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Synthesis and properties of low coefficient of thermal expansion copolyimides derived from biphenyltetracarboxylic dianhydride with p-phenylenediamine and 4,4'-oxydianiline

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Abstract: A series of copolyimides were prepared by thermal imidization of poly(amic acid)s (PAAs) derived from 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA), 2,2',3,3'-biphenyltetracarboxylic dianhydride (a-BPDA), p-phenylenediamine (PDA) and 4,4'-oxydianiline (4,4'-ODA) commonly used for the production of commercial polyimides. The flexible copolyimide films were obtained from that the molar ratio of s-BPDA, a-BPDA, PDA and 4,4'-ODA was 9:1:8:2 (Co-PIs-3), 8:2:9:1 (Co-PIs-5) and 8:2:8:2 (Co-PIs-6). These obtained copolyimide films were characterized by Fourier transform-infrared spectroscopy (FT-IR), wide angle X-ray (WAXD), Thermogravimetric (TG), dynamic mechanical thermal analysis (DMA), thermomechanical analysis (TMA), field-emission scanning electron microscopy (FE-SEM) and mechanical properties measurement. The results showed that three copolyimides remained semi-crystalline and exhibited high glass transition temperature (T_g), high thermal stability, great ultimate tensile strength and low coefficient of thermal expansion (CTE).

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The Co-PIs-5 had lower crystallinity, lower CTE, greater elongation at break, higher T_g and thermal stability and the greater dense extent, compared with Co-PIs-3 and Co-PIs-6. Structure and property relations of the prepared polyimides were also briefly discussed. The results revealed that the copolymerization of s-BPDA/PDA with a small number of 4,4'-ODA/a-BPDA was a useful means for enhancing flexibility without sacrificing low CTE.

Keywords: 4,4'-oxydianiline; biphenyltetracarboxylic dianhydride; copolyimide; low-CTE; p-phenylenediamine.

1 Introduction

Flexible printed circuit boards (FPC) require polymers to have low coefficient of thermal expansion (CTE), high glass transition temperature (T_g), good thermal stability (1–4). Aromatic polyimides (PI) show a low CTE, high T_g , good chemical resistance, good thermal stability, high electrical insulating properties and high mechanical strength (5–8), and therefore are employed in FPC. It is accepted that the linearity/stiffness of PI backbone structures is a very important factor when attempting to obtain low CTE (9–11). 3,3',4,4'-Biphenyltetracarboxylic dianhydride (s-BPDA) and p-phenylenediamine (PDA) system possesses a crank shaft-like but still a relatively linear structure, is widely known as a commercially available typical low-CTE polyimide film, which possesses CTE=6–15 ppm/K depending on the film thickness and processing conditions (12, 13). However, because of their rigidity and poor flexibility, s-BPDA/PDA films are difficult to apply to specific FPC filed that need PI films with good flexibility.

2,2',3,3'-Biphenyltetracarboxylic dianhydride (a-BPDA) has a highly irregular structure, which makes polyimides based on a-BPDA exhibit unusual properties relative to those polyimides from s-BPDA, such as higher glass transition temperatures, higher thermoplasticity, and higher flexibility (14, 15). More important, a-BPDA is not a flexible monomer, is bent and non-coplanar rigid monomer,

yet the special rigid structure of a-BPDA gives the polyimides from a-BPDA a good flexibility and a still low CTE. To improve flexibility of film based on s-BPDA/PDA by means of blending, a-BPDA has been proved to be an attractive and efficient technique. Moreover, a blend film consisting of s-BPDA/PDA (80 wt.%) and a-BPDA-based PIs (20 wt.%) displayed improved flexibility and a still low CTE (20 ppm/K) without an undesirable T_g decrease (16).

