

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

Hui Peng,¹ Shiyuan Cheng,¹ Zhiqiang Fan²

¹School of Chemistry and Materials Science, Hubei University, Wuhan, 430062, China

²Institute of Polymer Science and Engineering, Zhejiang University, Hangzhou, 310027, China

Received 30 September 2003; accepted 3 February 2004

ABSTRACT: Polystyrene-*b*-poly(dimethylsiloxane)-*b*-polystyrene (Pst-*b*-PDMS-*b*-PSt) triblock copolymers were synthesized by atom transfer radical polymerization (ATRP). Commercially available difunctional PDMS containing vinylsilyl terminal species was reacted with hydrogen bromide, resulting in the PDMS macroinitiators for the ATRP of styrene (St). The latter procedure was carried out at 130°C in a phenyl ether solution with CuCl and 4,4'-di(5-nonyl)-2,2'-bipyridine (dNbpy) as the catalyzing system. By using this technique, triblock copolymers consisting of a PDMS center block and polystyrene terminal blocks were synthesized.

The polymerization was controllable; ATRP of St from those macroinitiators showed linear increases in M_n with conversion. The block copolymers were characterized with IR and ¹H-NMR. The effects of molecular weight of macroinitiators, macroinitiator concentration, catalyst concentration, and temperature on the polymerization were also investigated. Thermodynamic data and activation parameters for the ATRP are reported. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3764–3770, 2004

Key words: ATRP; polysiloxanes; block copolymers

INTRODUCTION

Of all the inorganic polymers studied, polysiloxanes have been the most widely exploited.¹ Particularly, poly(dimethylsiloxane) (PDMS) is used in materials for its high oxygen permeability and heat transfer properties. However, because PDMS is a fluid at room temperature, the homopolymer lacks dimensional stability. In an effort to produce materials composed of silicones with more desirable mechanical properties, block, graft, and network copolymers containing PDMS segments were examined.^{2–4} The best results were obtained by using living anionic polymerization. However, these methods required stringent purification and stoichiometric conditions. Block and graft copolymers were prepared by 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) from PDMS macroinitia-

tors.^{9–11} ATRP was first reported by Matyjaszewski and Wang in 1995,¹² now 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,^{12,15–16} methacrylate,^{15,17} acrylate,^{18–19} dienes, and acrylonitrile²⁰ was developed by many researchers.^{21–22} 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 was successfully employed in the synthesis of a large range of previously unknown well-defined block copolymers.^{23–28} In this article, as shown in Figure 1, the difunctional PDMS macroinitiators that contained alkyl bromide end groups were used to initiate ATRP of styrene (St) under conditions that provided control over both chain length of the organic segment and overall composition. The effects of molecular weight of macroinitiators, macroinitiator concentration, catalyst concentration, and temperature on the polymerization were also investigated.

EXPERIMENTAL

Materials

Styrene (St) was dried over CaH₂ and distilled under vacuum. 4,4'-Di(5-nonyl)-2,2'-bipyridine (dNbpy) was obtained from Aldrich Chemical Co. and used as received. Cuprous chloride (CuCl) was purified according to literature.²⁹ Difunctional vinylsilyl-terminal PDMS, obtained from Sichuan Chenguang Chemical Regents Co. (China), was used as received.

Correspondence to: S. Cheng.

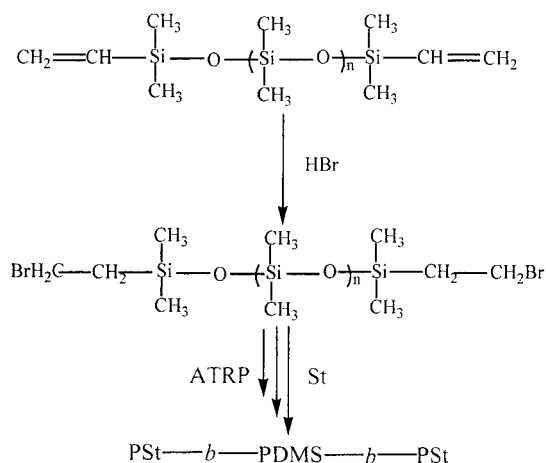


Figure 1 Synthesis of PDMS macroinitiators and copolymers.

