

# Poly(dimethylsiloxane-*b*-styrene) Diblock Copolymers Prepared by Reversible Addition–Fragmentation Chain-Transfer Polymerization: Synthesis and Characterization

Cheng-Mei Guan, Zheng-Hong Luo, Pei-Ping Tang

Department of Chemical and Biochemical Engineering, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, People's Republic of China

Received 12 September 2009; accepted 10 November 2009

DOI 10.1002/app.31780

Published online 22 February 2010 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Well-defined poly(dimethylsiloxane-*b*-styrene) diblock copolymers were prepared by reversible addition–fragmentation chain-transfer (RAFT) polymerization. Monohydroxyl-terminated polydimethylsiloxane was modified to form a functional polydimethylsiloxane/macro-RAFT agent, which was reacted with styrene to form the diblock copolymers. The chemical compositions and structures of the copolymers were characterized by proton nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy, and gel permeation chromatography. The surface properties and morphology of

the copolymers were investigated with static water contact-angle measurements, X-ray photoelectron spectroscopy, transmission electron microscopy, and atomic force microscopy, which showed a low surface energy and microphase separation surfaces that were composed of hydrophobic domains from polydimethylsiloxane segments. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3283–3290, 2010

**Key words:** RAFT polymerization; block copolymers; polysiloxanes

## INTRODUCTION

Poly(dimethylsiloxane-*b*-styrene) (PDMS-*b*-PS) combines the unique properties of silicone polymers with those of polystyrene (PS).<sup>1–5</sup> The excellent properties of silicone polymers include high stabilities toward heat and ultraviolet radiation, very low glass transition and melting temperatures, and good gas permeability and low surface tension, and most importantly, polysiloxanes are nontoxic and environmentally compatible,<sup>6</sup> whereas PS materials can find wide industrial applications because of their special properties, including light transmission capability, dimensional stability, and high tensility and flexibility.<sup>7</sup> New properties are expected if these two polymers are combined together. However, polydimethylsiloxane (PDMS) and PS are incompatible, and phase separation and nanostructures are observed.<sup>8–10</sup> Asso-

ciation between these two polymers opens the way to various industrial applications. For instance, PDMS-*b*-PS copolymers can be used as thermoplastic elastomers, compatibilizers, and surfactants in polymer blends,<sup>11–13</sup> and in practice, they have been made into contact lenses, gas permeable films and tubes, release surfaces for pressure-sensitive adhesives, and lithographic printing masters.<sup>13–16</sup>

Considerable attention has been paid to PDMS-*b*-PS copolymers.<sup>1,7,17–25</sup> Davies and Jones<sup>1</sup> studied the bulk composition and configuration of PDMS-*b*-PS copolymers. Chen and coworkers<sup>17,18</sup> studied the surface compositions and structures of PDMS-*b*-PS films cast from different solvents. Sokol et al.<sup>7</sup> evaluated the friction properties of PDMS-*b*-PS films on top of silicon wafers. Fukumine et al.<sup>19</sup> studied the micellization behavior of diblock copolymers in solution. Recently, Ma et al.<sup>20</sup> obtained materials based on the micellization of PDMS-*b*-PS copolymers. Generally speaking, PDMS-*b*-PS copolymers can form morphologies with strongly segregated PS and PDMS microphases and are possibly the most studied PDMS-containing block copolymers.<sup>26–30</sup> However, most of these studies were focused on interfacial behaviors,<sup>31–35</sup> and few studies were concerned with the relationship between the surface composition and morphology of the block copolymers.

Various polymerization techniques have been used to synthesize block copolymers, with living

Correspondence to: Z.-H. Luo (luozh@xmu.edu.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 20406016.

Contract grant sponsor: Nation Defense Key Laboratory of Ocean Corrosion and Anti-Corrosion of China; contract grant number: 51449020205QT8703.

Contract grant sponsor: Fujian Province Science and Technology Office of China; contract grant number: 2005H040.

anionic polymerization being the most widely studied.<sup>36–38</sup> Living anionic polymerization methods for nonpolar monomers (e.g., butadiene or styrene) have been successfully commercialized, whereas no commercial success exists for living anionic polymerization of acrylic monomers because of the need for high-purity monomers and solvents and a low reaction temperature and unwanted side reactions.<sup>38</sup> Living/controlled radical polymerization provides an efficient way to synthesize well-defined polymers. Successful methods of living radical polymerization include nitroxide-mediated radical polymerization, atom transfer radical polymerization (ATRP), and reversible addition–fragmentation chain-transfer (RAFT) polymerization. ATRP can be used to prepare well-defined block copolymers because of the ability to control the polymer architecture, molecular weight, and molar mass distribution and to moderate the experimental conditions.<sup>39–45</sup> With ATRP, the halide species is usually toxic, and the catalyst complex used is easily oxidized in air. The nitroxide-mediated radical polymerization technique also has restrictions of monomer choice and tends to operate at elevated temperatures.<sup>46</sup> The RAFT technique, however, is applicable to a wide range of monomers and can be applied to high-conversion bulk polymerizations.<sup>47–50</sup>

PDMS-*b*-PS copolymers have been achieved mainly by living anionic polymerization<sup>37,51,52</sup> and ATRP.<sup>53,54</sup> No detailed research has been done with the RAFT technique to prepare the PDMS-*b*-PS copolymers before this study. Therefore, it was desirable for us to develop a novel approach for the direct synthesis of PDMS-*b*-PS copolymers. In this study, we synthesized PDMS-*b*-PS diblock copolymers by RAFT with a PDMS/macro-RAFT agent.

## EXPERIMENTAL

### Materials

Monohydroxyl-terminated polydimethylsiloxane [PDMS-OH; 5000 g/mol, as determined by gel permeation chromatography (GPC)] and 2-bromoisobutrylbromide (98%) were obtained from A Better Choice for Research Chemicals GmbH & Co. KG (Hamburg, Germany) Triethylamine (99%) was supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and was stored over 4-Å molecular sieves. Styrene (Guangdong Xilong Chemical Co, Ltd., Guangzhou, China) was washed with a 5 wt % aqueous NaOH solution to remove the inhibitor. Azobisisobutyronitrile (AIBN; Shanghai No. 4 Reagent and H. V. Chemical Co, Ltd., Shanghai, China) was recrystallized from ethanol. Potassium *O*-ethyl xanthate was supplied by J&K Chemical Co, Ltd., (Beijing, China) and was used without further purification.

