

Synthesis and Characterization of PS-*b*-PDMS-*b*-PS Triblock Copolymer

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ABSTRACT: A series of polystyrene-*b*-poly(dimethylsiloxane)-*b*-polystyrene (PS/PDMS/PS) triblock copolymers had been synthesized by atom transfer radical polymerization (ATRP). The products had been characterized by Fourier transform infrared, gel permeation chromatography, differential scanning calorimetry, thermogravimetric analysis, contact angle, and scanning electron microscope. The results indicate that the PS chains have been successfully blocked onto the PDMS back bone, and the PS-*b*-PDMS-*b*-PS triblock copolymers have low-surface tension, good thermal stability, and microphase separation configuration. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 247–252, 2013

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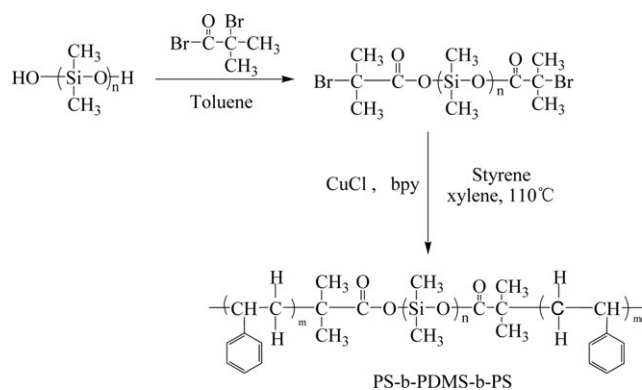
INTRODUCTION

Polysiloxanes are the major representatives of a class of polymers having inorganic main chains. Poly(dimethylsiloxane) (PDMS) is the choice of material for a wide range of applications, because it owns many advantages, such as stability to ultraviolet (UV), nontoxicity, thermostability, hydrophobicity, good gas permeability, low-coefficient friction, low-surface tension, biocompatibility, and commercial availability.^{1–3} However, its application is limited because of its awful film-forming property, poor cohesion, and low-glass transition temperature, which induce the cumbersome curing process of PDMS and poor mechanical performance. So many modification methods had been applied to improve mechanical performance of PDMS. Specifically, hybrid polymers containing PDMS have been reported for many different applications such as nanotechnology, electronics, filtration, two-dimensional liquid chromatography, and adsorption, among many others.^{4–9}

Block copolymers offer an attractive route to generate new types of materials that possess excellent properties because of the large variety of structural arrangements they give rise by spontaneous self-assembly into a diversity of mesophases.^{10,11} Many techniques have been used to synthesize block copolymers, atom transfer radical polymerization (ATRP) is one of the most robust and efficient method, yielding well-defined copolymers with precisely controlled functionality, composition, and topology.^{12–15} It is very little that block copolymers containing polysiloxanes were prepared, because polysiloxanes is susceptible to many reagents such as acid and alkali. Some kinds of block copolymers containing PDMS have been prepared by ATRP or

living anionic polymerization.^{16–20} Recently, Sun and Liu²¹ researched poly(methyl methacrylate) (PMMA)-*b*-PDMS-*b*-PMMA, which synthesized via activators generated by electron transfer atom transfer radical polymerization (AGET ATRP). Its results indicate that the polymers could self-assemble into various complex morphologies in different solvents, and the morphologies depended on the properties of solvents.²¹ Luo et al.²² synthesized the diblock copolymers of poly(dimethylsiloxane)-*block*-poly(2,2,3,3,4,4,4-heptafluorobutyl methacrylate) (PDMS-*b*-PHFBMA) via ATRP and found that the diblock copolymers are microphase-separated if the bulk contains enough PHFBMA segments. Also, the surface tension of PDMS-*b*-PHFBMA film is declined to 11.1 mN/m.

