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# Anionic polymerization of acrylates. XII. Polymerization of methyl methacrylate and *tert*-butyl acrylate initiated with alkylolithiums or methyl 2-lithioisobutyrate in the presence of lithium *tert*-butoxide

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## Abstract

Ligated anionic polymerization of methyl methacrylate (MMA) and *tert*-butyl acrylate (*t*-BuA) initiated either with 1,1-diphenyl-3-methylpentylolithium (DPMPLi) or  $\alpha$ -methyl styryllithium ( $\alpha$ -MStLi) or methyl 2-lithioisobutyrate (MIB-Li) stabilized with lithium *tert*-butoxide (*t*-BuOLi) was studied at  $-60^\circ\text{C}$ . In combination with DPMPLi, or  $\alpha$ -MStLi, stabilizing efficiency of the alkoxide is negligible; MMA polymerizes with high reaction rate, but the chains self-terminate after all the monomer has been consumed, which was tested in two-dose experiments. Ageing of mixed DPMPLi/*t*-BuOLi solutions as well as an excess of the alkoxide over the initiator have no effect on the stability of the growing chain-ends. In the presence of ten-fold excess of *t*-BuOLi, MIB-Li initiates slow polymerization of MMA with high stability of active centers. Three MMA doses were successively polymerized producing polymers with narrow MWDs in all steps, so that the active centers remained living for more than 4 h. *t*-BuA also polymerized in a living manner with the same system. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Ligated anionic polymerization; (Meth)acrylates; Lithium *tert*-butoxide

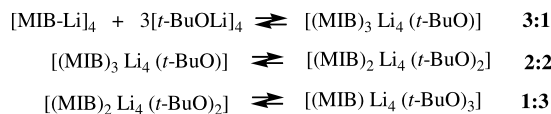
## 1. Introduction

Alkali metal *tert*-alkoxides rank among utilizable ligands stabilizing active centers of anionic polymerization of acrylic monomers [1–4]. In addition to *tert*-alkoxides, LiCl [5–7], bidentate alkoxides of the  $\text{CH}_3\text{-(OCH}_2\text{-CH}_2\text{)}_2\text{-OLi}$  type [8–10] and aluminium alkyls [11–13] were successfully used for preparation of tailor-made poly(meth)acrylates and their block copolymers. It was found in the studies of model systems that the individual ligands form with low-molecular-weight models of methacrylate active center cross-aggregates of various composition which are, among others, responsible for restriction of undesired side reactions during polymerization process [14–16]. In a THF solution of methyl 2-lithioisobutyrate (MIB-Li) and Li *tert*-butoxide (*t*-BuOLi), the alkoxide gradually replaces molecules of the ester-enolate in its tetramer forming cross-complexes with different mole ratios of both the components according to Scheme 1. The first

cross-aggregate with the mole ratio MIB-Li/*t*-BuOLi = 3:1 is formed virtually immediately after mixing the components and, during storing, it is transformed to the other two complexes with higher *t*-BuOLi contents. In a mixture with three-fold excess of the alkoxide over the ester-enolate, equilibrium population of the individual cross-aggregates is reached after ca 24 h ageing at  $-15^\circ\text{C}$  and, the complex with the MIB-Li/*t*-BuOLi ratio 1:3 probably prevails. The same effect can be reached with six-fold or higher excess of the alkoxide within 2 min standing at room temperature. It follows from NMR and theoretical studies that the core of cross-aggregates has cubic structure in which O and Li atoms alternate; the assumed structure of the 1:3 complex is given in Scheme 2. The effect of *t*-BuOLi excess and storage conditions on initiation behavior of the cross-complexes was studied in real polymerization systems [17]. The mixtures with starting MIB-Li/*t*-BuOLi ratios 1:3, 1:6 and 1:10 behave virtually in the same way assuming that they are mixed at room temperature and stored at  $-15^\circ\text{C}$  for 24 h, which indicates that, under the given conditions, all the mixtures are in an equilibrium state. If used without ageing, only 1:6 and 1:10 mixtures initiate quantitative methyl methacrylate (MMA) polymerization with linear

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Scheme 1.

