Colorless, heat resistant polyimide films derived from 2,3,3',4'-biphenyltetracarboxylic dianhydride

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Abstract. The development of high performance colorless polyimide (PI) films is one of the targets of PI chemistry, since heat resistant colorless PI films are key materials for reliable plastic substrates in image display devices. In the present work, 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA) was used to polymerize with diamines to afford a series of PI, as shown in Scheme 1. Due to the fully aromatic composition, the films displayed high thermal decomposition temperatures (T5%). PI-FDA and PI-FFDA had similar glass transition temperatures (Tg) around 425°C, and much higher than that of PI-TFMB. PI-TFMB and PI-FFDA showed a transparent and colorless feature, with high transparency at 400nm (T400). Coefficients of thermal expansion (CTE) were found around 55ppm°C−1 for the series of PI films, larger than the requirement of flexible substrate applications, which could be attributed to the distorted chain structure derived from the a-BPDA component.

1. Introduction
Colorless, heat-resistant polymer films are key materials in the applications of display devices, liquid crystal alignment layers, color filters and optical compensation films. In addition, plastic substrates alternative to the current inorganic glass substrates are urgently required in the field of image display devices [1,2].

Polyimides (PIs) have satisfactory heat resistance, and have been used as electrical insulation materials in a variety of electronic devices. Besides, PI films are known to have good dimensional stability (low-CTE) characteristics. Therefore, PI films should be good candidate for the heat resistant, colorless polymer films [3,4].

The key point to develop colorless PI films is to weaken the charge transfer complex of the polymer chains [5,6], therefore, the monomers with distorted and twisted conformation should be employed, to disrupt the electronic conjugation between the polyimide chains [7].

In the present article, dianhydride monomers with distorted biphenyl linkage: 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA) was used to prepare colorless PI films, and the properties were discussed from the viewpoint of structure-property relationship.

2. Experimental
2.1 Reactants and reagents
2,2'-Bis(trifluoromethyl)benzidine (TFMB) and a-BPDA was supplied by Sunlight Pharmaceutical Co., Ltd. (Jiangsu, China), 9,9-bis(4-aminophenyl)fluorene (FDA) and 9,9-bis(4-amin-3-fluorophenyl)fluorene (FFDA) were provided by Tokyo Chemical Industry
Co., Ltd. (Tokyo, Japan), N,N-dimethylacetamide (DMAc) and isoquinoline were purchased from Yonghua Chemical Technology Co., Ltd. (Jiangsu, China) and Meryer Chemical Technology Co., Ltd. (Shanghai, China), respectively, m-cresol was provided by Meryer Chemical Technology Co., Ltd. (Shanghai, China) and distilled under reduced pressure prior to use. All the other commercially available reagents were analytical grade and used without purification.

![Scheme 1. Synthesis of the polyimides.](image)

2.2 Characterizations

FT-IR spectra were obtained on a Bruker Vertex 70 spectrometer at a resolution of 4cm⁻¹ in the range of 400 cm⁻¹-4000 cm⁻¹. Mechanical properties were examined at room temperature on a Instron 5966 universal testing apparatus with crosshead speed of 5mm/min. Thermogravimetric analysis (TGA) was performed using a TA TGA 550 with a temperature ramp of 10°C/min in nitrogen atmosphere. Temperatures at which 5% weight loss occurred (T_d5) were taken as parameters to evaluate thermal stability. Differential scanning calorimetric (DSC) analysis were conducted with a TA DSC 250 with a heating rate of 20°C/min in nitrogen purge. Thermal dimensional stabilities of the PI films were examined by TA TMA Q400 at a heating rate of 10°C/min in film tension mode and a constant load of 2g was applied to the sample in nitrogen flow (the initial dimension of film samples: 15mm long, 4mm wide, 20μm thick). Dynamic mechanical analysis (DMA) was carried out with a TA DMA 850 at a heating rate of 5°C/min and a load frequency of 1Hz in film tension geometry, glass transition temperature (T_g) was determined from the peak point of the loss factor curve. Solubility of the PI resins was qualitatively tested with 10mg powder in 1mL of solvent. Ultraviolet-visible (UV-Vis) spectra of the PI films were recorded with a Shimadzu UV-Vis 2550 spectrometer in the range of 800nm-200nm in transmittance mode.

2.3 Polymerization and film preparation

The polyimides were prepared by equimolar polyaddition of tetracarboxylic dianhydride and diamine, via one-step method in m-cresol, as shown in Scheme 1. A typical procedure was as follows. a-BPDA (2.1185g, 7.20mmol), TFMB (2.3071g, 7.20mmol), isoquinoline (0.45g, 3.5mmol) and m-cresol (25g) was added into a three-necked 100ml flask, which was equipped with mechanical stirrer, condenser, and nitrogen inlet/outlet. The mixture was stirred at 160°C for 1h to completely dissolve the reactants, afterwards, the mixture was heated to 200 °C and kept for 10h. The resulting viscous solution was cooled and precipitated to excessive amount of ethanol. The fibrous product was washed with ethanol for several times,
and dried at 120°C under vacuum for 24h to afford polyimide a-BPDA/TFMB.

Polyimide solution was obtained by dissolving PI powder in DMAc with solid concentration of 10%wt. Prior to film casting, the solution was filtered to remove insoluble impurities and degassed by standing still overnight. Afterwards, the solution was cast onto flat glass substrate and dried in an air convection oven at 50°C for 2h, 80 °C for 1h, 150 °C for 1h, followed by 250 °C under vacuum for 1h. After cooling down, the film was peeled off from the substrate by immersion in tap water for a few minutes. The thickness of PI films were controlled to be 20μm approx..

