

# Polyimide–Polydimethylsiloxane Copolymers for Low-Dielectric-Constant and Moisture-Resistance Applications

Kai Xi,<sup>1</sup> Zhen Meng,<sup>1</sup> Liang Heng,<sup>1</sup> Renjie Ge,<sup>1</sup> Hui He,<sup>1</sup> Xuehai Yu,<sup>1</sup> Xudong Jia<sup>1,2</sup>

<sup>1</sup>Department of Polymer Science and Engineering, Nanjing University, Nanjing 210093, People's Republic of China

<sup>2</sup>National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, People's Republic of China

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**ABSTRACT:** Novel, randomly coupled, soluble, segmented polyimide–polydimethylsiloxane (PI–PDMS) copolymers were prepared from aminoalkyl-terminated polydimethylsiloxane (At–PDMS), 4,4'-oxydianiline diamine, pyromellitic dianhydride, and 4,4'-diphenylmethane diisocyanate (MDI). When At–PDMS was introduced into the polyimide chain, the polyimide copolymers exhibited lower dielectric constants and better moisture resistance and mechanical properties. The reductions in the dielectric constant of the PI–PDMS copolymers could be attributed to the incorporation of polydimethylsiloxane (PDMS) into

the polyimide chain and the nanopores in the film generated by carbon dioxide evolution during the reaction. The lowest dielectric constant was 2.58 with 25 wt % PDMS and 5 wt % MDI. In addition, the water contact angles of the resultant copolymers increased from 51 to 109° when the contents of PDMS increased from 0 to 25 wt %. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1633–1641, 2009

**Key words:** polyimides; polysiloxanes; dielectric property

## INTRODUCTION

Polyimides (PIs) have been widely used as protection and insulation layers for very large scale integration circuits and multichip modules for computers and aerospace applications because of their high thermal stability and excellent mechanical properties.<sup>1–3</sup> With the rapid development of ultra-large-scale integration, a novel low-dielectric-constant material is needed to replace the current interlayer dielectrics.<sup>4</sup> However, conventional PIs with dielectric constants of approximately 3.3–3.5 are insufficient in meeting the requirement of a dielectric constant less than 2.5 for the dielectrics needed for ultra-large-scale integration in the near future.<sup>5</sup> Additionally, air humidity can convert PIs back to poly(amic acid), and the dielectric constant of the materials will decrease as a result.

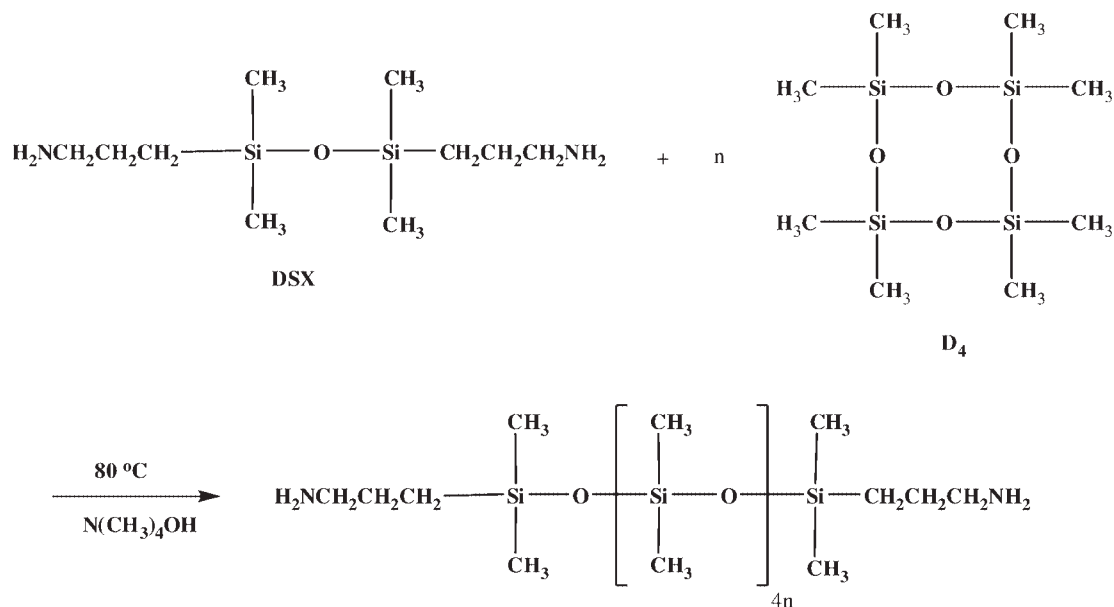
In recent years, there has been considerable interest in copolymer materials and their applications as low-dielectric-constant materials.<sup>6</sup> To decrease the dielectric constants of polymers, several research groups have explored the possibility of incorporating various nanofoams into polymer matrices to take advantage of the low dielectric constant of air (dielectric constant

= 1).<sup>7–11</sup> Unfortunately, the mechanical properties of nanofoaming PI materials fall, whereas the dielectric constants of the polymers decrease. Furthermore, the dielectric constant of PI will rise when water molecules appear. To the best of our knowledge, there are only limited publications related to improving the moisture resistance of PI materials.

