

Synthesis and Surface Characterization of Poly(methyl methacrylate)-Block-Polydimethylsiloxane Copolymers from Macroazoinitiator

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ABSTRACT: Poly(methyl methacrylate)-block-polydimethylsiloxane (PMMA-*b*-PDMS) copolymers with various compositions were synthesized with PDMS-containing macroazoinitiator (MAI), which was first prepared by a facile one-step method in our lab. Results from the characterizations of X-ray photoelectron spectroscopy (XPS), contact angle measurements, and atomic force microscopy (AFM) showed that the copolymer films took on a gradient of composition and more PDMS segments enriched at the film surfaces, which then resulted in the low surface free energy and little micro-

phase separation at the film surfaces. By contrast, transmission electron microscopy (TEM) analysis demonstrated that distinct microphase separation occurred in bulk. Slight cross-linking of the block copolymers led to much steady morphology and more distinct microphase separation, in particularly for copolymers with low content of PDMS. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3356–3366, 2007

Key words: block copolymers; macroazoinitiator; phase separation; polydimethylsiloxane; surfaces

INTRODUCTION

Multiphase polymeric systems are an important class of materials that have the ability to exhibit the physical property of each component. Block copolymers containing both polydimethylsiloxane (PDMS) and vinyl-monomer components are one of the multiphase polymeric systems, and methyl methacrylate (MMA) is one of the most frequently used vinyl-monomers. Incorporation of microphase-separated PDMS domains into a poly(methyl methacrylate) (PMMA) matrix often allows the system to exhibit many of the desirable properties of both components. The PMMA is known to possess very good optical clarity, good UV stability, high electrical resistibility, and hydrolytic stability.¹ Some of the desirable properties of PDMS include a very low glass transition temperature, biocompatibility, low surface free energy, high oxygen permeability, excellent thermal stability, and higher oxidative stability.^{2–4} A heterophase material, therefore, consisting of microphase-separated PDMS and PMMA domains, should

demonstrate the desirable properties of both components. There has been considerable effort to synthesize the PMMA-*b*-PDMS copolymers by various routes, such as anionic polymerization,⁵ atom transfer radical polymerization (ATRP),^{6,7} and free-radical polymerization with macroinitiators,^{8–10} for instance, azocontaining macroinitiator, namely, macroazoinitiator (MAI), etc. Though anionic polymerization and ATRP are efficient methods for synthesizing PMMA-*b*-PDMS block copolymers, these methods require stringent purification and rigorous conditions for polymerization. Thereupon, the method of using thermal decomposable MAI to synthesize PMMA-*b*-PDMS block copolymers is still very promising, since the polymerization reaction can be carried out under much mild conditions.

As far as the method of using MAI to synthesize block copolymers is concerned, MAI needs to be prepared first. The conventional method for synthesis of MAI is complicated, moreover, the synthetic process needs the rigorous conditions, even now, a relatively low yield of MAI is obtained generally.^{9,11,12} For synthesizing MAI efficiently, in our experiment, the MAI was synthesized via a facile one-step method under mild conditions, e.g., ambient temperature and moisture, and the yield of MAI could reach 80–90%.¹³ Then a series of PMMA-*b*-PDMS copolymers with various compositions were synthesized with the resulted PDMS-containing MAI to initiate the polymerization of MMA. Although bulk properties of

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PDMS-containing block copolymers have been studied extensively,^{14–16} few surface characterizations of these copolymers have been reported. Surface properties are quite important when these copolymers are applied to such materials as lubricants, water repellents, and antifouling agents. Therefore, in this paper, the surface properties of both the linear and slightly crosslinked block copolymers were investigated in detail.

EXPERIMENTAL

Materials

Bis(hydroxyalkyl)-terminated PDMS [HO-PDMS-OH, number-average molecular weight (M_n): 5600 g/mol; degree of polymerization (DP): 69] was obtained from Aldrich and used as received. 4, 4'-Azobis-4-cyanopentanoic acid (ACPA) was also from Aldrich but freeze-dried under vacuum for 48 h using liquid nitrogen as cooling agent before use. Dicyclohexylcarbodiimide (DCC) and methyl methacrylate (MMA) were purchased from Sinopharm Group Chemical Reagent. The former was used as received and the latter was treated with 5 wt % aqueous NaOH to remove the inhibitor and dried over anhydrous calcium chloride and then stored at low temperature prior to use. 1,6-Hexanediol dimethacrylate (HDM) was from Acros and used as received. Dichloromethane, *N,N*-dimethylformamide (DMF), and benzene, dried with 3 Å molecular sieves before use, and other solvents, such as *n*-hexane, ethanol, and methanol, used as received, were all from Sinopharm Group Chemical Reagent.

Preparation of MAI from HO-PDMS-OH and ACPA

Unlike to the conventional method for synthesizing the MAI, in our lab, the MAI was prepared via the direct one-step polycondensation of ACPA with HO-PDMS-OH by the use of DCC as an activating agent and DPTS¹⁷ as a catalyst under mild conditions, e.g., ambient temperature and moisture. The detailed procedure for synthesis of MAI was described elsewhere.¹³ Namely, HO-PDMS-OH, ACPA, and DPTS were firstly dissolved in a mixture of dichloromethane and DMF. Then, DCC solution in dichloromethane was added and the mixture reacted for 24 h at room temperature. The molar ratio of HO-PDMS-OH/ACPA/DPTS/DCC is 1/1/0.4/3. After purifying with methanol and dichloromethane, finally, a colorless and highly viscous oily product was obtained in a yield of 80–90%, M_n of 36,500–40,000 g/mol and M_w/M_n of ~1.96 (determined by GPC with narrow polystyrene as calibration standard).

