Lithium Diisopropylamide as Initiator for the Anionic Polymerization of Methacrylates

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ABSTRACT: The anionic polymerization of a series of methacrylates, i.e. methyl methacrylate (MMA), *tert*-butyl methacrylate (*t*BuMA), (dimethylamino)ethyl methacrylate (DMAEMA), and glycidyl methacrylate (GMA), has been investigated in THF at −78 °C, by using both lithium diisopropylamide (LDA) and α-lithioethyl isobutyrate (Li-EIB) complexed with LiCl as initiators. Compared to ligated Li-EIB, which is a model for the propagating enolate in the methacrylate anionic polymerization, ligated LDA has quite a comparable initiation efficiency (>90%) and gives rise to polymers with a predictable molecular weight and a narrow molecular weight distribution (MWD < 1.1). The effect of LiCl on the MWD of poly-GMA is less pronounced compared to the other polymethacrylates. An already narrow MWD in the absence of LiCl might be accounted for by an intramolecular coordination of the ion pair by the oxirane group of the (ante)penultimate unit(s) of growing poly GMA. As a direct consequence of the well-controlled anionic polymerization of these methacrylates, pairs of them have been polymerized in a sequential way with formation of well-defined block copolymers. Actually, there is no restriction on the addition order of the comonomers, so that both types of triblocks (ABA and BAB) can be successfully synthesized. Size exclusion chromatography supports that block copolymers are not contaminated by homopolymers, at least in detectable amounts.

Introduction

(Meth)acrylic esters are an important class of monomers available on a large scale (5 million tons per year) at steadily more attractive prices. The large variety of (meth)acrylates available, and particularly of functional groups in the ester substituent, accounts for the versatility of the derived polymers covering a large spectrum of materials: plastics, elastomers, adhesives, and protective coatings. Until ca. 15 years ago, the (meth)acrylic esters were polymerized only by radical methods. The need for a much better controlled polymerization and hopefully for efficient macromolecular engineering was a strong incentive to new polymerization strategies. The group transfer polymerization (GTP) was a first answer to this challenge. GTP is, however, incompatible with any traditional monomers other than carbonyl-containing ones.[1,2] Insertion mechanisms based on coordination complexes have proved to have high efficiency in tailoring the polymerization while usually keeping the polymerization rate rather slow.[3,4] Anionic polyaddition, which is the most obvious alternative mechanism for (meth)acrylate polymerization, has received special attention. In addition to all-organic large and delocalized ion pairs,[5,6] ligation of the anionic species[7−10] has been at the origin of remarkable progress in the control of living nucleophilic polymerization, with beneficial consequences for macromolecular engineering. Although it is not the only operating factor, steric hindrance appears to have a determining effect in maintaining the polymerization "living". This conclusion is in line with previous observations according to which sterically hindered initiators, such as (diphenylhexyl)lithium, (diphenylmethyl)lithium, and (α-methylstyryl)lithium,[11] minimize side reactions on the carbonyl group and increase the low initiation efficiency commonly reported for *n*-BuLi and *sec*-BuLi in THF at −78 °C.[12]

In the same vein, McGrath *et al.* have reported that PMMA of a predictable molecular weight and a rather narrow molecular weight distribution ($M_w/M_n = 1.3$) could be obtained by using lithium diisopropylamide (LDA) as an initiator in THF at −78 °C.[13]

Moreover, we have observed an increase in the initiation efficiency from 75% up to 94% upon ligation of LDA with LiCl.[14] This result is of a practical interest when micellization of amphiphilic diblock copolymers is studied by the time-resolved fluorescence technique.[15,16] Indeed, any aromatic species able to interfere with fluorescence measurements is prohibited, which makes LDA a very attractive initiator for the synthesis of well-defined block copolymers of the (meth)acrylate type.

This paper aims at reporting on the anionic polymerization of MMA, *t*-BuMA, DMAEMA, and GMA using both LDA and Li-EIB complexed with LiCl as initiators.

The ultimate purpose is the controlled sequential anionic polymerization of pairs of these monomers with formation of diblock and triblock copolymers which are free from any aromatic fragment.

