

Rigidity Enhancement of Polyimides Containing Benzimidazole Moieties

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ABSTRACT: A series of copolyimides were prepared by incorporating pyromellitic dianhydride (PMDA) into the homopolyimide derived from 5,4'-diamino-2-phenyl benzimidazole (DAPBI) and 3,3',4,4'-biphenyl tetracarboxylic dianhydride (s-BPDA), with the purpose of enhancing backbone rigidity of the homopolyimide. A systematic change in thermal, mechanical and optical properties was observed by changing the ratios of PMDA and s-BPDA components. Glass transition temperatures were in the range of 404–425°C, depending on the pyromellitimide content. Mechanical properties were significantly enhanced: Tensile modulus and strength ranged from 5.8 to 8.5 GPa and 249 to 263 MPa, respectively, and much higher than that of the homopolyimide (s-BPDA/DAPBI). Wide-angle X-ray diffractions showed that the copolymer films were amorphous, although locally ordered regions were observed with long periodicity larger than that of the homopolyimide. The properties enhancement was attributed to the increased overall rigidity of the polymer backbones and enhanced molecular in-plane orientation. Possible structure–property relationships were also discussed. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

KEYWORDS: polyimides; copolymers; structure–property relations; properties and characterization

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INTRODUCTION

Polyimide (PI) films having a favorable combination of properties such as high glass transition temperatures (T_g), excellent mechanical properties, and good dimensional stabilities have been extensively investigated with both academic and industrial viewpoints. They have been applied in a variety of electric, microelectronic and optoelectronic devices. Particularly, polyimides having rigid-rod backbones have attracted much attention because PI systems possessing linear and stiff backbone structures tend to afford low coefficient of thermal expansion (CTE), which is desirable since polyimides are frequently used as coatings and films adhered to metal or silicon substrates.^{1,2} Uniaxial or biaxial stretching of the polyamic acid (PAA, PI precursor) or PI film is an effective way to promote the degree of molecular orientation along the stretching directions. This method would improve the film's dimensional stability, mechanical property, and resistance to chemical and thermal attack.^{3–6} However, such mechanical procedures require precise control of process parameters thus complex and costly. Besides, even if ideal stretching process was possible, such mechanical steps could not be applied to the film/substrate laminates usually used in microelectronic applications.⁷

Incorporating heterocyclic units into PI main chain by using heteroaromatic monomers is also effective to improve thermal

and mechanical properties of polyimides, saving the complex procedures of mechanical stretching. This is because heterocyclic groups tend to increase the rigidity of the polymer backbones and provide strong intermolecular associations,⁸ as evidenced from the extraordinarily high performance of some aromatic heterocyclic polymers.^{9,10} Improved properties were obtained after quinazolinone¹¹ and benzothiazole¹² moieties were introduced into polyimide backbones.

In our previous study,¹³ homopolyimides containing benzimidazole moieties in the main chain were synthesized by using benzimidazole containing diamine monomer: 5,4'-diamino-2-phenyl benzimidazole (DAPBI), and the properties of resultant PI films were far more better than polyimides derived from common monomers. PI prepared from 3,3', 4,4'-biphenyl tetracarboxylic dianhydride (s-BPDA) and DAPBI had the best combination of properties, with T_g of 404°C and Young's modulus of 5.6 GPa. Pyromellitic dianhydride (PMDA), as the smallest rigid dianhydride monomer, was expected to react with DAPBI to form polyimide with better performance than PI (DAPBI/s-BPDA). However, homopolyimide film based on PMDA and DAPBI was highly brittle, probably due to of poor entanglement between the rod-like PI chains. As a continuation to that work, PMDA

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was incorporated into homo-PI (DABPI/s-BPDA) to form copolyimides, with the purpose of improving thermal and mechanical properties of the PI films by increasing polymer backbones' rigidity. The properties of the copolyimides were investigated and the composition dependence of the properties was discussed.

