Articles

Novel Cationic Macromonomers by Living Anionic Polymerization of (Dimethylamino)ethyl Methacrylate

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ABSTRACT: Water-soluble cationic macromonomers of (dimethylamino)ethyl methacrylate (DMAEMA) with terminal diallylmethylammonium or allylmethylphenylammonium group were synthesized by nitrogen anion (nitroanion) initiated living anionic polymerization of DMAEMA and subsequent quaternization. The initiators, lithium diallyamide and lithium allylphenylamide, were prepared by the reaction of corresponding N-substituted allylamine with butyllithium. The substituents on the nitroanion had a significant effect on the initiation efficiency. The initiator efficiencies of lithium allylamide, diallylamide, and allylphenylamide increased by the order 0 < 25% < 79% at −78 °C. The low initiator efficiency of lithium diallylamide was due to the reaction of the nitroanion with carbonyl groups in the monomer and polymer and could not be improved by optimizing polymerization conditions. A capping method using dimethylacrylamide (DMA) or *tert*-butyl methacrylate (tBMA) was then developed to modify the lithium diallylamide and thereby increased initiator efficiency. The DMA or tBMA capped lithium diallylamide had an initiator efficiency higher than 0.90, producing polymers with predicted molecular weight and nearly monodispersed polydispersity. Subsequent quaternization with CH_3I and dimethyl sulfate converted the polymer into cationic macromonomers with diallylmethylammonium or allylmethylphenylammonium terminal groups, which are readily copolymerizable with other vinyl monomers such as acrylamide and vinylformamide.

Introduction

Random copolymers of cationic monomers, such as diallyldimethylammonium chloride, with acrylamide are widely used to improve retention for fines and filters in papermaking processes and sludge dewatering in newsprint deinking plants, as well as many other applications in mineral processing, oil recovery, and drinking water treatment.[1] Recently, we demonstrated that graft copolymers with cationic pendant chains had better flocculation performance than their corresponding random polymers.[2,3] However, these graft copolymers were synthesized by a γ-radiation-initiated graft copolymerization. The copolymerization was difficult to control, and it was almost impossible to completely characterize the copolymer structure, e.g., the length of grafted chain and graft density.[2,3] Well-defined graft or comb-branched copolymers are thereby needed in order to investigate the relationship between the polymer structure and flocculation performance. Macromonomer copolymerization is an effective approach to prepare such copolymers of required chain length and side chain density through controlling the molecular weight and charged amount of macromonomer.[4] Therefore, the synthesis of cationic macromonomers with controlled molecular weight, narrow polymer dispersity, and polymerizable unsaturated terminal group is the key step in preparing the targeted copolymers.

Macromonomers with controlled molecular weight and structure can only be synthesized by living polymerization. Even though there are some reports about using new living polymerization techniques, such as atom transfer radical polymerization,[5−7] to prepare various macromonomers, living anionic polymerization is still most widely used for synthesizing macromonomers.[8] The macromonomer synthesis strategies by living anionic polymerization can be classified as the end-functionalization method using vinyl-containing agents and initiation method using functional initiator. The end-functionalization method involves either living polymer chain coupling with a termination reagent[9−11] or reacting functional polymer with unsaturated compound, such as ω-hydroxyl polymer with acrylyl chloride.[12] The main challenge for this method is that usually not all of the end groups can be capped. For the living chain coupling, the active center of polymer chain must be stable to avoid side reactions. Therefore, this method is only applicable for limited systems.

The initiation method using vinyl-containing initiators is the preferred approach for the preparation of macromonomers since each polymer chain so-prepared has one terminal vinyl group. The challenge for this method is to select a proper vinyl-containing initiator so that the vinyl moiety in it will not react during the polymerization of vinyl monomers. Furthermore, the vinyl moiety in the initiator should not react with the initiator's active center, e.g., alkyl−metal bond. Therefore, even though the living anionic polymerization of

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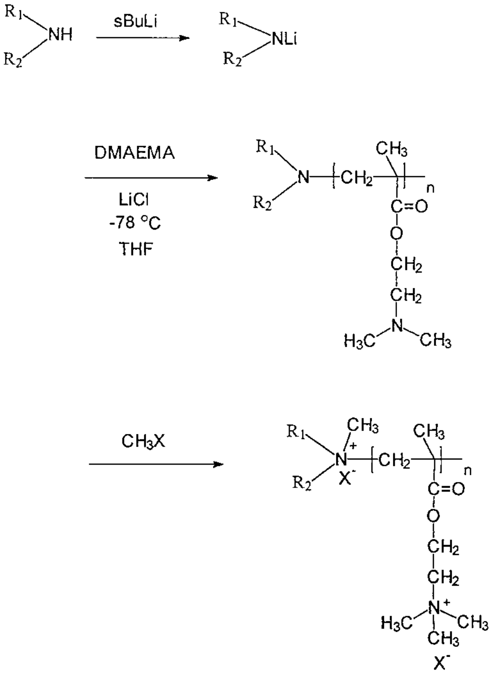
Scheme 1. Synthesis of DMAEMA Macromonomers by Nitroanion-Initiated Anionic Polymerization



