

Synthesis and properties of polyimides containing benzoxazole units in the main chain

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Abstract

A series of polyimide films were prepared with a benzoheterocyclic structure containing diamine monomer--5,4'-diamino-2-phenyl benzoxazole (DAPBO) and five commercially available dianhydrides in conventional two-step polymerization process. The films showed high level of mechanical properties with tensile modulus of up to 7.2GPa without any pre-drawing process. According to the results of thermal analysis, the glass transition temperatures(Tg) of the polymer films could reach as high as 412°C. Excellent properties of these polyimides were attributed to the existence of benzoxazole units in the main chain and accordingly strong intermolecular association.

Key Words: polyimide films; benzoxazole moiety; modulus; intermolecular interaction

Introduction

Polyimide films having a favorable combination of properties such as high glass transition temperatures, excellent mechanical properties, and good dimensional stability have been extensively investigated both in academia and application studies. Among these, polyimides having rod-like backbones attracted much attention because the polymer chains' rigidity could impart high tensile moduli, high glass transition temperatures and low CTEs (dimensional stability) to the resultant PI's properties. However, the thermal and mechanical properties were still far from the increasing demands for the rapid development of microelectronic industry, for example, the pre-orientation of PAAs is an effective way to enhance the tensile modulus and strength of the final PI films, but even if ideal stretching process was possible, such mechanical procedures could not be applied to the film/substrate laminates demanded in microelectronic applications^[1].

In our previous work^[2], polyimides containing benzimidazole moiety were synthesized by using a benzimidazole unit containing diamine monomer: 5, 4'-diamino-2-phenyl benzimidazole (DAPBI), the properties of the PI films obtained including glass transition temperatures, tensile moduli, thermal and thermoxidative stability were greatly enhanced owing to the introduction of benzoheterocyclic unit into the polymer backbone. In this study, a new diamine monomer containing benzoxazole moiety : 5,4'-diamino-2-phenyl benzoxazole (DAPBO) was used to prepare PI films and the properties were characterized to gain an insight to the influence of this unit on the polymers' properties.

Experimental Section

Materials

The following chemicals were obtained from the indicated sources and used without further purification. The diamine monomer 5,4'-diamino-2-phenyl benzoxazole (DAPBO) was purchased from Changzhou Sunshine Fine Chemicals Co.Ltd. 3,3',4,4'-biphenyl tetracarboxylic dianhydride(s-BPDA) and 3,3',4,4'-benzophenone tetracarboxylic dianhydride(BTDA) were supplied by Chriskev Company Inc . 3,3',4,4'- Oxydiphthalic dianhydride(ODPA) and bisphenol A di(phthalic anhydride)ether (BPADA) were obtained Beijing Jiaohua Company. Pyromellitic dianhydride(PMDA) was supplied by Beijing Chemical

Reagent (Beijing, China). These commercially available dianhydride monomers were dried under vacuum before use. N,N'-dimethylacetamide(DMAc) was distilled under reduced pressure and used as solvent.

Polymer synthesis

The polyimide films were prepared using a conventional two-step polymerization process. A typical example is as follows: to a solution of 2.1157g of DAPBO(9.39mmol) in 40 ml DMAc, 2.0487g of PMDA was gradually added under nitrogen atmosphere. The solid concentration was adjusted to 10% wt. The mixture was stirred for 10h after the addition of the dianhydride to form a homogeneous solution of poly(amic acid) (PAA) precursor. The PAA solutions obtained were stored in a refrigerator overnight.

PI films were cast from PAA solution onto a clean, flat glass plate with a programmed temperature procedure(40°C/2h;60°C/2h;80°C/2h;100 °C/2h;120 °C/1h;150 °C/1h;180 °C/1h) in air convection oven to remove the solvent and subsequently heated to 400°C under vacuum as the following steps: 250°C/1h; 320°C/1h; 400°C/1h, except that PI derived from DAPBO and BPADA was annealed at 350°C to avoid the degradation of aliphatic group in BPADA at high temperature. The freestanding films were obtained by soaking in water to get peeled off from the glass substrate. The thicknesses of the resultant films were controlled to be approximately 20µm.

