Living Anionic Homopolymerization and Block Copolymerization of (Dimethylamino)ethyl Methacrylate

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ABSTRACT: Anionic polymerization of (dimethylamino)ethyl methacrylate (DMAEMA) has been investigated in THF at −78 °C. The presence of lithium chloride has been shown to be desirable in order to afford a narrow molecular weight distribution as well as a good agreement between theoretical and observed molecular weight. The living character of the polymerization has been demonstrated. Thus the synthesis of block copolymers, some of them unattainable by GTP, has been carried out successfully. Finally, the anionic polymerization of mixtures of *tert*-butyl methacrylate (tBMA) and DMAEMA has been considered and their relative reactivity ratio estimated. The easy quaternization of (dimethylamino)ethyl methacrylate affords amphiphilic water-soluble copolymers displaying interesting characteristics as polymeric dispersants and surfactants.

Introduction

In his pioneering research, Szwarc[1] has demonstrated that some monomers could be polymerized in a living process, so providing a versatile methodology for the synthesis of polymers with controlled molecular weight and molecular weight distribution and for the macromolecular engineering of complex (multiphase) materials. However, the living polymerization of (meth)acrylates has proved not to be so straightforward. Indeed, nucleophilic attack of the active species on the carbonyl groups along the chain can easily occur. Among other strategies, the use of a bulky initiator combined with lithium chloride in THF at −78 °C has proved to be a very practical way to control the polymerization of those (meth)acrylates.[2,3]

Due to growing concerns on environmental protection, water-soluble polymers have undergone a fast development. Up to now, anionic and nonionic polymers, such as sulfonates, carboxylates, and poly(ethylene oxides) have been mostly studied. Cationic polyelectrolytes are now a center of growing interest in view of their various applications in areas such as flocculation (especially for water and wastewater treatment), adhesives, emulsion and dispersion stabilizers,[4,5] etc. In this regard, the anionic polymerization of DMAEMA, the quaternization of which is straightforward, has been considered to be promising. To our best knowledge, the only preceding report on its anionic polymerization has been published by Nazarov et al.,[6] who used butyllithium as initiator and observed side reactions on the ester functions. It must be stressed that DMAEMA has recently been polymerized in a controlled process by GTP.[7] Unfortunately, this method does not allow for the direct synthesis of block copolymers with monomers lacking carbonyl conjugated groups, i.e. in particular styrenes and dienes. In an attempt to avoid this drawback and have a possible access to a broader series of copolymers, we wish to report here the living anionic polymerization of DMAEMA and its block copolymerization with other momoners, as well as their products characterization by SEC.

Experimental Section

DMAEMA, methyl methacrylate (MMA), *tert*-butyl methacrylate (tBMA), α-methylstyrene (αMeSt), and styrene (St) were first vacuum distilled from calcium hydride and then stored under a nitrogen atmosphere at −20 °C. Before polymerization, a 50 vol % solution of DMAEMA in toluene, previously dried over calcium hydride, was treated with 5 vol % of 1 M triethylaluminum in toluene. A yellowish green color develops upon heating during the distillation. MMA and tBMA were similarly diluted with toluene, treated with 1 M triethylaluminum in toluene until a yellowish green color appeared, and finally redistilled under reduced pressure just prior to polymerization. α-Methylstyrene and styrene diluted with toluene were added dropwise with fluorenyllithium until a persistent orange color was observed and then distilled under reduced pressure just prior to polymerization. 1,1-Diphenylethylene was dried and redistilled over *sec*-butyllithium just before the polymerization.

(Diphenylmethyl)lithium was prepared at room temperature by reacting diphenylmethane with lithium naphthalenide prepared from lithium and naphthalene in THF at room temperature.

Lithium chloride was flame dried under vacuum just prior to polymerization and stored under nitrogen. THF was purified by refluxing over a freshly prepared sodium−benzophenone complex.

Polymerization was carried out under dry nitrogen in flasks equipped with three-way stopcocks. All glassware was flamed under vacuum before use. Solutions were transferred through stainless steel capillaries or with glass syringes through a rubber septum.

