

## Organosoluble and transparent polyimides derived from *trans*-1,2-bis(3,4-dicarboxyphenoxy)cyclohexane dianhydride

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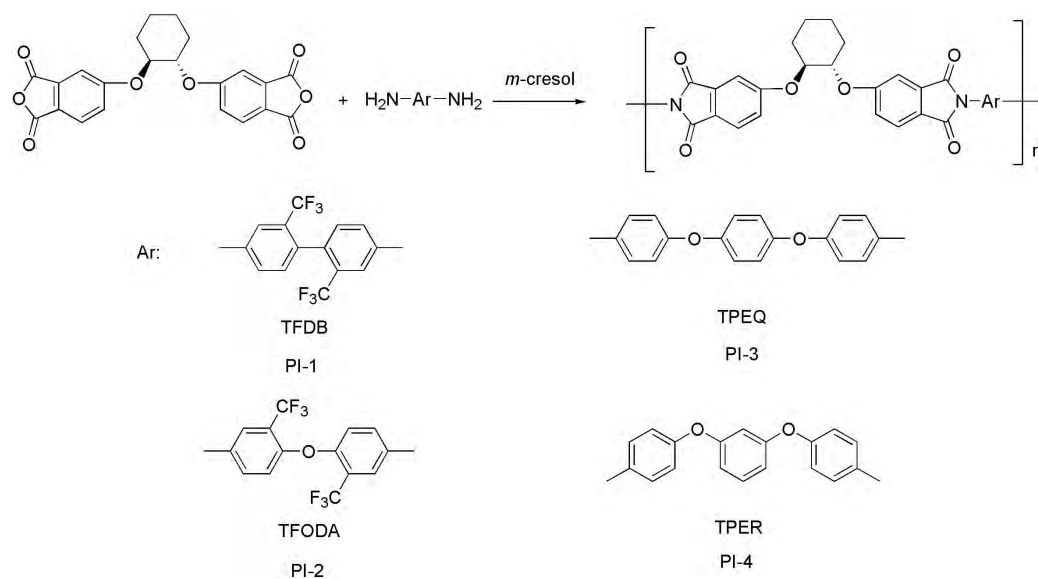
### Introduction

Colorless high-temperature polyimide materials are of special importance in application to flexible display substrates, nonlinear optical (NLO) waveguide materials and optical half-wave plates.<sup>[1-2]</sup> However, the wholly aromatic polyimides are pale yellow or deep reddish yellow because of their highly conjugated aromatic structures and inter-/intra-molecular charge transfer (CT) complex formation.<sup>[3]</sup> Besides, they have poor processability because of high softening temperatures and limited solubility in organic solvents owing to their rigid backbones and strong intermolecular interactions.<sup>[4-5]</sup> Therefore, many attempts have been made to decrease coloration and raise the solubility based on structural design by modification of dianhydrides and diamines, including incorporation of trifluoromethyl group, bulky group, unsymmetrical and alicyclic unit, ether chains into the polymers.<sup>[6-8]</sup>

We have previously reported the semi-aromatic transparent polyimides derived from dianhydrides or diamines containing cyclohexane-1,4-diol moiety, such as *trans*- and *cis*-1,4-bis(3,4-dicarboxyphenoxy)cyclohexane dianhydrides (*trans*- and *cis*-1,4-CHDPA),<sup>[9]</sup> 1,4-bis(4-aminophenoxy)cyclohexane diamines (1,4-HDA).<sup>[10]</sup> The polyimides with cyclohexane-1,4-diol exhibited good thermal stability and high optical transparency. On the other hand, compared with polyimides containing *para* linked phenylene units, the polyimides with *ortho* linked phenylene units exhibited lower coloration, higher optical transparency in the visible region, and better solubility in organic solvents, which prevented the extended close chain packing, and consequently, the charge transfer interactions.<sup>[11-13]</sup> Therefore, incorporation of more asymmetric and bulky alicyclic group, *trans*-cyclohexane-1,2-diol, into aromatic anhydrides would not only weaken electron-acceptability of dianhydride and enhance transparency, but also make the polymer chain more asymmetric and bent, increase the free volume and improve the organosolubility. Herein, a new dianhydride containing cyclohexane moiety, *trans*-1,2-bis(3,4-dicarboxyphenoxy)cyclohexane dianhydride (1,2-CHDPA), was designed and a series of polyimides were prepared by polycondensation of 1,2-CHDPA with various aromatic diamines. The solubility, thermal and optical properties of these polyimides as well as the isomeric effect of cyclohexane at different substituted position were also investigated.

