

2,2'-Bis[4-(6-amino-3-pyridinoxy) phenyl] Propane에서 유도된 새로운 폴리이미드 합성 및 분석

Zhun Li*, Yu Zhao*, Ying Wang**, and Shaomin Zhu***,†

*School of Materials Science and Engineering, Dalian Jiaotong University

**School of Environmental and Chemical Engineering, Dalian Jiaotong University

(2019년 10월 18일 접수, 2019년 12월 23일 수정, 2020년 1월 5일 채택)

Synthesis and Characterization of Novel Polyimides Derived from 2,2'-Bis[4-(6-amino-3-pyridinoxy) phenyl] Propane

Zhun Li*, Yu Zhao*, Ying Wang**, and Shaomin Zhu***,†

*School of Materials Science and Engineering, Dalian Jiaotong University, 116028, Dalian, People's Republic of China

**School of Environmental and Chemical Engineering, Dalian Jiaotong University, 116028, Dalian, People's Republic of China

(Received October 18, 2019; Revised December 23, 2019; Accepted January 5, 2020)

Abstract: A novel pyridine-containing aromatic diamine monomer, 2,2'-bis[4-(6-amino-3-pyridinoxy) phenyl] propane, was synthesized through nucleophilic substitution reaction. A series of polyimides (PIs) were obtained by the polycondensation reaction of synthesized monomer with four commercial dianhydrides. The structure and properties of the resulting PIs were characterized by Fourier transform infrared spectroscopy, differential scanning calorimetric analysis, dynamic mechanical thermal analysis, thermogravimetric analysis, and X-ray diffraction. The PIs exhibited good thermal stability with glass transition temperature of 231 to 303 °C by DSC and 205 to 274 °C by DMA. The temperature at 5% weight loss was 478 to 501 °C in nitrogen atmosphere, and the residual mass range at 800 °C was 42-55%. The excellent mechanical properties included tensile strength of 98-102 MPa, elongation at break of 6-18%, and tensile modulus of 2.8-3.0 GPa. The cut-off wavelength ranged from 391-440 nm, indicating that the resulting PIs had desirable optical performance.

Keywords: polyimides, pyridine heterocyclic ring, synthesis, structure and properties.

Introduction

Polyimide (PI) is divided into four types of pyromellitic PI, soluble PI, polyamide imide, and polyether imide, which are a class of polymers containing imide rings on the molecular main chain through the reaction of dianhydride and diamine.¹⁻⁵ Due to its five-membered ring structure, PI has several excellent properties, such as high modulus, great strength, excellent thermal stability, and flame retardancy. It has been widely used in the fields of aerospace, electrical and electronic, glass, locomotive, precision machinery, and automatic office machinery.⁶⁻¹⁰ More and more people have fully realized the wide application prospect of PI.

However, owing to the rigid backbones and the strong intermolecular interactions of the aromatic PIs,^{11,12} high melting or glass transition temperatures, low optical transmittance, and poor solubility were observed, greatly restricting their applications in some fields.¹³⁻¹⁶ Therefore, many researchers have made considerable efforts and contributions; for example, flexible linkages, non-coplanar structures, and heterocycle units are usually introduced into the polymer backbones to enhance the thermal properties, optical transparency, solubility, and so on.¹⁷⁻²¹

In this paper, a series of novel PIs based on pyridine were designed and synthesized. The introduction of pyridine into the main chain of PI has many advantages. Pyridine ring structure has aromaticity and symmetry, revealing excellent heat resistance and good mechanical properties.^{22,23} The structure of pyridine ring can significantly increase the orientation force between PI and solvent.²⁴ At the same time, the polarity of N

†To whom correspondence should be addressed.
zgdjld@163.com, ORCID[®]0000-0002-2555-8778
©2020 The Polymer Society of Korea. All rights reserved.

atoms in pyridine ring is larger; hence, it could correspondingly increase the polarity of PI, enhance the solubility of polymer in polar organic solvent, and improve the chemical resistance. Compared with the benzene ring structure, the mole refraction of the C=N=C bond in the pyridine ring structure is higher.^{25,26} Therefore, the introduction of pyridine ring in the PI molecular skeleton can effectively raise the refraction and optical transmittance, as well as greatly improve the color depth and bad transmittance of PI materials.²⁷⁻³⁰ It is of particular significance to design and synthesize new monomers containing pyridine and to incorporate new monomers into PI backbones while maintaining the desirable properties.

In this study, on the basis of previous work,³¹ a novel pyridine-containing diamine, 2,2'-bis[4-(6-amino-3-pyridinoxy) phenyl] propane (b), was prepared and characterized. A series of new PIs were successfully obtained with the reaction of monomer (b) and commercial dianhydrides through a traditional two-step procedure. The structural, thermal, mechanical, optical, and solubility properties of the resulting PIs were researched in detail. The resulting PIs derived from pyridine had a good combination of performances, such as higher tensile strength, better interesting optical property, which suggested promising potential applications in the optoelectronic devices and sensor applications fields.

Experimental

Materials. 5-Bromo-2-nitropyridine and bisphenol A (BPA) (Acros, Belgium) were of analytical grade and used without further purification. BPA was obtained from Acros in Shanghai. Pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 3,3',3,4'-biphenyltetracarboxylic dianhydride (s-BPDA), and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) were supplied by Sinopharm Chemical Reagent Beijing Co. Ltd. These aromatic dianhydrides were all recrystallized from acetic anhydride and then dried at 150 °C in vacuum for 10 h before using. Potassium carbonate (Acros), 80% hydrazine monohydrate (Acros), and 10% palladium on charcoal (Pd/C) (Acros) were used as received. Toluene and *N,N*-dimethylacetamide (DMAc) were purified by vacuum distillation over CaH₂ and stored over 4 Å molecular sieves before using. The other commercially available reagents and solvents were applied directly without further purification.