The solvent cooled at −78 °C was added dropwise with (diphenylmethyl)lithium until a persistent yellow/orange color was observed, and the required amount of this initiator was then transferred to the medium, followed by the purified monomer: polymerization was allowed to proceed for 1−2 h (in direct relation with the molecular weight). In the case of homopolymers, the polymerization was quenched by adding methanol. In the case of copolymerization, an aliquot was withdrawn for characterization and the second monomer was then injected. The copolymerization was finally quenched also with methanol. In the case of α-methylstyrene, a few drops of the latter were added to THF and then cooled to −78 °C. *sec*-Butyllithium was added slowly until a persistent red color was observed, and the required amount of this initiator was then added, followed by the purified αMeSt monomer. After 0.5 h, an aliquot was withdrawn for characterization and the second monomer injected. The copolymerization was finally quenched with methanol. The same procedure was followed for styrene, except that prior to DMAEMA addition, the living polystyrene chains were end-capped by 1,1-diphenylethylene. Complete conversions were always observed.

Polymerization of mixtures of tBMA and DMAEMA was carried out according to the DMAEMA homopolymerization procedure and was quenched after a few minutes to keep the conversion at a low level.

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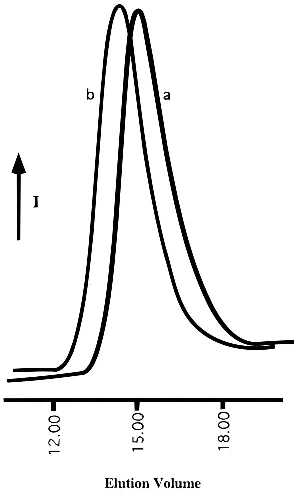

Figure 1. GPC chromatograms of poly(DMAEMA): (a) first feed, M_n(SEC) = 8800, M_w/M_n = 1.5, M_n(theor) = 5400; (b) second feed, M_n(SEC) = 15 600, M_w/M_n = 1.5, M_n(theor) = 10 800.

Quaternization of Poly(DMAEMA) with Alkyl Halides. A 5 wt % solution of the DMAEMA (co)polymer was first prepared in THF. Then an excess of alkyl halide was added and allowed to react at 40 °C for 12 h. The final product was recovered by complete removal of the solvent and the alkyl halide in excess. The degree of quaternization determined by ^{1}H NMR[7b] was quantitative.

Characterization. Size exclusion chromatography (SEC) was carried out at 35 °C in THF added with 1 vol % triethylamine, using a Hewlett-Packard 1050 liquid chromatograph equipped with two PLGel columns (1000 and 10000 Å) and a Hewlett-Packard 1047A refractive index detector. Poly(methyl methacrylate) standards were used for calibration. ^{1}H spectra were recorded at 400 MHz with a Bruker AM 400 superconducting magnet equipment.

Results and Discussion

Homopolymerization. Despite the extended potential applications of poly[(dimethylamino)ethyl methacrylate] and the report of DMAEMA polymerization by GTP,[7] a well-controlled anionic living polymerization process has astonishingly never been described. Since side reactions have been observed in the case of butyllithium as initiator,[6] a bulkier one, i.e. (diphenylmethyl)lithium, was used in a first approach at −78 °C in THF. After 1 h, an aliquot was withdrawn and a second feed was allowed to polymerize for an additional hour. SEC analysis was carried out in THF in the presence of 1% triethylamine in order to avoid any interaction with the columns, a common practice for 2-vinylpyridine.[8] Some discrepancy between the theoretical and the observed molecular weight is observed as well as a quite broad molecular weight distribution (Figure 1). However, a shift toward higher molecular weight without any significant broadening of the molecular weight distribution might already reflect some living character.

On the other hand, the broadness of the molecular weight distribution (1.5) probably reflects a kinetic problem. As exemplified by Teyssié et al.[9a] and Müller et al.,[9b] in the case of the anionic polymerization of *tert*-butyl acrylate or methyl methacrylate, the effect of lithium chloride on the molecular weight distribution of the final polymer is very pronounced. Indeed, the polydispersity drops below 1.1. They explained this phenomenon by the assumption that in the absence of LiCl, associated and nonassociated ion pairs are present. Since both species interconvert very slowly and propagate at very different rates upon monomer addition, a broad molecular weight distribution is observed, despite the living character of the polymerization. In contrast, addition of LiCl displaces the slowly interconverting associated and nonassociated ion pairs equilibrium toward the faster interconverting equilibrium between nonassociated and LiCl associated ion pairs. Thus, accordingly the main function of LiCl would be to deplete the system from the slowly interconverting aggregates.

Table 1. Anionic Homopolymerization of DMAEMA[a]

expt	initiator × 10^{-3} mol/L	M_n(theor)	M_n(SEC)	f^b	M_w/M_n
1	11.16	4500	4300	1.04	1.06
2	10.47	4800	5000	0.96	1.1
3	7.28	6900	6000	1.15	1.08
4	5.84	8600	8700	0.99	1.06
5	4.57	11000	12000	0.92	1.06
6	3.59	14000	13800	1.01	1.07
7	2.72	18500	20100	0.92	1.05
8	2.2	22800	24400	0.94	1.1

[a] Conditions: LiCl concentration = 10 × (diphenylmethyl)lithium mol; THF; −78 °C; 0.32 mol/L DMAEMA. [b] $f = M_n$(theor)/M_n(SEC). Mean f = 0.99.