PDMS-*b*-polystyrene (PS) diblock copolymers have been of scientific and technological interest for many years. The linear block copolymers based on PS and PDMS chains have been considered as good candidates for both technological applications and model systems. One of the particularities of the PS/PDMS system is the extremely large difference in chain flexibility of the blocks, PDMS being one of the most flexible polymers, whereas PS is a relatively stiff one. The material composed of monomers with extremely different characteristics exhibits interesting properties, making them desirable engineering and commodity materials.^{23,24} PDMS-*b*-PS considered as organic-siloxane copolymers have potential uses as compatibilizer, thermoplastic elastomer, or surfactants in polymer blends, and it has been incorporated into contact lenses, gas permeable films and tubes, release surfaces for pressure-sensitive adhesives, and lithographic printing masters.²⁵ But the introduced of PS



Scheme 1. Synthetic routes of PS-*b*-PDMS-*b*-PS.

section into PDMS-*b*-PS diblock copolymer is little and asymmetric, which bring the properties of copolymer declining. Thus, we can design and synthesize symmetrical structural PS-*b*-PDMS-*b*-PS triblock copolymers, which introduce more PS into copolymer in order to study the properties of PS-*b*-PDMS-*b*-PS triblock copolymer.

In this work, the hydroxyl-terminated polydimethyl siloxane has been used as a raw material to synthesize PDMS difunctional macroinitiator and the corresponding PS-*b*-PDMS-*b*-PS triblock copolymer (Scheme 1). The thermal properties and surface properties of PS-*b*-PDMS-*b*-PS triblock copolymer had been studied. The results showed that the PS-*b*-PDMS-*b*-PS had good film-forming property and high-thermal stability.

EXPERIMENTAL

Materials

PDMS [Jinan, China; $M_n = 38.0$ kg/mol and $M_w/M_n = 1.90$, which were decided by gel permeation chromatography (GPC)] was dissolved in tetrahydrofuran (THF; Shanghai, China), precipitated in miscible liquids of methyl alcohol for three times, and dried in vacuum before use. α -Bromoisobutyryl bromide (98%) and 2,2'-bipyridine (Shanghai, China) were used as received. CuCl (Shanghai, China) was purified by stirring in acetic acid and washing with ethanol and ether and dried in vacuum. Triethylamine (TEA, Shanghai, China) was stored over sodium hydroxide. Styrene (Shanghai, China) was washed three times with aqueous solution of NaOH (5%) and distilled water, respectively, dried with $MgSO_4$ overnight, and distilled over CaH_2 under vacuum.

Synthesis of Br-PDMS-Br Macroinitiator

PDMS (15 g, 0.29 mmol), dry toluene (40 mL), and TEA (0.15 mL, 1.07 mmol) were put into a 100-mL round-bottomed flask, which was fitted with a mechanical stirrer, freshly distilled α -bromoisobutyryl bromide (0.13 mL, 1.13 mmol) with the addition of 1 mL toluene into the flask. Then the reaction mixture was stirred at 0°C. After 1 h, the temperature was risen to room temperature. The reaction was continued under stirring for 10 h, and the solvent was centrifuged to remove the ammonium salt. The crude product was poured into methanol/ H_2O , and the product was precipitated and dried in vacuum.

Synthesis of PS-*b*-PDMS-*b*-PS

The Br-PDMS-Br macroinitiator (1.60 g, 0.028 mmol), CuCl (0.010 g, 0.10 mmol), and 2,2'-bipyridine (0.046 g, 0.30 mmol) was put into a Kolle flask with a mechanical stirrer and degassed three times. Then, styrene (3.5 mL, 30.5 mmol) and xylene (5 mL) were injected into the reaction flask. Then the flask was immersed in an oil bath at 110°C for different reaction time. The crude product was dissolved in THF, precipitated in methanol, and dried in vacuum.

Characterization

FTIR spectra were recorded on Nicolet 460 spectrometer. GPC was performed using THF as the eluent at a flow rate of 1 mL/min with a polystyrene standard as the reference by WATERS 515 gel permeation chromatography. 1H -NMR was performed on a 500-MHz Bruker NMR spectrometer (Model AVANCE-500) using $CDCl_3$ as solvent and tetramethylsilane as an internal reference. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere at a heating rate of 10°C/min on a NETZSCH TG 209F3 thermogravimetric analyzer. Differential scanning calorimetry (DSC) analyses were determined on a Diamond DSC PerkinElmer. The samples were heated from -30 to 150°C at the heating rate of 10°C/min. The contact angles of water and formamide were measured by HARKE-CA. The surface morphology of the copolymer was identified by JSM-6360LA SEM.

RESULTS AND DISCUSSION

As shown in Scheme 1, PDMS was transformed into a macroinitiator by direct reaction of difunctional PDMS-containing hydroxyl end groups with α -bromoisobutyryl bromide in toluene, which was used to initiate the polymerization of styrene in order to form triblock copolymers of PS-*b*-PDMS-*b*-PS.