All other reagents and solvents were obtained from Sinopharm Chemical Reagent and were used without further purification.

### Measurements

Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectroscopy was performed on a Bruker AV400 instrument (Bruker, Switzerland) with deuterated chloroform as the solvent. Fourier transform infrared (FTIR) spectra were obtained on an Avatar 360 FTIR spectrophotometer (USA). GPC was carried out with tetrahydrofuran (THF) at a flow rate of 1 mL/min with a Waters (USA) 1515 isocratic high-performance liquid chromatography pump equipped with a Waters 2414 refractive-index detector and three Waters Styragel HR columns (1 × 10<sup>4</sup>, 1 × 10<sup>3</sup>, and 500-Å pore sizes). Monodisperse PS standards were used for calibration. Static water contact angles of the diblock copolymer films (prepared by the casting of 3 wt % THF polymer solutions on glass slides) were measured on a telescopic goniometer (SL-200B) (Shanghai, China). For each angle reported, at least seven sample readings from different surface locations were averaged. X-ray photoelectron spectroscopy (XPS) spectra were recorded with a PHI quantum 2000 scanning ESCA microprobe (USA) equipped with an Al K<sub>α1,2</sub> monochromatic source of 1486.60 eV. The beam was 200 μm in diameter, and the analysis area was 1.5 × 0.2 mm<sup>2</sup>. The measurements were typically operated at 35 W. A typical multiplex pass energy was 29.35 eV, and a typical survey pass energy was 187.85 eV. XPS samples were prepared as follows: the block copolymers were dissolved in THF, then cast onto aluminum foil, and dried *in vacuo* at room temperature. The morphology of the PDMS-*b*-PS diblock copolymers was identified by transmission electron microscopy (TEM). The film surface was obtained from the slow evaporation technique: 25 mL of THF was placed in a dry and sealed desiccator to form a solvent atmosphere. A drop of 1 wt % polymer solution was applied onto a copper grid coated with carbon, and then, the grid was placed in the desiccator for 72 h to eliminate trace solvent. A transmission electron microscope (Tecnaif30) was used with an accelerating voltage of 300 kV. Atomic force microscopy (AFM) observation was made on a NanoScope SPM (Veeco, USA) in ultralight tapping mode under ambient conditions (25°C, 40% RH). We prepared the AFM samples by dispensing a drop of the THF solution on freshly cleaned Si wafer and then drying them *in vacuo* at room temperature.

### Synthesis of PDMS end-capped with bromine (PDMS-Br)

The synthesis of PDMS-Br via the esterification reaction of 2-bromoisobutrylbromide with a

commercially available PDMS-OH (Scheme 1) has been described previously.<sup>55–57</sup> The product is a pale yellow oil (yield = 4.1712 g, 85%), and it was used for the preparation of the PDMS/macro-RAFT agent.

<sup>1</sup>H-NMR ( $\delta$ , ppm, in CDCl<sub>3</sub>): 0.1 [m, 396H, –Si(CH<sub>3</sub>)<sub>2</sub>], 0.55 (m, 4H, –SiCH<sub>2</sub>), 0.90 (m, 3H, –CH<sub>3</sub>), 1.33 (m, 4H, –CH<sub>2</sub>), 1.58 (m, 2H, –CH<sub>2</sub>CH<sub>2</sub>O), 1.96 [s, 6H, –C(CH<sub>3</sub>)<sub>2</sub>Br], 3.46 (t, 2H, –CH<sub>2</sub>O), 3.70 (t, 2H, –OCH<sub>2</sub>), 4.34 (t, 2H, –CH<sub>2</sub>OCO). FTIR (liquid): 2964 (alkyl C–H stretching), 1742 (–C=O stretching), 1260 [–Si(CH<sub>3</sub>)<sub>2</sub> flexing], 1000–1100 cm<sup>–1</sup> (Si–O stretching).

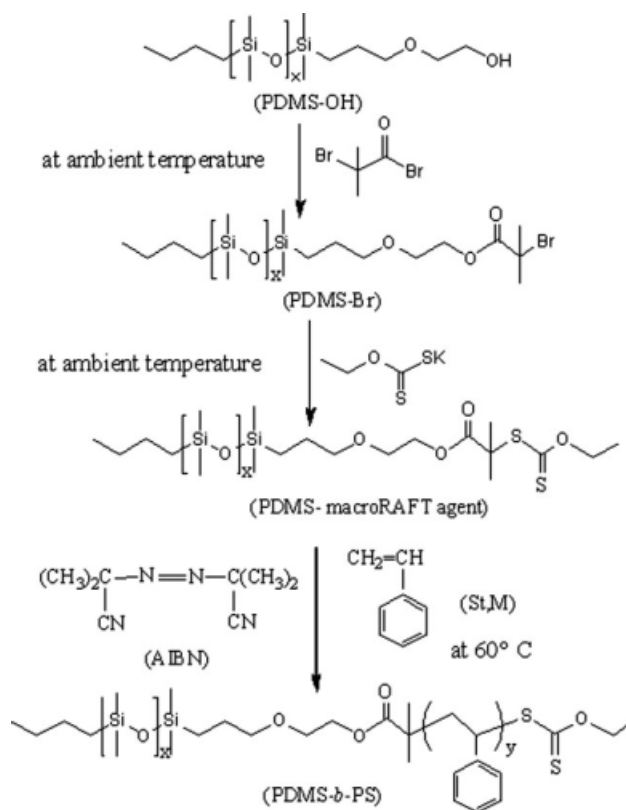
### Synthesis of PDMS end-capped with a dithioester group (the PDMS/macro-RAFT agent)

As shown in Scheme 1, PDMS end-capped with a dithioester group was prepared as the PDMS/macro-RAFT agent. In a 100-mL, round-bottom flask, potassium *O*-ethylxanthate (0.1040 g, 0.650 mmol) was dissolved in ethanol (20 mL), and PDMS-Br (1.357 g, 0.26 mmol) was added; then, the mixture was stirred for 12 h at room temperature. The precipitate was isolated by filtration and washed three times with dichloromethane. The solvent was evaporated to obtain a pale yellow liquid (yield = 1.1721 g, 80%).<sup>58</sup> The obtained liquid was used as the PDMS/macro-RAFT agent for the preparation of the diblock copolymers.

