RAPID COMMUNICATION

Atom Transfer Radical Polymerization of 2-(Dimethylamino)ethyl Methacrylate in Aqueous Media

FAQUAN ZENG, YOUQING SHEN, SHIPING ZHU, ROBERT PELTON

Department of Chemical Engineering, McMaster University, 1280 Main Street West, Hamilton, Ontario, Canada L8S 4L7

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INTRODUCTION

Living radical polymerization mediated by a metal complex, termed *atom transfer radical polymerization* (ATRP), is a versatile method for synthesizing various types of vinyl monomers.[1,2] ATRP is usually performed in bulk or in an organic solvent. Water is always the most preferable reaction medium because of its environmental and cost advantages. Coca et al.[3] first reported the polymerization of 2-hydroxyethyl acrylate in aqueous media at 90 °C. Recently, Ashford et al.[4] reported the polymerization of sodium methacrylate with a poly(ethylene oxide)-based macroinitiator in a water solution at 90 °C. Wang et al.[5,6] reported monomethoxy-capped oligo(ethylene oxide) methacrylate and sodium 4-vinylbenzoate polymerization at ambient temperature. However, the polymerization of aminoethyl methacrylate was not successful, giving poor control over the molecular weight.[7] We are interested in the polymerization of 2-(dimethylamino)ethyl methacrylate (DMAEMA) because poly(DMAEMA) is a useful water-soluble and temperature-sensitive polymer. Poly(DMAEMA) has a lower critical solution temperature (LCST), around 50 °C.[8,9] DMAEMA has been polymerized via living anionic polymerization,[10] group transfer polymerization,[11] and ATRP[12–14] in various organic solvents. Nevertheless, the ATRP of DMAEMA in aqueous media remains a challenge.

In this communication, we report an aqueous ATRP of DMAEMA with a CuBr-based catalyst system. The effects of the ligand and initiator types on the polymerization behavior were examined.

EXPERIMENTAL

Materials

The catalyst, Cu(I)Br; the initiators, methyl α-bromophenylacetate (MBP), allyl 2-bromoisobutyrate (ABIB), ethyl 2-bromoisobutyrate (EBIB), and α-bromo γ-butyrolactone; and the ligands, 2,2′-bypyridine (Bpy) and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), were provided by Aldrich and used without further purification. 2-Vinyloxyethyl 2-bromoisobutyrate (VBIB) was synthesized by our group.[14] DMAEMA, also from Aldrich, was distilled from CaH_2 prior to use. Deuterium oxide (D_2O; Cambridge Isotope Laboratories, Inc) and deionized water were used as reaction solvents. The molecular structures of all the initiators and ligands used in this work are shown in Scheme 1.

Polymerization

The ATRP polymerization of DMAEMA was carried out in D_2O or deionized water solutions via two methods. In method 1, 1 g (6.36 mmol) of DMAEMA, 9.14 mg (0.0636 mmol) of Cu(I)Br, and 19.87 mg (0.1272 mmol) of Bpy were first charged to a 10-mL glass ampule. The ampule reactor was sealed with a rubber septum. The mixture was allowed to react for 10 min under nitrogen

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Correspondence to: S. Zhu (E-mail: zhuship@mcmaster.ca)

