Synthesis and Characterization of Comb-Branched Polyelectrolytes. 1. Preparation of Cationic Macromonomer of 2-(Dimethylamino)ethyl Methacrylate by Atom Transfer Radical Polymerization

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ABSTRACT: The synthesis of water-soluble macromonomers of 2-(dimethylamino)ethyl methacrylate (DMAEMA) by atom transfer radical polymerization (ATRP) was studied in detail. The survival of the unsaturated groups in the initiators during the macromonomer preparation as well as the initiator efficiency depended on the nature of initiator and type of ligand used. The kinetics of the ATRP of DMAEMA catalyzed by allyl 2-bromoisobutyrate (ABIB)/copper bromide (CuBr)/*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) system at different conditions indicated that the low initiator efficiency of the ATRP system could not be improved by increasing temperature or changing solvents. It was found that ABIB/CuBr/tris(2-di(butylacrylate)aminoethyl)amine (BA_6-TREN) and allyl trichloroacetamide (ATCA)/CuBr/BA_6-TREN gave high initiator efficiencies and excellent control over the molecular weights and molecular weight distributions in the ATRP of DMAEMA. ^{1}H NMR studies confirmed that each polyDMAEMA chain had a polymerizable allyl end group. These allyl-terminated polyDMAEMAs after quaternized were proven to be reactive in the copolymerization with acrylamide.

Introduction

Water-soluble polymers have played an important role in papermaking, mineral processing, and wastewater treatment.[1] Random copolymers of acrylamide with cationic monomers are widely used for flocculation in wastewater treatment and for fines retention in papermaking process. Recently, we have shown that graft polymers with active cationic units concentrated on pendant chains gave better flocculation performance than the corresponding random copolymers.[2−4] The graft copolymers were prepared by γ-irradiation of the aqueous mixtures of poly(acrylamide) and poly(diallyldimethylammonium chloride). This procedure was not very selective and was difficult to control and resulted in a mixture of structures. On the basis of these promising initial results, we undertook an investigation to determine the detailed links between flocculation efficiency and graft copolymer structure. For this, well-defined graft copolymers were required. The macromonomer copolymerization technique was chosen as the best approach. The length of the pendant side chain and its density in the copolymer can be controlled by varying the macromonomer molecular weight and charged amount. Therefore, the major challenge is to prepare well-defined macromonomers.

Traditionally, well-defined macromonomers with narrow molecular weight distributions and terminal unsaturated groups are best prepared via living anionic polymerization,[5−8] group transfer polymerization,[9] and living cationic polymerization.[10,11] The reactive vinyl terminal groups can be introduced by end-capping or living polymer deactivation. For example, Ishizu and coworkers synthesized styrenic-functionalized poly(acrylic acid) by using chain transfer agent, followed by end-capping with 4-chloromethylstyrene.[12−14] There were only a few reports on direct synthesis of vinyl macromonomers of polymethacrylates because of the high selectivity of the initiator type. Recently, Nagasaki et al. and Lascelles et al. reported the synthesis of macromonomers of 2-di(ethylamino)ethyl methacrylate (DEAEMA)[15] and 2-(dimethylamino)ethyl methacrylate (DMAEMA) with terminal unsaturated groups by oxyanion-initiated polymerization.[16,17] However, these oxyanionic polymerizations had low initiator efficiencies and imprecise molecular weight control. In addition, living ionic polymerization requires stringent experimental conditions that often make industrial applications difficult and are limited to only a small number of monomer systems.

A new living radical polymerization process called atom transfer radical polymerization (ATRP) has been proven to be versatile for various vinyl polymerizations, such as styrene,[18,19] methacrylate,[19,20] acrylonitrile,[21] 2-(dimethylamino)ethyl methacrylate,[22] and 4-vinylpyridine,[23] as well as their block copolymers. An advantage of ATRP is that it does not require strict experimental conditions such as anionic and cationic polymerization. Therefore, this living process provides a new approach for the synthesis of macromonomers with controlled molecular weight and molecular weight distribution. For example, well-defined polystyrene macromonomers were prepared by ATRP of styrene initiated by vinyl chloroacetate or allyl bromide mediated by CuBr/bipyridine.[24,25] However, the initiators and ligands for the synthesis of macromonomers by copper-based ATRP were found to be very selective. For example, mediated by CuBr/bipyridine, vinyl chloroacetate was able to initiate styrene polymerization without damaging its vinyl group, while our work showed that vinyl chloroacetate could not initiate DMAEMA polymerization using CuBr as catalyst and BA_6-TREN or HMTETA as ligands at 60 °C. Similarly, the allyl group was found to polymerize and cause crosslinking in the ATRP polymerization of allyl acrylates

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catalyzed by CuBr/bipyridine system.[26] But this work showed that the allyl group in the initiator, allyl 2-bromoisobutyrate, was not consumed during the ATRP polymerization of DMAEMA catalyzed by CuBr/multidentate amine ligands, and thus polyDMAEMA macromonomers with terminal allyl group were obtained. Most importantly, these terminal allyl groups could copolymerize with acrylamide.

In this paper, we report the synthesis of DMAEMA macromonomers with terminal allyl group using CuBr-based ATRP system. The effects of ligands, initiators bearing allyl or vinyl functional groups, and experimental conditions were investigated in detail. The kinetics of the selected systems were also examined. After quaternization, the macromonomers were used to copolymerize with acrylamide to give comb-branched copolymers.

