:3 ratio at −60 °C and used without additional ageing, which is predominantly syndiotactic (Table 4, run 7). This corroborates the idea mentioned above that if the initiating complex is prepared from a 1:3 MIB-Li/*t*-BuOLi mixture at –60 °C and used without ageing, the polymerization is initiated with neat MIB-Li and the cross-aggregates of growing centres with the alkoxide are formed later on, during the propagation reaction (Table 3, run 1). The same effect of *t*-BuOLi was observed recently[7] in the study of MMA polymerization initiated with (diphenylmethyl)lithium but in 9/1 (v/v) toluene/THF mixture at –78 °C. In the absence of *t*-BuOLi under the same conditions, the initiator gives prevailingly syndiotactic PMMA, i.e., the microstructure is governed by a polar solvent even if used in a low concentration. The results in Table 4 show that all the considered MIB-Li/*t*-BuOLi complexes lead to formation of prevailingly isotactic polymer, which is a quite unexpected finding requiring further investigation.

Table 4: Microstructures of poly(methyl methacrylate)s prepared with MIB-Li/*t*-BuOLi complexes formed under various conditions[a]

Run	Z^b	$T_m{}^c$ min	Ageing time (min)	Ageing temp. (°C)	Tacticity (triad %) iso	hetero	syndio
1[d]	1:3	r.t.[e]	2	r.t.	66.6	7.2	26.2
2[d]	1:6	r.t.[e]	2	r.t.	61.8	7.9	30.3
3	1:10	r.t.[e]	2	r.t.	63.5	7.5	29.0
4[d]	1:10	r.t.[e]	2	r.t.	64.1	7.9	28.0
5	1:3	r.t.[e]	1440	-15	63.4	7.5	29.1
6	1:10	r.t.[e]	1440	-15	64.9	8.6	26.5
7	1:3	-60	2	-60	3.9	23.2	72.9
8	1:10	-60	2	-60	64.7	7.2	28.1

[a] $[\mathrm{MMA}]_0$ = 0.468 mol/l, $[\mathrm{MIB\text{-}Li}]_0$ = 0.0093 mol/l; [b] [MIB-Li]/*t*-BuOLi mole ratio; [c] temperature of mixing the initiator components; [d] $[\mathrm{MMA}]_0$ = 0.936 mol/l, $[\mathrm{MIB\text{-}Li}]_0$ = 0.0187 mol/l; [e] room temperature

Polymerization of 2-ethylhexyl acrylate

Preliminarily, the complexes formed in a 1:10 MIB-Li/*t*-BuOLi mixture and aged at –15 °C for 24 h were also used for initiation of polymerization of 2-ethylhexyl acrylate (EtHA), the monomer whose polymerization initiated with *tert*-butyl 2-lithioisobutyrate (tBIB-Li)/*t*-BuOLi complexes was studied earlier[11,25]. Polymerizations of EtHA were performed either in neat THF or in a 9/1 (v/v) toluene/THF mixture at –60 °C (see Table 5).

Table 5: Polymerization of 2-ethylhexyl acrylate initiated with a 1:10 MIB-Li/*t*-BuOLi mixture prepared at room temperature and aged at –15 °C for 24 h[a]

Run	X^b %	SEC $10^{-3}\,M_n$	SEC M_w/M_n	φ^c %
1[d]	~ 100	18.88	1.05	50
2[e]	94	28.05	1.10	35

[a] $[\mathrm{EtHA}]_0$ = 0.024, $[\mathrm{MIB\text{-}Li}]_0$ = 0.00048 mol/l; [b] EtHA conversion; [c] initiating efficiency of MIB-Li; [d] in a 9:1 (v/v) toluene/THF mixture, 5 min; [e] in THF, 10 min

In a toluene/THF mixture (Table 5, run 1), polymerization proceeds quantitatively within 2 min. Its semilogarithmic conversion plot is linear during the whole process (Fig. 11) and the product has a very narrow MWD (Fig. 12). In neat THF, the monomer conversion is over 90 % (Table 5, run 2) but not quantitative even after a long reaction time (Fig. 11). Molecular weight of the product is higher than that of poly(EtHA) prepared in the mixed solvent indicating a lower initiating efficiency of MIB-Li under these conditions. Moreover, the MWD of the former polymer (run 2) is slightly broader than that of the latter (run 1) and its MWD curve (Fig. 12) tails toward the low-molecular-weight region, which indicates a certain extent of self-termination.

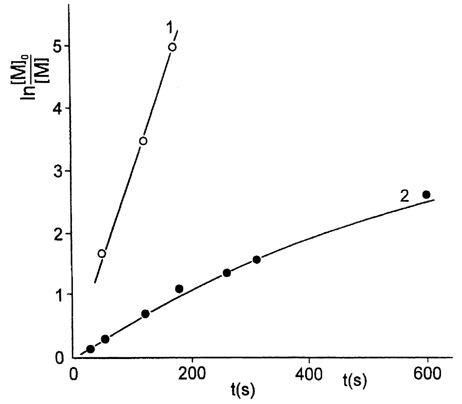


Fig. 11: Plots ln $[M]_0/[M]$ versus time of EtHA polymerizations initiated with the 1:10 MIB-Li/*t*-BuOLi mixtures aged for 24 h at –15 °C. (The curve numbers correspond to the runs in Table 5.)

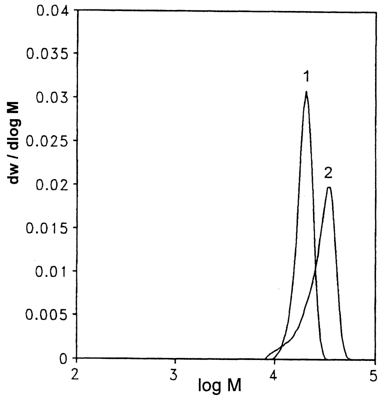


Fig. 12: MWD curves of poly(EtHA)s prepared with the 1:10 MIB-Li/*t*-BuOLi mixtures aged at –15 °C for 24 h. (The curve numbers correspond to the runs in Table 5.)

It can be said that the results of these polymerizations, initiated with the aged MIB-Li/*t*-BuOLi system are in agreement with recent studies of polymerization of EtHA initiated with the tBIB-Li/*t*-BuOLi complex[25] and, consequently, virtually no effect of ageing of the initiating complex was observed in this case. On the basis of the present results, it is difficult to make conclusions why ageing of the initiating mixture is efficient in the MMA polymerization and not in the EtHA polymerization; it can only be speculated about the importance of different reaction rates of anionic polymerizations of these two monomers.

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