Synthesis and Characterization of Poly(*n*-butyl methacrylate)-*b*-Polystyrene Diblock Copolymers by Atom Transfer Radical Emulsion Polymerization

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ABSTRACT: Poly(*n*-butyl methacrylate) (PBMA)-*b*-polystyrene (PSt) diblock copolymers were synthesized by emulsion atom transfer radical polymerization (ATRP). PBMA macroinitiators that contained alkyl bromide end groups were obtained by the emulsion ATRP of *n*-butyl methacrylate with $BrCH_3CHCOOC_2H_5$ as the initiator; these were used to initiate the ATRP of styrene (St). The latter procedure was carried out at 85°C with CuCl/4,4'-di(5-nonyl)-2,2'-bipyridine as the catalyst and polyoxyethylene(23) lauryl ether as the surfactant. With this technique, PBMA-*b*-PSt diblock copolymers were synthesized. The polymerization was nearly controlled; the ATRP of St from the macroinitiators showed linear increases in number-average molecular weight with conversion. The block copolymers were characterized with IR spectroscopy, ^{1}H-NMR, and differential scanning calorimetry. The effects of the molecular weight of the macroinitiators, macroinitiator concentration, catalyst concentration, surfactant concentration, and temperature on the polymerization were also investigated. Thermodynamic data and activation parameters for the ATRP are also reported. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 2123–2129, 2005

Key words: atom transfer radical polymerization (ATRP); block copolymers; emulsion polymerization

INTRODUCTION

The syntheses of polymers that have well-defined structures (e.g., predictable molecular weights and low polydispersities) and functionalities with radical intermediates have been an area of intense interest in recent years.[1] However, most of controlled/living radical polymerization has been confined to bulk or solution polymerization.[2] During past years, several attempts at applying the existing controlled radical polymerization techniques to the aqueous dispersed systems have been reported. The methods include stable free-radical polymerization,[3] atom transfer radical polymerization (ATRP),[4–6] reversible addition–fragmentation chain transfer,[7] and degenerative transfer polymerization based on the iodine atom exchange.[8]

Of all controlled/living radical polymerizations, ATRP in aqueous dispersed systems is of the most interesting ones. Although most transition metal complexes decompose rapidly in water, the Pd, Ru, and Cu complexes that catalyze ATRP are fortunately quite stable. With ruthenium[9] and palladium[10] catalytic systems, a relatively well-controlled polymerization can be achieved in aqueous systems with or without surfactant. The copper-mediated waterborne ATRP is so far the most versatile system.[11] It has been successfully employed for the (co)polymerization of styrene (St), acrylate, and methacrylates. Most studies have focused on the polymerization of *n*-butyl methacrylate (BMA).[12–17] ATRP is initiated by alkyl halides, and therefore, any polymer that has a sufficiently active alkyl halide end groups could initiate ATRP to afford block copolymers. This method has been successfully employed in the synthesis of a large range of previously unknown well-defined block copolymers.[18–23] However, only a few block copolymers have been prepared by emulsion ATRP.[24,25]

Recently, we reported our work on atom transfer radical solution and emulsion polymerization;[26–29] in this study, poly(*n*-butyl methacrylate) (PBMA) macroinitiators that contained alkyl bromide end groups were used to initiate the ATRP of St under aqueous conditions. With this technique, PBMA-*b*-polystyrene (PSt) diblock copolymers were synthesized. The effects of the molecular weight of the macroinitiators, macroinitiator concentration, catalyst concentration, surfactant concentration, and temperature on polymerization were also investigated.

EXPERIMENTAL

Materials

St was dried over CaH_2 and distilled *in vacuo*. BMA was distilled *in vacuo* immediately before use. Ethyl

2-bromopropinate (BrCH$_3$CHCOOC$_2$H$_5$) was synthesized according to a modified literature procedure. 4,4'-Di(5-nonyl)-2,2'-bipyridine (dNbpy) was obtained from Aldrich Chemical Co. (Shanghai, China) and was used as received. Cuprous Chloride (CuCl) was purified according to the literature.[30] Polyoxyethylene(23) lauryl ether (Brij35) was from commercial sources and was used as received.
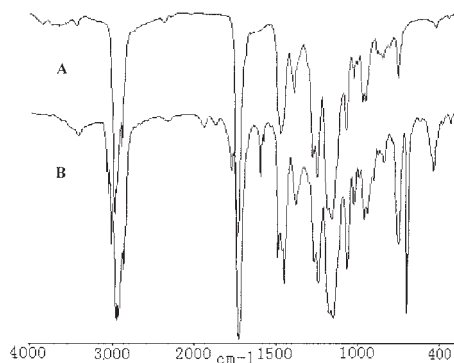
Synthesis of the PBMA macroinitiators

