Anionic Polymerization of Acrylic Monomers. 21. Anionic Sequential Polymerization of 2-Ethylhexyl Acrylate and Methyl Methacrylate

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ABSTRACT: A mixed complex of a polydentate lithium alkoxide, i.e., lithium 2-(2-methoxyethoxy) ethoxide (LiOEEM), and of a mono- or bisfunctional organolithium initiator, i.e., (diphenylmethyl)lithium (DPMLi) or lithium naphthalene/diphenylethylene, has been used to synthesize well-controlled AB (BA), ABA, and BAB block copolymers of methyl methacrylate (MMA) (A) and 2-ethylhexyl acrylate (2EtHA) (B), irrespective of the monomer addition order. Although the 2EtHA block copolymerization initiated with monofunctional living PMMA macroanions at −78 °C in a 75/25 toluene/THF mixture gives rise to a precisely-tailored PMMA-*b*-P2EtHA diblock polymer, the reverse sequence, i.e., from P2EtHA anions to the MMA type monomer, always results in contamination by homo-P2EtHA. This has been interpreted in terms of the short shelf lifetime of P2EtHA anions present. Nevertheless, a pure P2EtHA-*b*-PMMA type diblock copolymer can be produced at −100 °C, while keeping other conditions unchanged. More importantly, a well-controlled PMMA-*b*-P2EtHA-*b*-PMMA triblock copolymer has been prepared through a three-stage process with a monofunctional initiator, acutally providing a potential pathway toward the direct synthesis of a novel type of fully acrylic thermoplastic elastomer, instead of the more complicated hydrolysis/transalcoholysis process previously demonstrated by us.

Introduction

It has been recently demonstrated by us that μ/σ dual polydentate lithium alkoxides, such as 2-(2-methoxyethoxy) ethoxide (LiOEEM), can efficiently form a stable and bulky μ/σ complex with lithium ester enolates in solution[1] and should consequently be very effective in promoting the living anionic polymerization of (meth)acrylic ester monomers.[2] For instance, it has been reported for the first time that a living anionic polymerization process of 2-ethylhexyl acrylate (2EtHA) becomes possible,[3] when some of these LiOEEM-complexed organolithium initiators are used. Moreover, a highly syndiotactic living poly(methyl methacrylate) (PMMA) (75–85%) can be efficiently produced even in pure toluene at moderate temperature by using the same initiator systems.[4]

On those bases, attention has been paid to the potential block copolymerization of these two monomers. Indeed, soft P2EtHA ($T_g \sim -60$ °C) and hard syndiotactic PMMA ($\sim 80\%$) syndiotacticity; $T_g \sim 130$ °C) represent an acrylic adhesive elastomer and a methacrylic plastic, respectively. Also, a novel type of fully acrylic-based thermoplastic elastomer (TPE) can thus be generated by the association of PMMA and P2EtHA in a triblock structure.

The present work aims at producing A–B (B–A) diblock and ABA or BAB triblock copolymers by using (diphenylmethyl)lithium or lithium naphthalenamide as a mono- or bisfunctional initiator, and LiOEEM (10 mol equiv) as a ligand, in a 75/25 toluene/THF mixture at low temperature. To our knowledge, this is the first report on well-controlled block copolymers of PMMA and P2EtHA synthesized by means of "ligated" living anionic polymerization, whichever the order of monomer addition.

Experimental Section

Reagents and Solvents. 2EtHA and MMA obtained from Norsolor (France) were first vacuum distilled after reflux over CaH_2 and stored under a nitrogen atmosphere at −20 °C. Before polymerization, the monomer was added with 10 wt % $AlEt_3$ solution in hexane until a persistent yellowish green color was observed and then distilled under reduced pressure. THF was purified by refluxing over a fresh sodium benzophenone complex (a deep purple color indicating an oxygen- and moisture-free solvent). Toluene and hexane were refluxed over CaH_2 for 48 h and redistilled over oligo(styryllithium) immediately prior to use. Alcohols from Aldrich were distilled from CaH_2 and stored under nitrogen.

Initiator. (Diphenylmethyl)lithium (DPMLi) was prepared at room temperature by treating diphenylmethane with lithium naphthalene in THF for 24 h. The lithium naphthalene/THF solution was prepared by reacting lithium metal with naphthalene in THF at room temperature.

Preparation of LiOEEM. Two different methods were envisioned to prepare the ligand. (1) Under oxygen-and moisture-free argon, an equimolar amount of lithium metal (wire) and corresponding alcohol were added into THF in a dry flask equipped with an inert gas inlet, a magnetic stir bar, and a water-cooled condenser. The solution was heated to reflux and the reaction allowed to continue at reflux overnight. (2) Lithium alkoxide was generated by treating the suitable alcohol in dry hexane with an equimolar amount of n-BuLi at 0 °C. In this case, a few drops of 1 M dihenylethylene in hexane were used as a color indicator.