Experimental Section

Materials. The catalyst Cu(I)Br, the initiators allyl 2-bromoisobutyrate (ABIB), allyl bromide (AB), vinyl chloroacetate (VCA), vinyl benzyl chloride (VBC), and 2,2′-azobis(2-methylpropionamidine) dihydrochloride (AIBA, used as a radical initiator for the conventional copolymerization of acrylamide with macromonomers), and ligands *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), 18-crown-6, and tris(2-aminoethyl)amine (TREN, used as a precursor for synthesizing two new ligands described later) were obtained from Aldrich and used without further purification. Vinyl monomers 2-(dimethylamino)ethyl methacrylate (DMAEMA), methyl acrylate (MA), and *n*-butyl acrylate (BA) (MA and BA used as precursors for the two new ligands), all supplied by Aldrich, were distilled from CaH_2 prior to use. Solvents tetrahydrofuran (THF), methanol (MeOH), ethyl acetate (EtOAc), butyl acetate (BuOAc), dimethylformamide (DMF), γ-butyrolactone, 2-propanol, dimethyl sulfoxide (DMSO), formamide, and ethylene glycol were used after distillation. Acrylamide (AM) from Aldrich was recrytallized. Chemicals allylamine, trichloroacetate, 2-methyl-3-buten-2-ol, 2-bromopropionyl bromide, and triethylamine as precursors for preparing two new initiators were used as received from Aldrich.

Synthesis of Allyl Trichloroacetamide (ATCA) and (2-Methylbutenyl) 2-Bromopropionate (MBBP). To a solution of allylamine (5 mL, 66.64 mmol) and triethylamine (9.30 mL, 66.80 mmol) in 50 mL of dried THF cooled in ice−water bath was added dropwise trichloroacetate chloride (7.48 mL, 66.64 mmol) (allylamine reacted with trichloroacetate chloride to yield ATCA and HCl with the HCl absorbed by triethylamine). The mixture was magnetically stirred for 1 h at 0 °C and then 2 h at room temperature. Triethylamine hydroxy chloride salt was filtrated and washed with 10 mL of THF three times. After THF was evaporated, the crude product was distilled under vacuum. The product was recrystallized in hexane to give a colorless powder. Yield: 79.0% (10.7 g) with respect to allylamine or trichloroacetate chloride. ^{1}H NMR ($CDCl_3$, 200 MHz): 4.05 ppm (2H, m, NH−CH_2−CH=CH_2), 5.29 ppm (2H, m, NH−CH_2−CH=CH_2), 5.93 ppm (1H, m, NH−CH_2−CH=CH_2), 6.82 ppm (1H, br, NH−).

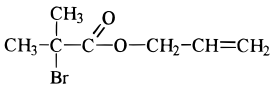
Following the same procedure, (2-methylbutenyl) 2-bromopropionate (MBBP) was prepared using 2-methyl-3-buten-2-ol, 2-bromopropionyl bromide, and triethylamine with a yield of 73.4%. ^{1}H NMR ($CDCl_3$, 200 MHz): 1.54 (6H, br, CH_2=CH−C(CH_3)$_2$−O), 1.75 (3H, d, CH_3−CHBr−COO−), 4.26 (1H, q, CH_3−CHBr−COO−), 5.13 (2H, q, CH_2=CH−C(CH_3)$_2$−O), 6.04 (1H, q, CH_2=CH−C(CH_3)$_2$−O).

The molecular structures of all the initiators used in this paper are shown in Scheme 1.

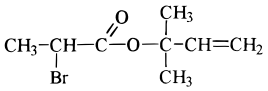
Synthesis of Tris(2-di(butylacrylate)aminoethyl)amine (BA_6-TREN) and Tris(2-di(methylacrylate)aminoethyl)-amine (MA_6-TREN). The two products were synthesized by a slightly modified method of Klee et al.[27] To 26.3 g (0.205 mol) of butyl acrylate was added dropwise tris(2-aminoethyl)-amine (5.0 g, 34.2 mmol) at 0−5 °C. The mixture was magnetically stirred for 2 h at 0−5 °C and then was reacted for further 24 h at room temperature. After evacuating the residual butyl acrylate, the purified crude product, yellowish liquid, was obtained. Yield: 98.7% (30.8 g). ^{1}H NMR ($CDCl_3$, 200 MHz): 0.88 (18H, m, 6 −CH_3), 1.28 (12H, m, 6 −CH_2−CH_3), 1.55 (12H, m, 6 −CH_2−CH_2−CH_3), 2.39 (24H, m, 3 N−CH_2−CH_2−N−(CH_2−CH_2−COO)$_2$), 2.70 (12H, t, 6 N−CH_2−CH_2−COO), 4.04 (12H, m, 6 COO−CH_2−).

Tris(2-di(methyl acrylate)aminoethyl)amine (MA_6-TREN) was prepared by the same procedure using methyl acrylate and tris(2-aminoethyl)amine. Yield: 97.9% (22.2 g). ^{1}H NMR ($CDCl_3$, 200 MHz): 2.44 (24H, m, 3 N−CH_2−CH_2−N−(CH_2−CH_2−COO)$_2$), 2.72 (12H, t, 6 N−CH_2−CH_2−COO), 3.63 (18H, br, 6 −CH_3).

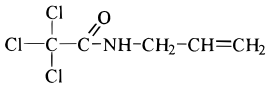
Scheme 1



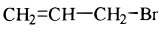
allyl 2-bromoisobutyrate (ABIB)



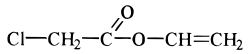
(2-methyl butenyl) 2-bromo propionate(MBBP)



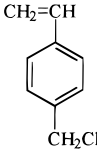
allyl trichloroacetamide(ATCA)



allylbromide (AB)

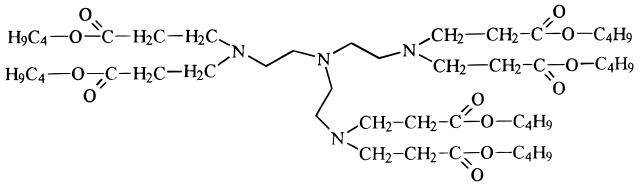


vinyl chloroacetate(VCA)