Instead of simple polymer blending, copolymerization is an applicable method to tune certain properties so that some problems have been solved thus far in the field of polymer chemistry. Some studies showed that practically low CTE PI films with sufficient flexibility could be readily obtained through copolymerization with an adequate fraction of some flexible monomers such as, typically, 4,4'-oxydianiline (4,4'-ODA) (17) or some bent and non-coplanar monomers such as, typically, a-BPDA (18). Moreover, copolymerization can solve the issues that poor mechanical properties of PIs caused by simple blending. Nevertheless, the flexibility of copolyimides from the reaction of PDA with mixtures of a-BPDA and s-BPDA has still not been good enough. And the introduction of high content 4,4'-ODA into an s-BPDA/PDA PI chain could decrease the thermal stability and enhance CTE values. Moreover, it was difficult to improve the flexibility of s-BPDA/PDA through copolymerization with low content 4,4'-ODA. Therefore, combined with structural advantages of a-BPDA and 4,4'-ODA monomer, we expected to obtain copolyimides based on s-BPDA/PDA with a low CTE and excellent flexibility. However, to our knowledge, a few examples of s-BPDA/PDA-based polyimides simultaneously containing a-BPDA and 4,4'-ODA by means of copolymerization have been reported. Therefore, the main aim of this work is to enhance the film flexibility of s-BPDA/PDA without sacrificing its intrinsic ultra-low CTE characteristics through copolymerization with 4,4'-ODA, PDA, a-BPDA and s-BPDA.

In this study, we report on the copolymerization reaction of 4,4'-ODA, PDA, a-BPDA and s-BPDA to obtain three modified s-BPDA/PDA-based copolyimides with different content of 4,4'-ODA and a-BPDA. The effects of the modification degree on some properties such as the mechanical properties, polymer's structure and morphological, CTE, and thermal stability have been studied and are reported in detail. Structure and property relations of the prepared polyimides are also discussed.

2 Experimental

2.1 Materials

The a-BPDA, s-BPDA and 4,4'-ODA were obtained from Shandong Wanda Chemical Industries Co Ltd (China). PDA was purchased from Shanghai Jindaimao Chemical Industries Co Ltd (China). The diamines were used as received after vacuum-drying at 70°C for 24 h. The dianhydrides before synthesis were heated after vacuum-drying at 200°C for 24 h. N,N-Dimethylacetamide (99.8%, DMAC) was provided from Chengdu Chemical Reagent Factory (China) and used as-received.

2.2 Synthesis of co-poly(amic acid)

The co-poly(amic acid)s (PAAs) were synthesized by adding solid forms of a-BPDA and s-BPDA to a stirred mixture solution of 4,4'-ODA and PDA in DMAC in a nitrogen atmosphere at 0°C. The reaction mixture was stirred for 0.5 h at this 0°C, after that it was heated to room temperature and stirred for 48 h. The molar ratio of the dianhydrides and diamines, and the inherent film qualities of

Table 1: The inherent film qualities of polyamic acids.

Copolyimides acids	Molar amount of monomers				Film ^a	M_w (g/mol)
	a-BPDA	s-BPDA	4,4'-ODA	PDA		
Co-PIs-1	0.1	0.9	0	1	Crack, small pieces	82,100
Co-PIs-2	0.1	0.9	0.1	0.9	Crack, big pieces	80,500
Co-PIs-3	0.1	0.9	0.2	0.8	No crack, flexible	74,600
Co-PIs-4	0.2	0.8	0	1	Crack, big pieces	79,500
Co-PIs-5	0.2	0.8	0.1	0.9	No crack, flexible	78,000
Co-PIs-6	0.2	0.8	0.2	0.8	No crack, flexible	73,200
Co-PIs-7	0.3	0.7	0	1	Crack, small pieces	45,800
Co-PIs-8	0.3	0.7	0.1	0.9	Crack, small pieces	37,600
Co-PIs-9	0.3	0.7	0.2	0.8	Crack, small pieces	36,900

^aPolyamic acids after drying in 145°C.

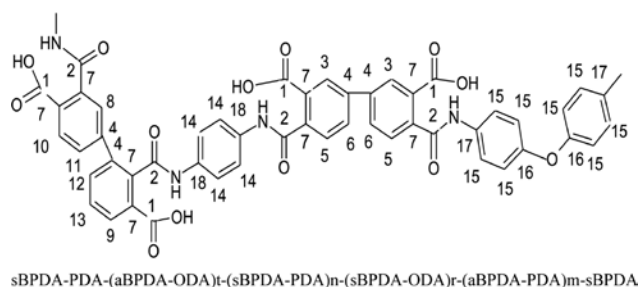


Figure 1: The structure of obtained flexible polyamic acids.

poly(amic acid)s dried in 145°C are presented in Table 1. The PAAs structure of obtained no crack films are shown in Figure 1. The IR and ^{13}C NMR data of those PAAs are as follow.