CuBr (0.0068 g), dNbpy (0.0428 g), and BMA were put into a flask equipped with a magnetic stirring bar. The flask was degassed three times by repeated freeze/vacuum/thaw cycles; then, the surfactant solution (0.2 g of Brij35 + 10 g of H$_2$O) was added via syringe. After an emulsion formed, the flask was placed in a 85°C oil bath under argon. The initiator BrCH$_3$CHCOOC$_2$H$_5$ (0.0085 g) was finally added, which corresponded to the zero point of the polymerization. After the heating was stopped, the reaction mixture was dried overnight at 50°C *in vacuo*; then, it was diluted with tetrahydrofuran (THF) and filtered through a 0.45-μm film. After precipitation into methanol from THF, the product was dried overnight at 60°C *in vacuo*.
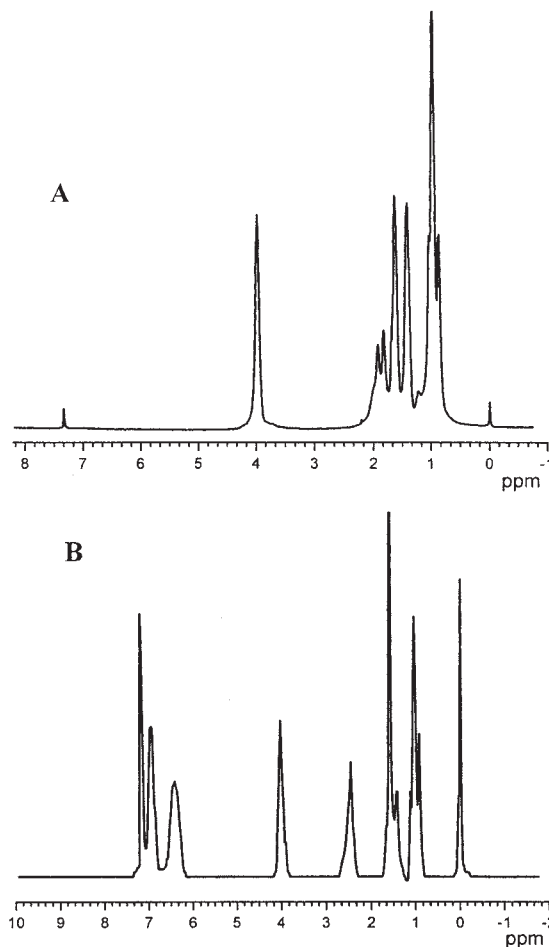
Synthesis of the PBMA-*b*-PSt diblock copolymers

The polymerization was carried out in a previously dried flask equipped with a magnetic stirrer bar under argon. The PBMA macroinitiator, CuCl, dNbpy, St, and the surfactant solution were added in sequence with stirring under an argon atmosphere and finally immersed in an oil bath at the reaction temperature. After heating was stopped, the product was purified by precipitation into methanol from THF.

Characterization

The conversion of the polymerization was determined gravimetrically. The molecular weight and molecular

Figure 2 ^{1}H-NMR spectra: (A) PBMA macroinitiators and (B) PBMA-*b*-St copolymer.

weight distribution were obtained by gel permeation chromatography (GPC) and multi-angle laser light scattering (MALLS) made in a Wyatt Technology Corp. (Santa Barbara, CA) instrument. The GPC–