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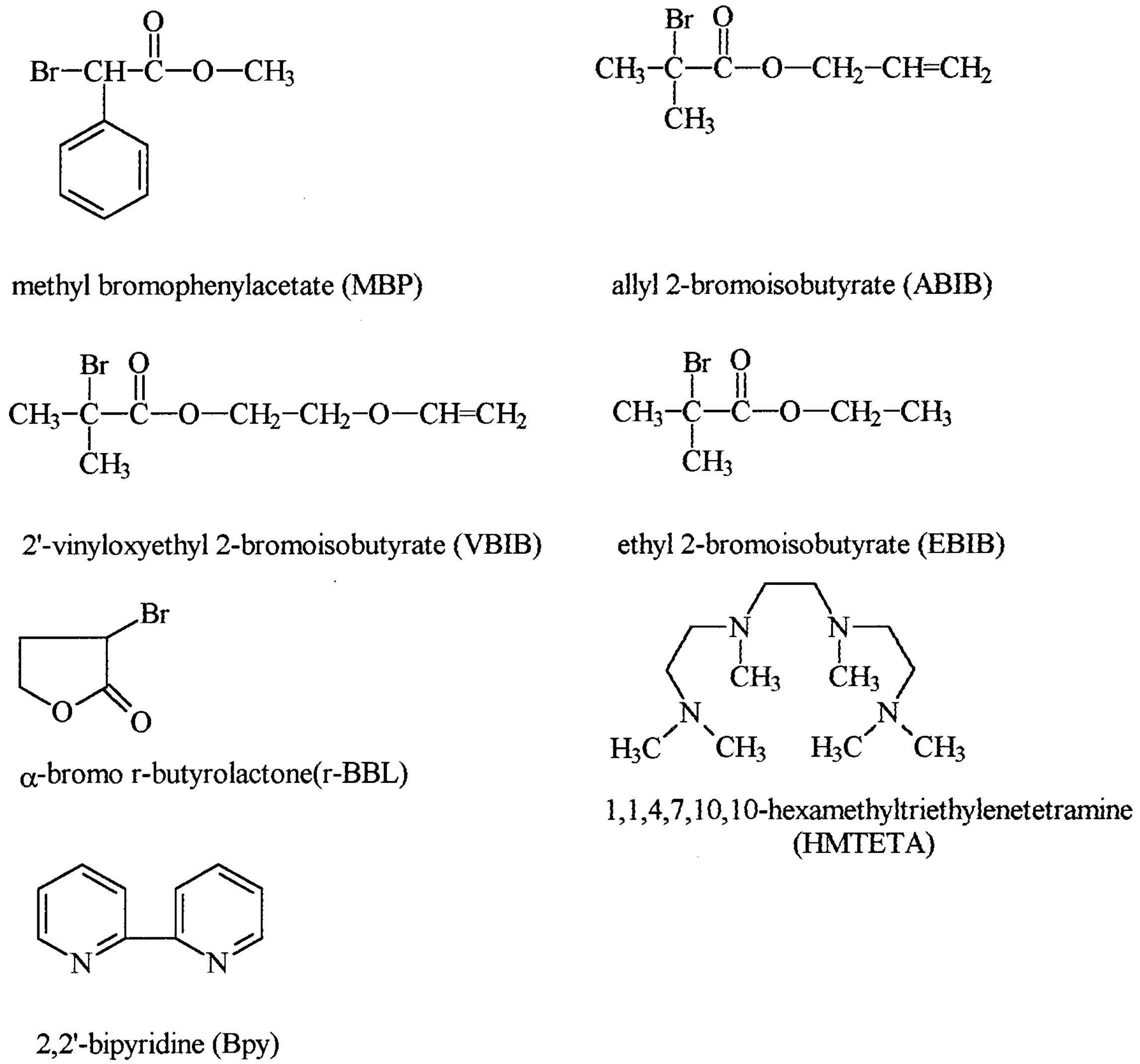

methyl bromophenylacetate (MBP)

allyl 2-bromoisobutyrate (ABIB)

2'-vinyloxyethyl 2-bromoisobutyrate (VBIB)

ethyl 2-bromoisobutyrate (EBIB)

α-bromo r-butyrolactone(r-BBL)

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

2,2'-bipyridine (Bpy)

Scheme 1. Molecular structures of the initiators and ligands.

protection, and then 1 g of D_2O was added and degassed for another 10 min. Degassed MBP (10.0 μL, 0.0636 mmol) was added to the reactor with a microsyringe. The ampule was then immersed in a 20 °C water bath. In method 2, 1 g (6.36 mmol) of DMAEMA, 9.14 mg (0.0636 mmol) of Cu(I)Br, 19.87 mg (0.1272 mmol) of Bpy, and 1 g of D_2O were charged to a 10-mL glass ampule. The ampule reactor was sealed with a rubber septum and degassed for 10 min under nitrogen. Sampling was done with a degassed syringe in time intervals. The polymerization was terminated by the addition of the sampled polymer mixture to 0.1 mL of a $CuBr_2$ D_2O solution. Conversion was determined by ^1H NMR. The molecular weight and molecular weight distribution of the polymer were measured by gel permeation chromatography (GPC) with tetrahydrofuran (THF) containing 2% triethylamine (v/v) as an eluent, and polystyrene standards were used to generate the calibration curve.