Polymerization. Anionic block copolymerization of 2EtHA and MMA was carried out in a flamed glass reactor under a nitrogen atmosphere. Solvent, ligand, and initiator were transferred into the glass reactor byusing a rubber septum and a stainless steel capillary or a syringe. The initiator solution was added dropwise to the solvent, containing the polydentate lithium alkoxide ligand, until the initiator color persisted; ca. 5 drops of a 0.2 M initiator soluton to 100 mL of solution was generally required to get a persistent color. After adding the desired amount of initiator, the solution was cooled to −78 or −100 °C, the required quantity of MMA or 2EtHA was introduced, and the polymerization was performed at that temperature for a few minutes. Upon addition of the monomer, a sudden change of the initiator color from deep red to light yellow indicates that initiation was practically instantaneous. An aliquot of the reaction medium was withdrawn for anlysis by SEC in order to determine the molecular weight and molecular weight distribution of the first block. The second monomer was then added to the solution containing the first living polymer at −78 or −100 °C,

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Table 1. Characterization Data for PMMA-*b*-P2EtHA Diblock Copolymerizations in a 75/25 Toluene/THF Mixture at −78 °C, Using a 10 Molar Ratio LiOEEM/DPMLi Initiator System

	DPMLi	monomer (mol)		% total	for PMMA				for diblock copolymer				
no.	(10^3 mol)	MMA	2EtHA	yield	M_n (calc)	M_n (SEC)	M_w/M_n (SEC)	f^a	M_n (calc)	M_n (SEC)	M_n (^{1}H NMR)	M_w/M_n (SEC)	f^b
1	0.364	0.02	0.027	99	5 500	6 000	1.03	0.92	18 500	19 600	19 200	1.09	0.96
2	0.428	0.03	0.015	100	7 000	7 200	1.06	0.97	12 500	13 600	13 000	1.09	0.96
3	0.129	0.04	0.0105	100	31 000	33 000	1.08	0.94	45 200	46 400	46 000	1.09	0.98
4	0.129	0.08	0.0071	100	62 000	64 500	1.10	0.96	72 700	76 600	77 000	1.10	0.94

[a] f (initiator efficiency) = M_n(calc)/M_n(SEC), where M_n(calc) = (moles of monomer/moles of initiator)(M_w of monomer). [b] f (initiator efficiency) = M_n(calc)/M_n(^{1}H NMR).

Table 2. Characterization Data for P2EtHA-*b*-PMMA Diblock Copolymerization in a 75/25 (v/v) Toluene/THF Mixture, Using a 10 Molar Ratio LiOEEM/DPMLi Initiator System

	DPMLi	monomer (mol)		temp	% total	for P2EtHA				for diblock copolymer				
no.	(10^3 mol)	2EtHA	MMA	(°C)	yield	M_n (calc)	M_n (SEC)	M_w/M_n (SEC)	f	M_n (calc)	M_n (SEC)	M_n (^{1}H NMR)	M_w/M_n (SEC)	f
1	0.392	0.0135	0.0375	−78	96	5100	5600	1.09	0.91	15 000	81 100^a		1.04^a	
2	0.217	0.0135	0.0461	−78	100	9200	10000	1.09	0.92	31 200	122 000^a		1.07^a	
3	0.375	0.0201	0.0596	−78	99	8000	8100	1.09	0.99	24 000	43 300^a		1.09^a	
4	0.455	0.0135	0.110	−100	95	4400	4900	1.10	0.90	29 000	31 400	31 500	1.10	0.92
5	0.472	0.0168	0.0552	−100	100	5300	5300	1.06	1.00	17 000	19 100	19 000	1.04	0.90
6	0.426	0.0268	0.0213	−100	100	9400	10000	1.05	0.94	15 000	16 000	16 500	1.06	0.91

[a] Only one peak on the high molecular weight side (i.e., diblock copolymer) is considered.

and the copolymerization was carried out for an additional few minutes. It was then stopped by adding acidic methanol, and the copolymer was recovered by precipitation into methanol. The crude polymer was dried under vacuum at 60 °C for 48 h.

Characterization. SEC was carried out by using a Hewlett-Packard 1090 liquid chromatograph equipped with columns (10^5, 10^3, 500 and 100 Å) and a Hewlett-Packard 1037A refractive index detector. Polystyrene standards were used for calibration and the number- ($\bar{M}_n$) and weight-average ($\bar{M}_w$) molecular weights as well as polydispersity of the polymer were accordingly calculated. The copolymer's composition was determined by ^{1}H NMr using a Bruker AM 400 spectrometer.

