Synthesis and Characterization of PBMA-*b*-PDMS-*b*-PBMA Copolymers by Atom Transfer Radical Polymerization

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ABSTRACT: Poly(butyl methylacrylate)–*b*–poly(dimethylsiloxane)–*b*–poly(butyl methylacrylate) (PBMA–*b*–PDMS–*b*–PBMA) triblock copolymers were synthesized by atom transfer radical polymerization (ATRP). The reaction of α,ω-dichloride PDMS with 2′-hydroxyethyl-2-bromo-2-methylpropanoate gave suitable macroinitiators for the ATRP of BMA. The latter procedure was carried out at 110°C in a phenyl ether solution with CuCl and 4,4′-di (5-nonyl)-2,2′-bipyridine (dNbpy) as the catalyzing system. The polymerization was controllable, with the increase of the monomer conversion, there was a nearly linear increase of molecular weight and a decrease of polydispersity in the process of the polymerization, and the rate of the polymerization was first-order with respect to monomer conversion. The block copolymers were characterized with IR and ^{1}H-NMR and differential scanning calorimetry. The effects of macroinitiator concentration, catalyst concentration, and temperature on the polymerization were also investigated. Thermodynamic data and activation parameters for the ATRP were reported. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 532–538, 2004

Key words: ATRP; polysiloxanes; block copolymers

INTRODUCTION

Poly(dimethylsiloxane) (PDMS) block and graft copolymers are expected to possess unique physical properties making them viable candidates for materials such as thermoplastic elastomers, compatibilizers for silicone rubbers, and surfactants for supercritical carbon dioxide. Several synthetic methods for PDMS copolymers have been reported.[1–8] The best results were obtained using living anionic polymerization. However these methods required stringent purification and stoichiometric conditions. Block and graft copolymers have been prepared using free radical polymerization. For example, PDMS containing internal tetraphenylethylene moieties were used for the synthesis of segmented multiblock copolymers with various vinyl monomers.[5,6] While the use of macroinitiators for free radical polymerization appeared to be very promising, conventional methods introduced problems such as functionalization of polymer end groups, incomplete initiators efficiency, and homopolymer formation.[7,8]

These problems are avoided by atom transfer radical polymerization (ATRP)[9] from PDMS macroinitiators.[10–12] ATRP catalyzed by copper halides complexed with 2,2′-bipyridine (bpy) derivatives [such as 4,4′-di (5-nonyl)-2,2′-bipyridine (dNbpy)[13,14]] for the polymerization of various styrene,[15] methacrylate,[16,17] acrylate,[18] dienes, and acrylonitrile[19] has been developed by many researchers.[20,21] ATRP is initiated by alkyl halides, and therefore, any polymer that has a sufficiently active alkyl halide end-group could initiate ATRP to afford block copolymers. It has been successfully employed in the synthesis of a large range of previously unknown well-defined block copolymers.[22–25] As shown in Figure 1, this paper reports the synthesis of well-defined samples of PDMS end-capped with a group possessing an active C–Br bond and their subsequent applications as macroinitiators in the ATRP of butyl methylacrylate (BMA). The purpose of this study was to expand the scope of the ATRP method to produce block copolymers from PDMS macroinitiators.

EXPERIMENTAL

Materials

BMA was distilled under vacuum immediately before use. dNbpy was obtained from Aldrich Chem Co and used as received. Cuprous chloride (CuCl) was purified according to the literature.[26] α,ω-Dichloride PDMS (M_n = 8,200), obtained from Sichuan Chenguang Chemical Regents Co was used as received.