Characterization. Nuclear magnetic resonance (NMR) was adopted to characterize the synthesized precursor and monomer,

and a series of PIs were characterized by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetric (DSC) analysis, dynamic mechanical thermal analysis (DMA), thermogravimetric analysis (TGA), ultraviolet–visible (UV-Vis) spectroscopy, X-ray diffraction (XRD), gel permeation chromatography (GPC), and so on. ¹H and ¹³C NMR spectra were recorded on a BRUKER-300 spectrometer (Germany) operating at 300 and 75 MHz, respectively. FTIR spectroscopy was performed using a Bruker Vector 22 spectrometer (Germany) at a resolution of 4 cm⁻¹ in the range of 400–4000 cm⁻¹ for 128 scanning times. The powder samples were measured after KBr pressing, and the film samples were directly tested. Weight average molecular weights (*M*_w) and number-average molecular weights (*M*_n) were determined on the basis of polystyrene calibration on a PL-GPC 220 instrument (USA) at a flow rate of 1.0 mL/min as an eluent for DMF. Inherent viscosities (*η*_{inh}) of PIs were obtained at a 0.5 g/dL of DMAc solution concentration with an Ubbelohde viscometer at 25 °C. DSC analysis was conducted on a TA instrument DSC Q100 at a scanning rate of 10 °C/min under N₂ flow of 50 mL/min. The glass transition temperature of the polymer was tested two times, the thermal history was eliminated for the first time, and the second test data were adopted. DMA was conducted on a TA instrument DMA Q800 (USA) at a heating rate of 5 °C/min and a load frequency of 1 Hz in film tension geometry under nitrogen atmosphere. TGA was conducted with a TA-2050 (USA) at a heating rate of 10 °C/min under nitrogen atmosphere. The UV-vis spectra of PI films were recorded with a Shimadzu UV-Vis 2501 spectrometer (Japan) in transmittance mode at room temperature. The cut-off wavelength (*λ*_{cut-off}) was used as the parameter to evaluate the transparency of the films. XRD (D/MAX 2500 H; Rigaku Co. Japan) was used for measuring the morphology of PI thin films. Copper *K*_α (*λ*=1.54 Å) radiation was operated and filtered using a monochromator. An X-ray generator was run at 40 kV and 50 mA.

In addition, the mechanical properties of the synthesized PI films were tested using an AG-I universal testing apparatus (Shimadzu, Japan) with a tensile rate of 5 mm/min. The films were tested at room temperature (thickness of approximately 30 μm, width of 3 mm, and length of 6 cm), and the tensile strength (*T*_s), tensile modulus (*T*_M), and elongation at break (*E*_B) were calculated by the experimental subsidiary computer. Solubility test was performed, that is, to place 10 mg PI in 1 mL solvent at room temperature for 24 h, and then to observe its dissolution state. Selected solvent included *N,N*-

dimethylformamide (DMF), DMAc, *N*-methyl-2-pyrrolidone (NMP), dimethyl sulphoxide (DMSO), tetrahydrofuran (THF), chloroform, and acetic acid.

Monomer Synthesis. **2,2'-Bis[4-(6-nitro-3-pyridinoxy)phenyl] Propane (a):** Under the protection of nitrogen, a mixture of 5-bromo-2-nitropyridine (13.40 g, 66 mmol) and BPA (6.85 g, 30 mmol) were added into a 250 mL flask fitted with a mechanical stirrer, thermometer, and reflux condenser. Then potassium carbonate (9.12 g, 66 mmol) and 60 mL of DMF were added to the reaction bottle. After stirring for 30 min at room temperature, the mixture was dissolved, heated to 80 °C, and continuously stirred for 6 h. After cooling the mixture to room temperature, the mixture was poured into 500 mL of deionized water, and the solid product was precipitated. After filtering, the product was collected and washed with the deionized water. The obtained crude product was dried in vacuum at 80 °C for 10 h. The crude product was recrystallized and purified with DMF/ethanol, and the yellow solid product was obtained and marked as (a). The yield of the product was 85%, and the melting point was 156.8 °C (DSC peak at a heating rate of 10 °C/min under N₂). ¹H NMR (DMSO-*d*₆, ppm) -9.04 (dd, 1H), 8.61 (dd, 1H), 7.37 (m, H), 7.24 (dd, 1H), 7.16 (m, H), 1.72 (s, 3H).³¹

2,2'-Bis[4-(6-amino-3-pyridinoxy)phenyl] Propane (b): Under nitrogen protection, 2,2'-bis[4-(6-nitro-3-pyridinoxy)phenyl] propane (a, 9.45 g, 20.0 mmol), 1.0 g of palladium on activated carbon (Pd/C 10%), and 150 mL of anhydrous dioxane were added in a 250 mL reaction bottle with a mechanical stirrer, thermometer, and reflux condenser. The mixing solution was heated to the reflux temperature, dripping 12.5 g (200 mmol) of hydrazine hydrate (80%) within 1 h, and maintaining the reflux temperature to react for 8 h. Then heat filtration was performed to remove the Pd/C. Most of the organic solvents were removed by redistilling filtrate. The filtrate was poured