Synthesis of PDMS macroinitiators

Sixty-six grams (0.01 mol) of vinylsilyl-terminal PDMS and 200 ml of anhydrous ethyl ether were put into a 500-ml three-necked flask with a magnetic stir bar. The dry HBr gas was introduced to the mixture in an ice-water bath. The mixture was stirred at 0°C for 1 h, before the gas introduction was stopped; then, the mixture was stirred overnight, warming to room temperature over that period, and the mixture was filtered. The solvent, anhydrous ethyl ether, was removed by room-temperature distillation. Distillation was continued until no more bubbling was observed, at which time the pressure was reduced to 1 mmHg to remove any volatile byproducts. The liquid was dried at 55°C under vacuum overnight. Yield = 56 g (84.8%). The molecular weight and molecular weight distribu-

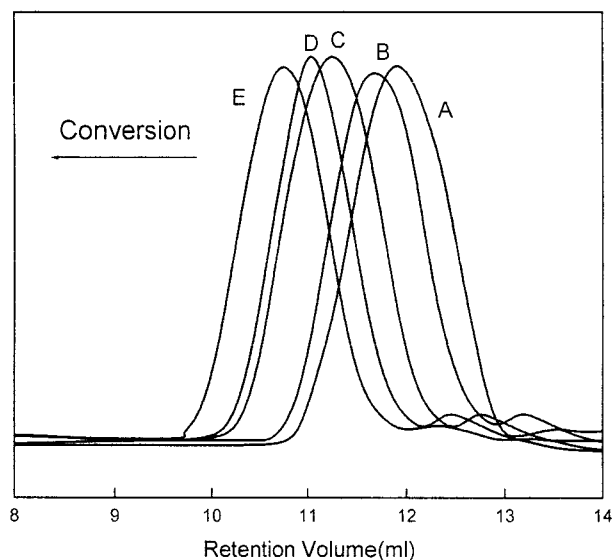


Figure 3 GPC traces for the progress of ATRP of St with PDMS macroinitiator in phenyl ether. From right to left, the GPC peaks are (A) $M_n = 64400$, $M_w/M_n = 1.37$; (B) $M_n = 9560$, $M_w/M_n = 1.36$; (C) $M_n = 12700$, $M_n/M_n = 1.34$; (D) $M_n = 16800$, $M_w/M_n = 1.34$; (E) $M_n = 18200$, $M_w/M_n = 1.33$.

tion of the PDMS macroinitiators were obtained by GPC ($M_n = 6400$, $M_w/M_n = 1.37$).

Synthesis of PSt-*b*-PDMS-*b*-PSt triblock copolymers

The polymerization was carried out in a previously dried flask equipped with a magnetic stirrer bar under argon. The PDMS macroinitiator (1.09 g) ($M_n = 6400$, $M_w/M_n = 1.37$), CuCl (0.0216 g), dNbpy (0.178 g), and phenyl ether (1.25 g) were put into the flask. Then the

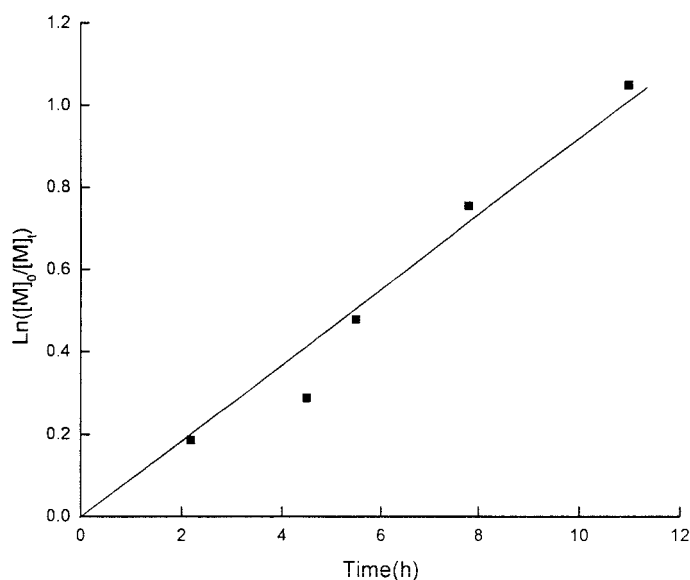


Figure 2 First-order kinetic plot for the ATRP of St in phenyl ether.