Experimental Section

Reagents and Solvents. Methyl methacrylate (MMA), glycidyl methacrylate (GMA), and (dimethylamino)ethyl methacrylate (DMAEMA) from Aldrich and *tert*-butyl methacrylate (*t*-BuMA) from BASF (Belgium) were first vacuum distilled from CaH_2 and stored under nitrogen at −20 °C. Just prior to polymerization, MMA, DMAEMA, and *t*-BuMA were titrated with a 10 wt % triethylaluminum solution in hexane until a persistent yellowish green color was observed, and then distilled under reduced pressure. GMA was titrated with styryllithium oligomers and then distilled as reported elsewhere.[17]

Pure LiCl (99.9%) (Aldrich) was dried overnight at 130 °C. Tetrahydrofuran (THF) was purified by refluxing over fresh sodium benzophenone complex (a deep purple color indicating an oxygen and moisture-free solvent). It was further distilled over oligomers of styryllithium under reduced pressure immediately before use.

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A 2 M solution of lithium diisopropylamide (LDA: Janssen Chimica) in THF/*n*-heptane was diluted 10 times its weight in dry hexane. α-Lithioethyl isobutyrate (Li-EIB) was prepared under nitrogen by reacting LDA with an equimolar amount of ethyl isobutyrate in hexane at −78 °C as previously reported.[18]

Polymerization was carried out in a previously flamed glass reactor under an inert atmosphere. Monomer, solvent, and initiator were transferred with a syringe and/or stainless steel capillaries. The reactor was first loaded with LiCl, which was dried “in situ” at 130 °C. Solvent was then added, followed by the initiator. The reactor was cooled to −78 °C before addition of the monomer. The monomer conversion was inferred from the weight of the polymer precipitated into cold methanol, filtered, and dried under vacuum. In the case of block copolymerization, an aliquot of the polymerization medium was withdrawn for analysis before adding the second monomer still at −78 °C.

The as-formed homopolymers and diblock copolymers were analyzed by size exclusion chromatography (SEC) with a Waters GPC apparatus equipped with two Ultrastyragel linear columns, eluted with THF at 35 °C. In the case of poly-DMAEMA, 1% of triethylamine was added to the eluent in order to prevent the polyamine from interacting with the columns, which was observed to broaden and to shift the elution peak toward longer retention times.

The composition of the block copolymers was analyzed by ^{1}H-NMR using a Bruker AN-400 spectrometer.

Results and Discussion

Homopolymerization. With the purpose of synthesizing polymethacrylates and parent block copolymers without any aromatic moiety, two sterically hindered aliphatic initiators were selected: lithium diisopropylamide (LDA) and α-lithioethyl isobutyrate (Li-EIB). The latter initiator is nothing but a monomeric model structurally comparable to the propagating species of living poly(alkyl methacrylate)s, the alkyl group being ethyl in this case. This type of monomeric model has proved to be quite suitable for the study of the ion pairs in THF and THF/toluene mixtures at different temperatures and in the presence of various ligands,[19,20] particularly LiCl.[21,22] Li-EIB is thus an ideal reference for the behavior and efficiency of LDA as an aliphatic anionic initiator. In this study, each initiator has been systematically mixed with 5 equiv of LiCl, since the aggregation equilibrium of the ion pairs has been shown to be shifted toward the formation of a single type of LiCl-complexed species at LiCl/monomeric model molar ratios of 1 and higher.[21] This situation provides the living PMMA chains with a very low polydispersity in THF at low temperature. It must also be pointed out that lithium alkylamides have been previously studied as initiators for MMA polymerization.[13] Due to steric hindrance, lithium diisopropylamide has an intrinsically high initiation efficiency (75%), which is further improved up to ca. 94% in the presence of LiCl in THF at −78 °C.[14]

Results listed in Table 1 confirm that the MMA polymerization is under complete control in THF at −78 °C when initiated by ligated LDA. The molecular weight is predictable, at least until 10^4, and the molecular weight distribution is very narrow ($M_w/M_n = 1.05$). The beneficial effect of LiCl on this polymer characteristic is obvious since M_w/M_n is ca. 1.3 in the absence of ligand. There is no apparent difference between LDA and Li-EIB used as an aliphatic initiator. This observation indicates that LDA is as efficient as the monomeric model for the propagating species in preventing side reactions from occurring.

Table 1. Anionic Polymerization of MMA Initiated by α-Lithioethyl Isobutyrate (Li-EIB) or Lithium Diisopropylamide (LDA) Complexed with a 5-Fold Molar Excess of LiCl in THF at −78 °C for 0.5 h

initiator	[initiator] (mol/L × 10^{-3})	M_n(cal)[a] × 10^{-3}	M_n(SEC) × 10^{-3}	M_w/ M_n	yield (%)	f[b]
Li-EIB	5	2	2.2	1.04	100	0.91
Li-EIB	6.8	4.7	5.1	1.03	98	0.92
LDA	2.9	2.1	2.2	1.05	100	0.95
LDA	2.9	4.0	4.1	1.04	100	0.97
LDA	1.8	6.0	6.1	1.04	98	0.96
LDA	2.5	8.0	8.6	1.06	100	0.92

[a] M_n(cal) ≅ [monomer mass (g)]/mol of initiator]. [b] Initiator efficiency = M_n(cal)/M_n(SEC).

