Anionic Polymerization of Acrylates. Synthesis of (Meth)acrylate Di- and Triblock Copolymers Using the Li Ester−Enolate/*tert*-Alkoxide Initiating System

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ABSTRACT: Methacrylate di- and triblock copolymers composed of methyl (MMA), butyl (BuMA), 2-(dimethylamino)ethyl (DMAMA), and 2-ethylhexyl (EtHMA) methacrylates and *tert*-butyl acrylate (*t*-BuA) blocks were prepared by ligated anionic polymerization and characterized by SEC and NMR. The process was initiated with the system methyl 2-lithioisobutyrate/lithium *tert*-butoxide (MIB−Li/*t*-BuOLi) at the 1/10 mole ratio, which was recently described as the optimum composition, at THF at −60 °C. The monomers were added to the reaction mixture successively after chosen polymerization intervals and products of the individual polymerization steps were isolated and analyzed. Molecular weights of methacrylate copolymers increased with increasing total amount of the monomers added, and the products of the two- or three-step polymerizations were not detectably contaminated with the products of the foregoing steps, so that the corresponding MWD curves were unimodal and symmetric. The product of MMA/*t*-BuA block copolymerization exhibited bimodal MWD, originating probably by the self-termination proceeding at the beginning of the second polymerization step after addition of an acrylate monomer to the "living" polymethacrylate. A possible mechanism of self-termination and reactions of polymethacrylate chains bearing a few terminal acrylate units are briefly discussed.

Introduction

Ligated anionic polymerization (LAP)[1] is one of the classic methods for tailoring polymers based mainly on acrylic and methacrylic esters and styrene. The main types of the ligands protecting growing chain ends from undesired side reaction (in particular, self-termination by backbiting reaction) are Li halides[2] (almost exclusively LiCl), didentate alkoxides of the CH_3O-$(CH_2-CH_2O)_nLi$ general structure,[3] alkylaluminums,[4] and alkali metal *tert*-alkoxides.[1] The last ligands are the oldest ones and have been studied in a number of papers as stabilizing additives in polymerizations of methacrylic and acrylic monomers.[1,5] The above-mentioned ligands can be combined with various organometallic initiators; LiCl and didentate alkoxides (Li 2-(methoxyethoxy)ethoxide, MEEOLi) give best results in combination with bulky alkyllithiums,[6] for instance 1,1-diphenylhexyllithium (DPHLi) or α-methylstyryllithium (αMeStLi), whereas alkylaluminums stabilize perfectly methacrylate polymerization initiated with *tert*-butyllithium (*t*-BuLi).[7] Also, *tert*-alkoxides were used and studied in combination with butyllithium[8] (BuLi) or 1,1-diphenyl-3-methylpentyllthium[9] (DPMPLi) as initiating complexes for acrylate and methacrylate polymerization; however, the results were not completely satisfactory, in particular those obtained with the DPMPLi/Li-*tert*-butoxide (*t*-BuOLi) initiating system. The alkoxides exhibit the highest stabilizing efficiency when combined with the initiators of ester-enolate type, mostly esters of 2-metaloisobutyric acid, e.g., methyl or *tert*-butyl 2-lithioisobutyrates (MIB−Li or tBIB−Li). The systems, containing from 3- to 10-fold excess of the alkoxide over the metaloester, initiate controlled polymerization of methacrylates[9,10] and acrylates[5,11] with a very low extent of self-termination, and so they can be used for a synthesis of diblock copolymers composed, for instance, of blocks of different acrylates.[12] In addition, styrene can be polymerized by BuLi in the presence of an excess of *t*-BuOLi, which leads to slower polymerization rate and slightly broader MWD of the formed polystyrene. However, this living polystyrene combined with the alkoxide can be used as a macroinitiator for polymerization of methacrylate monomers[13] even without commonly practiced Rempp's modification of the living polystyryllithium with 1,1-diphenylethylene.[14] Thus, *tert*-alkoxide-stabilized LAP of (meth)acrylates is compatible with the anionic polymerization of styrene giving the corresponding block copolymers in good yields and with acceptable MWDs.

The structure of complex active species was studied in a number of works using model systems composed of 2-metaloester and appropriate ligand. It was found that the individual ligands form with ester−enolates cross-aggregates having a nonequal, but a favorable, effect on the course of polymerization, namely on the extent of side reactions and/or MWD of products. Structure and composition of the complexes depend on the type of ligand, mole ratio of components, storage time, and temperature. LiCl and MEEOLi form with MIB−Li one type of cross-aggregate. The former gives complexes with MIB−Li/LiCl in mole ratios 3/1 or 2/2 or 1/3,[15] in dependence on the ratio of starting concentrations of the components; the latter forms complexes with the MIB−Li/MEEOLi in the mole ratio 1/2. This prevents the polymerization system from possible multiplicity of active species and leads to formation of polymer with a very narrow MWD. Nevertheless, the cross-aggregates of MIB−Li with LiCl exhibit rather moderate stabilizing efficiency, which is sufficient in the polymerization of

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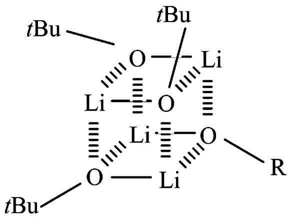
Scheme 1

$$3\,[(\text{MIB-Li})_4] + (t\text{-BuOLi})_4 \longrightarrow 4\,[(\text{MIB-Li})_3\,(t\text{-BuOLi})_1]$$

$$2\,[(\text{MIB-Li})_3\,(t\text{-BuOLi})_1] + (t\text{-BuOLi})_4 \rightleftharpoons 3\,[(\text{MIB-Li})_2\,(t\text{-BuOLi})_2]$$

$$[(\text{MIB-Li})_2\,(t\text{-BuOLi})_2] + (t\text{-BuOLi})_4 \rightleftharpoons 2\,[(\text{MIB-Li})_1\,(t\text{-BuOLi})_3]$$