Measurements

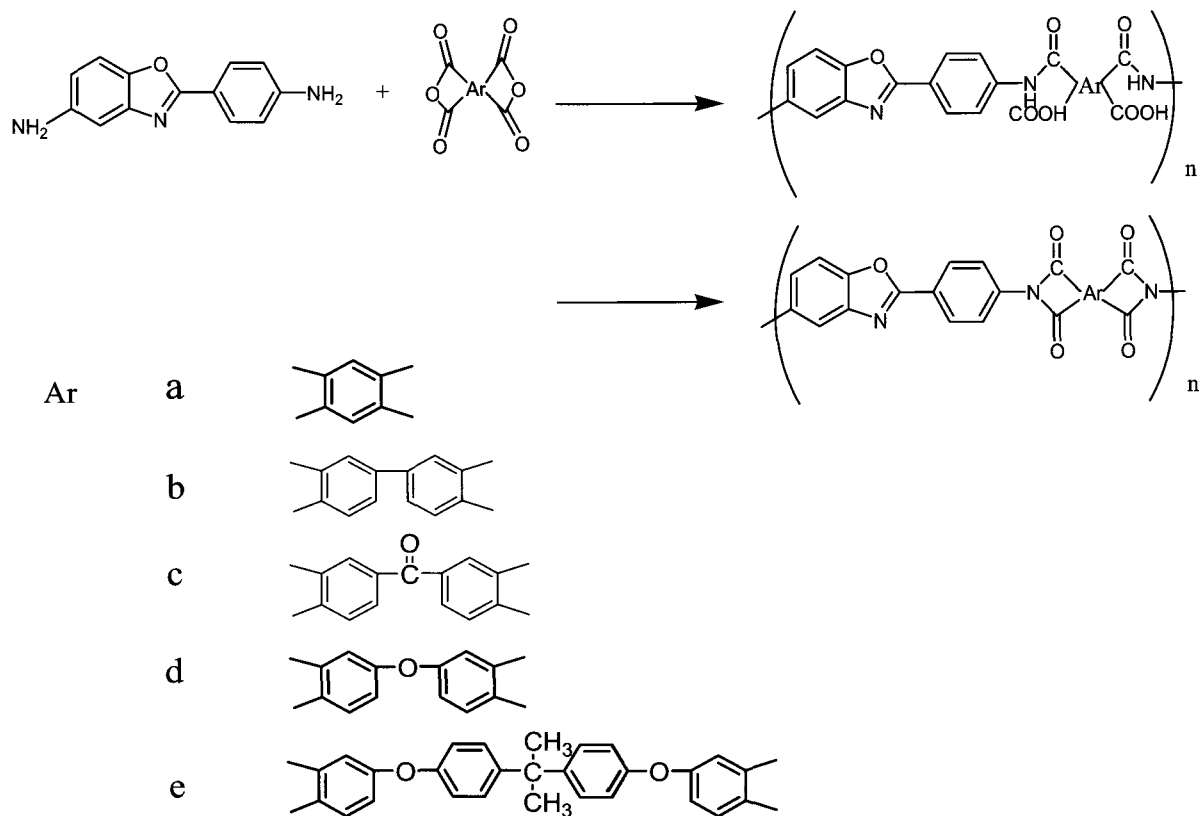
Intrinsic viscosities of the PAA solutions were determined at 0.5g/dL concentration in DMAc with an Ubbelohde capillary viscometer at 25°C. Mechanical properties including tensile modulus, tensile strength and elongation at break were measured on a Shimadzu AG-I universal testing apparatus using samples of 5mm width and 20mm length with a strain rate of 8mm/min, the results were calculated as the average of ten specimens for one certain kind of PI film. Thermogravimetric analysis(TGA) was obtained using a TA instrument TA-2050 thermogravimetric analyser, film samples were heated at a temperature ramp of 5°C/min in nitrogen and air atmosphere, respectively. Differential scanning calorimetry(DSC) experiments were performed with a TA instrument DSC Q100 system with a heating rate of 20°C/min under nitrogen atmosphere. Dynamic mechanical analysis(DMA) was carried out on film specimens on a TA instrument DMA Q800 at a heating rate of 5°C/min and a load frequency of 1Hz with film tension mode in nitrogen atmosphere. The peak of tan delta value as a function of temperature was regarded as Tg of the film. Thermal mechanical analysis(TMA) was examined using a Mettler Toledo TMA/SDTA 841e at a heating rate of 5°C/min with film tension mode and a constant load of 5g was applied to the sample in nitrogen flow. In this case, the in-plane CTE values were measured as an average within 100°C-200 °C and 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 residual stress. The water absorption rates were measured, specimens were immersed in 23°C water for 24h, and the weight differences were measured.