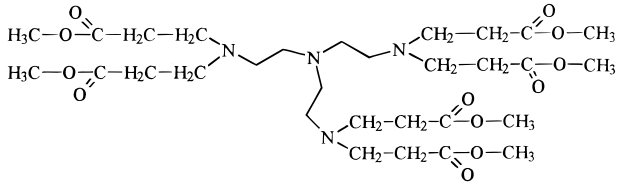


vinyl benzylchloride (VBC)

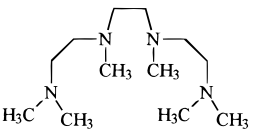
Scheme 2



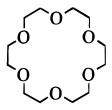
tris [2-di(butyl acrylate)amino ethyl]amine (BA_6-TREN)



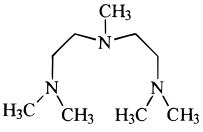
tris [2-di(methyl acrylate)amino ethyl]amine(MA_6-TREN)



1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA)

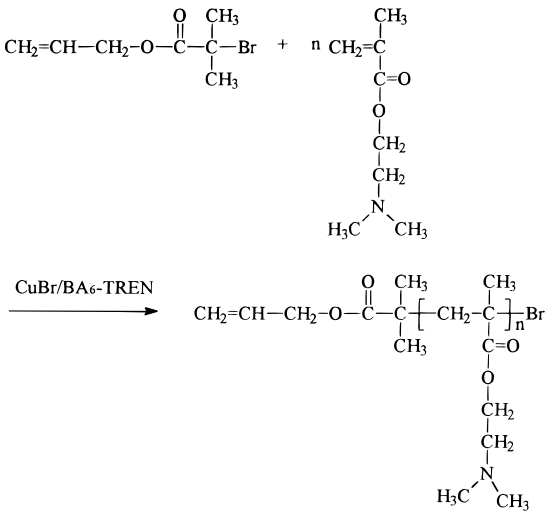


18-crown-6



N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA)

Scheme 3



Scheme 2 shows the molecular structures of the ligands used in this work

ATRP of DMAEMA. The ATRP polymerization of DMAEMA was carried out in bulk and in solution. In a typical experiment, 1 g (6.36 mmol) of DMAEMA, 9.14 mg (0.0636 mmol) of Cu(I)Br, 58.14 mg (0.0636 mmol) of BA_6-TREN, and 1.1 mL of THF were charged to a 10 mL tube reactor. The tube was degassed with argon for 10 min before being sealed with a rubber septum. Initiator was also degassed before being added to the tube by a microsyringe. The tube was then immersed into an oil bath set to a required temperature. The polymerization was terminated by immersing the tube into an ice−water bath. The mixture was diluted by THF, and the polymer was then precipitated in hexane or petroleum ether and dried in a vacuum. Conversion was determined either gravimetrically or by ^{1}H NMR (only for bulk polymerization). The resulting macromonomers were purified by passing through a silica gel column.

Macromonomer Quaternization and Copolymerization with Acrylamide. To a solution of 2 g of purified macromonomer (0.286 mmol from 99-18-5, M_n = 6500) in 30 mL of acetone was added methyl iodide (1.79 g, 12.7 mmol). The mixture was magnetically stirred for 1 h at room temperature. Then the quaternized macromonomer was separated by filtration and washed with 10 mL of acetone for three times and dried under vacuum to give a colorless powder. Yield: 96.8% (3.67 g). ^{1}H NMR ($CDCl_3$, 200 MHz): 0.90 (3H, br, (−CH_2−C(CH_3)−COO−), 1.92 (2H, br, (−CH_2−C(CH_3)−COO−), 3.17 (9H, (−N(CH_3)$_3^+$I$^-$), 3.75 (2H, (−O−CH_2−CH_2−N(CH_3)$_3^+$I$^-$), 4.39 (2H, (−O−CH_2−CH_2−N(CH_3)$_3^+$I$^-$), 5.19 ppm (2H, allyl proton), 5.80 ppm (1H, allyl proton).

Copolymerization of the quaternized macromonomer with acrylamide was conducted using AIBA as a radical initiator. A 0.2 g (0.016 mmol from above sample, M_n = 12 400) sample of the macromonomer, 0.2 g (2.8 mmol) of acrylamide, 1 mg of AIBA, and 2 mL of water were charged to a 10 mL tube reactor. The tube was degassed with argon for 10 min and sealed with a rubber septum. The tube was then immersed into a water bath at 60 °C. After reaction for 4 h, the polymer was precipitated in methanol and dried in a vacuum to yield 0.38 g of comb polymer with conversion 95% with respect to the total monomers charged.

Measurements. ^{1}H NMR spectra were obtained on a Bruker AC-P200 Fourier transform spectrometer (200 MHz for ^{1}H) in $CDCl_3$ or D_2O solvent. The chemical shifts were reported in ppm with signals of trace of $CHCl_3$ or H_2O as internal standard. GPC measurements were carried out using a Waters 590 liquid chromatography equipped with three Varian MicroPak columns (G1,000, 3,000, and 7,000HXL) with a 410 differential refractometer detector. THF with 2% triethylamine was used as solvent. Narrow polystyrene standards (Polysciences) were used to generate the calibration curve. Data were recorded and processed using the Millennium 2.0 software package.

Results and Discussion

Effects of Initiator and Ligand on the Synthesis of Macromonomers by ATRP Process. A key criterion for macromonomer synthesis (see Scheme 3) is that the vinyl group associated with the initiator is not consumed during macromonomer synthesis because this terminal group becomes the reactive center for subsequent macromonomer copolymerization. Therefore, different combinations of initiators and ligands were screened for the synthesis of macromonomers by ATRP of DMAEMA mediated by copper bromide. The results are summarized in Table 1.