Low-dielectric-constant materials made of organic silicon,<sup>12–17</sup> such as polymethylsilsesquioxane and polydimethylsiloxane (PDMS), are frequently reported.<sup>18–24</sup> These materials show good thermal stability and moisture resistance. For PIs as low-dielectric-constant materials,<sup>25–29</sup> two methods of synthesis have mostly been reported in the recent literature. One is the dehydration of a diamine and a dianhydride with poly(amic acid), and the other is the elimination of carbon dioxide between a dianhydride and a diisocyanate. By combining these methods, we synthesized a novel series of polyimide–polydimethylsiloxane (PI–PDMS) copolymers with aminoalkyl-terminated polydimethylsiloxane (At–PDMS), 4,4'-oxydianiline diamine (ODA), pyromellitic dianhydride (PMDA), and 4,4'-diphenylmethane diisocyanate (MDI) as comonomers. A series of PI copolymers were then prepared by the adjustment of the molar ratios of PDMS and MDI.<sup>30</sup> The obtained PI–PDMS copolymers exhibited lower dielectric constants because the introduction of PDMS and the free volume in the samples increased with the absorption of carbon dioxide onto the PI–

Correspondence to: X. Jia (jiaxd@netra.nju.edu.cn).

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Scheme 1 Synthesis of At-PDMS.

PDMS microphase-separation interfaces. Meanwhile, the moisture resistance was improved when PDMS was enriched on the copolymer surfaces. Clearly, these materials with low dielectric constants and good moisture resistance and mechanical properties have great potential for applications in the microelectronics industry.

## EXPERIMENTAL

### Materials

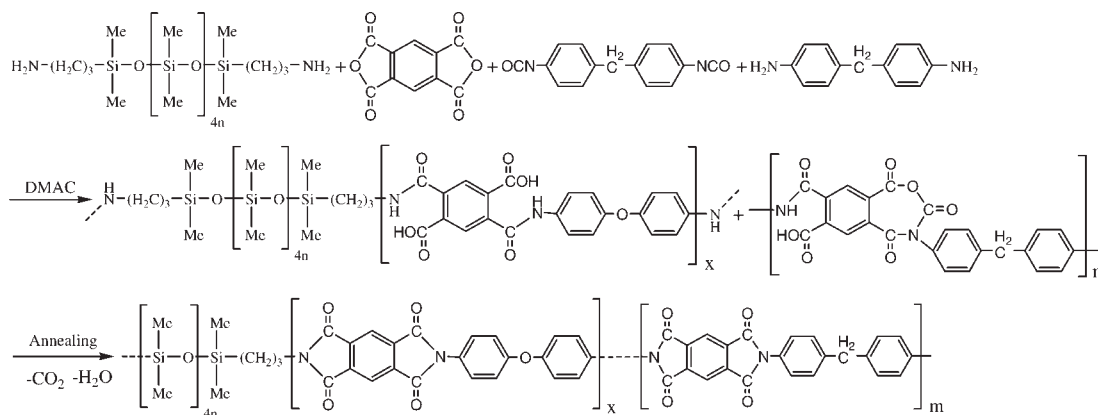
PMDA from Shanghai Chemical Co. (Shanghai, China) was purified by sublimation. ODA and MDI were purchased from Shanghai Chemical, and MDI was distilled *in vacuo*. Aminoalkyl disiloxane was purchased from United Chemical Technologies, Inc., (Bristol, CT) and used as received. Cyclic tetramer, *N,N'*-dimethylacetamide (DMAC), and tetrahydrofuran (THF) were purchased from Shanghai Chemical

and were dried over 4-Å molecular sieves for at least 24 h and distilled *in vacuo* before use.

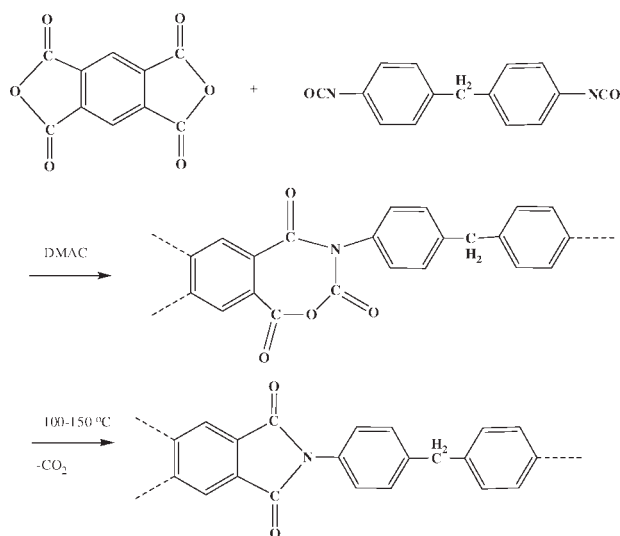
### Preparation of the samples

At-PDMS was prepared according to the literature.<sup>6,31</sup> The number-average molecular weight of At-PDMS was 2100, as measured by <sup>1</sup>H-NMR (Scheme 1).