Results and Discussion

Synthesis of AB and BA Diblock Copolymers of Methyl Methacrylate (MMA) (A) and 2-Ethylhexyl Acrylate (2EtHA) (B). Tables 1 and 2 report the characteristic features of diblock copolymers of PMMA and P2EtHA prepared from polyanions of either the MMA or the 2EtHA type. When these precursors are synthesized in a 75/25 toluene/THF mixture at −78 and/or −100 °C by using a 10-fold excess LiOEEM-complexed DPMLi as an initiator, the data summarized in Tables 1 and 2 show that the expected molecular weight is actually obtained for *both* PMMA and P2EtHA; the moleuclar weight distribution is very narrow (<1.10), altogether indicating a living process.[2,3]

When monofunctional polyanions of that MMA or 2EtHA type are subsequently used as a macroinitiator for 2EtHA or the MMA sequential anionic polymerization, respectively, the overall conversion is found to be nearly quantitative, which ever the order of monomer addition (Tables 1 and 2). However, the corresponding initiator efficiency for the block copolymerization strongly depends on the order of monomer addition.

(a) Synthesis of PMMA-*b*-P2EtHA (AB) Copolymer. When the copolymerization of 2EtHA is initiated by a living 10 molar ratio LiOEEM/PMMA$^-$Li$^+$ in 75/25 toluene/THF at −78 °C, the experimental data indicate a well-controlled block copolymerization process (Table 1): a very narrow molecular distribution (<1.10), a high efficiency (0.95 as an average), and above all the absence of any homo-PMMA in the raw final product (see SEC trace in Figure 1). These results indicate that a pure PMMA-*b*-P2EtHA diblock copolymer has been successfully produced.

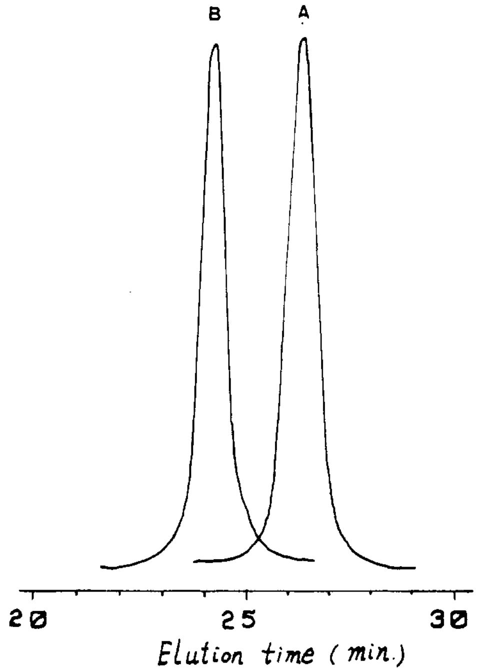

Figure 1. SEC of sample 1 (Table 1). (A) PMMA block: M_n = 6000, M_w/M_n = 1.03. (B) PMMA-*b*-P2EtHA block copolymer: M_n = 19 600, M_w/M_n = 1.09; prepared in 75/25 toluene/THF at −78 °C using DPMLi as an initiator and in the presence of 10 mol equiv of LiOEEM.

At this point, it is worth recalling that,[5] although LiCl-complexed organolithium initiator gives rise to a "perfectly" living anionic homopolymerization of MMA and *tert*-butyl acrylate (tBuA), respectively, as well as a precisely-controlled sequential polymerization of MMA initiated with living PtBuA macroanions, in THF, at −78 °C, the reverse block copolymerization process, i.e., tBuA initiated with a living PMMA, always leads to a ca. 5% homo–PMMA present according to the SEC diagram of the final product. This has been accounted for by a selective nucleophilic attack of the short methyl ester groups by the rather moderately hindered acrylate-type anions (backbiting termination reaction).[6] In terms of the structurally comparable steric hindrance at the α-substituted group of PtBuA and P2EtHA anions, the absence of the above-described backbiting termination reactions between MMA units in the polymer chains and living