Figure 1 shows the FTIR spectra of pure PDMS, Br-PDMS-Br, and PS-*b*-PDMS-*b*-PS copolymer. In Figure 1(A), the peaks at 787 and 1263 cm^{-1} are attributed to the $-Si-CH_3$ of PDMS. There is a strong absorption band at 1109 cm^{-1} , which is

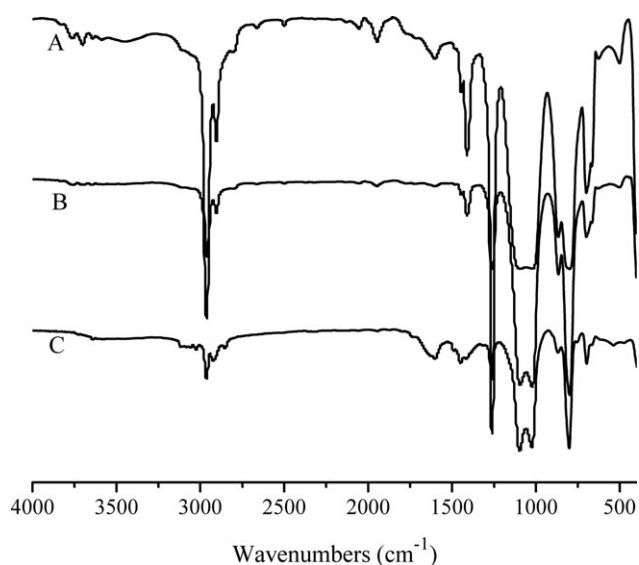


Figure 1. FTIR spectra of (A) PDMS, (B) macroinitiator, and (C) PS-*b*-PDMS-*b*-PS triblock copolymer.

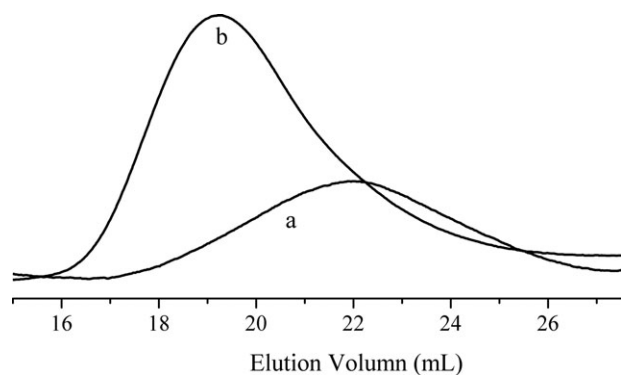


Figure 2. GPC chromatograms of (a) PDMS and (b) PS-*b*-PDMS-*b*-PS triblock copolymer.

assigned to the —Si—O—Si— stretching vibration. The absorption peaks at 2952 and 2868 cm^{-1} are due to the methylene of PDMS, and Si—OH stretching vibration peak is about at 3700 cm^{-1} . The macroinitiator [Figure 1(B)] that expected the —Si—OH stretching vibration peak at 3700 cm^{-1} disappeared because of the reaction of hydroxyl and α -bromoisobutyryl bromide, but other main absorption peaks of PDMS do not change, which suggest that the macroinitiator of Br-PDMS-Br had been prepared. Figure 1(C) shows the FTIR spectra of the triblock copolymer (PS-*b*-PDMS-*b*-PS). The characteristic spectra of PDMS, —Si—CH_3 in 1263 cm^{-1} , —Si—O—Si— in $1000\text{—}1100\text{ cm}^{-1}$ still exist. The peaks of PS that appear at 3080 , 3062 , 2922 , and 2851 cm^{-1} are ascribed to characteristics absorption peaks of benzene, and 1159 cm^{-1} is attributed to single instead of benzene. These results confirm that the PS-*b*-PDMS-*b*-PS triblock copolymers have been synthesized successfully.

The molecular weights and distribution of raw material and copolymer were tested by gel permeation chromatography for raw material PDMS, $M_n = 38.0\text{ kg/mol}$, and $M_w/M_n = 1.90$. As is shown in Figure 2, the GPC chromatograms of copolymer (polymerization time = 20 h) are single peak that confirmed that the product is the PS-*b*-PDMS-*b*-PS block copolymer ($M_n = 88.7\text{ kg/mol}$, $M_w/M_n = 2.06$), for the styrene corresponding to 89.6% percent conversion. And the mass fraction of PS in PS-*b*-PDMS-*b*-PS is 57.18%, which is in good agreement with the relevant TGA data presented below (see Table II, sample b, 56.85% PS).