Co-PIs-3 PAA, IR (KBr) 3295, 2921, 1712, 1658, 1604, 1515, 1404, 1321, 1255, 1019, 838, 795, 742 and 709 cm^{-1} . ^{13}C NMR (DMSO d_6) δ 170.07 (C-1), 167.66(C-2), 149.70(C-16), 139.77(C-7), 138.66(C-17,18), 131.06(C-6,11,13), 127.31(C-5,10), 123.58(C-3,8,9,12), 120.07(C-14), 112.47(C-15) and 99.74(C-4) ppm.

Co-PIs-5 PAA, IR (KBr) 2908, 2357, 1714, 1605, 1515, 1405, 1321, 1258, 1019, 837, 795, 744 and 708 cm^{-1} . ^{13}C NMR (DMSO d_6) δ 170.07 (C-1), 167.66(C-2), 149.80(C-16), 140.11(C-7), 135.69(C-17, 18), 130.39(C-6, 11, 13), 128.34(C-5, 10), 121.43(C-3, 8, 9, 12) and 120.39(C-14, 15) ppm.

Co-PIs-6 PAA, IR (KBr) 3291, 2960, 2358, 1720, 1666, 1605, 1511, 1406, 1322, 1255, 1019, 839, 795 and 746 cm^{-1} . ^{13}C NMR (DMSO d_6) δ 170.06 (C-1), 167.66(C-2), 143.50(C-7), 135.99(C-17, 18), 127.99(C-5, 10), 121.42(C-3, 8, 9, 12) and 120.07(C-14, 15) ppm.

2.3 Films of copolyimides preparation

Thin films were prepared from DMAC solutions of PAAs. The solutions were coated onto clean, dry plate-glass and then dried at 60°C for 2 h in an air-convection oven. The coatings were cured by heating under mild thermal conditions in follow stages: at 100°C for 40 min, 125°C for 30 min, 145°C for 20 min, 185°C for 10 min, 220°C for 20 min, 260°C for 20 min, 300°C for 40 min, 330°C for 20 min, 350°C for 20 min. The thickness of the films was 60–80 μm .

2.4 Characterizations

The chemical structure information of polyimide films was collected using infrared measurements (Version BM Spectrometer). ^{13}C NMR spectra were recorded on a

