

Synthesis and Properties of Poly(imide siloxane) Block Copolymers with Different Block Lengths

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ABSTRACT: Several poly(imide siloxane) block copolymers with the same bis(γ -aminopropyl)polydimethylsiloxane (APPS) content were prepared. The polyimide hard block was composed of 4,4'-oxydianiline and 3,3',4,4'-diphenylthioether dianhydride (TDPA), and the polysiloxane soft block was composed of APPS and TDPA. The length of polysiloxane soft block increased simultaneously with increasing the length of polyimide hard block. For better understanding the structure–property relations, the corresponding randomly segmented poly(imide siloxane) copolymer was also prepared. These copolymers were characterized by FT-IR, $^1\text{H-NMR}$, dynamic mechanical thermal analysis, thermogravimetric analysis, polarized optical microscope, rheology and tensile test. Two glass transition temperatures (T_g) were found in the randomly segmented copolymer, while three T_g s were found in the block copolymers. In addition, the T_g s, storage modulus, tensile modulus, solubility, elastic recovery, surface morphology and complex viscosity of the copolymers varied regularly with increasing the lengths of both blocks. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 3718–3727, 2013

KEYWORDS: poly(imide siloxane) copolymers; glass transition temperature; mechanical properties; structure-property relations; thermal properties

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INTRODUCTION

Copolymerization is one of the most general and successful ways for preparation of new materials with specifically desired properties, due to the incorporation of two structures with different chemical or physical properties in the same polymer chain.¹ It has been established that the combination of polysiloxane and polyimide not only can increase the solubility and processability of polyimide but also can improve the mechanical property of polysiloxane.² In addition, a number of other beneficial properties in the poly(imide siloxane) copolymers were also observed, such as high hydrophobicity, resistance to degradation in aggressive oxygen environment, excellent adhesion, low dielectric constants, high flexibility and impact resistance.^{3–9} Moreover, the poly(imide siloxane) copolymers can range from thermoplastics to thermoplastic elastomers depending on composition and structure.^{10,11} Therefore, the copolymers have become attractive candidates for microelectronic, adhesives, printed circuit, organophilic pervaporation, thermoplastic elastomers and aerospace applications.^{3–11}

Various kinds of poly(imide siloxane) copolymers have been prepared over the past decades. In the most general preparation method, the polysiloxane diamine [predominantly bis(γ -aminopropyl)polydimethylsiloxane (APPS)] was first added to

the solution of dianhydride, and then the non-siloxane diamine was added to the free dianhydride and anhydride-capped polysiloxane.^{3,12,13} The polysiloxane diamine was randomly distributed in the polymer chain. As a result, the length of polysiloxane soft block was determined by the molecular weight of polysiloxane diamine, and the length of polyimide hard block was a function of composition.^{6,14} The obtained copolymers were called randomly segmented poly(imide siloxane) copolymers.^{6,15}

Another different synthesis method for poly(imide siloxane) copolymers was also developed, in which two or more polysiloxane diamines were first linked together by dianhydride to form extended polysiloxane soft block, and then the extended polysiloxane soft block was further reacted with polyimide hard block or non-siloxane diamine and dianhydride.^{14,16,17} The lengths of polyimide hard block and polysiloxane soft block could be adjusted by creating different stoichiometric imbalances of monomers. The obtained copolymers were called poly(imide siloxane) block copolymers.^{14,16,17} It was found that the poly(imide siloxane) block copolymers had much higher glass transition temperature (T_g) of the polyimide hard block than the corresponding randomly segmented poly(imide siloxane) copolymer, and the T_g of polyimide hard block increased with increasing its length.^{14,16,17}

However, some other information about the property differences between the randomly segmented poly(imide siloxane) copolymer and the poly(imide siloxane) block copolymer, and the effect of the polyimide hard block and polysiloxane soft block lengths on the properties of the poly(imide siloxane) block copolymers is still insufficient. Herein, a series of poly(imide siloxane) block copolymers and corresponding randomly segmented poly(imide siloxane) copolymer with the same polysiloxane content were synthesized, and some new discoveries were found in the study. First, in dynamic mechanical thermal analysis (DMTA) testing, three T_g s were found in the block copolymers, and the T_g s and storage modulus varied regularly with increasing the lengths of polyimide hard block and polysiloxane soft block. Second, with increasing the lengths of both blocks, the tensile modulus decreased and the elastic recovery increased, and these phenomena could be explained according to the result of DMTA. Third, the solubility decreased and the complex viscosity increased with increasing the lengths of both blocks, resulting in difficulty in processing. Moreover, the block copolymers and the corresponding randomly segmented copolymer were found to have different surface morphologies. These discoveries are very useful in understanding the structure–property relations of the poly(imide siloxane) copolymer system. It enables the synthetic polymer chemists to tailor the lengths of both blocks to achieve desirable processability and physical properties of this kind of material.

EXPERIMENTAL

Materials

3,3',4,4'-Diphenylthioether dianhydride (TDPA) was synthesized as literature reported.¹⁸ APPS ($M_n = 953$ g/mol) was purchased from Gelest, and used as received. 4,4'-Oxydianiline (ODA) was purified by sublimation in vacuum. *N*-methyl-2-pyrrolidone (NMP) and 1,2-dichlorobenzene (ODCB) were distilled under vacuum over phosphorus pentoxide and stored over 4 Å molecular sieves. All other reagents were guaranteed grade and were used as received without further purification.

Measurements

Inherent viscosity was measured with an Ubbelohde viscometer at $30 \pm 0.1^\circ\text{C}$ in NMP at a concentration of 0.5 g/dL. The molecular weights and molecular weight distributions were determined by a Waters 1515 gel permeation chromatograph equipped with a Waters 2414 differential refractometer, using chloroform (CHCl_3) as eluent. $^1\text{H-NMR}$ spectra were performed at 400 MHz on a Bruker 400 AVANCE III in deuterated chloroform (CDCl_3). Fourier transform infrared (FT-IR) spectra of the copolymer films were recorded with a Thermo Nicolet 6700 FT-IR spectrometer. DMTA was conducted with a Mettler Toledo DMA in a tensile mode at a heating rate of $5^\circ\text{C}/\text{min}$ and a frequency of 1 Hz. Thermogravimetric analysis (TGA) was performed in both nitrogen and air atmospheres (flow rate of 50 mL/min) at a heating rate of $10^\circ\text{C}/\text{min}$ from 50 to 800°C with a Mettler Toledo-TGA/differential scanning calorimetry (DSC) I instrument. Mechanical properties were measured and averaged on at least six film specimens by an Instron model 5567 tensile tester at room temperature. The specimen gauge length was 50 mm and the specimen width was 10 mm. Two types of mechanical tests were performed. In the monotonic tensile test, samples

