Synthesis and characterization of polyimides containing pyridine ring

Zhun Li 1, Ying Wang 2 and Shaomin Zhu 1,2,*

1 School of Materials Science and Engineering, Dalian Jiaotong University, Dalian, China
2 School of Environmental and Chemical Engineering, Dalian Jiaotong University, Dalian, China

*Corresponding author e-mail: zgdljd@163.com

Abstract. Monomer 2,2'-bis [4-(5-amino-3-methyl-2-pyridoxy) phenyl] propane was successfully synthesized by 2-chloro-3-methyl-5-nitropyridine and bisphenol A, and the structure of pyridine diamine monomer was confirmed by 1HNMR. A series of polyimides were prepared by two-step polymerization of the pyridine diamine monomer with five aromatic dianhydride monomers. The results show that the polyimide films had good thermal stability and mechanical properties. Tg was 236-300 °C in DSC test and 240-299 °C from DMA test, T5% and T10% weight loss at N2 were 470-492 and 499-515 °C, respectively. Moreover, the polyimide films showed outstanding mechanical properties with tensile strength of 72-90 MPa, tensile modulus of 1.8-2.4 GPa, and breaking elongation of 5-12%. The cut-off wavelength was 338-399nm.

1. Introduction

Polyimides have excellent heat resistance, chemical resistance, electrical and mechanical properties. They have been extensively used in so many fields, such as optoelectronic industry, liquid crystal materials, aerospace industry, and functional films, etc [1-5]. A large number of studies have shown that the structure of polymer segments determines the properties of polyimides. The synthesis of polyimide is usually obtained by polycondensation of diamine monomer and dianhydride monomer, and the most frequently used methods include one-step, two-step and chemical ones [6,7]. Different preparation methods have certain influence on the properties of polyimide, but the main properties of polyimide are greatly determined by the chemical structure of main chain. Recently, the introduction of nitrogen-containing aromatic heterocyclic units into the main chain of polyimide has been widely reported, for example, the introduction of benzimidazole, pyridazine, pyridine, and pyrimidine has largely made polyimide possess outstanding heat resistance and mechanical properties [8,10].

Because it is extremely easy to get pyridine ring and its cost is low, and its rigidity is stronger than that of benzene ring, its heat resistance is similar to that of benzene ring [11]. In this work, pyridine ring structure was introduced into diamine monomers to synthesize 2,2'-bis [4-(5-amino-3-methyl-2-pyridoxy) phenyl] propane. A series of polyimide films were successfully prepared by two-step reaction of the obtained pyridine diamine monomers with PMDA, BTDA, s-BPDA, ODPA and 6FDA, respectively. The purpose is to improve the glass transition temperature and optical properties of polyimides, while maintaining their inherent thermal and mechanical properties.
2. Experimental

2.1. Materials

Pyromellitic dianhydride (PMDA), 3,3',4,4'-Benzophenone tetracarboxylic dianhydride (BTDA), 3,3',4,4'-Biphenyl tetracarboxylic dianhydride (s-BPDA), 4,4'-Oxydiphthalic anhydride (ODPA) and 4,4'- (Hexafluoroisopropylidene) diphthalic anhydride (6FDA) were thoroughly dried with acetic anhydride for 10h under 150 °C in vacuum before using. Potassium carbonate was carefully dried at 130 °C for 10h in vacuum. Toluene and DMAc were refluxed with calcium hydride, and then had a vacuum distillation and were stored in reagent bottle, adding molecular sieve for drying. Other raw materials and reagents could be used directly without being treated.

2.2. Instruments and Methods

Fourier transform infrared spectrometer (Vector-22 Bruker, Germany); Nuclear magnetic resonance spectrometer (BRUKER-300, Germany); Differential scanning calorimeter (DSC-Q100 TA, USA), temperature range: 50-350 °C, heating rate: 10 °C/min, N2; Thermogravimetric analyzer (TGA-2050 TA, USA), temperature range: 100-800 °C, heating rate: 10 °C/min, N2; Dynamic thermomechanical analyzer (DMA-Q800 TA, USA), tensile mode of thin film, temperature range: 50-300 °C, heating rate: 5 °C/min, testing frequency: 1Hz. Shimadzu UV-Vis 2501 ultraviolet visible light analyzer, transmission mode; X-ray Diffractometer (D/MAX 2500 Japan), 5-50 °, λ=1.54Å, 40kV, 50mA.

The mechanical properties were tested by AG-I universal testing machine (Shimadzu, Japan). The test conditions were as follows: tensile rate was 5mm/min, film thickness was about 30μm, width was 3mm, length was 4cm, and tensile strength (TS), modulus (TM) and elongation at break (EB) were obtained by the auxiliary computer.