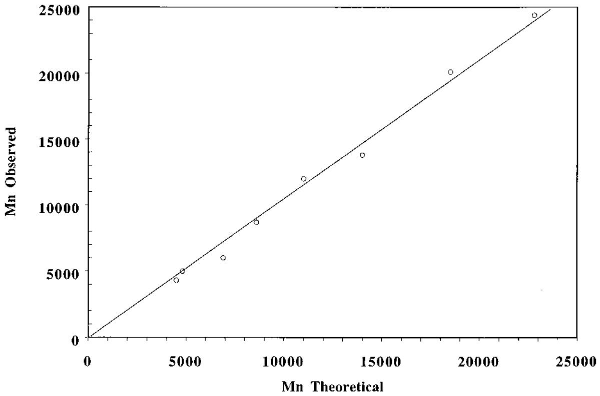

Figure 2. Anionic polymerization of DMAEMA in the presence of LiCl.

Our experiments were accordingly repeated in the presence of lithium chloride. A narrow molecular weight distribution was then observed (<1.1) as well as a higher initiator efficiency (Table 1). So although some living character is already observed in the absence of lithium chloride, its presence is necessary in order to obtain a good kinetic control of the molecular parameters. Homopolymers with different molecular weights were then synthesized with a good correlation between observed and theoretical molecular weight (Figure 2). Moreover, the living character was tested by adding a second feed of monomer to living poly[(dimethylamino)ethyl methacrylate] anions. The final product and the intermediate one exhibit the expected molecular weight in accordance with the feeds (Figure 3).

Block Copolymerization. The living character of DMAEMA homopolymerization being demonstrated as above, its block copolymerization was examined. In a first approach, living poly(methyl methacrylate) anions were used to initiate a second sequence of DMAEMA, and the final product moved to the expected higher molecular weight with a narrow molecular weight distribution (see Table 2 and Figure 4a). ^{1}H NMR confirms the theoretical composition. The block copolymerization was then repeated backward in order to check the interconvertibility of the two methacrylates. The final product exhibits once again the right molecular characteristics (see Table 2 and Figure 4b).

Table 2. Anionic Synthesis of DMAEMA Copolymers

	first block					block copolymer						
expt	monomer	M_n(theor)	M_n(SEC)	f	M_w/M_n	monomer	comp[a]	M_n(theor)	M_n(SEC)	M_n(NMR)[b]	f^c	M_w/M_n
9	MMA	2100	2200	0.95	1.1	DMAEMA	24−76	8500	7200	9100	0.93	1.07
10	DMAEMA	8600	8700	0.99	1.06	MMA	77−23	11500	15900	11300	1.02	1.06
11	tBMA	2700	3100	0.87	1.1	DMAEMA	52−48	5500	5400	6000	0.92	1.08
12	St	5800	6000	0.97	1.1	DMAEMA	48−52	12000	12300	12500	0.96	1.08
13	αMeSt	4300	4600	0.93	1.2	DMAEMA	40−60	12000	11300	11500	0.96	1.1

[a] Weight composition determined by NMR. [b] M_n(NMR) = M_n(SEC) of first sequence divided by the NMR weight composition percentage of the first sequence. [c] $f = M_n$(theor)/M_n(NMR).

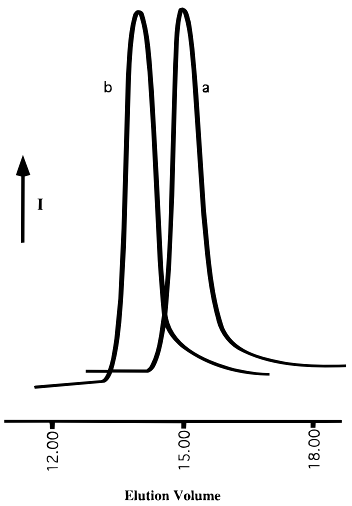

Figure 3. GPC chromatograms of poly(DMAEMA): (a) first feed, M_n(SEC) = 12 000 (expt 5); (b) second feed, M_n(SEC) = 24 400 (expt 8).