Scheme 2



methacrylates and *tert*-butyl acrylate only, but not in polymerization of *n*-alkyl acrylates. Stabilizing efficiency of the MIB−Li/MEEOLi complexes is much higher, and thus, they can be successfully used for "living" polymerization of *n*-alkyl acrylates at low temperatures.[16]

In contrast to these two ligands, formation of MIB−Li/*t*-BuOLi cross-aggregates is a more complex process. When mixed in THF solution, the alkoxide gradually replaces MIB−Li molecules in its tetramer,[17] forming at room temperature immediately after mixing the components the complex with MIB−Li/*t*-BuOLi mole ratio 3/1, which is further transformed during storage into the 2/2 complex and, finally, after long enough storage, the cross-aggregate with the MIB−Li/*t*-BuOLi mole ratio 1/3. The process is roughly described by Scheme 1. In equilibrium, i.e., after 24 h storage at −15 °C, the solution contains all three complexes, probably in different concentrations (see Scheme 1) with slightly prevailing relative population of the 1/3 complex. The core of these cross-aggregates has cubic structure with alternating C and O atoms as in Scheme 2, in which R stands for isobutyrate unit or growing polymer chain. The effect of *t*-BuOLi excess, storage time, and temperature on initiation behavior of the cross complexes was studied in MMA polymerization described in the foregoing paper.[9] It was found that the mixtures with 3-, 6-, and 10-fold excess of the alkoxide over MIB−Li behave virtually in the same way, giving controlled process when mixed at room temperature and stored at −15 °C for 24 h. Therefore, one can assume that all the mixtures are in equilibrium, whatever starting MIB−Li/*t*-BuOLi ratio was used, after sufficiently long aging at the given temperature. Without aging, only 1/6 and 1/10 mixtures initiate controlled polymerization with a negligible extent of self-termination, whereas the 1/3 mixture does not reach the equilibrium and, thus, initiates polymerization with a nonlinear semilogarithmic conversion curve producing PMMA with a broad MWD. Thus, transformation of the MIB−Li/*t*-BuOLi cross-aggregates can be distinctly accelerated using a higher excess of the alkoxide. The stabilizing efficiency of the optimized initiation complex, i.e., that with 10-fold excess of *t*-BuOLi over MIB−Li, was tested in the recent study[10] of two- and three-dose MMA polymerization. It was shown that the second and third monomer doses perfectly polymerize on the "living" chains formed from the first MMA dose without a detectable extent of self-termination; thus, the optimized polymerization system remains active for the total polymerization time of all monomer doses, i.e., approximately 4 h. In this paper, synthesis of di- and triblock copolymers is presented, composed of different methacrylate or *t*-BuA blocks using the MIB−Li/*t*-BuOLi initiating system in the 1/10 mole ratio.

Experimental Part

Materials. The monomers, i.e., MMA, BuMA, DMAMA, EtHMA, and *t*-BuA (Fluka, >99%), were purified first by vacuum distillation with calcium hydride and, prior to use, by distillation with triisobutylaluminum. THF (Fluka, >99%) was first distilled with CaH_2 and, prior to use, with sodium benzophenone ketyl. Preparation and purification of MIB−Li and *t*-BuOLi were described earlier.[18,19] Other solvents, hexane, methanol, and acetonitrile (AN), were used as received.

Synthesis of Polymers. Polymerizations were performed at −60 °C in a stirred tank reactor with side dosing cells,[8] allowing to quickly mix the reaction components at the polymerization temperature and to withdraw samples of the reaction mixture at various time intervals. All operations were performed under an inert atmosphere of dry argon. Conversions of the monomers in the individual reaction steps were determined gravimetrically or by gas chromatography (GC). Typical block copolymerization, diblock poly(MMA-*b*-BuMA), run 1, Table 1: Before use, the reactor was dried by heating with flame under vacuum and flushing with dry argon; the cycle was repeated 10 times. Then, the main flask of the reactor was filled with 60 mL of dry THF and 20 mL of a THF solution containing 0.93 mmol of MIB−Li and 9.3 mmol of *t*-BuOLi, prepared in a separate flask under inert conditions at room temperature. The reactor was immersed into a −60 °C ethanol bath, and one of the dosing cells was filled with 15 mL of THF and 5 mL (46.8 mmol) of MMA. After 5 min temperation, the THF solution of MMA was quickly (within 1−2 s) transferred from the side cell into the main flask, containing the initiator/ligand solution, under vigorous stirring using argon overpressure, and polymerized at the given temperature for 1 h. Then, 30 mL of sample of the reaction mixture was withdrawn for analysis, using argon overpressure and a stainless capillary equipped with gastight stopcock. Subsequently, 25 mL of THF and 5.2 mL (32.7 mmol) of BuMA as the second monomer were added into the second dosing cell and temperated for 5 min; then, it was transferred into the reaction mixture and polymerized for 1.5 h. Conversion of MMA in the first step as well as that of BuMA in the second was over 95%, determined gravimetrically. For the characterization of the product, see Table 1, run 1. When triblock copolymer was to be synthesized, a sample of the reaction mixture containing "living" diblock was withdrawn, and the third monomer was added in the same way as in the second polymerization step. Finally, polymerization was stopped by adding a THF/CH_3OH mixture. The products, containing MMA, BuMA, EtHMA, or *t*-BuA blocks, were isolated by precipitation into a 9/1 (v/v) methanol/water mixture; those containing DMAMA blocks were precipitated into hexane.