Preparation of 2′-hydroxyethyl-2-bromo-2-methylpropanoate

The synthesis of 2′-hydroxyethyl-2-bromo-2-methylpropanoate was based on the reported proce-
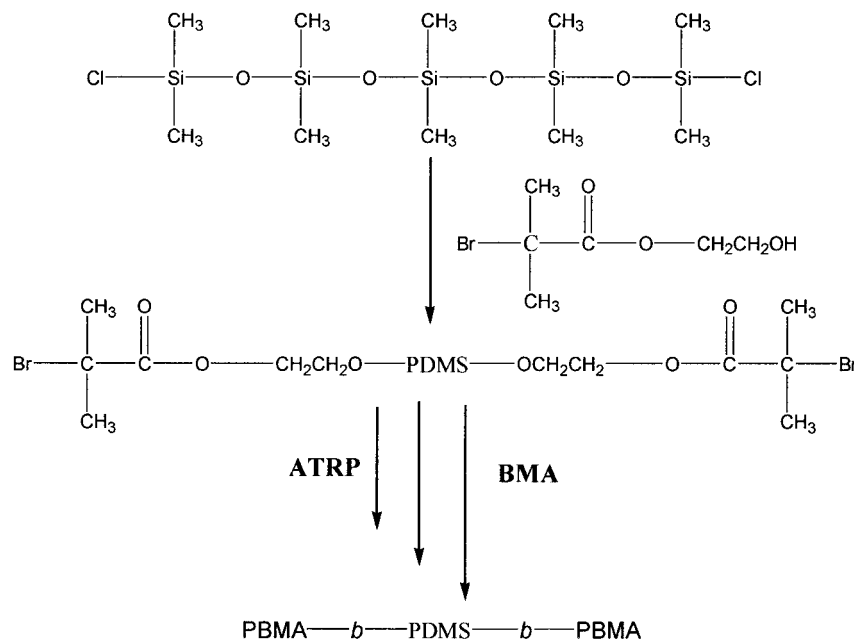
Figure 1   Reaction scheme for the synthesis of PDMS macroinitiators.

dure.[27] 2-Methyl-2-bromoproprionyl bromide (0.2 mol, 25 mL) was added dropwise to excess ethylene glycol (0.528 mol, 30 mL) in the presence of triethylamine (0.18 mol, 25 mL) and diethyl ether (70 mL). The reaction vessel was cooled with an ice bath. After the reaction had subsided, any remaining solvents were removed *in vacuo*, and the product was redissolved in diethyl ether. The solution was washed several times with a saturated sodium bicarbonate solution and then with water. The crude product was purified with flash chromatography with an eluent made up of a 50/50 (v/v) mixture of hexane and ethyl acetate. The final product was obtained as a transparent, colorless liquid. The structure of the product was confirmed by ^{1}H-NMR and IR spectroscopy.

^{1}H-NMR (CDCl$_3$, δ, ppm): C(Br)(**CH$_3$**)$_2$ (1.8), OH (3.0). –CO$_2$—CH$_2$—**CH$_2$** (3.72), –CO$_2$—**CH$_2$**—CH$_2$ (4.1). IR (KBr, cm^{-1}): O—H (3300), C—H (2970), C=O (1735).
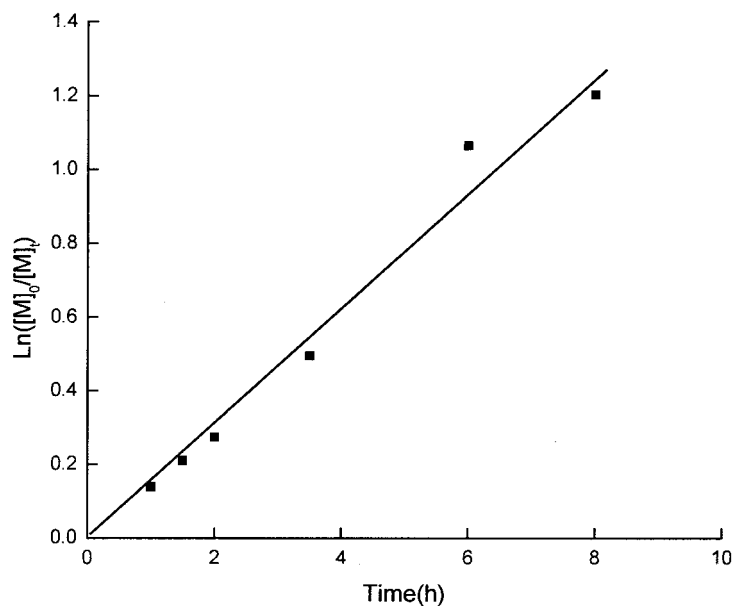