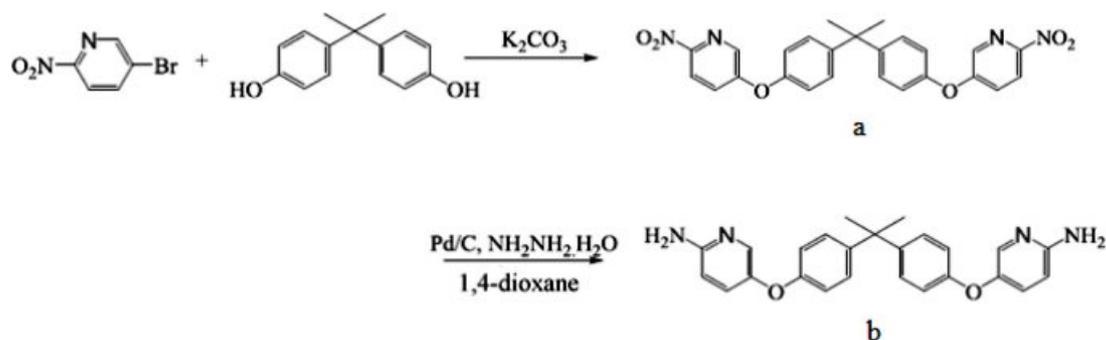
into 500 mL of deionized water, and the solid product was precipitated. After filtration, the resulting precipitate was collected and dried at 60 °C overnight under vacuum. After filtration again, the filter cake was washed with deionized water and dried in vacuum. The crude product was recrystallized and purified with ethanol/water, and the yellow solid product was obtained. The yield of the product was 90%, and the melting point was 175.8 °C (DSC peak at a heating rate of 10 °C/min under N₂). ¹H NMR (DMSO-*d*₆, ppm) -7.55 (m, 1H), 7.19 (m, H), 7.09 (m, 1H), 6.86 (m, H), 6.75 (m, 1H), 5.09 (s, 2H), 1.60 (m, 3H); ¹³C NMR (DMSO-*d*₆, ppm) -153.9, 153.5, 144.7, 141.8, 132.3, 127.4, 125.3, 118.3, 112.7, 41.5, 30.6.³¹

Scheme 1 shows the reaction formula for the preparation of the monomers.

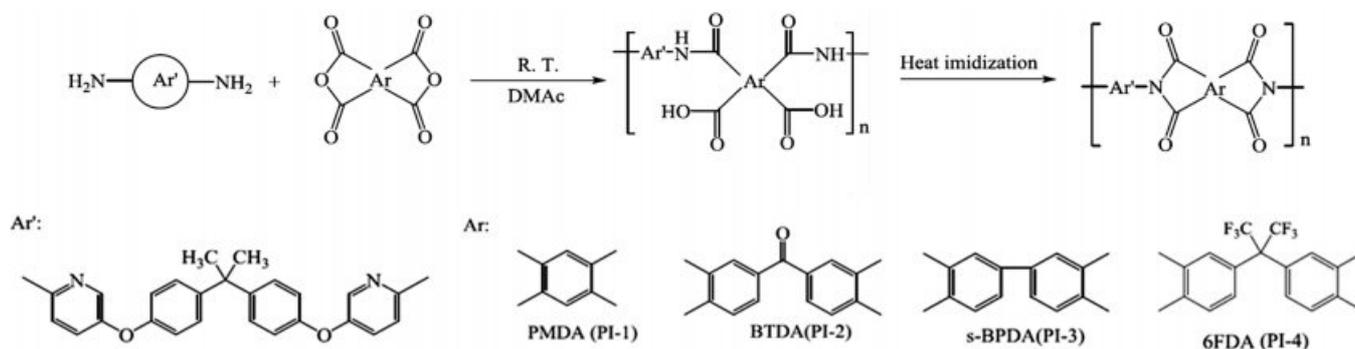
Polymer Synthesis. PIs were synthesized by polycondensation reaction. DMAc was used as solvent, and the resulting 2,2'-bis[4-(6-amino-3-pyridinoxy)phenyl] propane (b) reacted with aromatic dianhydride PMDA, BTDA, s-BPDA, and 6FDA. Polyamic acid (PAA) precursors were obtained. Next, thermal imidization was carried out at high temperature. Finally, a series of PIs were obtained and labeled as PI-1, PI-2, PI-3, and PI-4.

Taking PI-1 as an example, a typical polymerization procedure was as follows. 2,2'-Bis[4-(6-amino-3-pyridinoxy)phenyl] propane (b) (2.00 g, 4.8 mmol) and 10.0 g of DMAc were added to a 50 mL flask and stirred constantly to dissolve completely. Then PMDA (1.0470 g, 4.8 mmol) was added to the above mixture in two batches. In addition, extra 7.1 g of DMAc were added to the solution to maintain 15% solid content of the system. The above reaction solution was stirred at room temperature for 24 h to obtain a viscous PAA solution.

On a flat and clean glass board, the PAA solution was coated with a scraper. Then the glass plate was placed in an oven and was predried to remove the solvent according to the following



Scheme 1. Preparation of the monomer.



Scheme 2. Preparation of the PIs.

heating program: 80 °C/3 h, 100 °C/1 h, and 120 °C/0.5 h. After cooling to room temperature, the glass plate was placed into the vacuum oven, and the thermal imidization process was carried out according to the following heating program: 200 °C/0.5 h, 250 °C/0.5 h, and 300 °C/1 h. After the thermal imidization process, the film was immersed in deionized water. After a period of time, the film naturally separated from the glass plate, and then was dried under 110 °C for 3 h.

PI-2, PI-3, and PI-4 were synthesized by the above same method. The related synthesis process is shown in Scheme 2. In addition, PI-6 in previous work³¹ was abbreviated as Ref-PI in this paper, that is, a polymer synthesized from (b) and ODPDA. In particular, the polymer data of Ref-PI mentioned in the following sections were cited from reference 31. Therefore, the properties of the polymers synthesized from five commercial dianhydrides were discussed systematically in this paper.