RESULTS AND DISCUSSION

Effects of the Solvent, Initiator, and Ligand on the ATRP Polymerization of DMAEMA

CuBr combined with multidentate amines was proven to be a good catalyst system for the ATRP of DMAEMA in organic solvents such as dichlorobenzene or THF.[12–14] However, polymerizations in high polar solvents such as ethylene glycol were less controlled.[13] The molecular weight distributions of the resulting poly(DMAEMA) were broader [weight-average molecular weight/number-average molecular weight (M_w/M_n) $\cong$ 1.6)]. Further study indicated that the DMAEMA ATRP could also be carried out in aqueous media, and the initiator, ligand, and catalyst preparation strongly affected the polymerization. Table I summarizes the results for the ATRP of DMAEMA in water catalyzed by CuBr–Bpy or CuBr–HMTETA with various initiators.

Table I. Effects of the Initiator Type and Ligand Type on the Aqueous ATRP of DMAEMA at 20 °C

Run	Initiator	Ligand	Time (h)	Conversion (%)	$M_{n,\mathrm{cal}}$	$M_{n,\mathrm{SEC}}$	$M_{w,\mathrm{SEC}}/M_{n,\mathrm{SEC}}$	$f = M_{n,\mathrm{cal}}/M_{n,\mathrm{SEC}}$
1[a]	MBP	Bpy	0.5	32.6	5,130	5,340	1.12	0.96
2[a]	MBP	Bpy	2	84.5	13,000	12,800	1.21	1
3[a]	ABIB	Bpy	0.5	91.1	14,330	16,300	1.77	0.87
4[a]	VBIB	Bpy	0.5	95.2	14,900	19,100	2.10	0.78
5[a]	EBIB	Bpy	0.5	88.2	13,860	15,900	1.71	0.87
6[a]	*r*-BBL	Bpy	0.5	81.3	12,800	59,700	2.09	0.21
7[a]	MBP	HMTETA	0.5	53.28	8,370	12,680	1.46	0.66
8[a]	MBP	HMTETA	2.0	84.5	13,280	18,400	1.50	0.72
9[a]	ABIB	HMTETA	0.5	92.70	14,570	17,900	1.66	0.81
10[a]	VBIB	HMTETA	0.5	94.5	14,850	18,500	2.18	0.80
11[a]	EBIB	HMTETA	0.5	94.8	14,900	17,180	1.95	0.86
12[a]	*r*-BBL	HMTETA	0.5	90.3	14,190	28,000	1.74	0.51
13[b]	MBP	Bpy	1.0	89.1	14,000	21,300	1.46	0.66

DMAEMA/initiator/CuBr/ligand = 100/1/1/2 (for Bpy) and 100/1/1/1 (for HMTETA) in moles; DMAEMA/water = 1/1 (w/w); *f* = initiator efficiency.

[a] The catalyst was prepared via method 1.

[b] The catalyst was prepared via method 2.

The initiator was the most important factor for the DMAEMA ATRP. Catalyzed by CuBr–Bpy, MBP initiated a living polymerization of DMAEMA in water, producing polymers with controlled molecular weights and very low polydispersities, whereas others such as bromoisobutyrate and α-bromo *r*-butyrolactone (*r*-BBL) yielded polymers with broad molecular weight distributions. All the initiators dissolved quickly once they were added to the DMAEMA/H_2O mixture (1/1 w/w). Therefore, this difference did not result from the solubility of the initiators.

The ligands also affected the aqueous ATRP of DMAEMA. When HMTETA was used, DMAEMA polymerization was very fast but poorly controlled, producing polymers with molecular weights much higher than predicated and broad polydispersities, as shown in runs 7 and 8 in Table I. When Bpy was used as the ligand with MBP as an initiator, the polymerization rate was relatively slow but well controlled, as indicated in runs 1 and 2 in Table I. The molecular weight of poly(DMAEMA) agreed with the predicated weight, and the polydispersity of the polymer was about 1.20.

The procedure of the catalyst preparation also had influence on the polymerization rate and molecular weight development. When CuBr, Bpy, and DMAEMA were mixed under nitrogen before water addition (method 1), the polymerization proceeded smoothly, and the resulting polymers had predefined molecular weights and narrow molecular weight distributions. However, when water was added with CuBr, Bpy, and DMAEMA at the same time (method 2), the polymerization rate was very fast, and the produced polymers had high molecular weights and broad molecular weight distributions ($M_w/M_n > 1.5$; Table I, run 13).