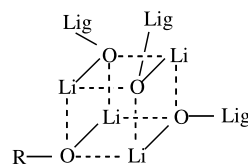
semilogarithmic conversion plots, producing polymers with narrow MWDs. However, the 1:3 mixture remains under these conditions in a non-equilibrium state, so that the polymerization initiated with these systems has a non-linear  $\ln [M]_0/[M]$  versus time dependence and the product has a broad bimodal MWD. Thus, for a controlled process to be achieved the initiating systems have to be stored at moderately low temperature for rather long time or a high extent of the stabilizing alkoxide must be used.

Similarly, cross-aggregates are formed from *tert*-butyl 2-lithioisobutyrate (*t*BIB-Li) and *t*-BuOLi; however, no cross-complex with *t*BIB-Li/*t*-BuOLi mole ratio 3:1 was found in systems regardless of the extent of the alkoxide and ageing time [18]. These combinations with various mole ratios of the components were found to be efficient initiators for acrylate polymerizations leading to products with narrow MWDs [1] and, also, to block copolymers composed of two different acrylate blocks [19]. In addition to this, *t*-BuOLi can also be used in the preparation of styrene/methacrylate block copolymers, initiated with butyllithium [20], where the alkoxide distinctly restricts reaction of the living polystyrene with methacrylate carbonyl, so that no modification of polystyryllithium with 1,1-diphenylethene [21] is needed in this special case.

In this paper, polymerization of MMA and *t*-BuA was studied, initiated with solutions of MIB-Li and *t*-BuOLi at a starting mole ratio 1:10 and used without ageing; special attention was paid to kinetics of the process and stability of the growing chain-ends in two- and three-dose experiments. Also, a short study of MMA polymerization initiated with DPMP Li or  $\alpha$ -MStLi in the presence of *t*-BuOLi was performed under various conditions and stabilizing efficiency of the alkoxide was tested in these systems.

## 2. Experimental

MMA and *t*-BuA (Fluka) were purified by usual methods, solvents (THF and toluene) were distilled with sodium benzophenone ketyl. Preparation and purification of MIB-Li and *t*-BuOLi were described elsewhere [22,23]. DPMP Li was prepared in THF according to the literature [24] and its concentration was verified by acidimetric titration.  $\alpha$ -MStLi was prepared by the reaction of *s*-BuLi with a small amount of  $\alpha$ -methylstyrene so that MMA polymerization was initiated with short chains of oligo- $\alpha$ -MStLi [5]. Polymerizations were performed in a stirred tank reactor with side dosing cell [25] allowing to quickly mix monomer solution with initiating system at a chosen temperature and to withdraw samples of the reaction



Scheme 2.

mixture in various time intervals for the determination of the monomer conversion and molecular weight of the formed polymer. In some experiments, the reactor content had been purified in situ by titration with DPMP Li solution until the red color persisted. Then, the calculated amount of the initiator was added (Tables 1 and 2). All manipulations with the components of the reaction mixture were performed under atmosphere of dry argon. The content of residual monomer in the samples was determined by gas chromatography, for measurements of molecular weights, GPC with a separation system composed of two columns (porosity  $10^3$  and  $10^5$  Å), equipped with UV and refractometric detectors was used. The system was calibrated with PMMA standards.

## 3. Results and discussion

### 3.1. MMA polymerization initiated with DPMP Li/*t*-BuOLi or $\alpha$ -MStLi/*t*-BuOLi

DPMP Li was prepared in THF solution separately and mixed with a solution of *t*-BuOLi either in flask at room temperature or directly in the reactor at  $-60$  °C. Both the ways of preparation of the initiating system gave the same results when used in polymerization; hence the conditions of mixing of the components have virtually no effect. DPMP Li was thus mixed with either an equivalent, or three- or ten-fold excess of *t*-BuOLi and then used as initiator. Mole ratios of the starting concentrations of MMA and initiator,  $[MMA]_0/[initiator]_0$ , were equal to 100 in all the experiments discussed in this chapter. As can be seen from the results in Table 1, *t*-BuOLi has virtually no effect on the polymerization; experiments proceeded with the same high reaction rate and produced in quantitative yield polymers with narrow MWDs. The only differences can be seen in molecular weights attained in the individual runs; this, however, is most probably caused by the fact that in some of the experiments, the reaction mixtures had been purified in situ before the monomer was added and the other not, so that traces of protic impurities decomposed a part of the initiator.