<sup>1</sup>H-NMR ( $\delta$ , ppm, in CDCl<sub>3</sub>): 0.1 [m, 396H, –Si(CH<sub>3</sub>)<sub>2</sub>], 0.55 (m, 4H, –SiCH<sub>2</sub>), 0.90 (m, 3H, –CH<sub>3</sub>), 1.33 (m, 4H, –CH<sub>2</sub>), 1.45 (s, 3H, –OCH<sub>2</sub>CH<sub>3</sub>), 1.58 (m, 2H, –CH<sub>2</sub>CH<sub>2</sub>O), 1.96 [s, 6H, –C(CH<sub>3</sub>)<sub>2</sub>Br], 3.46 (t, 2H, –CH<sub>2</sub>O), 3.70 (t, 4H, –OCH<sub>2</sub>), 4.34 (t, 2H, –CH<sub>2</sub>OCO). FTIR (liquid): 2964 (alkyl C–H stretching), 1742 (–C=O stretching), 1260 [–Si(CH<sub>3</sub>)<sub>2</sub> flexing], 1000–1100 cm<sup>–1</sup> (Si–O stretching).

### Synthesis of the PDMS-*b*-PS diblock copolymers

RAFT polymerization was carried out in a dry flask under an inert atmosphere of nitrogen. The typical styrene polymerization with AIBN as the initiator proceeded with an initial monomer/RAFT agent/initiator molar ratio of 100 : 1 : 1 (Scheme 1). AIBN (0.0978 g, 0.058 mmol) and the PDMS/macro-RAFT agent (0.3000 g, 0.0578 mmol) were charged into a dry two-necked flask along with a magnetic stirrer bar. A vacuum was then applied, and the flask was flushed with nitrogen, which was run three times. Styrene (0.663 mL, 5.78 mmol) and toluene (1 mL) were added to the flask with degassed syringes. The solution was flushed with nitrogen as described previously and heated to 60°C in an oil bath. Samples were taken periodically with a syringe. The reaction was stopped after 5 h. The reaction mixtures were diluted with THF and precipitated in methanol. The



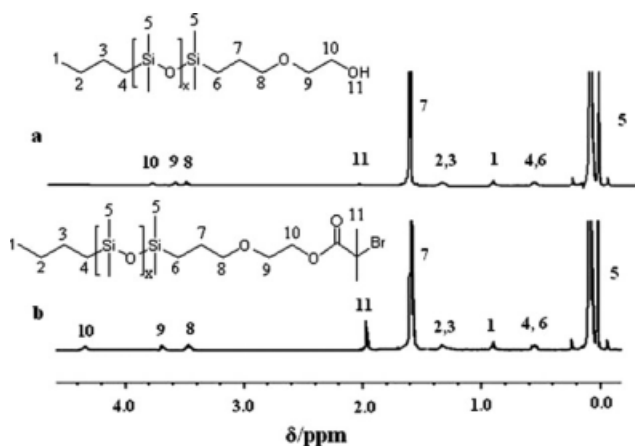
**Scheme 1** Synthetic schemes for the PDMS/macro-RAFT agent and the PDMS-*b*-PS diblock copolymers (St = styrene).

obtained polymer was rinsed with methanol several times and dried to a constant weight *in vacuo* at 50°C (yield = 0.7102 g, 79%). The final conversion of styrene monomer was 85%.

## RESULTS AND DISCUSSION

### Synthesis of PDMS-Br

Our choice of PDMS was governed primarily by the availability of appropriate molecular-weight and end-group structures. The reaction was achieved with a high yield, and the chemical structure of the resulting product was fully characterized by <sup>1</sup>H-NMR [Fig. 1(b)] and FTIR [Fig. 2(b)] before polymerization. The sharp singlet at 1.96 ppm (11) in the <sup>1</sup>H-NMR spectra corresponded to the two methyl groups  $\alpha$  to the bromide atom. The chemical shift at 4.34 ppm (10) belonged to the monocarbinol-terminated PDMS-OH that was converted to PDMS-Br. PDMS-Br had a distinctive peak in the <sup>1</sup>H-NMR spectrum, which was assigned to the dimethylsiloxane repeat units at 0.1 ppm (5). The integral ratio of the dimethylsiloxane repeat units to the region at 4.34 ppm (10) was used to calculate the absolute number-average molecular weight value. The IR absorption at 1740 cm<sup>–1</sup> was ascribed to the ester



**Figure 1**  $^1\text{H-NMR}$  spectra of (a) PDMS-OH and (b) PDMS-Br.

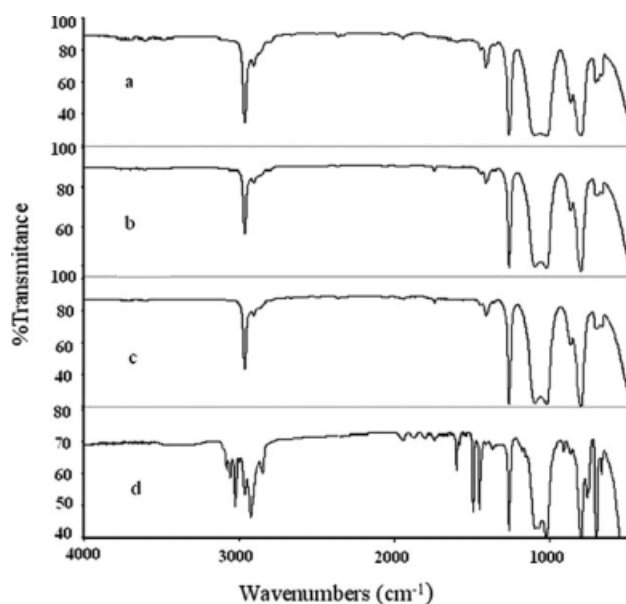
group and suggested that PDMS-Br was successfully synthesized.