NMR Measurement. ^1H NMR spectra of 5 wt % solutions of the copolymers in $CDCl_3$ were measured at 300.13 MHz using a Bruker Avance DPX 300 spectrometer at 330 K using hexamethyldisiloxane (HMDS) as the internal standard. The measurement conditions were as follows: pulse width 15.3 μs (90° pulse), relaxation delay 10 s, spectral width 6000 Hz, acquisition time 1.36 s, 16 scans. The integrated intensities were determined by integration software of the spectrometer. Compositions of copolymers were calculated from the integrated relative intensities of the peaks at 3.58 ppm (OCH_3 in MMA), 3.90−4.10 ppm (OCH_2- in BuMA and DMAMA), 2.26 and 2.56 ppm ($N(CH_3)_2$ and $CH_2N=$ in DMAMA), and 1.42 ppm ($OC(CH_3)_3$ in *t*-BuA).

Analyses of Polymers. Molecular weights of products (apparent values for block copolymers) were measured by SEC (Labora HP-5001, Czech Republic) in THF at 20 °C with a separation system composed of two 300 × 8 mm columns filled with SDV gel (bead size 5 μm, porosity 10^5 and 10^3 Å), equipped with differential refractometer Labora RIDK 102 and UV detector Labora LCD 2040 adjusted at 260 nm. The flow rate of THF was 1 mL/min, the system was calibrated with PMMA

Table 1. Synthesis and Characterization of (Meth)acrylate Diblock Copolymers[a]

	M_1,[b]	M_2			m_1:m_2	PM_1		$P(M_1$-*b*-$M_2)$		
run	mmol	type	mmol	time, h	(NMR)[c]	M_n (SEC)	M_w/M_n	M_n (SEC)	M_w/M_n	M_n (NMR)
1	31.2			1		7400	1.19			
	31.2	BuMA	13.0	1.5	2.6:1			12 400	1.19	11 400
2	32.7			1		8200	1.18			
	32.7	BuMA	32.8	1.5	1:1			21 900	1.19	19 800
3	34.5			1.5		9500	1.20			
	34.0	DMAMA	28.0	18	1.2:1			29 500	1.29	21 900
4	32.8			1.5		7000	1.22			
	32.8	*t*-BuA	69.0	17	1:2			25 500[d]	1.70	
					1:4.6			50 500[e]	1.08	
								8 800[f]	1.17	

[a] $[M_1]_0 = 0.468$ mol/L, $[MIB{-}Li]_0 = 0.0093$ mol/L. [b] M_1 = MMA. [c] Mole ratio M_1:M_2 units in the copolymer. [d] Bimodal MWD, both the low- and high-molecular-weight parts considered in calculation. [e] High-molecular-weight part. [f] Low-molecular-weight part.

Table 2. Synthesis and Characterization of (Meth)acrylate Triblock Copolymers

				NMR[e]		PM_1		$P(M_1$-*b*-$M_2)$			$P(M_1$-*b*-M_2-*b*-$M_3)$		
run	M_1, mmol	M_2, mmol	M_3, mmol	m_1:m_2	m_1:m_2:m_3	M_n (SEC)	PDI[f]	M_n (SEC)	PDI[f]	M_n (NMR)	M_n (SEC)	PDI[f]	M_n (NMR)
1[a]	17.3					7300	1.21						
	17.3	17.5		1:1.2				21 000	1.22	19 500			
	17.3	17.5	26.4		1:1.2:2.1						38 300	1.15	34 400
2[b]	23.0					8400	1.16						
	23.0	23.0		1.1:1						20 500			
	23.0	23.0	23.0		1.1:1:1.1						33 100	1.21	29 400
3[c]	18.3					7700	1.19						
	18.3	18.2						22 700	1.20				
	18.3	18.3	18.3								42 700	1.17	
4[d]	22.9					6300	1.21						
	22.9	23.0		1.1:1				16 600	1.19	14 500			
	22.9	23.0	25.0		1.1:1:1						23 300	1.18	21 800

[a] ABA-type triblock, $M_1 = M_3$ = MMA, M_2 = BuMA; $[M_1]_0 = 0.468$ mol/L, $[MIB{-}Li]_0 = 0.0093$ mol/L; reaction time: 1.5 h (first step), 1.5 h (second step), 2.5 h (third step), $T = -60$ °C. [b] ABA-type triblock, $M_1 = M_3$ = MMA, M_2 = DMAMA; reaction time: 1.5 h (first step), 2.5 h (second step), 17 h (third step). [c] ABC-type triblock, M_1 = MMA; M_2 = BuMA, M_3 = EtHMA,; reaction time: 1.5 h (first step), 2 h (second step), 17 h (third step). [d] ABC-type triblock, M_1 = MMA, M_2 = BuMA, M_3 = *t*-BuA; reaction time: 1.5 h (first step), 2 h (second step), 3 h (third step). [e] Mole ratios M_1:M_2 and M_1:M_2:M_3 units in the copolymers. [f] M_w/M_n.

standards (PSS Germany), and its separation range was from 10^3 to 10^6 Da. Eluograms were treated as PMMAs using professional software Caliber (Polymer Laboratories). To obtain real values of molecular weights of copolymers, their composition was determined by ^{1}H NMR spectroscopy; then, from a combination of NMR results and molecular weights of the first PMMA blocks, determined by SEC, more accurate M_n values of block copolymers were calculated. For SEC of poly(MMA-*b*-DMAMA-*b*-MMA) triblock (run 2, Table 2) and poly(MMA-*b*-DMAMA) diblock (run 3, Table 1), THF with 1% (v/v) of triethylamine was used as a mobile phase to avoid special attractions of PDMAMA to SDV gel, complicating the analysis.[20,21] The product of the second polymerization step in run 2, Table 2, became poorly soluble in THF after precipitation and storage in the solid state so that the SEC gave nonacceptable eluograms; this is why the results of NMR analysis only are presented in this case.

Extraction Tests. Poly(MMA-*b*-*t*-BuA) copolymer, the final product with bimodal MWD (run 4, Table 1), was extracted with acetonitrile to separate self-terminated PMMA from the first polymerization step and block copolymer. A weighed amount of the crude product was placed in a flask, acetonitrile (AN) was added, and the mixture was vigorously shaken overnight at room temperature. Acetonitrile is a good solvent for PMMA, which does not dissolve P*t*-BuA; this was verified by of solubility tests for P*t*-BuA. Then, the insoluble portion was separated by centrifugation, and the solution was carefully transferred into weighed flask with a syringe. The AN solution was evaporated to dryness; then, both the AN-soluble and -insoluble portions were dried in vacuo at 40 °C, weighed, and, finally, analyzed by SEC and ^{1}H NMR.