2.3. Synthesis of Monomers

Synthesis of 2, 2-bis [4-(5-nitro-3-methyl-2-pyridinoxy) phenyl] propane (a)

Under N2 protection, 2-chloro-3-methyl-5-nitropyridine (12.08g, 70mmol) and bisphenol A (7.31g, 32mmol) were added to 250mL boiling flask-3-neck with mechanical agitator, thermometer and reflux condensation unit. And then, potassium carbonate (9.67g, 70mmol) and 70mL DMF were added into the reaction bottle and stirred at room temperature for 30min until completely dissolved, the system was heated to 80 °C and stirred continuously for 6h. The mixture was cooled to room temperature and then introduced into 500mL deionized water, solid product was precipitated, filtered and washed with deionized water, and the obtained crude product was dried in vacuum at 80 °C for 10h. The crude product was recrystallized and purified by ethanol to obtain white solid product with 90% yield.

Synthesis of 2,2'-bis [4-(5-amino-3-methyl-2-pyridinoxy) phenyl] propane (b)

Under nitrogen protection, 2,2-bis [4-(5-nitro-3-methyl-2-pyridinoxy) phenyl] propane (a, 10.00g, 20.0mmol), 1.0g palladium carbon (10%), 150 mL anhydrous dioxane ring were added to a 250mL reaction bottle with mechanical agitator, thermometer and reflux condensation unit. And then, potassium carbonate (9.67g, 70mmol) and 70mL DMF were added into the reaction bottle and stirred at room temperature for 30min until completely dissolved, the system was heated to 80 °C and stirred continuously for 6h. The mixture was cooled to room temperature and then introduced into 500mL deionized water, solid product was precipitated, filtered and washed with deionized water, and the obtained crude product was dried in vacuum at 80 °C for 10h. The crude product was recrystallized and purified by ethanol to obtain white solid product with 90% yield.
and the white powder 2,2'-bis [4-(5-amino-3-methyl-2-pyridoxy) phenyl] propane (b) was received for 7.7g. The yield of the product was 87 %. The monomer reaction formula is shown in Fig 1.

Characterization of Monomers

Molecular structure and NMR spectra of (a) and (b) are shown in Figures 2 and 3. It can be seen from the figure that the chemical shifts of H atoms in (a) belong to: $^1$H NMR (DMSO-d$_6$, ppm)—8.83 (d, 1H), 8.54(d, 1H), 7.37-7.29 (m, H), 7.17-7.10 (m, H), 2.41 (d, 1H), 1.72 (t, 3H); $^{13}$C NMR (DMSO-d$_6$, ppm)—164.7, 150.7, 147.1, 141.4, 140.2, 134.6, 127.7, 122.2, 121.1, 41.9, 39.5, 30.4, 15.3. Chemical shift attribution of H atoms in (b): $^1$H NMR (DMSO-d$_6$, ppm)—7.38 (d, H), 7.17-7.11(m, H), 6.95 (d, 1H), 6.81-6.76 (m, H), 5.02 (d, 2H), 2.10 (s, 3H), 1.61 (s, 3H); $^{13}$C NMR (DMSO-d$_6$, ppm)—154.2, 151.6, 144.3, 142.1, 129.9, 127.3, 125.8, 122.3, 117.8, 41.4, 39.5, 30.6, 15.6. Among them, 1 is the methyl proton peak in propane, 2 and 3 are ascribed to the methylene proton peak in different substitution positions of benzene ring, 4 and 5 are both the methylene proton peak in different substitution positions of pyridine ring, 6 attributes to the methyl proton peak in pyridine ring, and the attribution of the peaks for 13 carbon atoms in (a) and (b) is very clear.

By analyzing and identifying the polymers and comparing the $^1$H NMR spectra of (a) and (b), it is found that in (b) spectrum there is a single absorption peak of H atom on -NH$_2$ labeled as 7, and the chemical shift signal appeared in $\delta$5.02, proving that -NO$_2$ in (a) was completely reduced to -NH$_2$, which further confirms the reductive reaction process from (a) to (b).

2.4. Synthesis of polyimides

Polyimide was synthesized by condensation reaction. The monomer (b) was polycondensated with aromatic dianhydride PMDA, BTDA, s-BPDA, ODPA and 6FDA respectively in DMAc solvent to form PAA(polyacrylic acid) precursor. Polyimide was prepared by thermal imidization at high temperature and labeled as PI-1, PI-2, PI-3, PI-4 and PI-5, respectively.
Taking PI-1 as an example, the specific reaction process is as follows: the monomer (b) (1.7622g, 4mmol) and 8g DMA were placed into 50mL reaction bottle, and to stir until dissolve completely, and then PMDA (0.8725g, 4mmol) was added into the above mixture in two batches. In addition, 6.53g DMAc was added to adjust the solid content of the system for 15%. The viscous PAA solution was gained by stirring the reaction solution at room temperature for 24h.