At-PDMS (0.0012 mol) and ODA (0.0078 mol) were added to a 100-mL, round-bottom flask with a mixture of DMAC and THF (1 : 1 v/v) and stirred under an N<sub>2</sub> atmosphere. After PMDA (0.01 mol) was added slowly, the solution was stirred at 40°C for 6 h. MDI (0.001 mol) was then added, and the solution was stirred at room temperature for 24 h. To obtain the PI-PDMS copolymer film (PI-25-5), the aforementioned solution was finally cast onto a Teflon dish, and the solvent was removed at room



Scheme 2 Synthesis of PI and organic silicon composites.



**Scheme 3** Reaction of MDI and PMDA with PI and  $\text{CO}_2$ .

temperature for 24 h, at 100°C for 2 h, and at 250°C for 1 h. The reactions are described in Schemes 2 and 3. The other PI-PDMS films with different components were obtained with a similar approach.

### Characterization

Infrared spectra were taken with a Nexus 870 spectrometer (Madison, WI) in the range of 4000–400  $\text{cm}^{-1}$  with a resolution of 1.0  $\text{cm}^{-1}$ . The preparations of all samples were performed under a continuous flow of nitrogen to ensure minimal oxidation or degradation of the samples.

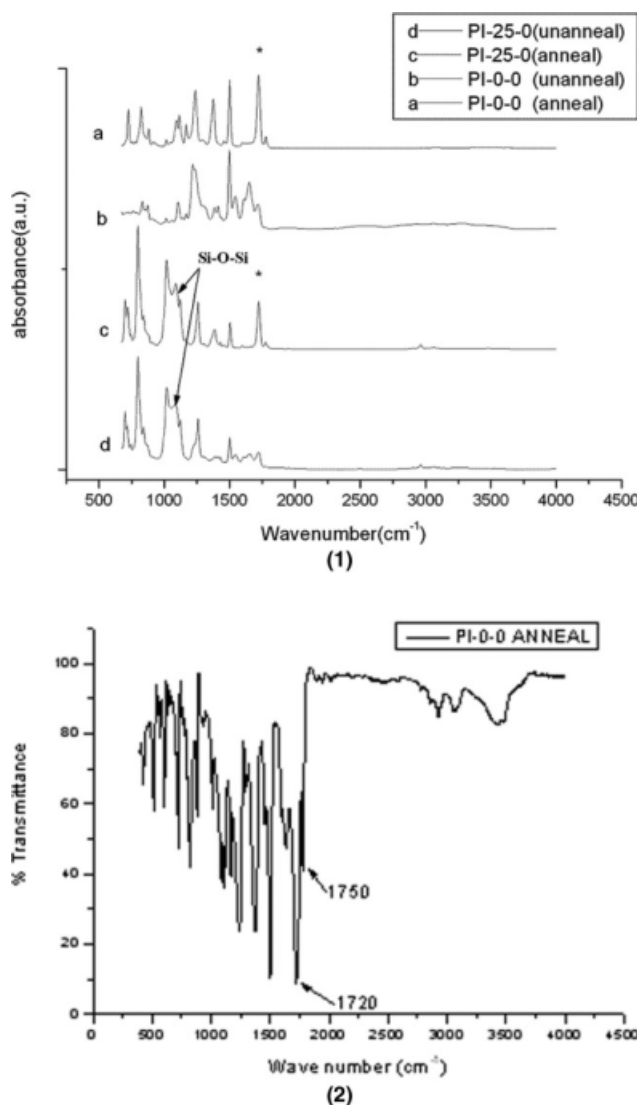
The  $^1\text{H-NMR}$  spectrum of primary At-PDMS in  $\text{CDCl}_3$  (Bruker, Switzerland) was taken with a Bruker Avance 300 at room temperature.

**TABLE I**  
Components of the PI-PDMS Block Polymers

Sample	PMDA and ODA (wt %)	PDMS (wt %)	MDI (wt %)
PI-0-0	100	0	0
PI-0-2	98	0	2
PI-0-5	95	0	5
PI-0-10	90	0	10
PI-6-0	94	6	0
PI-6-2	92	6	2
PI-6-5	89	6	5
PI-6-10	84	6	10
PI-12-0	88	12	0
PI-12-2	86	12	2
PI-12-5	83	12	5
PI-12-10	78	12	10
PI-25-0	75	25	0
PI-25-2	73	25	2
PI-25-5	70	25	5
PI-25-10	65	25	10

The water contact angles were measured with a KSV Instruments, Ltd., (Helsinki, Finland) optical contact-angle meter. The data were collected 1 min after a drop of double-distilled water had been placed on a film surface. At least 10 measurements were used, and the average contact angle was then calculated.