Results and discussion

Synthesis of polyimide films

The synthetic route for PIa-e was shown in **Scheme 1**. Solution-polycondensation process between DAPBO and five dianhydrides in DMAc led to pale-yellow colored homogeneous PAA solutions, followed by thermal imidization process to obtain yellow-brown PI films. The diamine monomer used in this work contained benzoxazole unit and the PI molecular chains formed were expected to adopt rigid-rod conformations, among those the one based on PMDA and DAPBO (PI-a) was of fully rigid structure. Inherent viscosities and film-forming ability of PAAs were listed in **Table 1**. The values of inherent viscosities measured tended to be smaller than those of highly-polymerized PAAs, however, this did not prohibit the

formation of good, flexible PI films.



Scheme 1 Synthesis of PIs derived from DAPBO

Table 1 Inherent viscosity of PAAs and film-forming ability

sample	inherent viscosity (dL/g)	PI film quality
PI-a	0.81	flexible and creasible
PI-b	0.60	flexible and creasible
PI-c	0.39	flexible and creasible
PI-d	0.37	flexible and creasible
PI-e	0.38	flexible and creasible

Mechanical properties

The tensile properties of PI films were listed in **Table 2**. As shown in the table, PI-a-d all had remarkable tensile modulus and strength values, while common polyimide films have tensile modulus no more than 4GPa. Among these the film derived from PMDA had modulus up to 7.2GPa, and strength up to 278.9MPa, owing to its fully rigid structure and thus extended conformation. Such high level of mechanical properties were attributed to the existence of benzoxazole moiety in the molecular chain which served to enhance the chains' rigidity and strengthen the intermolecular association. D.Bhaumik et al^[3] calculated the intermolecular energies of benzobisoxazole polymers to get an insight into the extraordinarily high mechanical strength of these materials, the

calculations indicated that the interaction energies were very large and the intermolecular interaction was notably strong, they elucidated that the polymer chains' rigidity as well as the intermolecular association related to the benzoheterocyclic unit enhanced the mechanical properties and solvent resistance of these kind of materials remarkably. In this study, benzoxazole as well as imide structure should have strengthened the chains' stiffness intensively and contributed to the remarkable mechanical properties. PI-e, derived from BPADA, had the lowest value of tensile modulus, owing to the decrease in the chain's stiffness on account of the existence of ether linkage and isopropyl group in tetraacid dianhydride moiety.