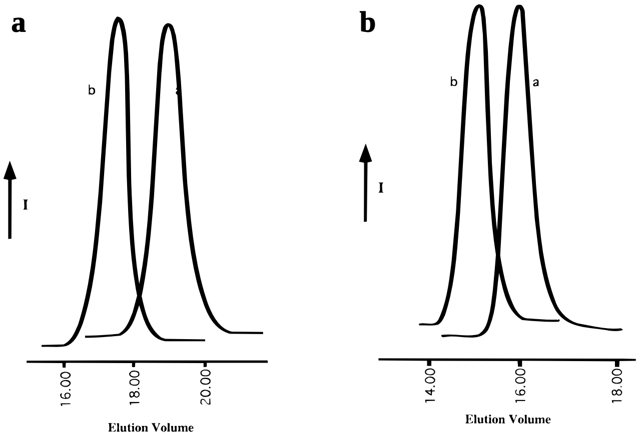

Figure 4. (a) GPC chromatograms of expt 9: (a) poly(MMA), M_n(SEC) = 2200; (b) poly(MMA-*b*-DMAEMA), M_n(SEC) = 7200. (b) GPC chromatograms of expt 10: (a) poly(DMAEMA), M_n(SEC) = 8700; (b) poly(DMAEMA-*b*-MMA), M_n(SEC) = 15 900.

The anionic cross-polymerization of DMAEMA with methyl methacrylate so being demonstrated, its block copolymerization with *tert*-butyl methacrylate was examined. Indeed, after easy hydrolysis of the *tert*-butyl ester into methacrylic acid, the water-soluble copolymer exhibits excellent properties as a pigment dispersant.[10] Moreover, if the amine moiety is quaternized before hydrolysis, the final polyampholyte product should have potential properties as a reverse osmosis membrane for desalination.[11] The living poly(*tert*-butyl methacrylate) anion has thus been used successfully as an initiator for DMAEMA. The final product again exhibits the expected shift toward higher molecular weight as well as a narrow molecular weight distribution (Table 2).

Finally, block copolymerization of DMAEMA with styrene derivatives, i.e. α-methylstyrene and styrene, was studied. The latter living chains were end-capped with 1,1-diphenylethylene prior to DMAEMA addition in order to afford a smooth initiation of the second sequence. Once again, the final products as well as the intermediate ones exhibit the right molecular characteristics (Table 2). This gives access to styrene-based block copolymers, unattainable by GTP. Moreover, one may expect also access to diene-based copolymers, since diene type living chains may be end-capped with 1,1-diphenylethylene.

Table 3. Anionic Copolymerization of a 62/38 wt % tBMA/DMAEMA Mixture[a]

time, min	M_n(SEC)	M_w/M_n	NMR wt comp
15	5000	1.25	53−47
30	5400	1.16	54−46
60	6700	1.12	59−41
180	7400	1.08	62−38

[a] Conditions: THF; −78 °C; LiCl concentration = 10 × (diphenylmethyl)lithium mol.

The poly(α-methylstyrene-*b*-DMAEMA) and poly(methyl methacrylate-*b*-DMAEMA) copolymers can be quaternized with alkyl halides, such as methyl iodide, to afford amphiphilic water-soluble copolymers. The so-obtained water-soluble block copolymers display a remarkable efficiency as dispersing agents for pigments in the presence of poly(vinyl alcohol).[5]

Copolymerization of Mixtures of DMAEMA and tBMA. As mentioned above, poly(DMAEMA) bonded to a water-soluble counterpart, i.e. poly(methacrylic acid salts), anchors strongly onto pigments, and imparts remarkable properties to the final dispersions.[10] In order to evaluate the influence of the sequence distribution (i.e. a diblock character as opposed to some random character, upon the dispersion properties), mixtures of tBMA and DMAEMA were polymerized. First, the living character of the mixture anionic copolymerization was checked. A 62/38 tBMA/DMAEMA mixture was polymerized at −78 °C in THF in the presence of lithium chloride. The progression of the copolymerization was monitored by withdrawing an aliquot for SEC and NMR characterization. As exemplified in Table 3, a regular increase in molecular weight associated with a narrow molecular weight distribution is observed, indicating the living character of the copolymerization. The copolymer composition was determined by comparing the dimethylamino peak at 2.33 ppm (DMAEMA) to the *tert*-butyl peak at 1.44 ppm (tBMA). The composition exhibits a preference for DMAEMA in the early steps of the polymerization and tends to the feed composition with increasing conversion. DMAEMA is thus expected to be somewhat more reactive than tBMA.