Table 2. Anionic Polymerization of *t*-BuMA Initiated by Lithium Diisopropylamide (LDA) Complexed with a 5-Fold Molar Excess of LiCl in THF at − 78 °C for 3 h

[initiator] (mol/L × 10^{-3})	M_n(cal) × 10^{-3}	M_n(SEC) × 10^{-3}	M_w/ M_n	yield (%)	f
9.5	5.7	6.05	1.04	100	0.94
6.1	4	4.1	1.06	100	0.97
6.1	15	16.3	1.02	100	0.91

When *tert*-butyl methacrylate is substituted for MMA, the molecular weight distribution is much broader (1.6), all the other conditions being the same. This molecular characteristic feature decreases however with increasing temperature. The basic explanation for this unexpected behavior has to be found in an equilibrium between THF nonsolvated species and THF-solvated active species slowly exchanging at low temperature, at least compared to the monomer addition rate. Since temperature influences the kinetics of both the solvation equilibrium and the chain propagation, it is not surprising that the chain polydispersity decreases as the temperature is increased. Once again the beneficial effect of LiCl on the chain polydispersity is obvious since M_w/M_n is then as low as 1.05 (Table 2). Accordingly, LiCl has a high propensity to coordinate with a lithium ester enolate and at the same time to either promote a fast-exchanging ligation equilibrium or form a simple type of active complex. Also in contrast to the anionic polymerization of MMA, which is very fast (100% yield within a few minutes for experiments reported in Table 1), *t*-BuMA is less reactive as assessed by a reaction time of 3 h under the same experimental conditions. The steric and electronic effect of the *tert*-butyl substituent can explain this difference in kinetics.

When (dimethylamino)ethyl methacrylate (DMAEMA) is anionically polymerized in THF at −78 °C without LiCl, the molecular weight distribution is broad ($M_w/M_n > 1.5$) whatever the initiator, i.e. LDA or Li-EIB. Nevertheless, the initiation efficiency is high (over 90%) compared to the anionic polymerization of MMA under the same experimental conditions ($M_w/M_n = 1.3$; $f = 75\%$).[14] These results might indicate that the dimethylamino substituent of both the monomer and the penultimate unit in the growing chain can coordinate with the Li counterion, which perturbs the aggregation and solvatation by THF of both the initiator (f is higher) and the propagating species (M_w/M_n is broader). No significant difference can be detected between the two initiators, even in the presence of LiCl, which results again in a narrower molecular weight distribution.

In order to confirm the apparently living polymerization mechanism (good agreement between the calculated and theoretical M_n), a monomer resumption experiment has been carried out. Thus a first dose of DMAEMA was polymerized by LDA ligated by LiCl

Table 3. Living Anionic Polymerization of DMAEMA Initiated by LDA or Li-EIB Complexed with 5 equiv of LiCl in THF at −78 °C

initiator	[initiator] (mol/L × 10^{-3})	M_n(cal)[b] × 10^{-3}	M_n(SEC) × 10^{-3}	M_w/M_n	time (h)	yield (%)	f[c]
LDA[a,d]	8.8	5.2	5.4	1.5	1		
LDA[a,d]	8.8	12	12.5	1.55	1	96	0.94
LDA	5.86	3.50	3.6	1.07	2	100	0.98
LDA[e]	6.0	3.8	3.9	1.09	2		
LDA	10.0	4.2	4.3	1.05	2	97	0.97
LDA	7.1	6.3	6.6	1.08	1.5	95	0.95
LDA[e]	6.0	9.4	9.5	1.05	2	97	0.98
Li-EIB	6.25	6.3	6.6	1.08	2	100	0.95
Li-EIB	3.33	9.4	10.2	1.10	2	94	0.92
Li-EIB	10.0	4.2	4.3	1.75	1.5	98	0.96

[a] Without LiCl. [b] M_n(cal) ≅ [monomer mass (g)]/[mol of initiator]. [c] Initiator efficiency = M_n(cal)/M_n(SEC). [d,e] Pairs of samples being part of resumption experiments.