Allylamine: $R_1 = H$, R_2 = allyl
Diallylamine: $R_1 = R_2$ = allyl
Allylaniline: R_1 = allyl, R_2 = phenyl

vinyl monomers has been well developed using alkyllithium systems,[8,13] the application of the initiation method in the synthesis of macromonomers is still very limited because it is difficult for an initiator such as alkyllithium to bear an unsaturated group. Recently, Nagasaki[14] and Lascelles[15] synthesized macromonomers of poly(diethylaminoethyl methacrylate) (polyDEAEMA) and poly(dimethylaminoethyl methacrylate) (polyDMAEMA) using less active oxyanionic initiators. However, the molecular weights of the prepared polymers were higher than predicted, and the polymer dispersities were about 1.3.

Hindered lithium alkylamides initiated a living polymerization of methacrylic esters.[16−18] We found that the nitrogen anion (nitroanion) was stable with allyl group, and therefore polyDMAEMA with allylamino end group can be synthesized.[19] We here report the synthesis and characterization of cationic macromonomers of DMAEMA with diallylmethylammonium or allylmethylphenylammonium terminal group by nitroanion-initiated living polymerization of DMAEMA and subsequent quaternization (Scheme 1). The prepared macromonomers are readily copolymerizable with acrylamide and vinylformamide, yielding water-soluble comb-branched copolymers with cationic teeth and nonionic backbones.

Experimental Section

Reagents and Solvents. (Dimethylamino)ethyl methacrylate (DMAEMA), dimethylacrylamide (DMA), and *tert*-butyl methacrylate (tBMA) from Aldrich were stirred over CaH_2 for 24 h, then was distilled from CaH_2 under a reduced pressure, and stored over CaH_2 under nitrogen in a refrigerator. LiCl (99.9%) from Aldrich was dried at 130 °C and then dried again at 100 °C under vacuum just before use. THF was refluxed over potassium under nitrogen atmosphere. Diallylamine, allylamine, and allylaniline were distilled over CaH_2. *sec*-Butyllithium (sBuLi) was purchased from Aldrich, and its concentration was titrated by a standard method.

Preparation of Initiator and Polymerization. In a glass reactor previously treated with chlorotrimethylsilane and flame-dried, weighted LiCl was added and heated to 100 °C under vacuum and purged with nitrogen five cycles. Then 30 mL of THF and the required amount of N-substituted allylamine were charged to the reactor. The reactor was cooled to −78 °C. A stoichiometric amount of *sec*-butyllithium was added in a dropwise manner with stirring. After 1 h of stirring, the monomer was introduced. In the runs with a capping agent, 2-fold (molar) dimethylacrylamide or *tert*-butyl methacrylate with respect to N-substituted allylamine was introduced and stirred at −78 °C for half an hour prior to monomer addition. The polymerization was terminated by adding 0.2 mL of methanol. The aliquot was then poured into 200 mL of petroleum ether. Finally the polymer was separated and dried in a vacuum at 30 °C for 24 h.

Quaternization of the Polymers. 1 g of polymer was dissolved in 10 mL of acetone or DMSO or dimethylformamide (DMF) at room temperature. 0.5 mL of CH_3I was then added in a dropwise manner and stirred for 2 h. 0.1 mL of dimethyl sulfate was then added, and the solution was stirred for another hour. When using acetone as solvent, the quaternized polymer precipitated very quickly after adding CH_3I. The precipitate was isolated and dried in the vacuum oven. When DMSO or DMF was used as solvent, the quaternized polymer was soluble in DMSO, and therefore the reaction in DMSO or DMF was homogeneous. The quaternized polymer was precipitated in acetone and also dried in a vacuum.

Characterization. *Nuclear Magnetic Resonance (NMR) Spectroscopy.* Proton (^1H) NMR spectra were recorded on a Bruker ARX-200 spectrometer at 200 MHz. ^1H NMR chemical shifts in $CDCl_3$ were reported downfield from 0.00 ppm using residual $CHCl_3$ signal at 7.23 ppm as an internal reference. When D_2O was used as solvent, the residual H_2O signal at 4.63 ppm was used as reference.