Figure 1 IR spectra: (A) PBMA macroinitiators and (B) PBMA-*b*-PSt copolymer.
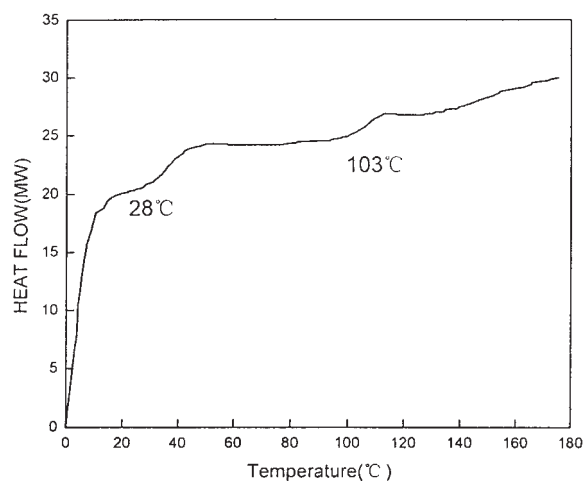
Figure 3 DSC analysis of the PBMA-*b*-PSt copolymer.

Figure 4 GPC curves of the PBMA macroinitiators.

Figure 5 M_n and M_w/M_n dependence on the conversion for the emulsion ATRP of St with PBMA macroinitiators.
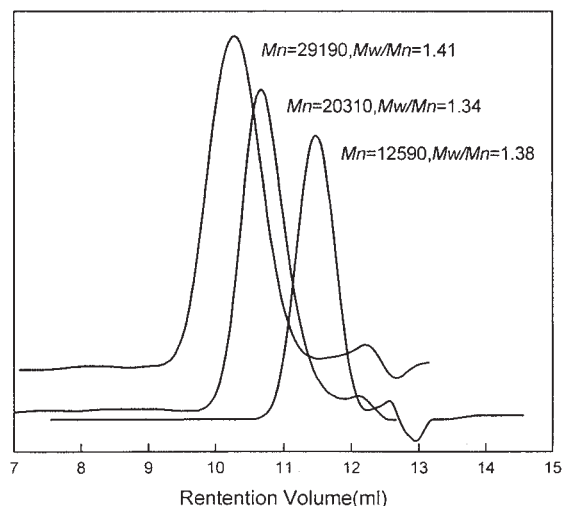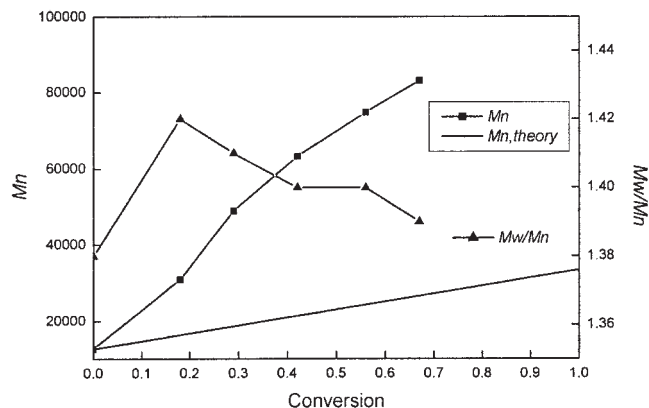
MALLS system involved a Styagel HWN 6E GPC column, a Wyatt OPTILAB RI detector, and a Wyatt MALLS detector (DAWN E). All samples were run in THF at 25°C with a flow rate of 0.8 mL/min. The theory number average molecular weight ($M_{n,theory}$) was calculated according to the following formula:

$$M_{n,theory} = M_{n,Macroinitiator} + \frac{[M]_{St}}{[M]_{Macroinitiator}} \times M_{n,St} \times \text{Conversion}$$

where the $M_{n,theory}$ is the theory number average molecular weight of the copolymer, $M_{n,macroinitiator}$ is the number average molecular weight of the macroinitiator, $[M]_{St}$ is the concentration of the styrene monomer, $[M]_{macroinitiator}$ is the concentraiton of the macroinitiator and $M_{n,St}$ is the molecular weight of the styrene monomer.

The ^{1}H-NMR spectrum was recorded on a Varian Mercury-300 spectrometer (Varian Corp., Palo Alto, CA) at room temperature in CDCl$_3$. The IR spectrum was recorded on a Daojin Japan IR-440 spectrometer (Shimadzu Corp., Chiyoda-Ku, Japan) at room temperature (KBr performing). Differential scanning calorimetry (DSC) measurement was carried out under a nitrogen flow with a PerkinElmer DSC7 instrument

(PerkinElmer, Foster City, CA) (heating rate = 20°C/min).