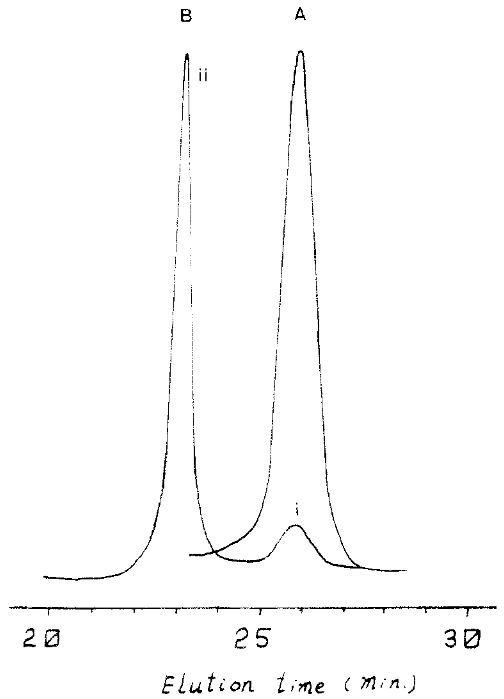

Figure 2. SEC of sample 3 (Table 2). (A) P2EtHA precursor: M_n = 8100, M_w/M_n = 1.09. (B(ii)) P2EtHA-*b*-PMMA block copolymer: M_n = 43 300, M_w/M_n = 1.09; prepared in 75/25 toluene/THF at −78 °C using DPMLi as an initiator in the presence of 10 mol equiv of LiOEEM.

P2EtHA anions might imply that the complexation of polyacrylate-type anions by LiOEEM can practically suppress such side termination reactions. In fact, it has already been demonstrated that, in sharp contrast to an ill-controlled anionic copolymerizations of MMA and tBuA mixtures in THF at −78 °C using LiCl-complexes initiator, the use of LiOEEM induces a "living random" copolymerization process under the same experimental conditions,[7] which might strongly suppor the above idea. Actually, these results can be interpreted in terms of an important role of ligand bulkiness in the ligated living anionic (co)-polymerization of (meth)acrylates, as already discussed elsewhere.[8]

(b) Synthesis of P2EtHA-*b*-PMMA (BA) Copolymer. In contrast to the preceding results, when the block copolymerization of MMA is initiated with a living P2EtHA macroanion under the same experimental conditions, i.e., at −78 °C and in 75/25 toluene/THF, it has been found that homo-P2EtHA always contaminates the block polymer. As indicated in Figure 2B, two peaks, namely, peaks i and ii, clearly show up in the SEC trace of the final product. In comparison with the elution curve of the P2EtHA precursor (Figure 2A), the peak on the high molecular weight side (i.e., peak ii) can be reasonably ascribed to a P2EtHA-*b*-PMMa diblock copolymer since peak i in Figure 2B obviously corresponds to the initial homo-P2EtHA (Figure 2A). Interestingly, enough, the MWD of P2EtHA-*b*-PMMA diblock copolymers is still very narrow (Table 2) and even sometimes narrower than the one observed for the P2EtHA precursor (e.g., 1.04 versus 1.09).

From the many attempts reported in the literature to elucidate the termination mechanism in anionic polymerization of (meth)acrylates,[9] it appears that the experimental conditions may be the determining factor in deciding between three pathways: termination with monomer, intermolecular terination with ester groups of another polymer chain, and intramolecular termination with the penultimate or antepenultimate ester group of the same chain (backbiting reaction). It seems most likely that none of these potential termination reactions can convincingly explain the experimental observations for the following reasons. First of all, in comparison with a possible nucleophilic attack of the methyl ester group by polyacrylate anions, the alternative reaction, i.e., the attack of a 2-ethylhexyl ester group by a PMMA anion (backbiting), is definitely much less probable because of the presence of greater steric hindrance in the transition state between the α-methyl group of the PMMA anion and the 2-ethylhexyl ester group and of the length and crowding of the latter. Since LiOEEM-complexed active species can efficiently diminish the backbiting attack in the case of PMMA-*b*-P2EtHA (see above), it is thus reasonable to rule out such a termination reaction in the opposite order, i.e., from PMMA anion to P2EtHA amount. Moreover, it is generally accepted that either a termination reaction with monomer or an intermolecular termination reaction may result in a grafting polymer,[10] leading to a broadening of the molecular weight distribution of the final product (sometimes with tailing on the high molecular weight side). The fact that all P2EtHA-*b*-PMMA block copolymers obtained in the present study have very low polydispersity (down to 1.04) together with a symmetric distribution might likely imply the absence of such termination reactions.

Up to this point, it may be otherwise first argued that a sluggish crossover reaction from the P2EtHA macroanion to MMA might result in the formation of homo-P2EtHA. Should this occur, the MWD of the block copolymer is usually found to be broader compared to the corresponding precursor,[11,12] contrary, as described above, to the experimental dispersity values of P2EtHA-*b*-PMMA diblock copolymers which are often smaller than that of the first block (i.e., P2EtHA) (Table 2), suggesting that this possible interpretation has to be disregarded.