Differential scanning calorimetry (DSC) thermograms were recorded with a 20°C/min heating rate under an  $\text{N}_2$  atmosphere from 50 to 300°C with a PerkinElmer Pyris 1 thermal analysis system (Waltham, MA). Before the scanning was carried out, the samples were annealed at 100°C for 10 min to eliminate the remaining stress during the membrane formation. Thermogravimetric analysis (TGA) was carried out with a PerkinElmer TGA thermogravimetric analyzer at a heating rate of 10°C/min from



**Figure 1** (1) FTIR spectra of PI-25-0 and pure PI before and after annealing (obtained by reflection absorbance) and (2) FTIR spectrum of PI-0-0 after annealing (obtained by the transmission method).

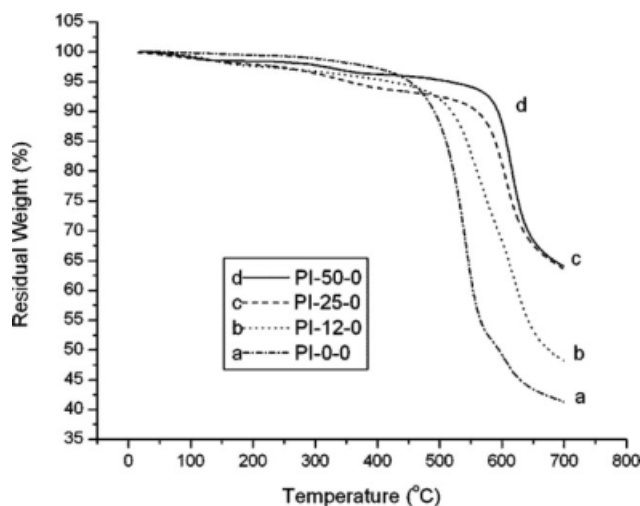


Figure 2 TGA of the PI-PDMS block polymers.

room temperature to 700°C under a continuous nitrogen flow. Dynamic mechanical thermal analysis (DMTA, Rheology, USA) measurements were performed with a DMTA V in a tension mode over the temperature range of  $-120$  to  $350^{\circ}\text{C}$ . Data acquisition and analysis of the storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) were recorded automatically by the system.

The mechanical properties were determined on an Instron series IX (Norwood, MA) table automated materials testing system with an interface type of 4200. The samples were stamped with an ASTM 1708 standard die and tested with a crosshead speed of  $50\text{ mm/min}$  at room temperature (ca.  $18^{\circ}\text{C}$ ) under 50% humidity.

The current-voltage characteristics were measured with an HP4145B (USA) semiconductor parameter analyzer. The dielectric constant of the film was calculated through the measurement of the capacitance

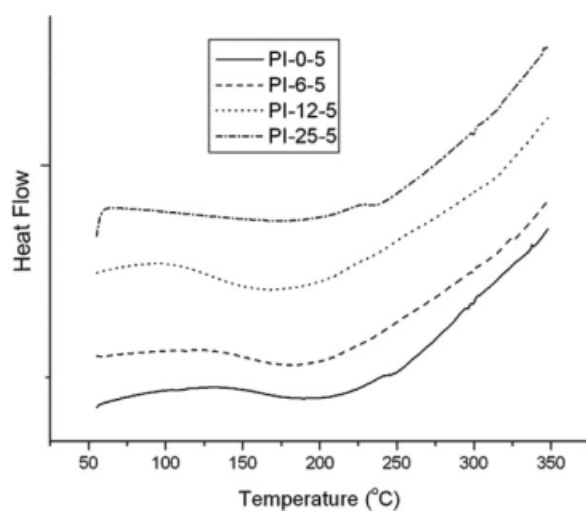


Figure 3 DSC of the PI-PDMS block polymers.

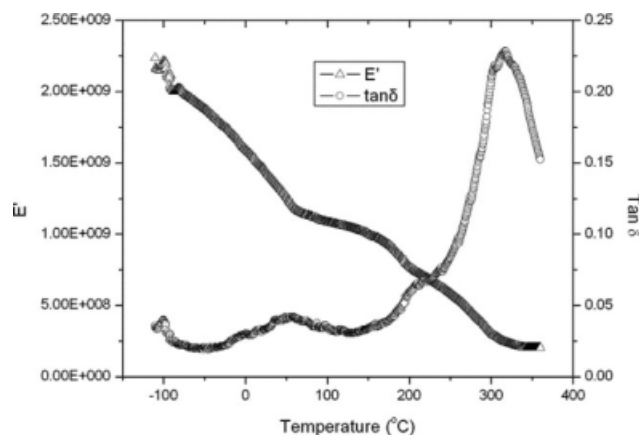


Figure 4 DMTA of PI-12-5.

of the metal-insulator-metal structure with the HP4145B semiconductor parameter analyzer according to the following equation:  $k = C \times d / (A \times \epsilon_0)$ , where  $k$  is the dielectric constant,  $C$  is the capacitance,  $d$  is the thickness of the thin film,  $A$  is the area of the thin film, and  $\epsilon_0$  is a constant.