#### Synthesis of the PDMS/macro-RAFT agent

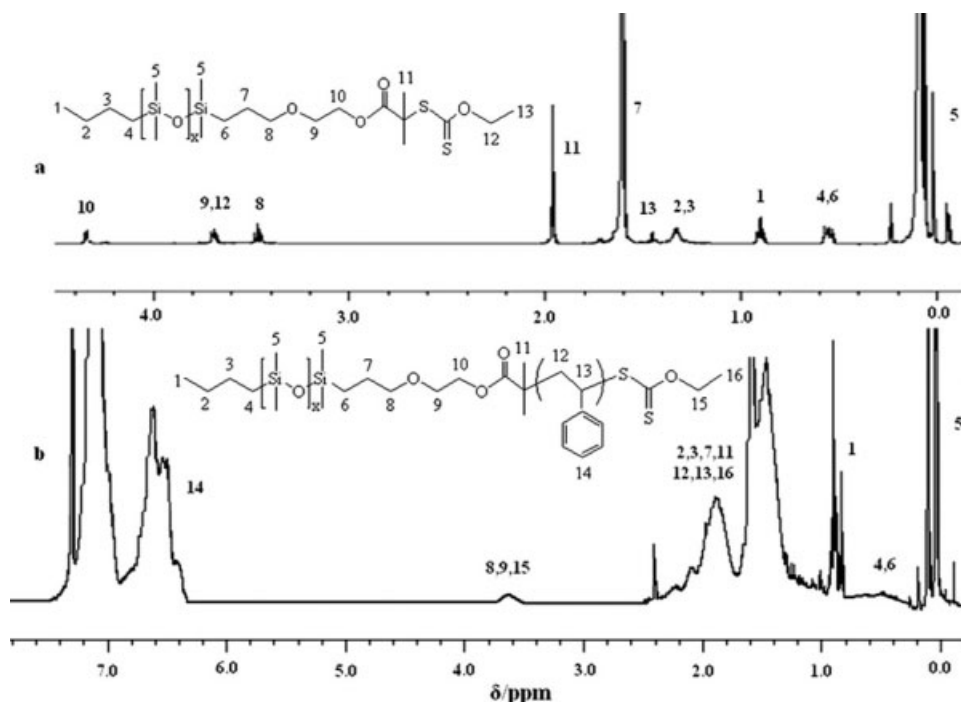
RAFT polymerization is accomplished by radical polymerization in the presence of certain compounds, which all act as reversible chain-transfer agents (including dithioesters, dithiocarbamates, trithiocarbonates, and xanthates).<sup>47–50</sup> Few RAFT agents are commercially available; it was necessary to synthesize a suitable agent before polymerization in this study. The attachment of a RAFT agent to a compound via functional groups has been used for the synthesis of complex polymer architectures. Hydroxyl-terminated PDMS allows the coupling of a RAFT agent via ester formation on both chain ends, which results in polymeric RAFT agents suitable for the preparation of diblock copolymers. In this study, a PDMS/macro-RAFT agent with a xanthate group was prepared for RAFT polymerization to form one block of the copolymers. The structure of the resulting macro-RAFT agent was similar to that of xanthates with a longer chain, which can be used to mediate the polymerization of styrene. The FTIR peaks of the  $-\text{C}=\text{S}$  and  $-\text{C}-\text{S}$  group at 1020–1065 and 1000–1054  $\text{cm}^{-1}$ , respectively, overlapped with peaks at 1000–1100  $\text{cm}^{-1}$ , which corresponded to the characteristic peaks of the  $\text{Si}-\text{O}$  group. Therefore, the FTIR spectrum [Fig. 2(c)] of PDMS/macro-RAFT was nearly the same as that of PDMS-Br. In the  $^1\text{H-NMR}$  spectrum [Fig. 3(a)], there was a peak at 1.45 ppm (13), and it was assigned to the methyl group next to the  $-\text{OCH}_2$  group; this indicated that the PDMS/macro-RAFT agent with xanthate groups was successfully synthesized. The molecular weight calculated from MS agreed with the theoretical value.

#### Synthesis of the PDMS-*b*-PS diblock copolymers

Well-defined PDMS-*b*-PS diblock copolymers were prepared by RAFT polymerization. Oxygen has significant influence on RAFT polymerization and can inhibit polymerization and terminate radicals, so the system needed to be strictly deoxygenated before heating. The polymerization was carried out with an initial monomer/RAFT agent/initiator molar ratio of 100 : 1 : 1; this gave us a theoretical absolute number-average molecular weight value of approximately 15,590 g/mol with 100% conversion. After the PDMS-*b*-PS diblock copolymers were purified, their chemical structures were measured by  $^1\text{H-NMR}$  [Fig. 3(b)] and FTIR [Fig. 2(d)]. The PDMS-*b*-PS diblock copolymers had two distinct peaks in the  $^1\text{H-NMR}$  spectrum [Fig. 3(b)]: one at 6.5–7.16 ppm (14), which corresponded to the aromatic hydrogen in the PS moiety, and the other at 0.1 ppm (5), which corresponded to the PDMS moiety. Integral ratios of the two regions were used to calculate the absolute number-average molecular weight values for the diblock copolymers. The FTIR spectrum of the PDMS-*b*-PS shown in Figure 2(d) also proved that the PDMS polymers had distinctive peaks centered between 1000 and 1100  $\text{cm}^{-1}$ , which corresponded to the  $-\text{Si}-\text{O}$  group, whereas peaks at 1260  $\text{cm}^{-1}$  were attributed to the  $-\text{[Si(CH}_3)_2]$  group. Characteristic peaks of the PS block appeared at 700, 760, 1600, and 3000–3100  $\text{cm}^{-1}$ . We measured monomer conversion through gravimetry by drying the sampled PDMS-*b*-PS solution to a constant weight *in vacuo* at 50°C. Figure 4 shows the first-order plots for the polymerization of styrene. The linearity of the plots suggested first-order kinetics, and



