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Soluble Polyimides Derived from a Novel Aromatic Diamine Containing an Imidazole Unit and Trifluoromethyl Groups

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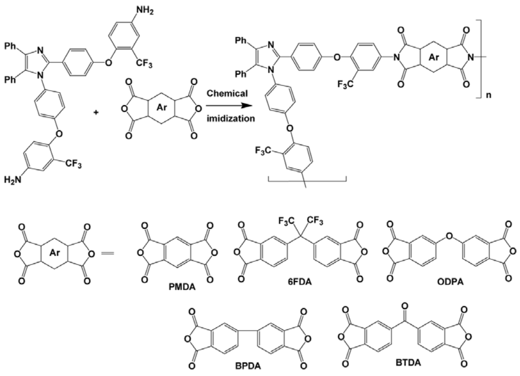
Abstract: A series of polyimide (PI) films were prepared through a two-step polycondensation process *via* chemical imidization using five commercial aromatic dianhydrides and a novel diamine containing an imidazole unit and trifluoromethyl groups, *i.e.*, 4,4′-(((4,5-diphenyl-1H-imidazole-1,2-diyl)bis(4,1-phenylene))bis(oxy))bis(3-(trifluoromethyl)aniline) (referred to as diamine **3**). The number average molecular weights of the resulting PIs ranged from 1.57 × 10^4 to 3.17 × 10^4 g·mol^{-1} with polydispersity indices between 2.53 and 3.60, which were obtained through gel permeation chromatography measurements using a polystyrene standard. All the PIs prepared using diamine **3** were amorphous because of the large side group and kink structure of the diamine. They are soluble in common high-boiling point solvents, such as N-methyl pyrrolidone, dimethyl acetamide, and *m*-cresol, as well as several low-boiling point solvents, including chloroform and tetrahydrofuran. They exhibit the thermal stability with 10% weight loss temperatures in the range of 545 to 562 °C and 5% weight loss temperatures in the range of 500 to 541 °C in a nitrogen atmosphere. Their glass transition temperatures exceed 245 °C. All the resulting PI films show transmittances of over 74% in the visible light region ranging from 400 to 760 nm. The tensile strength of the PI films is in the range of 30.1 to 52.8 MPa, while the tensile modulus ranges from 1.0 to 1.7 GPa.



Keywords: imidazole, trifluoromethyl, polyimide, film, soluble, transparent.

1. Introduction

Nowadays, polyimides (PIs) are widely utilized in several applications in various fields, such as aerospace, microelectronics, and flexible displays, owing to their outstanding properties, including excellent thermal stability, high chemical resistance, good mechanical performance, and reliable electrical insulation abilities.[1-9] However, poor processability and low transparency are the main problems inhibiting the development of aromatic PIs for a wider range of applications, such as optoelectronic devices.[10-12] The difficulty in processing in solution or melting state can be attributed to their rigid structures and strong intermolecular interactions.[13,14] The deep color and low transparency issues are mainly due to the formation of intra- and inter-molecular charge-transfer complexes (CTCs).[15,16] The most common and effective approach to overcome the above-mentioned problems to obtain ideal properties entails the incorporation of side groups into PI structures by designing and synthesizing novel monomers.[17] These methods mainly include the integration of bulky pendent groups (*e.g.*, *tert*-butyl, cyclohexane, *etc.*),[18-21] flexible linkages (*e.g.*, -O-, -SO_2-, isopropylidene, -S-, *etc.*),[22-24] unsymmetrical or noncoplanar (*i.e.*, kink, spiro, and cardo) structures,[25-27] and fluorinated structures, including the trifluoromethyl (CF_3) group.[28] It has been reported that introducing flexible linkages into PI chains can reduce the energy barrier of rotation in the polymer chain and the degree of conjugation between aromatic rings, thereby enhancing the solubility and transparency of the PIs; however, the inherent thermal stability can diminish, especially the value of the glass transition temperatures (T_gs).[7] Fortunately, introducing bulky pendent or CF_3 groups has been established to be an acceptable strategy to improve the solubility and transparency of PIs without significantly influencing their inherent thermal stability.[29,30] Introducing bulky pendent groups into the polymer chains can hinder the segmental mobility, as well as reduce close packing and intermolecular charge-transfer interactions.[31] There have been several reports on introducing imidazole units into polymer chains to enhance the solubility and thermal stability, including increased T_gs, owing to the hindrance in segmental mobility and increased molecular irregularity.[32-34] In addition,

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incorporating CF_3 groups can impede the interactions and chain packing between the PI chains, as well as reduce the CTC formation owing to the low polarizability of the C-F bond and the electron withdrawing inductive effect of -CF_3 group.[35] In this work, we report a series of novel soluble PIs derived from a new diamine containing an imidazole unit and CF_3 groups. On the one hand, it is envisaged to provide enhanced molecular irregularity and solubility, as well as decreased interchain interaction and segmental mobility by introducing the imidazole unit into polymer chains.[36] On the other hand, the introduction of CF_3 groups aims to provide weakened intermolecular cohesive forces and reduce CTC formation.[37] The novel 4,4'-(((4,5-diphenyl-1H-imidazole-1,2-diyl)bis(4,1-phenylene))bis(oxy))bis(3-(trifluoromethyl)aniline) (diamine **3**) was designed and synthesized successfully following a three-step reaction methodology. Diamine **3** was used to prepare a series of PIs with five commercial aromatic dianhydrides, including pyromellitic dianhydride (PMDA), 2,2-bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride (6FDA), 3,3',4,4'-diphenylether tetracarboxylic dianhydride (ODPA), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), and 3,3',4,4'-benzophenone-tetracarboxylic dianhydride (BTDA), through a two-step polycondensation process *via* chemical imidization at room temperature. The corresponding PI films were obtained by means of the blade-coating method. Consequently, the chemical structures of the resulting PIs were confirmed, and the thermal properties, transparency, solubility, and mechanical properties were investigated and comprehensively discussed.