It can be seen that the initiators can be classified into three groups. The first group initiators are those who showed no activity in the ATRP of DMAEMA. For example, VCA could not initiate the DMAEMA polymerization mediated by CuBr with BA6-TREN or HMTEMA as ligand. This is very different from Coca and Matyjaszewski's results that VCA initiated a living polymerization of styrene polymerization and produced macromonomers.[26] The activity of the initiators also depended on the type of ligand used. For example, AB could initiate DMAEMA polymerization when BA_6-

Table 1. Effects of Initiator Type and Ligand Type on Bulk Polymerization of DMAEMA at 60 °C[a]

run	initiator	ligand	time (h)	conv (%)	$M_{n,cal}$	$M_{n,SEC}$	$M_{n,NMR}$	$M_{w,SEC}/M_{n,SEC}$	$f = M_{n,cal}/M_{n,NMR}$
99−18−4	VCA	BA_6-TREN	20.0	0					
99−18−2	AB	BA_6-TREN	5.0	53.0	4200	30600		2.6	0.14[b]
99−18−3	VBC	BA_6-TREN	2.0	gel					
99−17−1	ABIB	BA_6-TREN	0.5	98.5	7700	8000	8600	1.34	0.90
99−18−1	MBBP	BA_6-TREN	0.5	92.4	7200	8900	8500	1.70	0.85
99−18−5	ATCA	BA_6-TREN	5.0	89.4	7000	6500	7000	1.18	0.99
99−11−5	VCA	HMTETA	20.0	0					
99−11−6	AB	HMTETA	20.0	0					
99−11−4	VBC	HMTETA	5.0	96.3	7500	11400		2.01	0.66[b]
99−11−1	ABIB	HMTETA	0.5	96.7	7601	7700	8800	1.27	0.86
99−11−2	MBBP	HMTETA	2.0	90.3	7100	8600	8050	1.67	0.88
99−11−3	ATCA	HMTETA	5.0	76.2	5990	5600	6000	1.18	0.99
99−17−4a	VBC	PMDETA	5.0	Gel					
99−17−4	ABIB	PMDETA	0.5	99.5	7800	21100		1.30	0.37[b]
99−17−2	ABIB	MA6-TREN	0.5	97.5	7700	6600	8300	1.39	0.92
99−17−5	ABIB	18-crown-6	20	87.1	6800	9200		1.50	0.74[b]
99−17−6	ABIB	no ligand	20	93.3	7300	5500		2.31	

[a] DMAEMA/initiator/CuBr/ligand = 50:1:1:1 in moles. f = initiator efficiency; $b = M_{n,cal}/M_{n.SEC}$.

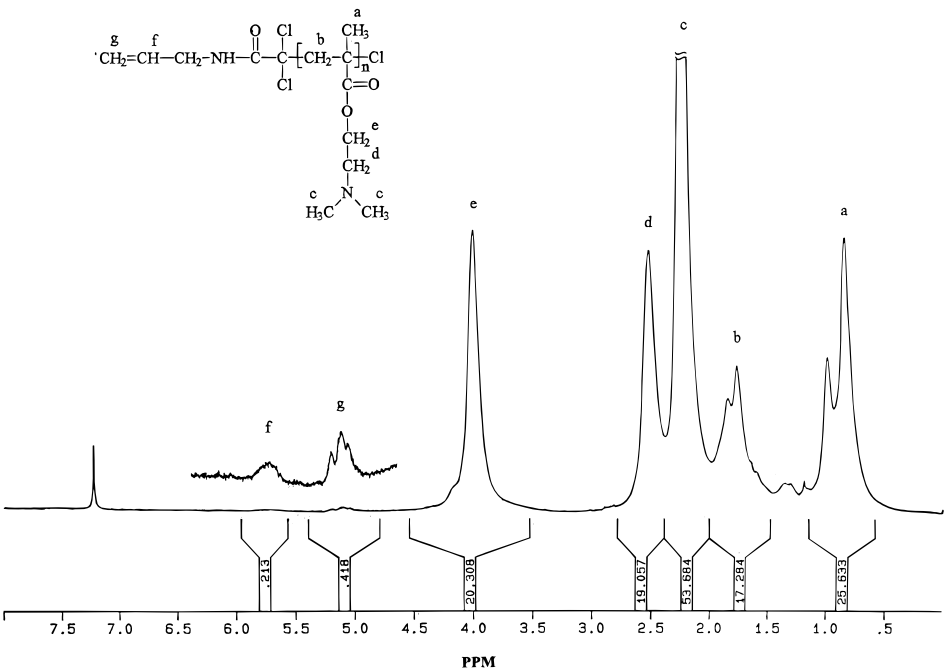


Figure 1. ^{1}H NMR spectrum of polyDMAEMA macromonomer: DMAEMA/ATCA/CuBr/BA_6-TREN = 50:1:1:1 in moles with molecular weight M_n = 7000 from GPC (sample 99-18-5).

TREN was used as ligand, while it could not when HMTEMA used as ligand.

The second group of initiators could initiate the DMAEMA polymerization but caused cross-linking or broad molecular weight distribution. The typical example was VBC. For example, with VBC as initiator, DMAEMA polymerization mediated by CuBr−BA_6-TREN or CuBr−PMDETA became cross-linked even at very low conversions. This means that the VBC's styrenyl group was also (co)polymerized during the ATRP process of DMAEMA. By contrast, mediated by CuBr−HMTEMA, the polymerization did not cross-link, but the molecular weight distribution of the resulting poly(DMAEMA) was up to 2.

The third group initiators initiated the ATRP of DMAEMA yielded the desired narrow molecular weight distribution macromonomers. These initiators included ABIB and ATCA. For example, with ATCA and ABIB as initiators and mediated by CuBr−BA_6-TREN, the polydispersities of polyDMAEMA were 1.18 and 1.34, respectively, with high initiator efficiencies (higher than 90%).