**Figure 2** FTIR spectra of (a) PDMS-OH, (b) PDMS-Br, (c) the PDMS/macro-RAFT agent, and (d) PDMS-*b*-PS.

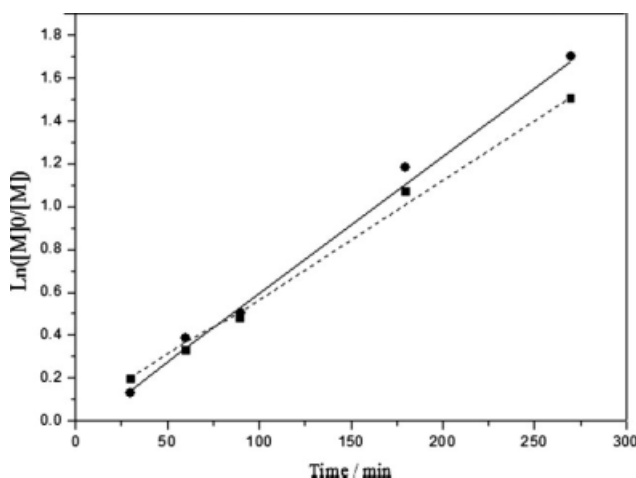


**Figure 3**  $^1\text{H-NMR}$  spectra of (a) the PDMS/macro-RAFT agent and (b) PDMS-*b*-PS.

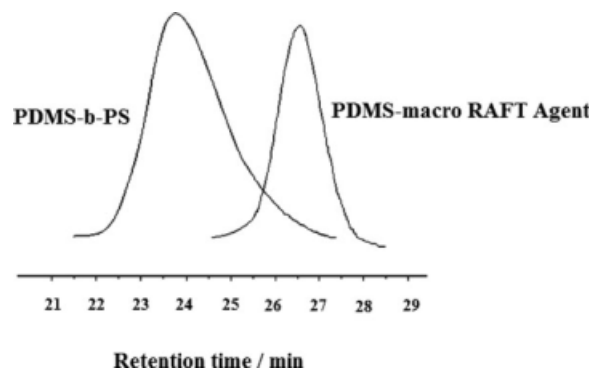
furthermore, the reaction rate increased with increasing styrene monomer concentration. GPC was used to study the molecular weights and molar weight distributions of the resulting copolymers. GPC traces of the PDMS/macro-RAFT agent and PDMS-*b*-PS diblock copolymers are displayed in Figure 5. For the sample examined, the molecular weight was 14,370 g/mol, and the polydispersity was 1.67. The molecular weights determined by  $^1\text{H-NMR}$  [14,240 g/mol; Fig. 3(b)] and GPC agreed with the theoretically predicted ones. The molecular weight distribu-

tions suggested that the reaction proceeded in a controlled manner.

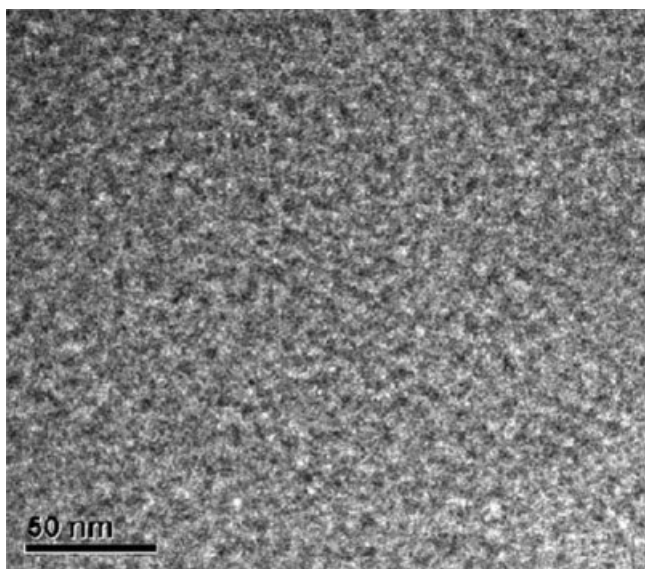
The morphology of the PDMS-*b*-PS diblock copolymers was investigated by TEM and AFM measurements. The high electron density of the PDMS microphase, as compared to the PS microphase, gave sufficient contrast without the need for staining. In the TEM bright-field pictures (Fig. 6), the PDMS microdomains appeared black, whereas regions corresponding to the PS block were bright. Figure 7 illustrates the typical AFM images of the PDMS-*b*-PS copolymers, which were believed to be the result of the phase separation. Furthermore,



**Figure 4** First-order kinetic plots for the polymerization of styrene in a toluene solution ( $[M]$  = monomer concentration;  $[M]_0$  = initial monomer concentration). The monomer/CTR/initiator molar ratios were 100 : 1 : 1 (34 vol %) and 80 : 1 : 1 : 2 (29 vol %).



**Figure 5** GPC traces for PDMS-*b*-PS (sample = DMS<sub>65</sub>St<sub>87</sub>, number-average molecular weight = 14,370, weight-average molecular weight/number-average molecular weight = 1.67) prepared from the PDMS/macro-RAFT agent (number-average molecular weight = 5720, weight-average molecular weight/number-average molecular weight = 1.06).