2. Experimental

2.1. Materials

Benzil, 4-aminophenol, ammonium acetate, 4-hydroxybenzaldehyde, and 10% palladium on carbon (Pd/C) were purchased from Inokai Technology Co. Ltd. (Beijing, China) and used as received without further purification. Acetic acid, 2-chloro-5-nitrobenzotrifluoride, and anhydrous potassium carbonate (K_2CO_3) were purchased from Titan Scientific Co. Ltd. (Shanghai, China) and used as received. Additionally, PMDA, 6FDA, ODPA, BPDA, and BTDA were purchased from Adamas Reagent Co. Ltd. and purified by recrystallization from acetic anhydride before use, while DMAc (Sinopharm Chemical Reagent Co. Ltd.) was purified through vacuum distillation before use. Acetic anhydride (Sinopharm Chemical Reagent Co. Ltd.), pyridine (Adamas Reagent Co. Ltd.), *N*-methyl pyrrolidone (NMP, Adamas Reagent Co. Ltd.), *m*-cresol (Macklin Biochemical Co. Ltd.), and other commercially available reagents and solvents were used without further purification.

2.2. Diamine syntheses

2.2.1. Synthesis of 4,4'-(4,5-diphenyl-1*H*-imidazole-1,2-diyl)diphenol (1)

A mixture of 40 mmol of benzil, 40 mmol of 4-aminophenol, 160 mmol of ammonium acetate, and 40 mmol of 4-hydroxybenzaldehyde in 120 mL of acetonitrile were added in a 250 mL round-bottom flask. Thereafter, 2 mL of acetic acid was added and heated to reflux with stirring in an oil bath for 8 h. After the reaction was finished and cooled to room temperature, the mixture was washed repeatedly with deionized water to remove acetic acid, and filtered to obtain a white solid product. Finally, the solid was recrystallized from methanol to generate white crystals (**1**) and dried overnight in a vacuum oven at 80 °C. Yield: 64% (10.40 g); m.p. > 280 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.72 (s, 1H), 9.65 (s, 1H), 7.47-7.44 (m, 2H), 7.30 (dd, J = 5.0, 1.9 Hz, 3H), 7.24-7.19 (m, 6H), 7.17-7.12 (m, 1H), 7.02-6.98 (m, 2H), 6.68-6.64 (m, 4H).

2.2.2. Synthesis of 1,2-bis(4-(4-nitro-2-(trifluoromethyl)phenoxy)phenyl)-4,5-diphenyl-1H-imidazole (2)

A mixture of 5 mmol of 4,4'-(4,5-diphenyl-1H-imidazole-1,2-diyl)diphenol (**1**), 5 mmol of 2-chloro-5-nitrobenzotrifluoride, and 20 mmol of K_2CO_3 were dissolved in 30 mL of DMAc in a 100 mL round-bottom flask equipped with a condenser, magnetic stirrer bar, and nitrogen inlet. After 30 min of stirring at room temperature, the mixture was heated at 110 °C for 12 h. After cooling, the mixture was poured into methanol/water (1:1, v:v) and the yellow precipitate was collected through filtration. Finally, the solid was recrystallized in acetonitrile to precipitate yellow crystals (**2**) and dried overnight in a vacuum oven at 80 °C. Yield: 46% (1.66 g); m.p.: 233 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.61-8.49 (m, 4H), 7.65-7.57 (m, 4H), 7.52-7.48 (m, 2H), 7.44 (m, 3H), 7.36-7.24 (m, 9H), 7.20 (d, J = 9.2 Hz, 1H), 6.94 (d, J = 9.1 Hz, 1H).

2.2.3. Synthesis of 4,4'-(((4,5-diphenyl-1H-imidazole-1,2-diyl)bis(4,1-phenylene))bis(oxy))bis(3-(trifluoromethyl)aniline) (3)

15 mmol (11.74 g) of 1,2-bis(4-(4-nitro-2-(trifluoromethyl)phenoxy)phenyl)-4,5-diphenyl-1*H*-imidazole (**2**) was dissolved in a mixture of 10 mL ethanol and 90 mL tetrahydrofuran (THF), and 0.5 g of Pd/C (10%) was added into it as a catalyst. The hydrogenation reaction was performed in a high-pressure reactor at 45 °C for 24 h in hydrogen atmosphere. After the reaction, the solution was filtered to remove Pd/C, and the filtrate was concentrated to obtain a white solid. The crude product was recrystallized from a mixture of ethyl acetate and hexane (3:1, v:v) and dried overnight in a vacuum oven at 80 °C. Yield: 94% (10.22 g); m.p.: 225 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.49-7.46 (m, 2H), 7.35-7.29 (m, 5H), 7.26-7.15 (m, 7H), 6.95-6.87 (m, 3H), 6.87-6.76 (m, 7H), 5.51 (d, J = 1.9 Hz, 4H). HRMS (ESI, m/z): $[M+H]^+$ calculated for $C_{41}H_{28}F_6N_4O_2^+$, 723.2116; found, 723.2222.

2.3. Polyimide syntheses

Equimolar amounts of diamine **3** and a dianhydride were polycondensed to prepare PI through a low-temperature two-step method *via* chemical imidization. In this work, five different commercial dianhydrides were used, including PMDA, 6FDA, ODPA, BPDA, and BTDA. The corresponding PIs were named as PI-1, PI-2, PI-3, PI-4, and PI-5, respectively. A typical polymerization procedure is described as follows: Firstly, diamine **3** (0.542 g, 0.75 mmol) was dissolved in 5 mL of dry NMP in a 25 mL threenecked flask equipped with a magnetic stirrer bar and a nitrogen inlet. After the diamine **3** was fully dissolved, PMDA (0.1636 g, 0.75 mmol) was added and stirred at room temperature for 24 h in N_2 atmosphere to form a viscous poly (amic acid) (PAA) solution. Thereafter, 1 mL of pyridine and 2 mL of acetic anhydride were added to the PAA solution and stirred for another 24 h in N_2 atmosphere for imidization. After the reaction, the solution was diluted with 30 mL of chloroform ($CHCl_3$) under stirring and was carefully poured into 500 mL of methanol to give a yellow fiber-like precipitate. Finally, **PI-1 (3-PMDA)** was collected by filtration and dried at 150 °C in a vacuum oven for 24 h. It was purified by reprecipitating two times. Yield: 94%. FTIR (blade-coating film, cm^{-1}): ν = 3064 (CH$_2$-H), 1780 (C=O), 1732 (C=O), 1604, 1496, 1374 (C-N), 1251, 1139, 1102, 1055, 960, 918, 851, 829, 777. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.31 (q, J = 10 Hz, 2H), 7.99 (s, 2H), 7.78 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 7.8 Hz, 4H), 7.42–7.10 (m, 15H), 7.03 (d, J = 9.1 Hz, 1H). Elemental analysis: calculated for $C_{51}H_{26}F_6N_4O_6$: C, 67.70; H, 2.90; N, 6.19. Found: C, 66.87; H, 3.44; N, 5.94.