Results and Discussion

Monomer Synthesis. The melting point of the precursor and monomer was measured by DSC method. Thus, the melting point of 2,2'-bis[4-(6-nitro-3-pyridinoxy)phenyl] propane (a) and 2,2'-bis[4-(6-amino-3-pyridinoxy)phenyl] propane (b) were 156.8 and 175.8 °C, respectively, which agreed with reported values.³¹ This result indicated that the different substituents on the benzene ring can directly affect the melting point of monomer; the melting point of monomer is higher than that of -NO₂ when the substituent is -NH₂.

The ¹H NMR and ¹³C NMR spectra were obtained. The molecular structures and NMR spectra of (a) and (b) were found in Figure 1. From the figures, the peak marked as 1 was the peak of the methyl proton on propane; the peaks marked 2 and 3 were the submethyl proton peaks on different

substitutions of benzene ring; and the peaks marked 4, 5, and 6 were the submethyl proton peaks on the different substitutions of the pyridine ring. In ¹³C NMR spectra, the carbon 13 atoms in monomer (b) showed 11 signals, which resonated in the regions of 31-155 ppm and all the spectroscopic data obtained agreed with the expected structures.

By analyzing the monomers and comparing the two ¹H NMR spectra of (a) and (b), the single absorption peak of the H atom on -NH₂ marked in the (b) spectrum was found to be δ5.09, which proved that -NO₂ in (a) was completely reduced to generate -NH₂. This finding further confirmed the process from (a) to (b) reduction.

Synthesis of PIs. The diamine monomer (b) was reacted with four kinds of commercially available aromatic dianhydrides, PMDA, BTDA, s-BPDA, and 6FDA, to give the corresponding PIs, as shown in Scheme 2. Two-step thermal imidization method was adopted to synthesize the PIs, which was performed through PAA intermediate. Equimolar amounts of diamine monomer with aromatic dianhydrides were used, and polymerization was carried out with a 15 % solid concentration in DMAc at room temperature for 2–24 h to yield PAA precursors, e.g. PMDA for 24 h, BTDA for 24 h, s-BPDA for 10 h, and 6FDA for 2 h. Tough and flexible PI films were obtained by casting the PAA solutions on the glass plate followed by thermal curing process at 300 °C.

As listed in Table 1, the inherent viscosities of PIs were 0.22-0.82 dL/g in DMAc at 25 °C, suggesting that the polymers had relatively high molecular weights. Moreover, gel permeation chromatography (GPC) measurements also further established these results. *M_w* and polydispersities (*M_w*/*M_n*) were in the range of 7989-47349 and 1.60-1.72, respectively.

Figure 2 presents the vertically offset FTIR spectra of PIs containing pyridine heterocyclic rings derived from 2,2'-bis[4-

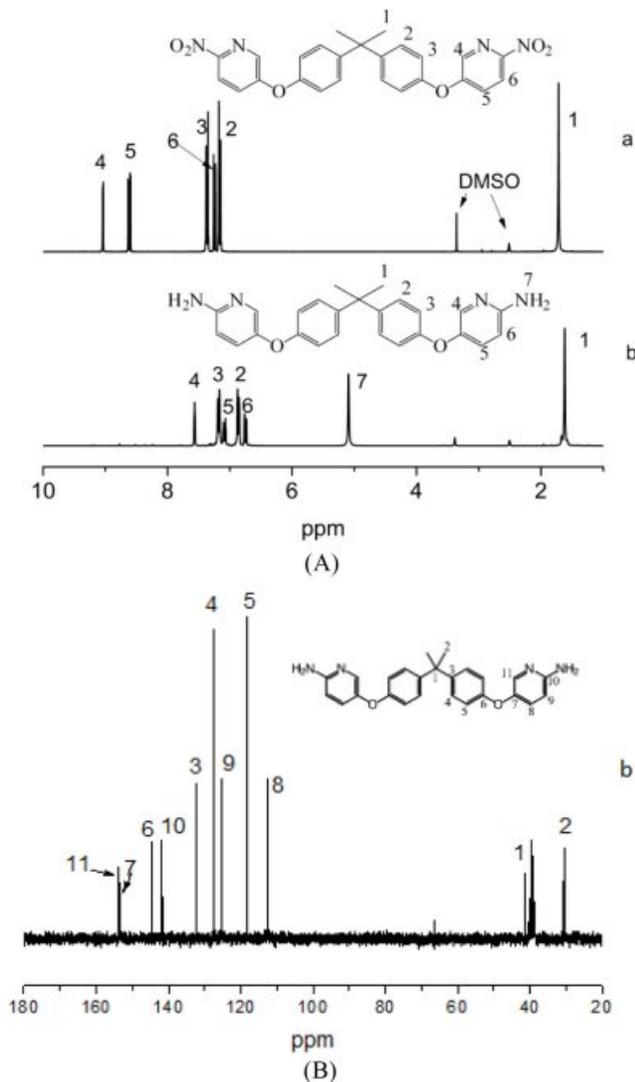


Figure 1. (A) ^1H NMR spectra; (B) ^{13}C NMR spectra of monomers.