The effects of the initiator, ligand, and catalyst preparation on the controllability of the polymerization might have resulted from the different reaction rates. The LCST of DMAEMA monomer was very low (ca. 36 °C).[8,9] Therefore, it was very sensitive to temperature changes. If the polymerization was fast, the released polymerization heat raised the solution temperature higher than the LCST of DMAEMA, so DMAEMA separated from the solution. The polymerization medium was clear only for the CuBr/Bpy/MBP system, whereas others were cloudy, suggesting a phase separation. This heterogeneity might have resulted in poor control in the polymerization.

Kinetics of the ATRP of DMAEMA in Aqueous Media

All the aqueous ATRPs of DMAEMA were carried out in a 50% (w/w) water solution. Figure 1 shows the DMAEMA polymerization at 20 and 30 °C with MBP/CuBr/Bpy (1/1/2 in moles). The polymerization reached a 90% conversion in 1 h at 30 °C. However, the reaction was much slower at 20 °C. The reaction took 6 h to reach a 90% conversion. The linear plots of $\ln([M]_0/[M])$ versus time suggests a first-order kinetics with a constant concentration of growing radicals. Lowering the catalyst concentration to half (DMAEMA/MBP/CuBr/Bpy = 100/1/0.5/1 in moles) slightly decreased the polymerization rate (Fig. 2).

The GPC analysis showed that the number-average molecular weight increased linearly with increasing monomer conversion for the polymers at 20 and 30 °C or at lower catalyst concentrations (Fig. 3). The polydispersities remained low, about 1.2–1.3, throughout

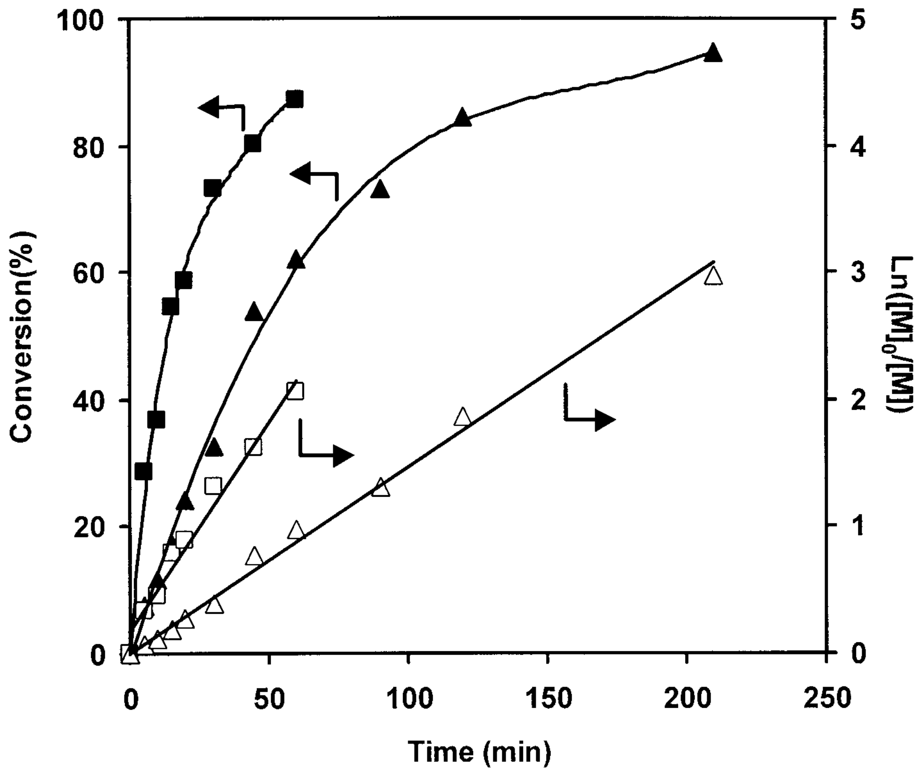

Figure 1. Aqueous ATRP of DMAEMA catalyzed by CuBr–Bpy at 20 and 30 °C. $[\text{DMAEMA}]_0/[\text{MBP}]_0/[\text{CuBr}]_0/[\text{Bpy}]_0$ = 100/1/1/2 (in moles); $\text{DMAEMA}/\text{D}_2\text{O}$ = 1/1 (w/w); temperature = 20 °C (■, □) and 30 °C (▲, △).