In a similar way, poly(MMA-*b*-DMAMA) (run 3, Table 1) was extracted with methanol, which is a good solvent for PDMAMA but does not dissolve PMMA; however, the sample was completely soluble (see below).

Results and Discussion

Diblock Copolymers. As the ligated anionic polymerization of methacrylates initiated with Li ester enolate in the presence of 10-fold excess of Li-*tert*-butoxide is at low temperature (−60 °C) stable and "living" for several hours so that three doses of MMA can be successively polymerized,[10] we applied the initiating system to a synthesis of block copolymers composed of various methacrylate or *tert*-butyl acrylate blocks using the same technique and under the same reaction conditions. The results of preparation of diblock copolymers are summarized in Table 1.

Poly(MMA-*b*-BuMA). Runs 1 and 2 document the synthesis of poly(MMA-*b*-BuMA) copolymers with either different (run 1) or the same (run 2) block lengths. SEC eluograms of the products (Figure 1) show clearly shifts of the peaks of copolymers (traces B) compared with PMMA precursors (traces A), thus indicating an increase in molecular weights as well as symmetric and unimodal MWDs of the block copolymers without a detectable hint of the presence of PMMAs from the first reaction steps. Also, the polydispersities of copolymers are virtually the same as those of the corresponding PMMA precursors. Gravimetrically determined monomer conversions in the first and second reaction steps were ≥95% in both the experiments. Compositions of the copolymers were determined from ^{1}H NMR spectra by comparing intensities of the OCH_3 and OCH_2 protons at 3.58 and 3.93−3.97 ppm, respectively; the calculated mole ratios of units in PMMA and PBuMA blocks correspond approximately to the mole ratios of the

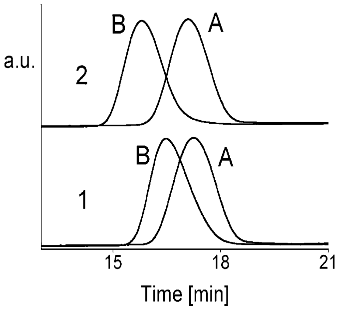


Figure 1. SEC eluograms of poly(MMA-*b*-BuMA) copolymers (B) and the corresponding PMMAs (A); RI detection; 1, run 1; 2, run 2; Table 1.

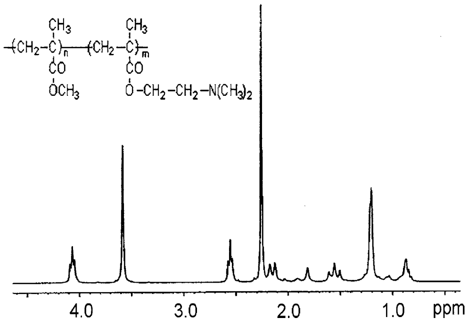


Figure 2. ^{1}H NMR spectrum of poly(MMA-*b*-DMAMA) copolymer; run 3, Table 1.

monomers used. Using a combination of NMR and SEC, more accurate M_n values of the block copolymers were determined; they are not far from those calculated from SEC (Table 1). All these findings document the "living" nature of PMMAs prepared in the first steps leading to the corresponding poly(MMA-*b*-BuMA) copolymers; moreover, because polydispersities of PMMAs and copolymers are the same, it can be reasonably assumed that the systems exhibit a negligible extent of self-termination for the total polymerization time, i.e., 2.5 h.

Poly(MMA-*b*-DMAMA). Run 3 represents the diblock copolymer with PMMA and PDMAMA block. MMA was polymerized for 1.5 h; then, DMAMA was added as a precooled THF solution and polymerized for 18 h. By GC, MMA conversion was >99% and that of DMAMA, calculated from the copolymer yield, was >95%, i.e., nearly quantitative. As mentioned above, apparent molecular weight of the copolymer (M_n) was determined by SEC using the mixed mobile phase; however, more accurate data were obtained by combining M_n values of the PMMA block obtained from SEC and chemical composition of the copolymer, calculated from ^{1}H NMR spectra. The spectrum of poly(MMA-*b*-DMAMA) in Figure 2 shows perfectly separated peaks of OCH_2, $CH_2{-}N{=}$ and $(CH_3)_2N$ protons of DMAMA units at 4.07–4.09, 2.56, and 2.26 ppm, respectively, and OCH_3 protons at 3.58 ppm belonging to MMA units. From the intensities of these peaks, composition of the final block copolymer was determined, MMA/DMAMA mole ratio 1.2:1, which corresponds well to the mole ratio of monomers in copolymerization. The isolated copolymer was extracted with methanol, which is a good solvent for PDMAMA but does not dissolve PMMA (see Experimental Part); the material was almost completely soluble, and a negligible portion only remained as a solid. This shows that the product of copolymerization is a true block copolymer and not a mixture of corresponding homopolymers.

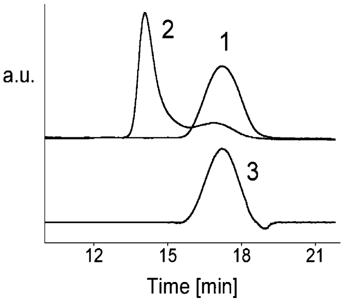


Figure 3. SEC eluograms of poly(MMA-*b*-*t*-BuA) copolymer with RI (2) and UV detections (3) and the PMMA homopolymer with RI detection (1); run 4, Table 1.

