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Synthesis of (meth)acrylate Block Copolymers by Ligated Anionic Polymerization

Petr Vlček, Eva Čadová, Miroslav Janata, Petra Látalová, Luděk Toman, Jaroslav Kříž, Dana Kurková*

Summary: Synthetic potential of the ligated anionic polymerization (LAP) of acrylic and metacrylic esters initiated with methyl 2-lithioisobutyrate (MIB-Li) in the presence of an excess of alkali metal *tert*-alkoxides (prevailingly Li *tert*-butoxide) is presented. *tert*-Alkoxides form with ester-enolates, like MIB-Li, cross-aggregates of various composition, which tailor the environment of growing chain-ends, lower their nucleophilicity and restrict in this way the extent of side reactions, in particular self-termination of growing macroanions by back-biting reaction. Thus, stability of polymethacrylate living chains is sufficiently high for methacrylate and acrylate block copolymers to be synthesized. In the case of acrylate polymerization, reaction conditions must be optimized due to their high tendency to self-termination.

Keywords: anionic polymerization; block copolymers; ester-enolates; (meth)acrylates *tert*-alkoxides

Introduction

Anionic polymerization of polar vinyl monomers, namely acrylic and methacrylic esters, is complicated with a number of side reactions, originating from the condensation of organometallic initiator (e.g. butyllithium – BuLi) and/or living chain-end with carbonyl group of monomer or polymer and leading to loss of control over the process[1–4]. Typically, the living chain-end of growing (meth)acrylate polymer can react with the carbonyl group of the penultimate unit (back-biting reaction) forming, after the splitting off alkoxide molecule, cyclic oxoester which means virtually irreversible self-termination of polymerization. Thus, two main reactions compete in every propagation step, see Scheme **1**: propagation of the polymer and self-termination by back-biting reaction. Therefore, livingness of the process is given by the ratio of the rates of propagation and self-termination, which can be expressed as the k_p/k_t ratio. To overcome these problems, a number of methods have been developed such as group-transfer polymerization (GTP) by DuPont[5,6], initiated with 1-methoxy-1-trimethylsilyloxy-2-methylpropene and catalyzed with nucleophilic or electrophilic catalysts, metal-free anionic polymerization[7] initiated with tetraalkylammonium salts (MFP), polymerization initiated with metalloporphyrine derivatives[8] or with lanthanocenes[9].

Ligated anionic polymerization is in fact the first successful attempt to polymerize (meth)acrylates in a controlled way. It is based on a modification of classical anionic polymerization, initiated with organometallic initiators like *tert*-BuLi (*t*-BuLi), 1,1-diphenylhexyllithium (DPHLi) or ester-enolates. The basic strategy followed here was to decrease the reactivity of the living chain-end toward the carbonyl group of (meth)acrylate and the acid α-hydrogen in acrylate[10,11]. This has been performed by tailoring the environment of the propagating chain-end by electronically well-balanced ligands which cause steric

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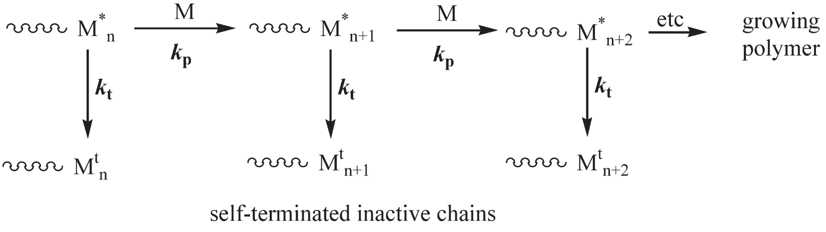
Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 16206 Prague 6, Czech Republic
Fax: (420) 296809410
E-mail: vlcek@imc.cas.cz



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Scheme 1.

hindrance and, at the same time, lower nucleophilicity of the growing carbanion. The living chain-end, however, remains reactive enough to add further monomer molecule. At present, the following stabilizing additives (ligands) are mainly used in the (meth)acrylate polymerization: (i) alkali metal *tert*-alkoxides[12,13] (the oldest type of ligand), (ii) alkali metal halides[14] (prevailingly LiCl), (iii) alkali metal polydentate alkoxides[15] (dual ligands) and, (iv) alkylaluminums[16]. In addition, other compounds ($LiClO_4$, tertiary diamines, Li silanolates, etc) were tested as ligands.