This experimental situation consequently encourages us to invoke another mechanism, which might well explain the observed results. As recently noted by several authors,[13] the lifetime of the resulting active species is obviously one of the determining factors in controlling a living polymerization process. Actually, this crucial parameter becomes still more serious in the case of sequential copolymerization. In order to produce a pure block copolymer, it is indeed mandatory that the resulting living precursor retains its integrity for a sufficiently long time to complete the initiation of the second monomer, a common sense requirement which is however sometimes overlooked in the case of very active but moderately stable species.

Indeed, it has been already observed that the shelf time of the LiOEEM-complexed P2EtHA macroanions is not that long at −78 °C in a 9/1 toluene/THF mixture, so that the resumption experiment always leads to a small amount of precursor polymer present within the shortest possible laboratory experimental time scale (ca. 1 min).[3b] Supposing the same situation prevails in the present sequential polymerization, it is highly probable that some already dead P2EtHA chains possibly are present in the system before reacting with MMA, resulting in the observed homo–P2EtHA fraction.

Nevertheless, when the polymerization temperature was decreased down to −100 °C, the situation was improved to the point where homo-P2EtHA was no longer observed. In fact, as clearly seen in Table 2, the MW of block copolymers as calculated from ^{1}H NMR is very close to the theoretical one (f = 0.95 for block copolymerization),

Table 3. Characterization Data for P2EtHA-*b*-PMMA-*b*-P2EtHA (I) and PMMA-*b*-P2EtHA-*b*-PMMA (II) Triblock Copolymers through a Two-Stage Process Using a 10 Molar Ratio LiOEEM/(DPE + NaphLi) Initiator System in 75/25 Toluene/THF

				for central block				for triblock copolymer				
no.	sequence	temp (°C)	% total yield	M_n (calc)	M_n (SEC)	M_w/M_n	*f*	M_n (calc)	M_n (SEC)	M_n (^{1}H NMR)	M_w/M_n	*f*
1	I	−78	100	4 600	4 600	1.08	1.00	22 400	21 100	22 800	1.15	0.98
2	I	−78	100	15 000	16 000	1.10	0.94	45 000	47 000	46 500	1.15	0.97
3	II	−100	99	8 800	9 000	1.20	0.98	30 000	*a*		1.22	
4	II	−100	100	30 000	32 100	1.25	0.93	50 000	*a*		1.50	

[a] Multimodal distribution.

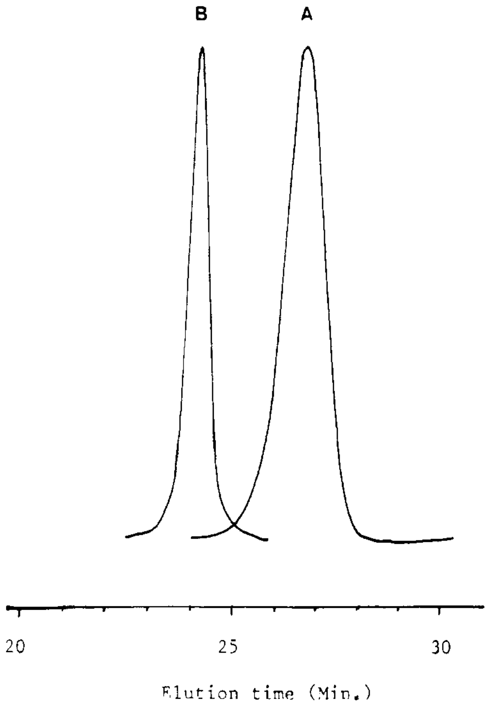

Figure 3. SEC of sample 5 (Table 2). (A) P2EtHA precursor: $M_n = 5300, M_w/M_n = 1.06$. (B) P2EtHA-*b*-PMMA: $M_n = 19\,000$, $M_w/M_n = 1.04$; prepared in 75/25 toluene/THF at −100 °C using DPMLi as an initiator and in the presence of 10 mol equiv of LiOEEM.

