

Synthesis and Characterization of the Hydrophobic Diblock Copolymers of Poly(dimethylsiloxane)-*block*-poly(ethyl methyl acrylate) Through Atom Transfer Radical Polymerization

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ABSTRACT: The poly(dimethylsiloxane)-*block*-poly(ethyl methylacrylate) diblock copolymers (PDMS-*b*-PEMA) were synthesized by atom transfer radical polymerization (ATRP). The chemical structure of the copolymers was characterized by nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy. Thermal behaviors were observed via differential scanning calorimetry (DSC). In the DSC curve, the resulting copolymers appear two glass transition temperatures (T_g 's), one at -123°C corresponding to the PDMS block and the other at 65°C ascribed to the PEMA segment. Moreover, the copolymer microstructure was investigated by transmission

electron microscopy (TEM). The results show that the diblock copolymers are microphase separated if the bulk contains enough PEMA segment. The surface properties of the PDMS-*b*-PEMA diblock copolymers were searched by contact angle. The PDMS-*b*-PEMA diblock copolymers are of low surface energy. The polymerization kinetics was also investigated, and the results show that the reaction proceeds in a living manner. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1201–1208, 2008

Key words: PDMS-*b*-PEMA; low surface energy; ATRP; living polymerization

INTRODUCTION

Living polymerizations, such as anionic polymerization,^{1,2} group transfer polymerization (GTP),³ and some other controlled radical polymerizations are extremely useful to prepare a wide range of useful polymer architectures including block copolymers, graft copolymers, telechelic polymers, and star polymers.⁴ Among them, the anionic polymerization has been most intensely searched.⁵ Although the anionic polymerizations of nonpolar monomers such as butadiene and styrene have been successfully commercialized,^{6,7} the need for high-purity monomers, solvents, other reagents, very low temperatures usually required shows that the anionic polymerization of acrylic monomers makes little commercial success

especially because of side reactions.^{8–13} Among the living polymerizations, atom transfer radical polymerization (ATRP) is the most ideal and has been intensely searched since its discovery in 1995^{14–16} due to its ability to control polymer architecture, molecular weight and molar mass distribution, moderate experimental conditions, and its applicability to a wide range of monomers.^{17,18} Polydimethylsiloxane (PDMS) materials have been applied in a variety of industrial areas due to their well-established surface-modifying properties.^{19–21} PDMS-containing polymers are usually hydrophobic and exhibit properties such as low irritation potential, low melting and glass-transition temperatures, very low surface tension,^{22,23} and, probably most important, nontoxic and environmentally compatible. Such polymers can be used as surfactants, lubricants, water repellents, and antifoaming agents.^{24–26}

When compared with other major organic polymers, they are thermally stable, transparent to ultraviolet radiation, and highly permeable to small molecules. Because of these interesting and useful properties, there has been recently considerable interest in block copolymers that incorporate PDMS as one segment.²⁷ It was traditionally achieved through anionic polymerization or GTP, but these techniques have their own disadvantages, such as rigorous reaction conditions or limited monomers and so on.

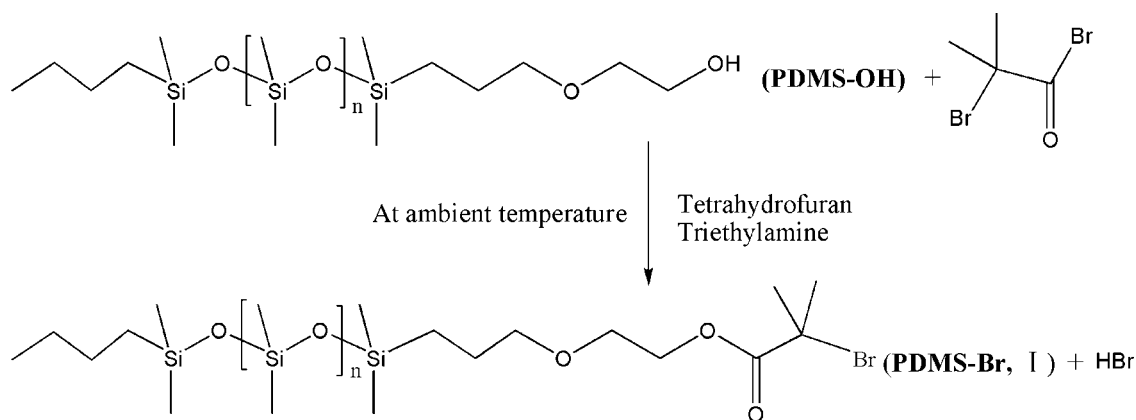
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Scheme 1 Synthetic scheme of polydimethylsiloxane macroinitiator.

The diblock copolymers-containing PDMS block and polyethylmethacrylate (PEMA) segment were not reported in the previous literatures due to the difficulty of synthesizing these polymers via anionic polymerization. In this article, we synthesized the hydrophobic PDMS-*b*-PEMA diblock copolymers by ATRP. The surface properties of the resulting copolymers were also surveyed by static water contact angle in this study.