It was found in a number of studies that alkali metal *tert*-alkoxides form with enolate-type initiators and/or enolate type living chain-ends cross-complexes affecting their reactivity, in particular that toward carbonyl groups of monomer or polymer[17,18]. Model studies of interaction of methyl 2-lithioisobutyrate (MIB-Li) and lithium *tert*-butoxide (*t*-BuOLi) demonstrated that the cross-aggregation proceeds in solution as a stepwise process according to Scheme **2**, leading to an equilibrium mixture of the individual cross-complexes, in which that with MIB-Li/*t*-BuOLi mole ratio 1/3 prevails[19]. As indicated in other papers[13,20], an equilibrium mixture of MIB-Li with at least three-fold excess of *t*-BuOLi initiates controlled polymerization of MMA; most probably, the 1/3 cross-complex is the true initiating compound. Let us note that the equilibrium is reached within a few minutes after both the components have been mixed in THF at room temperature (see below).

Polymerization of methacrylates

MMA polymerization, initiated with neat MIB-Li in THF proceeds at −60 °C very quickly and quantitatively, giving product with broad and bimodal MWD[13] (Run 4 in Table 1). The strongly favorable effect of a ten-fold excess of *t*-BuOLi over the initiator is clearly seen from the results of Runs 1–3, regardless of the method of preparation of the initiating complex or solvent used. The complexes were used either just after preparation at room temperature or after ageing at low temperature – see Table 1. Linear semilogarithmic plots of monomer consumption versus time, Figure 1, evidence living polymerization in all these three experiments. Stability of growing chains was investigated in a three-dose experiment, under the same polymerization

$$3\,[\mathrm{MIB\text{-}Li}]_4 + [t\text{-}\mathrm{BuOLi}]_4 \longrightarrow 4\,[\mathrm{MIB_3Li_4}(t\text{-}\mathrm{BuO})] \qquad (3{:}1)$$

$$2\,[\mathrm{MIB_3Li_4}(t\text{-}\mathrm{BuO})] + [t\text{-}\mathrm{BuOLi}]_4 \longrightarrow 3\,[\mathrm{MIB_2Li_4}(t\text{-}\mathrm{BuO})_2] \qquad (2{:}2)$$

$$[\mathrm{MIB_2Li_4}(t\text{-}\mathrm{BuO})_2] + [t\text{-}\mathrm{BuOLi}]_4 \longrightarrow 2\,[\mathrm{MIB\ Li_4}(t\text{-}\mathrm{BuO})_3] \qquad (1{:}3)$$

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Scheme 2.

Table 1.
MMA polymerization initiated with 1/10 MIB-Li/*t*-BuOLi complex at −60 °C[a]

Run	Solvent	Time (min)	Conv. (%)	SEC	
				$10^{-3}M_n$	M_w/M_n
1[b]	THF	120	100	7.46	1.22
2[c]	THF	90	100	7.95	1.22
3[b]	5/5[d]	60		9.04	1.14
4[e]	THF	1	100	12.1	2.13[f]

[a] $[MMA]_o/[MIB\text{-}Li]_o = 50$.
[b] fresh complex.
[c] complex aged for 24 h at −15 °C.
[d] toluene/THF volume ratio.
[e] no *t*-BuOLi.
[f] bimodal MWD.

conditions as in Run 1, Table 1. The first MMA dose was polymerized for 60 min, then a sample was withdrawn for analysis ($M_n = 7800$, $M_w/M_n = 1.20$) and the second dose was added and polymerized for 90 min ($M_n = 19000$, $M_w/M_n = 1.11$). After this time, the third monomer dose was introduced and polymerized for 100 min giving final product with $M_n = 30100$ and $M_w/M_n = 1.12$. The amounts of MMA in the doses were comparable. The long total reaction time, 250 min, documents a high stability of the growing chain-ends and SEC traces (Figure 2) show virtually quantitative initiating efficiencies of the corresponding "macroinitiators" in both second and third steps of polymerizations.