These results showed that the initiator activity depended on the type of the carbon−halogen bond. The secondary (MBBP) and tertiary carbon bromide (ABIB) as well as the multiple chlorine-based initiators (ATCA) were highly active, giving high initiator efficiencies, while the compounds having a strong carbon−halogen bond, such as AB, VCA, and VBC, were poor initiators for the methacrylate. This agreed with the Matyjaszewski's results.[21,28−30] It was also observed that the survival of the vinyl moiety in the initiator during the macromonomer preparation depended on the relative reactivity of the vinyl moiety with respect to the monomer. The low reactivity of the allyl group with respect to methacrylate was the determining factor for the survival of the vinyl moiety in ABIB, MBBP, and ATCA. However, the catalyst also played some role in the survival of the vinyl moiety. For example, when CuBr−HMTETA was used as catalyst, VBC did not have cross-linking although the polydispersity of poly-

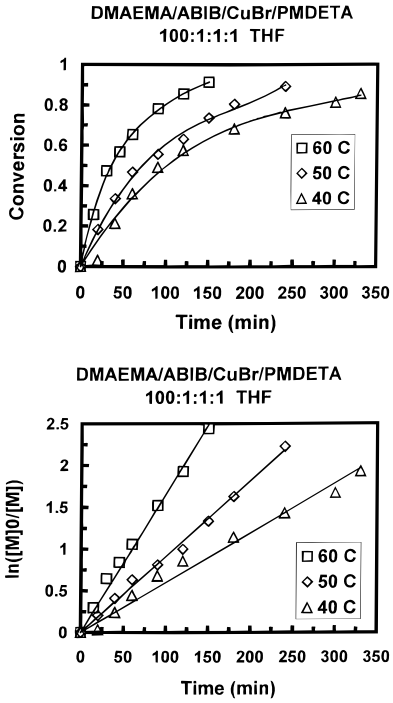


Figure 2. Monomer conversion of THF solution polymerization of DMAEMA at 40, 50, and 60 °C with $[DMAEMA]_0$ = 2.96 M and $[ABIB]_0 = [CuBr]_0 = [PMDETA]_0$ = 0.0296 M: (A) conversion versus time, (B) $\ln([M]_0/[M])$ versus time.

DMAEMA was high. For comparison, when CuBr−BA_6-TREN or CuBr−PMDEDA was used, VBC experienced gelation even at very low conversions.

The ligand type also strongly affected the activity of the initiators and the polymer properties, as shown in Table 1. AB could initiate the DMAEMA polymerization catalyzed by CuBr−BA_6-TREN, while it showed no activity when HMTEMA replaced BA_6-TREN. The initiator efficiency depended on the ligand type. With CuBr as catalyst and ABIB as initiator, the initiator efficiency increased by the order PMDETA < 18-crown-6

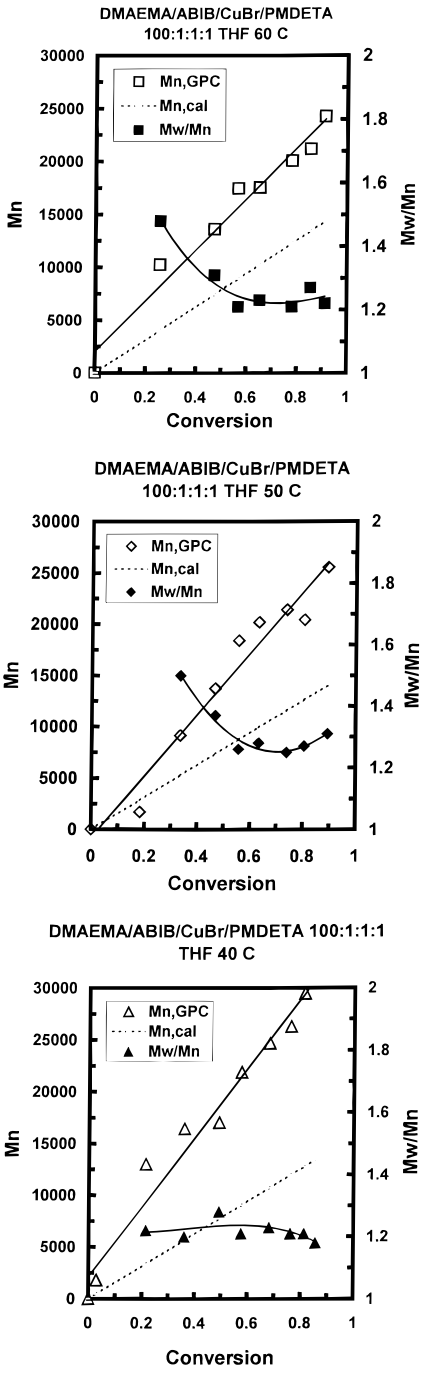


Figure 3. Molecular weight development of THF solution polymerization of DMAEMA at (A) 60, (B) 50, and (C) 40 °C with $[DMAEMA]_0 = 2.96$ M and $[ABIB]_0 = [CuBr]_0 = [PMDETA]_0 = 0.0296$ M. The molecular weights were measured by GPC.

< HMTETA < MA_6-TREN ≅ BA_6-TREN. The polydispersity of polyDMAEMA was also related to the ligand type. The polydispersities of polyDMAEMA were between 1.2 and 1.3 when BA_6-TREN, MA_6-TREN, HMTEMA, and PMDEMA were used. By contrast, the polydispersity of polyDMAEMA was higher than 1.5 when 16-crown-6 ether was used.