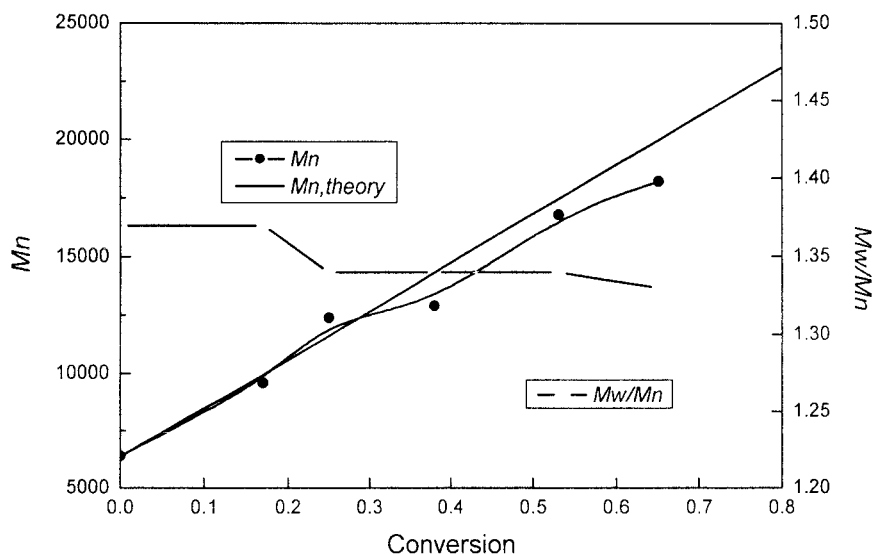


Figure 4 M_n and M_w/M_n dependence on conversion for the ATRP of St.

flask was degassed three times by repeated freeze/vacuum/thaw cycles under 10 mmHg. Previously dried St (2.5 ml) was purged into the flask. The mixture was stirred at room temperature under argon for 15 min, and the flask was placed into a 130°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.;

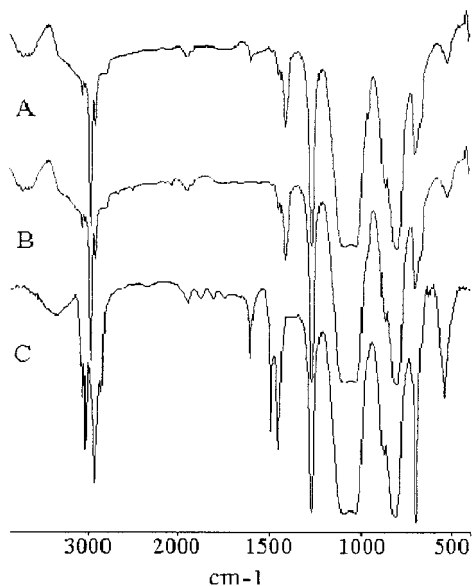


Figure 5 IR spectrum. (A) Vinylsilyl-terminal PDMS. (B) PDMS macroinitiators. (C) copolymer.