Consequently, the initiating system was used for synthesis of block copolymers, composed of different methacrylates[21]. MMA was used as the first monomer and polymerized by the 1/10 MIB-Li/*t*-BuOLi complex in THF at −60 °C for one hour and than, the second monomer was added and polymerized for a selected time. Characteristics of diblock copolymers containing MMA, butyl (BuMA) or 2-(dimethylamino)ethyl (DMAMA) methacrylates are given in Table 2 and Figure 3. It is seen from the data and SEC traces that the copolymers do not contain detectable amounts of the corresponding homopolymers. Thus, the homopolymers remain living at −60 °C and capable of initiation of polymerization of the second monomers even after a long time period.

Further, the same initiating system was used for synthesis of methacrylate triblock

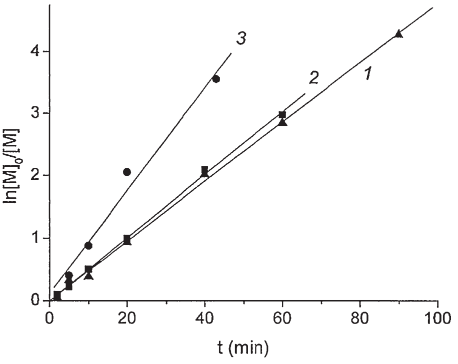


Figure 1.
Semilogarithmic conversion plots for MMA polymerizations, Runs 1–3 in Table 1.

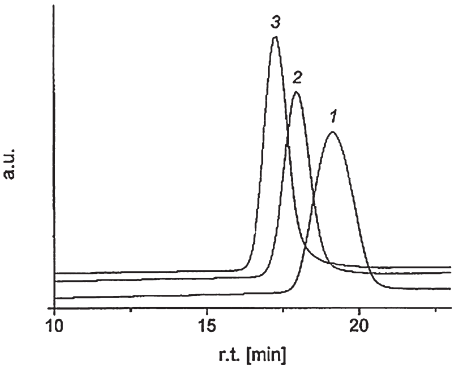


Figure 2.
SEC curves of products of the three-step MMA polymerization. The curve numbers correspond to the steps. For conditions see run 1, Table 1.

Table 2.
Synthesis of methacrylate diblock copolymers[a]

Run	M_2[b]	PMMA		M_1/M_2[c] (NMR)	P (MMA-*b*-M_2)		
		M_n (SEC)	M_w/M_n		M_n (SEC)	M_n (NMR)	M_w/M_n
1	BuMA	7400	1.19	2.6/1	12400	11400	1.19
2	BuMA	8200	1.18	1/1	21900	19800	1.19
3	DMAMA	9500	1.20	1.2/1	29500	21900	1.29

[a] Conditions: MMA/MIB-Li/*t*-BuOLi=1/10; $T=-60\,^{\circ}$C; THF.
[b] second monomer.
[c] mole ratio of monomers in the products.

copolymers, ABA and ABC-type. Here, the first monomer was polymerized at $-60\,^{\circ}$C again for 60 min; then, the second monomer was added and polymerized for 90 min under the same conditions. Finally, the third monomer was introduced into the reaction mixture and polymerized for 100 min. The results are summarized in Table 3, the SEC traces in Fig. 4. Also here, SEC traces are strictly unimodal and symmetrical, thus indicating that the products of the first and second steps are completely consumed in the subsequent steps of copolymerization. Therefore, the extent of spontaneous self-termination is negligible. It has to be noted that the M_n values of di- and triblock copolymers, determined by SEC, are only apparent ones, due to that the eluograms were treated as PMMAs and, also the SEC separation system was calibrated with PMMA standards. The same is valid for methacrylate/acrylate block copolymers. The exact M_n values were calculated on the basis of NMR analysis. It is seen from the above-mentioned results that the complex initiating systems, composed of the ester-enolate type initiator and alkali metal *tert*-alkoxide stabilizing ligand are advantageous combinations, inducing living and controlled polymerization of methacrylate esters leading to polymers and block copolymers with predetermined molecular parameters and chemical structure.