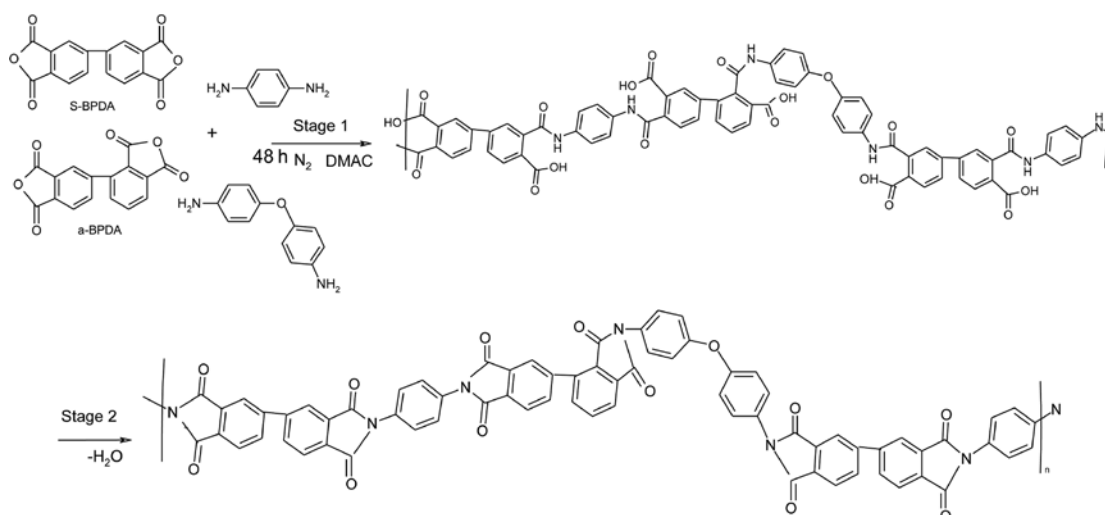
Brucker Avance 600 spectrometer with dimethylsulfoxide- d_6 (DMSO- d_6) as the solvents, and tetramethylsilane (TMS) as the internal reference. The molecular weights were determined by gel permeation chromatography (PL-GPC220). Wide angle X-ray diffract (WAXD) patterns of the films were obtained with a diffractometer (Cu Ka, 40 kV, 100 mA, Xpert MPD Pro). The surface morphologies of the films were studied by field-emission scanning electron microscopy (FE-SEM, Ultra 55). Thermogravimetric (TG) analyses of the films were performed with a TA Instrument SDT Q600 in a nitrogen atmosphere at a heating rate of 10°C/min. Mechanical properties were determined from stress-strain curves with a Toyo Instron UTM-III-500 with a load cell of 10 kg at a drawing speed of 5 cm/min. Measurement was performed at 25°C with film specimens (about 50 μm thick, 1.0 cm wide and 5 cm long) and an average of at least five individual determinations was used. Dynamic mechanical thermal analysis (DMA) was performed on thin film specimens (23.7 mm long, 5 mm wide and 0.05 mm thick) on a TA Instruments Q800 DMA at a heating rate of 3°C/min and a load frequency of 1 Hz in an air atmosphere as a function of temperature from 20°C to 400°C. Coefficients of thermal expansion (CTE) of PI specimens (10 mm long, 3 mm wide, 0.05 mm thick) were measured as the average within 50–150°C for the in-plane direction on a Perkin-Elmer Thermal Mechanical Analyzer-7 at a heating rate of 2°C/min and load of 14 g (0.3 g per a unit film thickness in μm , typically, 14 g load for 50 μm thick films) were measured.

3 Results and discussion

3.1 Synthesis of copolyimides

To obtain the copolyimides, we have employed the most popular way of polyimide synthesis, the reaction of two aromatic dianhydrides with two aromatic diamines to form soluble PAA as a precursor (stage 1), which is thermally converted (stage 2) to a copolyimide (Scheme 1).

In order to investigate the flexibility of copolyimide film, the inherent film qualities of polyamic acids dried in 145°C were observed. Because of the strong rigidity structure of monomers, the PAAs from Co-PIs-1, Co-PIs-2 and Co-PIs-4 failed to provide flexible films. The films of Co-PIs-7, Co-PIs-8 and Co-PIs-9 had some cracks and many small pieces, as results of low molecular weights (Table 1). Flexible copolyimide films (Co-PIs-3, Co-PIs-5 and Co-PIs-6) could be produced by thermal imidization using the following steps: 100°C for 40 min, 125°C for 30



Scheme 1: Two-stage synthesis of copolyimides.

min, 145°C for 20 min, 185°C for 10 min, 220°C for 20 min, 260°C for 20 min, 300°C for 40 min, 340°C for 20 min. The infrared and ¹³C NMR data of obtained flexible PAAs confirmed that 4,4'-ODA, PDA, a-BPDA and s-BPDA entered into the macromolecular chain of copolyamic acids. The complete imidization of polyimide from polyamic acids was proved by Fourier transform infrared (FT-IR) spectroscopy.

The FT-IR spectra of three flexible copolyimide films showed the characteristic imide bands at 1775, 1717, 1360 and 725 cm⁻¹ (Figure 2). Additionally, band at