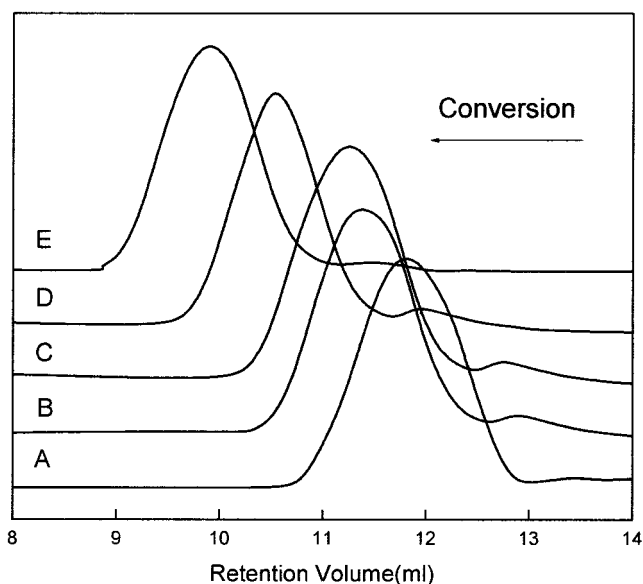**Figure 2**   First-order kinetic plot for the ATRP of BMA in phenyl ether.

Figure 3 GPC traces for the progress of ATRP reaction of BMA with PDMS macroinitiators. From right to left, the GPC peaks are (A) M_n = 8,200, M_w/M_n = 1.6; (B) M_n = 13,600, M_w/M_n = 1.58; (C) M_n = 17,600, M_w/M_n = 1.51; (D) M_n = 20,500, M_w/M_n = 1.43; (E) M_n = 31,200, M_w/M_n = 1.4.

Preparation of the PDMS macroinitiators

Typical PDMS macroinitiators were prepared as follows. α,ω-dichloride PDMS (8.16 $\times$ 10^{-4} mol, 6.5 g) was added to 2′-hydroxyethyl-2-bromo-2-methylpropanoate (1.66 $\times$ 10^{-3} mol, 0.25 g) and 1,8-diazabicylo[5.4.0]undec-7ene (DBU) (1.66 $\times$ 10^{-3}mol, 0.35 g) in tetrahydrofuran (THF; 30 mL) and stirred for 1 h at room temperature. After three reprecipitations into hexane, the macroinitiators were isolated and dried *in vacuo*. The molecular weight and molecular

weight distribution of the PDMS macroinitiators were obtained by GPC (M_n = 8,200, M_w/M_n = 1.6).

Preparation of the PBMA-*b*-PDMS-*b*-PBMA triblock copolymers

The polymerization was carried out in a previously dried flask equipped with a magnetic stirrer bar under argon. The PDMS macroinitiator (0.645 g), CuCl (0.0312 g), dNbpy (0.305 g), and phenyl ether (2.5 g) were put into the flask, and then the flask was degassed three times by repeated freeze/vacuum/thaw cycles under 10 mmHg. Previously dried BMA (5.0 mL) was purged into the flask. The mixture was stirred at room temperature under argon for 15min, and the flask was placed into a 110°C oil bath under argon. After the heating was stopped, the reaction mixture was purified by filtration through a short Al_2O_3 column followed by precipitation into methanol from THF. The filtered product was dried overnight at 60°C under vacuum.