Synthesis of linear PMMA-*b*-PDMS copolymers

The linear poly(methyl methacrylate)-*b*-polydimethylsiloxane (PMMA-*b*-PDMS) copolymers were synthesized using the resulted MAI to initiate the polymerization of MMA. The polymerization was carried out in a 100 mL four-necked flask equipped with a mechanical stirrer, an N₂ inlet, a thermometer with temperature controller, a Graham condenser, and a heating mantle. MAI and MMA in different molar compositions were dissolved in 40 g benzene to create a solution with a concentration of 25 wt %. The polymerization was carried out at 75°C for 12 h under nitrogen gas. The resulted block copolymer (PMMA-*b*-PDMS) was isolated by slow precipitation with an *n*-hexane/ethanol mixture (1 : 2 by volume) and further purified by dissolution in benzene once more and precipitation in the mixed solvents of *n*-hexane and ethanol. The final product was vacuum-dried at 40°C for 12 h. The resulted block copolymer was designated as Bx where x represents the content of DMS mol % in copolymer.

Synthesis of slightly crosslinked block copolymers

The procedure for synthesis of slightly crosslinked PMMA-*b*-PDMS copolymers was the same as that of the linear PMMA-*b*-PDMS copolymers except that 0.2 mol % HDM (based on the content of MMA) was additionally charged with MMA. The resulted crosslinked block copolymer was designated as Cy where y represents the content of DMS mol % in the crosslinked copolymer.

The whole process of syntheses of MAI and its based block copolymers was described in Scheme 1.

Characterization and sample preparation

FTIR analysis

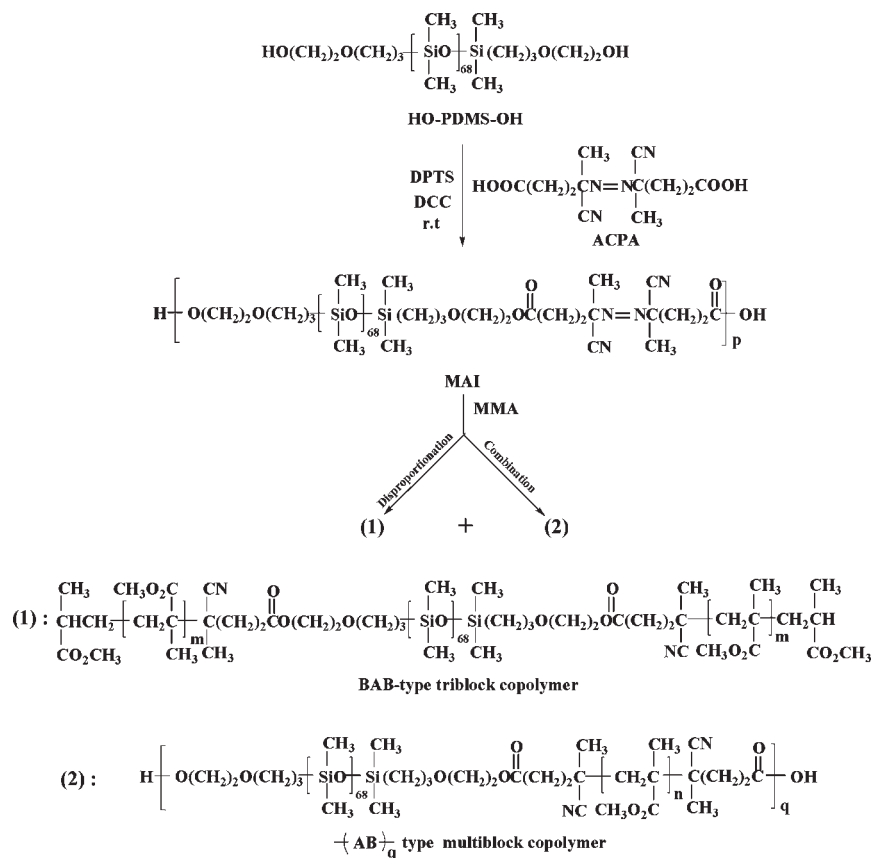
Fourier transform infrared spectra (FTIR) were carried out on a Nexus 470 FTIR spectrometer (Nicolet). HO-PDMS-OH and MAI were measured using films on KBr crystals and the block copolymers were measured using KBr pellets.

¹H-NMR analysis

¹H-NMR spectra were recorded on a VANCE DSX-500 spectrometer (Bruker, Germany), and chloroform-*d* (CDCl₃) was used as a solvent.

GPC measurement

The molecular weight and its distribution were determined by gel permeation chromatography (GPC) with a Waters Breeze 1515 instrument (USA), and



Scheme 1 Formation of MAI, BAB-type triblock, and $-(AB)_q$ -type multiblock copolymers (A = PDMS, B = PMMA).

tetrahydrofuran (THF) was used as an eluant and narrow polystyrene as the calibration standards.

AFM observation

The surface morphology of the film was observed by an atomic force microscope (AFM, SPA 300HV, Seiko Instruments, Japan) in ultra-light-tapping mode at ambient conditions. Samples for AFM measurements were prepared by cast-coating of 5 wt % toluene solution of the block copolymer onto the freshly cleaned silicon wafers with the appropriate size. All films were allowed to dry slowly at room temperature for 48 h, and the residual solvent was removed under vacuum at 40°C for 24 h. The thickness of the resulted films was ~ 30 μm . A micro-fabrication cantilever with constant of approximately 20 N m^{-1} and a scan rate of 2 Hz were used.

TEM observation

Transmission electron micrographs were observed with an H600 (HITACHI, Japan) transmission electron microscope at an accelerating voltage of 75 kV. Samples for TEM measurements were prepared by direct casting a drop of 5 wt % PMMA-*b*-PDMS copolymer solution in toluene on the carbon-coated copper

grids. The solvent was allowed to evaporate at room temperature for 2 days, and then the samples were annealed at 120°C in vacuum for 24 h. Subsequently, the resulted films were vapor-stained with an aqueous solution of 0.5 wt % RuO_4 in glass-covered dishes.¹⁸

XPS analysis

Samples for X-ray photoelectron spectroscopy (XPS) measurements were prepared with the same procedure as that of AFM analysis. XPS characterization was carried out on a PHI 5000C ESCA instrument (Perkin-Elmer) with an Mg/Al dual anode, using Al $K\alpha$ exciting radiation.

Contact angle measurement

Samples for contact angle measurements were cast-coated on clean glass flakes and treated with the same procedure as that of AFM measurements. Contact angle measurements were performed by sessile drop technique using OCA15 instrument (Dataphysics Instruments Company, Germany) at room temperature. The static contact angles (θ) were measured on the films at contact time of $t = 15$ s after application of a drop of test liquid (2 μL). The reported

values were an average of five individual measurements on different regions of the same sample.