Other PI-(2-5) compounds were synthesized by means of a similar procedure as described above.

2.3.1. PI-2 (3-6FDA)

Yield: 93%. FTIR (blade-coating film, cm^{-1}): ν = 3066 (CH$_2$–H), 1787 (C=O), 1732 (C=O), 1605, 1497, 1378 (C–N), 1251, 1143, 1103, 1054, 962, 910, 850, 776. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.19 (dd, J = 8.2, 4.3 Hz, 2H), 8.04–7.87 (m, 4H), 7.74 (s, 4H), 7.51 (dd, J = 8.1, 4.8 Hz, 4H), 7.44–6.98 (m, 16H). Elemental analysis: Calculated for $C_{60}H_{30}F_{12}N_4O_6$: C, 63.72; H, 2.67; N, 4.95. Found: C, 63.16; H, 3.03; N, 4.78.

2.3.2. PI-3 (3-ODPA)

Yield: 94%. FTIR (blade-coating film, cm^{-1}): ν = 3066 (CH$_2$–H), 1782 (C=O), 1727 (C=O), 1609, 1497, 1377 (C-N), 1250, 1139, 1108, 1054, 960, 908, 853, 837, 778. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.05 (dd, J = 6.0, 4.3 Hz, 2H), 7.98-7.90 (m, 2H), 7.75 (t, J = 7.7 Hz, 2H), 7.56 (dt, J = 47.5, 8.2 Hz, 8H), 7.35 (d, J = 12.5 Hz, 5H), 7.31-7.22 (m, 5H), 7.20-7.09 (m, 5H), 7.07-6.99 (m, 1H). Elemental analysis: Calculated for $C_{57}H_{30}F_6N_4O_7$: C, 68.68; H, 3.03; N, 5.62. Found: C, 67.75; H, 3.37; N, 5.41.

2.3.3. PI-4 (3-BPDA)

Yield: 96%. FTIR (blade-coating film, cm^{-1}): ν = 3063 (CH$_2$-H), 1778 (C=O), 1727 (C=O), 1606, 1497, 1377 (C-N), 1250, 1139, 1099, 1054, 960, 910, 860, 842, 776. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.99-7.59 (m, 10H), 7.52-7.47 (m, 4H), 7.42-7.13 (m, 12H), 7.05 (s, 3H), 6.93 (d, J = 10.0 Hz, 1H). Elemental analysis: Calculated for $C_{57}H_{30}F_6N_4O_6$: C, 69.80; H, 3.08; N, 5.71. Found: C, 68.83; H, 3.27; N, 5.60.

2.3.4. PI-5 (3-BTDA)

Yield: 95%. FTIR (blade-coating film, cm^{-1}): ν = 3064 (CH$_2$-H), 1780 (C=O), 1730 (C=O), 1604, 1497, 1375 (C-N), 1251, 1139, 1102, 1055, 960, 918, 859, 828, 777. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.28-8.06 (m, 6H), 7.97 (s, 2H), 7.78 (d, J = 8.8 Hz, 2H), 7.58-7.47 (m, 4H), 7.37 (m, 5H), 7.27 (m, 5H), 7.21-7.10 (m, 5H), 7.05 (d, J = 8.6 Hz, 1H). Elemental analysis: Calculated for $C_{58}H_{30}F_6N_4O_7$: C, 69.05; H, 3.00; N, 5.55. Found: C, 68.18; H, 3.26; N, 5.43.

2.4. Film preparation

The PI films were prepared *via* the blade-coating method. One of the obtained PIs was dissolved in freshly distilled DMAc with a solid content of 15 wt% at room temperature. Thereafter, the homogeneous PI solution was filtered using a 0.7 μm fiberglass syringe filter to remove impurities and coated on a glass substrate at 60 °C by using an Elcometer 4340 Automatic Film Applicator (blade height: 500 μm; coating speed: 0.2 in/s). After keeping it at 60 °C for 12 h, the PI film with the glass substrate was placed in vacuum to evaporate the residual solvent according to the following heating procedure: 100 °C/3 h, 150 °C/3 h, and 200 °C/12 h. Finally, the glass substrate was immersed in deionized water at room temperature to obtain a PI film.

2.5. Measurements

^{1}H nuclear magnetic resonance (NMR) measurements of the intermediate compounds, diamine, and PIs were performed on a 500 MHz Bruker NMR spectrometer with dimethyl sulfoxide (DMSO)-d_6 as the solvent. The liquid chromatography–mass spectrometry and high-resolution mass spectrometry (HRMS) spectra were determined using an ACQUITYTM UPLC & Q-TOF MS Premier. Fourier-transform infrared (FTIR) spectra were obtained on a Perkin-Elmer FTIR spectrometer using 5-15-μm-thick PI films. The molecular weights were measured *via* a Perkin-Elmer series 200 gel permeation chromatography (GPC) (polystyrene calibration) system using *N,N*-dimethylformamide (DMF) as an eluent containing 0.02 M LiBr (0.6 mL·min^{-1}). Elemental analysis was performed on a vario EL cube elemental analyzer. The mechanical properties of the PI films were measured using an INSTRON 4465 tensile tester based on the ASTM D882 method at a crosshead speed of 1 mm·min^{-1}. Five measurements were averaged. The sample dimensions were 25 mm in length and 5 mm in width. The optical properties of the PI films were measured on a Perkin-Elmer Lambda 20 ultraviolet-visible (UV-Vis) spectrometer. The thickness of the films was adjusted to 21-26 μm. The yellowness index (YI) was measured on a Perkin-Elmer Lambda 950 ultraviolet-visible-near infrared (UV-Vis-NIR) spectrometer based on the ASTM E313 method. The thickness of the films was also adjusted to 21-26 μm. X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu/Kα radiation with 2θ in the range of 5° to 50° at 40 kV and 40 mA. The water absorption rates of the PI films were investigated according to their weight changes before and after immersion in deionized water at 25 °C for 72 h. The dimensions are the same as those used for the mechanical tests, and each film was tested three times. The solubility of the resulting PIs was measured by dissolving 10 mg of PIs in 1 mL of solvent at 30 °C for 2 h. Thermogravimetric analysis (TGA) was carried out using a TA Discovery TGA Q5000 thermal analyzer in N_2 atmosphere at a heating rate of 20 °C·min^{-1} from 50 to 800 °C. Differential scanning calorimetry (DSC) curves were measured on a TA Discovery DSC 2500 thermal analyzer in N_2 atmosphere at a heating rate of 10 °C·min^{-1} from 40 °C to 400 °C. The T_g data were taken from the second heating scan using the onset method.