(6-amino-3-pyridinoxy) phenyl] propane. FTIR spectra are used to estimate whether the synthesized product is completely acylated and whether the resulting product is PI.³²

The figure clearly exhibits that no characteristic absorption peaks of hydrogen (N–H) and amide ($-\text{CO}-\text{N}-\text{H}$) were present on the amino group in the region of $3100\text{--}3500\text{ cm}^{-1}$ (belonging to N–H stretching vibration). Among them, at 1781 cm^{-1} (belonging to asymmetric C=O stretching vibration peak), 1728 cm^{-1} (belonging to symmetrical C=O stretching vibration peak), 1387 cm^{-1} (belonging to C–N stretching vibration peak), and $1200\text{--}1100\text{ cm}^{-1}$ range (belonging to C–O stretching vibration peak), strong absorption peaks were observed, displaying obvious characteristic absorption peaks of the imide group.³³ In a word, through FTIR spectra, the polymer was

Table 1. Viscosity and Molecular Weights of PIs

Polyimides	η_{inh} (dL/g)	M_n	M_w	M_w/M_n
PI-1	0.22	4645	7989	1.72
PI-2	0.54	15435	25313	1.64
PI-3	0.76	26820	44521	1.66
PI-4	0.82	29228	47349	1.62
Ref-PI	0.78	27120	43392	1.60

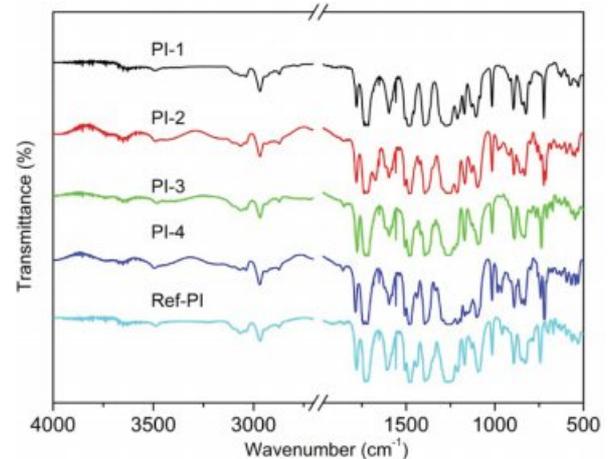


Figure 2. FTIR spectra of the PIs.

confirmed to have been completely amidated, and the synthesized product was PI.

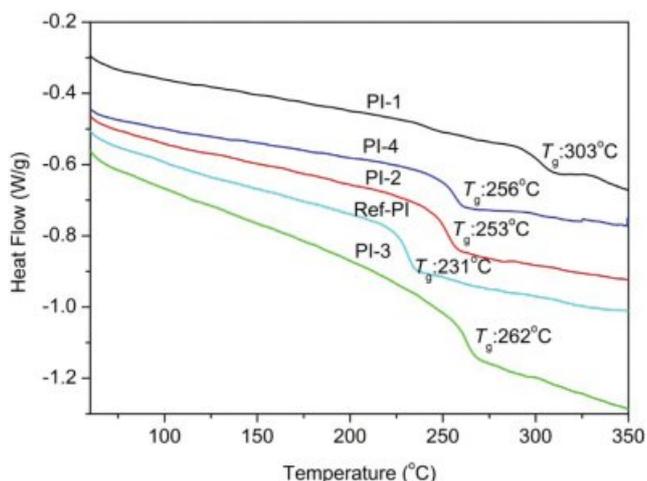
Thermal Properties of the PIs. The thermal properties of PIs were determined by DSC, DMA, and TGA; and the results are listed in Table 2. The glass transition temperature (T_g) of PIs detected by DSC (as in vertically offset Figure 3) is distributed between 231 and $303\text{ }^\circ\text{C}$, and the T_g of PI (Figure 4) detected by DMA is distributed between 205 and $274\text{ }^\circ\text{C}$. The T_g variation tendency of the PIs obtained by two methods is exactly the same. In DMA analysis, T_g is the peak temperature of the loss modulus (E'') curve. The T_g values obtained by DSC and DMA are slightly different mainly because of the different responses of the two instruments for the samples.³⁴ In general, the T_g of polymers was decided by the accumulation of molecular chains and the stiffness of the polymer backbone. Furthermore, in comparison of T_g in reference 34 (There was no N atom on the benzene ring),³⁵ T_g in this study was basically the same as that in reference 34, which implied that the introduction of N atoms on pyridine ring has not decreased the thermal stability of polymers, while maintaining a certain rigidity.

The main chain of PI-1 (b/PMDA) polymer has the highest

Table 2. Physical and Thermal Properties of the PI films

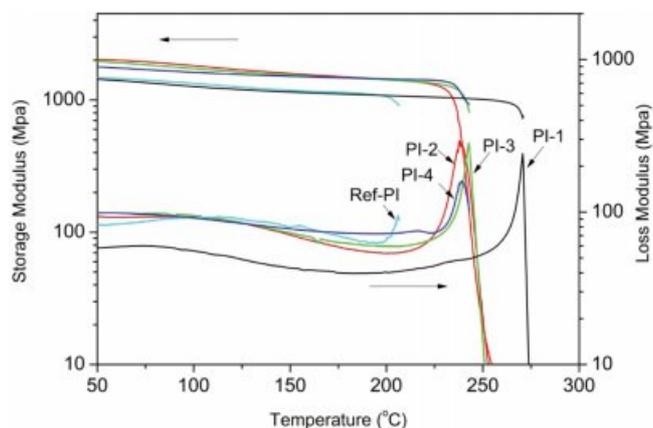
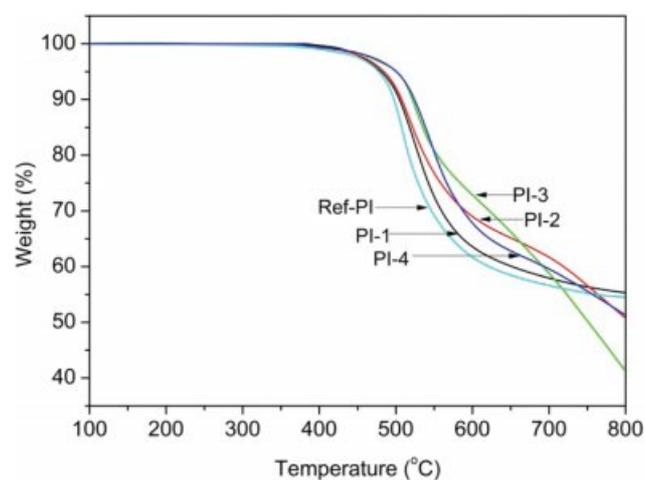
Polyimides	T_g (°C)		$T_{5\%}$ ^c (°C)	$T_{10\%}$ ^c (°C)	R_w ^d (%)
	DSC ^a	DMA ^b			
PI-1	303	274	480	505	55
PI-2	253	238	484	508	51
PI-3	262	243	501	522	42
PI-4	256	239	501	524	51
Ref-PI	231	205	478	497	55