Characterization

The conversion of the polymerization was determined gravimetrically. The molecular weight and molecular weight distribution were obtained by gel permeation chromatography (GPC) and many angle laser light scatter (MALLS) made by Wyatt Technology Corp. The GPC—MALLS system involves 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 data were processed with Wyatt Technology (Astra 473) software, and the $M_{n,theory}$ was calculated according to the following formula:
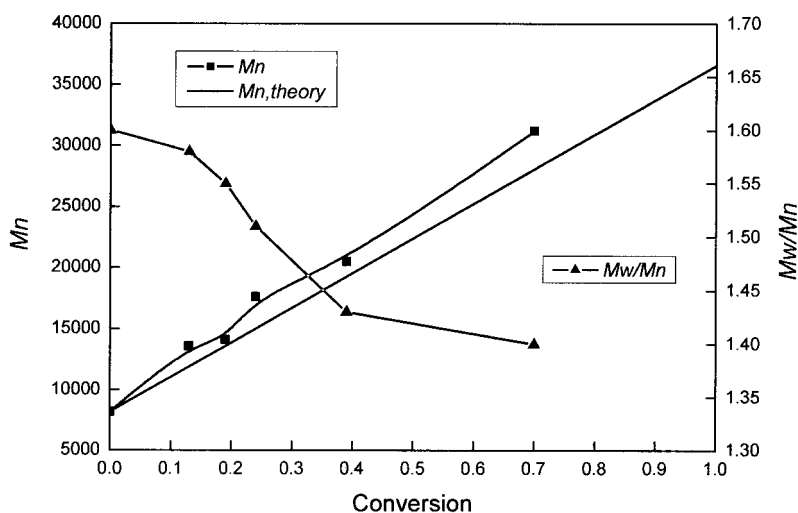

Figure 4 M_n and M_w/M_n dependence on conversion for the ATRP of BMA. [CuCl]$_0$: [dNbpy]$_0$: [PDMS]$_0$: [BMA]$_0$ = 1 : 2 : 0.25 : 100, BMA/phenyl ether = 4.47 g/2.5 g, T = 110°C.
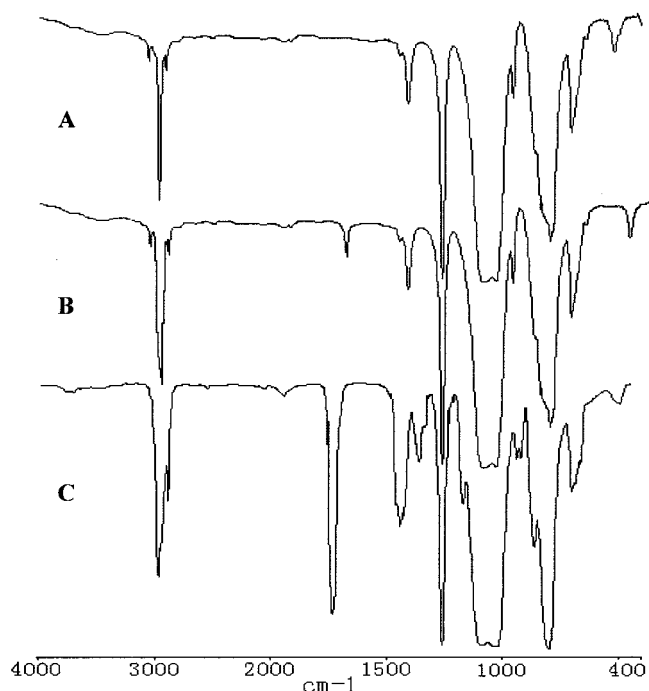
Figure 5 IR spectrum. (A) α,ω-dichloride polydimethylsiloxane. (B) PDMS macroinitiator. (C) PBMA-*b*-PDMS-*b*-PBMA copolymer.

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

The ^{1}H-NMR spectrum was recorded on a Varian Mercury—300 Spectrometer at room temperature in CDCl$_3$. The IR spectrum was recorded on a Daojin Japan IR-440 Spectroscopy at room temperature (KBr performing). Differential scanning calorimeter (DSC) measurements were carried out under a nitrogen flow with a Perkin–Elmer DSC7 (heating rate = 20°C/min).

RESULTS AND DISCUSSION

Polymerization of BMA initiated by PDMS macroinitiator

Polymerization of BMA initiated by the difunctional PDMS macroinitiators was carried out with a CuCl/dNbpy catalyst in phenyl ether at 110°C. The macroinitiator, catalyst, and growing triblock copolymer were soluble.