The surface morphology was recorded by an atomic force microscopy (AFM) (SPI3800, Seiko Instruments Inc., Japan) at room temperature with a BS-Tap300AI tapping mode needle at a resonant frequency of 300 Hz, a force constant of  $40\text{ N/m}$  and a scanning speed of 1 Hz. Cross-sectional images of PI-PDMS (0.2–0.5 mm) were studied with scanning electron microscopy (SEM). The SEM images were obtained with a Leo 1530VP microscope operating at an acceleration voltage of 5 kV.

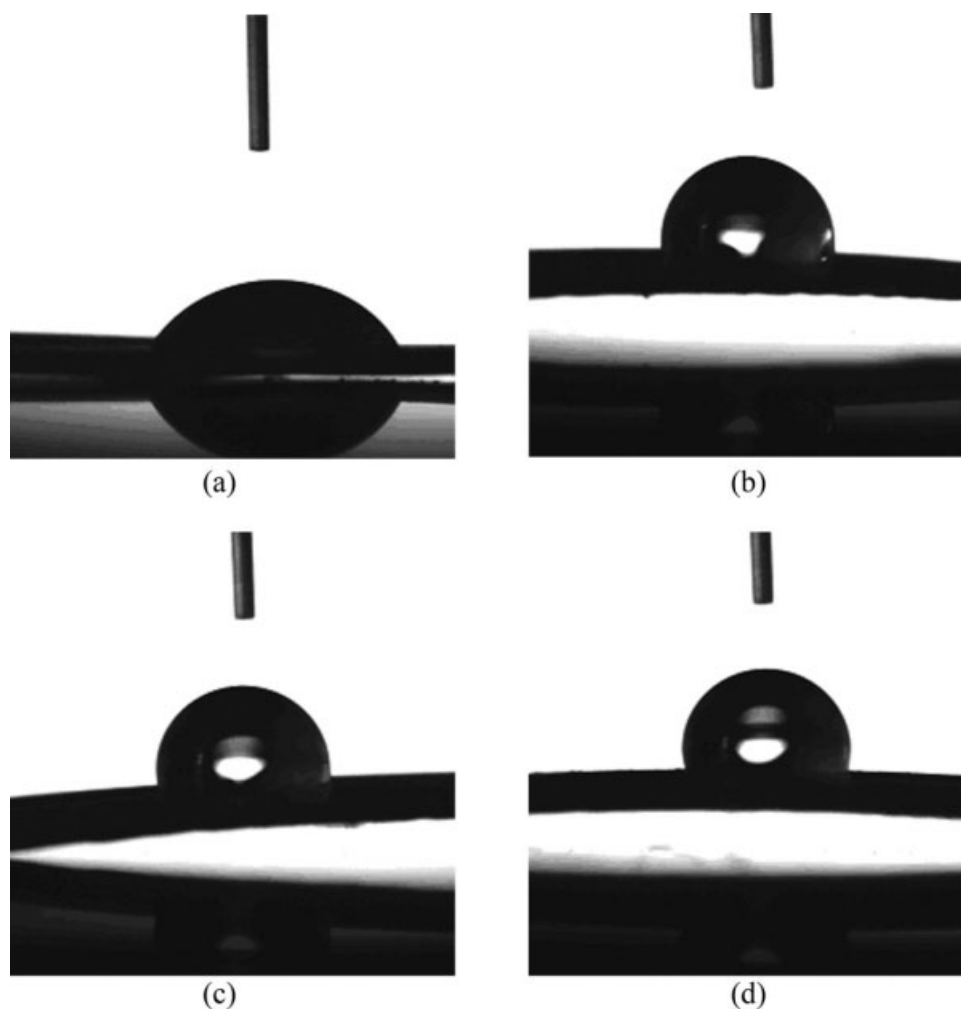
## RESULTS AND DISCUSSION

### Preparation of the PI-PDMS copolymers

In this study, we developed a novel synthetic method to condense At-PDMS, ODA, PMDA, and MDI in one pot. This approach provided a novel and convenient method for preparing a series of PI-PDMS copolymers with a wide range of dielectric and mechanical properties. The compositions of the films are listed in Table I.