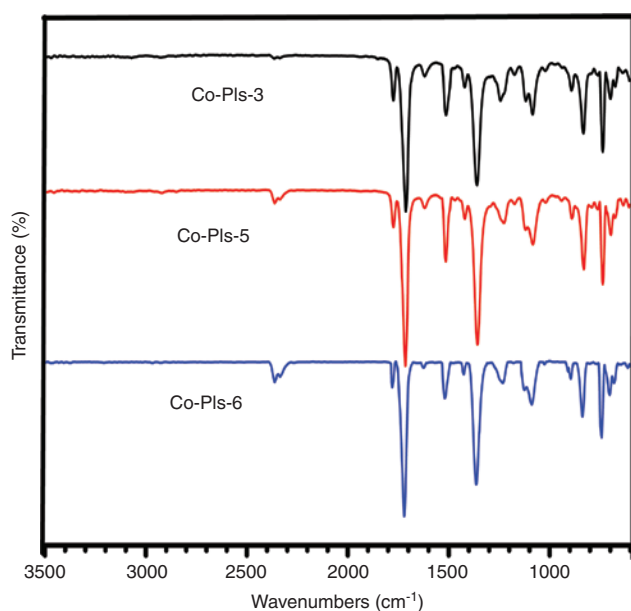


Figure 2: The FTIR spectra of Co-PIs-3, Co-PIs-5 and Co-PIs-6 films.

3284–3400 cm⁻¹ that was related to the N-H bond of amine group in the diamine was disappeared, which was also a proof of a complete imidization of those films. Furthermore, due to copolymerization with 4,4'-ODA of those films, in the FTIR spectra of those films, the =C-O-C= stretching of Aryl ether at 1229 cm⁻¹ could be observed.

3.2 Wide-angle X-ray diffraction of copolyimides

Representative WAXDs of films of three polymers (Co-PIs-3, Co-PIs-5 and Co-PIs-6) are shown in Figure 3. Three films had non-Gaussian distribution curves that revealed

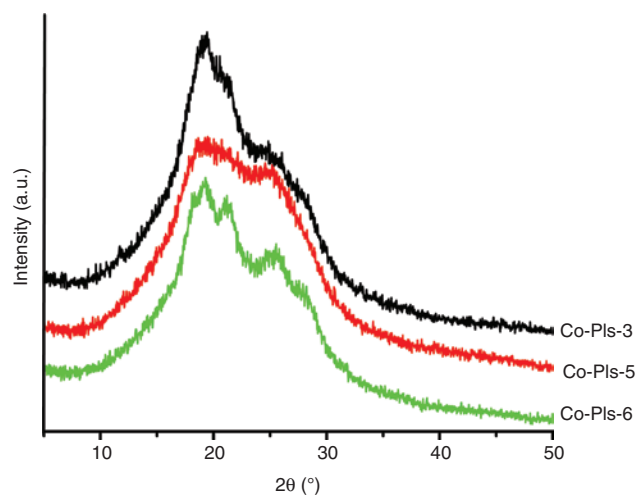


Figure 3: The WAXD of Co-PIs-3, Co-PIs-5 and Co-PIs-6 films.

a semi-crystalline structure of those polymers. Such diffraction peaks were attributed to the molecular chain orientation along the chain axis as well as to a good lateral packing order. Compared with the three films, Co-PIs-5 had lowest crystallinity. Co-PIs-6 had lower crystallinity than Co-PIs-3, which indicated that the increasing part of a-BPDA as a more bent and non-coplanar unit decreased the crystallinity of the product.

3.3 The glass transition temperature and thermal stability of copolyimides

Glass transition temperatures were determined by DMA. It can be seen from Table 2 and Figure 4, the T_g s of the prepared copolyimide films are about 358°C for the Co-PIs-3 and 369°C to 353°C for Co-PIs-5 to Co-PIs-6. The slight decrease of Co-PIs-3 to Co-PIs-6 in T_g is ascribed to a partial substitution of a-BPDA for s-BPDA, as the a-BPDA monomer has greater bend and non-coplanar structure than the s-BPDA monomer, as results from the weaker intermolecular interaction in Co-PIs-6 than in Co-PIs-3. The substitution of ODA for PDA also decreases the rigidity of the polymer chains, as well as the T_g of corresponding polyimides. The polyimides with less content of flexible ODA and higher content of rigid PDA have higher T_g . The decrease of Co-PIs-5 to Co-PIs-6 in T_g can be explained by a partial substitution of 4,4'-ODA for PDA monomer.