The macromonomer structure was confirmed by ^{1}H NMR spectra (see Figure 1). The allyl proton signals of polyDMAEMA using ATCA as an initiator appeared at 5.15 (2H, C*H*$_2$═CH−) and 5.72 (1H, CH$_2$═C*H*−). The polymers prepared by ABIB systems also showed similar allyl proton signals. ATCA may act as a bifunctional

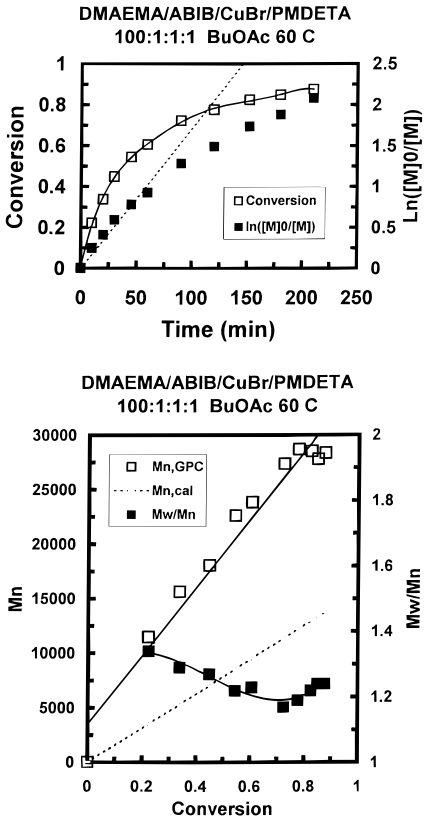


Figure 4. Monomer conversion and molecular weight development of *n*-butyl acetate solution polymerization of DMAEMA at 60 °C with $[DMAEMA]_0 = 2.96$ M and $[ABIB]_0 = [CuBr]_0 = [PMDETA]_0 = 0.0296$ M: (A) conversion and ln($[M]_0/[M]$) versus time and (B) number-average molecular weight and polydispersity versus conversion.

initiator, resulting in chain growth in two directions with the ally group in the center of the polymer chain.[31] The higher initiator efficiencies of ATCA/CuBr/BA_6-TREN, ABIB/CuBr/BA_6-TREN, and ABIB/CuBr/HMTETA systems and the narrow molecular weight distributions of their resulting polymers indicated that the terminal allyl groups were not (co)polymerized during the ATRP process of DMAEMA. The number-average molecular weights by ^{1}H NMR were in agreement with the theoretical values. These results are different from a recent report that the allyl group of allyl acrylate was polymerized during the polymerization of allyl acrylate monomers and resulted in cross-linking when the CuBr/bipyridine system was used.[27]

Kinetics of the DMAEMA Polymerization Mediated by CuBr−PMDETA and CuBr−BA_6-TREN with ABIB as Initiator. Table 1 showed that the ligand type had a very strong effect on the initiator efficiency and the polymer chain properties. To further understand the effects of other experimental factors such as temperature and solvent, two selected systems, ABIB/CuBr/PMDETA and ABIB/CuBr/BA_6-TREN, were studied in detail for the kinetics of the ATRP of DMAEMA.

First, the ABIB/CuBr/PMDETA system, which had low initiator efficiencies, was investigated to see whether varying other experimental factors such as temperature and solvent type could enhance the initiator efficiency. When PMDETA was used as ligand, the polymerization solution was heterogeneous both in bulk and in solution. The effect of temperature on the polymerization rate was investigated at temperatures 40, 50, and 60 °C.

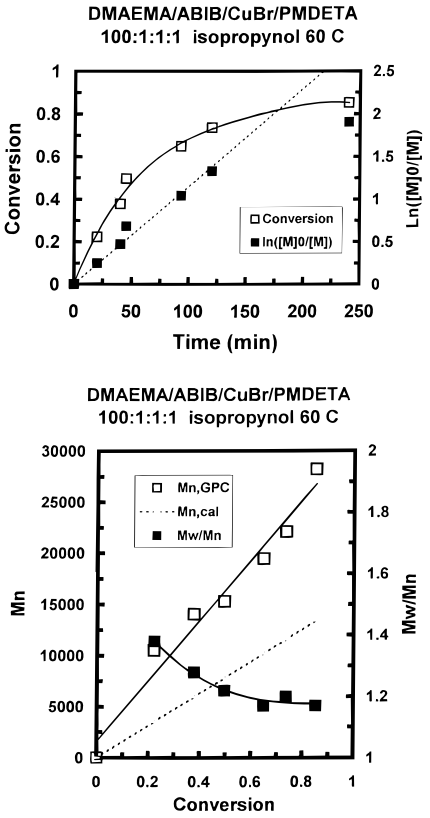


Figure 5. Monomer conversion and molecular weight development of 2-propanol solution polymerization of DMAEMA at 60 °C with $[DMAEMA]_0 = 2.96$ M and $[ABIB]_0 = [CuBr]_0 = [PMDETA]_0 = 0.0296$ M: (A) conversion and $\ln([M]_0/[M])$ versus time and (B) number-average molecular weight and polydispersity versus conversion.