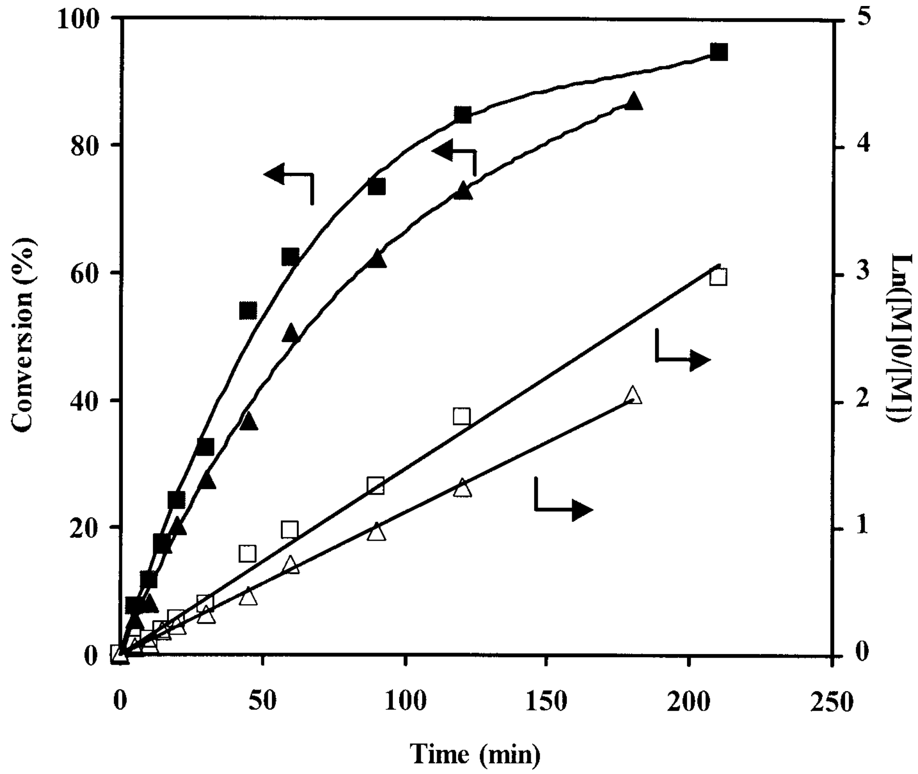

Figure 2. Aqueous ATRP of DMAEMA catalyzed by CuBr–Bpy at 20 °C at different catalyst concentrations. $[\text{DMAEMA}]_0/[\text{MBP}]_0/[\text{CuBr}]_0/[\text{Bpy}]_0$ = 100/1/1/2 (in moles; ■, □); $[\text{DMAEMA}]_0/[\text{MBP}]_0/[\text{CuBr}]_0/[\text{Bpy}]_0$ = 100/1/0.5/1 (in moles; ▲, △).