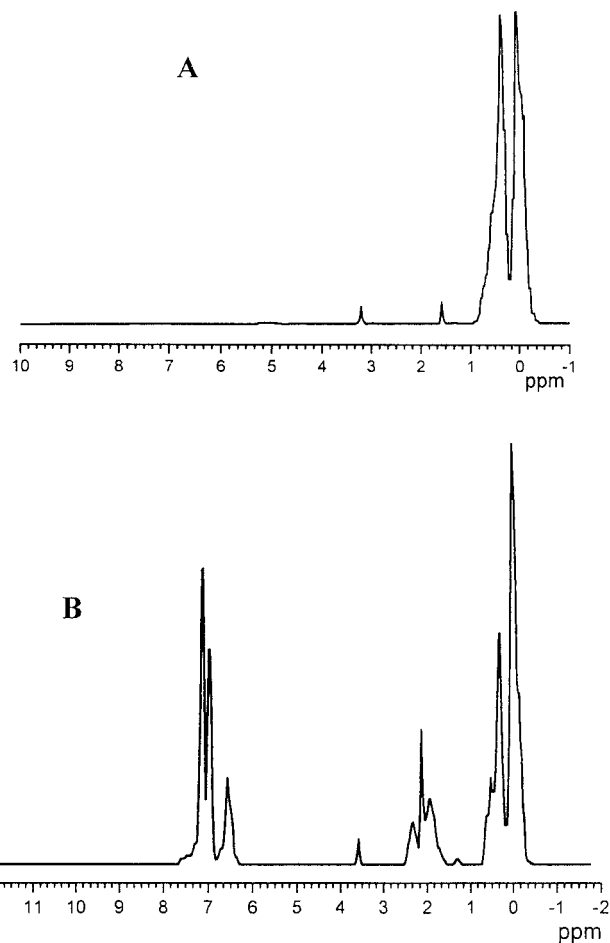


Figure 6 ^1H NMR spectrum, (A) PDMS macroinitiator. (B) copolymer.

TABLE I
The Molecular Characteristics of PSt-*b*-PDMS-*b*-PSt Triblock Copolymers

Copolymer (COP)	$M_{n, \text{initiators}}$	Conversion (%)	$M_{n, \text{theory}}$	$M_{n, \text{GPC}}$	$M_w/M_{n, \text{GPC}}$
COP-1	1800	74.1	17,200	16,400	1.29
COP-2	1800	76.2	17,600	16,800	1.31
COP-3	6400	65.3	19,900	18,200	1.33
COP-4	6400	68.1	20,500	18,900	1.33
COP-5	6400	66.2	20,100	21,700	1.34
COP-6	10,000	59.3	22,200	19,700	1.39
COP-7	10,000	61.1	22,700	19,200	1.42

the GPC-MALLS system involves a Styragel® 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 manipulated with Wyatt Technology (Astra 473) software, and the $M_{n, \text{theory}}$ was calculated according to

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

The $^1\text{H-NMR}$ 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 spectroscope at room temperature (KBr disc). Differential scanning calorimeter (DSC) measurement was carried out under a nitrogen flow with a Perkin-Elmer DSC7 (heating rate = 20°C/min).

RESULTS AND DISCUSSION

Polymerization of St initiated by PDMS macroinitiator

The first-order kinetic plot of the polymerization of St is shown in Figure 2. In ATRP, the first-order plot is usually linear because of a constant concentration of radicals. 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 St with PDMS macroinitiators are shown in Figure 3. The polymer peak continuously shifted to higher molecular weights with monomer conversion; the molecular weight of the macroinitiator was $M_n = 6400$, $M_w/M_n = 1.37$. After polymerization, the measured values of copolymer had increased to $M_n = 18,200$, $M_w/M_n = 1.33$.

The plot of number-average molecular weight, M_n , and polydispersity, M_w/M_n , and 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, demonstrated that the reaction was controllable.

The IR spectrum of the vinylsilyl-terminal PDMS, the PDMS macroinitiators, and the final copolymer are shown in Figure 5. Figure 5(A) is the IR spectrum of vinylsilyl-terminal PDMS: observed are a strong Si—O—Si characteristic spectrum in 1100–1000 cm^{-1} ; CH_3 characteristic spectrum in 1261 cm^{-1} ; C—Si—C characteristic spectrum in 800 cm^{-1} ; and C=C characteristic spectrum in 1596 cm^{-1} . The IR spectrum of the PDMS macroinitiators is shown in Figure 5(B): the strong the strong characteristic spectrum of Si—O—Si, CH_3 , and C—Si—C a still exist but the C=C characteristic spectrum in 1596 cm^{-1} disappears, indicating that there exists additional reaction between vinylsilyl-terminal PDMS and hydrogen bromide, and the alkyl bromide-terminal PDMS was obtained. Figure 5(C) reveals that the copolymer consists of polystyrene and PDMS. The characteristic spectra of PDMS, Si—O—Si in 1100–1000 cm^{-1} , CH_3 in 1261 cm^{-1} , C—Si—C in 800 cm^{-1} , still exist. The characteristic spectrum of polystyrene appeared at 698 cm, 758, 2925, 3000, 3026, 3059, and 3081 cm^{-1} .