In the next series of experiments, two-dose polymerizations were performed and stability of the active 'living' chains formed in the first reaction step was tested under various conditions. The first-step polymerization was performed in the same way as mentioned in the foregoing paragraph; after 3 min, a part of the polymerization mixture was withdrawn from the reactor for analyses and the second

Table 1  
MMA polymerization initiated with DPMPLi/*t*-BuOLi mixtures

Run	<i>t</i> -BuOLi <sup>a</sup>	Time (s)	Conversion (%)	GPC <sup>b</sup>	
				10 <sup>-3</sup> <i>M</i> <sub>n</sub>	<i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub>
1	– <sup>c</sup>	20	78.5	15.2	1.16
		40	97.1	15.6	1.25
		60	100	16.1	1.22
2	1	20	74.0	13.2	1.28
		40	95.4	17.2	1.22
		60	100	17.4	1.20
3 <sup>d</sup>	3	20	83.7	9.9	1.31
		40	97.6	–	–
		60	100	13.1	1.21
4 <sup>d</sup>	10	30	96.0	11.4	1.15
		50	100	12.2	1.13

[MMA]<sub>0</sub> = 0.468 mol/l; [DPMPLi]<sub>0</sub> = 0.047 mol/l; THF; –60 °C.

<sup>a</sup> Molar excess of *t*-BuOLi over DPMPLi.

<sup>b</sup> Crude reaction mixtures.

<sup>c</sup> In the absence of *t*-BuOLi.

<sup>d</sup> Purified in situ.

dose of MMA, diluted with THF and pre-cooled to the reaction temperature, was added and polymerized for 10 min. Thus, the time intervals between the first and second monomer doses were 3–4 min in these cases. The amounts of MMA added in the 1st and 2nd doses, were almost the same, i.e. 28–30 mmol each. The results are summarized in Table 2. In the first experiment, when the initiator components were premixed at the polymerization temperature and used without ageing, the final product of both the monomer doses has clearly bimodal MWD with separated peaks. This indicates that approximately one half of the growing chains only remained living and is able to polymerize the second dose of the monomer. If DPMPLi and *t*-BuOLi were mixed at –30 °C (run 2), the results are similar to those in the former case; it can also be documented by MWD curves in Fig. 1. Conversions of the second MMA doses were over 95% in the both above-

Table 2  
Two-dose polymerizations of MMA initiated with DPMPLi or α-MStLi in the presence of ten-fold excess of *t*-BuOLi

Run	Initiator	First step		Final product	
		10 <sup>-3</sup> <i>M</i> <sub>n</sub>	<i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub>	10 <sup>-3</sup> <i>M</i> <sub>n</sub>	<i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub>
1 <sup>a</sup>	DPMPLi <sup>b</sup>	11.6	1.14	25.3	1.65
2 <sup>a</sup>	DPMPLi <sup>c</sup>	13.2	1.11	25.4	1.56
3	α-MStLi <sup>d</sup>	16.7	1.20	30.2	2.18
4	α-MStLi <sup>e</sup>	51.9	1.38	80.4	2.64

<sup>a</sup> Purified in situ.

<sup>b</sup> DPMPLi and *t*-BuOLi mixed directly in the reactor at –60 °C.

<sup>c</sup> DPMPLi and *t*-BuOLi mixed at –30 °C in the reactor, then cooled down to –60 °C and MMA added.

<sup>d</sup> *s*-BuLi added to the reactor containing *t*-BuOLi and α-MSt at room temperature, then cooled down to –60 °C, non-aged, and MMA added.

<sup>e</sup> α-MStLi and *t*-BuOLi mixed in the reactor at room temperature, aged 20 h at –30 °C before the addition of MMA.

