Preparation and Properties of Rigid Polyimides from Dianhydrides Having Various Number of Phenylene Units and p-Phenylenediamine

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Rigid aromatic polyimides PI-PP-m (m = 0, 1, 2, 3, 4) were synthesized from p-phenylenediamine and dianhydride DA-m having various numbers (m) of phenylene units, 3,3’4,4’-biphenyltetracarboxylic dianhydride (DA-0), 3,3”4,4”-p-terphenyltetra-carboxylic dianhydride (DA-1), 3,3””4,4””-p-quarterphenyltetra-carboxylic dianhydride (DA-2), 3,3”””4,4”””-p-quinquephenyltetra-carboxylic dianhydride (DA-3), and 3,3””””4,4””””-p-sexiphenyltetra-carboxylic dianhydride (DA-4), by a conventional two-step procedure that included ring-opening polymerization and subsequent thermal cyclic dehydration. The PI-PP-m (m = 0, 1, 2, 3) films were characterized by wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), thermogravimetry (TG), dynamic mechanical analysis (DMA), and stress-strain curves. The properties were compared on the basis of the number (m) of phenylene units. The glass transition temperatures (T_g) were observed at 270-280 °C as tan δ peak temperatures of DMA, and the values did not depend on m. The decrement of storage modulus at the T_g was smaller with increasing m. The thermal properties of PI-PP-0 were compared with those previously reported for Upilex-S type polyimides prepared from p-phenylenediamine and DA-0.

Keywords: Rigid aromatic polyimides, PI-PP-m, p-Phenylenediamine, 3,3””4,4””-p-Quarterphenyltetra-carboxylic dianhydride, 3,3”””4,4”””-p-Quinquephenyltetra-carboxylic dianhydride

1. Introduction

We synthesized dianhydrides DA-m having various numbers (m) of phenylene units, DA-2, DA-3, and DA-4. These were used to prepare aromatic polyimides containing p-quarterphenyl [1], p-quinquephenyl [2], and p-sexiphenyl [3] with commercially available aromatic diamines, such as 4,4’-oxydianiline, 3,4’-oxydianiline, 4,4’-diaminodiphenyl methane, p-phenylenediamine, and 4,4’-bis(4-aminoophenoxy) biphenyl, and diamines which authors had synthesized [4-11]. The properties were compared with those of polyimides from 3,3’, 4,4’-biphenyltetra-carboxylic dianhydride (DA-0) and 3,3””, 4,4”’-p-terphenyltetra-carboxylic dianhydride (DA-1), and discussed on the basis of the number (m) of phenylene units [1-13]. The T_g values depended on the connecting group and the structure of the diamine moiety, but did not depend on m, whereas there was a smaller decrease in the modulus above T_g with increasing m. It is reported that the rotational barrier of the connecting group played a determining role in the value of T_g [14,15]. The polyimides from p-phenylenediamine, which did not have a connecting group, had the highest T_g. In this study, the properties of the polyimides PI-PP-m (m = 0, 1, 2, 3, 4) [1-13] prepared from p-phenylenediamine and DA-m (m = 0, 1, 2, 3, 4) were compared in detail and examined on the basis of the number (m) of phenylene unit. p-Phenylenediamine did not have a connecting group, and DA-2, DA-3, and DA-4 had more phenylene units than DA-0. The structures of
PI-PP-m (m = 2, 3, 4) from p-phenylenediamine were thought to be more linear than that of PI-PP-0. The effect of having more phenylene units in the dianhydride moiety was examined.

2. Experimental

2.1. Materials

p-Phenylenediamine, dry N,N-dimethylacetamide (DMAc), and N-methyl-2-pyrrolidone (NMP) were obtained commercially and purified by distillation under reduced pressure. DA-0 was obtained commercially and purified by sublimation under reduced pressure. DA-1 was supplied by Hitachi Kasei Kogyo Co., Japan, and purified by recrystallization from acetic anhydride. DA-2, DA-3, and DA-4 were synthesized according to methods reported previously [1-3].