Figure 3 shows the characteristic $^1\text{H-NMR}$ peaks of PDMS at 0.1 ppm ($\text{—Si(CH}_3)_2\text{O—}$) and the characteristic $^1\text{H-NMR}$ peaks of PS-*b*-PDMA-*b*-PS triblock copolymer at 0.1 ppm ($\text{—Si(CH}_3)_2\text{O—}$), 1.2–2.0 ppm ($\text{—CH}_2\text{—CH—}$), and 6.4–7.3 ppm (benzene), which

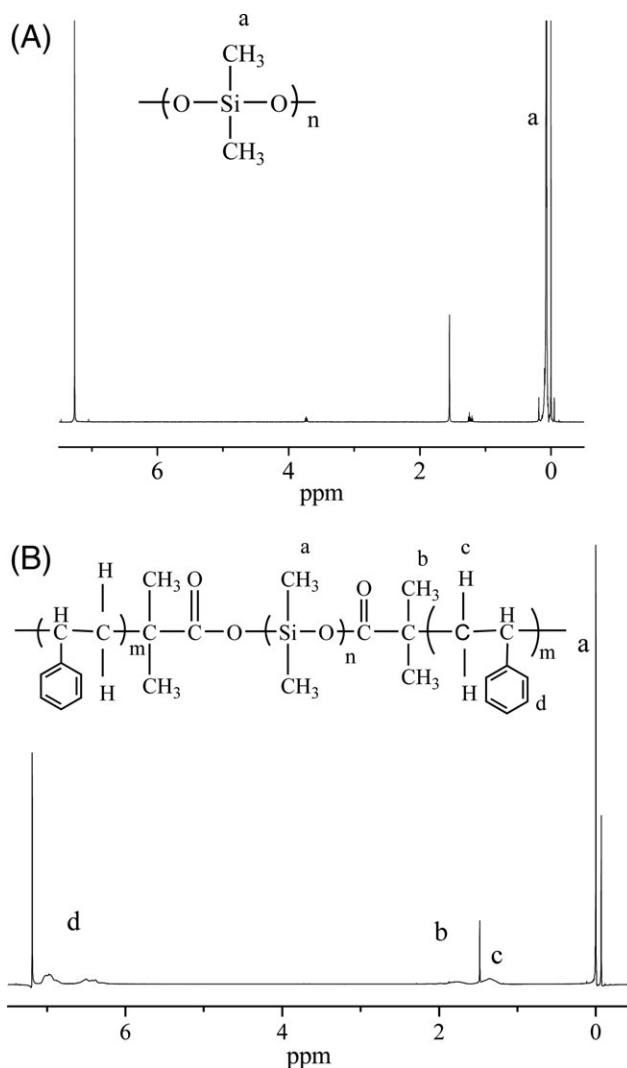


Figure 3. $^1\text{H-NMR}$ spectra of (A) PDMS and (B) PS-*b*-PDMA-*b*-PS.

were assigned to PS. The results showed that the final product included PDMS and PS phase structures. According to the proportion of area of H from benzene and $\text{—Si(CH}_3)_2\text{O—}$, the molar ratio of PS, PDMS, and the M_n (triblock copolymer) was obtained, and the data were listed in Table I, which indicated that the molecular weight of triblock copolymer was increased with the increase in the polymerization time.

The degradation data were obtained from the TGA thermograms in Figure 4. All samples own good thermal stability, because the

Table I. The Data of Triblock Copolymer

Sample	A_1 (H of benzene)	A_2 (H of $\text{—Si(CH}_3)_2\text{O—}$)	$n(\text{PS})/n(\text{PDMS})$	M_n (kg/mol)
PS- <i>b</i> -PDMS- <i>b</i> -PS (15 h)	0.29	1	0.35	56.9
PS- <i>b</i> -PDMS- <i>b</i> -PS (20 h)	0.76	1	0.91	87.1
PS- <i>b</i> -PDMS- <i>b</i> -PS (30 h)	1.27	1	1.49	118.3

A is the area of H; $n(\text{PS})/n(\text{PDMS}) = (A_1/5)/(A_2/6)$.