The thermal stability of three prepared copolyimide films was evaluated by TG (Figure 5 and Table 2). According to Table 2, when the partial substitution degree of a-BPDA for s-BPDA and 4,4'-ODA for PDA increases, the thermal stability decreases. In fact, Co-PIs-5 has the highest degradation temperature, at 602°C of T_5 and 627°C of T_{10} . This result indicates that a-BPDA moiety slightly reduces the thermal stability of the copolymers.

Table 2: Thermal properties of the copolyimides (according to data of DMA, TMA and TG).

Copolyimides no.	T_g (°C) ^c	T_5 (°C) ^a	T_{10} (°C) ^a	CTE (ppm/K) ^b
	DMA	TG	TG	TMA
Co-PIs-3	358	590	616	21
Co-PIs-5	369	602	627	13
Co-PIs-6	353	582	612	26

^a T_5 , °C and T_{10} , °C correspond to the temperatures at which a polymer undergoes 5% and 10% mass loss, respectively.

^bThe CTEs were obtained by average of temperature in the range of 50–150°C.

^cThe T_g s were obtained from temperature discrepancies of the mechanical loss tangent.

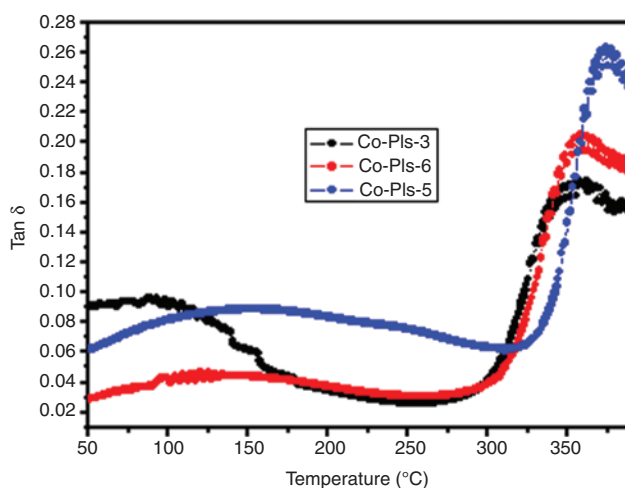


Figure 4: Tan δ of Co-PIs-3, Co-PIs-5 and Co-PIs-6 films.

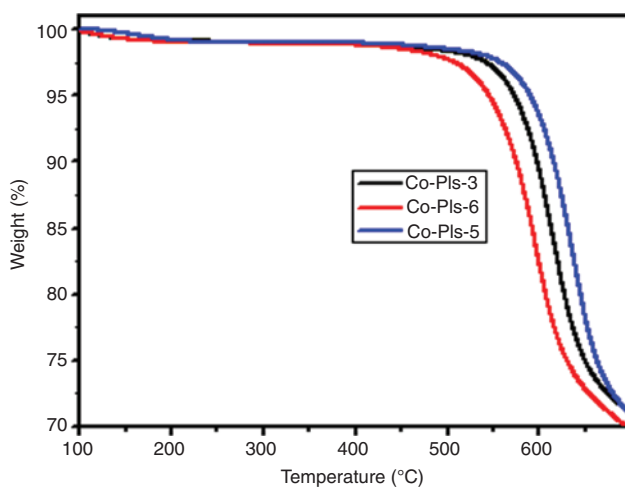


Figure 5: TG curves of Co-PIs-3, Co-PIs-5 and Co-PIs-6 films.

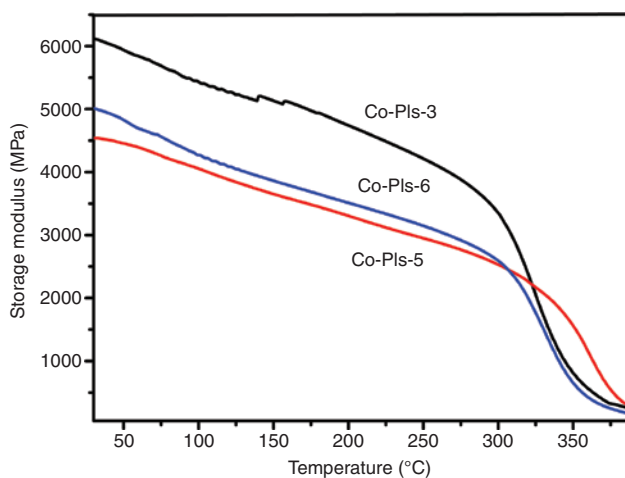


Figure 6: Dynamic storage modulus curves of Co-PIs-3, Co-PIs-5 and Co-PIs-6 films.