The static contact angles were further adopted to estimate the surface free energy (γ_s) of PMMA-*b*-PDMS copolymer films using the expression reported by Kobayashi and Owen¹⁹ as follows:

$$\gamma_l(1 + \cos \theta)/2 = (\gamma_s^d \gamma_l^d)^{1/2} + (\gamma_s^p \gamma_l^p)^{1/2} \quad (1)$$

$$\gamma_s = \gamma_s^d + \gamma_s^p, \quad \gamma_l = \gamma_l^d + \gamma_l^p \quad (2)$$

where θ was the contact angle and γ_s^d and γ_s^p were the dispersion and polar components of the surface free energy of the film, and γ_l , γ_l^d , and γ_l^p were the surface free energy of the liquid, its dispersion component and polar component, respectively. In this study, deionized water (DW) and ethylene glycol (EG) were chosen as the polar liquids whereas diiodomethane (DM) was used as the apolar liquid. Their dispersion components (γ_l^d) used for calculation were 18.70, 29.29, and 49.50 mN m⁻¹, and their polar components (γ_l^p) were 53.60, 18.91, and 1.30 mN m⁻¹ for DW, EG, and DM, respectively.

RESULTS AND DISCUSSION

Synthesis of PMMA-*b*-PDMS copolymers using MAI as a macroinitiator

In our experiments, the PDMS-containing MAI was first synthesized by direct one-step method under mild conditions as compared with the conventional method for synthesis of MAI. Then, PMMA-*b*-PDMS block copolymers were synthesized by the use of the resulted MAI as a macroinitiator to initiate the polymerization of MMA. The free radical polymerization of MMA over 60°C is known to terminate principally

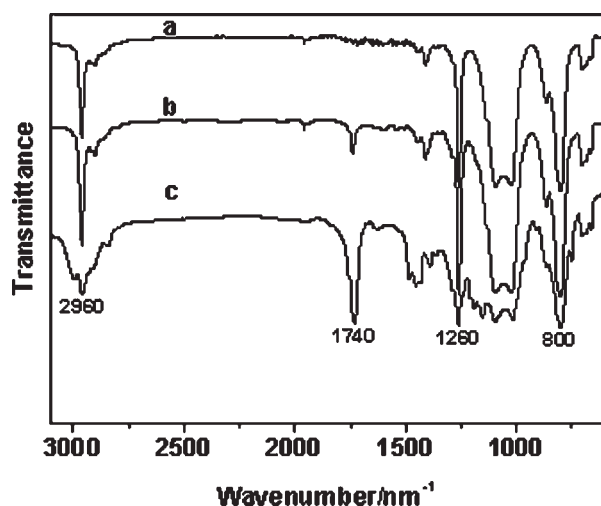


Figure 1 FTIR spectra for (a) HO-PDMS-OH, (b) MAI, and (c) PMMA-*b*-PDMS copolymer.

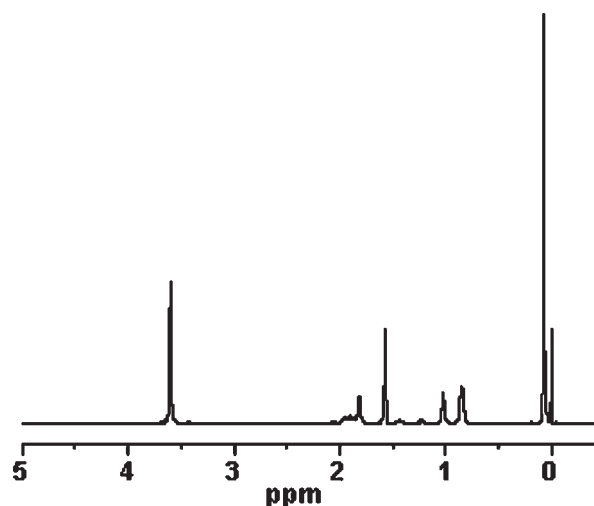


Figure 2 Typical ¹H-NMR spectrum of PMMA-*b*-PDMS copolymer (B44).

by disproportionation.²⁰ Thereupon, the preferential termination process for MMA would yield principally BAB-type triblock copolymers (where A = PDMS and B = PMMA segments, respectively) with the synthetic condition used herein. Meanwhile, some small amount of -(AB)_q- type multiblock copolymer could also be obtained due to the unavoidable combination termination, just as that described in Scheme 1.

The successful synthesis of PMMA-*b*-PDMS copolymer was confirmed by FTIR and ¹H-NMR spectra, shown in Figures 1 and 2, respectively. Compared with the spectra of HO-PDMS-OH and MAI, the strong absorption at 1740 cm⁻¹ principally due to ν_{CO} of PMMA blocks and the absorption bands at 1260 cm⁻¹ (Si-CH₃), 1000-1100 cm⁻¹ (Si-O-Si asymmetric stretching vibration), and 800 cm⁻¹ (Si-O asymmetric stretching vibration) due to PDMS blocks existed in the FTIR spectrum [Fig. 1(c)]. Meanwhile, the methoxy, methylene, and methyl protons at 3.6, 2.0-1.5, and 1.1-0.8 ppm due to PMMA segments and a sharp peak at 0.07 ppm attributing to the Si-CH₃ protons of PDMS segments all occurred in the ¹H-NMR spectrum. Comparing the relative intensity between the peak at 0.07 ppm and the peak at 3.6 ppm in the ¹H-NMR spectrum, the composition of the block copolymer could be calculated, and the results were shown in Table I. It was observed that the incorporated amounts of DMS were relatively close to the charged amounts, indicating the high initiation efficiency of MAI.