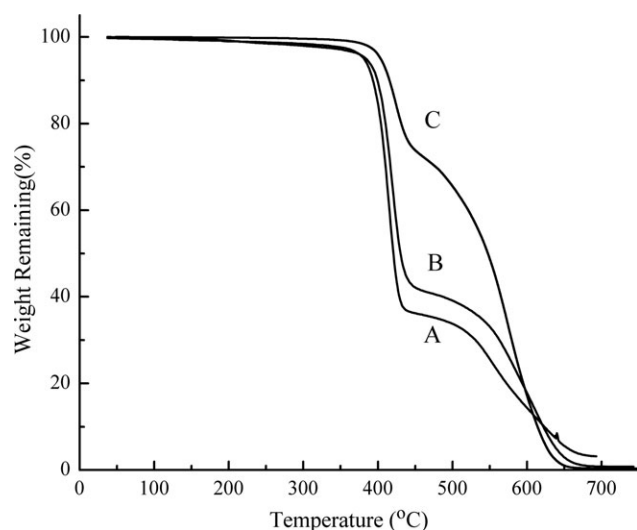


Figure 4. TGA curves of PS-*b*-PDMS-*b*-PS with different reaction time [(A) 30 h, (B) 20 h, and (C) 15 h].

decomposed temperatures are more than 300°C. The PS-*b*-PDMS-*b*-PS triblock copolymers [Figure 4(A–C)] have obvious two decomposition areas. The first step is corresponded to the thermal degradation of PS chains, and the second step is assigned to the thermal degradation of the PDMS main chains. The degradation with two steps for the PS-*b*-PDMS-*b*-PS triblock copolymers indicates the independent decomposition of two components of the copolymer. The temperature of the thermal

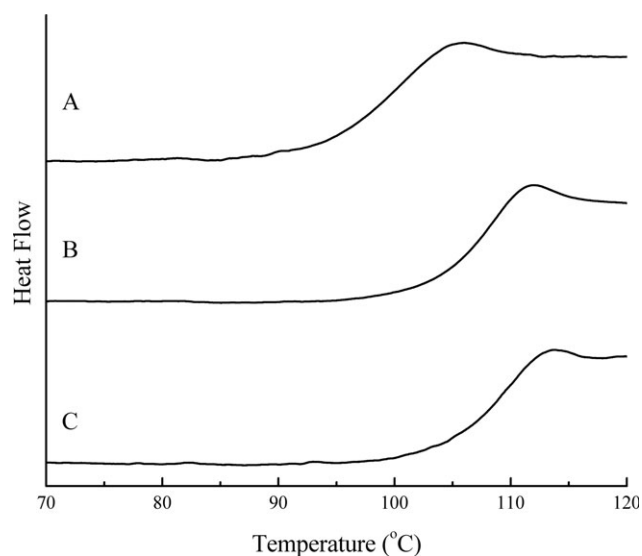


Figure 5. DSC thermograms of PS-*b*-PDMS-*b*-PS [(A) 15, (B) 20, and (C) 30 h].

degradation of PS segments decreased from 376 to 368°C as the polymerization time increased. Obviously, the existence of PDMS segments makes the initial decomposition temperature of the block copolymers considerably greater than that of pure PS (360°C), which indicated that the thermal stability of PS is improved by the polysiloxane in triblock copolymers. Dependence on the thermogravimetric data, we can obtain the average

Table II. TGA and DSC Data of Triblock Copolymer

Sample	Degradation interval ¹ (°C)	Mass loss ¹ (%)	T_g^2 (°C)	T_d^1 (°C)
a	368–342 (first step PS)	62.34	98	415
	468–676 (second step PDMS)	32.87	–	591
b	370–453 (first step PS)	56.85	107	419
	493–666 (second step PDMS)	40.11	–	587
c	376–445 (first step PS)	27.95	109	424
	445–648 (second step PDMS)	71.62	–	571

¹The data determined by TGA.

²Data determined by DSC.