3.4 Dynamic mechanical properties of copolyimides

The dynamic mechanical properties of copolyimides were measured. The dynamic viscoelastic curves for Co-PIs-3, Co-PIs-5 and Co-PIs-6 are shown in Figure 6. The storage modulus curves of three copolyimides displayed marked drop up to the T_g . The extent of the storage modulus drops of three copolyimides decreased with an

increase of a-BPDA. Comparing the three copolyimides, the storage modulus of Co-PIs-5 was lowest from 25°C to 300°C and the extent of the storage modulus drop of Co-PIs-5 was least, reflecting that the Co-PIs-5 had the best flexibility.

3.5 Mechanical properties of copolyimides

All polyimides formed flexible films by step imidization in a forced air oven. The mechanical properties of the films were measured at room temperature, and are summarized in Table 3.

One might note that generally the tensile strengths were higher when the amount of the PDA monomers were larger and the more s-BPDA monomers were in the macromolecule. These results of tensile strength might be attributed to the fact that more linear rigid structures were beneficial to the stacking of polymer chains and the

Table 3: Mechanical properties of Co-PIs-3, Co-PIs-5 and Co-PIs-6 films.

Copolyimides no.	23°C Mechanical properties	
	Tensile strength (MPa)	Elongation at break (%)
Co-PIs-3	209	13.2
Co-PIs-5	182	22.8
Co-PIs-6	154	20.6