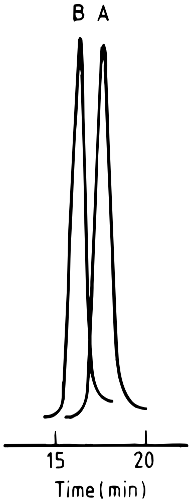

Figure 1. SEC traces for PDMAEMA synthesized in a two-step process with LDA/5LiCl as initiator: (A) first step, M_n = 3900; (B) second step, M_n = 9500.

Table 4. Living Anionic Polymerization of GMA Initiated by LDA and/or Li-EIB Complexed with 5 equiv of LiCl in THF at −78 °C

initiator	[initiator] (mol/L × 10^{-3})	M_n(cal) × 10^{-3}	M_n(SEC) × 10^{-3}	M_w/M_n	time (h)	yield (%)	f[c]
LDA	2.63	11.16	12.0	1.08	1.5	85	0.93
LDA	9.6	6.0	6.85	1.10	2	92	0.88
LDA	3.1	4.65	5.05	1.03	1.5	100	0.92
LDA[a,b]	7.7	2.48	3.60	1.09	1		
LDA[a,b]	7.7	4.78	5.50	1.14	1	98	0.85
Li-EIB	2.8	5.8	6.0	1.04	2	96	0.93
Li-EIB	7.0	8.75	8.95	1.14	1	95	0.98
Li-EIB	2.85	12.15	13.9	1.11	2	94	0.87
Li-EIB[a]	7.33	3.4	3.75	1.06	1	100	0.97

[a] Without LiCl. [b] Samples being part of resumption experiments. [c] Initiator efficiency.

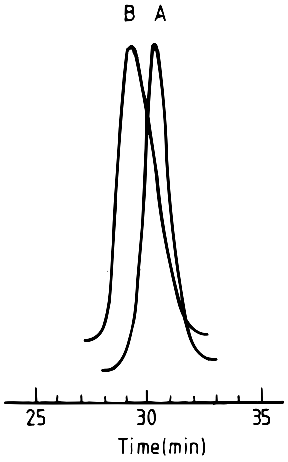

Figure 2. SEC traces for PGMA synthesized in a two-step process with LDA in THF at −78 °C: (A) first step, M_n = 3600; (B) second step, M_n = 5500.

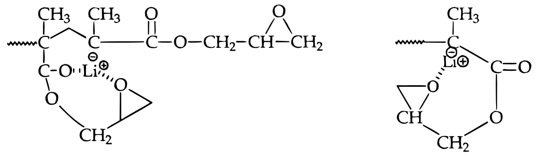

Figure 3. Intramolecular coordination of the active sites by the oxirane group.

(entry 4, Table 3) and 2 h later (which is enough for a 100% yield; see entry 3), a second monomer dose was added and polymerized for an additional 2 h. The final M_n is in close agreement with the expected value (entry 7, Table 3), and size exclusion chromatography (SEC) shows that no detectable amount of a low molecular weight fraction (first polymerization step) contaminates the final product (Figure 1), which is actually of a low polydispersity.

In 1990, Leemans *et al.* reported[17] for the first time on the living anionic polymerization of glycidyl methacrylate (GMA) initiated by (diphenylhexyl)lithium (DPHLi) and (α-methylstyryl)lithium (α-MeStyLi). When a more nucleophilic initiator is used, such as *sec*-BuLi complexed with LiCl, a cross-linking reaction occurs as result of the opening of the epoxy substituent.[12] Recently, Rempp *et al.* have confirmed the living anionic polymerization of GMA and formation of a polymer with a narrow molecular weight distribution (M_w/M_n = 1.1) when DPHLi is used in the presence of LiCl at −60 °C.[23]

Data in Table 4 (entries 4, 5, and 9) show that GMA contrasts with the other members of the methacrylate family, since the anionic polymerization is well controlled at −78 °C in THF (MWD = 1.1) in the absence of ligand at least in the range of low molecular weight (M_n ≤ 12 000), in which the polymer solubility is preserved at low temperature. Table 4 confirms this statement by reporting a monomer resumption experiment (entries 4 and 5). SEC analysis (Figure 2) shows that the elution peak of the polymer formed at the first step is shifted toward smaller elution volumes with a small increase in the polydispersity and a smaller initiation efficiency than usually observed. This last observation might however result from a discrepancy between theoretical and experimental M_n's at the end of the first step, rather than from a monomer resumption problem. This better control of the anionic polymerization of GMA compared to MMA, *t*-BuMA, and DMAEMA has something to do with the complexation capability of the oxirane substituent with the alkali metal cation by analogy with oxyalkylene chains.[24] Although their molecular structure is more favorable, crown ethers are chelating σ-ligands, known to be very efficient ligands in the control of the anionic polymerization of methacrylates.[9,25] On that basis, Figure 3 is a tentative explanation for the absence of noxious reactions of the GMA enolate propagating species on the carbonyl of the ester group. This kind of internal complexation that involves the penultimate or the antepenultimate monomer unit has been postulated elsewhere as a factor providing ionic vinyl polymerization with stereoregularity.[26] The addition of LiCl does

