

Controlled Radical Polymerization Catalyzed by CuCl/BDE Complex in Water Medium. I. Polymerization of Styrene and Synthesis of Poly(St-*b*-MMA)

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ABSTRACT: The controlled radical polymerization of styrene in water medium, in the presence of polyoxyethylene nonyl phenyl ether, catalyzed and initiated by CuCl/BDE [bis(*N,N'*-dimethylaminoethyl)ether]/R—X was studied. The results show that the molecular weight increased with conversion of the monomer. Using this controlled system, the block copolymer, poly(St-*b*-MMA), was successfully synthesized in water medium. In reference to the system of CuCl/BDE/PhCH₂Cl, the polymerization may also occur in the micelle to produce a superhigh molecular mass ($M_n = 1,500,000$) polymer with monodispersity (MWD, $M_w/M_n = 1.03$). The Cu(I) and Cu(II) partition ratio in two phases, which may affect the reversible deactivation and reduce the catalyst efficiency, was detected. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 802–807, 2000

Key words: “living”/controlled radical polymerization; emulsion polymerization; bis(*N,N'*-dimethylaminoethyl)ether; polystyrene; poly(methyl methacrylate); block copolymer

INTRODUCTION

Controlled/“living” radical polymerization has become the focus of recent free-radical polymerization research.^{1,2} Although many systems have been proposed, the two most widely used are nitroxyl-mediated polymerization^{3–5} and atom-transfer radical polymerization (ATRP) or transition-metal-mediated polymerization.^{6–8}

Various block and graft copolymers can be produced using ATRP or transition-metal-mediated polymerization methodology.^{9–13} Nearly all controlled/“living” radical polymerizations, however,

have been confined to bulk or solution polymerization. Although some polymerizations have been conducted in water, either as homogeneous¹⁴ or biphasic mixtures,^{15–19} detail studies via transition-metal-mediated polymerization on emulsion or a suspension system of styrene and preparation of a block copolymer by these systems have not been reported. Although the extension of ATRP to aqueous emulsion systems to prepare well-defined polymers of butyl methacrylate, methyl methacrylate, and butyl acrylate has been reported, the emulsion system of styrene has not been studied in detail.²⁰

In those reported aqueous emulsion systems, additionally, the ligands, 2,2'-bipyridine and its derivatives [4,4'-di(5-nonyl)-2,2'-bipyridine (dN-bpy)] or [4,4'-di(alkyl)-2,2'-bipyridine (dAbpy)] may be carcinogens to humans due to the conjugated aromatic ring structure in their molecules. We reported “living” radical bulk polymerization

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by a CuCl/bis(*N,N'*-dimethylaminoethyl)ether (BDE) catalyst system prior to this work.²¹ According to our prediction, the CuCl/BDE catalyst system was an excellent “living” system with zero-order kinetics up to a high monomer conversion for bulk polymerization of styrene or methyl methacrylate, and the molecular weight with $M_w/M_n = 1.12$ of those polymers corresponded with the theoretical one. Employing BDE as a ligand in a CuCl/ligand catalyst system may have a bright future in commercializing controlled/“living” radical polymerization because BDE is a product with low toxicity and cost and is widely used in manufacturing polyurethanes. Herein, we extended this catalyst system, CuCl/BDE, to a controlled aqueous polymerization system.

EXPERIMENTAL

Materials

CuCl (CP Shanghai No. 1 Chemical Plant, Shanghai, China) was purified according to the literature²²; benzyl chloride (PhCH₂Cl) (AR, Shanghai Chemicals Supply Station, Shanghai, China) was distilled in a vacuum; CCl₄ (AR, Shanghai No. 1 Chemical Plant) was distilled twice; styrene (St) and methyl methacrylate (MMA) (CP, Shanghai No. 1 Chemical Plant) were distilled twice in a vacuum just before use; 2,2'-bipyridine (bpy) (AR, Shanghai No. 1 Chemical Plant) was recrystallized with acetone; BDE (99%, from Witco Co., USA) was distilled twice under a vacuum; polyoxyethylene nonyl phenyl ether (OP-10) was synthesized by Shanghai Gaoqiao Petrochemical Co. (Shanghai, China) and purified in a 50% toluene solution by acid clay for 2 h at 90°C, then filtered and dried under a vacuum before use; and deionized water was used.