TABLE II  
Mechanical Properties of the Pure PI and PI-PDMS Block Polymers

Sample	Stress at maximum load (N)	Strain at maximum load (%)	Young's modulus (GPa)
PI-0-0	104	14	1.9
PI-6-2	89	10	1.4
PI-6-5	88	10	1.36
PI-6-10	86	9.8	1.3
PI-12-0	70	11	1.33
PI-12-10	42	10	1.22
PI-25-0	71	12.7	1.05



**Figure 5** Water contact angles of the PI-PDMS block polymers: (a) PI-0-0, (b) PI-6-0, (c) PI-12-0, and (d) PI-25-0.

### Infrared spectroscopy

Fourier transform infrared (FTIR) spectra of the pure PI and PI-25-0 (25 wt % PDMS) before and after annealing are shown in Figure 1. The broad and strong double peaks due to Si—O—Si stretching of the PDMS chain appear at 1020 and 1080  $\text{cm}^{-1}$ , respectively, and the characteristic band of the imide group at 1780  $\text{cm}^{-1}$  appears in the spectra of both pure PI and PI-25-0 after annealing. This indicates

**TABLE III**  
Water Contact Angles of the PI-PDMS Block Polymers

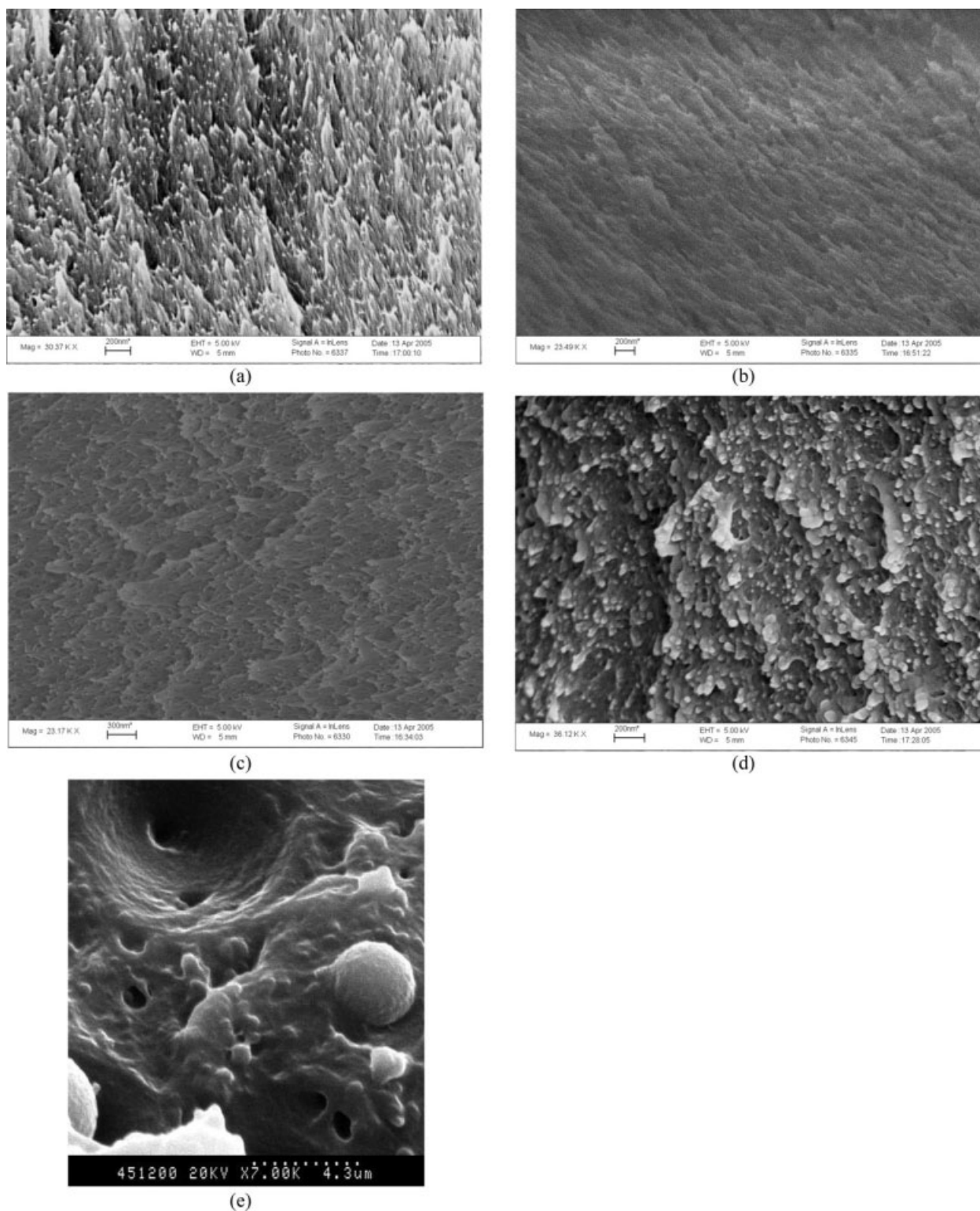
Sample	Water contact angle ( $^{\circ}$ )
PI-0-0	$51 \pm 1$
PI-6-0	$97 \pm 2$
PI-12-0	$104 \pm 2$
PI-25-0	$109 \pm 2$

the inclusion of PDMS in the final polymer, and the poly(amic acid) turns into PI after annealing [Fig. 1(1)]. Furthermore, the infrared spectrum of PI-0-0 (annealed) was also obtained by the transmission method. The characteristic peaks of the imide group at 1720 and 1775  $\text{cm}^{-1}$  are obvious [Fig. 1(2)].