Molecular Weight Measurements. Number- and weight-average molecular weights (M_n and M_w, respectively) were determined by gel permeation chromatography (GPC) using THF−2% (v/v) triethylamine as eluent at 25 °C with RI detector. Narrow polystyrene standards (Polysciences) were used to generate a calibration curve (Varian MicroPak column G1000, 3000, 7000 HXL). Data were recorded and processed using the Windows based Millenium 2.0 software package.

Results and Discussion

DMAEMA Polymerization by N-Substituted Allylamine−sBuLi Initiator System. The initiators, lithium N-substituted allylamide, were prepared in situ by the reaction of N-substituted allylamine with *sec*-butyllithium (Scheme 1). The reaction was thus investigated using diallylamine as model compound to see whether there were side reactions such as the addition reaction to the double bond and α-proton abstraction. First, diallylamine was allowed to react with equimolar sBuLi in THF at −78 °C, and then 2-fold *tert*-butyl methacrylate (tBMA) was added. The reaction was terminated by water. An oil-like liquid (*a*) was isolated. ^1H NMR spectra indicated that the product obtained was a dimer of tBMA with a terminal diallylamino group (Figure 1). The signals of the allyl group appeared at 5.7 ppm (m, $CH=$), 5.1 ppm (m, $CH_2=$), and 3.1 ppm (m, $-CH_2-$), slightly shifted to high field compared to those of diallylamine. Most importantly, the signal intensity ratio of methylene proton ($CH_2=$), methine ($=CH$), and methylene ($-CH_2-$) was close to 2:1:2, and there was no sign of N−H proton. This clearly indicates that sBuLi abstracted proton from N−H without reaction with the allyl groups, yielding lithium diallylamide. Therefore, lithium N-substituted allylamides were prepared by the reaction of corresponding N-substituted allylamine with sBuLi.

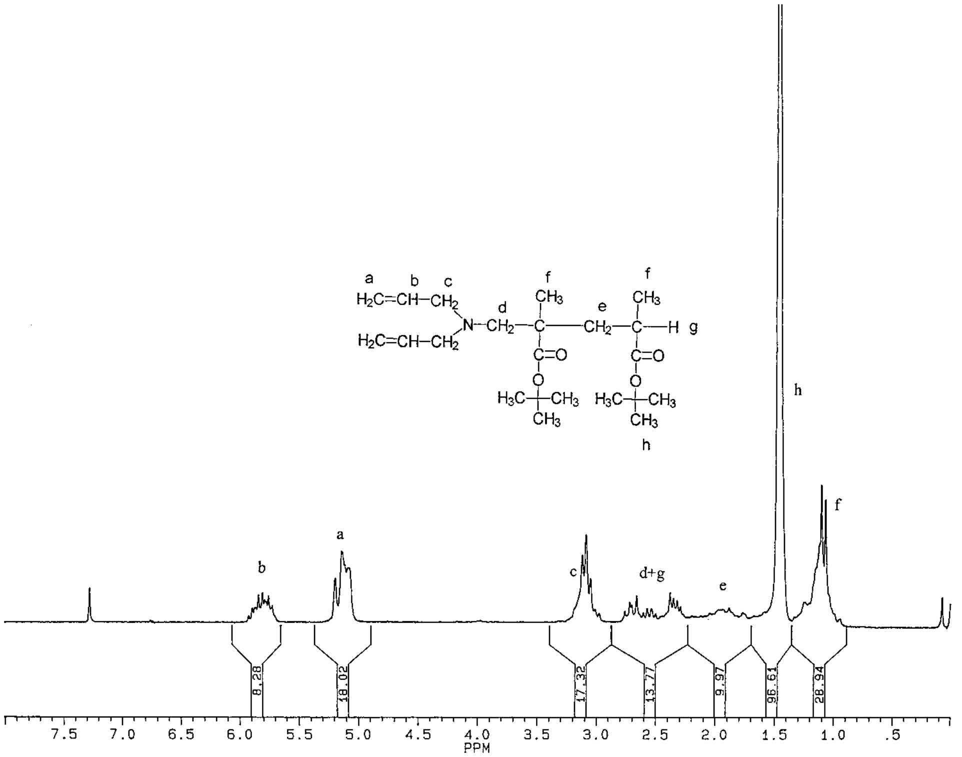


Figure 1. ^{1}H NMR spectra of the compound isolated from the reaction of diallylamine with sBuLi and *tert*-butyl methacrylate. [Diallylamine]/[sBuLi] = 1, [tBMA]/[diallylamine] = 2/1 in THF; −78 °C.