The molecular weights and their distributions of the linear and slightly crosslinked block copolymers were all shown in Table I. GPC traces (Fig. 3) of all block copolymers were symmetrically unimodal, which was also good evidence for the formation of block copolymers and further demonstrated the high efficiency of the purification process of copolymer by

TABLE I
Results of the Polymerization of Block Copolymers

Block copolymer	DMS units (mol %)		Molecular weight ^b		
	Feed	Copolymer ^a	M_n	M_w	M_w/M_n
B12	10	12	81500	150700	1.85
B25	25	25	66400	116900	1.76
B44	50	44	36800	63700	1.73
B63	70	63	29200	49200	1.68
B67	75	67	28800	44100	1.53
C14	10	14	78600	252400	3.21
C23	25	23	66200	197900	2.99
C47	50	47	42700	108100	2.53
C75	80	75	39300	78000	1.99

^a Determined by ¹H-NMR.

^b Determined by GPC.

using the pair of benzene-(*n*-hexane/ethanol) as the solvent and nonsolvent, respectively. It could also be seen from Table I that the molecular weights of the resulted copolymers decreased with increasing the charged amounts of DMS for both linear and slightly crosslinked series, namely, MAI content increased, which was consistent with the theory of traditional free radical polymerization, further manifesting the copolymers indeed prepared by the initiating of MAI. In addition, the molecular weights of slightly crosslinked copolymers were correspondingly higher than those of linear copolymer, suggesting the effective crosslink of HDM for PMMA-*b*-PDMS copolymers.

Surface morphology of PMMA-*b*-PDMS copolymer films

The PMMA-*b*-PDMS copolymers were expected to undergo microphase separation since they contain chemically distinct PMMA and PDMS segments. The morphology of the block copolymers were observed by AFM and TEM. Figure 4 showed the topographic images of the linear block copolymer films. According to the approaches in Refs. 21, 22 the brighter and darker regions in the images could be regarded as PMMA and PDMS components, respectively.

It could be seen from Figure 4 that surface morphologies of the block copolymer films were dependent on the composition of the copolymers. The blurred image was observed for copolymer B12, indicating low microphase separation between PMMA and PDMS components occurred at the film surface. There were maybe two reasons for engendering this situation: one may be the partial miscibility between PMMA and PDMS blocks due to chemical bonding, and the other was the migration of the entire copolymer chain brought by PDMS segments. As a result, the interfaces between PMMA and PDMS domains became blurry. With DMS content in the block copolymer up to 25 mol % (for copolymer B25), the morphology became much steady. Never-

theless, more darker regions occurred at the film surfaces when DMS content was over 44 mol %, such as copolymers B44 and B67, manifesting more PDMS components enriched at the film surfaces.

By contrast, TEM pictures clearly demonstrated that all of PMMA-*b*-PDMS copolymers had distinctly microphase-separated structures as shown in Figure 5. In these micrographs, the darker regions consisted of the PDMS component since only these segments can be stained by RuO₄.

The bulk morphology of the copolymers was strongly dependent upon DMS content. Specifically, at the very lower DMS content, for instance, sample B12, though microphase separation occurred, the interface between the two phases was very blurry [Fig. 5(a)], which was consistent with its surface morphology. The morphology was an island-sea texture with spherical and partial cylindrical PDMS domains dispersed in continuous PMMA matrix [Fig. 5(b)] when DMS content amounted to 25 mol %. With DMS content continuously increasing, PDMS phase gradually enlarged until it formed a continuous phase at about 44 mol% DMS content. As a result, bicontinuous PDMS and PMMA phases were formed for copolymer B44 [Fig. 5(c)] and even inverse sea-island structure, namely, PMMA domain dispersed in the continuous PDMS phase for copolymer B67 [Fig. 5(d)].

Surface chemical composition of PMMA-*b*-PDMS copolymers

Surface chemical compositions of block copolymers were not always the same as bulk compositions while they were usually dominated by the component with

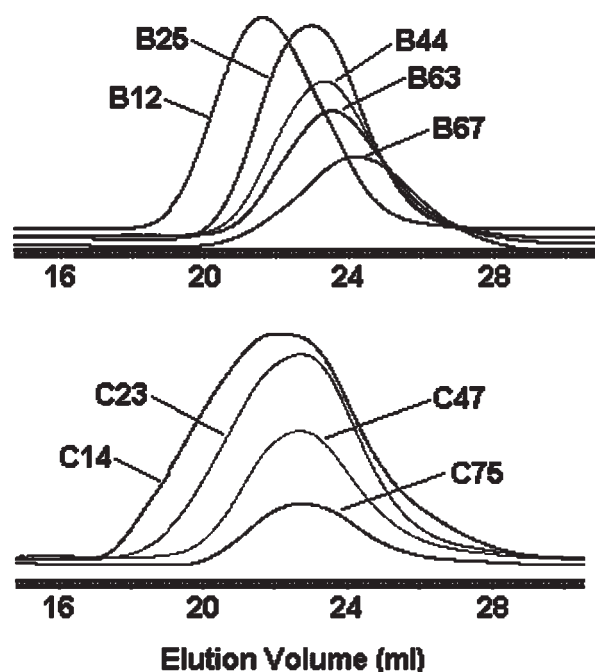


Figure 3 GPC traces of the block copolymers.