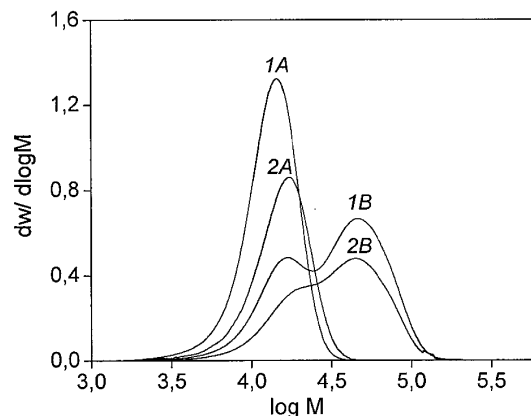


Fig. 1. MWD curves of PMMAs formed in one-dose (A) and two-dose (B) polymerizations initiated with a DPMPLi/*t*-BuOLi system (runs 1 and 2 in Table 2).

mentioned cases. α-MStLi, premixed with *t*-BuOLi at room temperature and used without ageing, initiates quick and quantitative polymerization of the first MMA dose; however, again, approximately one half of the growing chain-ends self-terminated before the addition of the second monomer dose. This is clearly documented by bimodal MWD curve of run 3 in Fig. 2. The same system, mixed at room temperature and stored for 20 h at –30 °C, initiates fast polymerization, giving, however, the product with a broadened MWD and hint of polymodality even in the first step (see the corresponding MWD curve in Fig. 2). This indicates multiplicity of active species in this case, generated likely during a relatively long interaction between the initiator and alkoxide. Again, only a part of these centers remains active and can initiate polymerization of the second MMA dose; consequently, the final product has broad MWD (Fig. 2), even broader than that formed from the first dose of the monomer. Also in these experiments, the second MMA doses were consumed almost quantitatively like in the processes initiated with DPMPLi. Thus, none of the

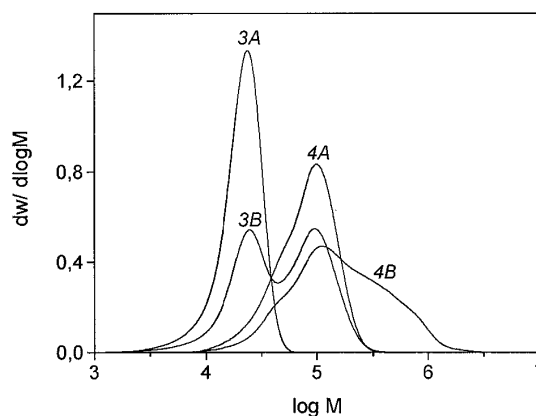


Fig. 2. MWD curves of PMMAs formed in one-dose (A) and two-dose (B) polymerizations initiated with an α-MStLi/*t*-BuOLi system (runs 3 and 4 in Table 2).

Table 3  
Polymerization of MMA initiated with a MIB-Li/*t*-BuOLi system

Run	Solvent	Time (min)	Conversion (%)	GPC	
				$10^{-3} M_n$	$M_w/M_n$
1 <sup>a</sup>	THF	120	100	7.46	1.22
2 <sup>b</sup>	THF	90	100	7.95	1.22
3 <sup>a</sup>	5/5 <sup>c</sup>	60	100	9.04	1.14
4 <sup>a,d</sup>	THF	60	>95	24.4	1.08
5 <sup>e</sup>	THF	30	100 <sup>f</sup>	12.1	2.13 <sup>g</sup>

[MMA]<sub>0</sub> = 0.486 mol/l; mole ratio [MMA]<sub>0</sub>/[MIB-Li]<sub>0</sub>/[*t*-BuOLi]<sub>0</sub> = 50/1/10; *T* = -60 °C.

<sup>a</sup> MIB-Li and *t*-BuOLi mixed at room temperature and used without ageing.

<sup>b</sup> MIB-Li and *t*-BuOLi mixed at room temperature and stored at -30 °C for 24 h before use.

<sup>c</sup> Toluene/THF mixture 5/5 (v/v).

<sup>d</sup> [MMA]<sub>0</sub> = 0.936 mol/l; mole ratio [MMA]<sub>0</sub>/[MIB-Li]<sub>0</sub>/[*t*-BuOLi]<sub>0</sub> = 100/1/10.

<sup>e</sup> Initiated with neat MIB-Li in the absence of *t*-BuOLi.