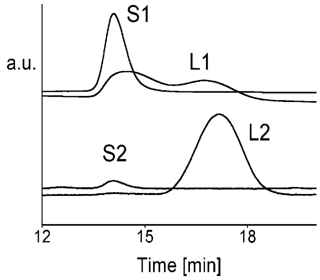


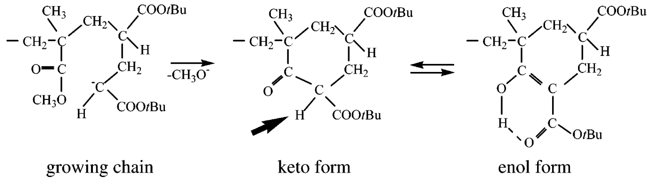
Figure 4. SEC eluograms of acetonitrile soluble (L) and insoluble (S) fractions of sample 4, Table 1: S1, L1—RI detection; S2, L2—UV detection; see Table 2.

Poly(MMA-*b*-*t*-BuA). In run 4, "living" PMMA was used for initiation of *t*-BuA polymerization under the same conditions as in the foregoing experiments. However, the obtained product, expected to be poly(MMA-*b*-*t*-BuA) diblock, had a broad bimodal distribution, as can be seen from SEC eluogram of the final product (Figure 3, trace 2, and Table 1, run 4). The low-molecular-weight part of the eluogram appears at almost the same retention time as that of PMMA homopolymer formed in the first reaction step (trace 1), so that it seems to be the residual self-terminated PMMA precursor. However, no hint of such bimodality was observed in the copolymerizations of different methacrylates, for instance MMA/BuMA (Table 1 and Figure 1); therefore, the spontaneous self-termination of the "living" pure PMMA chains during the first step of run 4, proceeding by a typical backbiting reaction of purely PMMA chain ends, does not seem to be likely in this case. Thus, the cyclic ketoester had to be formed after addition of *t*-BuA monomer. Moreover, the low-molecular-weight part of the product strongly absorbs in the UV region at 260 nm (see Figure 3, trace 3), which could be caused by the presence of the conjugated system of C=C and C=O double bonds in this part of the polymer, whereas the high-molecular-weight part virtually does not absorb in this region. The findings strongly indicate that the crude product of MMA/*t*-BuA block copolymerization is composed of two parts, and therefore, an attempt has been made to separate both the parts of the crude product (run 4, Table 1) by extraction with acetonitrile. A relatively high amount (36%, w/w) of the crude product was soluble in AN, whereas the rest (64%) remained as a slightly swollen solid. Both the portions of the sample, AN-soluble and AN-insoluble, were analyzed by SEC and ^{1}H NMR. SEC eluograms are in Figure 4, where S1 and S2 traces represent insoluble (solid) and L1 and L2 soluble (liquid) portions.

The eluogram of the soluble portion (RI detection, trace L1, Figure 4) shows bimodal MWD, most probably because some chains of the high-molecular-weight part of crude product were taken along with the low-molecular-weight part into the solution. The low-molecular-weight fraction of the soluble portion (trace L1), having an elution time not far from that of PMMA formed in the first polymerization step (see Figure 3, trace 1), strongly absorbs in the UV region at 260 nm (Figure 4, trace L2). The molecular weight calculated from this peak (Figure 4, trace L1, $M_n = 8900$) is virtually the same as that of the low-molecular-weight part of the crude product (Table 1, run 4, and Figure 3, trace 2, $M_n = 8800$); moreover, both these values are not too different from the molecular weight of PMMA homopolymer (Table 1, run 4, and Figure 3, trace 1, $M_n = 7000$). This indicates that these three polymers are basically PMMAs; however, the low-molecular-weight part in the crude product as well as the low-molecular-weight fraction in the AN-soluble portion most probably contain a certain amount of *t*-BuA units and, due to the strong absorption at 260 nm, also terminal ketoester groups. This is corroborated by NMR analysis of the AN-soluble portion, from which the average value of the MMA/*t*-BuA mole ratio 1:1 was determined, considering both the high- and low-molecular-weight fractions. The high-molecular-weight fraction of the AN-soluble portion is probably formed by poly(MMA-*b*-*t*-BuA) copolymer, which is more or less soluble in AN depending on lengths of the blocks. As this product exhibits almost no absorption at 260 nm (see Figure 4, trace L2), it can be assumed that the chains are prevailingly terminated by protonation and, therefore, do not contain cyclic ketoester at the chain ends to a perceptible extent.

The AN-insoluble portion of the crude product of MMA/*t*-BuA block copolymerization has a very narrow, unimodal MWD with polydispersity index 1.04 and $M_n = 47\,200$, as determined from RI response of SEC (Table 1, run 4, and Figure 4, trace S1). Absorption of this polymer at 260 nm is very weak (trace S2), most probably due to a very low content of chains with terminal cyclic ketoesters. It has to be noted that the higher-molecular-weight part of the crude product with $M_n = 50\,500$ also absorbs negligibly at this wavelength (Figure 3, trace 3). This, together with a high *t*-BuA conversion (97% by GC) indicates that the polymerization of the second monomer leading to the AN-insoluble portion of the crude product with MMA:*t*-BuA mole ratio 1:4.6, proceeded virtually without self-termination by backbiting reaction and its propagation was terminated prevailingly with methanol added at the end of polymerization. Thus, this part of the product of block copolymerization is reasonably assumed to be a true poly(MMA-*b*-*t*-BuA) copolymer with the P*t*-BuA blocks approximately 4.6 times longer than the PMMA blocks. These results strongly corroborate the above-mentioned assumption that the product of MMA/*t*-BuA block copolymerization, initiated with the MIB−Li/*t*-BuOLi system, is a mixture of two polymer components. That with the lower molecular weight roughly comparable with the molecular weight of PMMA precursor is composed probably of PMMA chains with several *t*-BuA units and, due to a relatively strong absorption at 260 nm, containing a terminal cyclic ketoester, probably in the enol form. Nevertheless, the literature data on this problem, published so far, have been somewhat inconsistent.