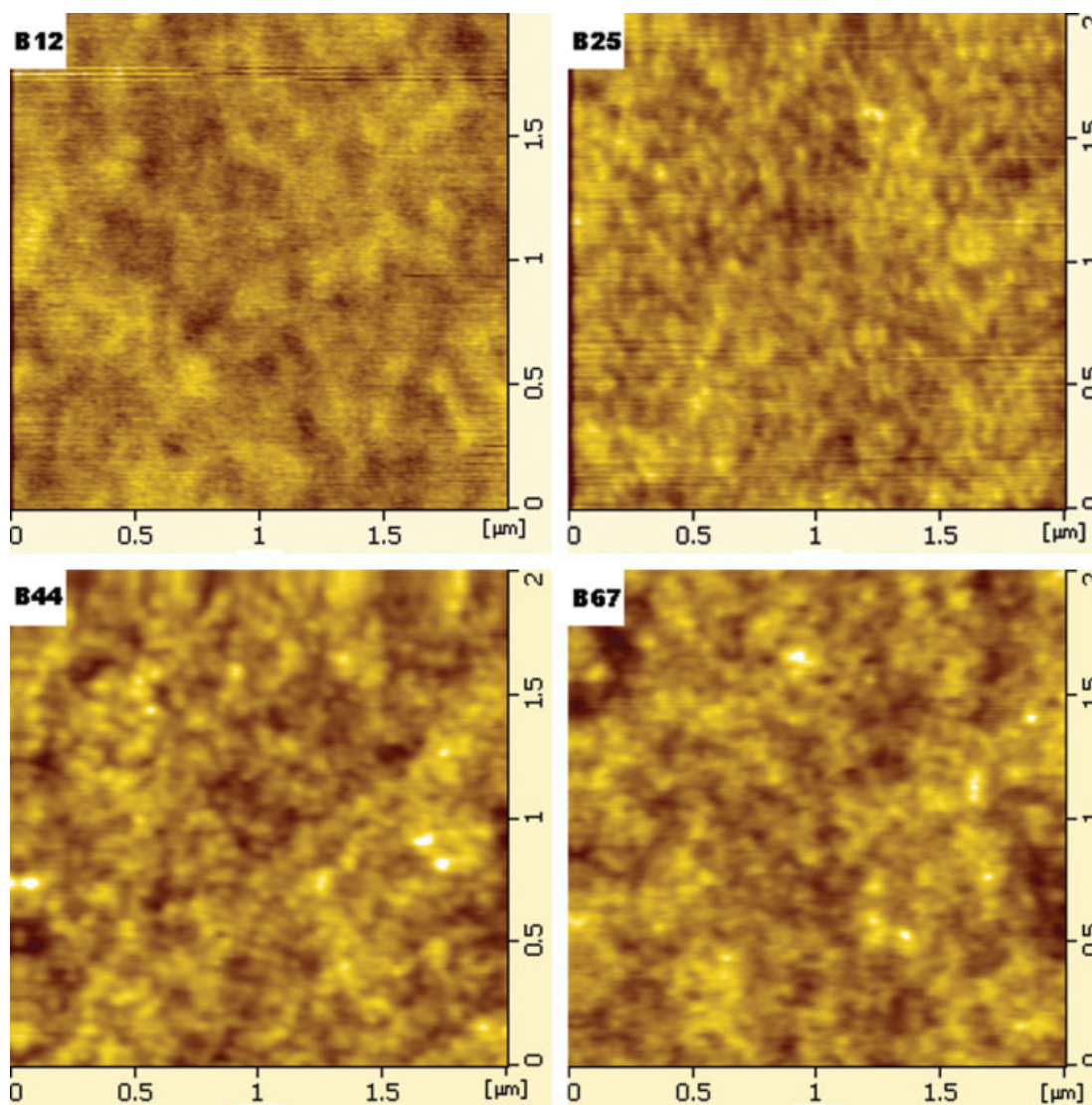


Figure 4 Topographic images of the linear block copolymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the lower surface free energy. Since PDMS had a low surface free energy and it existed in a microphase-separated system, it would dominate the air/solid interface in these block copolymers.²³ So the surface compositions of the copolymer films were evaluated using XPS at two different take-off angles (TOA): 90° and 45°. Figure 6 presented the typical XPS survey spectrum of PMMA-*b*-PDMS copolymer. Three elements were detectable, namely C, O, Si with C_{1s}, O_{1s}, Si_{2s} and Si_{2p} atomic signals assigned at 285, 530, 150, and 101 eV, respectively. The atomic quantification was determined using C_{1s}, O_{1s}, and Si_{2p}, and the obtained atomic ratios of Si/C at two different TOA for the film surfaces together with the theoretical atomic ratios of Si/C in bulk were plotted in Figure 7.

The sampling depth was approximately proportional to $\sin\theta$ (θ denoted the take-off angle).⁶ Higher

TOA meant that X-ray could penetrate more deeply into the surface of the sample. As an approximation, the measurement at TOA of 45° revealed the atomic composition about the top 6 nm of the surface, while the measurement at TOA of 90° measurement indicated the composition down to about 10 nm.^{24,25} Results in Figure 7 indicated that block copolymers with high atomic ratios of Si/C in bulk also had high DMS contents at the film surface, manifesting that the amounts of PDMS at the film surfaces increased with the increase of PDMS contents in the block copolymer. For each block copolymer, the atomic ratio of Si/C at the film surface was higher than their corresponding theoretical values in bulk, indicating enrichment of PDMS components at the surface regions in all cases due to the low surface free energy of PDMS, which agreed with