Table 1. Synthesis of DMAEMA Macromonomers by Living Polymerization of DMAEMA Initiated by Alkylamine/*sec*-Butyllithium in the Presence of Lithium Chloride[a]

entry	initiator	reaction temp (°C)	polym temp (°C)	LiCl/BuLi	DA/BuLi	conv (%)	M_n (calcd)	M_n (GPC)	efficiency	M_w/M_n
1	DA	0	0	10	1	33	1884	3 500		1.11
2	DA	25	−78	10	1	99	4700	32 700	0.16	1.09
3	DA	0	−78	10	1	99	4700	29 700	0.14	1.10
4	DA	−78	−78	0	1	99	4700	17 700	0.27	2.36
5	DA	−78	−78	1	1	99	4700	19 000	0.24	1.07
6	DA	−78	−78	3	1	98	4700	18 800	0.25	1.08
7	DA	−78	−78	10	1	99	4700	19 000	0.24	1.15
8	DA	−78	−78	10	10	97	9600	24 500	0.39	1.06
9	DA	−78	−78	10	10	97	12700	36 600	0.35	1.02
10	AAN	−78	−78	10	10	98	4700	5 888	0.79	1.06
11	AAM	−78	−78	10	10	0			0	

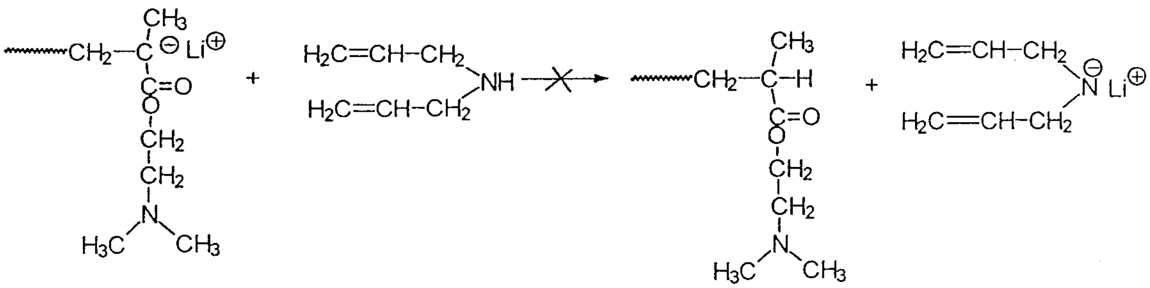
[a] −78 °C; [lithium amide] = 0.017 mol/L in THF; AAN = allylaniline; AAM = allylamine; DA = diallylamine.

After the catalyst was prepared, DMAEMA monomer was injected for polymerization. The effects of catalyst preparation and polymerization conditions are summarized in Table 1. If both the initiator preparation and polymerization of DMAEMA were carried out at 0 °C, the polymerization gave only 33% polymer (Table 1, entry 1). When the initiator was prepared at 0 or 25 °C while the polymerization was carried out at −78 °C, the conversion was almost complete, but the molecular weight of the resulting polymers was much higher than predicted (Table 1, entries 2 and 3). The initiation efficiency (the ratio of calculated M_n over measured M_n) with respect to diallylamine was only about 0.15. When both the initiator preparation and successive polymerization were carried out at −78 °C, the initiator efficiency increased to about 25% as shown in Table 1. The corresponding GPC trace shows a unimodal and extremely narrow molecular weight distribution. This result indicates that the initiation reaction was very fast, and once a polymer chain started to propagate, the propagating anions had no side reactions such as the reaction with carbonyl groups.

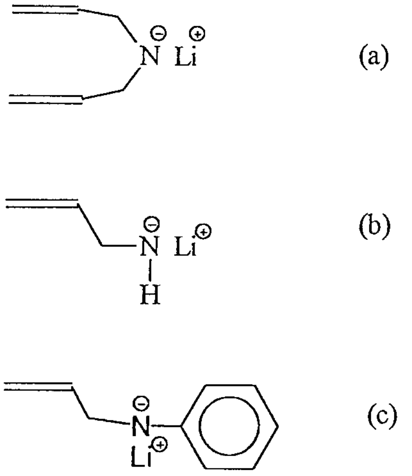
Experimental conditions were optimized in order to increase the initiator efficiency. The amount of added LiCl had some effect on the polymerization. In the absence of LiCl, the polymerization produced polymers with very broad molecular weight distribution (M_w/M_n = 2.36). But in the presence of LiCl, the polymers appeared to be nearly monodispersed (Table 1, entries 5−7). This agreed with the report that the presence of LiCl suppressed side reactions of carbon anions attacking the carbonyl groups in the polymer and monomer.[13] However, the presence of LiCl had no influence on the initiation efficiency. With or without LiCl, the initiation efficiencies of diallylamine were about 0.25.