3. Results and discussion

3.1. Syntheses and characterization of diamines

As shown in Scheme 1, the diamine monomer **3** containing CF_3 and the imidazole structure was synthesized through a three-step reaction methodology involving cyclocondensation, substitution (O-arylation to introduce nitro groups), and hydrogenation reaction (reduction of the nitro groups). Firstly, benzil, 4-aminophenol, ammonium acetate, and 4-hydroxybenzaldehyde were reacted to form tetra-substituted imidazole (compound **1**) using acetic acid as the catalyst and acetonitrile as the solvent. Thereafter, compound **1** was reacted with 2-chloro-5-nitrobenzotrifluoride in the presence of K_2CO_3 in DMAc to obtain the intermediate compound **2** with two nitro groups. Finally, a high-pressure reactor and hydrogen were used to reduce the nitro groups to amino groups, with a mixture of ethanol and THF as the solvent and Pd/C as the catalyst. Thus, diamine **3** with CF_3 groups and an imidazole unit was successfully synthesized.

The chemical structures of intermediate compounds **1** and **2**, as well as diamine **3** were confirmed by ^1H NMR and mass spectrometry.

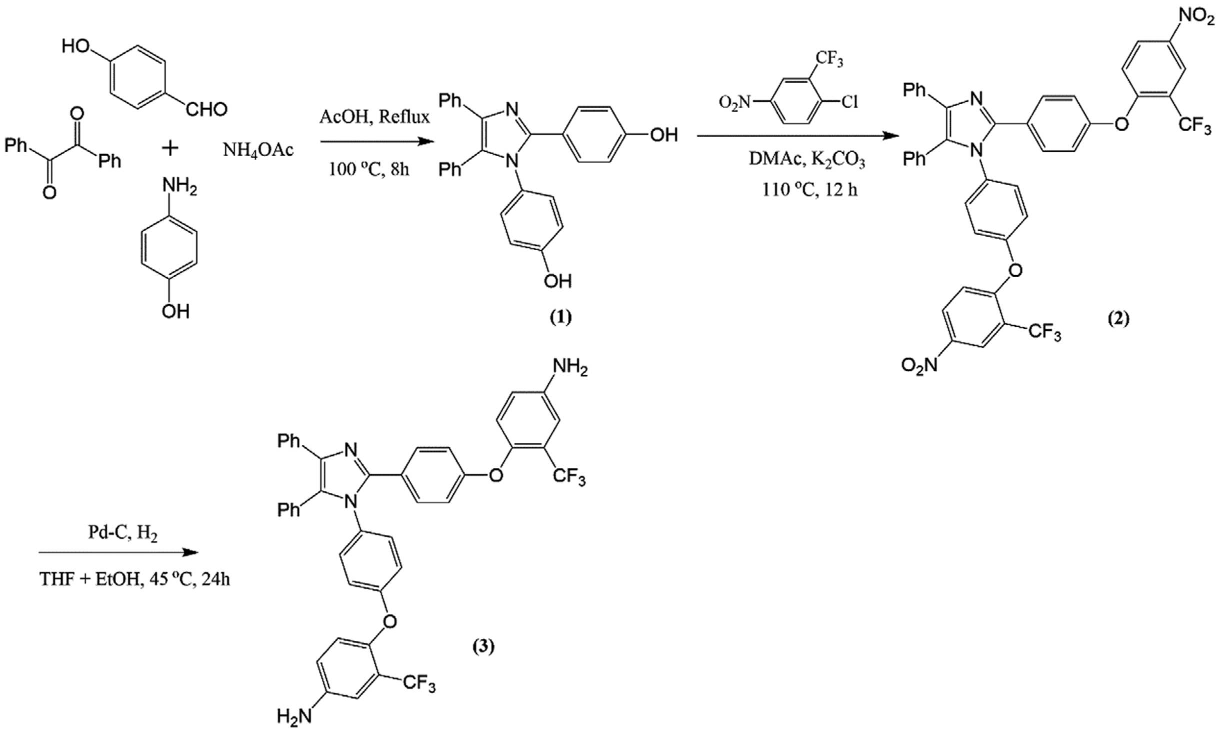
The ^1H NMR spectra of the intermediate compounds (**1** and **2**) are shown in Figure 1, and various proton signal peaks were analyzed and labeled in detail. From the ^1H NMR spectrum of compound **1**, it can be seen that the signal peaks ranging from 9.72 to 9.65 ppm are assigned to the protons of the hydroxyl groups on the benzene ring. The peaks from 7.47 to 6.64 ppm were assigned to the aromatic protons. From the ^1H NMR spectrum of compound **2**, it can be seen that the signal peaks ranging from 8.61 to 8.49 ppm are ascribed to the protons at the ortho position of the nitro groups on the benzene ring. The signal peaks from 7.65 to 6.94 ppm were assigned to the aromatic protons. Moreover, the integral area ratio of each signal peak was consistent with the ratio of the number of protons in the molecular structure of each compound, thereby indicating the successful syntheses of pure compounds **1** and **2**.