EXPERIMENTAL

Materials and procedure

Carbinol (hydroxyethylpropyl) terminated polydimethylsiloxane (PDMS-OH) obtained from ABCR GmbH (Karlsruhe, Germany). KG with average molecular weight of 5000 g/mol, and used without further purification, 2-bromo-2-methylpropionyl bromide (ABCR, 98%), triethylamine supplied by Sino-pharm Chemical Reagent (SCRC, 99%) and stored over 4 Å molecular sieves, tetrahydrofuran (SCRC, Shanghai, China, 99%), *n*-propylamine (ABCR, 98%), pyridine-2-carboxaldehyde (ABCR, 99%), Cu(I)Br (Aldrich, 98%) purified according to the method of Keller and Wycoff,²⁸ and ethyl methacrylate (EMA, SCRC, 99%) washed with 5% aqueous NaOH solution to remove inhibitor. All other reagents and solvents were obtained from SCRC and used without further purification.

All manipulations were carried out under nitrogen atmosphere using standard syringe technique. Immediately before polymerization, all solvents, monomers, and other reagents were bubbled with nitrogen for about 30 min.

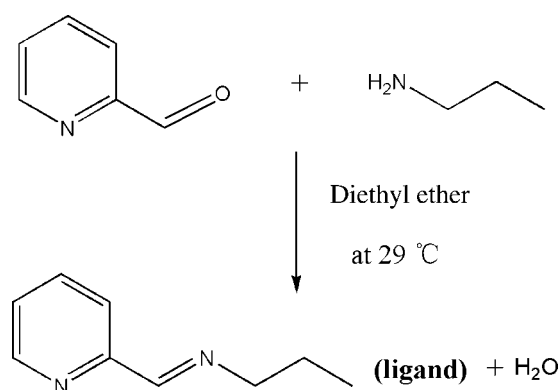
Preparation of carbinol-functional (mono) PDMS macroinitiators (PDMS-Br, I)

PDMS-OH (11 g, 2.2 mmol) was dissolved in anhydrous tetrahydrofuran (400 mL). Triethylamine

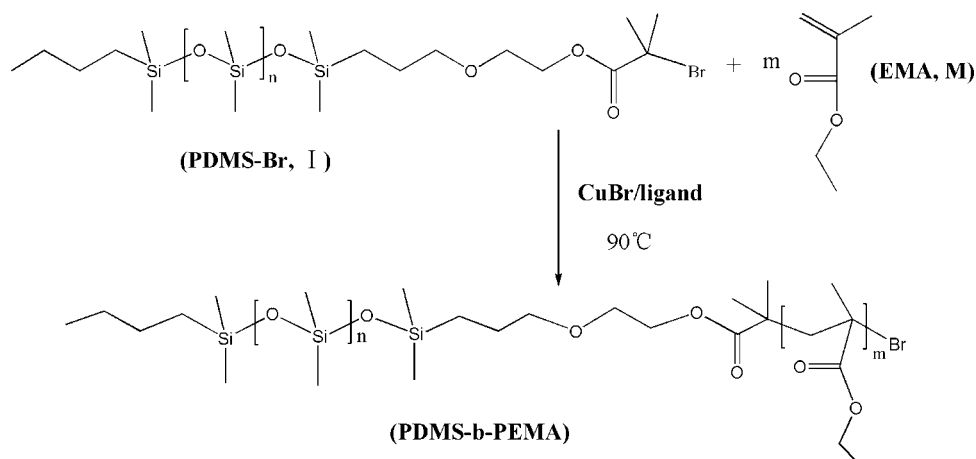
(1.54 mL, 11.1 mmol) was added to the stirred solution followed by 2-bromo-2-methylpropionyl bromide (0.69 mL, 5.55 mmol). The solution was left overnight at ambient temperature (the reaction scheme was shown in Scheme 1). The solution was filtered to remove the hydrochloride salt, and the solvent was removed under vacuum. The resulting yellow oil was taken up in dichloromethane (400 mL) and washed with saturated sodium-hydrogen carbonate solution (2 × 200 mL). The organic layer was isolated, dried over magnesium sulfate, and filtered. Then the resulting product was obtained as oil after the volatiles were removed *in vacuo*²⁹ (yield = 85 wt %).

Preparation of *N*-(*n*-propyl)-2-pyridinylmethanimine (ligand)

An excess of *n*-propylamine (4.11 mL, 35 mmol) was added dropwise to a stirred solution of pyridine-2-carboxaldehyde (4 mL, 42 mmol) in diethyl ether (4 mL) and cooled in an ice bath. After complete addition of the amine, anhydrous magnesium sulfate (1 g) was added, and the slurry was stirred for 2 h at 25°C (Scheme 2 shows the reaction). The solution



Scheme 2 Synthetic scheme of *N*-(*n*-propyl)-2-pyridinylmethanimine.