RESULTS AND DISCUSSION

Polymerization of St initiated by PBMA macroinitiators

The PBMA macroinitiators were prepared by emulsion the ATRP of BMA in waterborne media, catalyzed, and initiated by CuBr/dNbpy and BrCH$_3$CHCOOC$_2$H$_5$. Through the emulsion ATRP of St initiated by the PBMA macroinitiators, the PBMA-*b*-PSt diblock copolymers were obtained. The IR spectra of the PBMA macroinitiators and the final copolymer are shown in Figure 1. Figure 1(A) shows the PBMA macroinitiators; the characteristic spectra of PBMA appeared: C=O at 1728 cm^{-1}; C—O at 1268, 1241, and 1148 cm^{-1}; and —(CH$_2$)$_3$CH$_3$ at 1065, 965, and 844 cm^{-1}. Figure 1(B) shows that the copolymer consisted of PSt and PBMA. The characteristic spectra of PBMA still existed: C=O at 1728 cm^{-1};

TABLE I
Molecular Weight Characteristics of the PBMA Macroinitiators

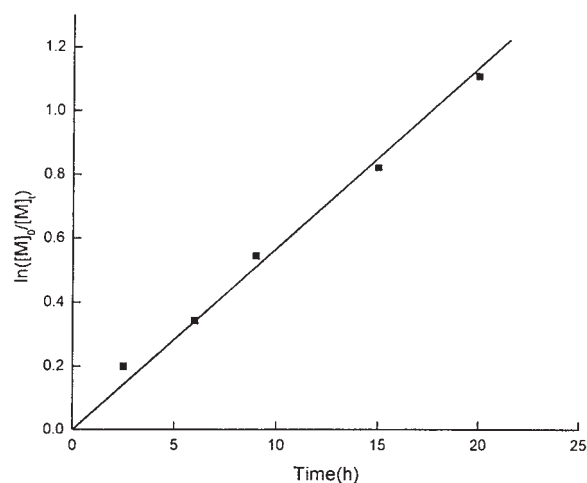| PBMA macroinitiator	Conversion (%)	$M_{n,theory}$	$M_{n,GPC}$	$M_w/M_{n,GPC}$
1	86	13,200	12,590	1.38
2	84	19,400	20,310	1.34
3	83	25,300	29,190	1.41

Figure 6 First-order kinetic plot for the emulsion ATRP of St.

TABLE II
Molecular Characteristics of the PBMA-*b*-PSt Diblock Copolymers

Copolymer (COP)	Initiators M_n	Conversion (%)	$M_{n,theory}$	$M_{n,GPC}$	$M_w/M_{n,GPC}$
COP-1	12,590	67.2	26,526	83,000	1.39
COP-2	20,310	63.3	33,414	111,200	1.41
COP-3	29,190	58.1	41,254	139,300	1.42

$[CuCl]_0[dNbpy]_0[PBMA-Br]_0[St]_0 = 1 : 2 : 1 : 200$; $St/H_2O = 1.5$ mL/10 mL; Brij35 = 0.2g; $T = 85$ °C.

C—O at 1268, 1241, and 1148 cm^{-1}; and —$(CH_2)_3CH_3$ at 1065, 965, and 844 cm^{-1}. The characteristic spectra of PSt also appeared at 698, 758, 2925, 3000, 3026, 3059, and 3081 cm^{-1}.

The ^{1}H-NMR spectrum of the PBMA macroinitiators and the final product are shown in Figure 2. In Figure 2(A), the signals at 0.8–1.19 ppm were attributed to the methyl protons of —$C(CH_3)(COOC_4H_9)$ and —$O(CH_2)_3CH_3$, and the signals at 1.35–2.10 ppm corresponded to the methylene groups of —CH_2—. The signals at 3.8–4.1 ppm were attributed to the methylene groups of —$COOCH_2(CH_2)_2CH_3$. In Figure 6(B) (shown later), in addition to the proton signals of PBMA, the signals at 6.2–7.3 ppm were attributed to the phenyl protons, and the signals at 1.2–2.0 ppm corresponded to the protons of vinyl in the main chain; this revealed that the polymer consisted of PBMA and PSt.