**TABLE IV**  
Dielectric Constants of the PI-PDMS Block Polymers

	Sample			
	PI-0-0	PI-0-5	PI-6-5	PI-12-5
Dielectric constant	3.51	3.42	3.14	3.04
Dielectric loss	0.01	0.01	0.01	0.01
	Sample			
	PI-25-0	PI-25-2	PI-25-5	PI-25-10
Dielectric constant	3.02	2.81	2.58	3.01
Dielectric loss	0.01	0.01	0.01	0.01



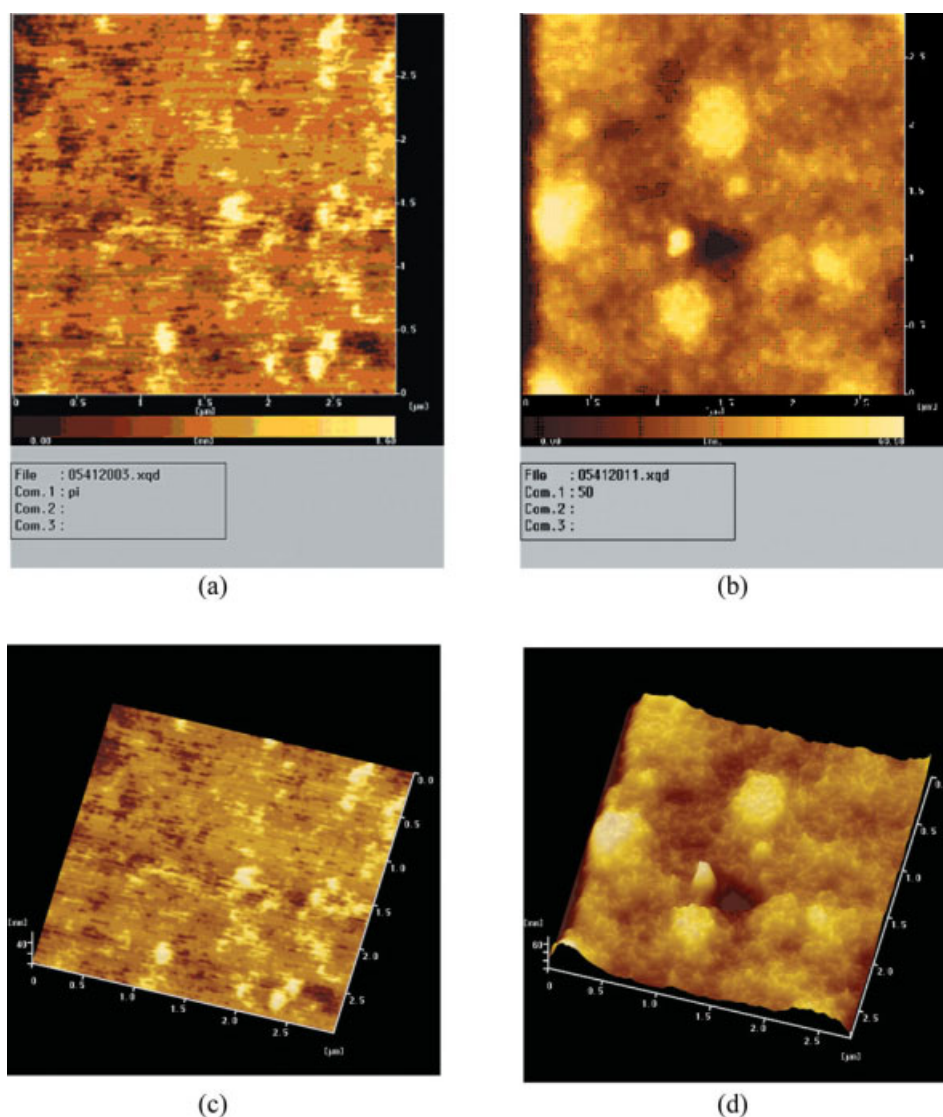


**Figure 6** SEM cross-section analysis of the PI-PDMS block polymers: (a) PI-0-0, (b) PI-6-0, (c) PI-12-0, (d) PI-25-0, and (e) PI-25-1.

### Thermal and mechanical properties of the PI-PDMS copolymers

Figure 2 presents TGA thermograms of pure PI and various PI-PDMS copolymers under a nitrogen

atmosphere. With the addition of PDMS, the decomposition temperatures of the PI-PDMS copolymers increase, and the residues ( $\text{SiO}_2$ ) are relevant to the amount of PDMS.