Scheme 3



Self-termination of a part of “living” PMMA in MMA/*t*-BuA block copolymerization, initiated with αMeStLi at −78 °C in the presence of LiCl, was already observed by Varshney et al.[22] The finding was explained on the basis of possible formation of “chemically heterogeneous” cyclic ketoester, i.e., composed of acrylate and methacrylate units, by the backbiting reaction between the terminal *t*-BuA$^-$ anion and antepenultimate MMA unit of the same chain. The mechanism of this self-termination (Scheme 3) was designed by Jacobs et al.[23] on the basis of results of a random copolymerization of MMA/*t*-BuA mixtures, initiated with the DPMPLi/LiCl system, leading, however, to almost pure P*t*-BuAs with low molecular weights and broad MWDs. This idea is in accordance with the fact that “living” PMMA chains lacking the favorable effect of a bulky *t*-BuO group not only at the end, but also along the chain, self-terminate more rapidly than the “living” P*t*-BuA or poly(*tert*-butyl methacrylate).[24,25] However, using *t*-BuA as the first monomer and the diphenylmethyllithium/LiCl initiating system, the authors obtained poly(*t*-BuA-*b*-MMA) copolymer with an acceptably narrow and unimodal MWD. On the other hand, Klein et al.[26] obtained somewhat different results from a similar study. Here, an attempt to prepare poly(*t*-BuA-*b*-MMA) copolymer using the acrylate as the first monomer and DPMPLi/LiCl as an initiator at −55 °C completely failed, and the product was almost pure P*t*-BuA. Surprisingly and in contrast to Varshney's observation,[22] the “living” PMMA prepared by 1,4-dilithio-1,1,4,4-tetraphenylbutane assisted with LiCl gave rise to a poly(*t*-BuA-*b*-MMA-*b*-*t*-BuA) triblock. Moreover, the authors did not mention bimodality of the product or self-termination upon *t*-BuA addition. Random copolymerization of MMA/*t*-BuA mixture initiated with DPMPLi in the presence of 5-fold excess of LiCl led to almost pure P*t*-BuA (>95%), i.e., to the same result as that of Jacobs;[23] nevertheless, a different explanation is considered. The authors assume that unequal electron affinities of the monomers make possible cross-initiation of *t*-BuA polymerization by PMMA$^-$ anion only, but not the reverse reaction. These results are in contrast with our findings and also with those of Varshney.[22] Our results also indicate a partial deactivation of “living” polymethacrylate chains by backbiting reaction upon addition of one or two molecules of *t*-BuA according to Scheme 3, leading to the low-molecular-weight portion of the crude product of block copolymerization (Figure 3, trace 2), which strongly absorbs at 260 nm (trace 3). Moreover, a certain extent of MMA/*t*-BuA random copolymerization cannot be excluded due to incomplete MMA conversion in the first step of block copolymerization (97% in run 4, Table 1); this also leads to a self-termination in accordance with literature data.[22,23] Therefore, the PMMA “living” chains only, which added three or more *t*-BuA units, self-terminate with much lower rate and, consequently, can grow further forming the corresponding poly(MMA-*b*-*t*-BuA) block copolymer with unimodal narrow MWD (Figure 3, trace 2, and Figure 4, trace S1), which absorbs very weakly in the UV region at 260 nm (Figure 4, trace S2). Similar behavior, i.e., a partial self-termination of polymethacrylate “living” chains after

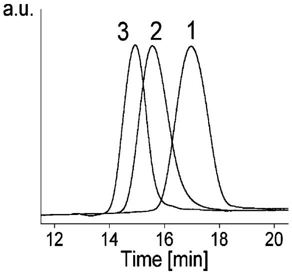


Figure 5. SEC eluograms of poly(MMA-*b*-BuMA-*b*-MMA) triblock (3) and poly(MMA-*b*-BuMA) diblock (2) copolymers and the PMMA homopolymer (1); RI detection, run 1, Table 2.

addition of an acrylate monomer, was also observed in the synthesis of triblock copolymers composed of methacrylate and acrylate blocks (see below). We also made an attempt to prepare *t*-BuA/MMA block copolymer in which *t*-BuA was polymerized with the MIB−Li/*t*-BuOLi system and subsequently used as a macroinitiator for MMA polymerization; however, the experiments did not give satisfactory results, as in Klein's work.[26]

Interesting results have to be noted, obtained by Müller et al., in the study of butyl acrylate and *t*-BuA polymerization initiated with *tert*-butyllithium or ethyl 2-lithioisobutyrate in toluene or mixture toluene/methyl pivalate at −78 °C in the presence of various trialkylaluminums.[27] Using MALDI−TOF analysis, he found that chains with two ketoester groups are present in the products, in addition to the chains terminated by deliberate protonation and those terminated by backbiting reaction and having thus one terminal cyclic ketoester group. The authors assume possible abstraction of proton from the C−H group localized between two carbonyls of the ketoester in keto form (see Scheme 3, the corresponding hydrogen is marked with the arrow) by a reaction with released Li alkoxide or with other "living" chain ends. The carbanion formed in this way might slowly reinitiate polymerization and cause further chain propagation. In addition, the enol form of cyclic ketoester can terminate propagation of another chain by the reaction of the "living" chain end with the acid hydrogen of the OH group.[28,29]

Thus, when one takes into account all above-mentioned findings and considerations, the cyclic ketoester formed by the well-known backbiting reaction at the end of "living" polyacrylate chain leads probably not only to a simple self-termination of this chain, but it can react further, complicating the polymerization process. Obviously, the self-termination steps are perceptibly different for anionic polymerizations of acrylates and methacrylates.

Triblock Copolymers. Using a three-step process under similar conditions, (meth)acrylate triblock copolymers were synthesized; the results of experiments are presented in Table 2.