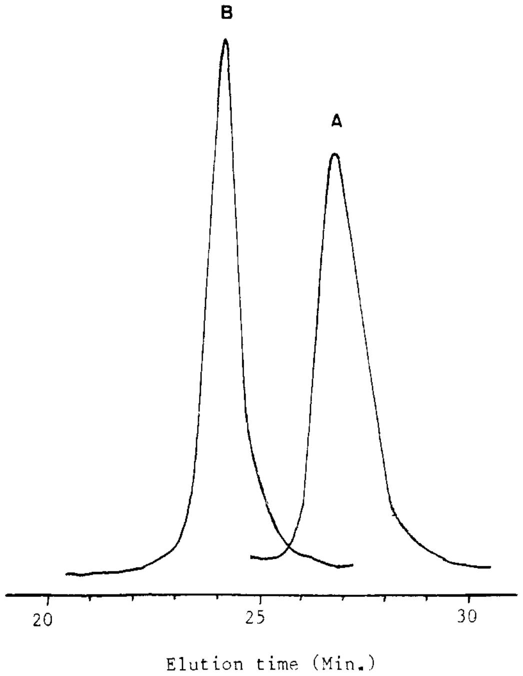

Figure 4. SEC of sample 1 (Table 3). (A) PMMA precursor: $M_n = 4600$, $M_w/M_n = 1.08$. (B) P2EtHA-*b*-PMMA-*b*-P2EtHA triblock copolymer: $M_n = 21\,100$, $M_w/M_n = 1.15$; prepared in 75/25 toluene/THF at −78 °C using NaphLi/DPE as an initiator in the presence of 10 mol equiv of LiOEEM.

and MWD is very narrow for both first and second blocks (<1.1). Moreover, within the limits of experimental error, SEC shows the absence of any homo-P2EtHA in the raw final products (Figure 3). It thus appears that lowering the temperature sufficiently enhances the stability of P2EtHA anions, while at the same time keeping their high reactivity and allowing all living P2EtHA chains to properly react with MMA monomer. Quite consistently, it has previously been found that,[3b] in the case of anionic homopolymerization of 2EtHA in a 9/1 toluene/THF mixture, two-step monomer resumption experiments always lead to the formation of a first dose fraction of P2EtHA at −78 °C but not at −100 °C.

Synthesis of A–B–A and B–A–B Triblock Copolymers. Since there is no problem of cross-reactivity when the sequential anionic polymerization of MMA (A) and 2EtHA (B) is considered, synthesis of A–B–A and B–A–B triblock copolymers should represent a straightforward valuable extension of the results described in the foregoing sections. In that prospect, two different pathways can be envisioned.

(a) Two-Stage Process Using a Difunctional Initiator. It should be feasible to substitute the monofunctional initiators by a difunctional one in order to synthesize the desired BAB block copolymer; the MMA anionic polymerization has accordingly been initiated by the lithium naphthalene/diphenylethylene adduct in the presence of a 10-fold excess of LiOEEM at −78 °C in a 75/25 toluene/THF mixture, leading to difunctional macroanion, i.e., a potential center block. As clearly indicated in Table 3, the resulting difunctional living PMMA is very comparable to the monofunctional one synthesized with DPMLi in terms of high initiator efficiency ($f > 0.93$) and very narrow MWD ($M_w/M_n < 1.10$). Furthermore, in the second step, 2EtHA propagatoin takes place on both sides of that first living PMMA sequence. The compositions and MW of recovered block copolymers fit very well with the expected ones, and the MWD is still narrow (ca. 1.15). In comparison with PMMA-*b*-P2EtHA diblock copolymer resulting from 2EtHA copolymerization with monofunctional living PMMA (Table 1), it seems however that 2EtHA polymerization with the difunctional one affords triblock copolymers having a slightly broader MWD (1.15 versus 1.09). Nevertheless, the SEC chromatogram of a typical P2EtHA-*b*-PMMA-*b*-P2EtHA triblock copolymer presented in Figure 4 and compared to the elution curve of the precursor PMMA shows practically no contamination by homo-PMMA within the sensitivity limits of the method.

Regarding the reverse sequence of monomer addition difunctional living P2EtHA anions have first been prepared at −100 °C and used to initiate the subsequent MMA anionic polymerization. In contrast to the above-mentioned results, experimental data illustrated in Table 3 and Figure 5 highlight a very complex process. Despite

Table 4. Characterization Data for PMMA-*b*-P2EtHA-*b*-PMMA Triblock Copolymerization through a Three-Stage Process Using a 10 Molar Ratio LiOEEM/DPMLi Initiator System in 75/25 Toluene/THF at −100 °C[a]

		for PMMA				for PMMA-*b*-P2EtHA				for PMMA-*b*-P2EtHA-*b*-PMMA			
no.	% total yield	M_n (calc)	M_n (SEC)	M_w/M_n	f	M_n (calc)	M_n (SEC)	M_w/M_n	f	M_n (calc)	M_n (SEC)	M_w/M_n	f
1	100	6250	6800	1.06	0.92	15 500	16 200	1.06	0.96	50 000	55 600	1.05	0.90
2	100	9400	10300	1.07	0.91	29 500	32 600	1.10	0.90	98 600	107 000	1.08	0.92

[a] Initiator concentration: 10^{-3} mol. Final monomer concentration: 6 wt %.