3. Results and discussion

3.1 Preparation of the PI films

Polyimides were prepared based on a-BPDA and several aromatic diamines. One-step polymerization was employed in m-cresol in the presence of isoquinoline, which acted as the catalyst. The polymerization proceeded smoothly and viscous homogenous solution was obtained after several hours of reaction. Figure 1 shows the FTIR spectra of the PI films, the absorptions of imide group were observed at 1780 cm⁻¹(C=O asymmetric), 1720 cm⁻¹(C=O symmetric) and 1370 cm⁻¹(C-N). The characteristic amide (1660 cm⁻¹) and -COOH (1710 cm⁻¹ and 3300 cm⁻¹) stretching vibrations derived from poly(amic acid) were not observed in the FTIR spectra, implying the polyimides had been imidized completely.

![Figure 1. FTIR spectra of PI films derived from a-BPDA.](image)

3.2 Solubility of the polyimides

The solubility of the polyimides was evaluated with several common organic solvents, as listed in Table 1. All of the polyimides could be dissolved in high boiling point polar solvents at room temperature, such as DMF, DMAc, NMP, m-cresol and DMSO. Besides, good solubility was observed in less strong solvents, such as dioxane, THF and chloroform. PI(DCBPDA/TFMB) was even soluble in ethyl acetate and acetone. It was noted that the solubility of polyimides was strongly dependent on the backbone structures, for polyimides based on a-BPDA, biphenyl-imide structures were highly twisted, this non-coplanar conformation disrupted the compact packing of the molecular chains and provided enhanced solubility.
Table 1. Solubility * of the polyimides.

| polyimide | DMAc | DMF | Dioxane | NMP | m-cresol | THF | CHCl₃ | EtOAc | Acetone | DMSO |
|-----------|------|-----|---------|-----|----------|-----|-------|-------|---------|------|
| PI-TFMB   | ++   | ++  | ++      | ++  | ++       | ++  | ++    | ++    | ++      | ++   |
| PI-FDA    | ++   | ++  | ++      | ++  | ++       | --  | ++    | --    | --      | ++   |
| PI-FFDA   | ++   | ++  | ++      | ++  | ++       | ++  | ++    | --    | --      | ++   |

* solubility was tested with 10mg of PI powder in 1mL solvent. (++) soluble at room temperature; (+−) soluble upon heating; (−−) insoluble upon heating.

3.3 Thermal and mechanical properties of the polyimides

Table 2. Thermal properties of the polyimide films.

| polyimide | Tg (°C) | T5% (°C) | CTE (ppm.K⁻¹) |
|-----------|---------|----------|---------------|
|           | DSC     | DMA      |               |
| PI-TFMB   | 363     | 361      | 583           | 55.3       |
| PI-FDA    | 429     | 430      | 572           | 54.4       |
| PI-FFDA   | 423     | 421      | 583           | 58.9       |

Thermal stability of the polyimides was evaluated by TGA in N₂ atmosphere, T5%, which was the parameter of thermal stability, was listed in Table 4. All the PI samples demonstrated good thermal stability with T5% beyond 570°C, attributed to the fully aromatic chemical composition of the polyimides.

DSC and DMA were employed to measure the glass transition temperatures (Tg) of the polyimides. Due to the bulky fluorene unit of FDA and FFDA, the corresponding PI displayed superior high Tg.

Thermal dimensional stability of the PI films was examined by TMA, the in plane CTE data in the solid state of the films were listed in Table 2. The data indicated that the CTE was pretty large for the series of PI films, which could be interpreted from the viewpoint of twisted, non-coplanar conformation.

The tensile properties of PI films were tested and the data were shown in Table 3. The series of films had similar values, due to the twisted and bended feature of the molecular chain, the PI films displayed moderate mechanical properties.

Table 3. Mechanical properties of the PI films.

| polyimide | Modulus (MPa) | Tensile strength (MPa) | Elongation at Break (%) |
|-----------|---------------|------------------------|-------------------------|
| PI-TFMB   | 2950.2 ± 31.0 | 141.2 ± 9.3            | 12.1 ± 2.3              |
| PI-FDA    | 2902.3 ± 35.5 | 139.7 ± 10.8           | 11.6 ± 1.9              |
| PI-FFDA   | 2891.7 ± 41.1 | 133.5 ± 11.9           | 11.2 ± 2.7              |

3.4 Optical transparency of the PI films

Optical transparency of the PI films were studied by the use of UV-Vis spectroscopy and shown in Figure 2. Compared to pale yellow colored PI-FDA, PI-TFMB and PI-FFDA exhibited a more transparent and colorless feature, an obvious blue shift of the spectra were observed compared to PI-FDA, as displayed in Figure 2. The good optical transparency of PI-TFMB and PI-FFDA was attributed to the suppressed formation of intra- and
inter-molecular charge transfer complex (CTC), due to the steric hindrance effect of 2,3,3’,4’-biphenyl linkage combined with the fluoro content.

![Figure 2. UV-vis spectra of PI films derived from a-BPDA.](image)

4. Conclusion

The dianhydride monomer a-BPDA had distorted and twisted biphenyl linkage, the electronic conjugation along the polymer chain could be disrupted and the optical transparency of the PI films would be improved. Based on this designed feature, colorless polyimide films were developed and the physical properties were examined. The series of PI films displayed high thermal stability and high Tg, due to the fully aromatic structures. Besides, good optical transparency was obtained as expected. The dimensional stability was rather inferior due to the bended and twisted chain conformation, which should be improved in the future work.

5. References

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