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## Results and discussion

1,2-CHDPA were prepared through the nitro displacement reaction of 4-nitrophthalonitrile with *trans*-cyclohexane-1,2-diol followed by hydrolysis and dehydration. Polyimides **PI-1~PI-4** were synthesized from 1,2-CHDPA and various diamines via a conventional one-step procedure (Scheme 1). The inherent viscosities of the polyimides were ranged from 0.37 dL/g to 0.51 dL/g, as shown in Table 1, which were sufficiently high to form flexible and tough polyimide films.

**Table 1** Thermal properties of the polyimides.

| PI          | $\eta_{inh}^a$ (dL/g) | $T_g^b$ (°C) | $T_d$ (°C)     |     |                |     | Char yield <sup>d</sup> (%) |
|-------------|-----------------------|--------------|----------------|-----|----------------|-----|-----------------------------|
|             |                       |              | $T_{d5\%}^c$   |     | $T_{d10\%}^c$  |     |                             |
|             |                       |              | N <sub>2</sub> | air | N <sub>2</sub> | air |                             |
| <b>PI-1</b> | 0.37                  | 240          | 425            | 421 | 439            | 430 | 40                          |
| <b>PI-2</b> | 0.47                  | 225          | 424            | 413 | 438            | 440 | 43                          |
| <b>PI-3</b> | 0.49                  | 213          | 442            | 422 | 458            | 443 | 36                          |
| <b>PI-4</b> | 0.51                  | 198          | 445            | 422 | 460            | 444 | 37                          |

<sup>a</sup>The inherent viscosities of polyimides were measured at a concentration of 0.5 g/dL in DMAc at 30 °C. <sup>b</sup>Baseline shift in the second heating DSC traces, with a heating rate of 20 °C /min. <sup>c</sup>Temperatures at which 5% weight loss and 10% weight loss were recorded by TGA at a heating rate of 10 °C /min in nitrogen and air. <sup>d</sup>Residual weight (%) when heated to 800 °C in nitrogen.

DSC and TGA were used to evaluate the thermal properties of the polymers. The thermal behavior data of polymers are presented in Table 1. The  $T_g$  of polyimides are in range of 198-240 °C. The **PI-1** obtained from TFDB showed the highest  $T_g$  of 240 °C due to its rigid structure, while lowest  $T_g$  of 198 °C was observed for **PI-4** derived from TPER due to the presence of two flexible ether linkages and *meta* substitution between the phthalimide units. The thermal stability of the polyimides was studied by TGA at a heating rate of 10 °C /min. The decomposition temperatures at a 5% weight loss were recorded in the range of 424-445 °C in nitrogen, and 413-422 °C in air, respectively. Polyimides left more than 36% char yield at 800 °C in nitrogen. Interestingly, the temperatures for  $T_{d5\%}$  and  $T_{d10\%}$  of these polyimides based on 1,2-CHDPA in nitrogen and air atmospheres showed 30 °C higher than that polyimides based on *trans*-1,4-CHDPA.<sup>[9]</sup>

**Table 2** Solubility of the polyimides.

| PI          | Solvents <sup>a</sup> |      |     |     |      |                   |     |
|-------------|-----------------------|------|-----|-----|------|-------------------|-----|
|             | <i>m</i> -cresol      | DMAc | DMF | NMP | DMSO | CHCl <sub>3</sub> | THF |
| <b>PI-1</b> | ++                    | ++   | ++  | ++  | ++   | ++                | ++  |
| <b>PI-2</b> | ++                    | ++   | ++  | ++  | ++   | ++                | ++  |
| <b>PI-3</b> | ++                    | ++   | ++  | ++  | +    | ++                | +–  |
| <b>PI-4</b> | ++                    | ++   | ++  | ++  | +    | ++                | +–  |

The qualitative solubility was tested with 10 mg samples in 1 mL of solvent. ++: soluble at room temperature; +: soluble on heating; +–: partial soluble on heating; –: insoluble even on heating. <sup>a</sup> DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; NMP: *N*-methylpyrrolidone; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

The solubility of the polyimides was tested in various solvents, and the results are summarized in Table 2. **PI-1** and **PI-2** exhibited excellent solubility both in strong dipolar solvents and in common organic solvents such as *m*-cresol, DMAc, DMF, NMP, DMSO, CHCl<sub>3</sub>, and THF, and this is possibly due to the presence of bulky CF<sub>3</sub> groups, which reducing the interchain interactions.<sup>[5]</sup> Moreover, **PI-3** and **PI-4** were also soluble in *m*-cresol, DMAc, DMF, NMP, CHCl<sub>3</sub>, but less soluble in DMSO and THF. In addition, compared with the polyimides derived from *trans*-1,4-CHDPA,<sup>[9]</sup> the polyimide based on 1,2-CHDPA showed better solubility. This is attributed to that the latter had more asymmetric structure as well as more bent configuration in the 1,2-position of cyclohexyl moiety, which disrupted regularity of polymer chains and hindered denser chain packing.<sup>[11]</sup>