EXPERIMENTAL

Materials

The diamine component 5,4'-diamino-2-phenyl benzimidazole (DAPBI) was prepared according to the published method.¹³ 3,3',4,4'-biphenyl tetracarboxylic dianhydride (s-BPDA, m.p.306°C) and Pyromellitic dianhydride (PMDA, m.p. 285°C) were supplied by Beijing Jiaohua Company, and dried under vacuum at 180°C prior to use. *N,N*-dimethylacetamide (DMAc) was the product of Tianjin Chemical Reagent and used as the polymerization solvent.

Polymer Synthesis and Film Preparation

The copolyimide films were prepared via a conventional two-step polycondensation of s-BPDA, PMDA and DAPBI, affording polyimides with different dianhydride compositions. PAA precursors were formed by adjusting the molar ratio of s-BPDA and PMDA at 90 : 10, 70 : 30, 50 : 50, 30 : 70, and 10 : 90, with stoichiometrically equal amount of DAPBI. The resultant polymers were abbreviated as CPI(90/10), CPI(70/30), CPI(50/50), CPI(30/70), and CPI(10/90), respectively. Homopolyimides with the repeating unit of DAPBI/s-BPDA and DAPBI/PMDA, which have been studied previously¹³ were signaled as CPI(100/0) and CPI(0/100) for convenience. The procedure for preparing CPI(10/90) was taken as an example: s-BPDA (0.7383 g, 2.51 mmol) was gradually added to a stirred mixture of DAPBI (5.6251 g, 25.11 mmol) dispersed in DMAc. The mixture was stirred under nitrogen flow for 3 h at room temperature to form opaque suspension. And then the stoichiometric amount of PMDA (4.9270 g, 22.60 mmol) was gradually added with additional DMAc to adjust the solid concentration to 7 wt %. The mixture was stirred for another 7 h to form a homogeneous viscous PAA solution.

Film was cast from PAA solution onto a flat glass plate and heated with a programmed procedure (80°C/1 h, 100°C/1 h, 120°C/1 h, 150°C/1 h, 180°C/1 h) in ventilated oven to remove the solvent, then the film was cured under vacuum at 250, 300, and 350°C each for 1 h to afford PI film. The freestanding film was obtained by soaking in water to release from the glass substrate. Film samples were heated at 120°C for 2 h to remove the absorbed water prior to all tests.

Characterization

FT-IR spectra of the polyimide films as deposited onto KBr pellets were recorded by Bruker Vector-22 FT-IR spectrometer at a resolution of 4 cm⁻¹ and were signal-averaged for 128 scans. Inherent viscosities (η_{inh}) of the PAAs were measured at 0.5 g dL⁻¹ in DMAc with a Ubbelohde capillary viscometer at 25°C. Mechanical properties were examined on a Shimadzu AG-I universal testing apparatus, using strips of 3-mm width with a 30-mm gauge length at a crosshead speed of 8 mm min⁻¹. Thermogravimetric analysis (TGA) was conducted using a TA

instrument TA-2050 thermogravimetric analyzer, film samples were heated at a temperature ramp of 5°C min⁻¹ in a nitrogen flow. Temperatures at which 5% weight loss occurred ($T_d^{5\%}$) were taken to evaluate thermal stabilities of the films. Differential scanning calorimetric (DSC) experiments were performed with a TA instrument DSC Q100 system with a heating rate of 20°C min⁻¹ under nitrogen flow of 50 cm³ min⁻¹. Dynamic mechanical analysis (DMA) was carried out using a TA instrument DMA Q800 at a heating rate of 5°C min⁻¹ and a load frequency of 1 Hz in film tension geometry. T_g was determined as the peak temperature of tan δ curve. CTE values of the PI films were measured as an average within 150–250°C in the film plane direction on a Mettler Toledo TMA/SDTA 841e thermomechanical analyzer with a constant load of 5 g and a heating rate of 5°C min⁻¹. The data were collected from the second heating run after the first run which was carried out up to the annealed temperature to eliminate the stresses in films. Ultraviolet–visible (UV–vis) spectra of the PI films were recorded with a Shimadzu UV–vis 2501 spectrometer in transmittance mode. Reflection mode wide-angle X-ray diffraction (WAXD) measurements for PI films were conducted on a Rigaku Wide-angle X-ray diffractometer (D/max rA, using Cu K α radiation at wavelength $\lambda = 1.541 \text{ \AA}$) with a rate of 0.5° min⁻¹, data were collected at 0.02° intervals in the range of $2\theta = 5^\circ\text{--}50^\circ$. Small-angle X-ray scattering (SAXS) was performed using the same instrument in the range of $2\theta = 0.5^\circ\text{--}5^\circ$ with a scan rate of 0.2° min⁻¹.