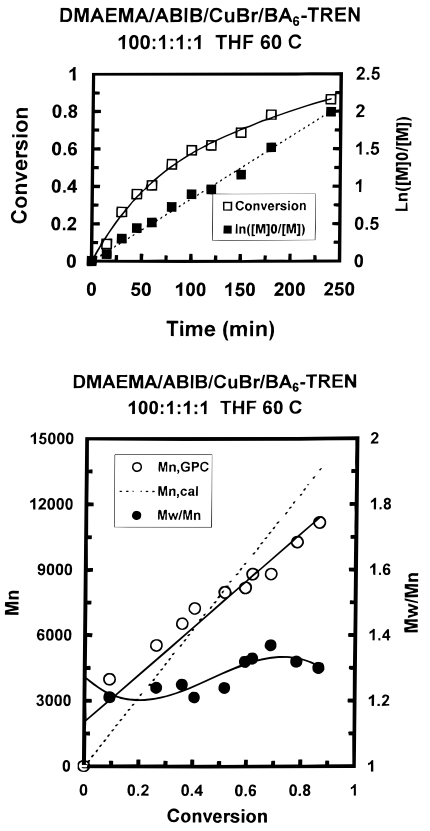


Figure 6. Monomer conversion and molecular weight development of THF solution polymerization of DMAEMA at 60 °C with $[DMAEMA]_0 = 2.96$ M and $[ABIB]_0 = [CuBr]_0 = [BA_6\text{-}TREN]_0 = 0.0296$ M: (A) conversion and $\ln([M]_0/[M])$ versus time and (B) number-average molecular weight and polydispersity versus conversion.

Figure 2A shows the conversion with time curves. At each temperature, the polymerization proceeded smoothly up to 85% conversion. The polymerization rate was increased with temperature. Figure 2B gives the first-order kinetic plot. The linearity between $\ln([M]_0/[M])$−time in all cases indicated that the concentration of the growing species remained constant. The apparent activation energy was calculated and found to be about 42 kJ/mol.

The GPC analysis shows that the number-average molecular weight increased linearly with increasing the monomer conversion at different temperatures (Figure 3A−C). The polydispersities remained narrow and decreased with the increase of monomer conversion at about 1.2−1.45. The polymerization at 40 °C (Figure 3C) yielded narrower distributions than 60 °C (Figure 3A) and 50 °C (Figure 3B). However, the $M_{n,SEC}$ deviated significantly from $M_{n,cal}$ at all the temperatures. The initiator efficiencies were lower than 0.50. Raising temperature did not increase the initiator efficiency.

The solvent effect on the polymerization was also investigated. When *n*-butyl acetate and 2-propanol were used as solvent for the polymerization of DMAEMA at 60 °C, the kinetic curves deviated from the first-order plot after the monomer conversion reached about 40% (Figures 4 and 5). These results indicated a significant amount of termination of the growing species. The molecular weights were also much higher than the predicted.

From the results of the ABIB/CuBr/PMDMEA system, we can conclude that the ligand plays an important role in ATRP of DMAEMA. Changing temperature or solvent type could not improve the initiator efficiency.

Table 2. Effects of Solvents on Solution Polymerization of DMAEMA at 60 °C[a]

run	solvent	time (h)	conv (%)	$M_{n,cal}$	$M_{n,SEC}$	M_w/M_n	$f = M_{n,cal}/M_{n,SEC}$
99−19−1	ethylene glycol	0.5	81.3	6300	6300	1.60	0.99
99−19−2	formamide	0.5	94.9	7460	7880	1.54	0.95
99−19−9	MeOH	2.0	96.3	7570	8790	1.45	0.86
99−19−3	DMSO	2.0	83.7	6600	6900	1.39	0.96
99−19−6	DMF	2.0	82.1	6450	6710	1.31	0.96
99−19−4	2-propanol	2.0	88.7	6970	7430	1.45	0.94
99−19−5	γ-butyrolactone	2.0	92.1	7240	7230	1.37	1.0
99−19−7	BuOAc	4.5	87.2	6900	6800	1.37	1.0
99−19−8	EtOAc	4.5	91.2	7200	7800	1.37	0.92
99−19−10	THF	4.5	90.1	7100	7400	1.23	0.96

[a] DMAEMA/ABIB/CuBr/BA_6-TREN = 50:1:1:1 in moles. [DMAEMA] = 2.97 M; f = initiator efficiency.

Table 1 shows that the ABIB/CuBr/ BA_6-TREN had very high initiator efficiency with good control over molecular weight and molecular weight distribution. Therefore, the ATRP polymerization of DMAEMA mediated by this system was also investigated in detail to further understand the role of ligand and other factors.

In contrast to the behavior of the ABIB/CuBr/ PMDETA system, the polymerization solution was completely homogeneous in bulk as well as in solution when BA_6-TREN was used as the ligand. The polymerization proceeded smoothly up to 90% conversion without cross-linking. The linear $\ln([M]_0/[M])-t$ plot also suggested a first-order kinetics with a constant radical concentration. The number-average molecular weight