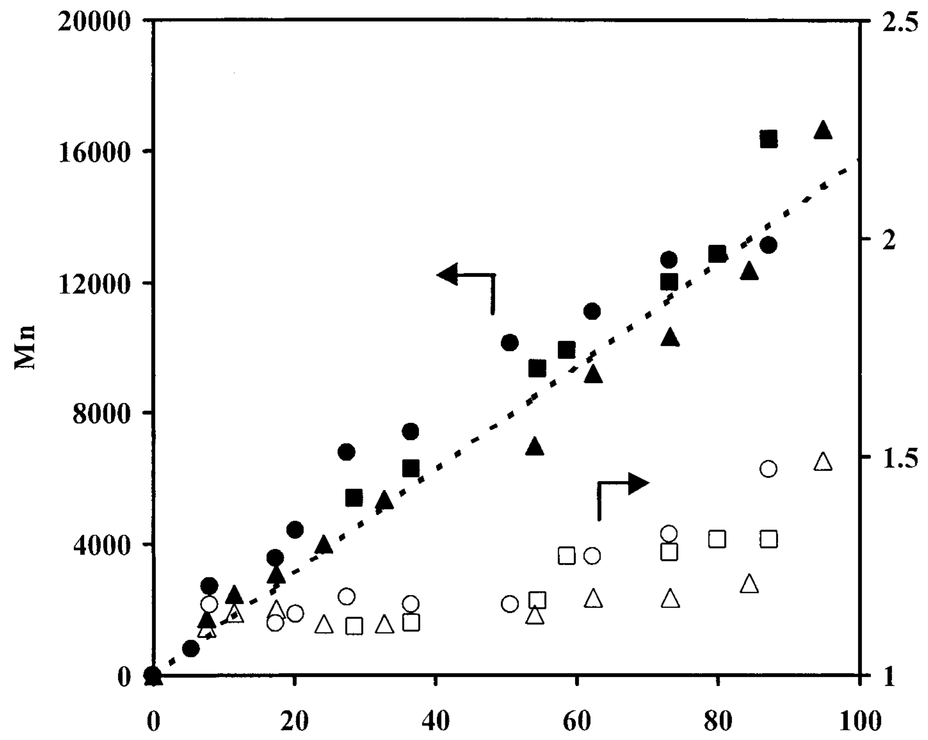

Figure 3. Molecular weight of poly(DMAEMA) as a function of conversion in the aqueous ATRP of DMAEMA. $[DMAEMA]_0/[MBP]_0/[CuBr]_0/[Bpy]_0$ = 100/1/1/2 and DMAEMA/D_2O = 1/1 (w/w) at 20 °C (■, □) and 30 °C (&▲, △); $[DMAEMA]_0/[MBP]_0/[CuBr]_0/[Bpy]_0$ = 100/1/0.5/1 and DMAEMA/D_2O = 1/1 (w/w) at 20 °C (●, ○). The dashed line shows the calculated molecular weight.

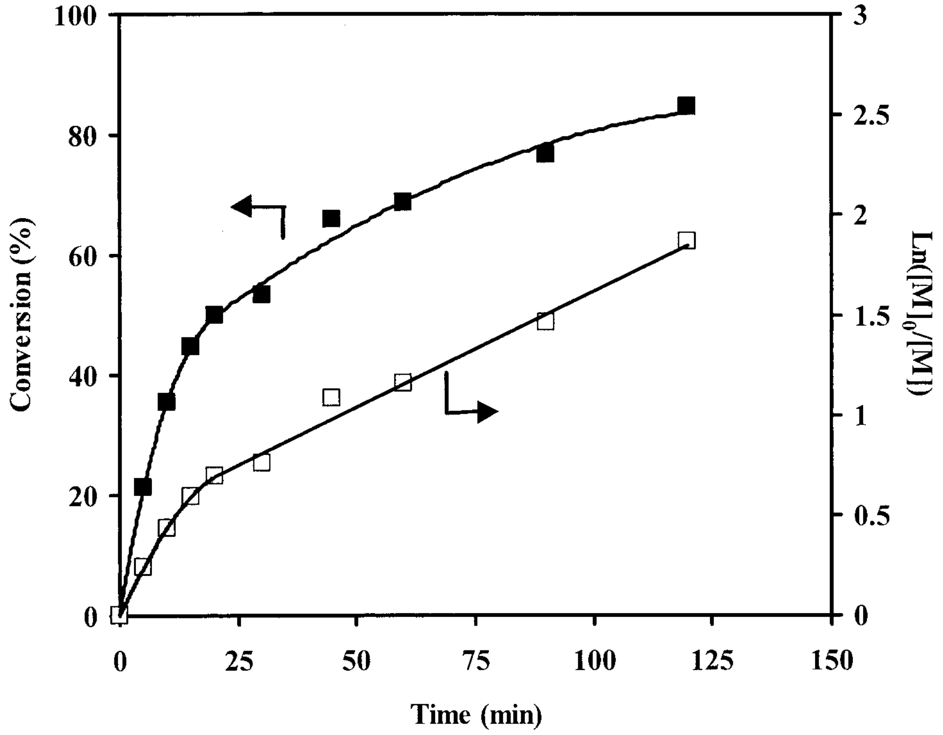

Figure 4. Aqueous ATRP of DMAEMA catalyzed by CuBr–HMTETA at 20 °C. $[DMAEMA]_0/[MBP]_0/[CuBr]_0/[HMTETA]_0$ = 100/1/1/1; DMAEMA/D_2O = 1/1 (w/w).