Scheme 3 Synthetic scheme of the PDMS-*b*-PEMA diblock copolymers.

was then filtered, followed by removing solvent, and the product purified by distillation under reduced pressure to give the golden yellow oil. Yield: 7.15 g (96.7%). The ligand was stored at 0°C under nitrogen atmosphere.^{30–32}

Synthesis of the PDMS-*b*-PEMA diblock copolymers

The PDMS-*b*-PEMA diblock copolymers were synthesized by copper (I) mediated living radical polymerization of EMA initiated by the PDMS-Br macroinitiator.

In a typical EMA(M) polymerization with the molar ratio of each components of $[M]/[I]/[CuBr]/[ligand] = 100/1/1/2$, Cu(I)Br (0.035 g, 0.246 mmol) along with a magnetic stirrer was placed in a dry three-necked flask, which was then evacuated and flushed with nitrogen three times. EMA (3.1 mL, 0.246 mmol), toluene (5.8 mL), and the PDMS-Br (1.256 g, 0.246 mmol) were added to the flask using degassed syringes. The solution was evacuated and flushed with nitrogen three times to deoxygenate. Finally, once the flask had reached 90°C the *n*-propyl-2-pyridinalmethanimine ligand (73 μ L, 0.5 mmol) was added with stirring. The reaction mixture immediately turned dark brown on addition of the ligand (the reaction scheme was shown in Scheme 3). Once ~90% conversion had been reached, the reaction was stopped, after which the catalyst was removed by passing the solution over basic alumina. The solution mixture then was precipitated into methanol several times to purify the resulting copolymers.³³

Measurement

Fourier transform infrared (FTIR) spectrum of the diblock copolymers was recorded on an Avatar 360 FTIR spectrophotometer by liquid sample. Proton

nuclear magnetic resonance (¹H NMR) was performed on a Bruker AV400 instrument with deuterated chloroform as the solvent. Gel permeation chromatography (GPC) was performed using THF as the eluent and polystyrene standards as the references. Differential scanning calorimetry (DSC) measurements were performed using a Netzsch DSC 204 apparatus at two temperature variation rates of 10°C/min for the heating run and 5°C/min for the cooling run. The morphology of the PDMS-*b*-PEMA diblock copolymers was characterized by transmission electron microscopy (TEM). A drop of copolymer solution (3 wt %) was applied onto a copper grid coated with carbon. The sample was used without any staining procedure. A transmission electron microscope (Tecnai F30) was used with an accelerating voltage of 300 kV. Static water contact angles of the diblock copolymer films were measured by casting the polymer solutions (3 wt % in tetrahydrofuran) on glass slides recorded on a telescopic goniometer (SL-200B). For each angle reported, at least seven sample readings from different surface locations were averaged. The angles reported have an accuracy of $\pm 2^\circ$.

RESULTS AND DISCUSSION

Synthesis of the PDMS-Br macroinitiator

Block copolymers containing PDMS segment are conveniently prepared from commercially available PDMS compounds with appropriate functionality at one or both termini. It is then possible to transform the end group(s) into active polymerization initiators. Our choice of PDMS was governed primarily by the availability of appropriate molecular weight and end group structures. Thus, we decided to use polysiloxanes with at least three methylene spacer groups connecting the silicon to the functional ter-

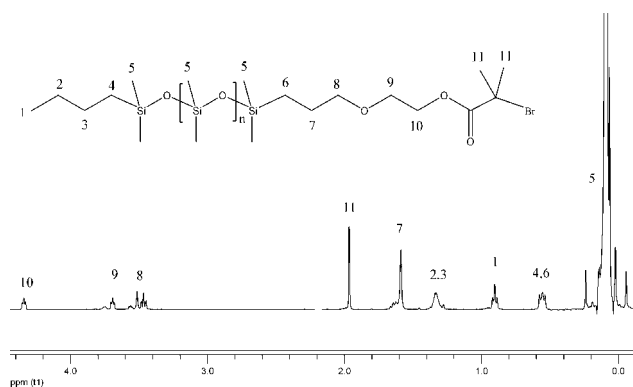


Figure 1 ^1H NMR spectrum of the bromine-encapped PDMS-Br macroinitiator.

mini. Accordingly, we synthesized the bromine-encapped PDMS-Br as macroinitiators for the ATRP to form one block of the copolymers. The reaction was achieved in a high yield, and the chemical structure of the resulting product was fully characterized before polymerization by ^1H NMR (Fig. 1) and FTIR [Fig. 2(b)]. The ^1H NMR spectroscopy shows the appearance of a sharp singlet at 1.96 ppm, assigned to the two methyl groups α to the bromide. The chemical shift of 4.34 ppm shows that the monocarbinol-terminated PDMS-OH has been converted into the bromine-encapped PDMS-Br macroinitiator. The PDMS macroinitiator has a distinctive peak in the ^1H NMR spectrum, which is assigned to the DMS repeat units at 0.0–0.2 ppm. Integral ratio of the DMS repeat units at 0.0–0.2 ppm to the region at 4.34 ppm can be used to calculate absolute number-average molecular weight (M_n) value. From the FTIR spectroscopy at 1742 cm^{-1} , which is ascribed to the ester group, we can also ascertain that the bromine-encapped PDMS-Br macroinitiators is successfully synthesized.