2.2. Polymerization

The polyimides were prepared by a conventional two-step method. The ring-opening polyaddition of DA-m (m = 0, 1, 2, 3, 4) in DMAc or NMP solutions of p-phenylenediamine yielded precursor polyamic acids PAA-PP-m (m = 0, 1, 2, 3, 4). The solution was cast on to a glass plate and the solvent was removed at 70°C to PAA-PP-m (m = 0, 1, 2, 3, 4) film. Thermal conversion of the film to polyimide PI-PP-m (m = 0, 1, 2, 3, 4) film was performed by successive heating at 100°C for 1 h, 200°C for 1 h, and finally 300°C for 1 h under vacuum (Scheme 1) [1-3, 12].

2.3. Measurement

For differential scanning calorimetry (DSC) and thermogravimetry (TG), a Shimadzu DSC-60 and Rigaku thermal analysis station TG 8110 were used, respectively, and measurements were made at a heating rate of 10°C min⁻¹ in air or nitrogen. Dynamic mechanical analysis (DMA) at 1.0 Hz and thermomechanical analysis were performed with the Advanced Rheometric Expansion System and thermomechanical analysis were performed by successive heating at 100°C for 1 h, 200°C for 1 h, and finally 300°C for 1 h under vacuum (Scheme 1) [1-3, 12].

3. Results and discussion

3.1. Polymer synthesis

The polyimides PI-PP-m (m = 0, 1, 2, 3, 4) were prepared by the usual two-step procedure involving the ring-opening polymerization of p-phenylenediamine to tetracarboxylic dianhydrides DA-m (m = 0, 1, 2, 3, 4) and subsequent thermal cyclodehydration as shown in Scheme 1. The ring-opening polyaddition of DA-m (m = 0, 1, 2) were carried out in DMAc at room temperature, leading to the formation of polyamic acids PAA-PP-m (m = 0, 1, 2) having inherent viscosities of 0.68-0.96 dLg⁻¹. The synthesis of PAA-PP-3 was conducted in NMP since the inherent viscosity in NMP was slightly higher than that in DMAc. The polymerizations proceeded homogeneously. In contrast, the solubility of PAA-PP-4 was very low, and the polyamic acid precipitated during polymerization. Table 1 summarizes the synthesis of the polyamic acids PAA-PP-m (m = 0, 1, 2, 3, 4) in the first step.

![Scheme 1. Preparation of PI-PP-m.](image)

Table 1. Synthesis of PAA-PP-m.

| Polyamic acid | Yield / % | ηinh / dL g⁻¹ |
|--------------|-----------|-------------|
| PAA-PP-0<sup>a</sup> | 97 | 0.96<sup>e</sup> |
| PAA-PP-1<sup>a</sup> | 95 | 0.91<sup>e</sup> |
| PAA-PP-2<sup>b</sup> | 93 | 0.68<sup>e</sup> |
| PAA-PP-3<sup>c</sup> | 94 | 1.12<sup>f</sup> |
| PAA-PP-4<sup>d</sup> | 95 | --<sup>g</sup> |

<sup>a</sup> Polymerization was carried out with DA (5.0 mmol) and p-phenylenediamine (5.0 mmol) in 20 mL DMAc at room temperature for 24 h.
<sup>b</sup> Polymerization was carried out with DA-2 (2.5 mmol) and p-phenylenediamine (2.5 mmol) in 30 mL DMAc at room temperature for 15 h.
<sup>c</sup> Polymerization was carried out with DA-3 (1.0 mmol) and p-phenylenediamine (1.0 mmol) in 30 mL NMP at room temperature for 5 h.
<sup>d</sup> Polymerization was carried out with DA-4 (1.25 mmol) and p-phenylenediamine (1.25 mmol) in 30 mL NMP at room temperature for 5 h.
<sup>e</sup> Measured at 0.5 g dL⁻¹ in DMAc at 30°C.
<sup>f</sup> Measured at 0.5 g dL⁻¹ in NMP at 30°C.
<sup>g</sup> Insoluble in NMP and DMAc.
In the second step, the thermal conversion of the polyamic acid to the polyimides was performed by heating the precursor polymers in the form of films successively at 100 °C for 1 h, 200 °C for 1 h, and finally 300 °C for 1 h under vacuum. The polyimides gave tough films with the exception of PI-PP-4, which could not be obtained as a film since PI-PP-4 was insoluble in NMP.