were stretched monotonically at a speed of 5 mm/min to fracture. In the step cyclic tensile test, samples were stretched with loading and unloading at a speed of 100 mm/min, a new cycle was started directly after the stress had decreased to zero and the strain step was 20%. The elastic recovery (ER) was defined as the strain recovered upon unloading divided by the maximum strain reached during the step. Rheological property was measured on a rotational Physica MCR 301 rheometer. Sample discs of 25-mm diameter and 1-mm thickness were prepared by press-molding of the copolymer powder at 150°C under 10 MPa pressure for 5 min, which were then loaded in the rheometer equipped with 25-mm diameter parallel plates. The upper plate was oscillated at a fixed strain of 1% and a fixed frequency of 1 Hz (well inside the linear viscoelastic range). The surface morphology of the copolymer films was performed on an Olympus BX51 polarized optical microscope (POM).

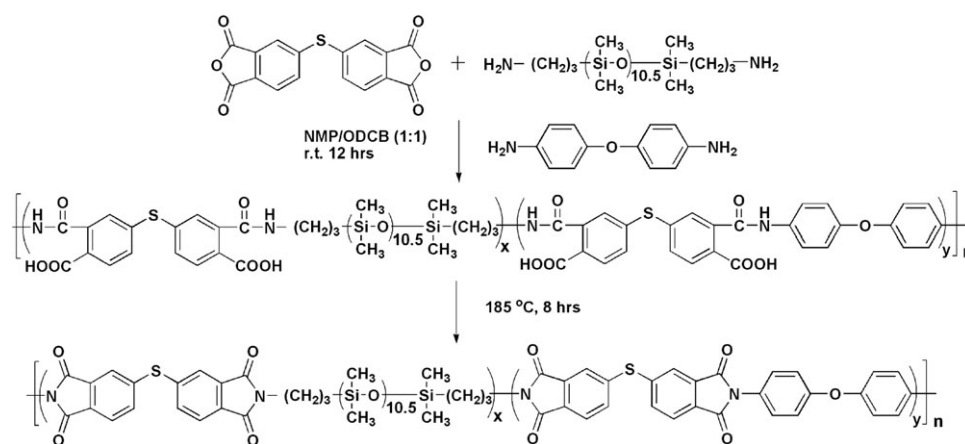
Polymer Synthesis

Preparation of Randomly Segmented Poly(imide siloxane) Copolymer R-1.

A flask was charged with TDPA (3.2628 g, 10.0 mmol), NMP (15 mL) and ODCB (10 mL) under nitrogen atmosphere. After the dianhydride was dissolved completely, APPS (3.5261 g, 3.70 mmol) in ODCB (5 mL) and ODA (1.2415 g, 6.20 mmol) were added sequentially. The mixture was stirred at room temperature for 12 h to yield a viscous poly(amic acid) solution. Then the reaction temperature was raised to 185°C and kept for 8 h. After the requisite time had elapsed, the viscous solution was cooled to room temperature, diluted with NMP and trickled into excess ethanol with stirring to afford a precipitate. The precipitate was collected, extracted with ethanol in a Soxhlet extractor and dried under vacuum at 120°C for 12 h to give the randomly segmented copolymer **R-1**. The structure of the copolymer **R-1** was identified by FT-IR and $^1\text{H-NMR}$ spectroscopies. FT-IR (thin film, cm^{-1}): 2962 (aliphatic C–H stretching), 1774 (asym C=O stretching), 1713 (sym C=O stretching), 1090 (asym Si–O–Si stretching), 1023 (sym Si–O–Si stretching), 801 (Si–C stretching). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ): 8.00–7.66 (m, 3.86H; Ar–H), 7.44–7.42 (d, $J = 8.0$ Hz, 1.63H; Ar–H), 7.21–7.19 (d, $J = 8.0$ Hz, 1.63H; Ar–H), 3.70–3.60 (m, 1H; CH_2), 1.74–1.62 (m, 1.03H; CH_2), 0.50–0.60 (m, 0.96H; CH_2), 0–0.20 (m, 14.83H; CH_3).

Preparation of Poly(imide siloxane) Block Copolymers. In the poly(imide siloxane) block copolymers, ODA and TDPA composed the polyimide hard block, while APPS and TDPA composed the polysiloxane soft block. The synthesis of the block copolymer **B-1** is used below as an example to illustrate the general synthetic route for the preparation of the block copolymers.

A flask was charged with TDPA (1.6445 g, 5.04 mmol), NMP (5 mL) and ODCB (5 mL) under nitrogen atmosphere. After the dianhydride was dissolved completely, APPS (3.5261 g, 3.70 mmol) in ODCB (5 mL) was slowly added and the mixture was stirred at room temperature for 6 h. Then the reaction temperature was raised to 185°C and kept for 1 h. After it was cooled to room temperature, the solution was transferred to another flask where TDPA (1.6183 g, 4.96 mmol) and ODA (1.2415 g, 6.20 mmol) had been dissolved and stirred in NMP (10 mL)



Scheme 1. Synthetic route of the randomly segmented poly(imide siloxane) copolymer **R-1**.

for 6 h. ODCB (5 mL) was used for complete transfer to avoid any loss. The mixture was stirred at room temperature for 12 h and then at 185°C for 8 h. The resulting viscous solution was cooled to room temperature, diluted with NMP and trickled into excess ethanol with stirring to afford a precipitate. The precipitate was collected, extracted with ethanol in a Soxhlet extractor and dried in vacuum at 120°C for 12 h to give the block copolymer **B-1**.

The preparation of other poly(imide siloxane) block copolymers was the same as the block copolymer **B-1**, and their structures were identified by FT-IR and ¹H-NMR spectroscopies.

Poly(imide siloxane) block copolymer B-1. FT-IR (thin film, cm⁻¹): 2962 (aliphatic C—H stretching), 1774 (asym C=O stretching), 1713 (sym C=O stretching), 1089 (asym Si—O—Si stretching), 1024 (sym Si—O—Si stretching), 804 (Si—C stretching). ¹H-NMR (400 MHz, CDCl₃, δ): 8.00–7.66 (m, 4.0H; Ar—H), 7.44–7.42 (d, *J* = 8.0 Hz, 1.68H; Ar—H), 7.21–7.19 (d, *J* = 8.0 Hz, 1.68H; Ar—H), 3.70–3.60 (m, 1H; CH₂), 1.74–1.62 (m, 1.06H; CH₂), 0.50–0.60 (m, 0.98H; CH₂), 0–0.20 (m, 15.33H; CH₃).