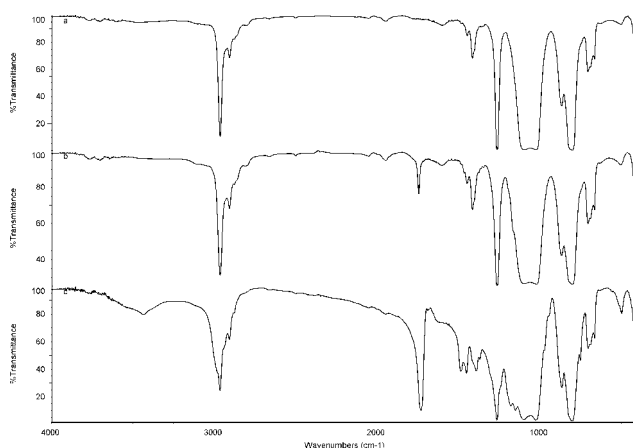


Figure 2 FTIR spectra (a) PDMS-OH, (b) PDMS-Br, and (c) PDMS-*b*-PEMA.

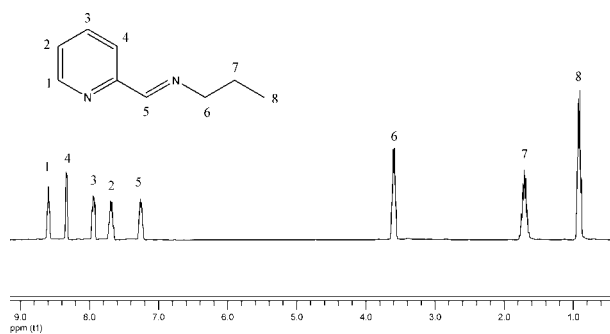


Figure 3 ^1H NMR spectrum of *N*-(*n*-propyl)-2-pyridinylmethanimine.

Synthesis of *N*-(*n*-propyl)-2-pyridinylmethanimine (ligand)

The Schiff base ligand of *N*-(*n*-propyl)-2-pyridinylmethanimine can be easily prepared by the condensation of primary amines with pyridine-2-carboxaldehyde in relatively short reaction time. It has already been demonstrated to provide efficient atom transfer polymerization catalysts for methyl methacrylate.^{31,34,35} In our study, we obtained *N*-(*n*-propyl)-2-pyridinylmethanimine ligand by the reaction of pyridine-2-carboxaldehyde with *n*-propylamine in a high yield (above 90%) at room temperature. The ligand was characterized by ^1H NMR (Fig. 3), FTIR (Fig. 4), and mass spectrum was recorded using a Finnigan MAT LCQTM mass spectrometer equipped with an electrospray ionization source. The chemical shift at 7.13 ppm, which is ascribed to $-\text{CH}=\text{N}$ group, shows that *N*-(*n*-propyl)-2-pyridyl methanimine ligand is successfully synthesized in ^1H NMR spectrum. From the FTIR spectrum in Figure 4, we can also ascertain that the ligand has been achieved according to the adsorption at 1650 cm^{-1} , which is assigned to flex oscillatory adsorption of the $-\text{C}=\text{N}$ group. The molecular weight calculated from mass spectrum agrees with the theoretical value. The ligand was then stored at 0°C under an inert atmosphere of nitrogen before polymerization.

Preparation of the PDMS-*b*-PEMA diblock copolymers

Well-defined PDMS-*b*-PEMA diblock copolymers were prepared by ATRP. This was achieved by the polymerization of EMA (in 33 vol % toluene) initiated by the PDMS-Br macroinitiator at 90°C . The solution was sampled and the molecular mass and monomer conversion were measured in each sample. After the PDMS-*b*-PEMA diblock copolymers were purified, the molecular structure of them was measured by ^1H NMR (Fig. 5) and FTIR [Fig. 2(c)]. The PDMS-*b*-PEMA diblock copolymers have two distinctive peaks in the ^1H NMR spectrum (Fig. 5),