The formation of the polyimides was confirmed by appearance of IR absorption bands at about 1780 cm⁻¹, 1720 cm⁻¹, and 1360 cm⁻¹, characteristic of imide group. Elemental analysis values were in close agreement with the calculated values, also supporting polyimide formation.

3.2. Polymer properties

The crystallinity of the PI-PP-m (m = 0, 1, 2, 3) films was estimated by wide-angle X-ray diffraction (WAXD) (Fig. 1). Diffraction peaks were not observed in PI-PP-m (m = 0, 1, 2, 3), which tended to be amorphous in nature. The structure of PI-PP-0 is the same as that of Upilex-S type polyimides which are known as crystalline polyimides [16-18]. The crystallinity may depend on the synthetic method of the polyimide, and heat treatment of Upilex-S type polyimide films was carried out by stepwise heating up to 400 °C [17].

Glass transition temperatures (T₉) of the PI-PP-m (m = 0, 1, 2, 3) films were observed as tan δ peak temperatures at 270-280 °C, and a highly modulus glassy region was followed by a decrease of the modulus above the T₉ in the temperature dependence storage modulus (Fig. 2). The T₉ values did not depend on m, and the decrement of storage modulus at the T₉ was smaller with increasing m, similar to the polyimides from diamines having connecting groups [1-13]. The decrements were smaller than those of the polyimides from diamines having connecting groups with equivalent m.

In DSC measurements, PI-PP-m (m = 0, 1, 2, 3) films showed exotherms starting at about 320 °C (Fig. 3). The exotherms were considered to be due to the ordering. Thus, the Upilex-S type polyimide

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### Table 2. Thermal properties of PI-PP-m.

| Polyimide | T₁₀ (°C) a | T₁₀ (°C) b | T₉ (°C) c |
|-----------|------------|------------|-----------|
| PI-PP-0   | 570        | 590        | 270       |
| PI-PP-1   | 568        | 592        | 280       |
| PI-PP-2   | 600        | 645        | 270       |
| PI-PP-3   | 565        | 637        | 280       |
| PI-PP-4   | 595        | 645        | -- d      |

- a Temperature at which 10% weight loss was recorded by TG at a heating rate of 10 °C min⁻¹ in air.
- b Temperature at which 10% weight loss was recorded by TG at a heating rate of 10 °C min⁻¹ in nitrogen.
- c Glass transition temperatures of polyimide films prepared by imidation at 300 °C, determined as tan δ peak temperatures by DMA.
- d PI-PP-4 film was not obtained.

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Fig. 1. X-ray diffraction patterns of PI-PP-m (m = 0, 1, 2, 3).

Fig. 2. Dynamic mechanical behaviors of PI-PP-m (m = 0, 1, 2, 3).

In DSC measurements, PI-PP-m (m = 0, 1, 2, 3) films showed exotherms starting at about 320 °C (Fig. 3). The exotherms were considered to be due to the ordering. Thus, the Upilex-S type polyimide
was crystalline [16-18], and the \( T_g \) was high (about 400\(^\circ\)C) [19], whereas the \( T_g \) value of \( \text{PI-PP-0} \) was thought to be lower despite having the same structure because the \( \text{PI-PP-0} \) film was not heated at 400\(^\circ\)C during imidation. The \( \text{PI-PP-m} \ (m = 0, 1, 2, 3) \) films were annealed at 400 \(^\circ\)C for 30 min to develop ordered structures.