A DSC analysis, as set forth in Figure 3, also confirmed these results, the glass-transition temperatures at 28 and 103°C were attributed to the PBMA and PSt blocks, respectively, indicating that the polymer consisted of PBMA and PSt. We concluded from the IR, ^{1}H-NMR, and DSC spectra that the PBMA-*b*-PSt copolymers were synthesized.

Three kinds of PBMA macroinitiators were obtained through emulsion ATRP. Figure 4 shows the GPC curves of the PBMA macroinitiators. The polymer peaks were narrow and monomodal, indicating that the PBMA macroinitiators had narrow polydispersities. The molecular weight and the molecular weight distribution of the three PBMA macroinitiators are listed in Table I.

With the PSt macromolecules [number-average molecular weight $(M_n) = 12{,}590$, weight-average molec-
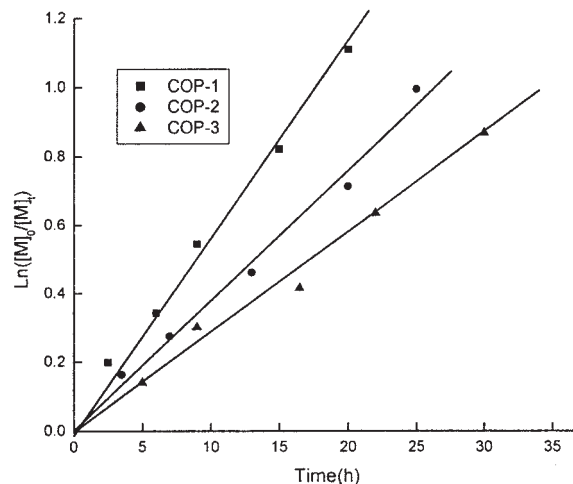
Figure 7 First-order kinetic plot for the emulsion ATRP of St.

ular weight $(M_w)/M_n = 1.38$] as macroinitiators, the emulsion polymerization of St with PBMA macroinitiator was investigated. The plot of M_n and polydispersity (M_w/M_n) dependence on conversion in this polymerization is shown in Figure 5; two important features of controlled radical polymerization were observed. The first one was the nearly linear increase of M_n versus monomer conversion, indicating that the number of chains was constant; in other words, chain-transfer reactions were negligible, but the molecular weight of the copolymers had a little more warp from the predicted value. The second feature was that the polydispersity decreased with the progress of the polymerization, meaning that nearly all of the chains started to grow simultaneously.

The first-order kinetic plot for the emulsion ATRP of St is shown in Figure 6. In ATRP, the first-order plot is usually linear due to a constant concentration. Within the bounds of experimental error, the first-order correlations were essentially linear, as required for a living polymerization. Figures 5 and 6 demonstrate that the reaction was nearly controlled.

Effect of the molecular weight of the macroinitiators on the polymerization

Table II shows the molecular weight and polydispersities of the copolymers with increasing molecular

TABLE III
ATRP of St at Various Concentrations of the PBMA Macroinitiators

$[I]_0$ (molL)	$[M]_0/[I]_0$	Conversion (%)	$M_{n,theory}$	$M_{n,GPC}$	$M_w/M_{n,GPC}$	$K_p^{app} \times 10^5/(S^{-1})$
0.0114	100	73.2	20,182	67,000	1.39	2.224
0.0057	200	67.3	26,526	83,000	1.39	1.531
0.0029	400	61.2	37,966	138,000	1.33	1.136