Table III. Contact Angles and Surface Tensions of Triblock Copolymer

Sample	Polymerization time (h)	θ (°)		Surface tension (mN/m)		
		H ₂ O	HCONH ₂	γ	γ^d	γ^p
H ₂ O	–	–	–	72.8	22.1	50
HCONH ₂	–	–	–	58.2	39.5	18.7
1	PDMS	105	85	19.0	1.0	20.0
2	PS- <i>b</i> -PDMS- <i>b</i> -PS (15)	97	82.5	23.4	0.8	24.2
3	PS- <i>b</i> -PDMS- <i>b</i> -PS (20)	95.7	80	26.9	0.5	27.4
4	PS- <i>b</i> -PDMS- <i>b</i> -PS (25)	92.3	75.3	30.9	0.6	31.4
5	PS- <i>b</i> -PDMS- <i>b</i> -PS (30)	87.7	71	31.7	1.2	32.9

γ = entire surface tension.

M_n of PS-*b*-PDMS-*b*-PS segment in the copolymers: 110.3 kg/mol (30 h), 91.9 kg/mol (20 h), and 53.1 kg/mol (15 h), respectively, corresponding to the data of $^1\text{H-NMR}$. And the proposed methods showed the characteristics of a “living” polymerization.

DSC measurements provided insight into the thermodynamical behavior of the copolymers. Figure 5 and Table II show the DSC thermograms and correlative data. In three cases, the T_g of copolymers is very visible due to the high-weight content of the PS component. With the change in the polymerizing time, the corresponding T_g of copolymers is 109°C (15 h), 107°C (20 h), and 98°C (30 h), respectively, which are located at lower temperatures than pure PS, in agreement with the earlier literature results.⁸ This suggests that the presence of the PDMS segregated phase in the copolymer causes a small plasticization effect on the PS matrix.

The PS-*b*-PDMS-*b*-PS copolymer films were injection-molded at a temperature of 150°C with a plate vulcanizing press. And the static contact angles were measured to characterize the wettability of the PS-*b*-PDMS-*b*-PS copolymer films. The water contact angles of the copolymer films were measured to demonstrate the effect of PS chains on the surface properties of triblock copolymers. All samples are hydrophobic, which is attributed to PDMS is typically hydrophobic, and PS is composed of nonpolar groups. The pure cross-linked PDMS has a high-water agent of 105.0°, and the pure PS has a water contact angle of 85.0°. As expected, PS increased the surface wettability of PDMS, and the water contact angles toward the air-side surface of the copolymer film decreased gradually with the increasing of PS block content. The average contact angles that exhibited on the PS-*b*-PDMS-*b*-PS films are 97.0° (15 h), 95.7° (20 h), 92.3° (25 h), and decrease to 87.7° (30 h), respectively. This may be because the molecular weight of PS segments is small during the earlier stage of polymerization, which makes more hydrophobic PDMS segments migrate toward the surface of film. With the increase in the polymerizing time, PS chain grows, which results in decrease in the water contact angle of copolymer. It is difficult that the PDMS segments migrate to the surface of film, because the long block chains of PS inter-twist with each other.

At the same time, we also tested the contact angle of the samples with formamide. From these θ data measured, the surface tension and its contributions of dispersion and polarity were obtained on the basis of expanded Fowkes²⁶ equations:

$$\gamma_L(1 + \cos \theta) = 2(\gamma_S^d \times \gamma_L^d)^{1/2} + 2(\gamma_S^p \times \gamma_L^p)^{1/2} \quad (1)$$

$$\gamma_S = \gamma_S^d + \gamma_S^p \quad (2)$$

$$\gamma_L = \gamma_L^d + \gamma_L^p \quad (3)$$

θ , γ_S , and γ_L were the contact angle, surface tension of the solid, and the surface tension of the tested liquid, respectively. γ^d and γ^p were dispersion and polar components of surface tension, and the data were shown in Table III. The results indicated that the surface tensions of copolymers increased as the increase in PS content, γ_S (15 h) = 24.2 mN/m, γ_S (20 h) = 27.4 mN/m, γ_S (25 h) = 31.4 mN/m, and γ_S (30 h) = 32.9 mN/m,

separately. The value of γ_S^p of all samples was very small, and the value of γ_S^d was added with the increase in PS content, which is because PDMS and PS are both nonpolar and PS possesses affluent electron of benzene ring. The chains with low-surface tension of the copolymer diffuse on the surface, which makes the copolymer surface tension declines significantly. All the results of surface tensions were agreeable with the contact angle measurements, and those results are also proven by the SEM.