<sup>f</sup> Complete conversion within 1 min.

<sup>g</sup> Bimodal MWD.

initiating systems, mentioned above, ensures sufficient stability of active species of the polymerization.

### 3.2. Polymerization of MMA initiated with MIB-Li/*t*-BuOLi system

In a number of our foregoing papers, controlled polymerizations of acrylates were described, initiated with *t*BIB-Li in the presence of *t*-BuOLi excess, allowing even synthesis of diblock copolymers composed of different acrylate blocks. The effect of *t*-BuOLi on MMA polymerization initiated with MIB-Li was studied in the recent paper [17] in dependence on the excess of the alkoxide over the ester-enolate and on the storage time of the system. Combination of MIB-Li/*t*-BuOLi with a mole ratio 1:10 in THF initiates virtually a living polymerization, giving the product with a narrow MWD, which indicates that the

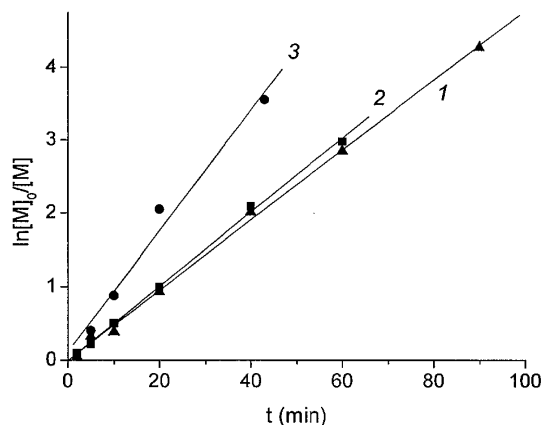


Fig. 3. Plots  $\ln [M]_0/[M]$  versus time for MMA polymerizations initiated with MIB-Li or its 1/10 mixtures with *t*-BuOLi (for conditions and numbering of the curves, see Table 3).

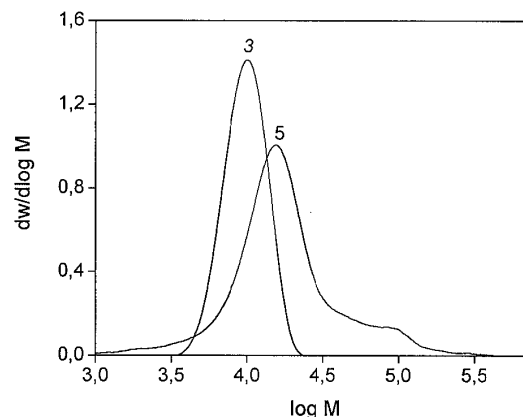


Fig. 4. MWD curves of PMMAs prepared by MIB-Li/*t*-BuOLi (the numbers correspond to the runs in Table 3).

system is in equilibrium. Here, the polymerization was studied in more detail, with various starting concentrations of reaction components and in different solvents. The results of these one-dose experiments are given in Table 3, semilogarithmic conversion curves in Fig. 3, and MWD curves of the polymers formed in the presence or in the absence of *t*-BuOLi are shown in Fig. 4. The polymerizations in all the reported experiments, performed in the presence of *t*-BuOLi, behave as living processes in both THF and toluene/THF mixture and the products have narrow MWDs (measured in reaction mixtures without isolation of polymers). Also, molecular weight of the formed polymer increases linearly with increasing monomer conversion and polydispersity index remains virtually unchanged within the whole range of the conversion (Fig. 5). The linear semilogarithmic conversion plots (Fig. 3) clearly document, that, in the presence of ten-fold excess of *t*-BuOLi, the extent of self-termination is virtually negligible in all cases.