Table 5. Microstructure of Polymethacrylates Anionically Synthesized in THF at Low Temperature

initiator	[initiator] (mol/L × 10^{-3})	*T* (°C)	monomer	[LiCl]/[initiator]	polymer microstructure syn (%)	hetero (%)	iso (%)	ref
DPHLi	3	−78	MMA		81	18	1	1
DPHLi	3	−78	MMA	1	81	18	1	1
LDA	0.6	−78	MMA	5	79	20	1	*a*
DPHLi		−60	GMA	5	64	34	2	22
LDA	0.6	−78	GMA		62	34	4	*a*

[a] This work.

not change at all the MWD whatever the initiator (Table 4), which suggests that the proposed intramolecular coordination is not perturbed by this μ-ligand. The narrow MWD even in the absence of external ligand is a good indication for a unique type of active species. Expectedly, the σ-type internal complexation shown in Figure 3 has an effect on the poly-GMA microstructure independently of the addition of LiCl. Indeed, Table 5 shows a decrease in the content of the syndiotactic triads in favor of the heterotactic triads compared to the chain microstructure reported for PMMA prepared under the same conditions of temperature (−78 °C) and solvent (THF). This general observation is consistent with the previously reported inability of a μ-ligand to perturb the anionic polymerization stereoregularity, which is essentially controlled by solvent polarity and temperature.[27] Conversely, σ-ligands such as macrocyclic crown ethers are known to be favorable to the formation of heterotactic triads at the expense of the syndiotactic ones in THF at low temperature.[9]

In order to confirm that ligated LDA is as efficient an initiator as ligated Li-EIB for the anionic polymerization of the four methacrylates under consideration, the experimental data are reported in Figure 4 as a plot of the theoretical molecular weight in the case of living polymerization (100% yield) against the experimental values for the two initiators (LiCl/initiator = 5 mol/mol). In the case of *t*-BuMA, only LDA was studied.

A straight line is observed with a slope which is usually higher than 0.9 and quite comparable for the two initiators. Thus LDA ligated by 5 mol of LiCl does not behave differently from an anionic species that mimics the propagating species in the living anionic polymerization of methacrylates ligated with the same ligand.

Therefore, LDA /5LiCl is an easily accessible and handled system, which increases the limited range of highly efficient initiators for the living anionic polymerization of alkyl methacrylates.

Block Copolymerization. Since the anionic polymerization of MMA, *t*-BuMA, DMAEMA, and GMA is living when initiated by the LDA/5LiCl and Li-EIB/5LiCl complexes in THF at −78 °C, each pair of these monomers could be sequentially polymerized with formation of well-defined block copolymers. The order of the monomer addition is thought to be of minor importance due to similar reactivity of the related methacrylate anions, so that the two types of triblock copolymers (ABA, BAB) could be made easily available.

Tables 6 and 7 report the complete characterization of a series of diblock copolymers prepared by the LDA/5LiCl complex (Table 7) and some of them by the Li-EIB/5LiCl initiator (Table 6). Not all the possible comonomer pairs have been investigated. Actually, the choice relied mainly upon the need of making some diblock copolymers available for micellization studies in aqueous solutions, most often after derivatization of one block into a polyelectrolyte one. Copolymerization of DMAEMA with MMA and *t*-BuMA, respectively, received much attention. MMA was also copolymerized with GMA, although its copolymerization with *t*-BuMA was reported elsewhere but with a different initiator.[12] All the syntheses of diblock copolymers reported in Tables 6 and 7 agree with a highly controlled copolymerization process, i.e. comonomer conversion close to completion, very narrow molecular weight distribution for the first block and the final diblock (M_w/M_n commonly in the 1.05−1.10 range), no homopolymer detected in the crude diblock by size exclusion chromatography as assessed by the comparison of the SEC traces of the first polymerized block and the final diblock (e.g. Figures 5a,b), and close matching of the theoretical and experimental molecular weight. M_n of the first block was measured by SEC, which in combination with the diblock composition allows M_n of the final copolymer to be calculated. The weight composition of the diblocks was calculated from the ^{1}H-NMR spectrum and particularly from the characteristic resonances: at 1.33 ppm for the *tert*-butyl group of *t*-BuMA, at 3.8 and 4.3