**Figure 6** TEM micrograph of the PDMS-*b*-PS diblock copolymers.

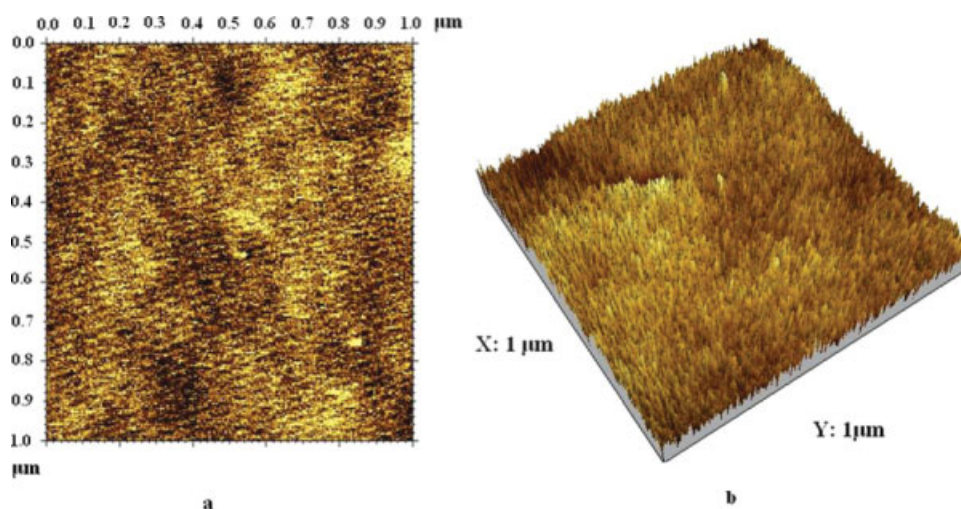
according to the consistency between TEM and AFM, we confirmed the attribution of two phases in the AFM image. In AFM images, the low spots appeared as dark patches, and the high spots appeared as bright areas. Hydrophobic patches appeared as low spots, and less hydrophobic areas appeared as high spots.<sup>59,60</sup> Therefore, the phase data for the hydrophobic patches were dark, and the hydrophilic areas were bright in the AFM topographical data obtained under ultralight tapping mode.<sup>61,62</sup> In Figure 7(a), dark patches are the hydrophobic PDMS domains, and the bright phases are the hydrophilic PS domains. The following data was obtained with the AFM software along with the NanoScope SPM Ila. The average height of the pro-

tuberant area shown in Figure 7(b) was 0.555 nm, the size of the distribution phase area was about 20–40 nm, and the root mean square roughness in an area of  $1000 \times 1000 \text{ nm}^2$  of this sample was 0.119 nm. The surface microphase separation in the PDMS-*b*-PS copolymers could be obtained. Furthermore, the surface microphase separation in the PDMS-*b*-PS copolymers was determined by the surface chemical composition, and the surface energy of the copolymers was influenced by the corresponding microphase separation behavior.<sup>63</sup>

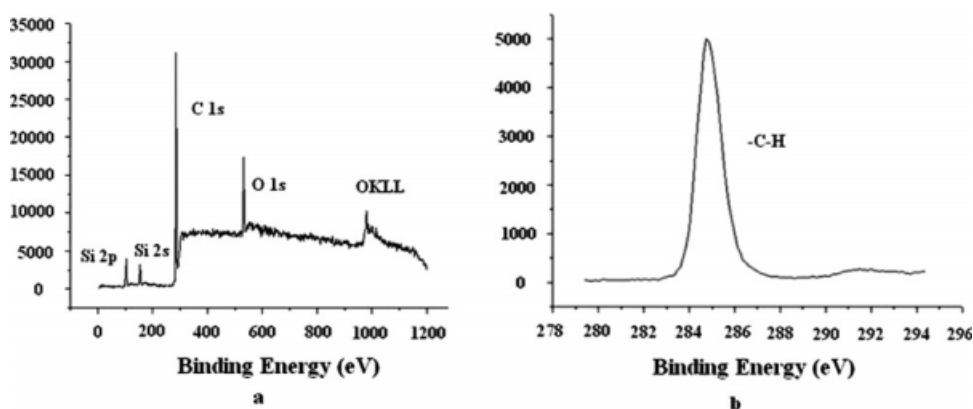
Surface composition was studied by XPS. The XPS images represent surface atomic ratios computed by software. Figure 8(a) is a broad scan of the binding-energy spectrum from 0 to 960 eV for PDMS-*b*-PS. It was composed of two strong peaks and three weak peaks at approximately 980, 532, 285, 152, and 102 eV, which resulted from direct photoionization from the  $O_{KLL}$ ,  $O_{1s}$ ,  $C_{1s}$ ,  $Si_{2s}$ , and  $Si_{2p}$  core levels, respectively. The high-resolution  $C_{1s}$  spectrum [Fig. 8(b)] of PDMS-*b*-PS exhibited a distinct peak at 284.7 eV, which was attributed to the  $-C-H$  species of PDMS-*b*-PS. According to the structures of the repeating units of PS (containing eight carbon atoms in each repeating unit) and PDMS (containing two carbon atoms and one silicon atom), the surface dimethylsiloxane molar fraction ( $X_{DMS}$ ) was expressed in terms of the  $X_C/X_{Si}$  ratio as follows:

$$X_{DMS} = 8 / (6 + X_C/X_{Si})$$

where  $X_C$  and  $X_{Si}$  are the atomic percentages of C and Si from XPS measurements, respectively.<sup>64,65</sup> The atom percentages of  $C_{1s}$ ,  $O_{1s}$ , and  $Si_{2p}$  were 70.7, 18.9, and 10.3, respectively, as computed by the software along with the XPS apparatus. The surface



**Figure 7** (a) AFM phase image and (b) 3D image of the PDMS-*b*-PS diblock copolymers. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 8** XPS of the PDMS-*b*-PS diblock copolymer films: (a) broad scan of the binding-energy spectrum and (b) high-resolution  $C_{1s}$  spectrum.

layer exhibited an  $X_C/X_{Si}$  ratio of 6.86. Therefore, we obtained an  $X_{DMS}$  value of 62.2, which was higher than that in the bulk [which was 44.8, as calculated from  $^1H$ -NMR, as shown in Fig. 3(b)]; this indicated that the surface was enriched with the PDMS component.