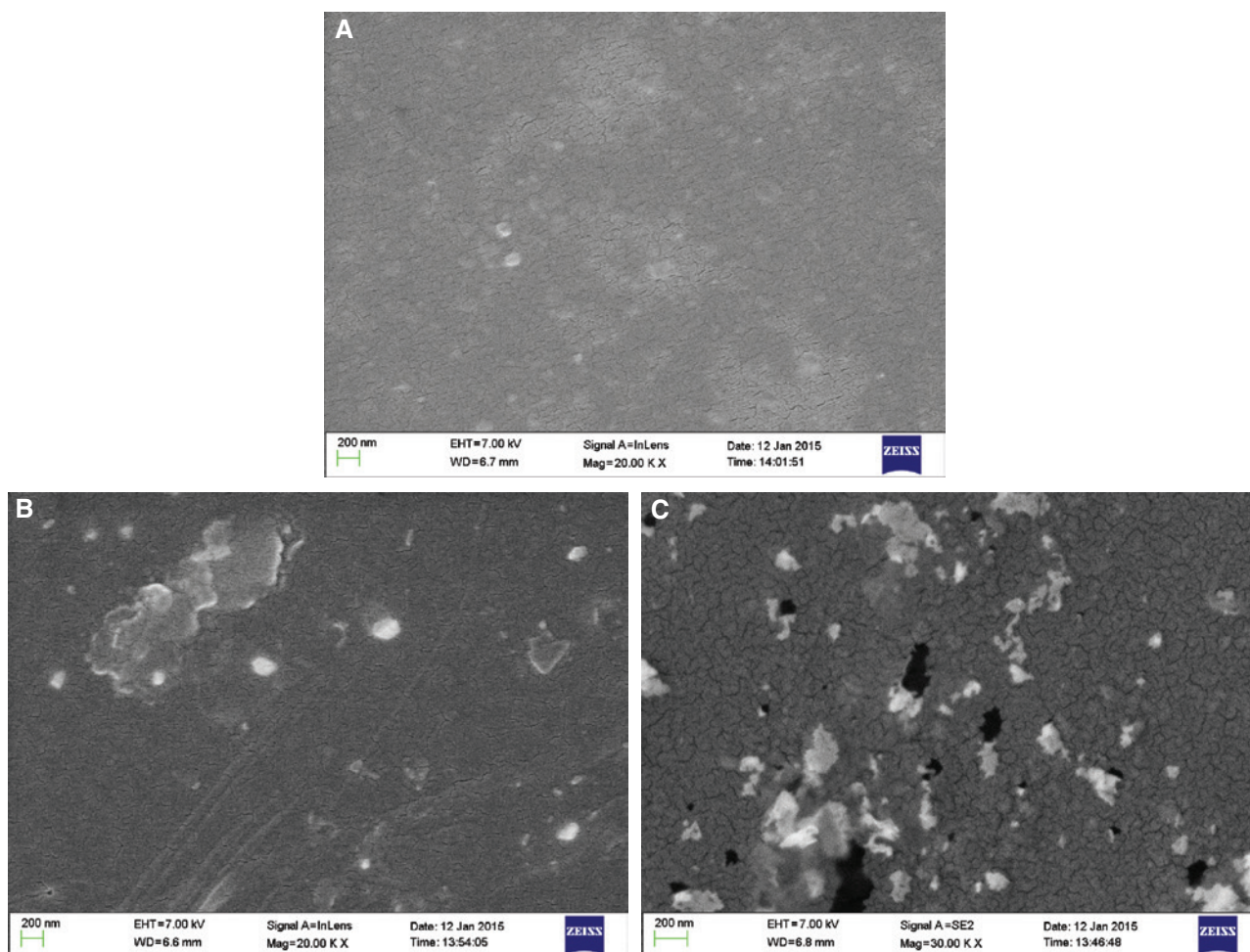


Figure 7: The SEM of the copolyimide films: (A) Co-PIs-3, (B) Co-PIs-5 and (C) Co-PIs-6.

enhancement of tensile strength. These analyses of tensile strength for three copolyimides can be confirmed by the SEM images of three copolyimides (Figure 7). The surface of the Co-PIs-6 sample had more and larger sized micro cracks than that of Co-PIs-3 and Co-PIs-5.

Due to an increase of a more kinked structure in the macromolecules and a more chain-chain entanglement, the elongation at break of copolyimides containing more s-BPDA monomers was less than that of copolyimides containing more a-BPDA monomers. Co-PIs-5 had excellent tensile strength, and its elongation at breaks the largest.

3.6 Coefficient of thermal expansion

The CTE of the copolyimide films are shown in Table 2.

The Co-PIs-5 film displayed a considerably low CTE of 13 ppm/K, which was much lower than that of Co-PIs-3 film (CTE=21 ppm/K) and that of Co-PIs-6 film (CTE=26 ppm/K). Based on their structural distinction, BPDA-PDA was regarded as rigid or planar structures and had larger in-plane molecular orientation (ordered structure) which was known to be responsible for their low CTE. The flexible (ODA) and bent and non-coplanar units (a-BPDA) in BPDA-PDA made the polymers in-plane orientation decrease and the CTE increase. In addition, the CTE was related to the molecular packing degree. The polymer chains were packed more densely and the polymer had smaller free volume that was favorable to form lower CTE polymers. The lowest CTE of Co-PIs-5 film is in accordance with the greatest packing degree as shown in Figure 7.

4 Conclusions

A series of copolymers were prepared from the reaction of 4,4'-ODA and a-BPDA with PDA and s-BPDA. The flexible films were obtained from the molar ratio of s-BPDA, a-BPDA, PDA and 4,4'-ODA was 9:1:8:2 (Co-PIs-3), 8:2:9:1 (Co-PIs-5) and 8:2:8:2 (Co-PIs-6). The complete imidization of three flexible copolyimide films was proved by FTIR. Three copolyimides remained semi-crystalline and exhibited high T_g , high thermal stability, great ultimate tensile strength and low CTE. The several properties of three copolyimides confirmed that the copolymerization of s-BPDA/PDA with a small number of 4,4'-ODA/a-BPDA enhanced the film flexibility of s-BPDA/PDA without sacrificing its intrinsic ultra-low CTE characteristics.

Compared with the three films, the Co-PIs-5 had the lowest crystallinity, lowest CTE, greatest elongation at break, highest T_g and thermal stability and the greatest dense extent. Those results may bear a close relationship to the micro-structure of most compact molecular chain and greatest nonlinear conformation in Co-PIs-5 chains.

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