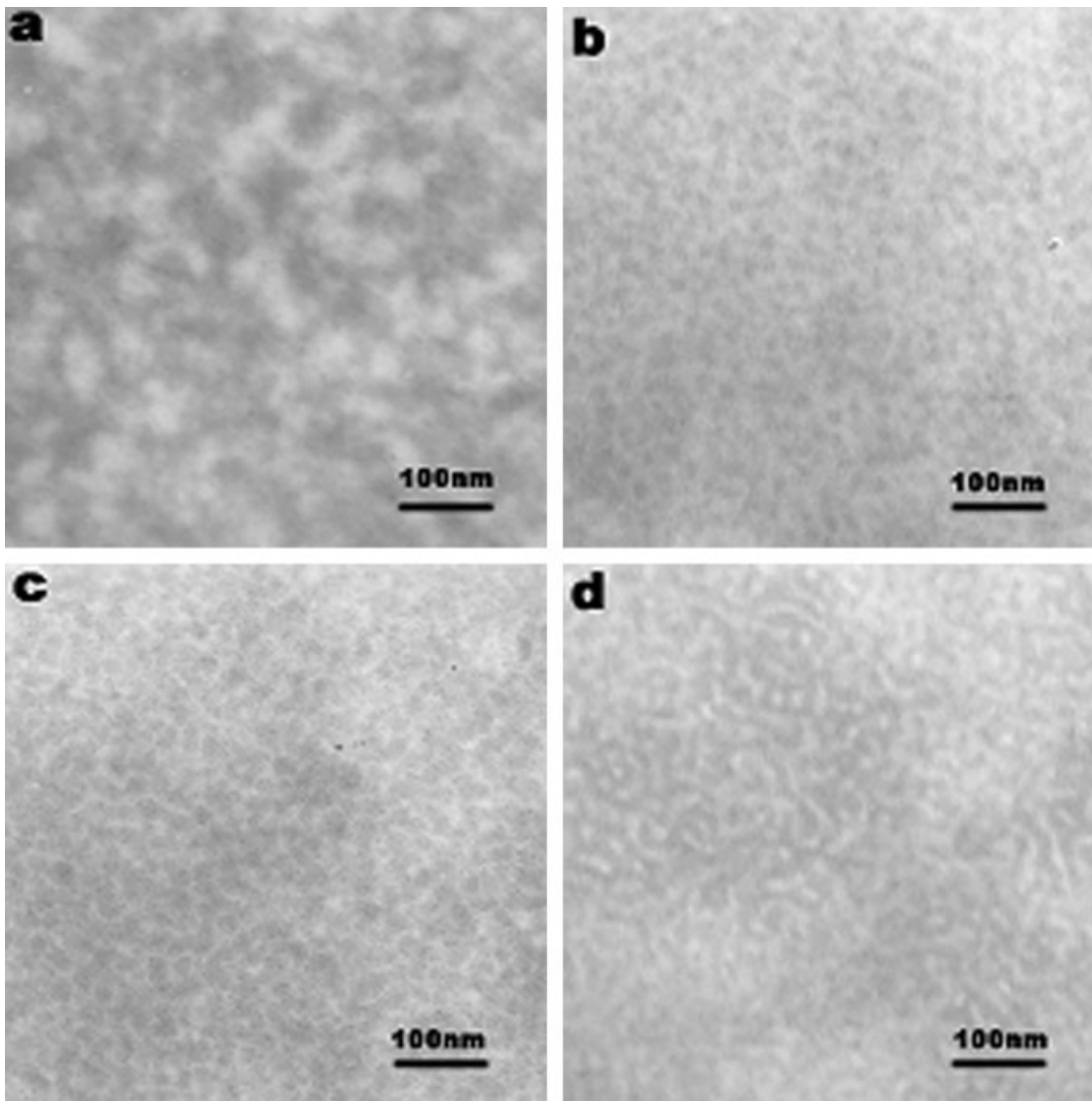


Figure 5 TEM pictures of PMMA-*b*-PDMS copolymers with various DMS molar contents: (a) 12% (B12), (b) 25% (B25), (c) 44% (B44), and (d) 67% (B67).

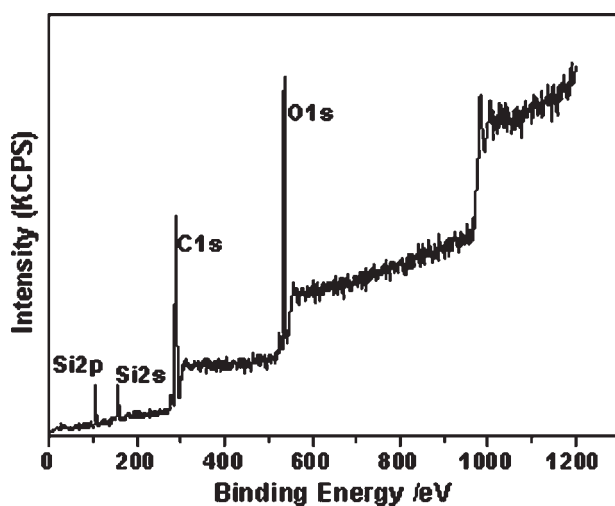


Figure 6 Wide scan XPS of the block copolymer (B44).

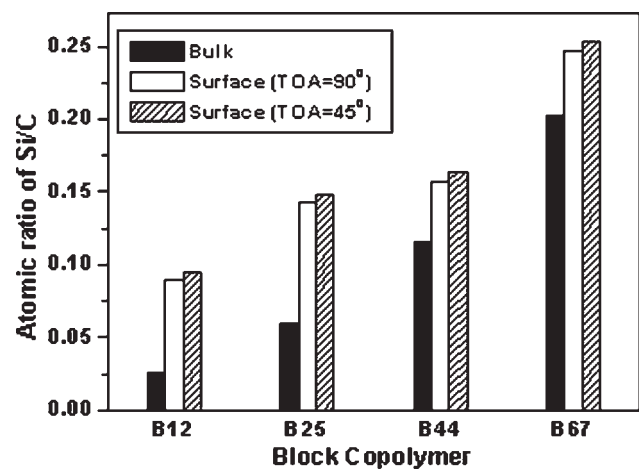


Figure 7 Atomic ratios of Si/C for various block copolymer films.

TABLE II
Contact Angles ($\theta \pm 1.0$) and the Surface Free Energy (γ_s) and Their Dispersion (γ_s^d) and Polar (γ_s^p)
Components of PMMA and Linear PMMA-*b*-PDMS Copolymer Films at 20°C

Sample	DMS content (mol %)	θ_{DW}^a (°)	θ_{EG}^b (°)	θ_{DM}^c (°)	γ_s^d (mN m ⁻¹)	γ_s^p (mN m ⁻¹)	γ_s (mN m ⁻¹)
PMMA	0	72.6	48.9	42.0	33.39 ± 0.57	6.09 ± 0.39	39.48 ± 0.69
B12	12	102.2	81.0	60.4	26.97 ± 0.64	0.22 ± 0.08	27.19 ± 0.65
B25	25	105.2	86.1	63.3	25.38 ± 0.64	0.07 ± 0.05	25.5 ± 0.64
B44	44	106.6	87.2	65.0	24.53 ± 0.63	0.05 ± 0.04	24.58 ± 0.63
B67	67	109.1	88.9	68.5	22.77 ± 0.62	0.04 ± 0.04	22.81 ± 0.62

^a Water (DW).

^b Ethylene Glycol (EG).

^c Diiodomethane (DM).

the morphological observation above. Meanwhile, there were also higher atomic ratios of Si/C at a TOA of 45° than those of 90°, indicating that amount

of PDMS gradually decreased from the outmost layer to the interior, as a result, gradient of compositions for the copolymer films were formed.