The effect of added amount of diallylamine was also investigated. An excessive amount of diallylamine slightly increased the initiator efficiency, as shown in Table 1, entries 8 and 9. The molecular weight distribution of prepared polyDMAEMA remained very narrow, regardless of the amount of added diallylamine. This indicates that the propagating carbonanions did not abstract the proton in N−H of diallylamine (Scheme 2). This allows sBuLi to react with an excessive amount of diallylamine

Scheme 2. No Chain Transfer of Polymer Anion to Diallylamine



Scheme 3. Schematic Structures of the N-Substituted Allylaminolithium



to minimize possible side reactions of sBuLi during the initiator preparation.

Allylaniline (AAn) and allylamine (AAm) were tested for the polymerization of DMAEMA to further investigate the effect of substituents on the initiator efficiency (Table 1, entries 10 and 11). With lithium monoallylamide (Scheme 3b) as initiator, no polymer was obtained, while lithium allylphenylamide (Scheme 3c), derived from the reaction of allylaniline with sBuLi, had much higher initiator efficiency, 0.79, than that of lithium diallylamide (Scheme 3a). Apparently, the substituent on the nitroanion influences the initiator efficiency. For N-substituted allylamines, the efficiency increased by the order $0 < 25\% < 79\%$ with the substituent changed from H, allyl, to phenyl. This trend suggests that the low initiator efficiency of lithium diallylamide was inherent due to its low steric hindrance of the two allyl groups. In fact, a similar initiator efficiency was obtained when using lithium diethylamide as initiator in the MMA polymerization.[18]

Diallylamine/sBuLi Capping Agent Initiated Polymerization of DMAEMA. The low initiator efficiency of a lithium amide with less bulky substituents was ascribed to the association and side reactions with carbonyl groups in the monomer and polymer.[18] Increasing steric hindrance of the substituent decreased such association and minimizes these side reactions and thus increased initiator efficiency. Therefore, lithium diallylamide was modified by reacting it with dimethylacrylamide (DMA), *tert*-butyl methacrylate (tBMA), or methacrylnitrile (MAN) (capping reaction) to convert it into an anion with bulky substituents (Scheme 4). Table 2 summarizes the results of the DMAEMA polymerization with the capped lithium diallylamide.

Scheme 4. Capping Reaction of Diallylaminolithium with DMA and tBMA

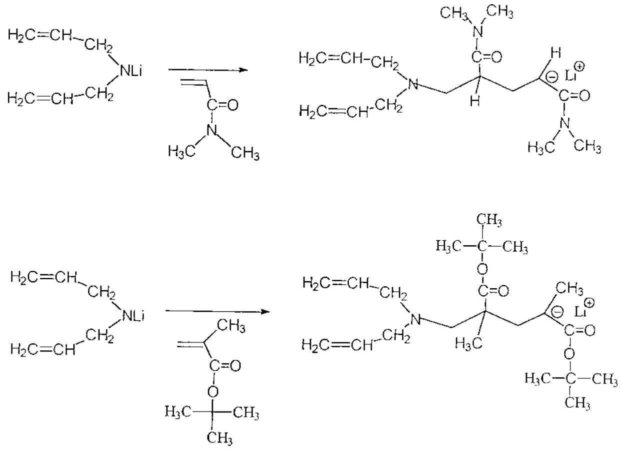


Table 2 shows that DMA or tBMA-capped lithium diallylamide had very high activities. The monomer conversions were almost complete. More importantly, the molecular weights of the polymers agreed well with predicted. The initiator efficiencies were as high as 0.90, in contrast to the low initiator efficiencies of the uncapped lithium diallylamide (Table 2, entries 2–5 and 9–11). The molecular weight distributions were also narrow, less than 1.1. The narrow GPC traces of the resulting polymers (Figure 2b,c) demonstrated that there was only a single type of initiation species. These results suggest that the capping reaction of lithium diallylamide with DMA or tBMA was complete, and the capped initiators did not associate each other in the solution and had no reactions with carbonyl groups. The complete capping reaction also indicates that lithium diallylamide did not have a strong association in the presence of LiCl, which was observed in the lithium diethylamide.[18] This conclusion was also confirmed by the lithium diallyamide-initiated homopolymerization of tBMA, in which high initiator efficiencies were also obtained.[20] Therefore, the low efficiency in the lithium diallylamide-initiated polymerization of DMAEMA (Table 1) was due to the reaction of lithium diallyamide with the carbonyl group, other than association.