Table 2 Mechanical properties of PI films obtained

sample	Modulus(GPa)	Strength(MPa)	Elongation at break(%)
PI-a	7.2±0.8	278.9±27.4	15.4±4.2
PI-b	5.1±0.6	271.3±36.1	26.9±9.8
PI-c	5.5±0.4	219.9±11.3	16.2±11.7
PI-d	4.9±0.8	213.8±35.9	21.4±3.4
PI-e	2.4±0.4	103.1±7.1	25.6±10.2

Thermal properties

Thermal properties of the polymers were identified by DSC, TGA, DMA, TMA method, the results were summarized in Table 3. TGA curves of the five PI films tested in nitrogen atmosphere were shown in Figure 1, the 5% weight-loss temperatures were detected between 484.9°C-579.0°C in nitrogen and 456.8°C -551.7°C in air, respectively. The heterocyclic moieties (imide ring and benzoxazole unit) in the polymer backbones imparted thermal resistance to the materials. Weight-loss temperatures of PI-d were the lowest among the series, because of the electron-donating methyl groups contained in this material.

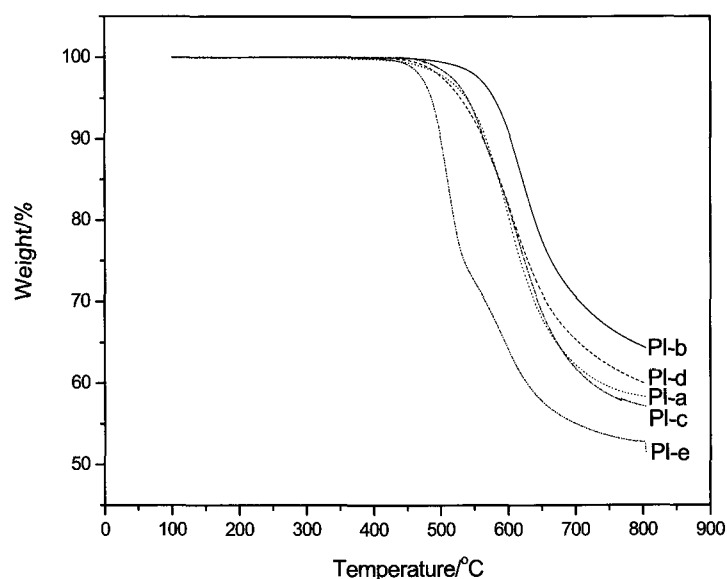


Figure 1 TGA curves of PIs in N₂ atmosphere

In the case of differential scanning calorimetry measurement, no well-defined glass transition except for PI-e was detected, which was common for wholly aromatic polyimide systems often possessing poor molecular mobility even above their T_g [4], while, like stated above, molecular backbone of PI-e tended to be rather flexible which induced distinct glass transition pattern in DSC analysis. On the other hand, PI derived from s-BPDA, ODA and BTDA all showed endothermic peak at 450°C approx. ,this might be due to the melting of crystallinity within the film, further consideration on this point will be given below.

Table 3 Thermal properties of PI films

sample	Tg(°C)		Tm(°C)	Td ⁵ (°C)	
	DSC	DMA	DSC	N ₂	Air
PI-a	--	411.8	--	540.3	514.6
PI-b	--	321.4	447.5	579.0	551.7
PI-c	--	349.8	461.3	529.3	503.7
PI-d	--	293.7	456.9	537.5	504.6
PI-e	252.3	262.9	--	484.9	456.8

Figure 2 is the results of DMA testing (storage modulus curves) of the five specimens

.DMA testing method is more sensitive in detecting polymers' transitions over DSC method owing to its specific nature. Tgs of these PIs were located in the range of 262.9°C-411.8 °C, depending on the structure of the dianhydride component and the stiffness of the polymer chain. For PI-a, the molecular chain was of fully rigid structure and without any flexible linkage thus tended to form a coplanar structure along the backbone, consequently leading to the highest Tg at 411.8°C; for PIb-d, glass transitions appeared between 293.7°C-349.8°C, owing to more or less rotational freedom of these chain segments depending on the dianhydrides used ,storage moduli of the four specimens mentioned above all decreased very gradually at the glass transition regions, this is often observed in highly cross-linked or highly crystallized polymers^[5],it's understandable here that the linear,rod-like chain segments of these PIs as well as the severe curing conditions(annealing at 400°C) induced strong interchain interactions and consequently formed highly-ordered structures. Besides, PIs from s-BPDA,BTDA and ODA underwent a second transition process at 450°C approx. after their glass transitions, corresponding to the occurrence of endothermic behavior in DSC analysis at this temperature range, these results again give an impression that there are crystallized structures within these film specimens. For PI-e, shape of E' curve was wholly different from the other four, E' went through a sharp decrease to less than 10MPa after the glass transition and no transition attributed to the melting of crystallinity was observed, this was related to the fact that this PI could take no ordered structure owing to the flexible and bent chain structure.