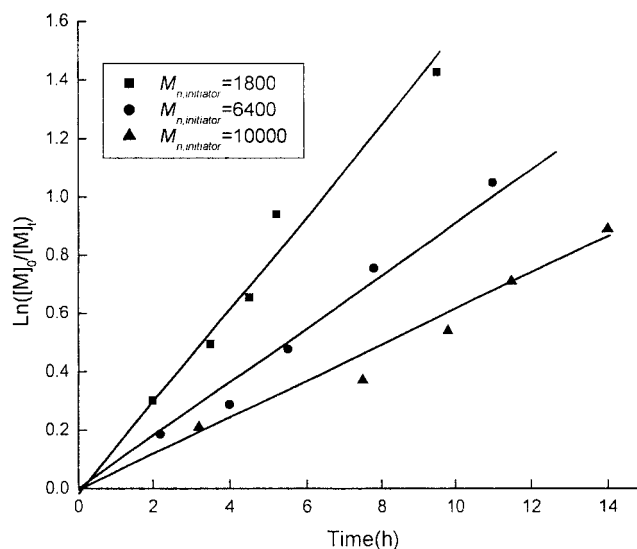


Figure 7 First-order kinetic plot for the ATRP of St with PDMS macroinitiator in phenyl ether.

TABLE II
ATRP of St at Various Concentrations of PDMS Macroinitiator

No.	$[I]_0$ (mol L ⁻¹)	Time (h)	Conversion (%)	$M_{n,theory}$	$M_{n,GPC}$	$M_w/M_{n,GPC}$	$k_p^{app} \times 10^5$ (S ⁻¹)
1	0.0075	20	51.2	27,500	16,700	1.39	1.20
2	0.015	11	65.3	19,900	18,200	1.33	2.35
3	0.030	7	79.2	14,600	13,800	1.33	5.24

The ¹H-NMR spectrum of PDMS macroinitiator and the final product are shown in Figure 6. In Figure 6(A), the observed peaks at 0.2–0.8 ppm are assigned to the protons of methyl groups of —Si(CH₃)₂O, and the signals at 3.2 ppm for the methylene group(—CH₂—CH₂—) next to the bromide. In Figure 6(A), besides the protons of methyl groups of —Si(CH₃)₂O (0.2–0.8 ppm), the methylene group next to the bromide (3.2 ppm), the signals at 6.56, 7.05 ppm are attributed to the phenyl protons, and the signals at 1.2–2 ppm correspond to the protons of vinyl (—CH₂—CH—) in the main chain. This revealed that the polymer consisted of polystyrene and PDMS. It was calculated from the area ratio between the 6H signal from PSt and the 5H signal from benzene that the ratio of sequence lengths of PSt and PDMS was $X = (A^*/5) / (A^*/6) = 1.76$ (A^* and A^* were the area of protons of methyl groups of —Si(CH₃)₂O and phenyl protons, respectively), which is close to that calculated from the GPC spectrum (1.84).

Effect of the molecular weight of macroinitiators on the polymerization

Table I shows the molecular weight and the polydispersities of copolymers with increasing molecular weight of macroinitiators. As can be seen, the polymerization was controllable; the molecular weights of copolymers approximately corresponded with those predicted by theory, but when the molecular weight of macroinitiators increased, the conversion decreased, and the departure of the molecular weight of copolymers from the theoretical value increased: the polydispersities were broader. Figure 7 shows a plot of $\ln[M]_0/[M]_t$ versus time for the ATRP systems. When the molecular weight of macroinitiators increased from 1800, 6400 to 10,000, the rate of polymerization (k_p^{app}) decreased from $4.18 \times 10^5 \text{S}^{-1}$, $2.35 \times 10^5 \text{S}^{-1}$ to $1.71 \times 10^5 \text{S}^{-1}$.

Effect of macroinitiator concentration on the polymerization

The polymerization of St with various PDMS macroinitiator concentration was investigated. Table II shows that a further increase in the amount of PDMS macroinitiator can increase the reaction rate. Shown in

Figure 8 is a plot of $\ln k_p^{app}$ versus $\ln[I]_0$ for the ATRP systems with different amounts of macroinitiators: the rate of polymerization is 1.06 order with respect to the concentration of the PDMS macroinitiators.