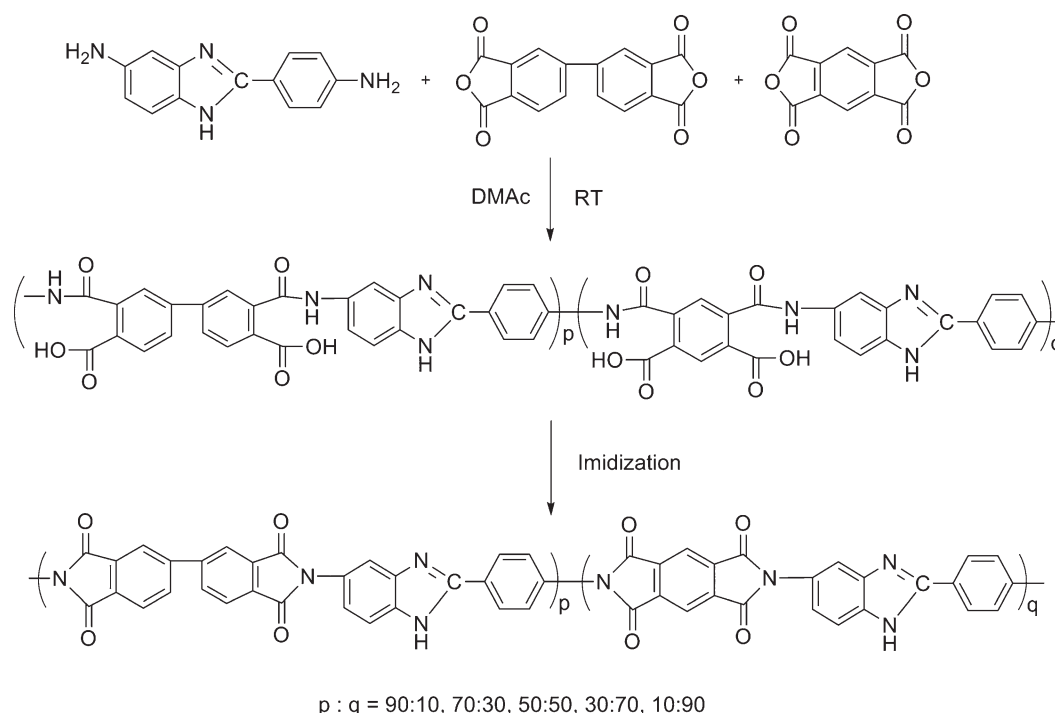
RESULTS AND DISCUSSION

Preparation of Copolyimide Films

A series of copolyimides with different compositions were prepared as shown in Scheme 1. Solution-polycondensation between the three monomers led to homogeneous PAA solution, followed by thermal cyclodehydration to obtain yellow-orange colored PI films. The complete transformation to polyimide from PAA was proved by IR analysis. All spectra demonstrated characteristic bands of imide ring at 1774 and 1718 cm⁻¹, and no bands that were assigned to amide linkages were detected, indicating that PAAs were fully imidized after the curing procedures. Data in Table I shows that reaction of DAPBI with the two dianhydride monomers led to high molecular weight PAAs, as evidenced from the high inherent viscosity values. The copolyimide films all showed the good toughness, although CPI(0/100) could not be obtained as tough film after thermal imidization of the corresponding PAA precursor, which possessed sufficiently high inherent viscosity. This is due to the poor entanglement between the rod-like molecular chains for CPI(0/100).¹⁴ In the case of copolyimides, the presence of not-rod-like biphenyldiimide structure improved the overall flexibility of the molecular chain, leading to better chain entanglement and consequently a toughness improvement.