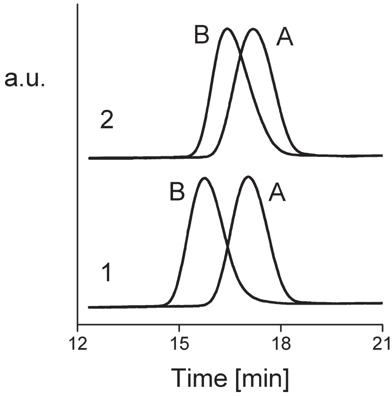


Figure 3.
SEC traces of PMMA (A) and block copolymers (B); runs 1 and 2 in Table 2.

Polymerization of acrylates

Controlled anionic polymerization of acrylic esters was not successful for a long time, due to their high tendency to side condensation reactions[22,23]. The only exceptions were esters with α-branched alkoxy groups, for instance cyclohexyl, isopropyl or, in particular, *tert*-butyl acrylates. Thus, the ester-enolate/*tert*-alkoxide initiating complexes have been used for acrylate polymerization[24]. As an example, the results of butyl acrylate (BuA) polymerization, initiated with *tert*-butyl 2-lithioisobutyrate (tBIB-Li) are presented in Table 4, documenting a favorable effect of the alkoxide addition on the course of polymerization[25]. In the absence of *t*-BuOLi, (run 1), polymerization spontaneously self-terminates at a low conversion and the product has extremely broad MWD, indicating a high extent of side reactions. Addition of the excess of *t*-BuOLi over the initiator, runs 2 and 3,

Table 3.
Synthesis of methacrylate triblock copolymers[a]

Run	M_1	M_2	M_3	M_1:M_2:M_3 NMR[b]	PM_1		$P(M_1$-*b*-$M_2)$		$P(M_1$-*b*-M_2-*b*-$M_3)$		
	mmol				M_n SEC	M_w/M_n	M_n SEC	M_w/M_n	M_n SEC	M_w/M_n	M_n NMR
1[c]	17.3				7300	1.21					
	17.3	17.5					21000	1.22			
	17.3	17.5	26.4	1:1.2:2.1					38300	1.15	34400
2[d]	23.0				8400	1.16					
	23.0	23.0					20500	1.18			
	23.0	23.	23.0	1.1:1:1.1					33100	1.21	29400
3[e]	18.3				7700	1.19					
	18.3	18.2					22700	1.20			
	18.3	18.2	18.3	1:1:1					42700	1.17	

[a] Conditions: M_1/MIB-Li/*t*-BuOLi = 50/1/10; T = −60 °C; THF.
[b] mole ratios in triblock copolymers.
[c] $M_1 = M_3$ = MMA, M_2 = BuMA.
[d] $M_1 = M_3$ = MMA, M_2 = DMAMA.
[e] M_1 = MMA, M_2 = BuMA; M_3 = 2-ethylhexyl methacrylate.