Because surface microphase separation and surface compositions had a great impact on the surface energy, the PDMS-*b*-PS diblock copolymers were investigated through contact-angle measurements. The result of the contact angles is shown in Figure 9. The water contact angles toward the air-side surface of the PDMS-*b*-PS film were about  $110^\circ$  [Fig. 9(b)]. The surface energies of the PDMS-*b*-PS diblock copolymers were indirectly obtained from the static water contact angles. The following equation, which was derived by Li and Neumann,<sup>66,67</sup> was applied to calculate the surface energies:

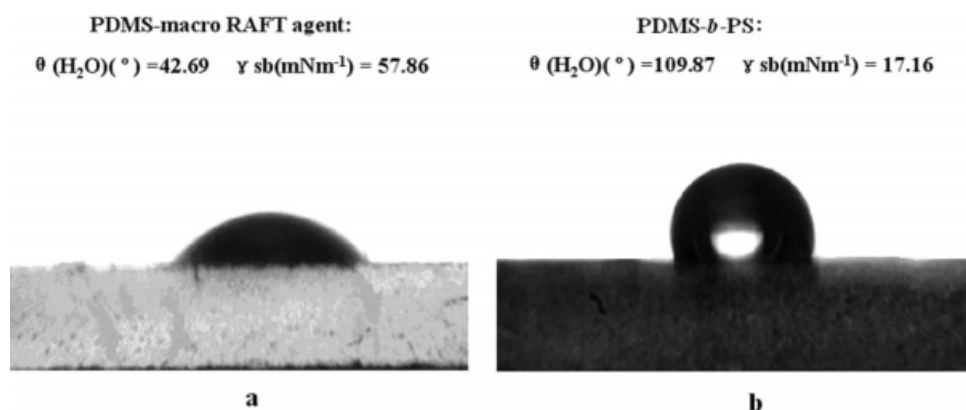
$$1 + \cos \theta = 2(\gamma_S/\gamma_L)^{1/2} \exp[-\beta(\gamma_L - \gamma_S)]^2$$

where  $\beta$  is a constant with a value of  $0.0001247 \text{ (m}^2/\text{mJ)}^2$ , determined from the contact-angle data for low-energy solids, and  $\gamma_S$ ,  $\gamma_L$ , and  $\theta$  are the surface energy of the solid, the surface energy of the test liq-

uid, and the contact angle, respectively. Therefore, we obtained surface energies of the PDMS-*b*-PS diblock copolymers and PDMS/macro-RAFT agent of 17.16 and 57.86 mN/m, respectively. Compared with the PDMS/macro-RAFT agent [Fig. 9(a)], the surface energy of the PDMS-*b*-PS diblock copolymers was much lower. The contact-angle measurements strongly implied that the PDMS-*b*-PS diblock copolymer films were hydrophobic. The hydrophobicity resulted from the higher molar fraction of the dimethylsiloxane moieties on the surface. In other words, the surface was enriched with the hydrophobic PDMS components.

## CONCLUSIONS

PDMS-*b*-PS diblock copolymers with well-defined structures were successfully synthesized via RAFT polymerization. The copolymer molecular weights measured by  $^1H$ -NMR and GPC were close to those predicted, and therefore, we confirmed that the polymerization proceeded in a controlled manner. This provided an applicable approach to the preparation of PDMS-containing block copolymers with a PDMS/macro-RAFT agent with a xanthate group.



**Figure 9** Static water contact-angle images: (a) the PDMS/macro-RAFT agent and (b) PDMS-*b*-PS.

Microphase separation surfaces primarily consisting of hydrophobic domains from PDMS segments were proven by the results of TEM, AFM, and XPS. In addition, the results of the static water contact-angle measurements indicated that the copolymers had a low surface energy.

The authors thank Bing-Wei Mao (State Key Laboratory for Physical Chemistry of Solid Surfaces and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University) for the AFM analyses.