The ^1H NMR spectrum of diamine **3** is depicted in Figure 2 and the signals of all peaks were ascribed to the protons of the compound. From the ^1H NMR spectrum of diamine **3**, signals corresponding to aromatic protons were observed in the range from 7.49 to 6.76 ppm. The peak at approximately 5.51 ppm was ascribed to the protons of the amino groups. In the ^1H NMR spectrum of the compound **2** of Figure 1, the peaks of four protons on the benzene ring from the ortho position of the nitro groups ranged from 8.61 to 8.49 ppm, which shifted to between 6.95 and 6.76 ppm after the hydrogenation reaction. These results indicated that the prepared diamine **3** was consistent with the proposed one.

Furthermore, the $[M+H]^+$ molecular ion peak of diamine **3** was found at 723.2222 in the mass spectrum, which was in accordance with the theoretical value (723.2116). The DSC analysis results indicated that the melting point of diamine **3** was approximately 225 °C.

3.2. Syntheses and characterization of polyimides

As shown in Scheme 2, the PIs were prepared through low-temperature two-step polycondensation by chemical imidization from diamine **3** with five commercial aromatic dianhydrides in dry NMP, with pyridine and acetic anhydride (1:2). The solid content during the polymerization process was maintained at approxi-



Scheme 1. Synthesis of the novel diamine 3.

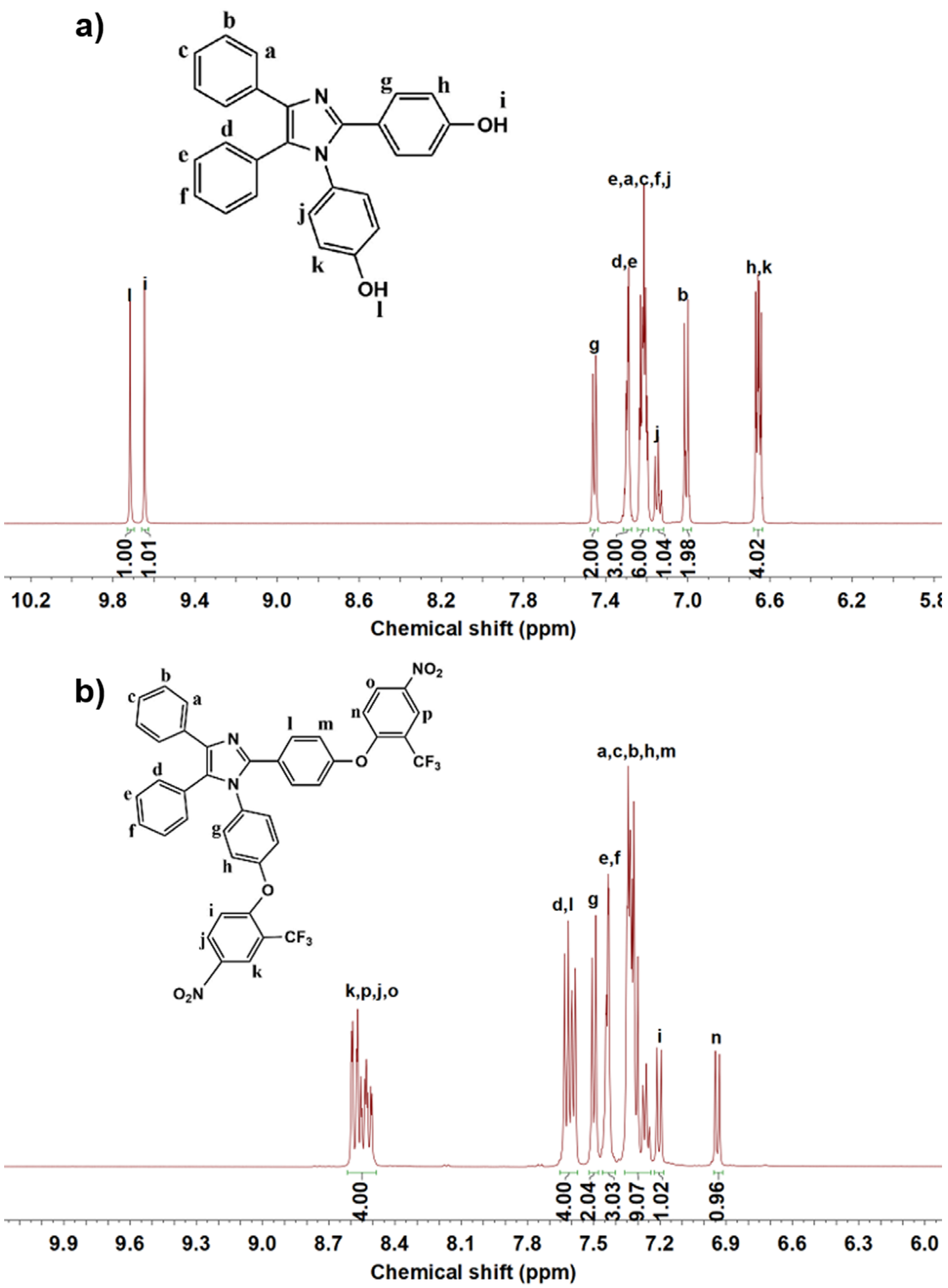


Figure 1. ^{1}H NMR spectra of (a) compound **1** and (b) compound **2**.

mately 15 wt%. Notably, the chemical imidization method was used here to convert the PAA solution to the corresponding PIs, rather than the thermal imidization method based on the following reasons:[7] Firstly, chemical imidization is unsuitable for insoluble PIs. Therefore, if a clear solution, and not a suspension, is obtained during chemical imidization, chemical imidization with a dehydrating agent is preferred. Secondly, chemically imidized PIs often exhibit better transparency and colorlessness because Ac_2O can cap the unstable terminal amino group of the PI chain during the chemical imidization process, while color problems always arise after high-temperature thermal imidization.

The resulting PIs were characterized *via* ^{1}H NMR, FTIR, elemental analysis measurements, and GPC.