The first-order kinetic plot of the polymerization of BMA is shown in Figure 2. 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.

GPC traces for the progress of ATRP reaction of BMA with PDMS macroinitiators are shown in Figure 3. The growing triblock copolymer peak remained monomodal throughout the reaction, indicating that all of the attachable initiator that did not react with the PDMS had been removed prior to polymerization. Furthermore, the polymer peak continuously shifted to higher molecular weights with monomer conversion; the molecular weight of the macroinitiator was $M_n = 8{,}200$, $M_w/M_n = 1.60$. After polymerization, the measured values of copolymer had increased to $M_n = 31{,}200$, $M_w/M_n = 1.40$.

The plot of number average molecular weight, M_n, and polydispersity, M_w/M_n, dependence on conversion in this polymerization are shown in Figure 4. A nearly linear increase of M_n versus monomer conversion was observed; the polydispersity decreased with the progress of the polymerization. Figures 1–3 demonstrate that the reaction was controlled and the poly(butyl methylacrylate) blocks had low polydispersities typical of radical polymerization by ATRP.

The IR spectrum of α,ω-dichloride PDMS, PDMS macroinitiator, and the final copolymer are shown in
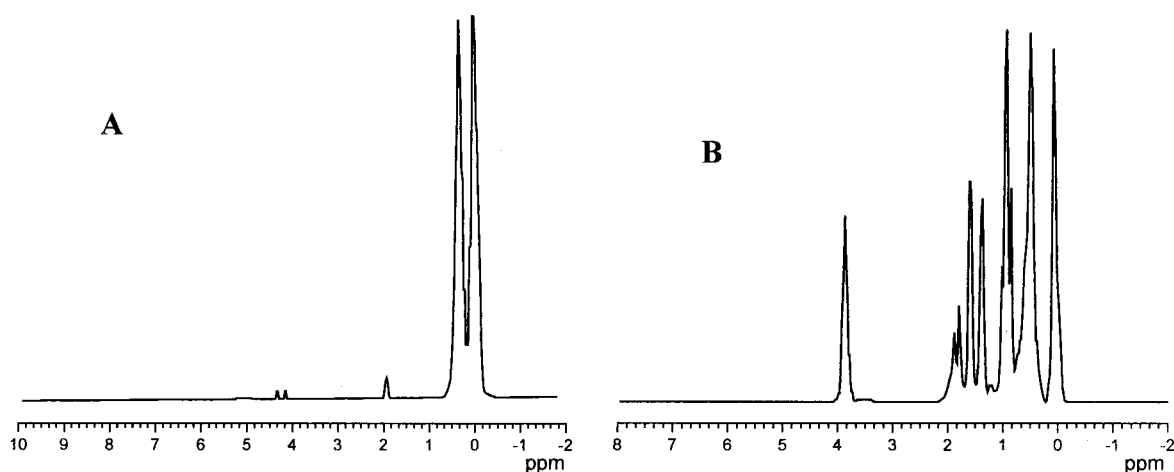

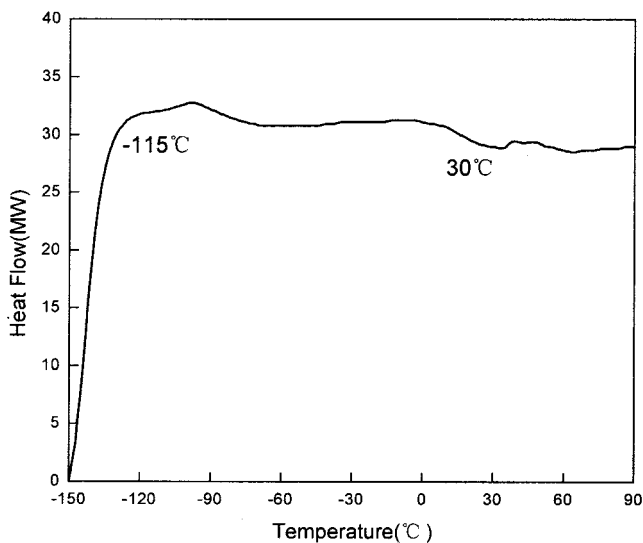**Figure 6** ^{1}H-NMR spectrum. (A) PDMS macroinitiator. (B) PBMA-*b*-PDMS-*b*-PBMA copolymer.