![Fig. 3. DSC curves of \( \text{PI-PP-m} \ (m = 0, 1, 2, 3) \).](image)

![Fig. 4. Dynamic mechanical behaviors of \( \text{PI-PP-m} \ (m = 0, 1, 2, 3) \) annealed at 400 \(^\circ\)C.](image)

The dynamic mechanical behaviors are shown in Fig. 4. The heights of the tan \( \delta \) peaks were considerably lower than those before annealing, and only that of \( \text{PI-PP-0} \) could be recognized as a tan \( \delta \) peak. The tan \( \delta \) peak temperature was 380 \(^\circ\)C, 110 \(^\circ\)C higher than that before annealing and approximately equal with \( T_g \) of Upilex-S type polyimides. In the temperature dependence storage modulus, decreases of the storage modulus above the \( T_g \) were smaller than those before annealing, and no discernible difference was found among annealed \( \text{PI-PP-m} \ (m = 1, 2, 3) \). Figure 5 shows the thermomechanical analysis of \( \text{PI-PP-m} \ (m = 0, 1, 2, 3) \). Only \( \text{PI-PP-0} \) showed remarkable expansion due to the \( T_g \) at around 420 \(^\circ\)C. Expansion changes of \( \text{PI-PP-1}, \text{PI-PP-2}, \) and \( \text{PI-PP-3} \) in the temperature range 50-450 \(^\circ\)C were 0.75\%, 0.57\%, and 0.46\%, respectively. The

![Fig. 5. Thermomechanical analysis of \( \text{PI-PP-m} \ (m = 0, 1, 2, 3) \).](image)

The increased \( T_g \) value of \( \text{PI-PP-0} \) and the smaller decreases of the storage modulus of \( \text{PI-PP-m} \ (m = 0, 1, 2, 3) \) were thought to be due to the development of ordered structures, but crystalline structures could not be detected in annealed \( \text{PI-PP-m} \ (m = 0, 1, 2, 3) \) films by X-ray diffraction, even for \( \text{PI-PP-0} \) (Fig. 6). Sharp diffraction peaks were not observed in annealed \( \text{PI-PP-1}, \text{PI-PP-2}, \) and \( \text{PI-PP-3}, \) and the interchain \( d \)-spacings were calculated from Bragg’s equation: \( d = \lambda/(2\sin\theta) \), with \( \theta \) determined as the maximum of the amorphous halo. The \( d \)-spacings thus obtained are considered to be the average interchain spacings [20]. The \( d \)-spacings of \( \text{PI-PP-1}, \text{PI-PP-2}, \) and \( \text{PI-PP-3} \) were 3.56 Å, 3.59 Å, and 3.75 Å, respectively, and increased with increasing \( m \), implying that the longer phenylene units had looser chain packings and larger free volumes.

![Fig. 6. X-ray diffraction patterns of annealed \( \text{PI-PP-m} \ (m = 0, 1, 2, 3) \).](image)
The mechanical properties of PI-PP-m (m = 0, 1, 2, 3) were measured and are summarized in Table 3. Tensile strength, elongation at break, and tensile modulus were 145-230 MPa, 11-17%, and 4.7-5.4 GPa, respectively, showing short elongation and high modulus due to the rigid structures. The elongations of PI-PP-m (m = 2, 3) were larger than those of PI-PP-m (m = 0, 1). The d-spacings of PI-PP-m (m = 0, 1, 2, 3) may have an influence on the tensile properties.

Table 3. Mechanical properties of PI-PP-m (m = 0, 1, 2, 3).

|       | Tensile strength (MPa) | Elongation at break (%) | Tensile modulus (GPa) |
|-------|------------------------|-------------------------|-----------------------|
| PI-PP-0 | 230                    | 12                      | 4.8                   |
| PI-PP-1 | 185                    | 11                      | 5.4                   |
| PI-PP-2 | 145                    | 16                      | 5.0                   |
| PI-PP-3 | 154                    | 17                      | 4.7                   |

4. Conclusion

Rigid polyimides PI-PP-m (m = 0, 1, 2, 3) were synthesized from p-phenylenediamine and tetracarboxylic dianhydrides having various number (m) of phenylene units by the usual two-step procedure involving thermal imidation at 300°C. The properties were compared on the basis of the number (m) of phenylene units. The T_g values were 270-280°C and did not depend on m, whereas the decrement of storage modulus at the T_g was smaller with increasing m. In the annealed PI-PP-m films at 400 °C, the decreases of the storage modulus above the T_g were smaller than those before annealing, and the T_g value of PI-PP-0 was highest at 380 °C. The tensile properties of the PI-PP-m (m = 0, 1, 2, 3) films did not depend on m.

References
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