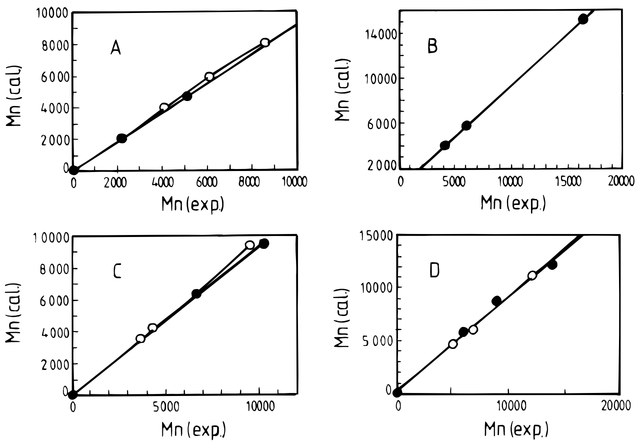

Figure 4. Plot of the theoretical M_n vs experimental M_n for the anionic polymerization (THF, −78 °C) of MMA (A), *t*-BuMA (B), DMAEMA (C), and GMA (D): (A) (○) LDA−5LiCl (slope: 0.93), (●) Li-EIB−5LiCl (slope: 0.92); (B) LDA−5LiCl (slope: 0.91); (C) (○) LDA−5LiCl (slope: 0.99), (●) Li-EIB−5LiCl (slope: 0.93); (D) (○) LDA−5LiCl (slope: 0.93), (●) Li-EIB−5LiCl (slope: 0.89).

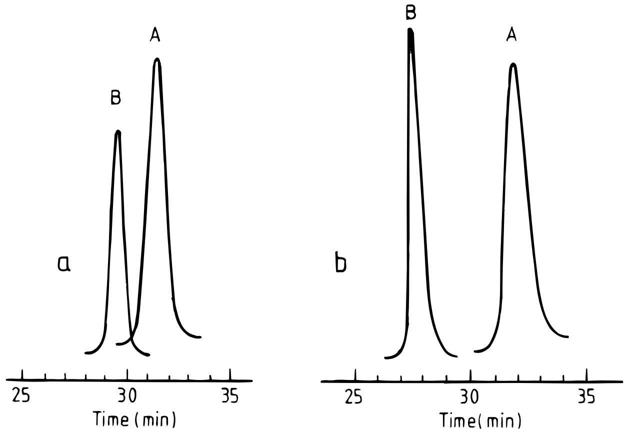

Figure 5. SEC chromatograms for diblock copolymers synthesized in THF at −78 °C with Li-EIB (a) and LDA (b) complexed with 5 equiv of LiCl. (a) Poly(MMA-*b*-DMAEMA) (Table 6, no. 3): (A) PMMA first block, M_n = 2900; (B) diblock copolymer, M_n = 5900. (b) Poly(MMA-*b*-DMAEMA) (Table 7, no. 10): (A) first block, M_n = 2200; (B) diblock copolymer, M_n = 16 600.

Table 6. Diblock Copolymerization of Different Methacrylate Pairs Initiated by Li-EIB Complexed with 5 equiv of LiCl in THF at −78 °C

		copolymer compn (wt %)		first block			copolymer			
no.	copolymer	theor	exp (NMR)	M_n(cal) × 10^{-3}	M_n(SEC) × 10^{-3}	M_w/M_n	M_n(cal) × 10^{-3}	M_n(exp) × 10^{-3}	M_w/M_n	yield (%)
1	DMAEMA−*t*-BuMA	83−17	80−20	5.2	3.9	1.05	6.24	4.9	1.1	100
2	*t*-BuMA−DMAEMA	50−50	49−51	2.7	2.9	1.05	5.28	5.9	1.05	98
3	MMA−DMAEMA	20−80	20−80	2.0	2.2	1.05	10.0	11.0	1.15	100
4	MMA−DMAEMA	50−50	48−52	3.93	3.7	1.05	7.9	8.2	1.10	100