## References

- Davies, W. G.; Jones, D. P. *Ind Eng Chem Res* 1971, 10, 168.
- Steinmeyer, R. D.; Becker, M. A. In *The Analytical Chemistry of Silicones*; Smith, A. L., Ed.; Wiley: New York, 1991.
- Krause, S.; Iskandar, M.; Iqbal, M. *Macromolecules* 1982, 15, 105.
- Emmanuel, P.; Jeff, T.; Cédric, E.; Patrick, L. D.; Bernard, B. *Macromolecules* 2006, 39, 6009.
- Andre, M. M.; Steven, K. P.; Kebede, B. *Macromolecules* 2002, 35, 4238.
- Luo, Z. H.; He, T. Y. *React Funct Polym* 2008, 68, 391.
- Sokol, N.; Patric, J.; Niels, B. L.; Kristoffer, A. *Langmuir* 1999, 15, 3859.
- Rosati, D.; Perrin, M.; Navard, P.; Harabagiu, V.; Pinteala, M.; Simionescu, B. C. *Macromolecules* 1998, 31, 4301.
- Rosati, D.; Loon, B. V.; Navard, P. *Polymer* 1999, 41, 367.
- Petitjean, S.; Ghitti, G.; Jerome, R.; Teyssie, P.; Marien, J.; Riga, J.; Verbist, J. *Macromolecules* 1994, 27, 4127.
- Dieng, A. C.; Lavielle, L.; Riess, G. *New Polym Mater* 1996, 5, 13.
- DeSimone, J. M.; Jones, T. A.; Shaffer, K. A. *Macromolecules* 1996, 29, 2704.
- DeSimone, J. M.; Betts, D. E.; Canelas, D. A. *Macromolecules* 1996, 29, 2818.
- DeSimone, J. M.; Canelas, D. A. *Macromolecules* 1997, 30, 5673.
- Yokota, M.; Goshima, T.; Fujioka, S. U.S. Pat.632,968 (1986).
- Mann, R. H.; Sun, E. L.; Plamthottam, S. S.; Newing, C. W. U.S. Pat. 5,728,469 (1998).
- Chen, J.; Gardella, J. A. *Macromolecules* 1998, 31, 9328.
- Chen, C.; Wang, J.; Chen, Z. *Langmuir* 2004, 20, 10186.
- Fukumine, Y.; Inomata, K.; Takano, A.; Nose, T. *Polymer* 2000, 41, 5367.
- Ma, X.; Xia, Y.; Chen, E. Q.; Mi, Y.; Wang, X.; Shi, A. C. *Langmuir* 2004, 20, 9520.
- Ndoni, S.; Jannasch, P.; Larsen, N. B.; Almdal, K. *Langmuir* 1999, 15, 3859.
- Chuai, C.; Li, S.; Almdal, K.; Alstrup, J.; Lyngaae-Jorgensen, J. *J Appl Polym Sci* 2004, 92, 2747.
- Li, H. Y.; Chen, S. T.; Zhang, X. F.; Cui, N. N.; Zhang, Z. C.; Lu, Y. Y.; Hu, Y. L. *React Funct Polym* 2005, 65, 285.
- Endo, K. *Prog Polym Sci* 2002, 27, 2021.
- Chung, T. G. *Prog Polym Sci* 2002, 27, 39.
- Chuai, C.; Li, S.; Almdal, K.; Alstrup, J.; Lyngaae-Jorgensen, J. *J Polym Sci Part A: Polym Chem* 2004, 42, 898.
- Maric, M.; Macosko, C. W. *J Polym Sci Part B: Polym Phys* 2002, 40, 346.
- Harrison, K. L.; Rocha, S. R. P.; Yates, M. Z.; Johnston, K. P.; Canelas, D.; DeSimone, J. M. *Langmuir* 1998, 14, 6855.
- Brown, D. A.; Price, G. J. *Polymer* 2001, 42, 4767.
- Nakagawa, Y.; Miller, P. J.; Matyjaszewski, K. *Polymer* 1998, 39, 5163.
- Hamurcu, E. E.; Hazer, B.; Misirli, Z.; Baysal, B. M. *J Appl Polym Sci* 1996, 62, 1415.
- Nair, C. P. R.; Clouet, G. *Macromolecules* 1990, 23, 1361.
- Chaumont, P.; Beinert, G.; Herz, J.; Rempp, P. *Polymer* 1981, 22, 663.
- Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem Rev* 2001, 101, 3689.
- Patten, T. E.; Matyjaszewski, K. *Adv Mater* 1998, 10, 901.
- Hou, Y. X.; George, S. T.; Paul, L. V.; Valint, J. J.; Joseph, A. G. *J Macromolecules* 2002, 35, 5953.
- Bellas, V.; Iatrou, H.; Hadjichristidis, N. *Macromolecules* 2000, 33, 6993.
- Hirahara, K.; Takano, A.; Yamamoto, M.; Kazama, T.; Isono, Y.; Fujimoto, T.; Watanabe, O. *React Funct Polym* 1998, 37, 169.
- Wang, J. S.; Matyjaszewski, K. *Macromolecules* 1995, 28, 7901.
- Hansen, N. M. L.; Jankova, K.; Hvilsted, S. *Eur Polym J* 2007, 43, 255.
- Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1995, 28, 1721.
- Matyjaszewski, K.; Xia, J. *Chem Rev* 2001, 101, 2921.
- Nagase, Y.; Ando, T.; Yun, C. M. *React Funct Polym* 2007, 67, 1252.
- Karatzas, A.; Bilalis, P.; Iatrou, H.; Pitsikalis, M.; Hadjichristidis, N. *React Funct Polym* 2009, 69, 435.
- Liu, Y. L.; Chen, M. H.; Hsu, K. Y. *React Funct Polym* 2009, 69, 424.
- Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem Rev* 2001, 101, 3661.
- Barner-Kowollik, C.; Davis, T. P.; Heuts, J. P.; Stenzel, M. H.; Vana, P.; Whittaker, M. *J Polym Sci Part A: Polym Chem* 2003, 41, 365.
- Vana, P.; Quinn, J. F.; Davis, T. P.; Barner-Kowollik, C. *Aust J Chem* 2002, 55, 425.
- Zhou, D.; Zhu, X. L.; Zhu, J.; Cheng, Z. P. *React Funct Polym* 2009, 69, 55.
- Mori, H.; Iwaya, H.; Endo, T. *React Funct Polym* 2007, 67, 916.
- Saam, J. C.; Gordon, D. J.; Lindsey, S. *Macromolecules* 1970, 3, 1.
- Bajaj, P.; Varshney, S. K. *Polymer* 1980, 21, 201.
- Bajaj, P.; Gupta, D. C.; Varshney, S. K. *Polym Eng Sci* 1983, 23, 820.
- Bajaj, P.; Varshney, S. K. *Polymer* 1980, 21, 201.
- Li, D. G.; Zhu, J.; Cheng, Z. P.; Zhang, W.; Zhu, X. L. *React Funct Polym* 2009, 69, 240.
- Chen, W. X.; Fan, X. D.; Huang, Y.; Liu, Y. Y.; Sun, L. *React Funct Polym* 2009, 69, 97.
- Luo, Z. H.; He, T. Y.; Yu, H. J.; Dai, L. Z. *Macromol React Eng* 2008, 2, 398.
- Tong, Y. Y.; Dong, Y. Q.; Du, F. S.; Li, Z. C. *Macromolecules* 2008, 41, 7339.
- Person, D. V.; Fitch, J. W.; Cassidy, P. E.; Kono, K.; Reddy, V. S. *React Funct Polym* 1996, 30, 141.
- Luo, Z. H.; Yu, H. J.; Zhang, W. *J Appl Polym Sci* 2009, 113, 4032.
- Sauer, B. B.; Mclean, R. S.; Thomas, R. R. *Langmuir* 1998, 14, 3045.
- Brandsch, R.; Bar, G.; Whangbo, M. H. *Langmuir* 1997, 13, 6349.
- Lipatov, Y. S.; Semenovich, G. M. *Polymer* 1999, 40, 6485.
- Chen, X.; Kumler, P. L.; Gardella, J. A., Jr. *Macromolecules* 1992, 25, 6621.
- Schmitt, R. L.; Gardella, J. A., Jr.; Chin, R. L.; Magill, J. H.; Salvati, L., Jr. *Macromolecules* 1985, 18, 2675.
- Li, D.; Neumann, A. W. *Colloid Interface Sci* 1990, 137, 304.
- Li, D.; Neumann, A. W. *Colloid Interface Sci* 1992, 148, 190.