General Procedure for Polymerization

The reaction vessel was a 250-mL three-necked flask. In the flask, there was a magnetic stirrer bar, and one neck was used for sample taking and the others were installed with a thermometer, vacuum tube, and an inert gas tube, respectively. The general procedure was as follows: Before adding materials, the flask was degassed under a vacuum and replaced with argon twice. After OP-10 (1.0 g/100 mL solution) and the catalyst ([CuCl]/[BDE] = 1:3 molar ratio) were added to the vessel, the system was degassed and replaced

with argon again, then water, St, and the initiator were added in sequence with stirring under an argon atmosphere, and, finally, it was immersed in an oil bath at 80°C.

Synthesis and Characterization of Poly(St-*b*-MMA)

When the aqueous polymerization of St was completed, the system was dried under a vacuum, 20.0 mL toluene was then added to resolve the polystyrene (polySt), and, finally, 100.0 mL water and 20.0 mL MMA was added with stirring in an argon atmosphere. The product was dried under a vacuum condition and purified by precipitation with a 1:1 water-methanol mixture after 100% monomer conversion under reaction for 3 h at 80°C. The purified polymer was separated by precipitation and solubility fractionation, respectively, with water and a cyclohexane-toluene mixture. The block copolymer was characterized by ¹H-NMR spectroscopy at 500 MHz (DRX500 instrument).

Determination and Calculation of Monomer Conversion

A 2-mL sample was taken from the vessel at a certain time and weighed accurately (W_1); then, the sample was placed in a vacuum oven for drying at 50°C. Up to an invariable mass (W_2), the sample was dissolved with THF for other uses. Monomer conversion was calculated according to the following formula:

$$\text{Conv (\%)} = [(W_1 - W_2 - W_1 \times C_1)/W_1]/C_2$$

with C_1 the emulsifier concentration, and C_2 , the initial St concentration.

Determination of Molecular Weight and Its Distribution

The above THF solution of the sample was settled overnight, and the clear liquid in the upper layer was filtered by a 0.45 μm filter film for two cycles. The filtered solution, in which the polymer concentration remained at 2 mg/mL, was used for SEC measurements. The molecular weight and its distribution were carried out in THF at a 1.0-mL/min flow rate on a Waters 150 GPC/ALC equipped with Waters HT2 and HT4 polySt gel columns at 25°C. Calibration was based on monodispersity molecular weight polySt standards from Waters Corp.

Table I Detected Copper Content (mg) in Each Phase (10 mL)

	BDE System	bpy System
CuCl added/[absolute Cu(I) weight] (mg)	44/[29.5]	40/[25.6]
CuCl ₂ added/[absolute Cu(II) weight] (mg)	55/[25.8]	84/[39.5]
Detected [Cu(I) in water phase] (mg)	24.0	22.0
Detected [Cu(I) in St phase] (mg)	1.2	1.3
Detected [Cu(II) in water phase] (mg)	29.0	46.0
Detected [Cu(II) in St phase] (mg)	0.4	0.2
Total recovered [Cu(I)] (mg)	25.2	23.3
Total recovered [Cu(II)] (mg)	29.4	46.2

Determination of Partition Ratio

CuCl, 40–90 mg (64% Cu content) or CuCl₂ (47% Cu content) was added to a single-necked flask and then degassed under a vacuum and replaced with argon twice. After this process, BDE or bpy at a mol ratio three times that of copper, 10.0 mL water, and 10.0 mL St were added to the flask in an argon atmosphere. The flask was immersed in an oil bath at 80°C for 6 h. Finally, a 2.0-mL sample was taken from the St phase and a 0.5-mL sample from the water phase and the two samples were put into a vacuum and oven dried at 50°C. HCl, 1.0 mL (36%), was added to each of the two dried samples; then, the solution was diluted to 50 mL with water. The copper content was measured by AAS (Hitachi-

80 AAS instrument). The copper partition ratio (K) was calculated by the following formula:

$$K = [\text{Cu}]_{\text{water phase}}/[\text{Cu}]_{\text{St phase}}$$

[Cu] was detected by AAS (Table I).