**Figure 7** AFM surface analysis of the PI-PDMS block polymers: (a) PI-0-0, (b) PI-0-0 (three-dimensional), (c) PI-25-0, and (d) PI-25-0 (three-dimensional). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

More thermal information can be found in the DSC thermograms in Figure 3. The glass-transition temperatures ( $T_g$ 's) of the PI-PDMS copolymers are similar to that of pure PI. Because  $T_g$  of the PDMS segment in PI is about  $-100^\circ\text{C}$ , it cannot be shown in the DSC thermograms.  $T_g$  of the hard segment in PI is about  $250^\circ\text{C}$ . With the addition of PDMS, the hard-segment ratio in the copolymer decreases, and  $T_g$  of the hard segment becomes much less visible. Figure 4 shows the results of the DMTA spectrum for PI-12-5. The separated peaks at about  $-100$  and  $320^\circ\text{C}$  on the  $\tan \delta$  curve, which correspond to the  $T_g$  values of typical PDMS chains and PI chains, respectively, indicate that the polymer is highly phase-separated. The great difference in the solubility parameters of the siloxane and imide segments

provides a driving force for microphase separation, particularly when higher molecular weight siloxane oligomers are incorporated.<sup>32</sup> The values of  $T_g$  for the PI chains are found at a higher temperature by DMTA than DSC.

Table II shows the mechanical properties of pure PI and PI-PDMS copolymers at room temperature. The modulus of pure PI is 1.9 GPa, whereas the modulus, stress, and strain of the other polymers regularly decrease with the addition of PDMS. The modulus of the film with 25 wt % PDMS (PI-25-0) is 1.05 GPa. The mechanical properties of the copolymers do not change much with the addition of MDI; this means that the PIs prepared with both MDI and ODA have similar compositions and behaviors.

### Water contact angles of the PI-PDMS copolymers

PIs can react with moisture and revert to poly(amic acid)s. The dielectric constants will then deteriorate, and mechanical deformation of the copolymer materials will be greatly weakened. The hydrophilicity of PI is a disadvantage for low-dielectric-constant materials. Water contact-angle analysis can show the affinity between the films and water. Figure 5 and Table III show that the moisture resistance of PI-PDMS copolymers is better than that of pure PI. The water contact angle becomes larger when the PDMS weight percentage increases. The water contact angles of the resultant copolymers increase from 51 to 109° when the contents of PDMS increase from 0 (PI-0-0) to 25 wt % (PI-25-0). Because PDMS possesses a relatively low surface energy, it tends to lead to surface enrichment, which results in the hydrophobicity of the PI-PDMS copolymer.<sup>33</sup>

### Dielectric constants of the PI-PDMS copolymers

A lower dielectric constant is one of the most desirable properties for the next generation of electronic devices. Table IV lists the dielectric constants of various PI-PDMS composites with different PDMS and MDI contents. The dielectric constants of the copolymers decrease as the components of PDMS increase, and the addition of 5 wt % MDI helps to yield a lower dielectric constant.

The most reasonable explanation for the observed reductions in the dielectric constant is more than likely a combination of two factors: the incorporation of PDMS into the PI chain and the nanopores in the film generated by carbon dioxide evolution during the reaction.<sup>34</sup>

### AFM and SEM analysis

The surface morphologies of PI-PDMS copolymers were studied with AFM and SEM. Figure 6 displays SEM images of cross sections of PI-PDMS copolymers. Figure 6(a-d) shows that the roughness of PI and PI-PDMS films apparently increases as the PDMS content increase. The cross section of the pure PI film [Fig. 6(a)] shows many hard-segment structures. The hard-segment domains of PI decrease with the increase in PDMS, and the microphase separation becomes more obvious. There are many nanospheres related to the PDMS domain in the image of the PI-25-0 cross section, and the diameter of the PDMS domain is about 30–100 nm [Fig. 6(d)]. The free volumes can be observed in the SEM image of PI-20-10 [Fig. 6(e)]. The interspaces between the microphase separation of PDMS and PI and the nanopores in the film are shown in the SEM image [Fig. 6(e)]. The phase morphologies of PI-PDMS

were also investigated with AFM. The images of pure PI [PI-0-0; Fig. 7(a,b)] show a smooth surface, and the images of PI-PDMS [Fig. 7(c,d)] show many high light points related to the microphase-separated areas in the polymer. The roughness of the two films changes greatly with the addition of PDMS.

### CONCLUSIONS

Novel, randomly coupled, soluble, segmented PI-PDMS copolymers have been developed through copolycondensation. In these copolymers, the molar ratio of the materials is adjustable, and the resultant PI-PDMS copolymers exhibit some certain variable properties. The reduction of the dielectric constant of the PI-PDMS copolymers can be explained in terms of loose PDMS chains introduced and free volume increased by the carbon dioxide produced by the reaction of MDI and PMDA. The PI-PDMS copolymers also exhibit better moisture resistance than pure PI. With this approach, the dielectric constant can be further reduced and the moisture resistance can be further reinforced by the adjustment of the PDMS and MDI contents. In brief, we intend to explore the possibility of incorporating different organic silicon moieties into PI chains in hopes of achieving PI copolymers with lower dielectric constants, better moisture resistance, and better mechanical properties.

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