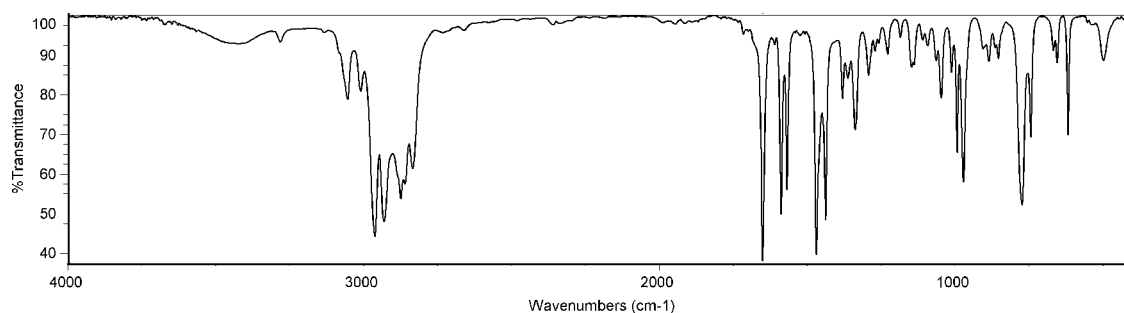


Figure 4 FTIR spectrum of *N*-(*n*-propyl)-2-pyridinylmethanimine.

which can be assigned to hydrogens of the $-\text{OCH}_2\text{CH}_3$ group at 4.05 ppm affected by the ester group and the DMS repeat units at 0.0–0.2 ppm. Integral ratio of the two regions can be used to calculate absolute number-average molecular weight (M_n) values for the diblock copolymers. Figure 2(c) shows the FTIR spectrum of the PDMS-*b*-PEMA diblock copolymers. The appearances of a $\nu_{\text{C}=\text{O}}$ at approximate 1730 cm^{-1} and a $\nu_{\text{C}-\text{O}}$ at about 1178 cm^{-1} were attributed to the ester carbonyl group of EMA. The monomer conversions were measured by gravimetry by drying to constant weight in a vacuum oven at 50°C . Figure 6 shows the first-order plots for the polymerization of EMA. The linearity of the plot suggests first-order kinetics, and furthermore, the reaction rate accelerates as the concentration of EMA increases. Figure 7 shows a plot of M_n as a function of conversion for the EMA polymerization. The plot gives excellent linearity indicative of living polymerization and the molecular weights determined by ^1H NMR are close to those predicted. The linearity of Figures 6 and 7 strongly implies that the polymerizations of EMA proceed in a controlled manner. The important data of the polymerization were shown in Table I.

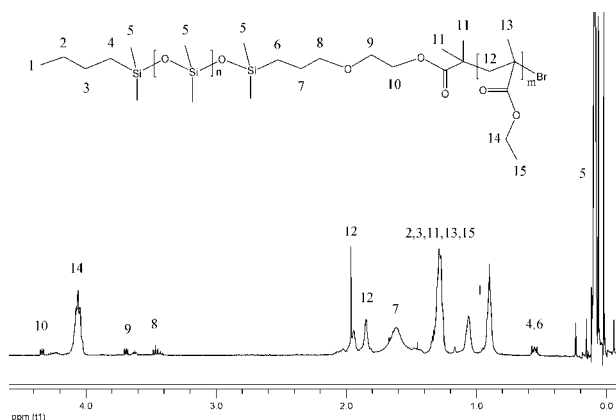


Figure 5 ^1H NMR spectrum of the PDMS-*b*-PEMA diblock copolymers.

The molar mass distribution of the resulting copolymers was measured using the GPC at room temperature, using tetrahydrofuran as the eluent and polystyrene standards as the references, at a flow rate of 1 mL/min. GPC traces of the PDMS-*b*-PHFBMA diblock copolymers were shown in Figure 8. For the polymerization of EMA with the four samples examined, the molecular weight of the resulting copolymers increased with increasing conversion while the polydispersity remained less than 1.2. The narrow molecular weight distributions of the resulting copolymers also suggest that the reaction proceeds in a controlled manner.

As the values of cohesive energy are quite different in the two blocks, the PDMS-*b*-PEMA diblock copolymers are expected to have phase-segregated morphology in the bulk. Usually, block copolymers synthesized by sequential anionic polymerization are microphase separated in toluene-cast films even at moderately low molecular weight. DSC measurements were performed using a Netzsch DSC 204 apparatus at two temperature variation rates of $10^\circ\text{C}/\text{min}$ for the heating run and $5^\circ\text{C}/\text{min}$ for the cooling