When methacrylonitrile (MAN), which has a similar vinyl group of tBMA but without the bulky *tert*-butyl group, was used as a capping agent, the polymerization was less controlled (Table 2, entry 13). The resulting polymer had a much higher molecular weight than predicted with a broad molecular weight distribution. Actually, it was found that when MAN was added to the lithium diallylamide solution at −78 °C, the solution turned into red, which suggested that some lithium diallylamide reacted the CN group.

Table 2. DMAEMA Polymerization Initiated by Capped Lithium Diallylamide at −78 °C[a]

entry	capping agent	DMAEMA/amide ratio	LiCl/amide	solvent	conv (%)	M_n calcd	M_n GPC	initiator efficiency	M_w/M_n
1	DMA	30	0	THF	99	4700	38500	0.12	2.89
2	DMA	30	1	THF	98	4700	5310	0.89	1.06
3	DMA	27	3	THF	99	4200	4440	0.95	1.04
4	DMA	78	3	THF	98	12300	13800	0.90	1.08
5	DMA	150	3	THF	99	23300	25500	0.93	1.04
6	DMA	30	3	THF−toluene[b]	95	4700	24600	0.19	4.86
7	DMA	30	10	THF	99	4700	9600	0.49	1.06
8	DMA	60	10	THF	100	7720	15200	0.51	1.08
9	tBMA	30	3	THF	99	4700	4900	0.96	1.03
10	tBMA	50	3	THF	99	7800	8300	0.94	1.05
11	tBMA	64	3	THF	99	10000	11500	0.87	1.07
12	tBMA	60	10	THF	97	9420	17000	0.55	1.04
13	MAN	30	3	THF	100	4700	19500	0.21	1.31

[a] [Diallylaminolithium] = 0.017 mol/L. [b] Toluene/THF = 9/1 (v/v).

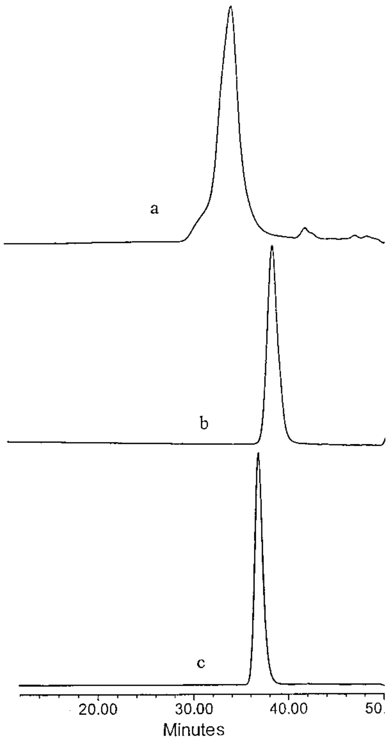


Figure 2. GPC traces of polyDMAEMA initiated by DMA-capped lithium diallylamide: (a) without LiCl (Table 2, entry 1), (b) with 3-fold LiCl (Table 2, entry 3), and (c) with 10-fold LiCl (Table 2, entry 7).

The LiCl concentration had a dramatic effect on the DMAEMA polymerization initiated by the capped lithium diallylamide. Without LiCl, DMA-capped lithium diallylamide had a very low initiation efficiency (Table 2, entry 1), even lower than that of uncapped initiator (Table 1). The polymer produced had a broad molecular weight distribution (Figure 2a). Adding 1−3-fold LiCl with respect to lithium diallylamide substantially increased the initiator efficiency to 0.90 and yielded polymers with extremely narrow molecular weight distributions (Table 2, entries 2−5) (Figure 2b). This agreed with the results in other polymerization systems.[21] However, we found that excessive amount of LiCl had a detrimental effect on the initiation efficiency for both DMA and tBMA-capped lithium diallylamide (Table 2, entries 7, 8, and 12). For example, the efficiencies of the capped lithium diallylamide decreased to about 0.5 with a 10-fold LiCl. This effect of excess LiCl may be due to the fact that too many LiCl molecules surrounded an initiator anion, and thus some initiators may become dormant in clusters and inactive in the initiation of DMAEMA. We also tested toluene/THF (9:1 v/v) as a solvent and found low initiator efficiency and very poor control of molecular weight (Table 2, entry 6).