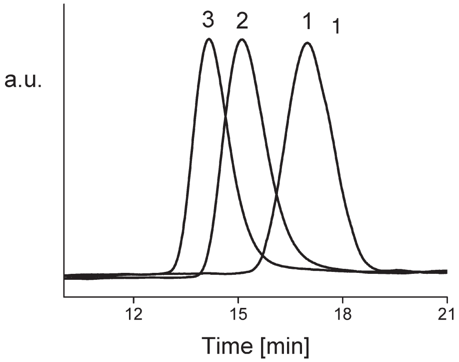


Figure 4.
SEC traces of PMMA (1), diblock (2) and triblock (3) copolymer; run 3 in Table 3.

strongly lowers the extent of self-termination so that the polymerization proceeds quantitatively and the formed polymers have narrow MWDs. Nevertheless, the semilogarithmic conversion plots in Figure 5 are not linear even if ten-fold excess of the alkoxide was used, which clearly indicates non-zero rate of self-termination. This is in contrast to the methacrylate polymerization under the same conditions, discussed above, and shows a perceptibly different tendency to back-biting reaction for methacrylate and acrylate polymerizations. Moreover, acrylate polymerization must be performed in a medium with moderate polarity, ie. toluene/THF mixtures containing a low amount of THF. In a neat THF, the extent of self-termination increases and

Table 4.
Polymerization of BuA[a]

Run	Solvent[b]	*t*-BuOLi excess	Time min	Conv. %	SEC	
					M_n[c]	M_w/M_n
1	9/1	—	5	22.7	3300	>10
2	9/1	3	5	99.6	14000	1.31
3	9/1	10	3	100	11700	1.21
4	19/1	10	3	100	11000	1.18
5	THF	10	5	67.5	11800	1.73

[a] $[BuA]_0/[tBIB\text{-}Li]_0 = 50$, $T = -60$ °C.
[b] toluene/THF volume ratio.
[c] eluograms were treated as poly(2-ethylhexyl acrylate), thus the values are apparent.

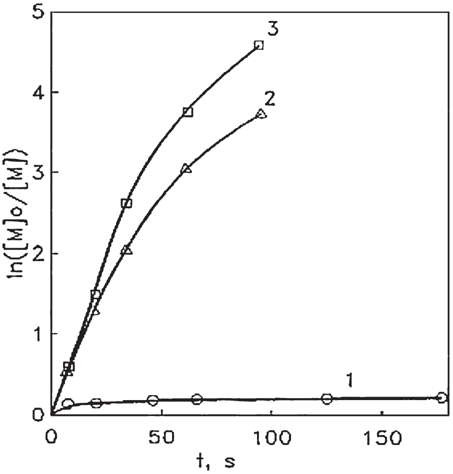


Figure 5.
Semilogarithmic conversion plots for BuA polymerization; effect of *t*-BuOLi and solvent. The curve numbers correspond to the runs in Table 4.

polymerization does not proceed up to 100 % monomer conversion. This can be clearly seen comparing runs 3 and 5 in Table 4. Further, reaction temperature affects both the kinetics of propagation and self-termination, however, the rate of the latter increases with increasing temperature more steeply[26]. This has been found in a short kinetic study of BuA polymerization, the results of which are presented in Table 5. Quantitative monomer conversion can be reached at temperatures $\leq -60\,^\circ$C, whereas at higher temperature ($-40\,^\circ$C), the rate of self-termination is already high and, consequently, the k_p/k_t ratio is too low. This is why the reaction spontaneously stops before the monomer has been consumed. Thus, not absolute values of rates of propagation and self-termination, but their ratio – or the ratio of the rate constants – is a key factor determining livingness of polymerization as has been mentioned above.

Methacrylate/acrylate block copolymerization

Due to a number of potential technological applications of block copolymers containing hard PMMA and rubbery polyacrylate blocks, the initiating complexes were used in a preparation of methacrylate/acrylate block copolymers[27]. Using the information obtained in the foregoing studies, MMA and 2-ethylhexyl acrylate (EtHA) were block-copolymerized under the conditions given in the footnote of Table 6. The time of MMA polymerization was 1 h, then a sample of the mixture was withdrawn, EtHA solution was added at the reaction temperature and polymerized for 15 min. At $-60\,^\circ$C, the product with a clear hint of bimodality was obtained, as shown in Figure 6. Also, this low-molecular-weight part of the copolymer perceptibly absorbs in UV region at 260 nm, which indicates that these chains do not contain only MMA units. Bimodality was not observed for the product of copolymerization prepared at $-78\,^\circ$C, see run 2 in the Table and Figure 7. Here, the copolymer has a unimodal and narrow MWD with a small tail only toward the lower molecular weight region, indicating a negligible extent of self-termination during the beginning of the second step of copolymerization. Thus, under sufficiently low temperature, a true diblock copolymer is formed containing perhaps an insignificant amount of the corresponding PMMA homopolymer.