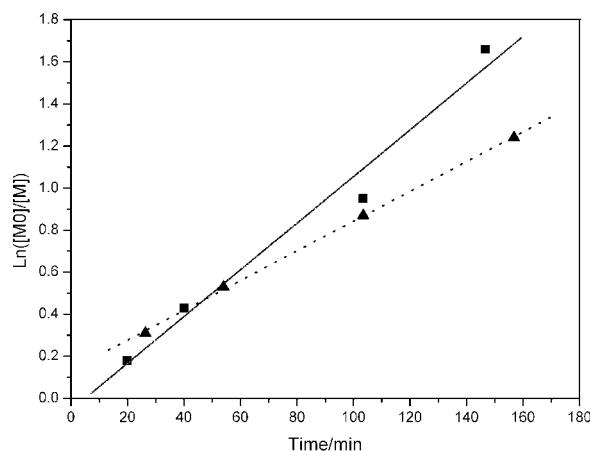


Figure 6 The kinetic plot of the polymerization of EMA using a $\text{Cu}(\text{I})\text{Br}$ catalyst in toluene solution at 90°C . \blacktriangle $[\text{M}]/[\text{I}]/[\text{Cu}]/[\text{ligand}] = 100 : 1 : 1 : 2$ (33 vol %), \blacksquare $[\text{M}]/[\text{I}]/[\text{Cu}]/[\text{ligand}] = 80 : 1 : 1 : 2$ (40 vol %).

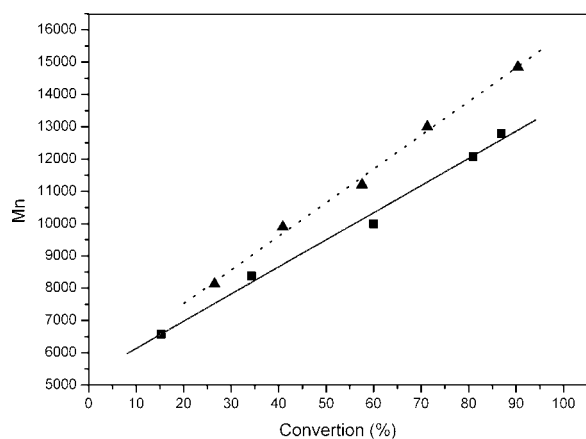


Figure 7 M_n versus conversion for the preparation of PDMS-*b*-PEMA using a Cu(I)Br catalyst in toluene solution at 90°C. ▲ [M]/[I]/[Cu]/[ligand] = 100 : 1 : 1 : 2 (33 vol %), ■ [M]/[I]/[Cu]/[ligand] = 80 : 1 : 1 : 2 (40 vol %).

run. The result of the heating run was shown in Figure 9. As can be seen, glass transition of the PEMA block occurs at about 65°C. The other T_g of the PDMS segment, which is about -123°C, is also observed. On the basis of the DSC measurements, the PDMS-*b*-PEMA diblock copolymers are also confirmed.

To observe the phase segregation of the PDMS-*b*-PEMA diblock copolymers, the toluene solvent, a good solvent for both blocks, was chosen. The morphology of the PDMS-*b*-PEMA diblock polymers was characterized by TEM. A drop of polymer solution (3 wt % in THF) was applied onto a copper grid coated with carbon. The sample was used without any staining procedure. A transmission electron microscope (TECNAI F30 HRTEM) was used with an accelerating voltage of 300 kV. The high-electron density of the PDMS microphase when compared with the PEMA microphase gave sufficient contrast

TABLE I
Important Data of the ATRP of EMA, in Toluene Solution, at 90°C

Sample	Time (min)	Conversion ^a (%)	M_n Theo	M_n^b	PDI ^c
PDMS ₆₅ -Br	—	—	—	5150	1.03
PDMS ₆₅ PEMA ₂₆	25	26	8110	8100	1.08
PDMS ₆₅ PEMA ₄₁	50	41	9820	9790	1.15
PDMS ₆₅ PEMA ₅₃	100	57	11650	11200	1.12
PDMS ₆₅ PEMA ₆₉	150	71	13240	12980	1.19

Where M_n Theo. = (weight of monomer/molar quantity of initiator) × conversion + M_n (PDMS).

^a This is calculated by gravimetry by drying to constant weight in a vacuum oven at 50°C.

^b This is measured by ¹H NMR.

^c PDI is obtained by GPC.

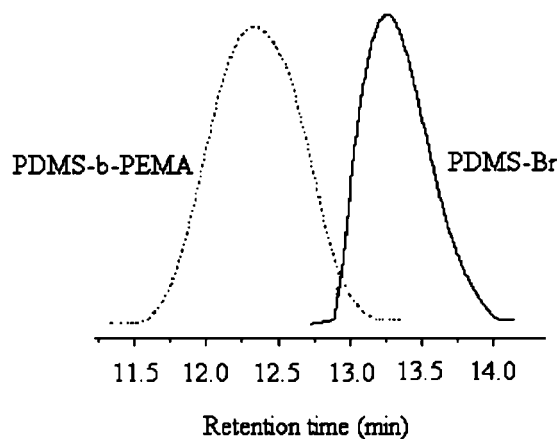


Figure 8 GPC traces of the PDMS-*b*-PEMA diblock copolymers (the sample is PDMS₆₅PEMA_{53.1}, $M_n = 10,970$, $M_w/M_n = 1.12$) prepared from PDMS-Br ($M_n = 5650$, $M_w/M_n = 1.03$).

without staining. On the TEM bright-field pictures, the PDMS microdomains appear black. The results were shown in Figure 10. The microphase separation appears obviously if the diblock copolymers contain enough PEMA segment both in (a) and (b) of Figure 10, with 56.7 and 61.6 wt % PEMA, respectively. The TEM observations agree with the results of DSC measurements.