Thermal Properties of Copolyimide Films

Thermal properties of the polyimides were examined by DSC, DMA, TGA, and TMA, and the results were summarized in Table I. TGA curves of the copolyimide films under nitrogen atmosphere were shown in Figure 1, 5% weight loss temperatures were detected in the range of 539–572°C, exhibiting good



Scheme 1. Synthesis and structures of the copolyimides.

thermal stabilities of the copolyimides. This could be attributed to the high content of aromatic heterocyclic moieties in the polymer backbones.

Thermal transitions were firstly evaluated by DSC, and no well-defined glass transition was detected in the range of 50–500°C. This is common for the wholly aromatic polyimides which often possess poor molecular mobility even above their T_g .¹⁴ Because there was no detectable glass transition in the DSC curve of CPI(100/0), it is understandable since the overall rigidity of the copolyimide backbones was increased after the introduction of pyromellitic moiety. No endothermic peaks assigned to the melting of crystallinity were detected in DSC curves, and

characterizations based on X-ray diffraction (WAXD and SAXS) will be performed to give a detailed discussion on the morphological structures of the films in latter sections.

Glass transitions of the copolyimide films were further examined by DMA and the results were displayed in Table I. DMA is more helpful in detecting polymer transitions over DSC owing to DMA's appreciably higher sensitivity.¹⁵ $\tan \delta$ and storage modulus of copolyimides as a function of temperature were shown in Figures 2 and 3, respectively, and T_g s were located in the range of 404–425°C. It was observed that T_g increased with the content of pyromellitic unit, and this can be explained by the increased rigidity of the polymer backbones.¹⁶ Storage

Table I. Inherent Viscosities and Thermal Properties of the Homo^a- and Copolyimide Films

Sample	η_{inh} (dL g ⁻¹)	T_g (°C)		T_5^b (°C)	R_{800} (%) ^d	CTE (ppm/°C)
		DSC	DMA			
CPI(100/0)	0.97	NF ^c	404	575	71	-6.7
CPI(90/10)	1.83	NF	404	572	71	-7.3
CPI(70/30)	2.00	NF	412	557	71	-8.7
CPI(50/50)	2.49	NF	414	545	70	-9.3
CPI(30/70)	1.92	NF	418	539	70	-9.8
CPI(10/90)	2.19	NF	425	539	68	-11.4
CPI(0/100)	0.98	NF	- ^d	548	68	-

^aData for homopolyimides were quoted from Ref. 13, as in the following diagrams for comparison convenience. ^bWeight retention when heated to 800°C in nitrogen atmosphere. ^cNot found. ^dNo tough film sample was available for testing.

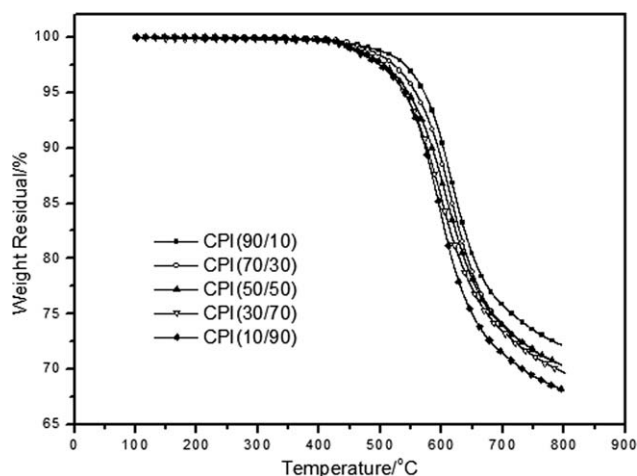


Figure 1. TGA curves of the copolyimides under N₂ atmosphere.