Poly(imide siloxane) block copolymer B-2. FT-IR (thin film, cm⁻¹): 2962 (aliphatic C—H stretching), 1774 (asym C=O stretching), 1713 (sym C=O stretching), 1090 (asym Si—O—Si stretching), 1024 (sym Si—O—Si stretching), 802 (Si—C stretching). ¹H-NMR (400 MHz, CDCl₃, δ): 8.00–7.66 (m, 3.99H; Ar—H), 7.44–7.42 (d, *J* = 8.0 Hz, 1.70H; Ar—H), 7.21–7.19 (d, *J* = 8.0 Hz, 1.68H; Ar—H), 3.70–3.60 (m, 1H; CH₂), 1.74–1.62 (m, 1.03H; CH₂), 0.50–0.60 (m, 0.96H; CH₂), 0–0.20 (m, 15.49H; CH₃).

Poly(imide siloxane) block copolymer B-3. FT-IR (thin film, cm⁻¹): 2962 (aliphatic C—H stretching), 1774 (asym C=O stretching), 1713 (sym C=O stretching), 1086 (asym Si—O—Si stretching), 1023 (sym Si—O—Si stretching), 801 (Si—C stretching). ¹H-NMR (400 MHz, CDCl₃, δ): 8.00–7.66 (m, 3.98H; Ar—H), 7.44–7.42 (d, *J* = 8.0 Hz, 1.67H; Ar—H), 7.21–7.19 (d, *J* = 8.0 Hz, 1.66H; Ar—H), 3.70–3.60 (m, 1H; CH₂), 1.74–1.62 (m, 1.14H; CH₂), 0.50–0.60 (m, 0.97H; CH₂), 0–0.20 (m, 15.23H; CH₃).

Poly(imide siloxane) block copolymer B-4. FT-IR (thin film, cm⁻¹): 2962 (aliphatic C—H stretching), 1774 (asym C=O stretch-

ing), 1713 (sym C=O stretching), 1089 (asym Si—O—Si stretching), 1025 (sym Si—O—Si stretching), 801 (Si—C stretching).

Film Preparation

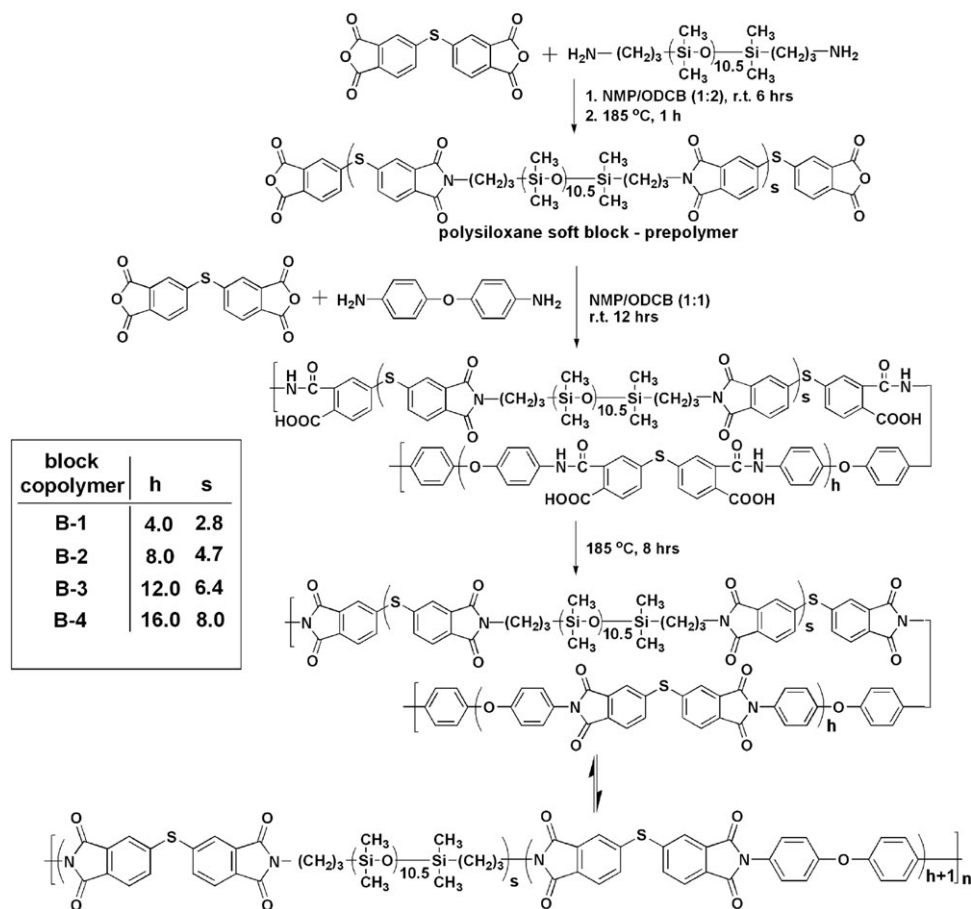
The copolymer films were prepared via the casting of 12 wt % homogenous solution of the copolymer powder in NMP onto clean glass plates, which were then placed in a 100°C oven overnight to evaporate most of the solvent and subjected to scheduled heating at 150, 200, and 250°C for 30 min at each temperature. The resulting films were stripped off the plates by immersion in hot water.

RESULTS AND DISCUSSION

Polymer Synthesis

Because of the vastly different solubility characteristics between the aromatic monomers and polysiloxane diamine APPs,³ the randomly segmented and block copolymers were synthesized in the co-solvent system consisting of NMP and ODCB. The randomly segmented copolymer **R-1** was prepared by conventional one-pot method, where the APPs was first added to the solution of dianhydride to effectively cap the APPs and then non-siloxane diamine ODA was added to the free dianhydride and anhydride capped APPs (Scheme 1).³ In the randomly segmented copolymer **R-1**, the APPs was randomly distributed in the polymer chain.

In contrast, the block copolymers were prepared by first linking two or more APPs together through TDPA to form anhydride terminated extended polysiloxane soft block, and then the anhydride terminated extended polysiloxane soft block was further reacted with ODA and additional dianhydride (Scheme 2).¹⁴ The block copolymers had the same APPs content but increasing lengths of polyimide hard block and polysiloxane soft block, which were adjusted by creating different stoichiometric imbalances of monomers according to the Carothers equation.^{19,20} The four different block copolymers were prepared with increasing average repeating unit number of the polyimide hard block (*h*+1) from 5.0 to 9.0, 13.0, and 17.0, and increasing average repeating unit number of the polysiloxane soft block (*s*) from 2.8 to 4.7, 6.4, and 8.0, respectively. The randomly segmented and block copolymers were obtained with similar molecular weights in order to compare properties (Table I).