Static water contact angles of the diblock copolymer films toward the air side were measured at 25°C on a telescopic goniometer (SL-200B) by casting polymer solutions (3 wt % in THF) on glass slides. For each angle reported, at least seven sample readings from different surface locations were averaged. The angles reported have an accuracy of ±2°. We show the results in Table II. The water contact angles toward the air-side surface of the PDMS-*b*-PEMA films can reach as high as 110°. The surface energy of the resulting copolymers is much lower than that of the PDMS-Br macroinitiator. Contact angle measurements strongly imply that the PDMS-

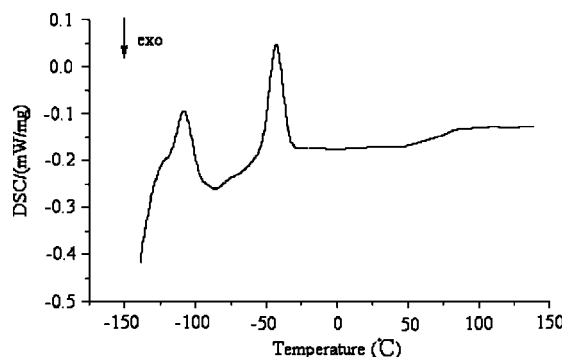


Figure 9 DSC curve of the PDMS-*b*-PEMA diblock copolymers in the heating run.

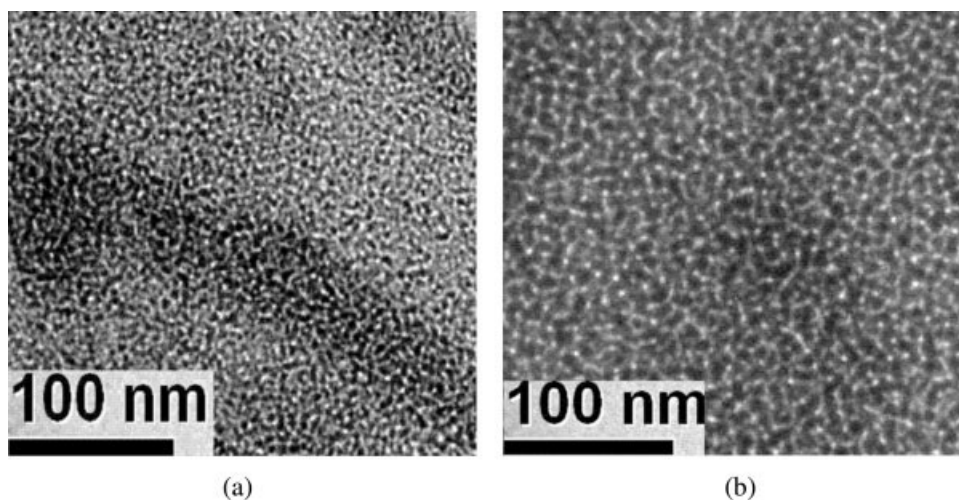


Figure 10 TEM micrographs of the PDMS-*b*-PEMA diblock copolymers: (a) (PDMS₆₅PEMA₆₀) and (b) (PDMS₆₅PEMA₇₂).

b-PEMA diblock copolymers create hydrophobic films.

CONCLUSIONS

Well-defined PDMS-*b*-PEMA diblock copolymers were successfully prepared via ATRP. The polymerization occurred in a controlled manner with the molecular weight measured by ¹H NMR close to that predicted. It provided a generally applicable approach to the preparation of PDMS-containing block copolymers initiated by the PDMS macroinitiator. The PDMS-*b*-PEMA diblock copolymers exhibited two T_g 's, one at an extremely low temperature of -123°C corresponding to the T_g of the PDMS microphase and the other at a higher temperature of 65°C ascribed to the T_g of the PEMA microdomain. TEM images evidenced microphase segregation mor-

phology in bulk for the PDMS-*b*-PEMA diblock copolymers. The analysis of contact angle showed that the PDMS-*b*-PEMA diblock copolymers created hydrophobic surface.