Table 7. Diblock Copolymerization Initiated by LDA Complexed with 5 equiv of LiCl in THF at −78 °C

		copolymer compn (wt %)		first block			copolymer			
no.	copolymer	theor	exp (NMR)	M_n(cal) × 10^{-3}	M_n(SEC) × 10^{-3}	M_w/M_n	M_n(cal) × 10^{-3}	M_n(exp) × 10^{-3}	M_w/M_n	yield (%)
1	DMAEMA−*t*-BuMA	77−23	85−15	10.0	6.9	1.10	13.0	8.1	1.11	100
2	*t*-BuMA−DMAEMA	50−50	49−51	5.4	5.5	1.05	10.8	11.2	1.05	92
3	GMA−MMA	54−46	60−40	4.6	5.0	1.05	8.6	8.4	1.1	100
4	MMA−GMA	20−80	18−82	3.98	4.1	1.05	20.5	22.1	1.10	96
5	DMAEMA−MMA	79−21	83−17	14.0	11.8	1.05	17.0	14.3	1.05	100
6	DMAEMA−MMA	84−16	81−19	3.55	3.6	1.05	4.25	4.5	1.10	100
7	DMAEMA−MMA	84−16	83−17	9.24	7.4	1.15	11.08	8.9	1.15	100
8	DMAEMA−MMA	84−16	82−18	11.10	9.9	1.05	13.34	12.1	1.05	96
9	MMA−DMAEMA	18−82	20−80	4.08	4.10	1.05	23.21	20.4	1.05	97
10	MMA−DMAEMA	16−82	15−85	2.25	2.2	1.05	14.25	16.6	1.05	100
11	DMAEMA−MMA	50−50	48−52	5.7	5.7	1.05	12.0	11.8	1.10	96

Table 8. Triblock Copolymerization of Methacrylates Initiated by LDA Complexed with 5 equiv of LiCl in THF at −78° C

	first block			diblock copolymer					triblock copolymer					
							comp (wt %)					comp (wt %)		
copolymer	M_n(cal) × 10^{-3}	M_n(SEC) × 10^{-3}	M_w/M_n	M_n(cal) × 10^{-3}	M_n(SEC) × 10^{-3}	M_w/M_n	theor	exp	M_n(cal) × 10^{-3}	M_n(SEC) × 10^{-3}	M_w/M_n	theor	exp	yield (%)
DMAEMA−MMA−DMAEMA	5.7	4.2	1.05	12	11.8	1.10	50−50	52−48	17.3	15.72	1.15	66−34	61−39	96
MMA−DMAEMA−MMA	2.25	2.20	1.05	14.25	14.60	1.05	16−84	15−85	16.5	18.3	1.05	32−68	32−68	100
MMA−GMA−MMA	1.88	1.9	1.05	7.5	7.0	1.04	24−76	27−73	9.76	8.5	1.05	38−62	40−60	95

ppm for the methylene protons of the glycidyl ester and at 3.3 ppm for the CH of the oxirane group of GMA, at 2.27 ppm for the dimethylamine protons of DMAEMA, and at 3.6 ppm for the (OCH_3) methyl ester group of MMA (Figure 6A,B).

Experiments 1 and 2 in Table 6 and experiments 1 and 2, 3 and 4, 8 and 9, and 10 and 11 in Table 7 confirm that the addition order of the comonomers for the *t*-BuMA−DMAEMA, GMA−MMA, and MMA−DMAEMA pairs has no effect on the course of the diblock copolymerization, whose implementation is thus highly flexible. Since the diblock copolymerization of the aforementioned comonomers has proved to be under tight control, there is no reason for the synthesis of the parent triblock copolymers to fail.

Table 8 accordingly shows that the three-step sequential polymerization of DMAEMA and MMA is as precisely controlled as the diblock copolymerization, whatever the order of the comonomer addition. The synthesis of MMA−GMA−MMA copolymers is additional evidence that there is no problem of cross-reactivity for the MMA−GMA pair, just as with the MMA−DMAEMA comonomers. In this respect, triblock copolymers show a remarkably narrow molecular weight distribution, in addition to the close matching of the theoretical and experimental compositions. SEC chromatograms for the first block (PMMA), the diblock (PMMA−PGMA), and the final triblock (PMMA−PGMA−PMMA) are compared in Figure 7 and show that the as-formed diblock and triblock are free from contamination by the precursors, at least within the limits of detection of SEC.