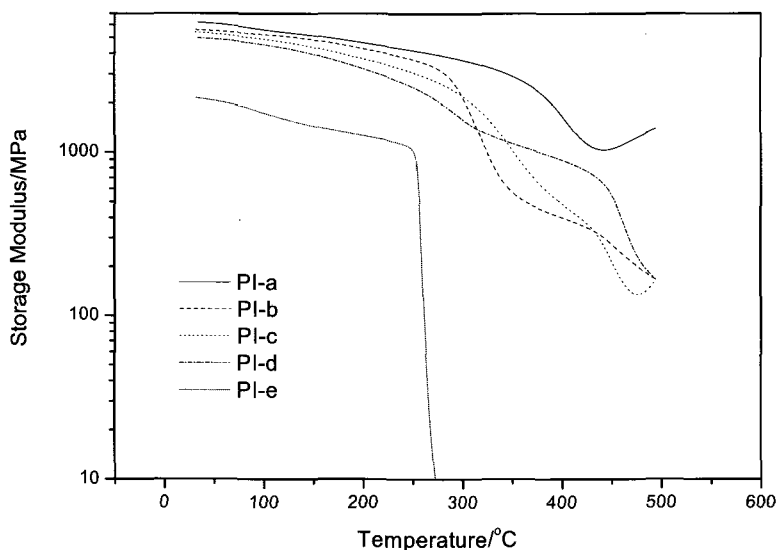


Figure 2 Dynamic storage modulus as a function of temperature for PI films obtained

Thermal expansion behavior was preliminarily examined by TMA method . Usually, the CTE of PI films tends to be inversely proportional to the degree of molecular in-plane orientation which depends on the linearity of the molecular chain and the film fabrication conditions.^[6] It was found that PI film derived from DAPBO and ODPa had CTE at 17ppm/K, this value was unexpectedly low because polyimides containing ether linkage in the backbone usually had a considerably high CTE such as 30ppm/K for PMDA-ODA type PI films (Kapton films). Rigid-rod structure of the polymer chains and high level of in-plane orientation induced by curing at high temperature should be responsible for keeping CTEs at low values. The diamine monomer containing rigid benzoxazole unit imparted stiffness and linearity to the polymer backbone, leading to greatly enhanced molecular orientation after curing and consequently considerably low CTEs.

Water absorption rate

Water absorption behavior of the five PI film specimens were measured as shown in **Table 4** ,that of Upilex-S was also measured for comparison. From the data, the films synthesized in this study had water absorption rate comparative to that of Upilex-S, implying that the introduction of benzoxazole moiety into the polymer backbone did not deteriorate the water absorption behavior of the PI films.

Table 4 Water absorption rate of the PI films

Sample	PI-a	PI-b	PI-c	PI-d	PI-e	Upilex-S
Waterabsorption(%)	1.83	0.92	1.51	0.72	0.34	1.49

Conclusion

In this study a series of polyimides containing benzoxazole moiety in the polymer backbone have been prepared by using a diamine monomer containing benzoxazole unit . The properties of the PI films obtained, such as mechanical properties, thermal and thermaloxidative stability, glass transition temperatures and dimensional stability were greatly enhanced due to the introduction of benzoheterocyclic unit into the main chain .

References

(Refs see p143)