Figure 7 DSC analysis of PBMA-*b*-PDMS-*b*-PBMA copolymer.

Figure 8 Dependence of kp^{aPP} on the concentration of PDMS macroinitiators.

Figure 5. Figure 5(A) shows the IR spectrum of α,ω-dichloride PDMS; a strong Si—O–Si characteristic spectrum in 1,100–1,000 cm^{-1}, a CH$_3$ characteristic spectrum in 1,261 cm^{-1}, and a C—Si–C characteristic spectrum in 800 cm^{-1} can be observed. The IR spectrum of the PDMS macroinitiator is shown in Figure 5(B); the strong characteristic spectra of Si–O–Si, CH$_3$, and C-Si-C still exist and the characteristic spectrum of C=O appears at 1,730 cm^{-1}, indicating that the alkyl bromide-terminal PDMS was obtained by the reaction between α,ω-dichloride PDMS and 2′-hydroxyethyl-2-bromo-2-methylpropanoate. Figure 5(C) reveals that the copolymer consists of PBMA and PDMS. The characteristic spectrums of PDMS: Si–O–Si in 1,100–1,000 cm^{-1}, CH$_3$ in 1,261 cm^{-1}, C—Si–C in 800 cm^{-1} still exist and the characteristic spectrums of PBMA appear: C=O in 1,728 cm^{-1}; C—O in 1,268, 1,241, and 1,148 cm^{-1}; and —(CH$_2$)$_3$CH$_3$ in 1,065, 965, and 844 cm^{-1}.

The ^{1}H-NMR spectrum of PDMS macroinitiator and the final product are shown in Figure 6. In Figure 6(A), the observed peaks at 0.2–0.6 ppm were assigned to the protons of methyl groups of —Si(CH$_3$)$_2$O, the signals at 2.0 ppm were for the methylene groups next to the bromide, the signals at 4.0–4.2 ppm were assigned to the methylene groups of —CH$_2$—CH$_2$—O, which

also indicating that the alkyl bromide-terminal PDMS was obtained by the reaction between α,ω-dichloride PDMS and 2′-hydroxyethyl-2-bromo-2-methylpropanoate. In Figure 6(B), besides the protons of methyl groups of —Si(CH$_3$)$_2$O (0.2–0.6 ppm), the protons of the methylene groups next to the bromide (2.0 ppm) et al. The signals at 0.8–1.19 ppm were attributed to the methyl protons of —C(CH$_3$)(COOC$_4$H$_9$) and —O(CH$_2$)$_3$CH$_3$, and the signals at 1.35–2.10 ppm correspond to the methylene groups of —CH$_2$—, and the signals at 3.8–4.1 ppm were attributed to the methylene groups of —COOCH$_2$(CH$_2$)$_2$CH$_3$, revealing that the polymer consisted of PBMA and PDMS.

A DSC analysis, set forth in Figure 7, also confirms the results: the Tg in 30°C and the Tg in −115°C were attributed to PBMA block and PDMS block respectively, indicating that the polymer consisted of PBMA and PDMS. It could be concluded from the IR, ^{1}H-NMR, and DSC spectrum that the triblcok copolymers PBMA–*b*–PDMS–*b*–PBMA consisting of a PDMS center block and PBMA terminal blocks were synthesized.