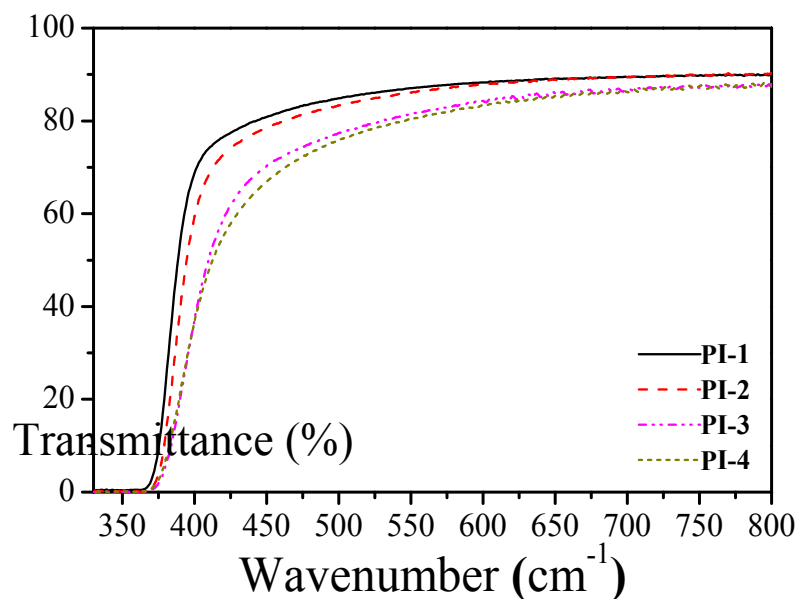
The UV-visible transmittance spectra were measured for polyimide films with thickness about 20 μm (Fig. 1). The cutoff wavelengths (absorption edge, λ<sub>0</sub>) and the transmittance at 400, 450, 500 nm from the UV–visible spectra are listed in Table 3. All polyimide films exhibited cut-off wavelengths shorter than 381 nm and were highly transparent. **PI-1**–**PI-2** with CF<sub>3</sub> group substituent showed obviously better transparent than **PI-3**–**PI-4** without CF<sub>3</sub> groups, which was attributed to the steric hindrance and inductive effect of bulky and electron-withdrawing CF<sub>3</sub> in diamine.<sup>[5]</sup> Besides, **PI-4** with *meta* substituent are slightly lighter in color than **PI-3**. The aliphatic cyclohexane moiety in dianhydride was presumably effective in decreasing electron-acceptability of dianhydride and weakening both intra- and intermolecular charge transfer interactions by breaking the conjugation.<sup>[9–10]</sup> Thus, the polyimides based on *trans*-1,2-CHDPA displayed high optical transparency, which was similar to polyimides based on *trans*-1,4-CHDPA.<sup>[10]</sup>

**Table 3** Optical properties of the polyimide films.

| PI          | d (μm) | λ <sub>0</sub> (nm) <sup>a</sup> | T <sub>400</sub> (%) <sup>b</sup> | T <sub>450</sub> (%) <sup>b</sup> | T <sub>500</sub> (%) <sup>b</sup> |
|-------------|--------|----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| <b>PI-1</b> | 20     | 370                              | 69                                | 81                                | 85                                |
| <b>PI-2</b> | 21     | 371                              | 59                                | 78                                | 83                                |
| <b>PI-3</b> | 19     | 380                              | 37                                | 67                                | 76                                |
| <b>PI-4</b> | 20     | 381                              | 37                                | 71                                | 78                                |

<sup>a</sup>λ<sub>0</sub>: UV cut-off wavelength.

<sup>b</sup>T<sub>400</sub>, T<sub>450</sub>, T<sub>500</sub>: transmittance at 400, 450, 500 nm.



**Figure 1.** UV-vis spectra of the polyimide films.

### Conclusions

A novel dianhydride containing *trans*-cyclohexane-1,2-diol moiety (1,2-CHDPA) was designed and successfully prepared to decrease the electron-acceptability of dianhydride and reduce the intra-/intermolecular interaction. Polyimides derived from 1,2-CHDPA with various diamines were synthesized in *m*-cresol via one-step method. All the polyimide films showed high optical transparency in the visible region, which proved the combination of 1,2-CHDPA and diamine monomers was a successful process for reducing charge transfer complex formation. In addition, isomeric effect of the dianhydride configuration between 1,2-position and 1,4-position of cyclohexyl moiety were also compared. It was found that 1,2-CHDPA-based polyimide exhibited better thermal stability and solubility. The improvement of solubility could be attributed to the bent structure of 1,2-CHDPA which increased their free volume, disrupted regularity of polymer chains and hindered denser chain stacking. The **PI-1** exhibited best optical transparency and highest  $T_g$  which may be a promising film for optical applications.

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