The extended Kelen−Tüdös method,[12] which takes into account the drift in the comonomer and copolymer compositions with conversion, was used to estimate the relative reactivity ratio of tBMA and DMAEMA. That Kelen−Tüdös method is expressed by the following

Table 4. Kelen−Tüdös Parameters for Anionic Copolymerization of DMAEMA/tBMA Mixtures[a]

expt	f_{DMAEMA}[c]	F_{DMAEMA}[c]	conv (wt frac)	X	Y	Z	F	G	ξ	η
14	0.856	0.895	0.07	5.94	8.52	1.452	4.04	5.18	0.962	1.233
15	0.766	0.845	0.06	3.27	5.45	1.691	1.91	2.63	0.922	1.27
16	0.651	0.757	0.13	1.86	3.12	1.735	1.04	1.22	0.866	1.015
17	0.258	0.6	0.12	0.348	1.5	4.864	0.064	0.103	0.284	0.457
18	0.157	0.428	0.05	0.186	0.748	4.243	0.042	−0.059	0.207	−0.29
19	0.086	0.436	0.1	0.094	0.773	10.954	0.0064	−0.021	0.0384	−0.125

[a] Conditions: THF; −78 °C; LiCl concentration = 10 × (diphenylmethyl)lithium mol. [b] DMAEMA molar fraction in monomer feed. [c] DMAEMA molar fraction in copolymer.

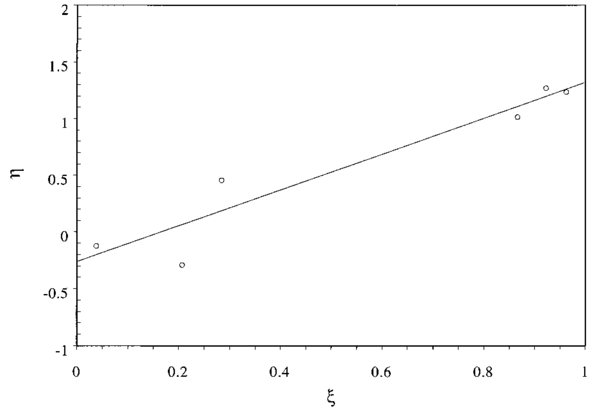

Figure 5. Extended Kelen−Tüdös plot $\eta = (r_{\mathrm{DMAEMA}} + r_{\mathrm{tBMA}}/\alpha)\xi - r_{\mathrm{tBMA}}/\alpha$.

equations:

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha$$

where

$$\eta = G/(\alpha + F)$$

$$\xi = F/(\alpha + F)$$

$$\alpha = (F_{\min}F_{\max})^{1/2}$$

$$F = Y/Z^2$$

$$G = (Y - 1)/Z$$

$$Z = \log(1 - \zeta_1)/\log(1 - \zeta_2)$$

where

$$\zeta_2 = w(\mu + X)/(\mu + Y)$$

$$\zeta_1 = \zeta_2\,(Y/X)$$

where X and Y represent the molar ratios of monomer 1 to monomer 2 in the comonomer feed and the resulting copolymer, respectively. w corresponds to the weight conversion of the copolymerization, and μ is the molecular weight ratio of monomer 2 to that of monomer 1.

The copolymerization data are reported in Table 4 and the extended Kelen−Tüdös plot in Figure 5. The intercepts at $\xi = 0$ and $\xi = 1$ of the ξ versus η plot gives as an estimation $r_{\mathrm{tBMA}} = 0.04 \pm 0.07$ and $r_{\mathrm{DMAEMA}} = 1.3 \pm 0.4$. This confirms the definitely higher reactivity of DMAEMA compared to tBMA. The copolymer could then be depicted as a "diblock" copolymer, probably "tapered" and composed of (i) one mixed sequence consisting of poly(DMAEMA) mixed with some tBMA and (ii) an essentially poly(tBMA) sequence formed after consumption of DMAEMA monomer, at least for a nonextreme composition. According to these results, it is also obvious that the random copolymers could be obtained by continuous controlled feeding of the more reactive partner, i.e. DMAEMA.

Conclusion

The homopolymerization of DMAEMA in a living process has been demonstrated. Well-defined (i.e. in terms of molecular weight and molecular weight distribution) homo- and copolymers, diblocks, and tapered diblocks can thus be synthesized thanks to the presence of lithium chloride. Even styrene type monomers can be successfully copolymerized sequentially with DMAEMA, in contrast to GTP. Quaternization of the amine moiety affords water-soluble cationic polymers, which, in combination with hydrophobic monomers, i.e. methyl methacrylate or α-methylstyrene, affords highly efficient dispersants or, in combination with methacrylic acid, affords polyampholytes or pigment dispersants.

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