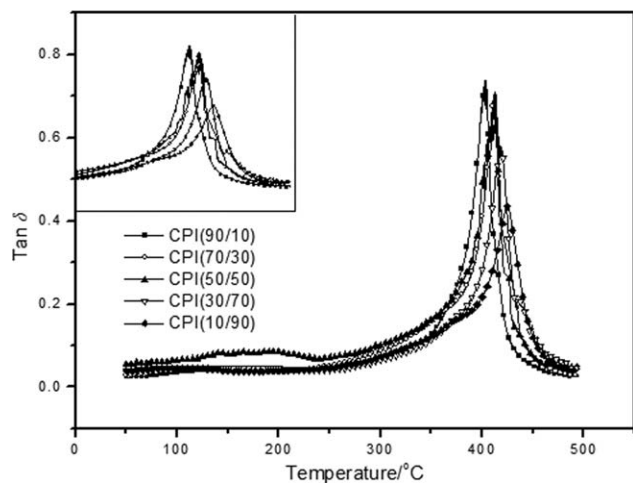


Figure 2. $\tan \delta$ of the copolyimide films as a function of temperature. The inset shows the profile in the range of 300–500°C.

modulus went through varying extents of decrease at the glass transitions as shown in Figure 3, in which higher degree of softening was observed for CPI(30/70), CPI(50/50), and CPI(70/30), while the decrease for CPI(10/90) and CPI(90/10) was less distinct. This can be interpreted by the varying extent of interruption of supramolecular regularity and symmetry^{17,18}: when the polymer backbones were composed of nearly equivalent amount of *s*-BPDA and PMDA (molar ratio = 30 : 70, 50 : 50, and 70 : 30), the polymer fragments packing is more disturbed compared to CPI(10/90) and CPI(90/10) with one dianhydride component majorly existing. Another interesting observation is the increase of storage modulus for all samples after glass transitions. This is related to the high temperature induced molecular rearrangement, like crystallization process or curing reaction. In this case curing could be ignored as the films had been fully cured, proved by the FT-IR results.

CTE was measured by TMA and the results were listed in Table I. Negative CTE values were obtained for all copolyimide films, with one typical TMA curve of CPI(100/0) shown in

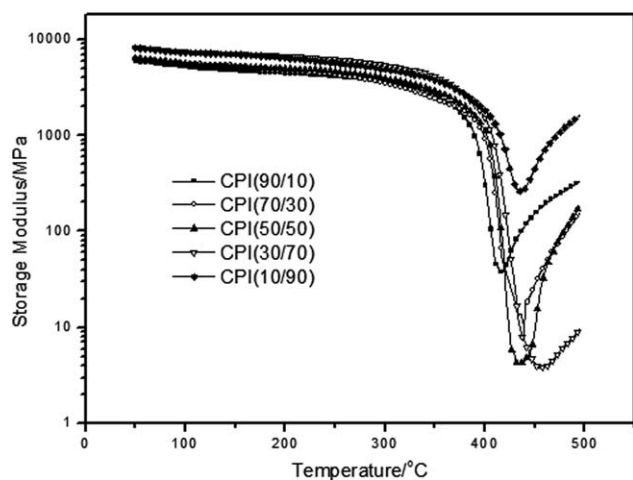


Figure 3. Storage modulus of the copolyimide films as a function of temperature.

Table II. Mechanical Properties of the Polyimide Films

Sample	Young's modulus (GPa)	Tensile strength (MPa)	Maximum elongation (%)
CPI(100/0)	5.6	234	12.3
CPI(90/10)	5.8	261	22.9
CPI(70/30)	5.8	258	17.2
CPI(50/50)	7.5	263	15.6
CPI(30/70)	7.7	262	10.2
CPI(10/90)	8.5	249	5.0

Supporting Information Figure S1. The curve was almost reversible after a heating/cooling cycle at the glassy state. This is direct evidence that the present negative CTE behavior quite differs from the irreversible relaxation of highly oriented polymer films or fibers. A combination of considerably high degree of in-plane orientation and less crystalline morphology was attributed to the negative CTE behavior.¹⁹ CTE dependence on the copolyimide composition is clear: the values decreased consistently as the content of PMDA increased. Because CTE of PI films tends to be inversely proportional to the degree of in-plane orientation, the adherence of CTE to the molar additivity rules could be interpreted from the enhanced in-plane orientation after the incorporation of PMDA.^{20,21}