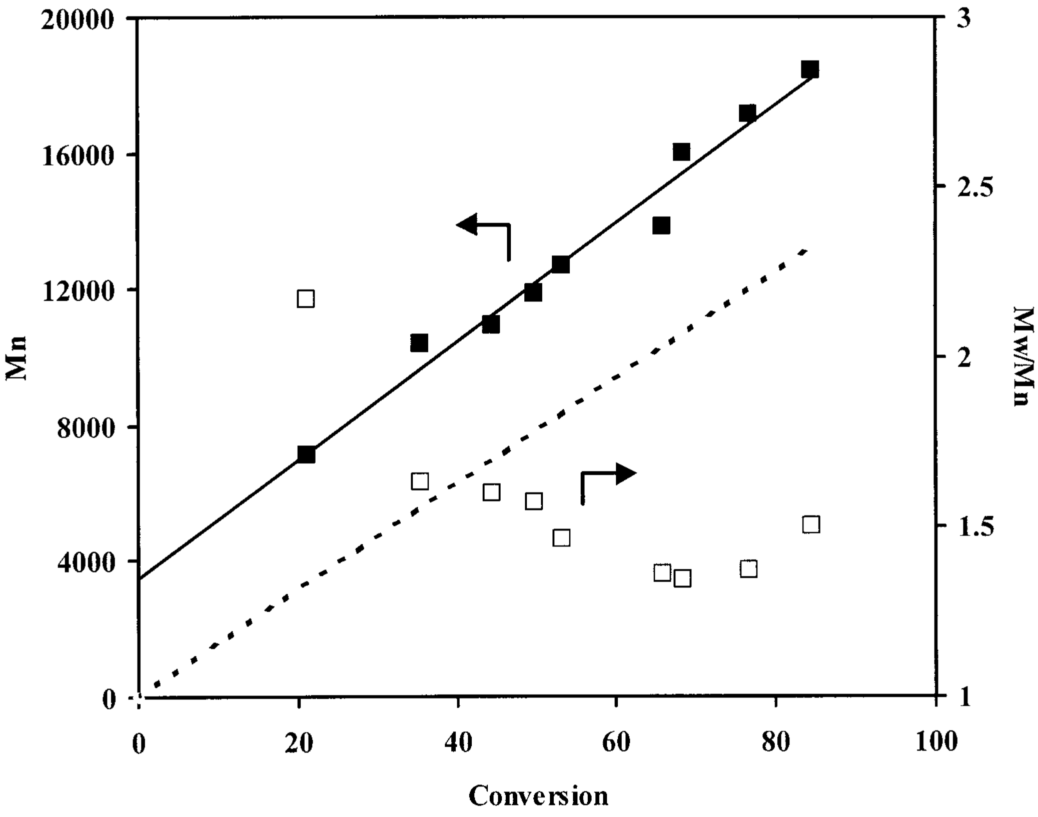

Figure 5. Molecular weight of poly(DMAEMA) as a function of conversion in the aqueous ATRP of DMAEMA. See Figure 4. for the conditions.

the polymerization. These results demonstrated the living feature of the aqueous ATRP of DMAEMA catalyzed by CuBr/Bpy with MBP as an initiator.

Figure 4 shows the DMAEMA polymerization at 20 °C in water with CuBr/HMTETA as a catalyst. The polymerization was very fast at the early stage but slowed down later. For example, the conversion reached 59% in the first 30 min but was only 84% in 2 h. The kinetic plot showed a significant curvature, indicating radical termination in the first 25 min. Correspondingly, the molecular weights were much higher than their theoretical values, and the molecular weight distributions were rather broad (M_w/M_n = 1.4–2.2), as shown in Figure 5.

CONCLUSION

Various combinations of two ligands and five initiators were examined for the ATRP of DMAEMA in aqueous media catalyzed by CuBr. The type of ligand, initiator, and catalyst preparation had strong effects on the polymerization. The living behavior was observed only with CuBr/Bpy as a catalyst and MBP as an initiator, which indicated first-order kinetics and a linear increase in the number-average molecular weight with monomer conversion. The molecular weight distribution of poly(DMAEMA) was narrow, with its polydispersity about 1.20.

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