Effect of macroinitiator concentration on the polymerization

The polymerization of BMA with various PDMS macroinitiator concentrations was investigated. Table I

TABLE I
ATRP of BMA at Various Concentrations of PDMS Macroinitiator

$[I]_0$ (mol/L)	$[M]_0/[I]_0$	Time (h)	Conversion (%)	$M_{n,theory}$	$M_{n,GPC}$	$M_w/M_{n,GPC}$	$kp^{aPP} \times 10^5$ (S^{-1})
0.005	800	13	63.2	44,090	60,800	1.46	2.56
0.011	400	8	70.1	28,080	31,200	1.40	4.41
0.022	200	5	75.4	18,906	21,900	1.40	6.91

$[CuCl]_0 : [dNbpy]_0 : [BMA]_0 = 1 : 2 : 100$; BMA/phenyl ether = 4.47 g/2.5 g; $T = 110$°C.
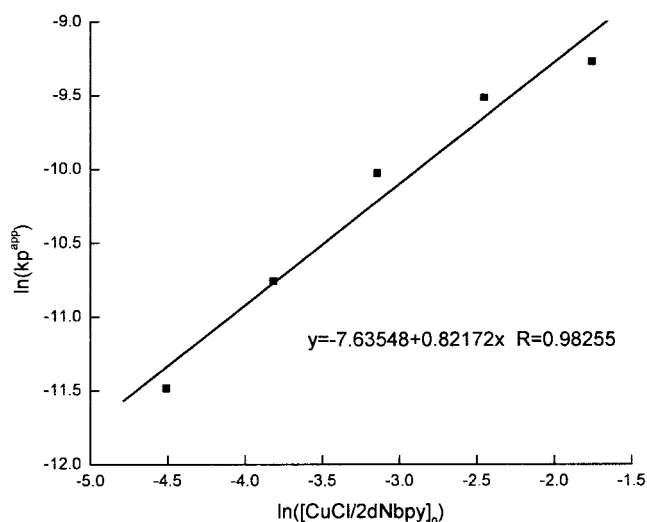
Figure 9 Dependence of kp^{app} on the concentration of $[CuCl/2dNbpy]_0$.

Figure 10 Kinetic plots of the ATRP of BMA with PDMS macroinitiator at different temperatures.

shows that a further increase in the amount of PDMS macroinitiator can increase the reaction rate, although the molecular weight distribution of the product keeps narrowing. Shown in Figure 8 is a plot of $\ln kp^{app}$ versus $\ln[I]_0$ for the ATRP systems with different amounts of initiator; the polymerization rate is proportional to the 0.67 index of the concentration of the PDMS macroinitiators.

Effect of catalyst concentration on the polymerization

The polymerization of BMA with various catalyst concentrations was also studied. The data are presented in Table II. When $[CuCl/2dNbpy]_0 = 0.011$ mol/L, the copolymer sample with $M_n = 28,400$ and $M_w/M_n = 1.38$ (Table II, NO 1) is obtained, whereas the product with a relatively high molecular weight and a relatively broad molecular distribution ($M_n = 34,500$, $M_w/M_n = 1.47$) is obtained if the $[CuCl/2dNbpy]_0$ concentration is increased to 0.172 mol/L. The rate of polymerization increases with increasing catalyst concentration. A plot of $\ln kp^{app}$ versus $\ln[CuCl/2dNbpy]_0$ for the ATRP systems shows that the polymerization

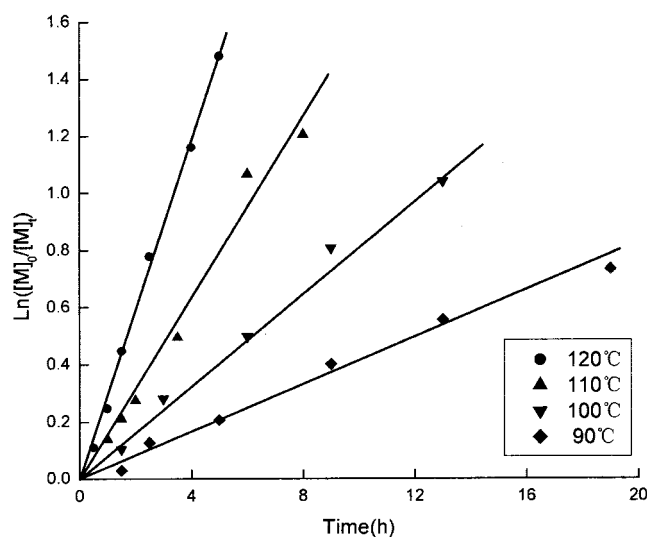rate is proportional to the 0.82 index of the concentration of the catalyst (Fig. 9).