Characterization and Quaternization of the Macromonomers. The macromonomers prepared were characterized by ^{1}H NMR. Figure 3 shows the NMR spectrum of polyDMAEMA. Signals of polyDMAEMA backbone are at 2.25 ppm ($N(CH_3)_2$), 2.55 ppm (NCH_2), 4.05 ppm ($COOCH_2$), 1.65−2.05 ppm ($CH_2{-}C{-}CH_3$), and 0.87−1.05 ppm ($CH_3{-}C$). Signals due to the diallylamino group appear at 5.1 ppm (m, $CH_2{=}$) and 5.7 ppm (m, $={CH}$) (Figure 3A), which are very similar to the signals of diallylamine. The signals of allyl group in allylphenylamino appear upfield, 5.6 ppm (m, $={CH}$) and 5.05 ppm (m, $CH_2{=}$), due to the conjugation of benzene ring with the nitrogen atom. These results indicated that the polymers had the desired diallylamino or allylphenylamino terminal groups.

The allyl group is not an reactive polymerizable group. But allyl on a quaternary nitrogen atom is readily polymerizable. For example, diallyldimethylammonium chloride (DADMAC) is an important cationic monomer for homopolymer and random copolymers widely used in industry.[1,22] Therefore, the allyl-terminated polymers were reacted with quaternization agents to prepare polymerizable cationic macromonomers. Two types of nitrogen atoms, in pendant dimethylamino and terminal diallyamino or allylphenylamino groups, need to be quaternized. The two types of nitrogen atoms showed very different activities toward quaternization. The nitrogen atoms in dimethylamino groups were easily quaternized by CH_3I at room temperature or by benzyl chloride at 40 °C. For example, after 1 h of reaction with CH_3I at room temperature, all the nitrogen atoms in dimethylamino groups were converted into trimethylammonium ($(CH_3)_3N^+$), as shown in Figure 4. The signal of NCH_3 at 2.25 ppm disappeared completely while a strong peak for N^+CH_3 appeared at 3.20 ppm. However, the signals of allyl groups did not change at all (Figure 4A). Increasing quaternization temperature or prolonging the reaction time could partially quaternize these terminal groups but caused some double bonds to disappear, possibly due to reactions with I_2 generated from the decomposition of CH_3I.

The more powerful methylizating agent, $(CH_3)_2SO_4$, can quantitatively quaternize both types of tertiary amino groups in the polymer. For example, after 1 h of reaction in DMSO at room temperature, the terminal

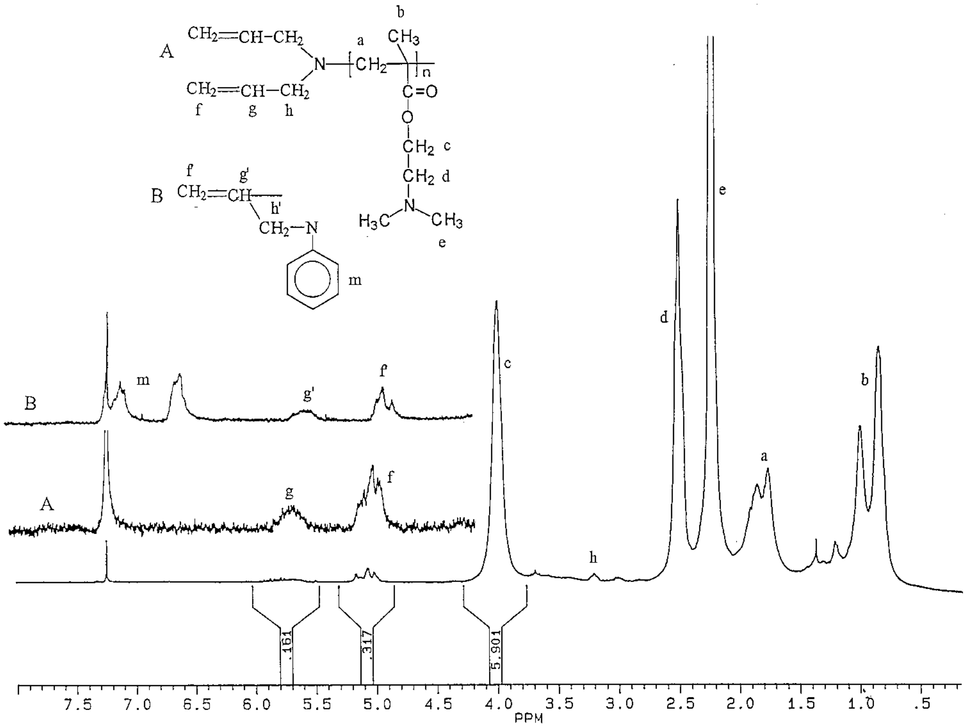


Figure 3. ^{1}H NMR spectra of polyDMAEMA macromonomers prepared by (a) diallylamine–sBuLi and (b) allylphenylamine–sBuLi.