On a flat and clean glass plate, PAA solution was scraped into a film with a scraper, and then the glass plate was put into the oven. The solvent was removed by pre-drying according to the heating procedure of 80°C/3h, 100°C/1 h, 120°C/0.5h. After cooling to room temperature, the glass plate was put into the vacuum oven and a thermoimidization was done according to 200°C/0.5h, 250°C/0.5h, 300°C/1h. After the thermal imidization reaction, the film was immersed in deionized water. After a period of time, the film naturally detached from the glass plate, and finally the polyimide film was obtained, which was recorded as PI-1. PI-2, PI-3, PI-4 and PI-5 were synthesized by the same method. The related synthesis process is shown in Fig 4.

3. Results and discussion

3.1. FT-IR characterization of Polyimide

Figure 5 shows the FTIR spectra of polyimides, from which the chemical structure of polymers can be determined. It can be seen from the figure that all polyimides showed distinct characteristic absorption peaks of imide groups. Among them, 1780cm⁻¹ belonged to an asymmetric stretching vibration absorption peak of C=O, 1725cm⁻¹ attributed to a symmetric stretching vibration peak of C=O, and the stretching vibration peaks of cyclic imides located on 1395 and 1092cm⁻¹. In addition, the characteristic peaks of benzene ring appeared at 1608 and 1505cm⁻¹. At the same time, there were no characteristic absorption peaks of hydrogen (N-H) on amino group and amide group (-CO-N-H) (3230, 3400, 1570cm⁻¹), and no characteristic absorption peaks of hydroxyl group (-COOH, 1680cm⁻¹), which confirmed that the polymer had been completely imidized.

3.2. Thermal properties of Polyimide

The thermal properties of the synthesized polyimides were tested by differential scanning calorimetry (DSC), dynamic thermomechanical analysis (DMA) and thermogravimetric analysis (TGA), as shown in Figures 6, 7 and 8; the analytical data are listed in Table 1.

Glass transition temperature refers to the transition temperature of polymer macromolecule chain segment from frozen state to free movement, represented by Tg. Meanwhile, the rigidity and flexibility of polymers can be changed by the chemical bonds and groups with different structures, which lead to different steric hindrances affecting chain motion. The introduction of rigid groups will increase Tg, while the introduction of flexible groups will reduce Tg.

DSC test is based on the relationship between power difference and temperature from the tested sample and the reference material under programmed temperature control, and the curve of heat flow
with temperature is obtained. In the DMA curve, the Tg is determined as the peak temperature of the loss modulus (E'') method. It should be noted that there are slight differences in Tg values measured by DSC and DMA, mainly due to the different responses of two instruments to the tested samples.

From the DSC curve, it could be clearly seen that the Tg of the synthesized polyimide was between 236-300°C, and the Tg of the polyimide was between 240-299°C in the DMA test. The Tg order from high to low was PI-1>PI-3>PI-5>PI-2>PI-4. PI-1 synthesized from b-PMDA had the highest Tg, which was basically because of the strongest rigidity of the polymer backbone[12]; PI-4 based on b-ODPA had lower Tg due to the flexibility of ether bonds between phthalimide units[13]; PI-5 synthesized from b-6FDA had higher Tg than PI-2, entirely owing to the inhibition of free rotation of the polymer backbone by trifluoromethyl groups.

T5% and T10% of polyimide in N2 were 470-492 and 499-515°C, respectively. The residual mass of polyimide at 800°C was 39-59%. Moreover, viewed from T5%, according to the order of s-BPDA, 6FDA, PMDA, ODPA and BTDA, the intermolecular force decreased gradually, the flexibility of molecular chain increased gradually, and the thermal stability of materials decreased accordingly. Generally, TGA results revealed that the synthesized polyimides had excellent thermal stability.
3.3. Mechanical properties of Polyimide

Table 2. Mechanical properties of PI films

| Polymides | $T_S$ a (MPa) | $T_M$ b (GPa) | $E_B$ c (%) |
|-----------|--------------|--------------|-------------|
| PI-1      | 72           | 2.4          | 5           |
| PI-2      | 74           | 2.2          | 12          |
| PI-3      | 84           | 2.3          | 12          |
| PI-4      | 90           | 2.0          | 12          |
| PI-5      | 78           | 1.8          | 6           |

a $T_S$: Tensile strength; b $T_M$: Tensile modulus; c $E_B$: Elongation at break