One of the incentives to consider the block polymerization of MMA, *t*-BuMA, DMAEMA, and GMA was to make available low molecular weight copolymers of a

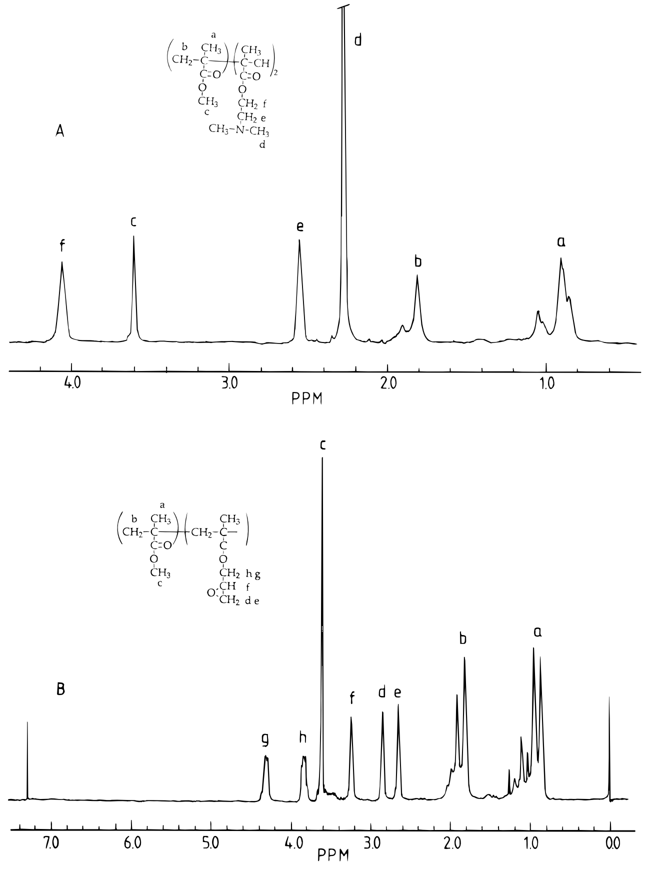

Figure 6. ^{1}H-NMR spectra for diblock copolymers in $CDCl_3$: (A) poly(MMA-*b*-DMAEMA) (Table7, no. 9); (B) poly(MMA-*b*-GMA) (Table 7, no. 3).

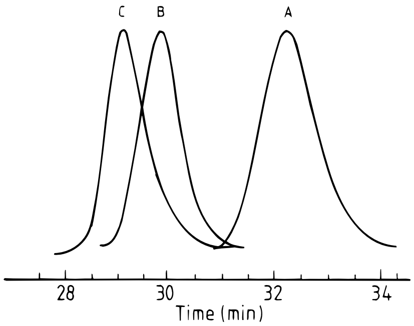

Figure 7. SEC traces for a triblock copolymer synthesized in THF at −78 °C with LDA−5LiCl (Table 8, no. 3): (A) PMMA first block, M_n = 1900; (B) poly(MMA-*b*-GMA) diblock, M_n = 7000; (C) poly(MMA-*b*-GMA-*b*-MMA) triblock, M_n = 8500.

well-defined and easily modulated composition and length and, above all, free from aromatic groups, including end groups. This target has been clearly reached, so that amphiphilic copolymers containing a polyelectrolyte block can be now studied in water, particularly their micellization by fluorescence techniques. For this purpose, the PDMAEMA block can be quaternized with an alkyl halide with formation of a polycationic block. Similarly, sulfonation of the PGMA block is known to provide a polyanionic block,[17] whereas hydrolysis of the P-*t*-BuMA block is an easy way to a polycarboxylate block. Details of this study will be reported in the future.

Conclusions

The experimental data reported in this paper strongly support that lithium diisopropylamide ligated with 5 equiv of LiCl is an initiator as highly efficient as lithium ethylisobutyrate for the anionic polymerization of MMA, *t*-BuMA, DMAEMA, and GMA, respectively, in THF at −78 °C. Although the polymerization appears to be living in the absence of LiCl, ligation of the initiator results in a much narrower molecular weight distribution, except for poly-GMA, which shows a low polydispersity independently of the ligand. An intramolecular coordination of the active site by the oxirane of the penultimate or antepenultimate unit is thought to be responsible for this effect.

Binary diblock and triblock copolymers of these methacrylates can be prepared in a quantitative way, with predictable molecular weight and narrow molecular weight distribution, whatever the addition order of the comonomers. It is noteworthy that these copolymers are free from homopolymers and aromatic species, which makes them suitable for the study of micellization by fluorescence techniques. Amphiphilic copolymers are easily derived by selective chemical modification of the poly-*t*-BuMA (hydrolysis), poly-DMAEMA (quaternization), and poly-GMA (sulfonation) blocks, so that polymeric surfactants for aqueous systems can be made available.

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