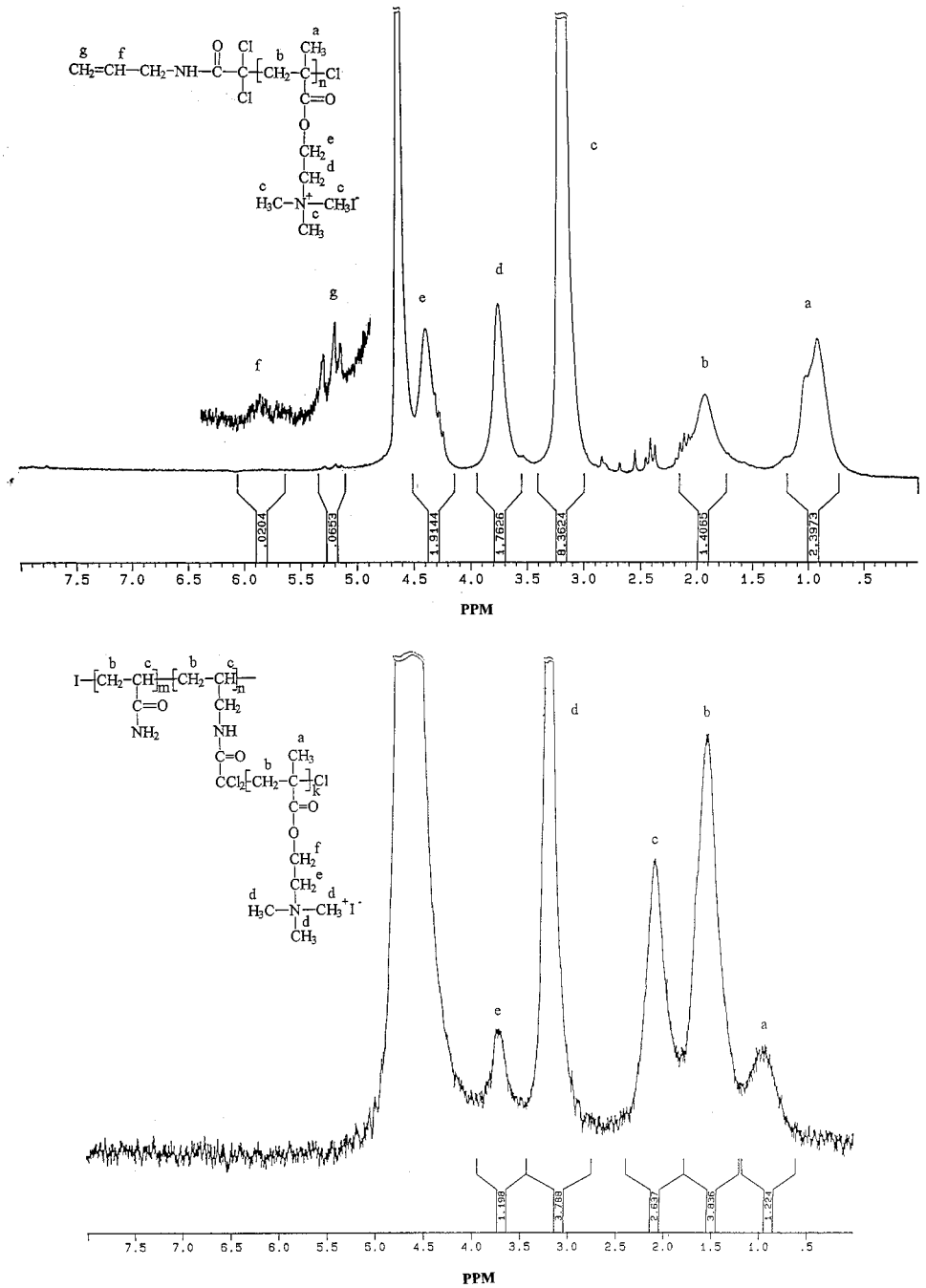


Figure 7. ^{1}H NMR spectrum of quaternized DMAEMA macromonomer and graft copolymer: (A, top) quaternized DMAEMA macromonomer and (B, bottom) graft copolymer of quaternized DMAEMA macromonomer with acrylamide. The copolymer molecular weight is $M_w = 112\,000$ measured by GPC.

increased linearly with the increase of monomer conversion with M_w/M_n around 1.2−1.4 (Figure 6B). The molecular weights of polyDMAEMA were very close to the theoretical values.

Table 2 shows the solvent effect on the ATRP of DMAEMA catalyzed by ABIB/CuBr/BA_6-TREN. The ATRP polymerization could proceed not only in THF but also in very polar solvents such as ethylene glycol, formamide, and DMSO. In high polar solvents, the polymerization was much faster than in the low polar solvent. For example, in formamide, the monomer conversion could go up to 95% in a half-hour with the molecular weight of the polymer close to the calculated value. The initiator efficiencies (calculated using the GPC data) in polar solvents were higher than 0.9. The molecular weight distributions of polyDMAEMA prepared in polar solvents were slightly broader than those prepared in low polar solvents.

Preparation of Quaternary Macromonomers and Their Copolymerization with Acrylamide. To examine whether the resulting macromonomers were copolymerizable, the polyDMAEMA macromonomers were quaternized and copolymerized with acrylamide in water. After precipitated from the aqueous solution using methanol, the copolymer was separated from unreacted macromonomers because the latter was soluble in the methanol/water mixture. Figure 7 shows the ^{1}H NMR spectra for the quaternized macromonomer and its copolymer with acrylamide. It can be seen that, besides the signals of acrylamide units (1.51, CH_2; 2.05, CH), the cationic macromonomer signals appeared at 3.15 [−O−CH_2−CH_2−N(CH_3)$_3^+$I$^-$] and 3.72 [−O−CH_2−

$CH_2-N(CH_3)_3^+I^-$]. The NMR spectra thus conformed that the cationic poly(DMAEMA) macromonomer was incorporated into the copolymer chains.

Conclusion

Based on the detailed studies on the synthesis of polyDMAEMA macromonomers by the ATRP process, the following conclusions were reached:

1. The nature of initiator and ligand type for the CuBr-based ATRP system determined whether the unsaturated group of the initiator was consumed during the ATRP process. Allyl groups in the ester or amide type of initiators survived in the ATRP of DMAEMA, while the styrenyl moiety of VBC took part in the polymerization giving cross-linking or broad MWD. Vinyl chloroacetate could not initiate the polymerization of DMAEMA.

2. The type of ligand affected the initiator efficiency. With ABIB as initiator, the initiator efficiency increased by the order PMDETA < 18-crown-6 < HMTETA ≅ MA_6-TREN ≅ BA_6-TREN. Varying temperature could not enhance the initiator efficiency of the ABIB/CuBr/PMDETA system.

3. Well-defined polyDMAEMA macromonomers with terminal allyl groups were synthesized by Cu(I)Br/BA_6-TREN with ATCA and ABIB as initiator. ^{1}H NMR showed that each polymer chain contained an allyl end group. The molecular weight distributions were at $M_w/M_n = 1.2-1.3$.

4. The corresponding cationic macromonomers were prepared by reacting polyDMAEMA macromonomers with methyl iodide. These cationic macromonomers showed high reactivities in their copolymerizations with acrylamide.

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