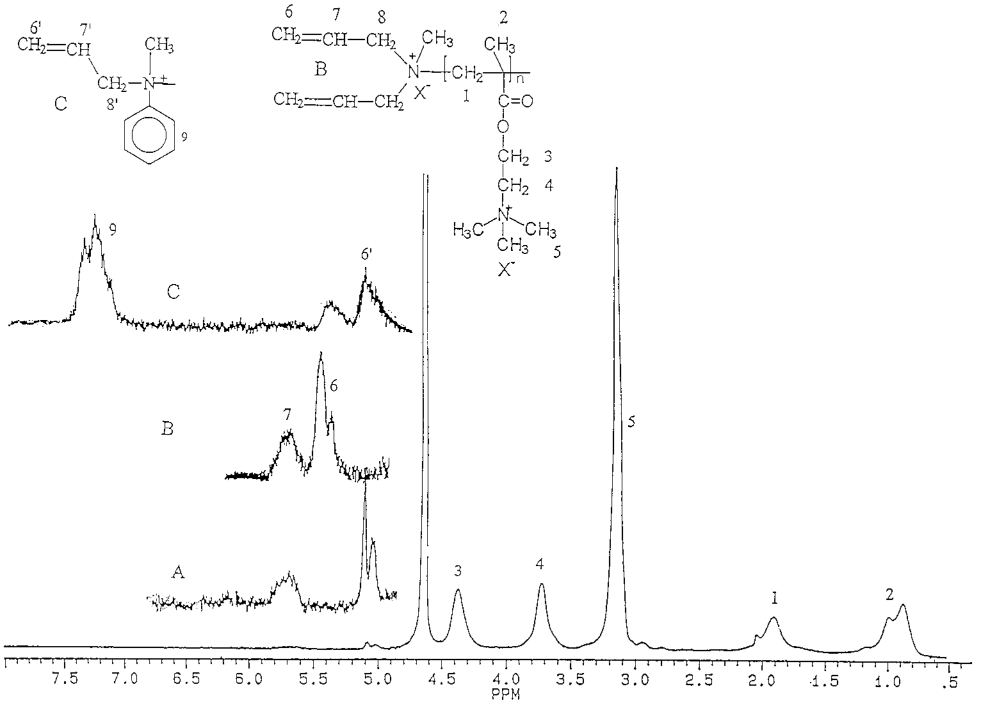


Figure 4. ^{1}H NMR spectra of quaternized polyDMAEMA macromonomers: (a) diallylamino-terminated polyDMAEMA reacted with CH_3I at room temperature for 1 h, (b) diallylamino-terminated polyDMAEMA reacted with $(CH_3)_2SO_4$ in DMSO for 1 h, and (c) allylphenylamino-terminated polyDMAEMA reacted with $(CH_3)_2SO_4$ in DMSO for 6 h.

diallylamino group was completely quaternized, as seen in NMR spectra (Figure 4B). The allyl proton signals at 5.1 ppm (CH_2=) in nonquaternized diallylamine shifted to 5.45 ppm after quaternization, which was the same as the signals of that in diallyldimethylammonium chloride. The complete quaternization of allylphenylamino group with dimethyl sulfate required longer time (Figure 4C). This lower reactivity of the allylphenylamino group may be due to the combination of high steric hindrance effect of the benzene ring and the conjugation of the nitrogen atom with benzene ring, which substantially decreases the electron density on the nitrogen atom.

The cationic macromonomer was found to have good reactivity in the copolymerization with acrylamide and vinylformamide, producing water-soluble comb-branched copolymer with uniform cationic side chains and nonionic backbones. These results will be reported soon.

Conclusions

(1) Cationic polyDMAEMA macromonomers with polymerizable terminal vinyl groups were successfully synthesized by a living anionic polymerization initiated by N-substituted lithium allylamide systems and subsequent quaternization.

(2) The substituent on the nitroanion strongly affected on the initiator efficiency, which increased by 0 < 25% < 79% with the substituent changed from H, allyl, to phenyl.

(3) A capping method for nitroanion was developed to increase the initiator efficiency. The initiator efficiency of lithium diallylamide was thus increased from 0.25 to 0.9 by capping it with dimethylacrylamide or *tert*-butyl methacrylate.

(4) One- to threefold LiCl with respect to initiator was necessary for a well-controlled polymerization of DMAEMA. However, an excess of LiCl reduced the initiator efficiency.

(5) The quaternization of terminal diallylamino and allylphenylamino groups required a strong methylizating agent such as $(CH_3)_2SO_4$, while the dimethylamino group in the polymer chain was readily quaternized by CH_3I.

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