Scheme 2. Synthetic route of the poly(imide siloxane) block copolymers.

The $^1\text{H-NMR}$ spectra of the randomly segmented and block copolymers are shown in Figure 1 except block copolymer **B-4** due to its insolubility in CDCl_3 . There were three kinds of possible structures (a, b, and c shown in Figure 1) in the copolymers, and the $^1\text{H-NMR}$ signals between 7.66–8.00 ppm were assigned to protons of TDPA in the three structures. In order to better understand the attribution, the $^1\text{H-NMR}$ spectrum of the homopolyimide (TDPA/APPS) synthesized from TDPA and

APPS is also shown, which exhibited the chemical shifts of the protons 4, 5, and 6 in the structure **b** obviously. It can be observed that, as the lengths of both blocks increased, the $^1\text{H-NMR}$ signal intensity from the protons of TDPA in the structures **a** and **b** increased, while the $^1\text{H-NMR}$ signal intensity from the protons of TDPA in the structure **c** decreased. This was consistent with the fact that, for multiblock copolymers, the longer both blocks the less the linkages between the two

Table I. Inherent Viscosities and Molecular Weights of the Copolymers

| Polymer | $h+1$ | s | Molecular weight of APPS ^a (g/mol) | η_{inh}^b (dL/g) | M_n (g/mol) | M_w (g/mol) | PDI |
|------------|-------|-----|---|------------------------------|----------------|----------------|----------------|
| R-1 | – | – | 832 | 0.381 | 22,200 | 49,700 | 2.24 |
| B-1 | 5.0 | 2.8 | 856 | 0.372 | 23,900 | 57,400 | 2.40 |
| B-2 | 9.0 | 4.7 | 864 | 0.366 | 22,500 | 55,300 | 2.46 |
| B-3 | 13.0 | 6.4 | 851 | 0.368 | 21,100 | 54,500 | 2.58 |
| B-4 | 17.0 | 8.0 | – ^c | 0.362 | – ^c | – ^c | – ^c |

$h+1$, the average repeating unit number of the polyimide hard block; s, the average repeating unit number of the polysiloxane soft block; M_n , number average molecular weight; M_w , weight average molecular weight; PDI, polydispersity index.

^aThe data were determined on the basis of $^1\text{H-NMR}$ spectra of the copolymers; ^bMeasured in NMP at a concentration of 0.5 g/dL at 30°C; ^cThe copolymer **B-4** was not measured by GPC and $^1\text{H-NMR}$ because of poor solubility in CHCl_3 .

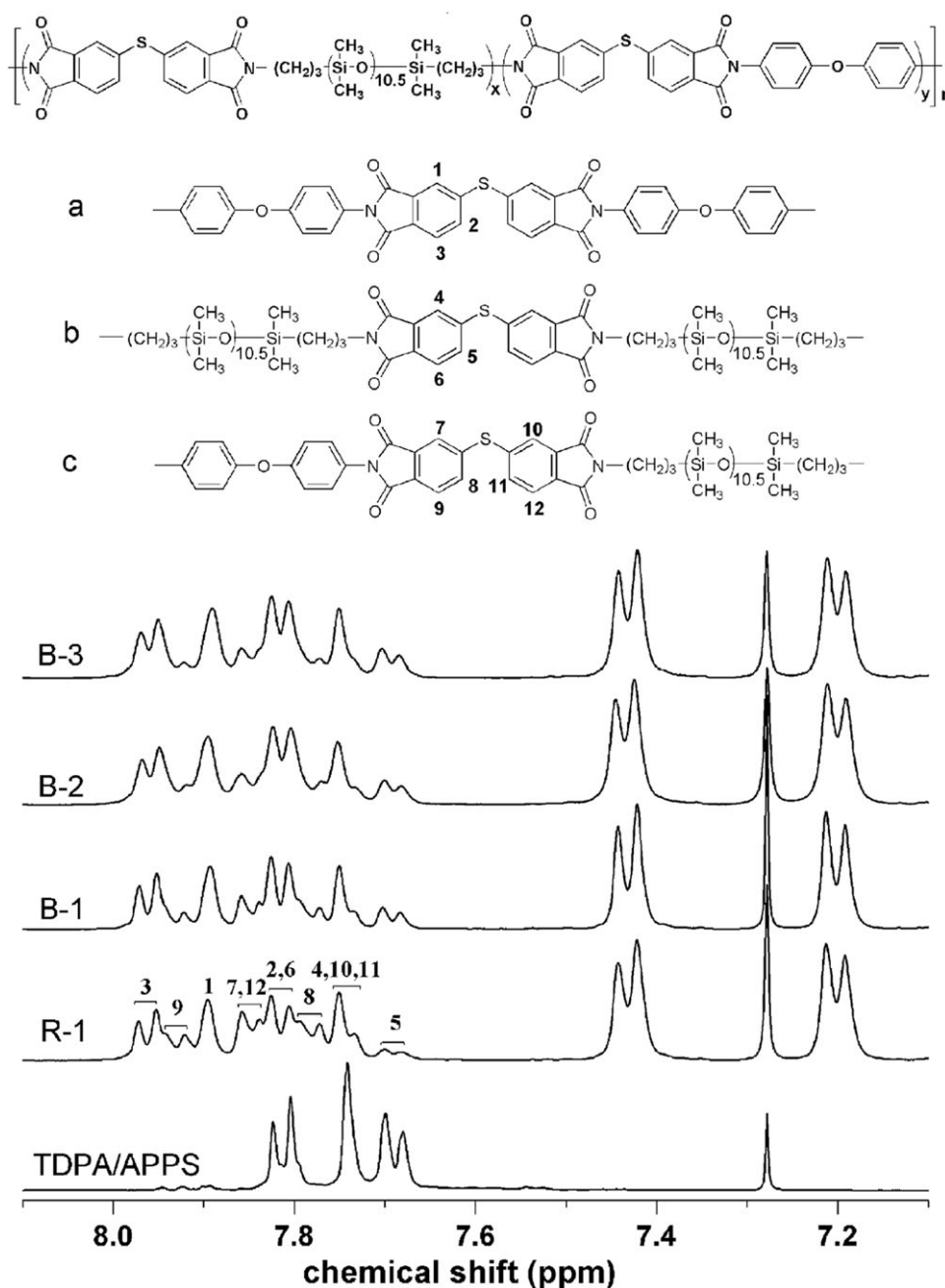


Figure 1. $^1\text{H-NMR}$ spectra of the copolymers.

blocks. Therefore, the block copolymers with increasing lengths of the polyimide hard block and polysiloxane soft block were successfully synthesized.