Table 2 exhibits the mechanical properties of the synthesized polyimides. It can be clearly displayed that polyimide films had good mechanical properties, including tensile strength of 72-90 MPa, tensile modulus of 1.8-2.4 GPa and elongation at break of 5-12%. The order of tensile strength of polyimide was ODPA > s-BPDA > 6FDA > BTDA > PMDA. PI-1 synthesized from b-PMDA had the lowest tensile strength and elongation at break, which was chiefly due to the strong rigidity and linearity of the formed molecular chains, but its low molecular weight and lack of entanglement between the molecular chains led to poor toughness of the films. PI-4 derived from b-ODPA had good elasticity because of the flexible ether bonds between phthalimide units. Comparing with the thermal stability of polymers, the thermal stability and mechanical properties of polyimides interfered with each other, and the mechanical properties of polyimides with excellent thermal stability were usually unsatisfactory, and vice versa. Therefore, how to optimize the reaction conditions of dianhydride and diamine and select the appropriate ratio were particularly important.

3.4. Optical properties and XRD characterization of Polyimide

![Figure 9: Ultraviolet-visible spectra of PI films](image)

Fig. 9 Ultraviolet-visible spectra of PI films

![Figure 10: Wide-angle X-ray diffraction patterns of PI films](image)

Fig. 10 Wide-angle X-ray diffraction patterns of PI films
Table 3. Optical properties of PI films

| Polymides | PI-1 | PI-2 | PI-3 | PI-4 | PI-5 |
|-----------|------|------|------|------|------|
| $\lambda_{\text{cut-off}}$ (nm) | 384  | 338  | 399  | 365  | 339  |
| Transmittance (%) | 79   | 89   | 13   | 88   | 60   |

$^a$ $\lambda_{\text{cut-off}}$, cut-off wavelength. $^b$ Transmittance, at 450nm.

The optical properties of polyimide were measured by ultraviolet-visible spectrometer, and the polyimide film was directly measured by transmission mode for thickness of about 10μm. The ultraviolet-visible spectra are observed in Figure 9, and the optical properties are measured and listed in Table 3. All of the polyimides showed excellent optical transmittance, and the cut-off wavelength was 338-399nm. Except for PI-3 the transmittance of other polymers at 450nm was 60-89%. PI-2 derived from b-BTDA exhibited higher transmittance(89%) and lower cut-off wavelength(338nm), which was primarily attributed to the fact that the deformed structure of BTDA weakened the chain stacking and thus reduced the formation of intermolecular charge transfer complexes(CTC). About its structure the C=O group on benzophenone had no or very little cross-linking phenomenon, which made the film exhibit excellent transparency and thus PI-2 had better transmittance than other polyimides[14]. PI-3 synthesized by b-s-BPDA revealed lower transmittance and higher cut-off wavelength, which was probably due to the cross-linking phenomenon during the polymerization process, and could be clearly identified from the yellowish color of the film.

The crystalline morphology of polyimide was analyzed by wide-angle X-ray diffractometer, scanning angle 2$\theta$ ranged from 5 to 50°, and the thin films were used as samples. As shown in Figure 10, X-ray diffraction curves of polyimide films exhibited a group of broad peaks, which indicated that polyimides were amorphous. The formation of this amorphous structure was primarily attributed to the introduction of flexible ether bonds and methyl substituted pyridine, which played a loosening role in the accumulation of polymer chains and chains. Meanwhile, the introduction of pyridine heterocycles caused the distortion of polymer skeleton and weakened the orderliness of polymer chains.

4. Conclusions

In this paper, 2,2'-bis[4-(5-amino-3-methyl-2-pyridoxy) phenyl] propane (b) monomer was prepared from 2-chloro-3-methyl-5-nitropyridine, and a series of polyimide were synthesized based on monomer (b). The characterization of thermal, mechanical and optical properties of polyimide was studied in detail. The results showed that the synthesized polyimides had excellent thermal stability. Tg was between 236-300°C in DSC test and 240-299°C from DMA test. PI-1 synthesized from b-PMDA had the highest Tg. T5% and T10% of polyimides in N$_2$ were 470-492 and 499-515°C, respectively. The residual mass of polyimide at 800°C was 39-59%. Polyimide films had good mechanical properties, including tensile strength of 72-90MPa, tensile modulus of 1.8-2.4Pa and elongation at break of 5-12%. All of the polyimides showed better optical transmittance, and the cut-off wavelength was 338-399nm. Except for PI-3 derived by b-s-BPDA, the transmittance of other polymers at 450nm was 60-89%.

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