RESULTS AND DISCUSSION

Aqueous Emulsion Polymerization of Styrene

Three kinds of initiators, 1-phenylethyl bromide (1-PEBr), CCl₄, and PhCH₂Cl, were used and the results are listed on Table II. Table II shows that

Table II Results of Emulsion Polymerization of St by Different Initiators Using OP-10 (2.0 g/100 mL Water) as Surfactant at 80°C

Run #	Initiator (mol/L)	Catalyst (mol/L)			Results				
		CuCl	BDE	St (mol/L)	Time (min)	Conv (%)	$M_{n,th}$	$M_{n,SEC}$	M_w/M_n
1	1-PE(Br) (0.025)	0.025	0.075	3.8	60	4.0	630	4640	1.35
					120	7.1	1120	20,000	1.42
					600	15.6	2470	24,200	1.53
2	CCl ₄ (0.025)	0.025	0.075	3.8	30	28.9	4570	65,700	1.70
					120	36.4	5750	70,600	1.66
					270	44.5	7034	73,200	1.52
					330	56.1	8870	83,200	1.44
					570	72.6	11,480	99,800	1.42
3	CCl ₄ (0.05)	0.05	0.15	1.9	300	100	3950	15,100	1.20
4	PhCH ₂ Cl (0.007)	0.007	0.021	2.5	30	22.0	8170	105,700	1.18
					120	36.5	13,560	125,700	1.37
					300	53.6	19,910	149,900	1.22
					600	74.5	27,670	172,800	1.22

Table III Copper Complex Partition Ratio in St-Water Mixture with Different Ligands at 80°C (Based on Table I)

BDE		bpy	
$K_{\text{Cu(I)}}^{\text{BDE}}$	$K_{\text{Cu(II)}}^{\text{BDE}}$	$K_{\text{Cu(I)}}^{\text{bpy}}$	$K_{\text{Cu(II)}}^{\text{bpy}}$
20.0	72.5	16.9	230.0

the molecular weight of polySt increased as the reaction time was extended, with monomer conversion increasing. Although increase of the molecular weight with conversion was not close to theory, the molecular weight was still controlled by the reaction time or monomer conversion. The difference in molecular weight between theory and that detected by SEC might be caused by a lower catalyst concentration in the St phase. From the partition ratio [$K_{\text{Cu(I)}}^{\text{BDE}} = 20.0$; see Table III], we know that the concentration of the Cu(I)/BDE complex in water was 20 times that in the St phase, which decreased the initiator efficiency and debased the catalyst efficiency.

Earlier attempts to use the CuCl/bpy system to perform controlled/"living" emulsion radical polymerization failed (Fig. 1). In the bpy system, the "living" species was "dead" at about 12% conversion; unexpectedly, the conversion increased without the M_n increasing. This uncontrolled system was attributed to higher solubility [$K_{\text{Cu(I)}}^{\text{BDE}} = 230.0$] of the CuCl₂/bpy complex (deactive species) in water than that [$K_{\text{Cu(I)}}^{\text{BDE}} = 72.5$] of CuCl₂/BDE (Table III). Compared to the CuCl/bpy system (Fig. 1), this novel system (CuCl/BDE)

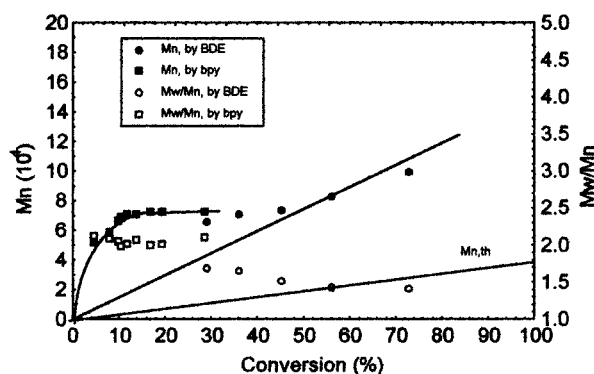


Figure 1 Comparison of molecular weight with different ligands for emulsion polymerization of St at 80°C. Concentrations of materials were the same as in Run £2 in Table II.

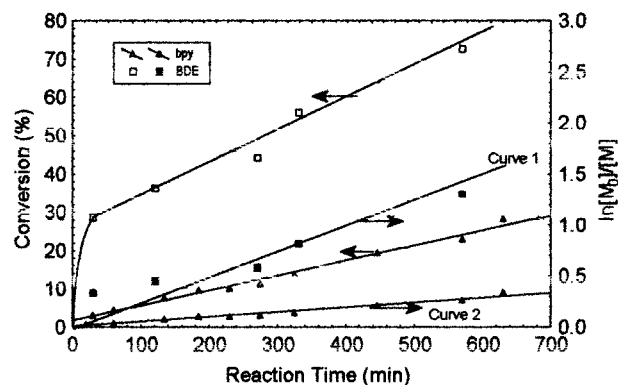


Figure 2 Comparison of kinetics on different ligands for emulsion polymerization of St at 80°C. Concentrations of materials were the same as for Run £2 in Table II.