The $^1\text{H-NMR}$ spectra also showed $^1\text{H-NMR}$ signals at about 3.65 ppm corresponding to the protons of the methylene adjacent to imide ring. Besides, $^1\text{H-NMR}$ signals corresponding to the protons of the middle methylene and the methylene attached to silicon appeared at about 1.7 and 0.57 ppm, respectively. It should be noted that a small amount of cyclic siloxanes (predominantly hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane) may be either present initially or generated during copolymerization as a result of siloxane redistribution.^{6,21} Therefore, the molecular weights of APPS in the

copolymers determined by $^1\text{H-NMR}$ spectroscopy were lower than 953 g/mol used for copolymerization (Table I).

Structural features of the copolymers were also confirmed by FT-IR spectroscopy. Figure 2 presents the FT-IR spectra of the copolymers **R-1**, **B-2** and **B-4**, as an example. No obvious discrepancy in absorption band positions and intensity was found among the randomly segmented and block copolymers. All of the copolymers showed absorption bands at about 2962 cm^{-1} (aliphatic C—H stretching), 1774 cm^{-1} (asymmetric C=O stretching), 1713 cm^{-1} (symmetric C=O stretching), 1089 cm^{-1} (Si—O—Si stretching), 1025 cm^{-1} (sym Si—O—Si stretching) and 801 cm^{-1} (Si—C stretching).

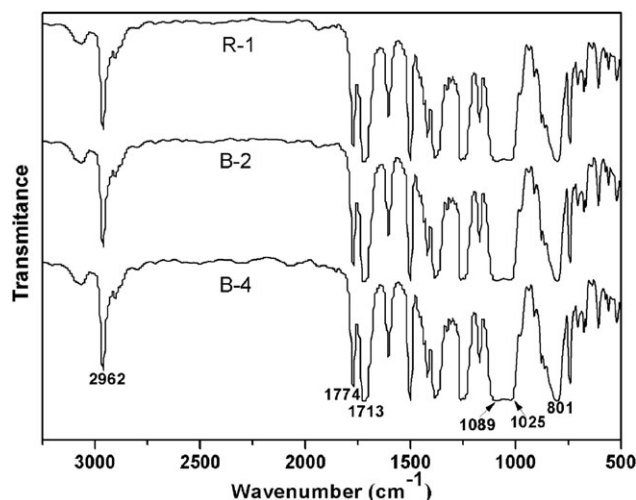


Figure 2. FT-IR spectra of the copolymers R-1, B-2, and B-4.

Table II. Solubility of the Copolymers

| Polymer | Solvents | | | | | |
|---------|----------|-----|------|------|------|-------------------|
| | NMP | DMF | DMAc | DMSO | ODCB | CHCl ₃ |
| R-1 | ++ | ++ | ++ | + | ++ | ++ |
| B-1 | ++ | ++ | ++ | + | ++ | ++ |
| B-2 | ++ | ++ | ++ | + | ++ | ++ |
| B-3 | ++ | + | ++ | + | + | ++ |
| B-4 | ++ | + | ++ | + | + | ± |

Key: ++, soluble at room temperature; +, soluble on heating; ±, partial swelling on heating.

Polymer Solubility

The solubility of the copolymers was tested qualitatively by putting 0.1 g of copolymer powder in 2 mL of organic solvents at room temperature for 24 h and heating up to the boiling points of solvents for samples which remained insoluble at room temperature. The results are presented in Table II. The randomly segmented copolymer R-1 was easily soluble in NMP, ODCB, CHCl₃, *N,N*-dimethyl formamide (DMF) and *N,N*-dimethylacetamide at room temperature, and soluble in dimethyl sulfoxide on heating, showing much better solubility than the homopolyimide synthesized from TDPA and ODA.²² The better solubility was due to the flexible polysiloxane, which increased the chain flexibility contributing to ease to solvent attack.²³ However, the solubility of the block copolymers in DMF, ODCB, and CHCl₃ turned out from easily soluble at room temperature to soluble or partial swelling on heating with increasing the lengths of both blocks. This was probably because the solubility of polyimide hard block decreased with increasing its length and thereby affected the solubility of copolymers.

DMTA

DMTA measurements for the copolymers were carried out to monitor the effect of both block lengths on the thermomechanical properties and T_g s of the copolymers. The storage modulus versus temperature curves and the loss tangent ($\tan \delta$) versus

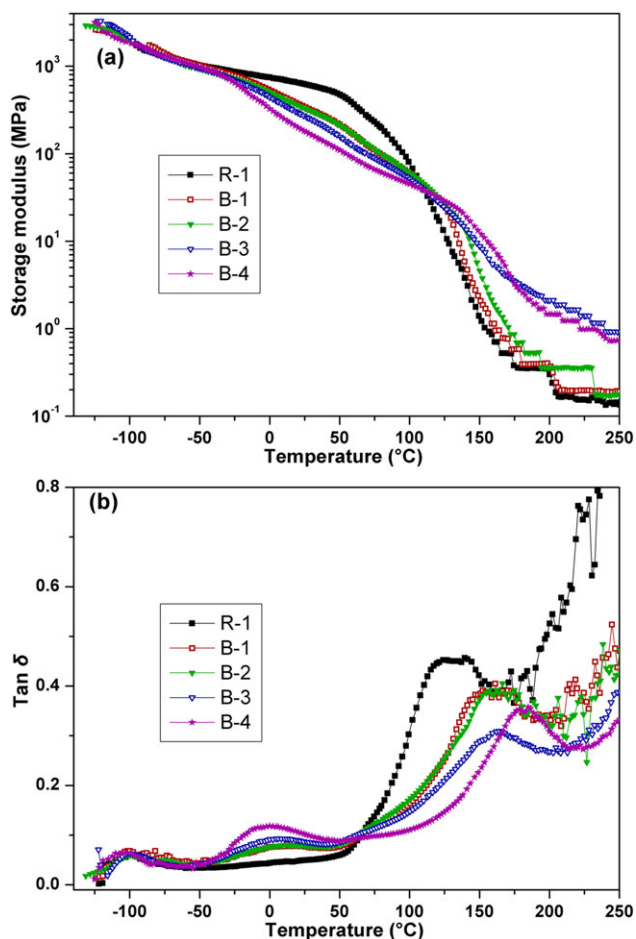


Figure 3. (a) Storage moduli of the copolymers as a function of temperature measured by DMTA in air. (b) Loss tangents ($\tan \delta$) of the copolymers as a function of temperature measured by DMTA in air. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

temperature curves of the copolymers determined by DMTA are shown in Figure 3(a,b), respectively. It was hard to discern the T_g s of the copolymers from their differential scanning calorimetry (DSC) curves. DMTA is generally more sensitive than the DSC method, and the T_g s of the copolymers identified by the peak temperatures of the $\tan \delta$ versus temperature curves are summarized in Table III.