The FTIR spectra were obtained using thin and transparent PI films. As shown in Figure 3, all the PIs exhibited typical absorption peaks at 1374-1378 cm^{-1} (C-N asymmetric stretching), 1778-1787 cm^{-1} (C=O asymmetrical stretching), and 1727-1732 cm^{-1} (C=O symmetrical stretching) due to the imide rings of the resulting PIs. Additionally, there were no evident N-H stretching vibration absorption peaks at 3220-3450 cm^{-1} nor N-H bending vibration absorption peaks at 1580-1650 cm^{-1}, thereby indicating complete imidization.[38]

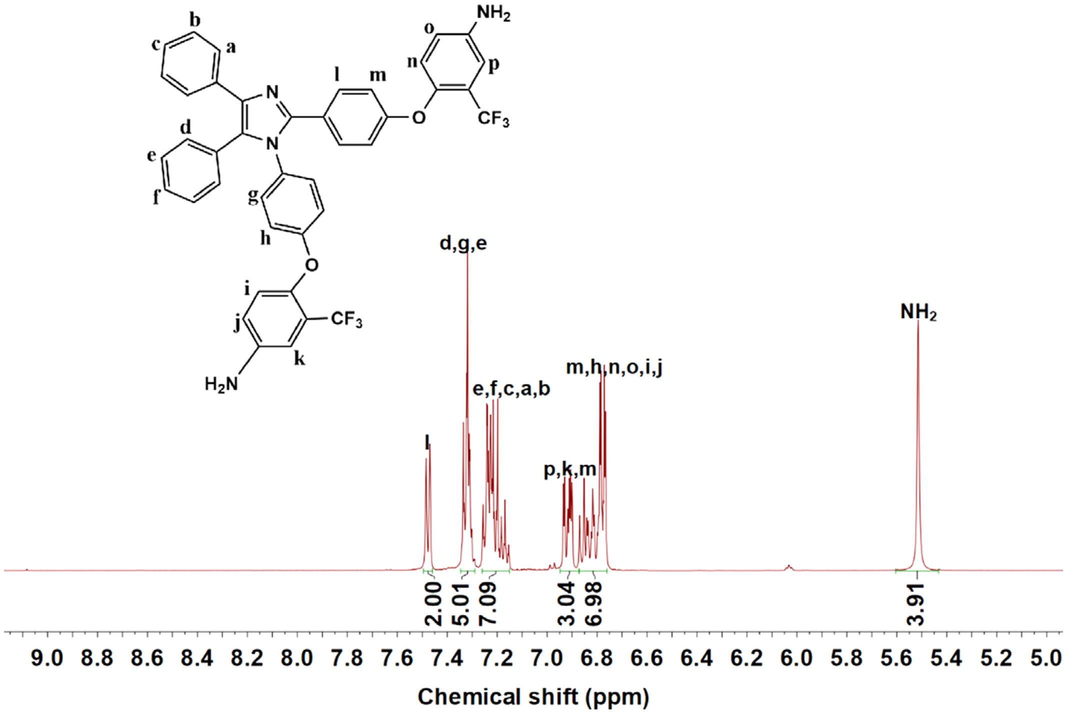
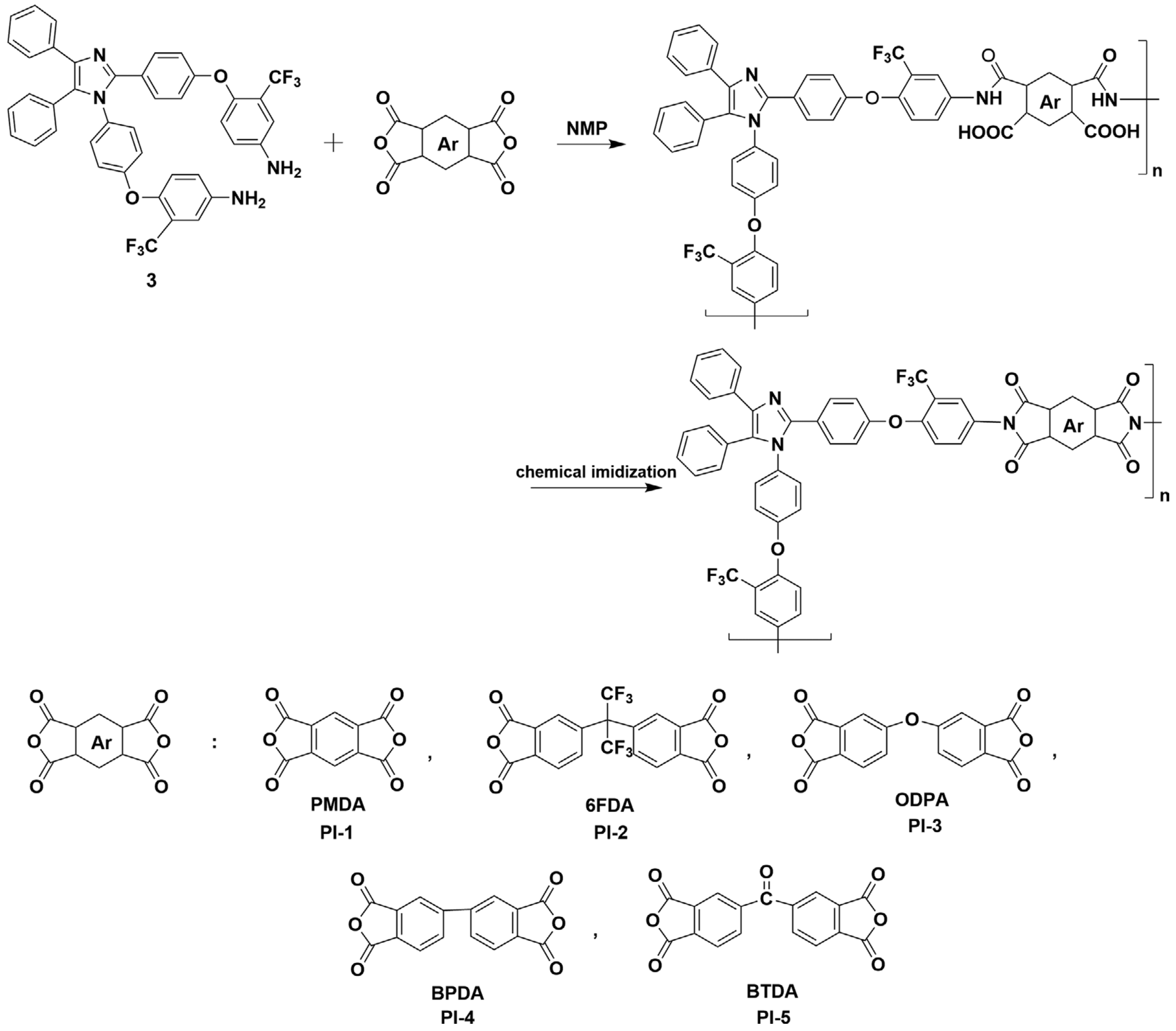


Figure 2. ^{1}H NMR spectrum of diamine **3**.