Poly(MMA-*b*-BuMA-*b*-MMA). In the first experiment, the ABA-type poly(MMA-*b*-BuMA-*b*-MMA) block copolymer was prepared. SEC eluograms of the intermediate and final products (Figure 5) clearly show that all the products have strictly unimodal and symmetric MWDs and that the diblock and triblock are not detectably contaminated with the products of the foregoing polymerization steps. MWDs of PMMA, poly(MMA-*b*-BuMA) diblock, and poly(MMA-*b*-BuMA-*b*-MMA) and their polydispersity indices are very similar (Table 2, run 1). Conversions of the monomers in the individual steps, as determined gravimetrically in samples of the reaction mixtures and in the final copolymer, were 95% or higher. This indicates that the "living" PMMA and diblock macroinitiator, formed in the first and second steps of the synthesis, exhibit a negligible extent of self-termination and, therefore, are quantitatively used up in the initiation of the next monomer polymerization. Taking into account the total polymerization time, it can be said that the system remains active for a period of about 5 h, which is in accordance with our previous results of three-dose polymerization of MMA.[9] To compare stabilizing efficiency of *t*-BuOLi with the LiCl-ligated system, three-dose polymerization of MMA was performed, initiated with MIB−Li in the presence of 10-fold excess of LiCl under otherwise the same conditions. As can be seen in SEC traces (Figure 6), PMMA with very narrow MWD was expectedly obtained in the first reaction step (M_n = 24 700, M_w/M_n = 1.03). However, the polymerization of the second MMA dose, added to the reaction mixture 60 min after the first dose and polymerized for 2 h, led to clearly bimodal product, the low-molecular-weight part of which has virtually the same retention time as the product of the first-dose polymerization (M_n = 26 000, M_w/M_n = 1.02), whereas the high-molecular-weight part is distinctly shifted toward the shorter retention time, having M_n = 71 100, M_w/M_n = 1.02. Obviously, a part only of the "living" PMMA from the first-dose polymerization remained active after 60 min, giving a product with correspondingly higher molecular weight, whereas the rest self-terminated during the chosen time interval. Moreover, the product of two-dose-polymerization self-terminated completely within 2 h, as documented by a coincidence of traces 2 and 3 in Figure 6. Thus, LiCl causes narrowing the MWD; however, its effect on the extent of self-termination is perceptibly lower than that of the *tert*-alkoxide.

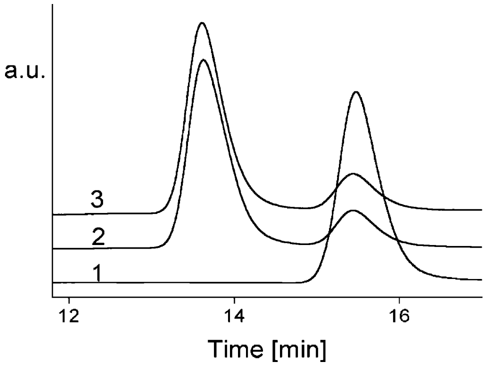


Figure 6. SEC traces (RI detection) of PMMAs resulting from the three-dose polymerization initiated with the 1:10 (m/m) MIB−Li/LiCl system in THF at −60 °C. The numbers of traces correspond to a number of MMA doses.

Poly(MMA-*b*-DMAMA-*b*-MMA). Run 2 affords the ABA-type triblock composed of PMMA outer blocks and PDMAMA central block. As in the foregoing experiment, MMA was polymerized first for 1.5 h, and a sample of the mixture was withdrawn. Then, the calculated amount of DMAMA in THF was added and polymerized for the chosen time period; after that, again, a sample of the reaction mixture was withdrawn for analysis and, finally, the third monomer dose, i.e., MMA, was added and polymerized for 17 h. As determined by GC of the samples and the final polymerization mixture, MMA conversion in the first step was almost 100% (traces of MMA only were found in the sample), conversion of

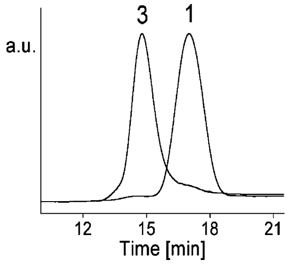


Figure 7. SEC traces (RI detection) of poly(MMA-*b*-DMAMA-*b*-MMA) triblock copolymer (3) and the corresponding PMMA precursor (1); Table 2, run 2. The copolymer was analyzed in THF plus 1% triethylamine as a mobile phase.

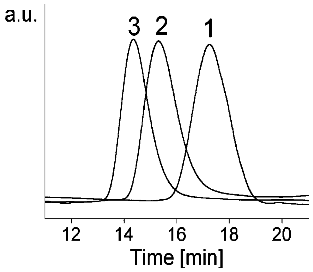


Figure 8. SEC eluograms of the poly(MMA-*b*-BuMA-*b*-EtHMA) triblock (3) and poly(MMA-*b*-BuMA) diblock (2) copolymers and the PMMA homopolymer (1); RI detection, run 3, Table 2.

DMAMA in the second step was ca. 99%, and no residual monomers were detected in the final mixture. As well as in the case of poly(MMA-*b*-DMAMA) diblock copolymer (see Table 1), molecular parameters of poly(MMA-*b*-DMAMA-*b*-MMA) triblock and the corresponding diblock precursor obtained in the second step were calculated using a combination of SEC (PMMA block) and ^{1}H NMR analyses (diblock and triblock compositions). Moreover, molecular weight and MWD of the poly(MMA-*b*-DMAMA-*b*-MMA) triblock were determined by SEC in the mixed mobile phase; for eluograms see Figure 7. It is seen that polydispersity of the triblock copolymer is very close to that of PMMA precursor, and also M_n values calculated from SEC and NMR are well comparable.