T_g : glass transition temperature; $T_{5\%}$: 5% weight loss temperature; $T_{10\%}$: 10% weight loss temperature; R_w : residual weight retention. ^aObtained at the baseline shift in the second heating DSC traces at a heating rate of 10 °Cmin⁻¹ under N₂ atmosphere. ^bObtained at a heating rate of 5 °Cmin⁻¹ and a load frequency of 1 Hz in film tension geometry. ^cObtained by TGA at a heating rate of 10 °Cmin⁻¹ under N₂ atmosphere. ^dObtained at 800 °C by TGA at a heating rate of 10 °Cmin⁻¹ under N₂ atmosphere.

**Figure 3.** DSC curves of PI films.

rigidity, showing the highest T_g ; however, the PI-2 synthesized by (b) and BTDA has the lowest T_g . As a result, PMDA-based PI-1 with the most rigid polymer backbone exhibited the highest T_g , whereas PI-2 derived from BTDA possessed the lowest T_g owing to its more flexible polymer chain structure than that of PI-1, PI-3 and PI-4. Moreover, the figure shows that the PI-3 synthesized by b/s-BPDA exhibited higher T_g than the PI-2 synthesized by b/BTDA. The former was 262 °C and the latter was 253 °C. The PI-4 synthesized by b/6FDA also had a slighter higher T_g than PI-2, which was derived from the -CF₃ structures in the backbone inhibited the free rotation of the polymer main chain.³⁶

In addition, the energy storage and loss modulus curves of the polymers tested by DMA are displayed in Figure 4. The

**Figure 4.** DMA curves of PI films.**Figure 5.** TGA curves of PI films.

storage moduli of all polymers were slightly lower or basically unchanged before the glass temperature, implying that the polymers had good mechanical properties.

In nitrogen atmosphere, the thermal stability of PI was evaluated by TGA. Figure 5 shows the thermogravimetric curves of the five synthesized PIs. The 5% and 10% thermogravimetric temperature ($T_{5\%}$ and $T_{10\%}$, respectively) of PIs and the residual mass at 800 °C in nitrogen atmosphere are listed in Table 2. The $T_{5\%}$ range of the synthesized PIs was 478 to 501 °C, and the residual mass was 42–55%. The order of $T_{5\%}$ was s-BPDA = 6FDA > BTDA > PMDA > ODP, and the trend of $T_{10\%}$ was in the same order as that of $T_{5\%}$. In addition, PI-1 (b/PMDA) and Ref-PI (b/ODPA) showed the highest residual mass (55%), which was mainly attributed to the high carbon content in the polymer molecular structures.

In summary, the thermal properties implicated that the obtained PIs had good thermal stability.

Table 3. Mechanical Properties of PI Films

Polyimides	T_S^a (MPa)	T_M^b (GPa)	E^c (%)
PI-2	99	3.0	20
PI-3	102	2.8	27
PI-4	101	2.9	27
Ref-PI	98	2.8	36

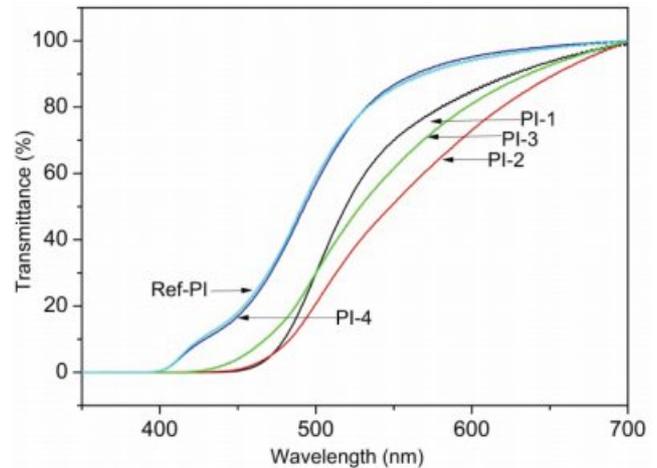
^aTensile strength. ^bTensile modulus. ^cElongation at break.

Mechanical Properties of the PIs. Four PIs can be prepared into high-quality PI films except for PI-1 synthesized from b/PMDA. Thus, mechanical properties, including tensile strength, tensile modulus, and elongation at break, were tested as shown in Table 3. The results displayed that tensile strength was 98–102 MPa, the elongation at break was 20%–36%, and the tensile modulus was 2.8–3.0 GPa, which revealed that the synthesized PIs possessed excellent mechanical properties.³⁷

The tensile strength of PI was the same as the rigidity order of dianhydride, that is, s-BPDA >6FDA >BTDA >ODPA. It should be noted that compared with previous work,³¹ the mechanical properties of PIs synthesized by 5-bromo-2-nitropyridine and BPA were significantly higher than those synthesized by 2-chloro-5-nitropyridine and BPA, which was mainly due to the different N atom positions on the pyridine ring. The substituent position of the nitrogen atom on the pyridine ring directly affected the mechanical properties of the prepared PIs. The above results indicated that the PI containing pyridine ring on the main chain kept the outstanding mechanical properties of the original polymer.