was suitable for better-controlled emulsion polymerization of St. Even with CuBr/dNbpy or CuBr/dAbpy as a high solubility catalyst in the organic phase, in which the conversion of St was not mentioned,²⁰ the polySt was not a well-defined polymer. As can also be seen in Figure 2, the rate with BDE (curve 1) was faster than that with bpy (curve 2). So, the reaction time for St with this novel catalyst system was shorter than that with bpy or its derivative systems, which diminished

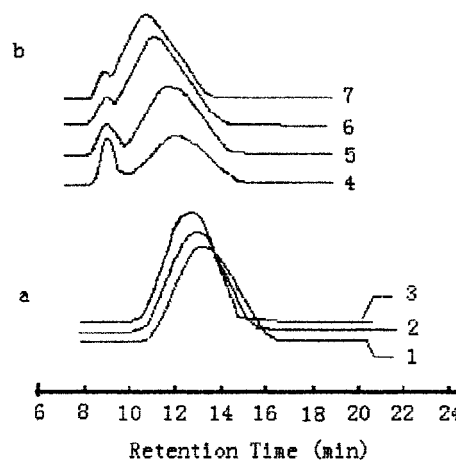


Figure 3 SEC trace for the emulsion system at 80°C. (a) Run £2 in Table II. (1) $t = 30$ min; $M_n = 65,700$; $M_w/M_n = 1.70$. (2) $t = 270$; $M_n = 73,200$; $M_w/M_n = 1.52$. (3) $t = 570$; $M_n = 99,800$; $M_w/M_n = 1.42$. (b) Run £4 in Table II, immobile peak: $M_n = 1,500,000$; $M_w/M_n = 1.03$. (4) $t = 30$; $M_n = 105,700$; $M_w/M_n = 1.18$. (5) $t = 120$; $M_n = 125,700$; $M_w/M_n = 1.37$. (6) $t = 300$; $M_n = 149,900$; $M_w/M_n = 1.22$. (7) $t = 600$; $M_n = 172,800$; $M_w/M_n = 1.22$.

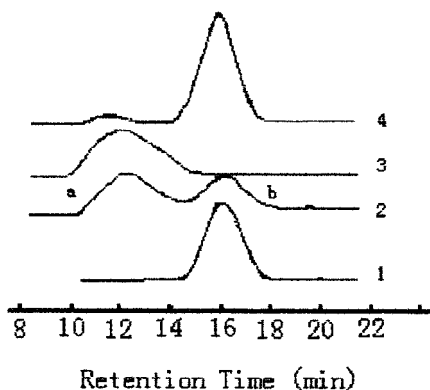


Figure 4 SEC of aqueous emulsion polymerization on block polymer system at 80°C. (1) Run £3 entry in Table II: PSt-Cl as macroinitiator. (2) purified polymer mixtures with M_n [(a) = 261,300, (b) = 14,500] and MWD [(a) = 1.49, (b) = 1.21] from aqueous block copolymerization for 180 min; [MMA] = 1.3M. (3) Block copolymer with M_n = 227,330 and M_w/M_n = 1.45 after separation. (4) Uninitiated PSt-Cl with M_n = 14,700 and MWD = 1.21 after separation.

side reactions, such as termination and dehydrohalogenation, to reach the higher conversion.

Unlike the CCl_4 initiator system (Run £2 in Table II), by which only a single peak with M_w/M_n = 1.4–1.7 was obtained on the SEC graph [Fig. 3(a)], the PhCH_2Cl (Run £4 in Table II) produced two peaks [Fig. 3(b)], on which the “dead” peak

with the superhigh molecular weight polymer (1,500,000) and monodistribution (M_w/M_n = 1.03) was formed at an early stage of polymerization, with the “moving” peak that shifted gradually to the left as polymerization proceeded behaving as a “living” one with a moderately narrower molecular weight distribution (MWD; about 1.2) than that with the CCl_4 initiator system (about 1.5). The “living” peak was probably produced in the St phase by microsuspension due to the oil-soluble initiator (PhCH_2Cl), and the “dead” peak with molecular mass to 1,500,000 could only be generated from a micelle as ordinary emulsion polymerization, which could occur when an initiator free radical diffused into a micelle to initiate polymerization of a monomer there and could be prolonged until a second free radical diffused,²³ so a superhigh molecular mass polymer with a monodistribution could be produced.