Figure 6(A–C) shows SEM images of the surface of copolymer films with different contents of PS. The copolymers that have strong microphase-separation configuration, which are

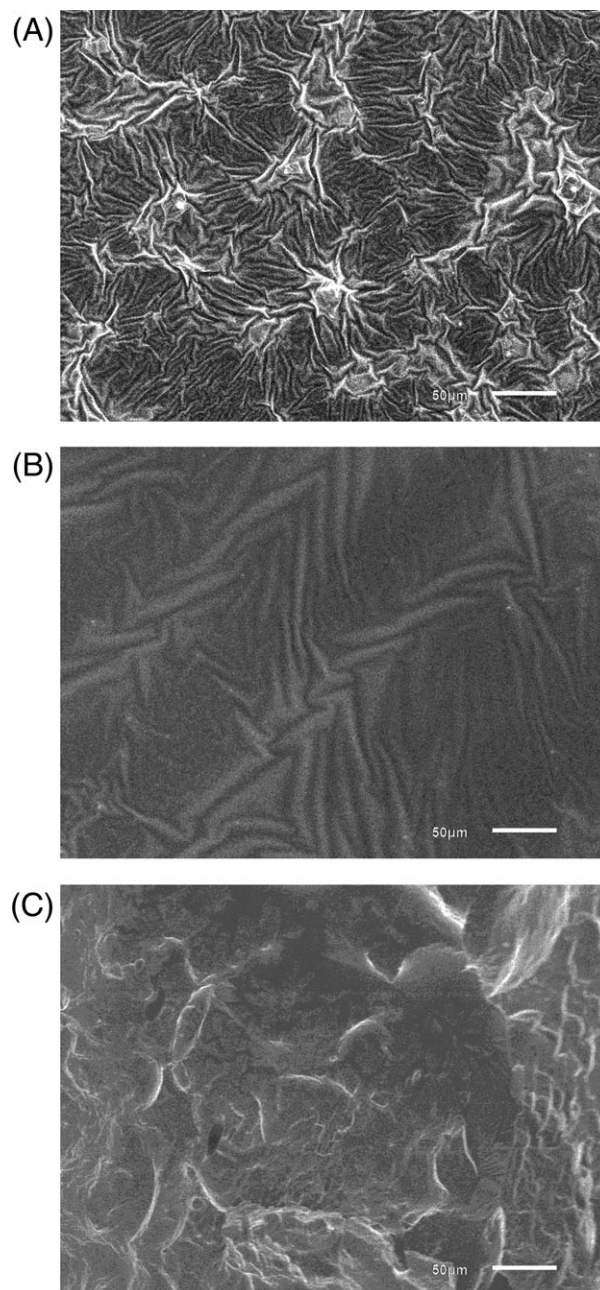


Figure 6. SEM micrographs of PS-*b*-PDMS-*b*-PS triblock copolymers. A: The surface of PS-*b*-PDMS-*b*-PS with 20 h. B: The surface of PS-*b*-PDMS-*b*-PS with 30 h. C: The fracture surface of PS-*b*-PDMS-*b*-PS with 30 h.

attributed to PDMS and PS segments, have different compositions. PS forms a continuous phase,^{23,27} and PDMS disperses equably in the continuous phase. Comparing Figure 6(A,B), the separation phenomenon is more apparent with the increase in the chain length of PS. Figure 6(C) shows the fracture surface of the PS-*b*-PDMS-*b*-PS. Comparing Figure 6(B) with Figure 6(C), the surface of triblock copolymer is more segregated than that of the interior. This is because the PDMS that possesses lower surface tension in the copolymers tends to migrate and distributes on the surface of triblock copolymer.

CONCLUSION

The PS-*b*-PDMS-*b*-PS triblock copolymers have been successfully prepared by ATRP with the catalysts of 2,2'-bipyridine and CuCl. The contents of PS in triblock copolymer increased with the polymerization time added, which result in different composition and properties of triblock copolymer. The triblock copolymers possess both PS and PDMS natural properties and strong microphase-separation configuration. The decomposed temperatures of PS-*b*-PDMS-*b*-PS triblock copolymers were more than 300°C, which indicated that PS-*b*-PDMS-*b*-PS owns good thermal stability. Furthermore, the surface tensions of PS-*b*-PDMS-*b*-PS copolymers increased as the increase in PS content.

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