References

- Wang, J. S.; Jerome, R.; Warin, R.; Teyssie, P. *Macromolecules* 1993, 26, 5984.
- Hunt, M. O.; Belu, A. M. *Macromolecules* 1993, 26, 4854.
- Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. *Macromolecules* 1987, 20, 1473.
- Pyun, J.; Matyjaszewski, K. *Chem Mater* 2001, 13, 3436.
- Ygor, I.; McGrath, J. E. *Advances in polymer Science*; Springer Press: New York, 1988; p 86.
- Szwarc, M.; Levy, M.; Milkovich, R. *J Am Chem Soc* 1956, 78, 2656.
- Szwarc, M. *Nature* 1956, 178, 1168.
- Hou, Y. X.; George, M.; Tulevski, P. L.; Valint, J.; Joseph, A.; Gardella, J. *Macromolecules* 2002, 35, 5953.
- Vasilios, B.; Hermis, I.; Nikos, H. *Macromolecules* 2000, 33, 6993.
- Yang, S.; Wang, J. G.; Ogino, K.; Valiyaveetil, S.; Christopher, K. O. *Chem Mater* 2000, 12, 33.
- Lim, K. T.; Webber, S. E.; Johnston, K. P. *Macromolecules* 1999, 32, 2811.
- Hwang, H. S.; Kim, H. J.; Jeong, Y. T.; Gal, Y. S.; Lim, K. T. *Macromolecules* 2004, 37, 9821.
- Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; Rajan, Babu, T. V. *J Am Chem Soc* 1983, 105, 5706.
- Wang, J. S.; Matyjaszewski, K. *Macromolecules* 1995, 28, 7901.
- Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1995, 28, 1721.
- Percec, V.; Barboiu, B. *Macromolecules* 1995, 28, 7970.
- Matyjaszewski, K.; Xia, J. *Chem Rev* 2001, 101, 2921.
- Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem Rev* 2001, 101, 3689.
- Javis, N. L. *J Phys Chem* 1966, 70, 3027.
- Owens, M. J.; Kendrick, T. C. *Macromolecules* 1970, 3, 458.
- Yilgor, I.; McGrath, J. E. *Adv Polym Sci* 1988, 86, 1.
- Owen, M. J.; Zeigler, J. M.; Fearon, F. W. G. *J Am Chem Soc* 1990, 224, 705.
- Clarson, S. J.; Semlyen, J. A. *Siloxane Polymers*; Ellis Horwood PTR Prentice Hall Press: New York, 1993.

TABLE II
Surface Characterization of the PDMS-*b*-PEMA Diblock Copolymers

Samples	DMS _x EMA _y	W_{PEMA}^a (%)	$\theta_{\text{H}_2\text{O}}$ ($^\circ$)	γ_s^b (mN m^{-1})
No. 1	PDMS-Br (PDMS ₆₅)	0	62	42.61
No. 2	PDMS ₆₅ PEMA ₂₄	34.7	90	23.73
No. 3	PDMS ₆₅ PEMA ₃₆	44.3	94	21.36
No. 4	PDMS ₆₅ PEMA ₅₁	53.0	106	14.20
No. 5	PDMS ₆₅ PEMA ₇₅	62.4	110	12.34
No. 6	PDMS ₆₅ PEMA ₈₁	64.2	110	12.34

^a Weight percent of the PEMA block (W_{PEMA}) calculated by the equation: $\text{PEMA}\% = (114 \times \text{DP}_n) / (5150 + 114 \times \text{DP}_n)$, DP_n is polymerization degree of the PEMA segment, 5150 is the molecular weight of PDMS-Br macroinitiators measured by ¹H NMR.

^b The values are obtained from a telescopic goniometer (SL-200B), and γ represents the surface energy of the PDMS-*b*-PEMA film.

24. Allcock, H. R. *Adv Mater* 1994, 6, 106.
25. Matsumoto, N. *J Appl Phys* 1998, 37, 5425.
26. Miller, R. D.; Michl, J. *Chem Rev* 1989, 89, 1359.
27. Miller, P. J.; Matyjaszewski, K. *Macromolecules* 1999, 32, 8760.
28. Keller, R. N.; Wycoff, H. D. *Inorg Synth* 1947, 2, 1.
29. Limer, A.; Haddleton, D. M. *Macromolecules* 2006, 39, 353.
30. Giuseppe, M.; François, L.; Lei, T.; David, M. H.; Joost, C.; Jeroen, J. L. M. C.; Kelly, V. *J Am Chem Soc* 2005, 127, 2966.
31. Haddleton, D. M.; Jasieczek, C. B.; Hannon, M. J.; Shooter, A. J. *Macromolecules* 1997, 30, 2190.
32. Haddleton, D. M.; Duncalf, D. J.; Kukulj, D.; Crossman, M. C.; Jackson, S. G.; Bon, S. A. F.; Clark, A. J.; Shooter, A. J. *Eur J Inorg Chem* 1998, 11, 1799.
33. Fukukawa, K.; Zhu, L.; Gopalan, P.; Ueda, M.; Yang, S. *Macromolecules* 2005, 38, 263.
34. Haddleton, D. M.; Waterson, C.; Derrick, P. J.; Jasieczek, C. B.; Shooter, A. J. *Chem Commun* 1997, 7, 683.
35. Haddleton, D. M.; Clark, A. J.; Crossman, M. C.; Duncalf, D. J.; Hemings, A. M.; Morsley, S. R.; Shooter, A. J. *Chem Commun* 1997, 13, 1173.