Mechanical Properties of Polyimide Films

Mechanical properties of polyimide films are summarized in Table II. All copolyimide films exhibited remarkable modulus and strength values, in the range of 5.8–8.5 GPa and 249–263 MPa, respectively. These values are far more than common polyimide films prepared under similar laboratory conditions, which have tensile modulus no more than 4GPa.²² Tensile modulus increased continuously as PMDA was gradually increased from 0 mol % (CPI(100/0)) to 90 mol % (CPI(10/90)), and CPI(10/90) had the largest tensile modulus of 8.5 GPa, which exceeded that of CPI(100/0) by 50%. Dependence of mechanical properties on the molar percentage of PMDA was expected and explained by the increased rigidity of the polymer backbone as the pyromellitic content increased. The content of benzimidazole moiety in the repeating unit, which tended to induce strong intermolecular association (hydrogen bonding),^{23,24} became higher as the PMDA content increased and served favorably in promoting the films' tensile properties.

Morphology Structures and Optical Properties of Polyimides

Reflection mode of WAXD diagrams for PI films were shown in Figure 4. No sign of crystallization was found from the broad and less-structured patterns, suggesting that all of the films were essentially amorphous.

Morphology structures were further analyzed by SAXS and the patterns were shown in Figure 5. Discernable dispersion peaks indicated regular arrangements of the polymer segments along the chain axis. The diagrams for the copolyimides displayed intensified signals at the Bragg angle $2\theta = 0.92^\circ$ – 1.3° , with respect to the periodicity of the polymer chains. The average length of the ordered regions could be calculated through

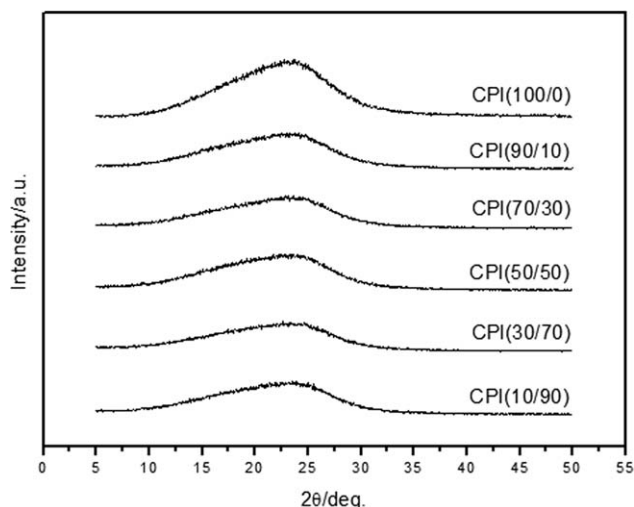


Figure 4. WAXD patterns of the homo- and copolyimide films.

Bragg's Law: $d = \lambda/2\sin\theta$, and the results were located in the range of 68–96 Å. These values were larger than that of CPI(100/0) (45.5 Å, with dispersion peak at 1.94°). This could be explained by the more defective and disturbed morphology structures after the introduction of PMDA-DAPBI segment, as discovered from the storage modulus curves. It should be stressed that the more aperiodic nature of the copolyimide chains' supramolecular structures, inferred from the DMA and SAXS results, is not in contradiction to the enhanced rigidity and in-plane orientation of the polymer backbones, which played a major role in improving thermal and mechanical properties of the copolyimides.