Further, attempts have been made to synthesize poly(MMA-*b*-BuA) and poly-

Table 5.
Effect of reaction temperature on BuA polymerization[a]

Run	T	Conv.	SEC		k_p	$k_t \cdot 10^3$	$k_p/k_t \cdot 10^{-3}$
	°C	%	M_n	M_w/M_n	$L \cdot mol^{-1} \cdot s^{-1}$	s^{-1}	$L.mol^{-1}$
1	−70	100	14600	1.18	15.71	6.0	2.62
2	−60	100	11300	1.13	26.17	15.3	1.74
3	−40	93	12100	1.38	55.55	76.2	0.73

[a] $[BuA]_0/[tBIB\text{-}Li]_0/[t\text{-}BuOLi]_0 = 50/1/10$; toluene/THF = 10/1; time 5 min.

Table 6.
Preparation of poly(MMA-*b*-EtHA) block copolymers

Run	T	1st step[a]		2nd step[b]	
	°C	M_n	M_w/M_n	M_n	M_w/M_n
1	−60	6700	1.16	22000[c] 31700[d]	1.20 1.04
2	−78	7700	1.23	21800[c]	1.26

[a] MMA/MIB-Li/*t*-BuOLi mole ratio = 50/1/10, toluene/THF 5/5.
[b] MMA/EtHA = 1/1.
[c] from the whole eluogram.
[d] from the major peak only.

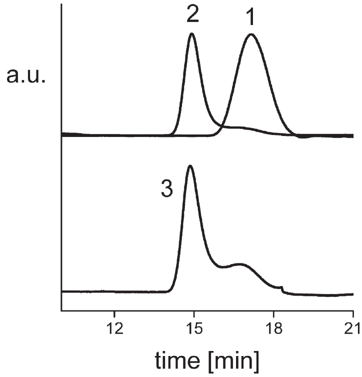


Figure 6.
SEC traces of: (1) PMMA, RI det., (2) poly(MMA-*b*-EtHA), RI det., (3) poly(MMA-*b*-EtHA), UV det. (run 1, Table 6).

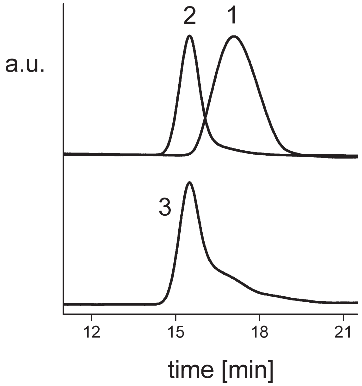


Figure 7.
SEC traces of: (1) PMMA, RI det., (2) poly(MMA-*b*-EtHA), RI det., (3) poly(MMA-*b*-EtHA), UV det.; run 2, Table 6.

(MMA-*b*-EtA) block copolymers under the same conditions. It should be noted that the rates of anionic polymerization of BuA and EtA initiated with an ester-enolate/*tert*-alkoxide system are perceptibly higher than that of EtHA; however, this is valid also for the rates of self-termination. It can be expected that these facts will affect also block copolymerization of BuA and EtA with MMA. Examples of MMA/BuA and MMA/EtA block copolymerizations are given in Table 7. Molecular weights of both the block copolymers are adequately higher than those of the precursors, nevertheless, the SEC traces show that the processes are not completely free of self-termination. SEC curve of the poly(MMA-*b*- BuA), Figure 8, is somewhat non-symmetrical with a tail toward the low-molecular-weight region. This indicates a certain extent of self-termination, proceeding most probably in the second step of the copolymerization, which is supported by a strong absorption of the copolymer in the