To obtain more information on the stability of growing chain-ends in the presence of *t*-BuOLi, two- and three-dose experiments were performed, initiated in the first step with the 1/10 (mol/mol) MIB-Li/*t*-BuOLi system, prepared at

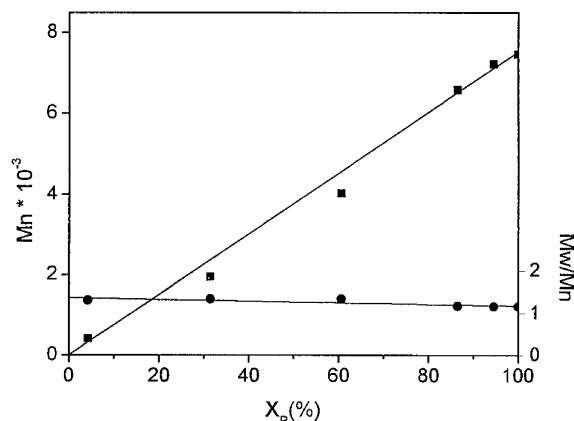


Fig. 5.  $M_n$  (■) and  $M_w/M_n$  (●) versus monomer conversion for MMA polymerization initiated with MIB-Li/*t*-BuOLi complex (run 1 in Table 3).

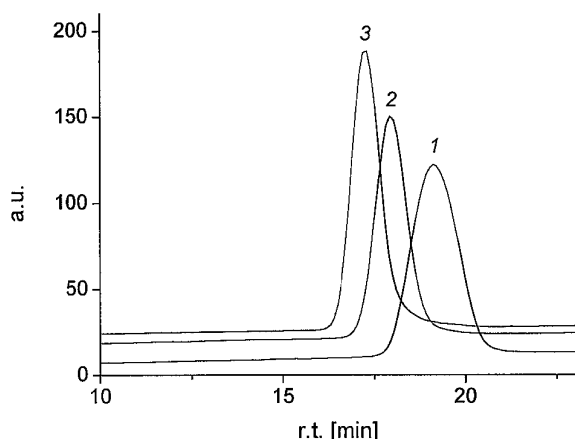


Fig. 6. GPC traces of polymers formed in three-dose polymerization of MMA. The numbers correspond to the monomer doses (see Table 4).

room temperature and used without ageing; i.e. with the same initiator as that used in run 1 in Table 3. The results of three-dose polymerization are given in Table 4. Sixty minutes after the mixing of the first MMA dose with an initiator solution in the reactor, approximately 50% of the reaction mixture was withdrawn and a dilute solution of the second MMA dose in THF was added to the reactor at the polymerization temperature and under vigorous stirring. The withdrawn sample was analyzed by GC and by GPC. The second dose of the monomer polymerized for 90 min; then, a part of the reaction mixture was again withdrawn for analyses. After this, 3rd MMA dose was added to the reactor in the same way as described for the second dose and polymerized for 100 min. Taking into account the above mentioned withdrawals of the reaction mixture in the individual polymerization steps, the amount of MMA used in the individual doses was estimated: 1st dose: 20.7 mmol; 2nd dose: 24.7 mmol, and 3rd dose: 28.1 mmol. Also, considering non-quantitative initiating efficiency of MIB-Li [1,17] (approx. 65%), the expected molecular weights of products of the two- and three-doses steps can be roughly calculated (Table 4). As determined by GC, conversion of the monomer was 90–100% in all of the doses. Molecular weights of the polymers increase with

Table 4  
Three-dose polymerization of MMA initiated with a MIB-Li/*t*-BuOLi system

Dose	$\Delta t^a$ (min)	$t^b$ (min)	Expected $M_n$ ( $\times 10^{-3}$ ) <sup>c</sup>	GPC	
				$10^{-3} M_n$	$M_w/M_n$
1	0	60	7.8	7.8	1.20
2	60	150	17.5	19.0	1.11
3	150	250	28.3	30.1	1.12

[MMA]<sub>0</sub> = 0.486 mol/l; mole ratio [MMA]<sub>0</sub>/[MIB-Li]<sub>0</sub>/[*t*-BuOLi]<sub>0</sub> = 50/1/10 in the first step; THF;  $T = -60$  °C.

<sup>a</sup> Time interval from the addition of the first dose.

<sup>b</sup> Total reaction time.

<sup>c</sup> Estimated from stoichiometry, see the text.