$[CuCl]_0[dNbpy]_0[St]_0 = 1 : 2 : 200$; $St/H_2O = 1.5$ mL/10 mL; Brij35 = 0.2 g; $T = 85$ °C.
$M_{n,GPC}$, the number average molecular weight of the copolymer measured by GPC.
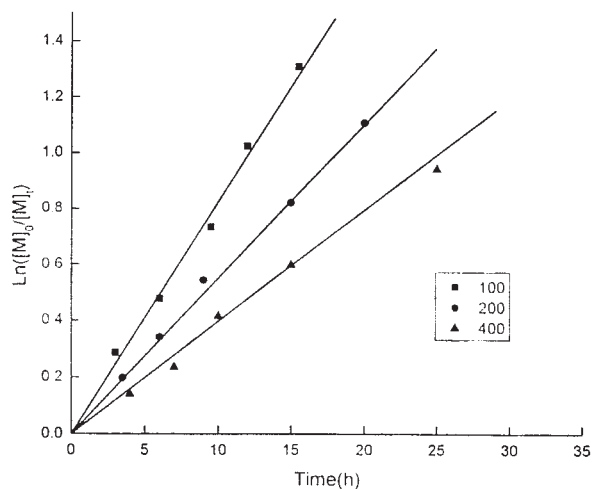
weight of the PBMA macroinitiators. The polymerization was controllable, and the molecular weight of the copolymers corresponded approximately with the predicted values, but with increasing macroinitiator molecular weight, the conversion decreased, the departure of the molecular weight of copolymers to the theoretical value increased, and the polydispersities broadened. Figure 7 shows a plot of ln $[M]_0/[M]_t$ versus time for the ATRP systems as the molecular weight of macroinitiators increased from 12,590 to 20,310 to 29,190 and the polymerization rate (k_p^{app}) decreased from 1.579×10^{-5} to 1.055×10^{-5} to 8.042×10^{-6} S^{-1}.

Effect of macroinitiator concentration on the polymerization
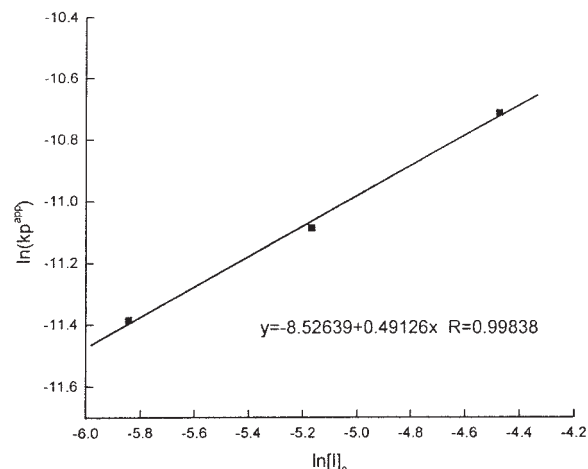
With the PBMA macroinitiators ($M_n = 12,590$, $M_w/M_n = 1.39$), the polymerization of St with various PBMA macroinitiator concentrations was investigated. Table III shows that a further increase in the amount of PBMA macroinitiator increased k_p^{app}, and the conversion and the molecular weight distribution of the product narrowed. Figure 8 shows the first-order kinetic plot for the ATRP of St with the PBMA macroinitiators when the PBMA macroinitiators concentration increased from 0.0114 to 0.0057 to 0.0029 mol/L and k_p^{app} decreased from 2.224×10^{-5} to 1.531×10^{-5} to 1.136×10^{-5} S^{-1}. Shown in Figure 9 is a plot of ln k_p^{app} versus ln $[I]_0$ for the ATRP systems with different amounts of initiator; k_p^{app} was on an order of 0.49 with respect to the PBMA macroinitiator concentration.

Effect of catalyst concentration on the polymerization

The polymerization of St with various catalyst concentrations was also studied. The data are shown in Table

Figure 9   Dependence of k_p^{app} on the concentration of the PBMA macroinitiators.

IV. When $[CuCl/2dNbpy]_0 = 0.00143$ mol/L, a copolymer sample with $M_n = 65,400$ and $M_w/M_n = 1.33$ was obtained, whereas a product with a relatively high molecular weight and a relatively broad molecular distribution ($M_n = 98,600$, $M_w/M_n = 1.45$) was obtained if $[CuCl/2dNbpy]_0$ was increased to 0.0228 mol/L, and the departure of the molecular weight of copolymers to the theoretical value increased. k_p^{app} increased with increasing catalyst concentration. A plot of ln k_p^{app} versus ln $[CuCl/2dNbpy]_0$ for the ATRP systems showed that the rate of polymerization was on the order of 0.61 with respect to the catalyst concentration (Fig. 10).
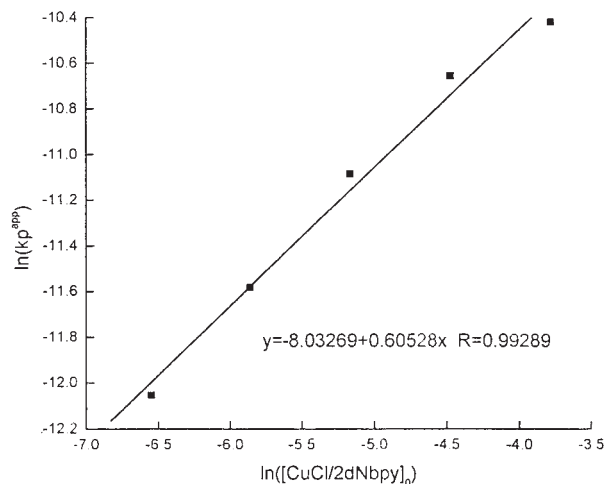
Effect of surfactant concentration on the polymerization