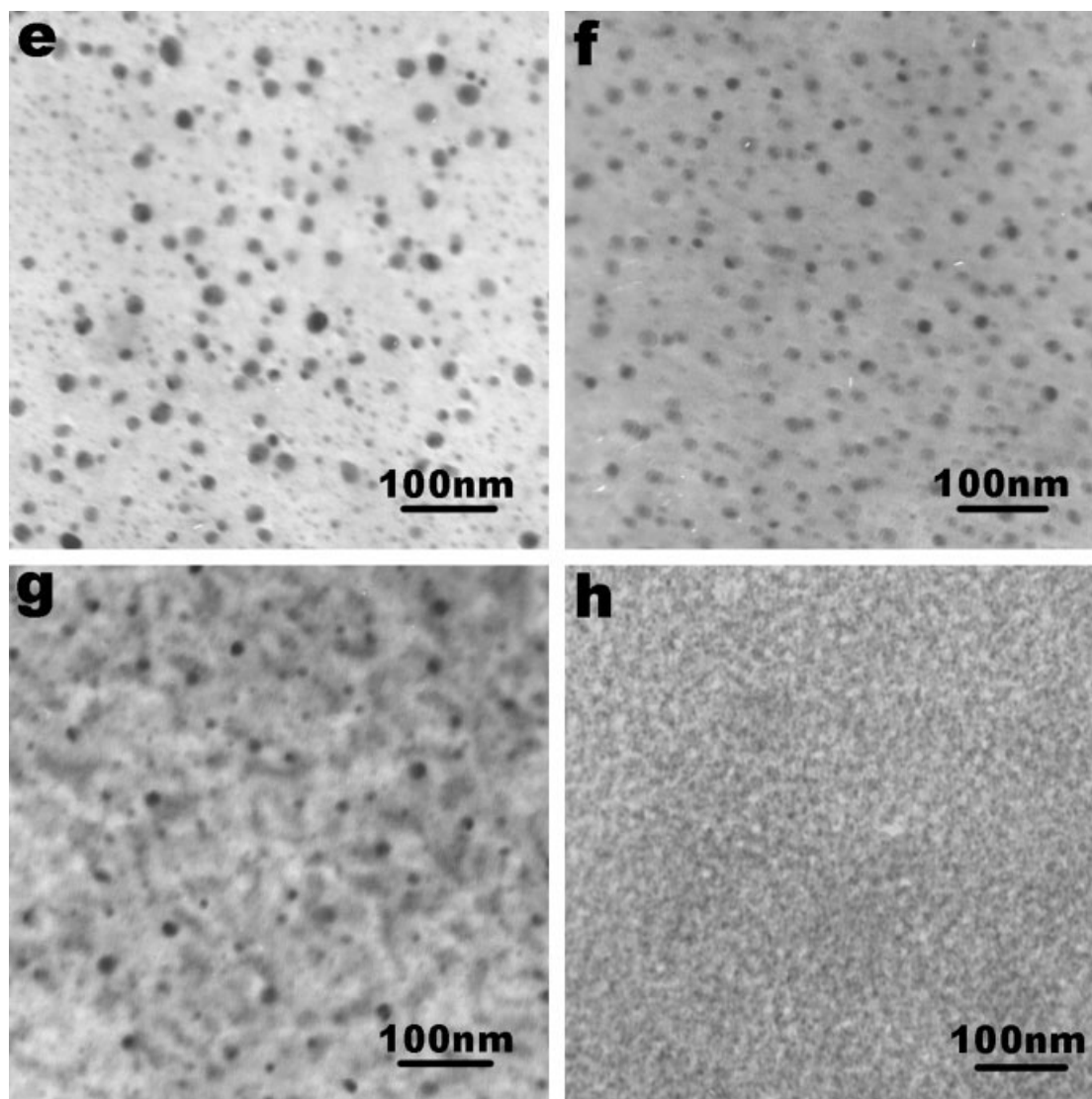


Figure 8 TEM pictures of slightly crosslinked PMMA-*b*-PDMS copolymers: (e) C14, (f) C23, (g) C47, and (h) C75.

Surface free energy of the linear block copolymer films

Since the surface chemical composition of the block copolymer film varied from copolymer to copolymer, as a result, the surface free energy of the copolymer would be different for various copolymers. Thereof, the static contact angles at the copolymer films were measured to calculate the surface free energy. Table II summarized their contact angles and calculated surface free energies (γ_s) together with their components (γ_s^d and γ_s^p). For comparison, the corresponding values for pure PMMA were also presented.

Data in Table II showed that contact angles measured on all copolymer films were higher than those on PMMA films for all probe liquids. It was noteworthy that the surface free energy of the film decreased after the incorporation of a small quantity

of PDMS (for instance, sample B12) in the block copolymers. This suggested that PDMS components enriched at the film surface even at very small amount of PDMS incorporated in the copolymers. With further increase of PDMS content in the copolymers, the surface free energy of the film decreased gradually until the surface free energy was close upon the surface free energy of the pure PDMS (19.15 mN m^{-1}),²⁶ indicating the amount of PDMS at the surface was nearly saturated.

Effect of crosslinking on the morphology of PMMA-*b*-PDMS copolymers

The free movement of the polymer chain can lead to the blurry interfaces between different phases, just as the morphologies of the linear copolymers as