Scheme 2. Synthesis route of the PIs.

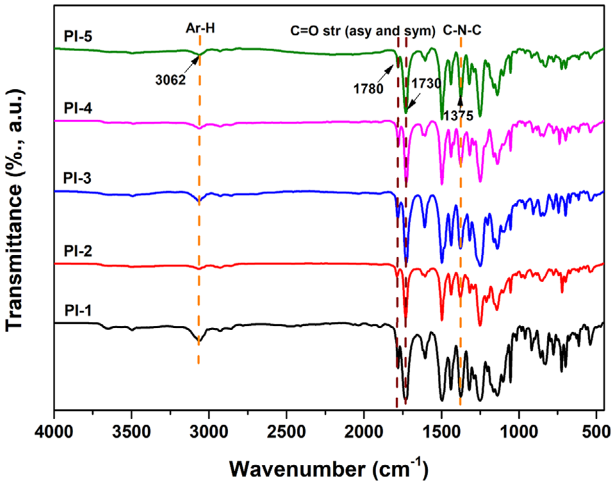


Figure 3. FTIR spectra of the resulting PIs.

As shown in Figure 4, all the peaks in the ^{1}H NMR spectra of the obtained PIs were assigned to the corresponding protons, which was in agreement with the proposed PI structures. Taking PI-1 as an example, the peak at 8.31 ppm was ascribed to the protons from the dianhydride part in the PI repeating unit, and the remaining peaks were assigned to the aromatic protons from the diamine. In addition, there were no amino group peaks (at around 5.5 ppm), thereby confirming the fully imidized structure. Moreover, the elemental analysis data of the resulting PIs shown in Table 1 also further confirm the successful preparation of the target PIs.

The molecular weights of the resulting PIs were measured *via* GPC. As shown in Table 2, the weight average molecular weights of the PIs were in the range of 4.64 × 10^4 to 8.68 × 10^4 g·mol^{-1}, while their number average molecular weights ranged from 1.57 × 10^4 to 3.17 × 10^4 g·mol^{-1}, with polydispersity indices in the range of 2.53 to 3.60.

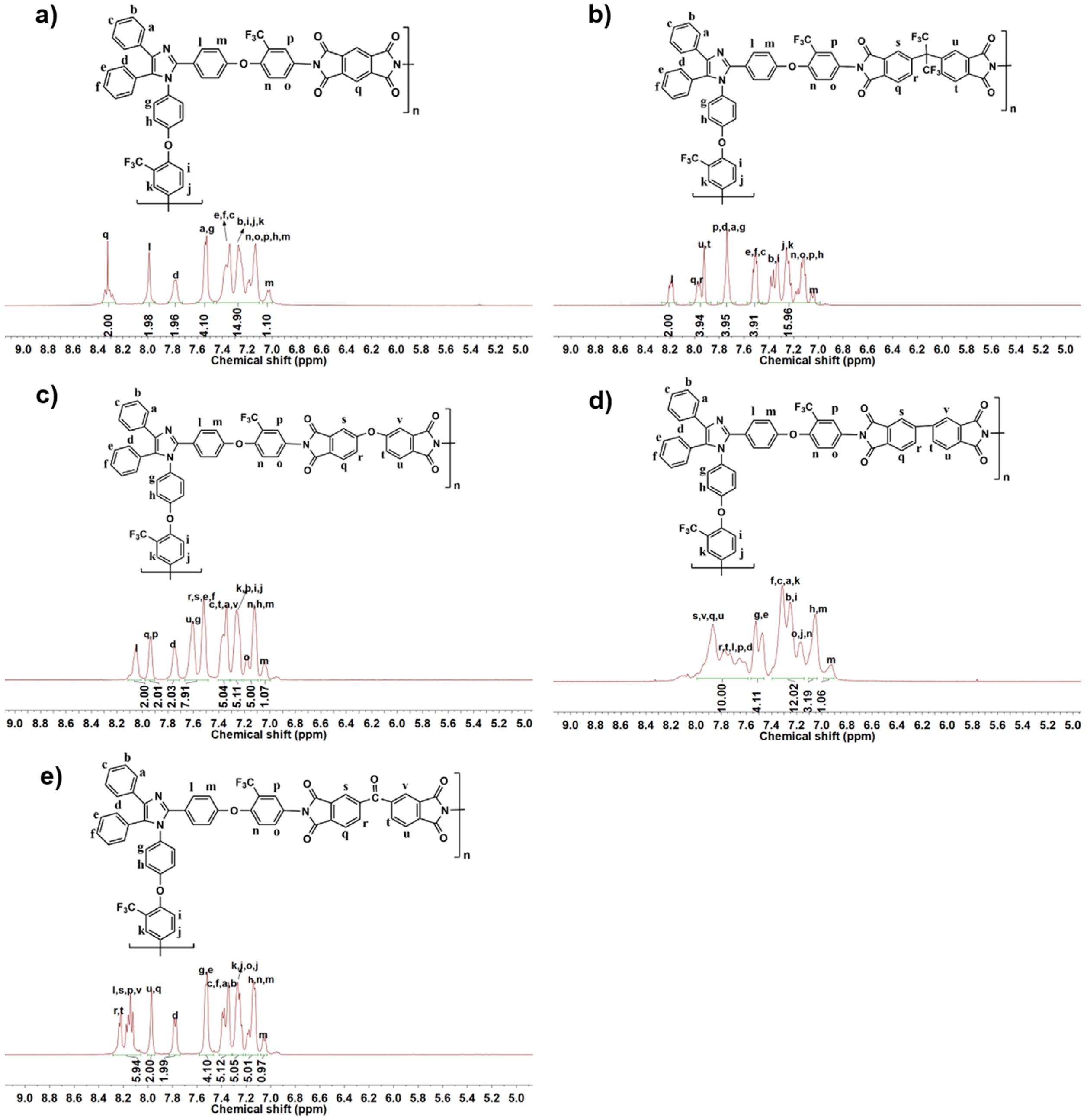


Figure 4. ^{1}H NMR spectra of the resulting PIs: (a) PI-1, (b) PI-2, (c) PI-3, (d) PI-4, and (e) PI-5.