All of the randomly segmented and block copolymers showed the T_g of the pure polydimethylsiloxane at about -100°C ,^{6,7,12} and the T_g varied little with the lengths of both blocks. Correspondingly, there was a significant fall in the storage moduli of the copolymers on passing through the T_g . Another T_g at about 0°C was only observed in the block copolymers, which should be attributed to the T_g of their polysiloxane soft blocks. The T_g decreased slightly and the magnitude of the $\tan \delta$ peak at this temperature increased with increasing the polysiloxane soft block length, indicating the mobility of polysiloxane soft block increased with increasing its length. As a result, in the range of -40 – 110°C , the randomly segmented copolymer R-1 exhibited the highest storage modulus among the copolymers, and block

Table III. Thermal Properties of the Copolymers

| Polymer | T_g^a (°C) | | | $T_{5\%}^b$ (°C) | | R_w^c (wt %) | |
|------------|--------------|---------|---------|------------------|-----|----------------|------|
| | T_g^1 | T_g^2 | T_g^3 | N ₂ | air | N ₂ | air |
| R-1 | -100 | - | 129 | 432 | 395 | 27.7 | 9.5 |
| B-1 | -100 | 9 | 162 | 431 | 388 | 28.5 | 14.3 |
| B-2 | -101 | 9 | 166 | 431 | 386 | 27.7 | 17.0 |
| B-3 | -100 | 7 | 165 | 429 | 394 | 27.5 | 10.4 |
| B-4 | -103 | -2 | 184 | 430 | 389 | 28.3 | 14.2 |

T_g^1 , T_g derived from the pure polydimethylsiloxane. T_g^2 , T_g derived from the polysiloxane soft blocks of the block copolymers. T_g^3 , T_g derived from the polyimide hard blocks of the randomly segmented and block copolymers; ^aObtained from DMTA at a heating rate of 5°C/min in air; ^bTemperature of 5% weight loss; ^cResidual weight when heated to 800°C.

copolymer with longer polysiloxane soft block exhibited relatively lower storage modulus. The T_g s derived from the polyimide hard blocks of the block copolymers were in the range of 162–184°C and mainly increased with increasing its length, which were much higher than the upper T_g (129°C) of the randomly segmented copolymer **R-1**. So, at high temperature (about >115°C), all the block copolymers exhibited higher storage modulus than the randomly segmented copolymer **R-1**, and the storage modulus of the block copolymers mainly increased with increasing the lengths of polyimide hard block, indicating the thermal stability of the copolymers could be improved by increasing the lengths of polyimide hard block.

TGA

TGA of the copolymers was measured under both nitrogen and air atmospheres, and the TGA curves of the copolymers are shown in Figure 4. We found that the thermal degradation behaviors of the randomly segmented and block copolymers were virtually identical and their 5% weight loss temperatures ($T_{5\%}$) were nearly the same under nitrogen atmosphere (Table III). It was probably because the thermal degradation began at the weak aliphatic *n*-propyl linkages in the poly(imide siloxane) copolymers that the $T_{5\%}$ of the copolymers was dependent on the APPS content rather than the lengths of both blocks.³ Under air atmosphere, the $T_{5\%}$ s were in the range of 386–395°C. A white residue was left after measurement, which corresponded to SiO₂.²⁴ Probably because SiO₂ from gas phase oxidation randomly fell on the sample pan or on the weighting arm of the balance,²⁵ the thermo-oxidative degradation behaviors under air atmosphere of the copolymers were different and the residues left varied from 9.5 to 17.0 wt % for different samples. Taking all of these phenomena together, we can conclude that the thermal and thermo-oxidative degradation behaviors of the copolymers had no association with the lengths of both blocks.

Mechanical Properties

All the copolymers could be processed into flexible films. The mechanical properties of the copolymer films were investigated using both monotonic and step cyclic tensile tests at room temperature. In the monotonic tensile test, the samples were stretched monotonically to fracture, and the tensile modulus,

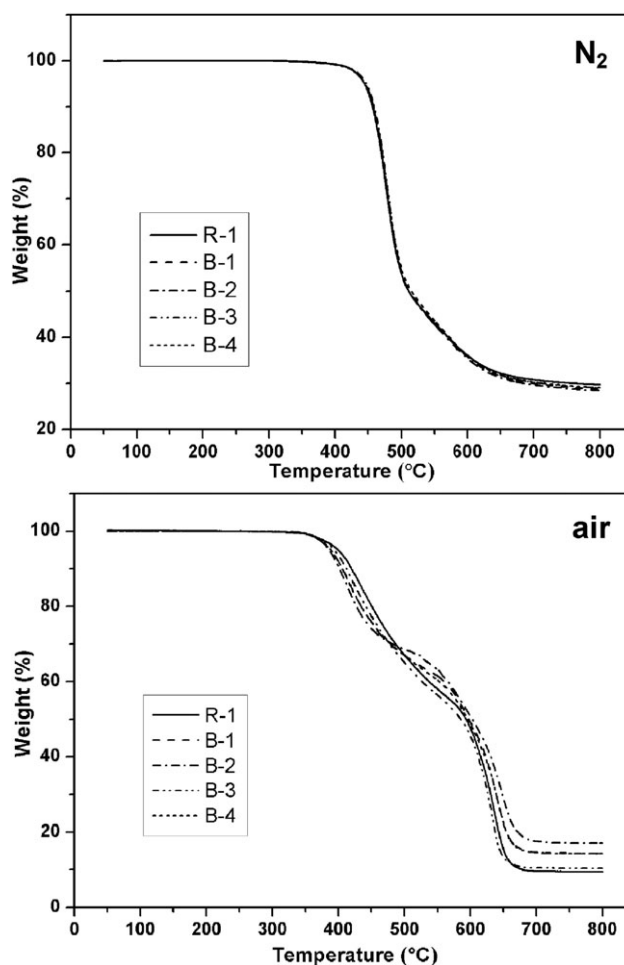


Figure 4. TGA curves of the copolymers at a heating rate of 10°C/min in N₂ and air.