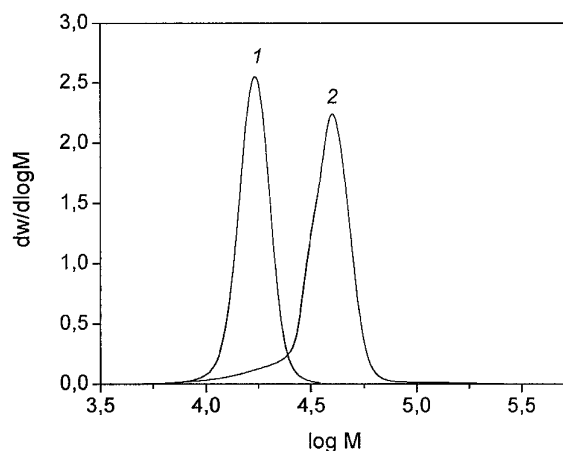


Fig. 7. MWD curves of poly(*t*-BuA)s formed in two-dose polymerization. (1) first dose:  $M_n = 16,940$ ,  $M_w/M_n = 1.06$ ; (2) first and second doses:  $M_n = 34,190$  (calculated value approximately 32,000),  $M_w/M_n = 1.14$ .

increasing total amounts of the added monomer, and the products in the individual reaction steps have narrow unimodal MWDs without detectable contamination by the product of the foregoing step as can be seen from GPC traces in Fig. 6. Thus, it can be concluded from the obtained results that the equilibrium initiation system MIB-Li/*t*-BuOLi with mole ratio 1/10 initiates at  $-60$  °C in THF polymerization with highly stable growing chain-ends, which remain active for more than 4 h.

### 3.3. Polymerization of *t*-BuA initiated with MIB-Li/*t*-BuOLi system

Under the same conditions, polymerization of *t*-BuA was followed, i.e. at  $-60$  °C in THF, with starting concentration [*t*-BuA]<sub>0</sub> = 0.468 mol/l and mole ratio [*t*-BuA]<sub>0</sub>/[MIB-Li]<sub>0</sub>/[*t*-BuOLi]<sub>0</sub> = 50/1/10. Polymerization time was 60 min; after that, approximately 40% of the reaction mixture was withdrawn for analyses. The residual mixture in the reactor was diluted with an appropriate amount of dry and pre-cooled THF and the second dose of *t*-BuA was added as a dilute THF solution under stirring. After 1 h polymerization, the process was terminated with a THF/methanol mixture and the crude reaction mixture was again analyzed by GC and GPC (calculated as PMMA). The amount of the monomer was 28 mmol in the 1st dose and 25 mmol in the 2nd dose, respectively. It can be seen from Fig. 7 that the second *t*-BuA dose polymerized quantitatively giving a product with correspondingly higher molecular weight than that of the first-dose polymer, with only slightly broadened MWD. Thus, under the given conditions, also polymerization of *t*-BuA is living and active for at least 2 h.

## 4. Conclusions

MMA polymerization initiated at  $-60$  °C in THF with

alkyllithiums (DPMPLi or  $\alpha$ -MStLi) in the presence of an excess of *t*-BuOLi proceeds with high reaction rate and produces polymer with a narrow MWD and, probably, with controllable molecular weight, at least to a certain extent. However, the second dose of monomer added after consumption of the first one, gives final polymer with bimodal or even polymodal MWD, which indicates that a part of active chains from the first-dose polymerization self-terminates and only the residual amount remains living under the given reaction conditions.

If, however, the process is initiated with a combination of ester-enolate initiator (MIB-Li) and ten-fold excess of *tert*-alkoxide (*t*-BuOLi) at the same temperature, polymerization rate is much slower than that in the foregoing case, but, it exhibits all features of a living process both in THF and in a mixture toluene/THF 5/5 (v/v). The stability of active chain-ends is high as was verified in two- and three-doses experiments with total polymerization time 250 min. Here, molecular weights of the formed polymers increase with increasing amounts of the added monomer and their MWDs remain virtually unchanged. Similar results were obtained in two-dose *t*-BuA polymerizations under identical conditions, which also remains active at least for 2 h. Thus, the polymerization initiated with the MIB-Li/*t*-BuOLi system with mole ratio 1/10 keeps its activity and ‘livingness’ without detectable extent of self-termination reaction for more than 4 h, which predetermines it for the synthesis of methacrylate block copolymers. This is now under study and will be reported in the next paper.

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