Table 7.
Block copolymerizations of MMA with BuA or EtA[a]

Run	M_2	M_1/M_2 (m/m)	1st step		2nd step			
			M_n(SEC)	M_w/M_n	M_n (SEC)	M_w/M_n	m_1/m_2	M_n (NMR)
1	BuA	0.93/1	6500	1.28	18500	1.26	0.92/1	15600
2	EtA	1.06/1	6400	1.34	13900	1.36	1.19/1	11800

[a] MMA/MIB-Li/*t*-BuOLi mole ratio = 50/1/10, toluene/THF = 5/5; $T = -78$ °C.

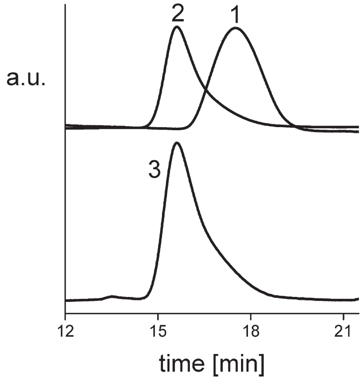


Figure 8.
SEC traces of (1) PMMA, RI det., (2) poly(MMA-*b*-BuA), RI det., (3) poly(MMA-*b*-BuA), UV det.; run 1, Table 7.

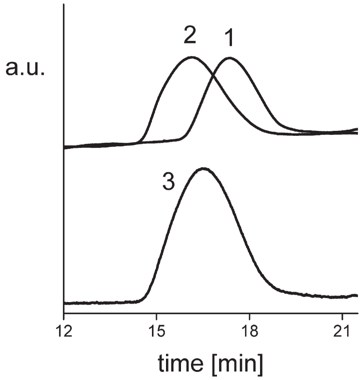


Figure 9.
SEC traces of (1) PMMA, RI det., (2) poly(MMA-*b*-EtA), RI det., (3) poly(MMA-*b*-EtA), UV det.; run 2, Table 7.

UV region at 260 nm. Similarly, block copolymerization of MMA with EtA gives product with non-symmetrical MWD and tail toward the low-molecular-weight region, as can be seen from SEC eluograms in Figure 9. Thus, BuA and EtA exhibit a perceptibly higher tendency to back-biting reaction than EHA so that the corresponding MMA/BuA and MMA/EtA copolymerizations proceed evidently in a less controlled way.

Somewhat surprisingly, block copolymerization of MMA with *t*-BuA, the tendency of which to self-termination is relatively very low, gives at −60 °C a clearly bimodal product with two separated peaks in SEC eluogram (Table 8, Figure 10). The retention time of the minor peak is virtually the same as that of the PMMA precursor so that it apparently belongs to self-terminated PMMA. As this part of the product absorbs in UV, the chains probably contain one or more *t*-BuA units at the ends. At −78 °C, the SEC trace of the copolymer is not composed of two separated peaks, nevertheless, the tail and hint of bimodality can clearly be seen (Figure 11). Thus, *t*-BuA exhibits a higher extent of self-termination when initiated with living PMMA than, for instance, EtHA (cf. Figs. 7 and 11). The main reason for this behavior lies most probably in the very different propagation rates of these two acrylates: EtHA polymerizes under the given conditions quanti-

Table 8.
Block copolymerization of MMA and *t*-BuA[a]

Run	T	1st step		2nd step	
	°C	M_n	M_w/M_n	M_n	M_w/M_n
1[b]	−60	7000	1.22	25500[d] 50500[e] 8800[f]	1.70 1.08 1.17
2[c]	−78	9600	1.31	24600[d] 33800[e]	1.27 1.04

[a] MMA/MIB-Li/*t*-BuOLi = 50/1/10, THF.
[b] $M_1/M_2 = 1/2$.
[c] 1/1.
[d] calculated from the whole eluogram.
[e] from the major peak.
[f] from the minor peak.