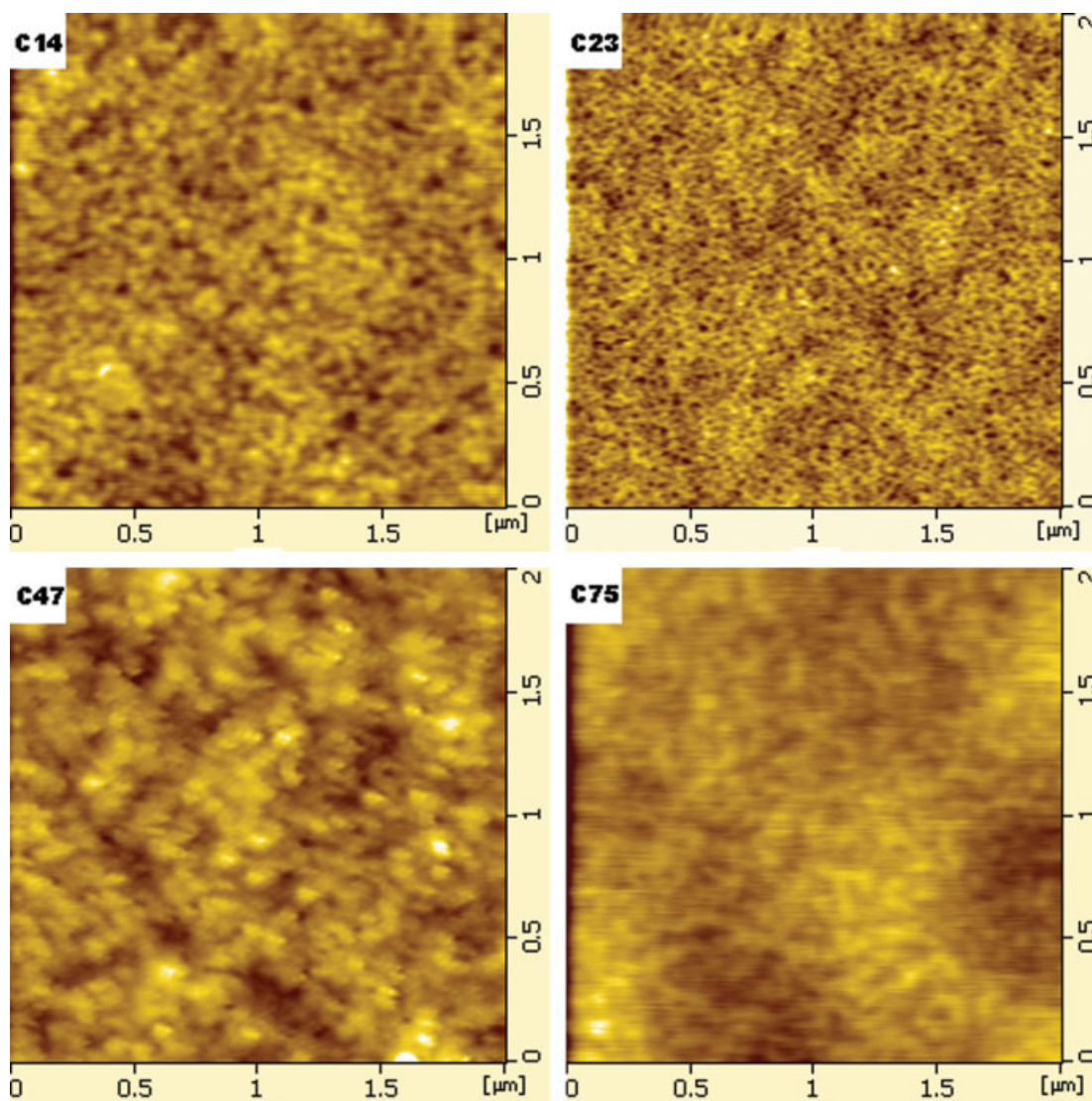


Figure 9 Topographic images of the linear and crosslinked block copolymer films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

shown in Figure 5. Thereupon, the copolymer was slightly crosslinked with HDM in the process of polymerization to improve this situation. Figure 8 showed TEM micrographs of the crosslinked block copolymers. It could be seen that bulky morphologies of the crosslinked copolymers changed as compared with that of the linear copolymers (Fig. 5). Specifically, the microphase separation was quite distinct at lower DMS contents in the crosslinked copolymers, and an island-sea structure with spherical PDMS dispersed in continuous PMMA matrix for copolymer C14 [Fig. 8(e)]. Moreover, the interfaces between PMMA and PDMS phases became quite apparent as compared with those of linear copolymer B12 [Fig. 5(a)]. With DMS content continuously increasing, more spherical PDMS occurred, just as that of C23 shown in Figure 8(f). Worm-like structure occurred with a little quantity of spherical PDMS when DMS content was up to 47 mol %, indicating that PDMS gradually became continuous phase and the bicontinuous structure began to form, as shown in Figure 8(g). That continuing increase of DMS content in the crosslinked copolymers resulted in the enlargement of PDMS phase, consequently, the microphase separation with bicontinuous structure became more apparent [Fig. 8(h)]. It was assumed that crosslinking led to more steady morphology with distinct microphase separation, in particularly for copolymers with low content of PDMS.

Likewise, the surface morphologies of the films were also changed after the block copolymers were crosslinked, just as shown in Figure 9. The interfaces between different domains became more distinct for crosslinked copolymers relative to those of the linear block copolymers, suggesting that the movement of the polymeric chains was restricted to some extent. This result further demonstrated that the blurred interfaces of the linear copolymers mainly resulted from the movement of polymeric chains. Meanwhile, some spinodal-like patterns existed at the surfaces of the crosslinked copolymer films with low content of DMS, such as C14 and C23, manifesting low microphase separation at the surface might occur. However, with DMS content increasing, these spinodal-like patterns progressively became less, suggesting more PDMS chains moved to the film surface, similar to those observed for linear block copolymers. This was caused by both the increase of PDMS amounts and the decrease of the crosslinking degree. Therefore, it could be assumed that crosslinking redounded to form more distinct and steady morphology, especially for copolymers with low DMS contents.

The surface free energies of the crosslinked copolymers were similar to those of the linear block copolymers with corresponding PDMS contents, indicating

that though the surface morphology changed to some extent, the PDMS still dominated the surface of the slightly crosslinked block copolymer.

CONCLUSIONS

PMMA-*b*-PDMS copolymers with various compositions were synthesized by the copolymerization of MMA and PDMS-containing MAI, which was first prepared via a facile one-step method in our lab. Results from characterizations of the morphology, surface free energy and the chemical composition of the block copolymers indicated that distinct microphase-separated structure occurred in bulk while the microphase separation was not apparent at the film surface due to the enrichment of PDMS components. The morphology tended to be much steady and the microphase separation became more distinct after the block copolymers were crosslinked, especially for copolymers with low contents of PDMS. In addition, gradient of compositions were established at the film surfaces and the surface free energies of the copolymer films slightly decreased with the increase of the PDMS contents in the copolymers.

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