tensile strength and elongation at break were recorded. In the step cyclic tensile test, the samples were stretched under loading and unloading, and the elastic recovery was recorded. These data are listed in Table IV and cyclic stress–strain curves of the copolymers under loading and unloading are presented in Figure 5. All the block copolymers showed much lower tensile modulus than the randomly segmented copolymer **R-1**, and the tensile modulus of the block copolymers basically decreased with increasing the lengths of both blocks. Furthermore, at the same strain, all the block copolymers showed much higher elastic recovery than the randomly segmented copolymer **R-1**, and the elastic recovery of the block copolymers basically increased with increasing the lengths of both blocks. From the DMTA results, the T_g at about 0°C was only observed in the block copolymers, which was attributed to the T_g of their polysiloxane soft blocks, indicating the polysiloxane soft blocks of the block copolymers had good mobility at room temperature. Probably for this reason, the block copolymers exhibited lower tensile modulus and higher elastic recovery than the randomly segmented copolymer at room temperature. Furthermore, because the mobility of polysiloxane soft block increased with increasing its length, the tensile modulus of the block copolymers basically

Table IV. Mechanical Properties of the Copolymers

| Polymer | Tensile strength (MPa) | Tensile modulus (MPa) | Elongation at break (%) | ER ^a at 20% strain (%) | ER ^a at 40% strain (%) | ER ^a at 60% strain (%) | ER ^a at 80% strain (%) | ER ^a at 100% strain (%) |
|---------|------------------------|-----------------------|-------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|------------------------------------|
| R-1 | 32.9 | 646 | 129.1 | 62 | 39 | 30 | 26 | 23 |
| B-1 | 33.3 | 132 | 124.3 | 85 | 62 | 47 | 38 | 33 |
| B-2 | 29.5 | 122 | 130.8 | 86 | 63 | 48 | 39 | 34 |
| B-3 | 26.6 | 99 | 126.7 | 88 | 64 | 49 | 41 | 35 |
| B-4 | 26.9 | 101 | 119.5 | 90 | 67 | 47 | 40 | 35 |

^aThe elastic recovery (ER) was defined as the strain recovered upon unloading divided by the maximum strain reached during the step.

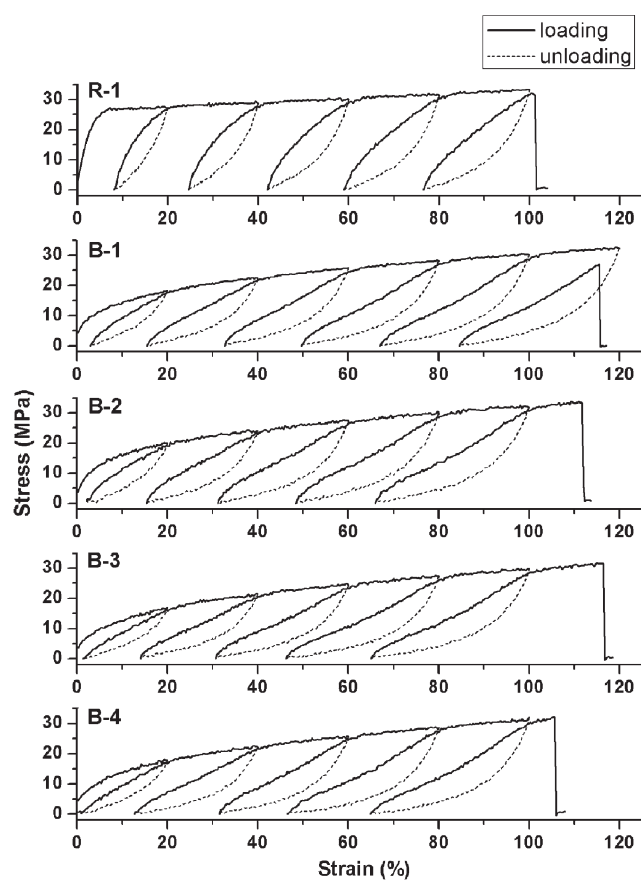


Figure 5. Cyclic stress–strain curves of the copolymers under loading and unloading at room temperature.

decreased and the elastic recovery of the block copolymers basically increased with increasing the length of polysiloxane soft block.

Rheology Properties

Melt processability was investigated by studying the rheological behavior of the copolymers with similar molecular weights under air atmosphere. Complex viscosity versus temperature curves of the three copolymers (R-1, B-2, and B-4) are shown in Figure 6(a). It was found that the complex viscosity increased in the order of R-1 < B-2 < B-4 at the same temperature. This was probably because the polyimide hard block functioned as a revers-

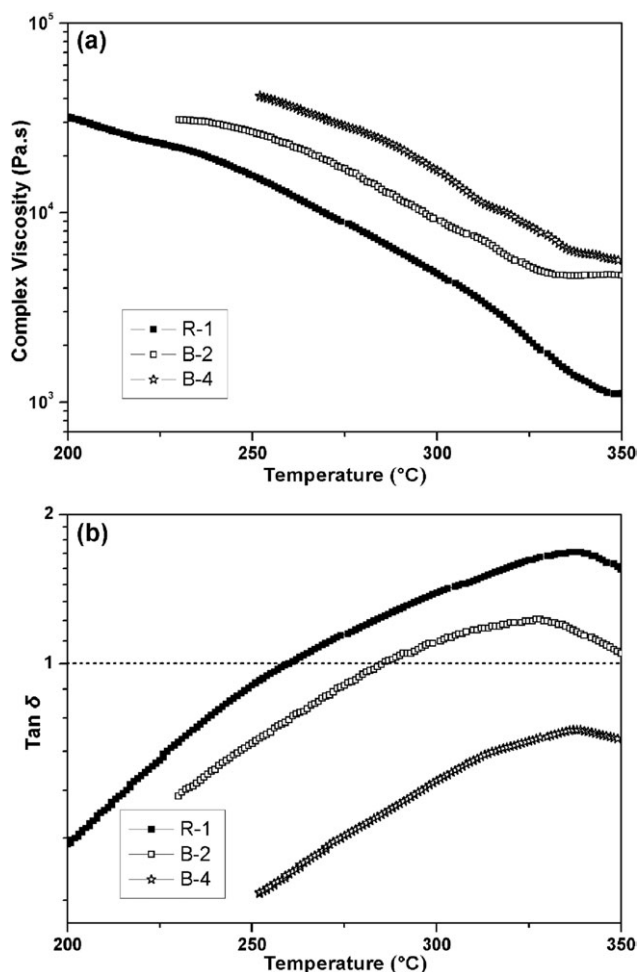


Figure 6. (a) Complex viscosities of the copolymers R-1, B-2, and B-4 as a function of temperature measured by rotational rheometer in air. (b) Loss tangents ($\tan \delta$) of the copolymers R-1, B-2, and B-4 as a function of temperature measured by rotational rheometer in air.

ible physical crosslink network and the physical crosslink network persisted in the melting state.²⁶ The increase in polyimide hard block length enhanced the entanglement extent of copolymer chain, resulting in the increase in complex viscosity of copolymer.