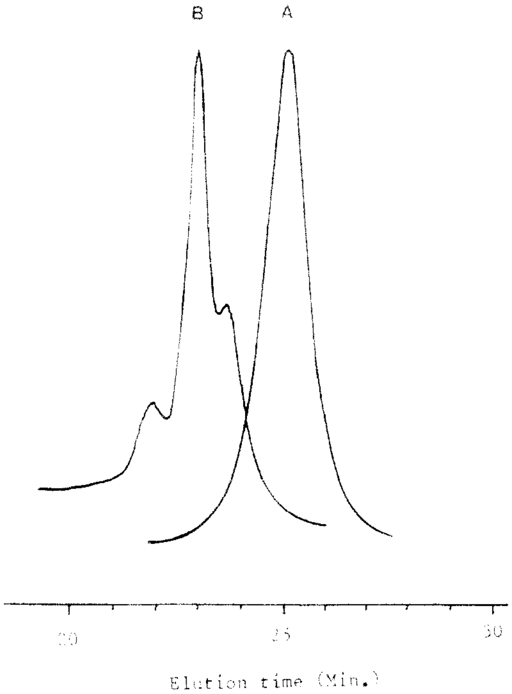

Figure 5. SEC of sample 3 (Table 3). (A) P2EtHA precursor: M_n = 9000, M_w/M_n = 1.20. (B) PMMA-*b*-P2EtHA-*b*-PMMA triblock copolymer: M_n = 30 000, M_w/M_n = 1.22; prepared in 75/25 toluene/THF at −100 °C using NaphLi/DPE as an initiator in the presence of 10 mol equiv. of LiOEEM.

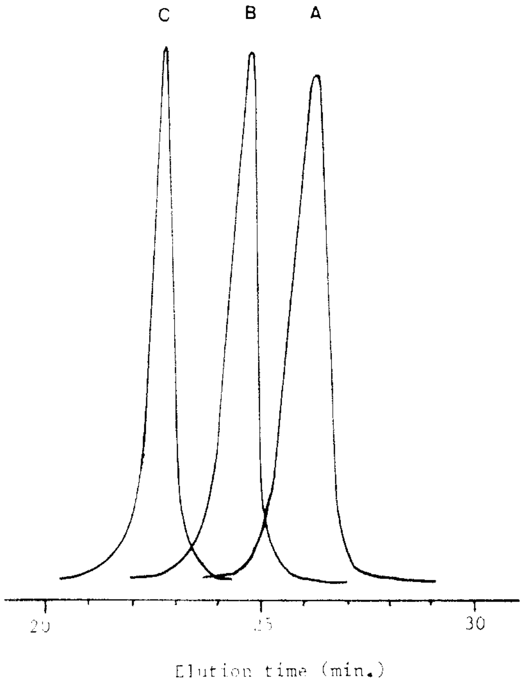

Figure 6. SEC of sample 1 (Table 4). (A) PMMA precursor: M_n = 6800, M_w/M_n = 1.06. (B) PMMA-*b*-P2EtHA diblock precursor: M_n = 16 200, M_w/M_n = 1.06. (C) PMMA-*b*-P2EtHA-*b*-PMMA triblock copolymer: M_n = 55 600, M_w/M_n = 1.05; prepared in 75/25 toluene/THF at −100 °C using a 10 molar ratio LiOEEM/DPMLi initiator system.

a nearly quantitative conversion of comonomers, and the absence of any homo-P2EtHA in the raw products (see SEC trace in Figure 5), a multimodal MWD was however surprisingly recorded. This might imply that several types of active species in slow equilibrium are involved, the reasons for which are not fully undestood as yet but should probably be sought in a misbehavior of the so-called difunctional initiator.

(b) Three-Stage Process with Monofunctional Initiator. In view of the importance of synthesizing a totally acrylate-based thermoplastic elastomer, serious efforts have been devoted to evaluate the feasibility of producing pure PMMA-*b*-P2EtHA-*b*-PMMA triblock copolymers through a three-stage process using a monofunctional initiator. In this regard, living PMMA anions were first generated with DPMLi as an initiator at −100 °C, followed by addition of 2EtHA to prepare living PMMA-*b*-P2EtHA macroanions. Finally, additional MMA was introduced to the above living solution, yielding the desired PMMA-*b*-P2EtHA-*b*-PMMA triblock copolymer. As noted in Table 4, each stage nicely gives rise to the block copolymer having expected composition and molecular weight as well as very narrow MWD (all <1.10). SEC traces also illustrate the absence of any precursors (Figure 6), indicating that a well-controlled triblock copolymer is produced. In addition, P2EtHA-*b*-PMMA-*b*-P2EtHA can be prepared following a similar strategy.