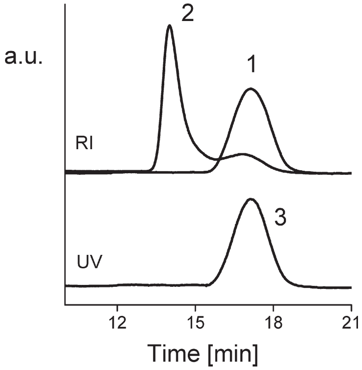


Figure 10.
SEC traces of (1) PMMA, RI det., poly(MMA-*b*-*t*-BuA) (2) RI det., (3) UV det.; run 1, Table 8

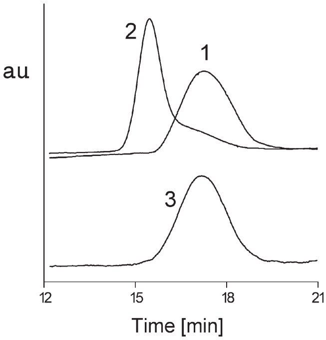
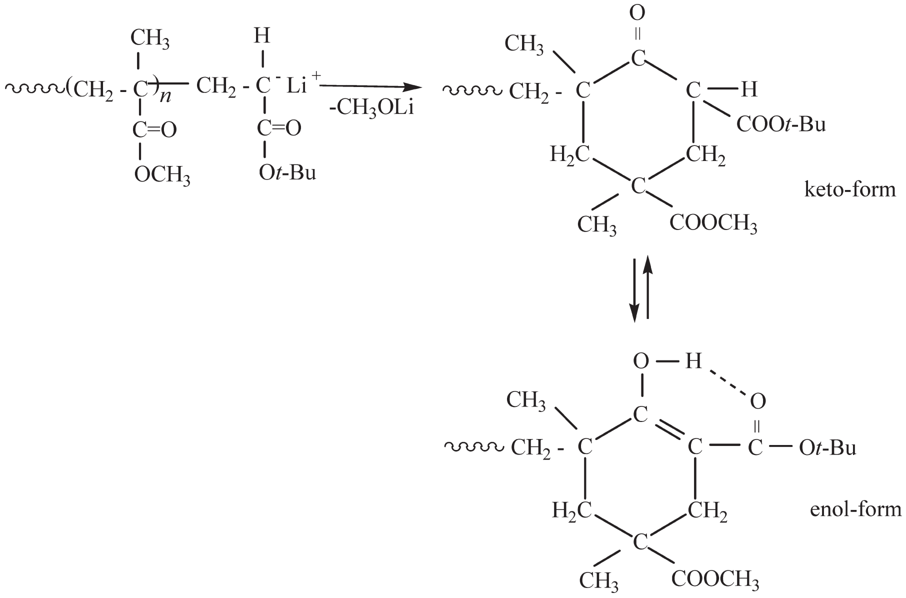


Figure 11.
SEC traces of (1) PMMA, RI det., poly(MMA-*b*-*t*-BuA) (2) RI det., (3) UV det.; run 2, Table 8

tatively within a couple of minutes, whereas *t*-BuA requires several hours.

It can be speculated that the self-termination proceeds on PMMA chains after addition of one or two acrylate units according to Scheme **3**. The idea is corroborated by the results of fractionation of a crude poly(MMA-*b*-*t*-BuA) with acetonitrile separating the low- and high-molecular-weight fractions of the product[21]. It was found that the low-molecular-weight fraction absorbs strongly in UV, whereas the higher part, being likely neat poly(MMA-*b*-*t*-BuA) does not. It is assumed that the conjugated system of C=C and C=O double bonds, being present in the enol-form of the "chemically heterogeneous" oxoester, causes the absorption [28,29]. However, the direct evidence of this structure is still missing.



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Scheme 3.

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