The polymerization of St with various surfactant concentrations was investigated, as shown in Table V. As shown, with increasing surfactant amount, k_p^{app} increased, the departure between the molecular weight of the copolymers to that of the theoretical value gradually decreased, and the molecular weight distribu-

Figure 8   First-order kinetic plot for the emulsion ATRP of St at various concentrations of the PBMA macroinitiators.

TABLE IV
ATRP Emulsion Polymerization of St with Different Amounts of Catalyst

[CuCl/ 2dNbpy]$_0$ (mol/L)	Conversion (%)	$M_{n,theory}$	$M_{n,GPC}$	$M_w/M_{n,GPC}$	$K_p^{app} \times 10^5$ (S^{-1})
0.00143	61.3	25,340	65,400	1.33	0.583
0.00285	63.3	25,756	71,000	1.35	0.932
0.0057	67.8	26,692	83,000	1.39	1.531
0.0114	72.6	27,690	91,000	1.42	2.354
0.0228	74.9	28,169	98,600	1.45	2.983

$[PBMA-Br]_0 [St]_0 = 1 : 200$; St/H$_2$O = 1.5 mL/10 mL; Brij 35 = 0.2 g; $T = 85$ °C.

Figure 10 Dependence of k_p^{app} on the concentration of $[CuCl/2dNbpy]_0$.

Figure 11 Dependence of k_p^{app} on the concentration of $[Brij35]_0$.

tion of the product narrowed. Shown in Figure 11 is a plot of $\ln k_p^{app}$ versus $\ln [Brij35]_0$ for the ATRP systems with different amounts of surfactant; k_p^{app} was on the order of 0.42 with respect to the surfactant concentration.

Dependence of the propagation rate on the temperature

The effect of temperature on k_p^{app} was studied over a range of 75–95°C. First-order kinetic plots are shown in Figure 12. The linearity between $\ln [M]_0/[M]$ and time in all cases indicated that the concentration of growing species remained constant and k_p^{app} increased with temperature. The Arrhenius plot obtained from the experimental data given in Figure 12 is given in Figure 13:
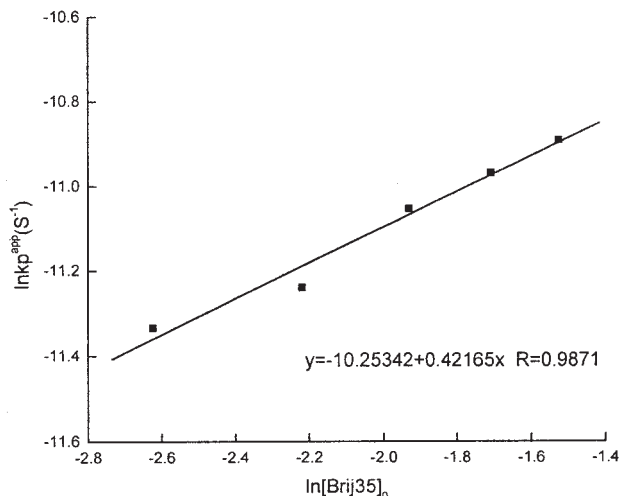
$$k_p^{app} = A \exp^{-E_{app}/RT}$$