Comparative Efficiency of Lithium *tert*-Butoxide (LiO*t*Bu) in Anionic Sequential Polymerization of MMA and 2EtHA. Recently, it has been claimed that a controlled anionic polymerization of 2EtHA can be achieved by using LiOtBu-complexed lithium *tert*-butylisobutyrate (tBuIBLi) in toluene/THF mixtures.[14] Since the same authors had previously shown that LiOtBu-complexed initiator is also effective in achieving the living polymerization of MMA,[15] it thus seemed of great interest to compare the effectiveness of a simple lithium alkoxide, i.e., LiOtBu, and that of polydentate one, i.e., LiOEEM, in the anionic sequential polymerization of MMA and 2EtHA, under the same experimental conditions: DMPLi as an initiator at −78 °C, in a 75/25 toluene/THF mixture, and in the presence of 10 mol equiv of ligand.

At this point, it must be pointed out that the PMMA-*b*-P2EtHA sequence, i.e., from PMMA anions to 2EtHA monomer, is considered only for the sake of comparison, since we have already found that LiOtBu-added DPMLi gives rise to a poorly-controlled polymerization process for 2EtHA in terms of both low initiator efficiency and broad MWD.[3b] Unlike with the LiOEEM-complexed system, it has been observed that sequential polymerization of 2EtHA initiated with LiOtBu-complexed living PMMA macroanions certainly induces the formation of a considerable amount of homo-PMMA. A typical example is clearly illustrated in Figure 7, where the SEC trace shows that ca. 25% PMMA contaminates the final product. It is actually no surprise to obtain such unsatisfactory results, since a rather low initiator efficiency had already been observed in the anionic polymerization of 2EtHA using LiOtBu-combined tBuBLi initiator system.[14]

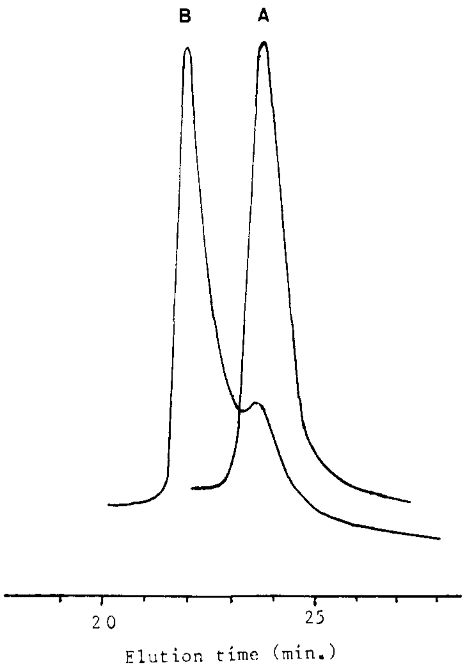

Figure 7. SEC of PMMA-*b*-P2EtHA block copolymer anionically prepared in 75/25 toluene/THF at −78 °C using DPMLi as an initiator in the presence of 10 mol equiv of LiOtBu. (A) PMMA precursor: M_n = 24 400, M_w/M_n = 1.15. (B) PMMA-*b*-P2EtHA diblock copolymer: M_n = 100 000, M_w/M_n = 1.25.

In good agreement with previously reported results,[3b] chelating LiOEEM (a μ/σ dual ligand) is clearly more efficient than a simple lithium alkoxide, i.e., LiOtBu (a μ-ligand), in promoting the living anionic polymerization of (meth)acrylates. As already demonstrated elsewhere,[7] in comparison with a simple μ-type mixed complex between LiOtBu and lithium ester enolate,[16] the formation of a bulkier μ/σ *dual* complex between LiOEEM and the same enolate[1] is at the origin of well-controlled anionic (co)polymerizations of (meth)acrylates.

In conclusion, the above-reported results again illustrate that ligated anionic living polymerization represents an efficient strategy for macromolecular engineering of poly(meth)acrylate-based materials and in particular for producing block copolymers of methyl methacrylate and primary acrylates with versatile architectures. It opens very attractive potentialities in the macromolecular engineering of (meth)acrylate-based materials, particularly the PMMA-*b*-P2EtHA-*b*-PMMA triblock copolymer which illustrates a novel type of thermoplastic elastomers; that new capability has promoted the investigation of the properties of this attractive class of physically cross-linked elastomers, which will be the subject of forthcoming papers.

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