Effect of catalyst concentration on the polymerization

The polymerization with various catalyst concentrations was studied and is shown in Table III. When $[\text{CuCl}/2\text{dNbpy}]_0 = 0.015 \text{mol L}^{-1}$, the copolymer sample with $M_n = 16,500$ and $M_w/M_n = 1.28$ (Table II, NO 1) is obtained, whereas a product with a relatively high molecular weight and broad molecular distribution ($M_n = 28900$, $M_w/M_n = 1.38$) is obtained if the $[\text{CuCl}/2\text{dNbpy}]_0$ concentration increases to 0.236mol L^{-1} . The rate of polymerization increases with increasing catalyst concentration. A plot of $\ln k_p^{app}$ versus $\ln[\text{CuCl}/2\text{dNbpy}]_0$ for the ATRP systems shows that the rate of polymerization is 0.86 order with respect to the concentration of the catalyst (Fig. 9).

Effect of temperature on the polymerization

The effect of temperature on the polymerization was studied over a range of 90–130°C. First-order kinetic

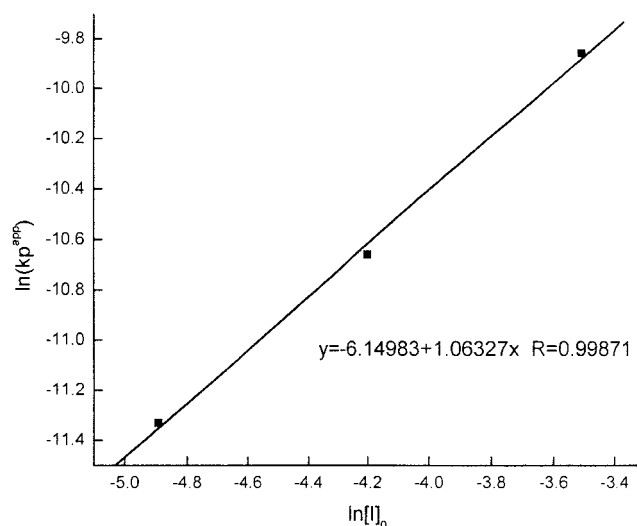


Figure 8 Dependence of k_p^{app} on the concentration of PDMS macroinitiators.

TABLE III
ATRP Polymerization of St with Different Amounts of Catalyst

$[\text{CuCl}/2\text{dNbpy}]_0$ (mol/L)	Conversion (%)	$M_{n,\text{theory}}$	$M_{n,\text{GPC}}$	$M_w/M_{n,\text{GPC}}$	k_p^{app} $\times 10^5$ (S ⁻¹)
0.015	55.2	17,881	16,500	1.28	0.576
0.030	56.3	18,110	17,300	1.29	1.068
0.059	65.7	20,065	18,200	1.33	2.354
0.118	74.8	21,958	24,500	1.34	4.116
0.236	77.5	22,520	28,900	1.38	5.734

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

k_p^{app} increased with temperature. The Arrhenius plot, obtained from the experimental data given in Figure 10, is given in Figure 11. The apparent activation en-

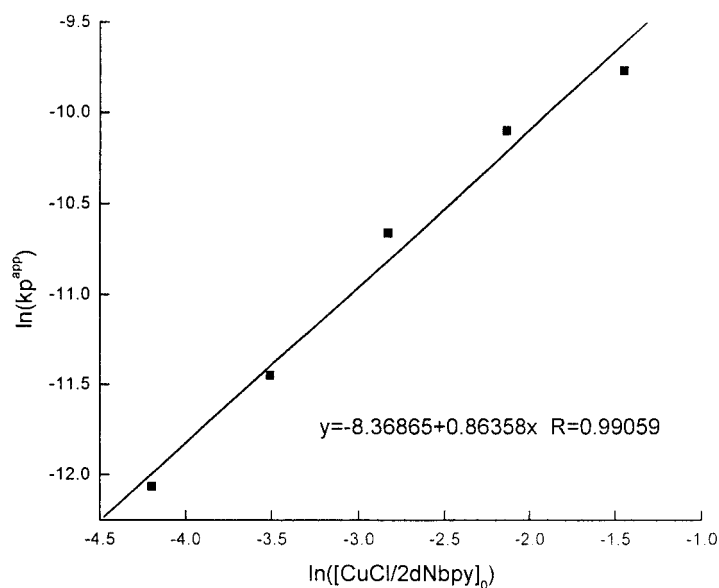


Figure 9 Dependence of k_p^{app} on the concentration of $[\text{CuCl}/2\text{dNbpy}]_0$