For the DAPBI derived homopolyimides studied in our previous research,¹³ densely packed layered ribbon-like morphology was

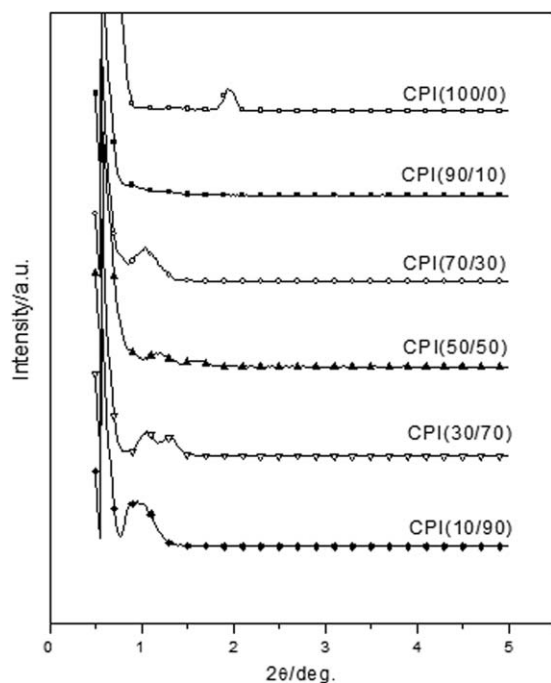


Figure 5. SAXS patterns of the homo- and copolyimide films.

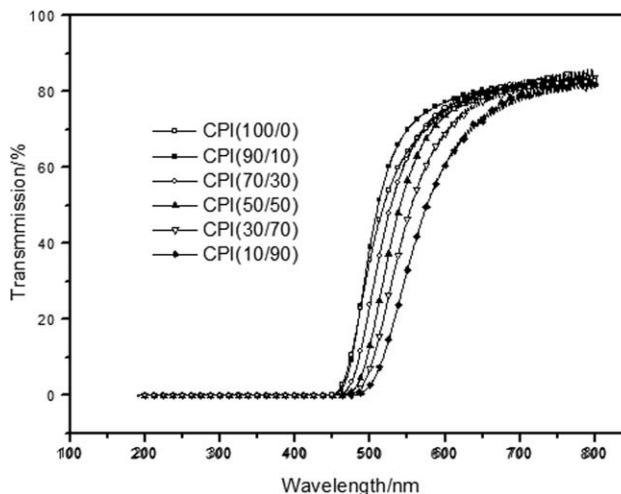


Figure 6. UV-vis spectra of the homo- and copolyimide films.

found along the direction of the film plane in the SEM photographs, indicating high degree of local ordering and orientation. However, no such feature was observed for the copolymers in the present study, it could also be attributed to the degradation of regularity when PMDA component was incorporated as stated above.

Optical properties of the PI films were examined by UV-vis spectroscopy and the spectra were displayed in Figure 6. The transmission onset and 80% transmission wavelength were used to evaluate the films' transparency²⁵ and the results were listed in Table III. The films were all relatively deep in color and the transmission onset and 80% transmission wavelength were located in the range of 439–465 nm and 485–533 nm, respectively, implying the UV-vis absorbance was strong. The poor transparency was attributed to the linear and rigid polymer backbones and high density of strongly polarized groups (imide ring and benzimidazole unit). The values in Table III increased with PMDA content and it is reasonable that the degree of linearity and coplanarity of the polymer backbones became higher as PMDA content increased, making it easier to form intermolecular charge-transfer complex(CTC).²⁶

CONCLUSIONS

With the purpose of enhancing thermal and mechanical properties of the homopolyimide based on DAPBI and s-BPDA, rigid

Table III. The Onset and 80% Transmission Wavelength of the Polyimide Films

Sample	Onset wavelength (nm)	80% Transmission (nm)
CPI(100/0)	439	485
CPI(90/10)	443	485
CPI(70/30)	445	496
CPI(50/50)	455	508
CPI(30/70)	458	518
CPI(10/90)	465	533

and symmetric pyromellitic unit was incorporated into the homopolymer system by copolymerizing with PMDA, and the copolyimide films were all tough and flexible. The results showed that thermal and mechanical properties of the polyimide films were remarkably promoted after the incorporation of PMDA component. The effect of varying the molar percentage of PMDA-DAPBI on thermal, mechanical and optical properties and morphology structures of the copolyimides were evaluated. It was observed that chain rigidity and linearity as well as structural symmetry played crucial roles in determining the properties of PI films. The structure–property relationships provided an opportunity for designing accurately the properties needed in specific applications.

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