Optical Properties and XRD of the PIs. The optical properties of the synthesized PIs were investigated using a UV-vis spectrometer, and the PI films were directly measured by transmission mode. The thickness of the tested PI film was approximately 30 μm , and the UV visible spectra are shown in Figure 6. The optical performance test data are listed in Table 4. The cut-off wavelength ($\lambda_{\text{cut-off}}$) was the intersection point value of the tangent line of a curve in the UV visible spectrum, and that for the synthesized PI was 392–440 nm.

From Table 4, in the same case of two amines, the $\lambda_{\text{cut-off}}$ and optical transmittance of Ref-PI (b/ODPA) were close to those of PI-4 (b/6FDA), followed by PI-3 (b/s-BPDA), PI-2 (b/BTDA), and PI-1 (b/PMDA). This finding was due to the fact that the $-\text{CF}_3$ group in PI-4 could inhibit the formation of charge transfer complex. At the same time, the low molar polarizability of the C–F bond in the $-\text{CF}_3$ group weakened the adhesive force between the main chain of the polymer, thereby

**Figure 6.** UV-vis spectra of PI films.**Table 4. Optical Properties of PI Films**

Polyimides	PI-1	PI-2	PI-3	PI-4	Ref-PI
$\lambda_{\text{cut-off}}^a$ (nm)	440	439	430	392	391
Transmittance (%) ^b	1	2	5	19	18

^aCut-off wavelength. ^bTransmittance, at 450 nm.

leading to PI-4 with a lower $\lambda_{\text{cut-off}}$ and higher optical transmittance than the PIs derived from other anhydrides.

The crystalline form of the synthesized PI was analyzed using a wide-angle X-ray diffractometer with a scanning 2θ angle range of 5° to 50° , and the film was used as a sample, as shown in vertically offset Figure 7. The XRD curves of all PI films appeared a wide range of diffraction peaks, which fully illustrated the amorphous structure of PIs. The formation of this structure was mainly attributed to the loosening of the

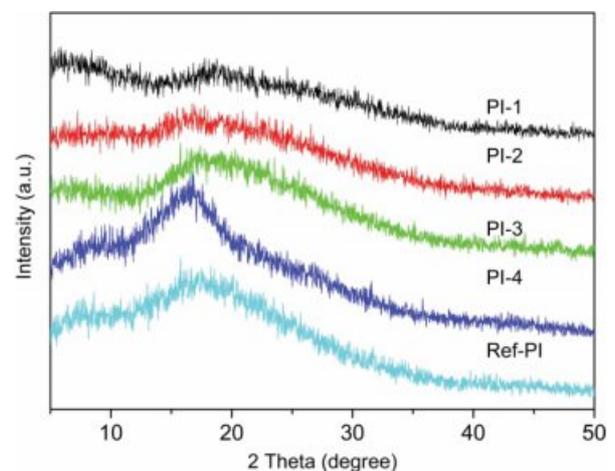
**Figure 7.** Wide-angle XRD patterns of PI films.

Table 5. Solubility of PIs in Organic Solvents^a

Solvent	PI-1	PI-2	PI-3	PI-4	Ref-PI
DMF	+ -	+ -	+ -	++	++
DMAc	+ -	+ -	+ -	++	++
NMP	+ -	+ -	+ -	+ -	++
DMSO	+ -	+ -	+ -	+ -	++
THF	—	—	—	+ -	++
Chloroform	+ -	+ -	+ -	+ -	++
Acetic acid	—	—	—	+ -	—

++: soluble at room temperature, + -: partial soluble, —: insoluble.
^aSolubility was determined with 10 mg of PIs in 1 mL of solvent at room temperature for 24 h.

accumulation on PI chains by the introduction of the flexible ether bonds and methyl-substituted pyridine, while the introduction of pyridine heterocyclic rings caused the distortion of the polymer skeleton and weakened the orderliness of the polymer chains.

Solubility of the PIs. Solubility of PIs is listed in Table 5. It could be seen that all PIs were soluble in polar solvent such as DMF, DMAc, NMP, DMSO, and chloroform. Pyridine ring nitrogen atom and $-(CH_3)_2-$ structures were introduced into the backbone of PIs, which could greatly increase the solubility. In addition, PI-4 (b/6FDA) exhibited better solubility in DMF and DMAc, which attributed to the introduction of the hexafluoroisopropylidene groups $-(CF_3)_2-$, and the groups could enhanced the chain flexibility and the affinity of the polymers.³⁸

Conclusions

In this paper, 2-bromo-5-nitropyridine and BPA were used as raw materials to prepare 2,2'-bis[4-(6-amino-3-pyridinoxy) phenyl] propane under certain conditions, demonstrating polycondensation reaction with aromatic dianhydrides, including PMDA, BTDA, s-BPDA, and 6FDA. After thermal imidization a series of PIs were obtained. The glass transition temperature of PIs tested by DSC was distributed at 231 to 303 °C; PI-1 (b/PMDA) polymer main chain has the highest rigidity, showing the highest T_g . The PI films possessed good mechanical properties, tensile strength of 98–102 MPa, elongation at break of 20%–36 %, and tensile modulus of 2.8–3.0 GPa. The optical performance test indicated that the cut-off wavelength was in the range of 391–440 nm. PI-4 (b/6FDA) had a lower cutoff wavelength and a higher optical

transmittance than other dianhydrides. The resulting PIs displayed great solubility. On the whole, the obtained series of PIs could be applied for high-performance materials with good properties.

Acknowledgements: This research was supported by the Doctoral Research Fund of Liaoning Province, China (no.20180540103).