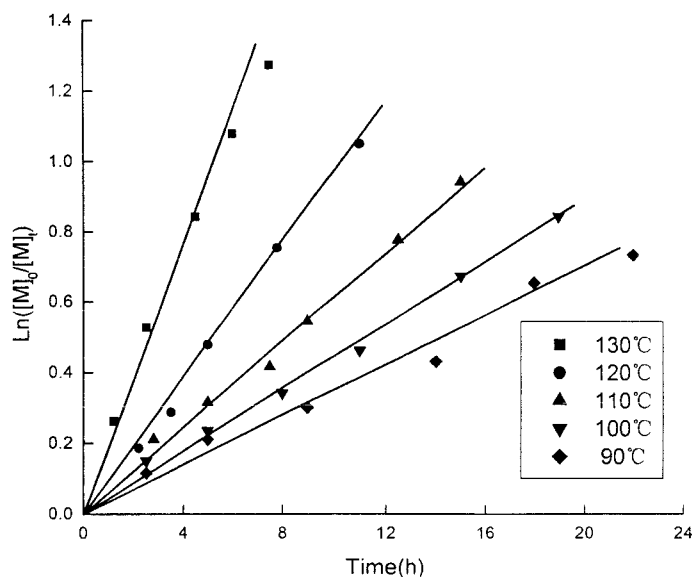


Figure 10 Kinetic plots of the ATRP of St with PDMS macroinitiator at different temperature.

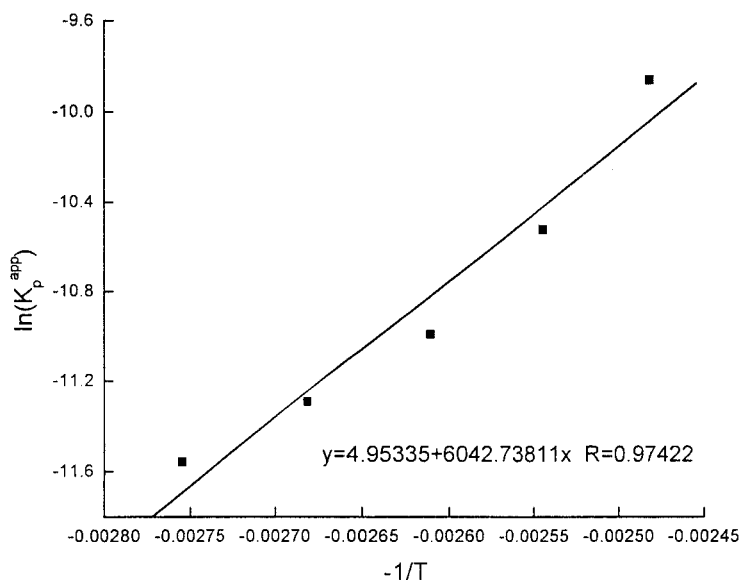


Figure 11 Effect of temperature on k_p^{app} for the ATRP of St with PDMS macroinitiator in phenyl ether.

ergy was calculated to be 11.96 kcal/mol. According to

$$\Delta H_{eq}^0 = \Delta H_{app} - \Delta H_{prop} \quad (1)$$

where ΔH_{eq}^0 is the enthalpy of the equilibrium, ΔH_{app} is the apparent enthalpy of activation, and ΔH_{prop} is the activation enthalpy of propagation ($\Delta H_{prop} = 7.1$ kcal/mol). Then, $\Delta H_{eq}^0 = 4.85$ kcal/mol was calculated for the ATRP of St initiated by PDMS macroinitiators, which was similar to the value of Matyjaszewski's.¹³

CONCLUSIONS

The ABA block copolymers, PSt-*b*-PDMS-*b*-PSt, were successfully synthesized with ATRP initiated from appropriately functionalized chain ends of PDMS macroinitiator. The rate of polymerization decreases with increasing molecular weight of PDMS macroinitiators and increases with increasing catalyst or PDMS macroinitiator concentration: the rate of polymerization is 1.06 order with respect to the macroinitiator concentration, and 0.86 order with respect to $[CuCl/2dNbpy]_0$. The apparent activation energy (ΔH_{app}) for the ATRP of St was 11.96 kcal/mol, and the enthalpy of the equilibrium was estimated to be $\Delta H_{eq}^0 = 4.85$ kcal/mol.