$$\ln k_p^{app} = \ln A + E_{app}/R \times (-1/T)$$

where A and R are constants, T is the temperature, and E_{app} is the apparent activation energy.
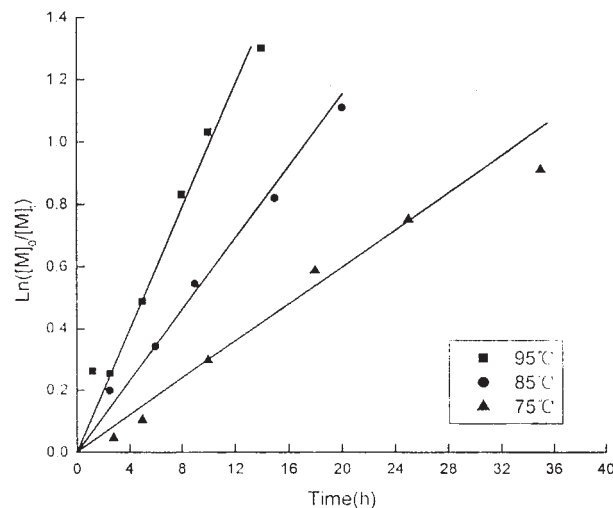
The apparent activation energy was calculated as 59.71 kJ/mol. According to the following equation

$$\Delta H_{eq}^0 = \Delta H_{app} - \Delta H_{prop}$$

where ΔH_{eq}^0 is the enthalpy of equilibrium, ΔH_{app} is the apparent enthalpy of activation, and ΔH_{prop} is the activation enthalpy of propagation. Values of ΔH_{prop} = 29.80 kJ/mol and ΔH_{eq}^0 = 29.91 kJ/mol were calculated for the ATRP emulsion of St initiated by PBMA macroinitiators.

CONCLUSIONS

PBMA-b-PSt diblock copolymers were successfully synthesized with emulsion ATRP initiated from ap-

TABLE V
ATRP Emulsion Polymerization of St with Different Amounts of Brij35

Brij35 vs water (%)	Conversion (%)	$M_{n,theory}$	$M_{n,GPC}$	$M_w/M_{n,GPC}$	$k_p^{app} \times 10^5$ (S^{-1})
1.0	62.1	25,506	36,000	1.41	1.196
1.5	65.4	26,193	35,500	1.39	1.314
2.0	68.1	26,754	81,900	1.39	1.583
2.5	71.2	27,399	37,700	1.38	1.724
3.0	72.3	27,628	39,300	1.37	1.862

$[CuCl]_0[dNbpy]_0[PBMA-Br]_0[St]_0 = 1: 2 : 1 : 200$; St/H$_2$O = 1.5 mL/10 mL, T = 85 °C.

Figure 12 Kinetic plots of the emulsion ATRP of St with PBMA macroinitiators at different temperatures.
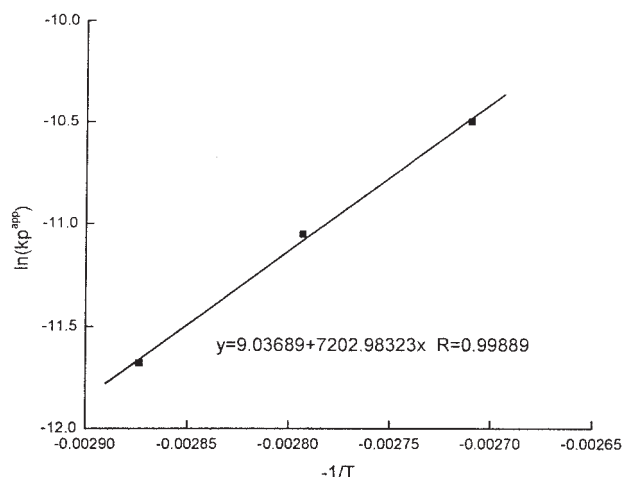
Figure 13 Effect of the temperature on k_p^{app} for the ATRP of St.

propriately functionalized chain ends of PBMA macroinitiators. The structure of the block copolymers and the living nature of the polymerization were characterized. The relationship between k_p^{app} with the concentration of the reactant was as follows:

$$k_p^{\text{app}} \propto [\text{CuCl}/2\text{dNbpy}]_0^{0.61}[\text{I}]_0^{0.49}[\text{Brij35}]_0^{0.42}$$

The apparent activation enthalpy (ΔH_{app}) for the ATRP of St initiated by PBMA macroinitiator was 59.71 kJ/mol, and ΔH_{eq}^0 was estimated to be 29.91 kJ/mol.

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