The loss tangent ($\tan \delta$) versus temperature curves of the three copolymers (R-1, B-2, and B-4) are shown in Figure 6(b). The

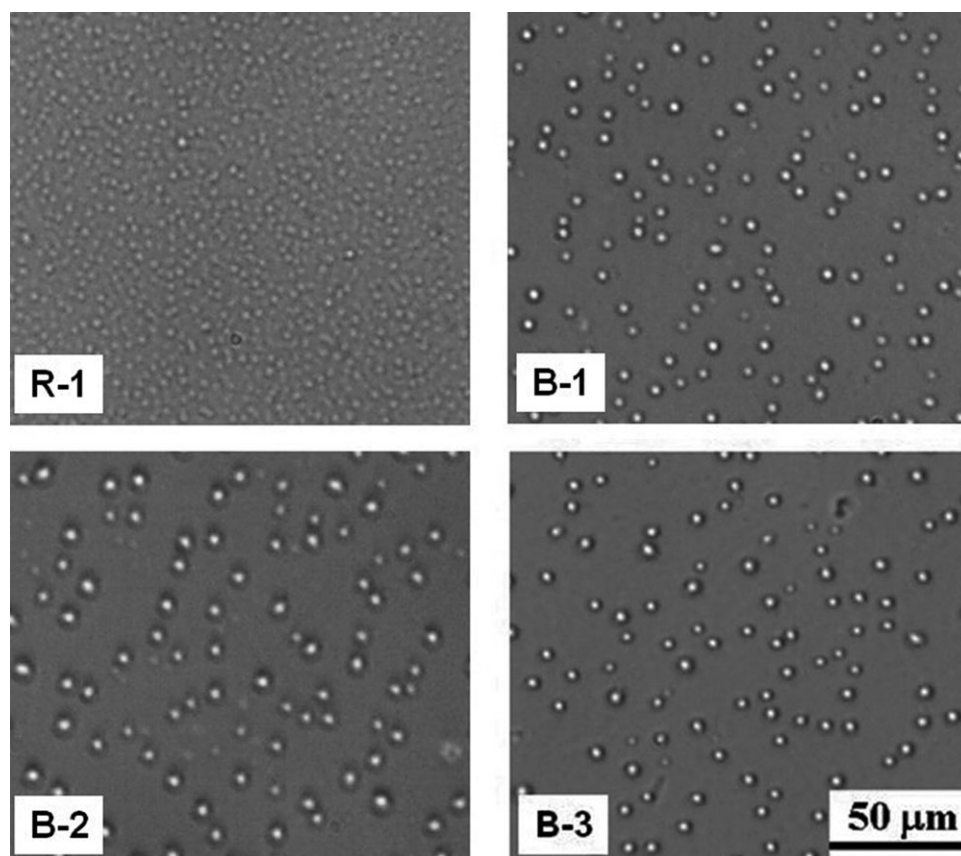


Figure 7. Surface morphology of the copolymer films under POM.

$\tan \delta$ is the ratio of the loss modulus G'' to the storage modulus G' . For a polymeric material, when the $\tan \delta > 1$, the material shows viscoelastic liquid-like behavior and is relatively easy to be melt-processed; when the $\tan \delta < 1$, the material shows viscoelastic solid-like behavior and is difficult to be melt-processed.²⁷ Both the $\tan \delta$ and transition from a viscoelastic solid-like behavior to a viscoelastic liquid-like behavior are strongly dependent on temperature and polymer structure. The randomly segmented copolymer **R-1** showed viscoelastic liquid-like behavior in the case of temperature higher than 260°C. The block copolymer **B-2** began to show viscoelastic liquid-like behavior at temperatures higher than 286°C. However, the block copolymer **B-4** showed a $\tan \delta < 1$ in the whole test temperature, which meant that the sample was not suitable for melt processing. From these results, we can conclude that the increase in the lengths of both blocks could decrease the processability of the copolymers.

Surface Morphology

The surface morphology of the randomly segmented copolymers has been extensively studied.^{13,28,29} However, the surface morphology of the block copolymers has not been studied. POM was used to study the surface morphology of the copolymer films. The observed films were prepared by dropping a 0.2 wt % CHCl_3 solution of copolymer onto slide glasses, which were then subjected to scheduled heating at 100, 150, 200, and 250°C for 30 min at each temperature. The film surface morphologies

of the randomly segmented and block copolymers under POM are shown in Figure 7 except block copolymer **B-4** due to its insolubility in CHCl_3 . Since the surface free energy of polysiloxane soft block is lower than that of polyimide hard block and the difference in solubility parameters between the polysiloxane soft block and polyimide hard block is large,^{29–32} the polysiloxane soft block tended to segregate to the surface and many aggregates were visible under POM. Interestingly, compared with the film surface of the randomly segmented copolymer **R-1**, the film surfaces of the block copolymers had less but bigger aggregates, which was probably because the polysiloxane soft blocks in the block copolymers were extended.

CONCLUSIONS

A series of poly(imide siloxane) block copolymers and the corresponding randomly segmented poly(imide siloxane) copolymer with the same polysiloxane content were prepared. In the randomly segmented copolymer, the polysiloxane diamine APPS was randomly distributed in the copolymer chain. While in the block copolymers, two or more APPSs were linked together by dianhydride in the copolymer chain. Probably because the polysiloxane soft blocks in the block copolymers were extended and the mobility of polysiloxane soft block increased with increasing its length, the block copolymers exhibited much lower tensile modulus and higher elastic recovery than the corresponding randomly segmented copolymer, and the tensile modulus of the block copolymers basically decreased and the elastic recovery of

the block copolymers basically increased with increasing the length of polysiloxane soft block. The extended polysiloxane soft blocks also had effect on the surface morphology of the block copolymers. In addition, block copolymer with longer both blocks basically exhibited lower T_g derived from the polysiloxane soft block but higher T_g derived from the polyimide hard block. Moreover, the increase in the lengths of both blocks increased the entanglement extent of copolymer chain, resulting in difficulty in processing. However, the thermal and thermo-oxidative degradation behaviors of the copolymers had no association with the lengths of both blocks.

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