References

1. Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: Englewood Cliffs, NJ, 1992.
2. Shinoda, H.; Matyjaszewski, K.; Okrasa, L.; Mierzwa, M.; Pakula, T. *Macromolecules* 2003, 36, 4772.
3. Shinoda, H.; Miller, P. J.; Matyjaszewski, K. *Macromolecules* 2001, 34, 3186.
4. Shinoda, H.; Matyjaszewski, K. *Macromol Rapid Commun* 2001, 22 (14), 1176.
5. Crivello, J. V.; Conlon, D. A.; and Lee, J. L. *J Polym Sci, Polym Chem Ed* 1986, 24, 1197.
6. Crivello, J. V.; Lee, J. L.; Conlon, D. A. *J Polym Sci, Polym Chem Ed* 1986, 24, 1251.
7. Nair, C. P. R.; Clouet, G. *Macromolecules* 1990, 23, 1361.
8. Harabagiu, V.; Hamciuc, V.; Giurgiu, D. *Makromol Chem, Rapid Commun* 1990, 11, 433.
9. Matyjaszewski, K. *Controlled Radical Polymerization*; ACS Symposium Series 685; American Chemical Society: Washington, DC, 1998.
10. Nakagawa, Y.; Miller, P. J.; Matyjaszewski, K. *Polymer* 1998, 39, 5613.
11. Miller, P. J.; Matyjaszewski, K. *Macromolecules* 1999, 32, 8760.
12. Wang, J. S.; Matyjaszewski, K. *J Am Chem Soc* 1995, 117, 5614.
13. Matyjaszewski, K.; Patten, T. E.; Xia, J. H. *J Am Chem Soc* 1997, 119, 674.
14. Patten, T. E.; Xia, J. H.; Matyjaszewski, K. *Science* 1996, 272, 866.
15. Wang, J. S.; Matyjaszewski, K. *Macromolecules* 1995, 28, 7901.
16. Qiu, J.; Matyjaszewski, K. *Macromolecules* 1997, 30, 5673.
17. Wang, J. L.; Grimand, T.; Matyjaszewski, K. *Macromolecules* 1997, 30, 6507.
18. Matyjaszewski, K.; Nakagawa, Y.; Jasieczek, C. B. *Macromolecules* 1998, 31, 1535.
19. Davis, K. A.; Paik, H. J.; Matyjaszewski, K. *Macromolecules* 1999, 32, 1767.
20. Matyjaszewski, K.; Jo, S. M.; Paik, H. J.; Gaynor S. G. *Macromolecules* 1997, 30, 6398.
21. Min, K.; Hu, J.; Wang, C. C.; Elaissari, A. *J Polym Sci, Part A: Polym Chem* 2002, 40 (7), 892.
22. Kotre, T.; Nuyken, O.; Weberskirch, R. *Macromol Rapid Commun* 2002, 23 (15), 871.
23. Gaynor, S. G.; Qiu, J.; Matyjaszewski, K. *Macromolecules* 1998, 31, 5951.
24. Tong, J. D.; Ni, S.; Winnk, M. M. *Macromolecules* 2000, 33, 1482.
25. Coca, S.; Paik, H. H.; Matyjaszewski, K. *Macromolecules* 1997, 30, 6513.
26. Kajiwarra, A.; Matyjaszewski, K. *Macromolecules* 1998, 31, 3489.
27. Patten, T. E.; Matyjaszewski, K. *Adv Mater* 1998, 10 (2), 901.
28. Coessens, V.; Pintauer, T.; Matyjaszewski, K. *Prog Polym Sci* 2001, 26, 337.
29. Keller, R. N.; Wycoff, H. O. *Inorg Synth* 1946, 2, 1.