Dependence of the propagation rate on the temperature

The effect of temperature on the rate of polymerization was studied over a range of 90–120°C. First-order kinetic plots are shown in Figure 10. The linearity between $\ln[M]_0/[M]$ and time in all cases indicates that the concentration of growing species remained constant, and kp^{app} increased with temperature. The Arrhenius plot obtained from the experimental data given in Figure 10 is given in Figure 11.

$$kp^{app} = A\exp^{-Eapp/RT}$$

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

The apparent activation energy was calculated to be 19.04 kcal/mol. According to eq (1),

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

TABLE II
ATRP Polymerization of BMA with Different Amount of Catalyst

$[CuCl/2dNbpy]_0$ (mol/L)	Conversion (%)	$M_{n,theory}$	$M_{n,GPC}$	$M_w/M_{n,GPC}$	$kp^{app} \times 10^5$ (S^{-1})
0.011	64.5	26,518	28,400	1.38	1.03
0.022	66.5	27,086	29,300	1.39	2.13
0.043	70.1	28,108	31,200	1.40	4.41
0.086	73.4	29,045	33,800	1.44	7.35
0.173	76.8	30,011	34,500	1.47	9.37

$[PDMS]_0 : [BMA]_0 = 0.25 : 100$; BMA/phenyl ether $= 4.47$ g/2.5 g; $T = 110°C$.
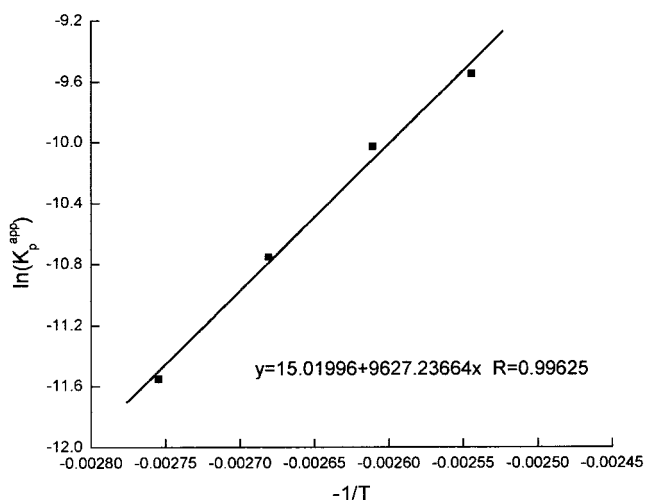
Figure 11 Effect of temperature on kp^{app} for the ATRP of BMA with PDMS macroinitiator in phenyl ether.

where

$$\Delta H^0_{\mathrm{eq}}$$

is the enthalpy of the equilibrium, ΔH_{app} is the apparent enthalpy of activation, and ΔH_{prop} is the activation enthalpy of propagation. $\Delta H_{\mathrm{prop}} = 4.2$ kcal/mol (the ΔH_{prop} of BA, which has similar structure to BMA). Then, $\Delta H^0_{\mathrm{eq}} = 14.85$ kcal/mol was calculated for the ATRP of BMA initiated by PDMS macroinitiators.

CONCLUSION

The ABA block copolymers, PBMA–*b*–PDMS–*b*–PBMA, have been successfully synthesized with ATRP initiated from appropriately functionalized chain ends of PDMS macroinitiator. The structure of the block copolymers and the living nature of the polymerization have been characterized. The rate of polymerization increases with increasing catalyst or PDMS macroinitiator concentration, the polymerization rate is proportional to the 0.82 index of the concentration of the catalyst [CuCl/2dNbpy]$_0$, and is proportional to the 0.67 index of the concentration of the PDMS macroinitiators. The apparent activation energy (ΔH_{app}) for

the ATRP of BMA was 19.04 kcal/mol, and the enthalpy of the equilibrium was estimated to be $\Delta H^0_{\mathrm{eq}} = 14.85$ kcal/mol.

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