Poly(MMA-*b*-BuMA-*b*-EtHMA). In run 3, the ABC-type poly(MMA-*b*-BuMA-*b*-EtHMA) triblock was synthesized in the same way; reaction times were 1.5 h for the first step, 2 h for the second step, and 17 h for the third step (see Table 2). SEC eluograms (Figure 8) show shifts of the peaks of products of the second and third steps compared with that of PMMA homopolymer, corresponding to the monomer added in the individual steps. Also, no detectable amounts of products of the first or second reaction step can be seen in the eluograms of diblock and triblock (traces 2 and 3) documenting the total initiating efficiency of both the PMMA homopolymer and poly(MMA-*b*-BuMA) diblock copolymer. Monomer conversions were checked by gas chromatography, and only traces of the corresponding methacrylates were found in reaction mixtures.

Poly(MMA-*b*-BuMA-*b*-*t*-BuA). Run 4 is an attempt to prepare ABC triblock copolymer composed of MMA, BuMA, and *t*-BuA blocks. Polymerization was performed in the same way as in the foregoing experiments. The time period between the first and second monomer additions was 1.5 h, that between the second and third monomer was 2 h, and the third monomer was polymerized for 3 h; the total reaction time was 6.5 h. In the first step, MMA conversion was 97% (by GC), BuMA conversion in the second step was 99%, and no unreacted MMA was found in this reaction mixture. A nonquantitative conversion of *t*-BuA in the third step (82% by GC) might be caused by rather low monomer and initiator concentrations in this mixture (0.23 and 0.0046 mol/L) and by the short reaction time. For comparison, the starting concentrations of MMA and initiator in the first step were 0.47 and 0.0094 mol/L, respectively. Moreover, the polymerization of *t*-BuA in the presence of *t*-BuOLi is much slower than that in the presence of LiCl.[29] All the products of this experiment exhibit unimodal and narrow MWDs as can be seen from SEC eluograms in Figure 9 (RI detection), and their polydispersities are virtually the same (run 4, Table 2). The third reaction step in this case is a certain analogy to the synthesis of poly(MMA-*b*-*t*-BuA) diblock (see run 4, Table 1) because, again, *t*-BuA polymerization is initiated with "living" polymethacrylate. However, in contrast to run 4 in Table 1, no hint of bimodality was found in RI trace of the poly(MMA-*b*-BuMA-*b*-*t*-BuA) triblock (Figure 9, trace 3), which could be considered as an indication of the absence of self-termination. Nevertheless, the UV trace of the triblock (Figure 7, trace 4) shows a detectable absorption of the poly(MMA-*b*-BuMA-*b*-*t*-BuA) copolymer at 260 nm with the elution time almost the same as that of the poly(MMA-*b*-BuMA) diblock obtained from RI detector (trace 2), prepared in the second step of this experiment. From the UV trace, the molecular weight M_n = 16 900 was calculated corresponding well to the molecular weight of the poly(MMA-*b*-BuMA) diblock, determined from RI trace (M_n = 16 600) (see Table 2). This is why the backbiting reaction of a certain part of poly(MMA-*b*-BuMA) diblock (Scheme 3) chains can be assumed after addition of *t*-BuA. Content of these self-terminated diblock chains in the final product is probably low, and consequently, their RI response can be overlapped by the eluogram of the poly(MMA-*b*-BuMA-*b*-*t*-BuA) as a major product. The extent of self-termination in this synthesis of the triblock copolymer seems to be perceptibly lower than that in the preparation of MMA/*t*-BuA diblock (Table 1, run 4); therefore, one can speculate that the extent of this side reaction might be affected by the amount of the residual unreacted methacrylate from the foregoing step and, perhaps, also by chemical structure of this methacrylate.

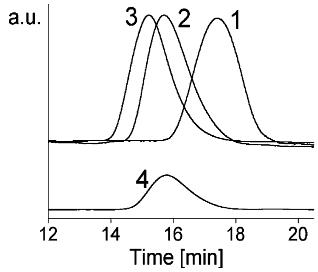


Figure 9. SEC eluograms of the poly(MMA-*b*-BuMA-*b*-*t*-BuA) triblock (3) and poly(MMA-*b*-BuMA) diblock (2) copolymers and the corresponding PMMA (1), RI detection, and the triblock (4); UV detection, run 4, Table 2.

Conclusions

Di- and triblock copolymers based on different methacrylate esters (MMA, BuMA, DMAMA, EtHMA) can be successfully prepared by the two- or three-step LAP initiated at −60 °C with the optimized complex composed of an ester−enolate initiator and a 10-fold excess of *tert*-alkoxide stabilizing ligand. The final copolymers have unimodal MWDs with the polydispersities virtually the same as those of homopolymers and/or diblock precursors and are not contaminated with products of the first or second reaction steps despite the rather long reaction times. Obviously, *tert*-alkoxide distinctly reduces an excess of selftermination and ensures a high stability of the methacrylate anionic polymerization. Let us note that stabilizig efficiency of *t*-BuOLi is perceptibly higher than that of LiCl; the halide is nonefficient in acrylate polymerization, and to our knowledge, synthesis of methacrylate triblock copolymers by three-step process in the presence of LiCl has not been described.

However, if a polymerization of *t*-BuA is initiated with a "living" polymethacrylate, a certain extent of self-termination of polymethacrylate chains can be observed after addition of the acrylate, in particular if some, even a small part, of the methacrylate monomer remains unreacted in the polymerization mixture. These self-terminated chains exhibit strong absorption in the UV region at ca. 260 nm, thus indicating the presence of a conjugated system of double bonds C=C and C=O. This system appears in the enol form of a cyclic ketoester (trimer) formed by the backbiting reaction taking place not only on purely polyacrylate "living" chains but probably also on polymethacrylate chains with one or two *t*-BuA terminal units. This acrylate-type "living" chain end can react with a carbonyl group of the antepenultimate MMA unit of the same chain, lacking the favorable effect of bulky *tert*-butoxy group and form in this way a "chemically heterogeneous" cyclic ketoester composed of the methacrylate and acrylate units. The structure of this group has not been verified, and therefore, the idea corroborated also by the results of some recent papers of other authors requires further investigation and will be studied more in detail in the following work.

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