Synthesis of Poly(St-*b*-MMA)

The block copolymer poly(St-*b*-MMA) was tentatively synthesized. The purified polymer is a mixture of a block copolymer [poly(St-*b*-MMA)] and unreacted PSt-Cl, so there are two peaks in Figure 4(2) (peaks a and b are the block copolymer and unreacted PSt-Cl, respectively). Then, the block copolymer and macroinitiator in the purified polymer mixture were separated by precipitation and solubility fractionation with water and

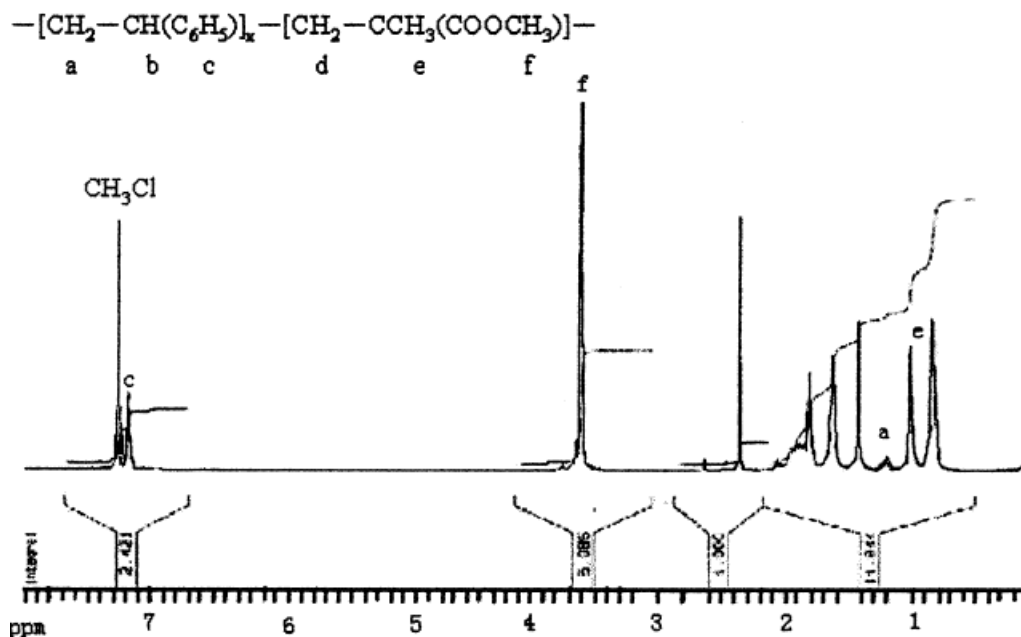


Figure 5 $^1\text{H-NMR}$ spectrum of poly(St-*b*-MMA).

a cyclohexane–toluene mixture, respectively. The block copolymer [Fig. 4(3)], P(St-*b*-MMA), was successfully obtained with a 67.8% yield. Moreover, peaks (2b) and (4) (Fig. 4) are identical to peak (1) (PSt-Cl before reaction) in molecular weight, which indicates that they are unreacted macroinitiators.

The structure of the block copolymer was analyzed by $^1\text{H-NMR}$ spectroscopy at 500 MHz. Figure 5 illustrates the $^1\text{H-NMR}$ spectra of the P(St-*b*-MMA) copolymer. The $^1\text{H-NMR}$ spectrum of the block copolymer shows the $-\text{COOCH}_3$ proton signal in the PMMA segment at 3.60 ppm and the phenyl ring proton signal in the PSt segment at 7.17 ppm. Based on the two kinds of proton signals, the molar ratio of the PMMA segment and the PSt segment in the block copolymer was 10:1, which agrees quite well with that (14:1) calculated from M_n on the SEC spectra. The tacticity of the PMMA segment in the block copolymer (based on $-\text{CH}_3$ group signals) was (*rr*) = 62%, (*rm*) = 38%.

CONCLUSIONS

Using the CuCl/BDE catalyst, we performed a controlled emulsion radical polymerization for St. The polymerization initiated by PhCH_2Cl may take place in both the St phase and in micelles to produce a polymer with double MWDs. The partition ratio, $K_{\text{Cu(I)}}$, affected the coherence of $M_{n,\text{SEC}}$ and $M_{n,\text{th}}$, because they probably debase the catalyst efficiency and decrease the initiator efficiency; $K_{\text{Cu(II)}}$ affected the emulsion system whether controlled or uncontrolled. The block copolymer of poly(St-*b*-MMA) was successfully synthesized in this novel controlled emulsion system.

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