References

- D. J. Liaw, K. L. Wang, Y. C. Huang, K. R. Lee, J. Y. Lai, and C. S. Ha, *Prog. Polym. Sci.*, **37**, 907 (2012).
- Y. T. Zhou, X. L. Liu, M. H. Wei, C. Song, Z. Z. Huang, and S. R. Sheng, *Polym. Bull.*, **11**, 1 (2018).
- Q. B. Hu, L. Zhang, R. J. Dai, J. H. Ru, and H. K. Wu, *Insulating Mater.*, **50**, 30 (2017).
- C. Aydın and A. A. Sacide, *Sep. Purif. Technol.*, **207**, 353 (2018).
- V. L. Bell, B. L. Stump, and H. Gager, *J. Polym. Sci., Part A: Polym. Chem.*, **14**, 2275 (2010).
- D. D. Sheng, H. T. Wang, and Z. H. Ying, *Plastics*, **42**, 46 (2013).
- A. B. Meddeb, Z. Ounaies, and M. Lanagan, *Chem. Phys. Lett.*, **649**, 111 (2016).
- Y. S. Lee, S. K. Lee, J. H. Kim, and K. H. Yoon, *Polym. Korea*, **43**, 331 (2019).
- Y. Y. Yu, T. J. Huang, W. Y. Lee, Y. C. Chen, and C. C. Kuo, *Org. Electron.*, **48**, 19 (2017).
- S. Escorihuela, A. Tena, S. Shishatskiy, S. Escolástico, T. Brinkmann, J. M. Serra, and V. Abetz, *Membranes*, **8**, 16 (2018).
- Z. Q. Jiang, T. T. Wang, F. P. Wu, J. D. Lin, and L. S. Liao, *J. Mater. Chem. A*, **36**, 17256 (2018).
- G. L. Song, Y. Zhang, D. M. Wang, C. H. Chen, H. W. Zhou, X. G. Zhao, and G. D. Dang, *Polymer*, **54**, 2335 (2013).
- H. Tian, X. Y. Kuang, A. J. Mao, Y. Yang, C. Xu, S. O. Sayedaghaee, and L. Bellaiche, *Phys. Rev. B.*, **97**, 020103 (2018).
- B. Chen, H. Li, X. Huang, and C. Wei, *Chin. J. Chem.*, **35**, 341 (2017).
- J. Un, J. H. Lee, H. J. Choi, S. Moon, I. D. Kim, and H. Lee, *Appl. Surf. Sci.*, **423**, 881 (2017).
- H. Zhang, L. S. Shao, S. M. Gong, Q. Gong, and Y. H. Wang, *Chin. J. Liq. Cryst. Displays*, **31**, 258 (2016).
- G. Lee, H. M. Lee, and Y. H. Kim, *Polym. Korea*, **43**, 113 (2019).
- Y. Q. Li, R. C. Fang, A. M. Zheng, Y. Y. Chu, X. Tao, H. H. Xu, S. J. Ding, and Y. Z. Shen, *J. Mater. Chem.*, **21**, 15643 (2011).
- W. J. Yang and J. H. Chang, *Polym. Korea*, **40**, 405 (2016).
- X. Huang, X. Pei, L. Wang, M. Mei, C. Liu, and C. Wei, *J. Appl. Polym. Sci.*, **133**, 43266 (2016).
- X. Y. Qiao and T. S. Chung, *AIChE J.*, **52**, 3462 (2010).
- E. Oikawa and H. Nozawa, *Polym. Bull.*, **13**, 481 (1985).
- S. Mehdipour-Ataiea and M. Nami, *Eur. Polym. J.*, **41**, 1024 (2005).

24. J. Kim, H. G. Jeon, P. Kang, and K. S. Jeong, *Chem. Commun.*, **53**, 6508 (2017).
25. A. M. Sanchez, J. Andrews, I. Hussein, G. N. Bennett, and K. Y. San, *Biotechnol. Progr.*, **22**, 420 (2010).
26. K. J. Weller, S. D. Gray, P. M. Briggs, and D. E. Wigley, *Organometallics*, **14**, 5588 (2002).
27. L. Zhao, K. Kou, L. Zhuo, and Y. Wang, *Chin. Plastics*, **27**, 57 (2013).
28. S. X. Chen, H. Y. Pan, Z. H. Chang, M. Jin, and H. T. Pu, *Ionics*, **7**, 1 (2018).
29. J. Yao, C. Wang, C. Tian, X. Zhao, H. Zhou, D. Wang, and C. H. Chen, *Des. Monomers Polym.*, **20**, 449 (2017).
30. A. F. Cannella, S. K. Dey, S. N. Macmillan, and D. C. Lacy, *Dalton Trans.*, **47**, 5171 (2018).
31. Z. Li, Y. Wen, Y. Wang, and S. M. Zhu, *High Perform. Polym.*, **29**, 161 (2016).
32. R. W. Snyder, B. Thomson, B. Bartges, D. Czerniawski, and P. C. Painter, *Macromolecules*, **22**, 4166 (1989).
33. F. D. M. Fernandez, J. W. Jang, and J. H. Yim, *Polym. Korea*, **43**, 420 (2019).
34. Y. Guan, D. Wang, G. Song, X. Zhang, C. Chen, H. Zhou, G. Dang, and X. Zhao, *High Perform. Polym.*, **26**, 455 (2014).
35. Y. Xu, C. Chen, P. Zhang, B. Sun, and J. Li, *J. Chem. Eng. Data*, **51**, 1841 (2006).
36. Y. Zhang, P. Luo, H. Yao, and S. Guan, *React. Funct. Polym.*, **72**, 621 (2012).
37. Y. T. Zhou, X. L. Liu, M. H. Wei, C. Song, Z. Z. Huang, and S. R. Sheng, *Polym. Bull.*, **11**, 1 (2018).
38. Y. Guan, D. Wang, G. Song, G. Dang, C. Chen, H. Zhou, and X. Zhao, *Polymer*, **55**, 3634 (2014).