Table 1. Elemental analysis data of the resulting PIs

PI	Formula		Elemental analysis (%)		
			C	H	N
PI-1	$C_{51}H_{26}F_6N_4O_6$	Calculated	67.70	2.90	6.19
		Found	66.87	3.44	5.94
PI-2	$C_{60}H_{30}F_{12}N_4O_6$	Calculated	63.72	2.67	4.95
		Found	63.16	3.03	4.78
PI-3	$C_{57}H_{30}F_6N_4O_7$	Calculated	68.68	3.03	5.62
		Found	67.75	3.37	5.41
PI-4	$C_{57}H_{30}F_6N_4O_6$	Calculated	69.80	3.08	5.71
		Found	68.83	3.27	5.60
PI-5	$C_{58}H_{30}F_6N_4O_7$	Calculated	69.05	3.00	5.55
		Found	68.18	3.26	5.43

Table 2. GPC data of the PIs

PIs	M_n[a] (g mol^{-1})	M_w[b] (g mol^{-1})	PDI[c]
PI-1	31,700	86,800	2.74
PI-2	19,700	66,900	3.40
PI-3	15,700	46,400	2.96
PI-4	17,300	62,200	3.60
PI-5	22,500	56,900	2.53

[a] M_n: number-average molecular weight. [b] M_w: weight-average molecular weight. [c] PDI: polydispersity index.

3.3. X-ray diffraction

XRD was conducted to study the microscopic crystallinity of the prepared PI films, and the corresponding results are shown in Figure 5. All the diffractograms were featureless and showed only wide diffraction peaks at a 2θ value of approximately 14°, thereby indicating that the obtained PIs were amorphous. This is mainly due to the introduction of CF_3 groups and the imidazole structure into the polymer main chain, which can increase the molecular chain spacing and free volume of the polymer, as well as reduce the symmetry and regularity of the main chain. Consequently, the crystallization of PI chains was impeded owing to the decreased interchain interactions and chain packing efficiency.

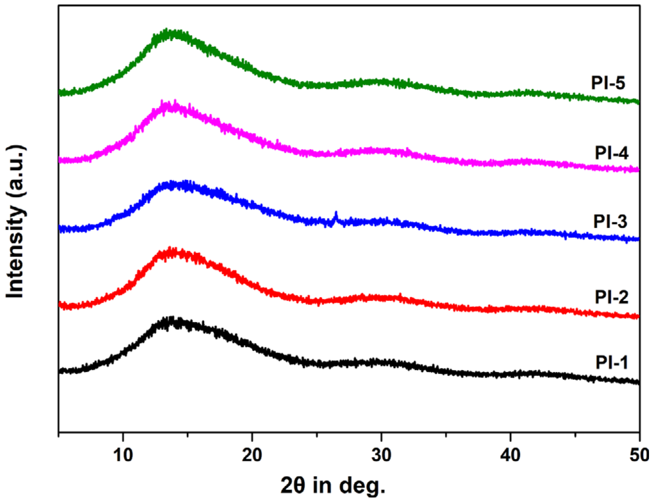


Figure 5. XRD patterns of the resulting PIs.

3.4. Solubility and water absorption rate

The solubility of the obtained aromatic PI resins was tested in diverse organic solvents by using 10 mg of the polymer dissolved in 1 mL solvent at 30 °C for 2 h. As presented in Table 3, all of the prepared PI resins displayed outstanding solubility in common high-boiling point solvents, such as DMF, DMAc, NMP, and *m*-cresol, as well as some low-boiling point solvents, including $CHCl_3$ and THF. This is because the introduction of CF_3 groups, ether bonds, and imidazole structures into the main polymer chain can effectively improve the solubility of the polymer.[7] Furthermore, CF_3 groups not only can hinder the interaction and close packing between the polymer chains, but also can weaken the intermolecular cohesion owing to the low polarizability of the C-F bond. The ether bond, as a flexible group, can reduce the energy barrier of rotation within the molecular chain, decrease the close chain packing density, and increase polymer flexibility. The imidazole structure can reduce the interaction between polymer chains, molecular regularity, and segmental mobility, thereby improving polymer solubility. Herein, the PI-2 derived from diamine **3** and 6FDA could also be easily dissolved in acetone, owing to the introduction of more fluorine atoms from the dianhydride, which could impede the stacking density of chains and reduce the intermolecular cohesive force.

Table 3. Solubility and water absorption rates of the resulting PIs[a]

PIs	DMF	DMAc	NMP	*m*-cresol	$CHCl_3$	THF	acetone	Water absorption (%)
PI-1	+	+	+	+	+	+	-	1.98
PI-2	+	+	+	+	+	+	+	1.81
PI-3	+	+	+	+	+	+	-	1.82
PI-4	+	+	+	+	+	+	-	1.80
PI-5	+	+	+	+	+	+	-	0.78

[a] DMF: *N*,*N*-dimethylformamide; DMAc: dimethylacetamide; NMP: *N*-methyl pyrrolidone; $CHCl_3$: trichloromethane; THF: tetrahydrofuran; +: soluble; -: insoluble.

The water absorption rates of the obtained PI films were investigated by calculating the weight changes before and after immersion in deionized water at room temperature for 72 h. The data are summarized in Table 3. It was shown that all the PI films possessed water absorption rates in a range of 0.78% to1.98%, indicating tolerable dimensional stability after moisture absorption.

3.5. Thermal properties

The thermal stability of the five PIs was characterized by means of TGA in nitrogen. The TGA curves are shown in Figure 6 (left), and the corresponding decomposition results are illustrated in Table 4. All of the PI films exhibited thermal stabilities with 10% weight loss temperatures ($T_{10\%}$) in the range of 545 to 562 °C and 5% weight loss temperatures ($T_{5\%}$) in the range of 500 to 541 °C, which indicated that incorporating CF_3 groups and imidazole units into the polymer chains did not reduce their inherent thermal stability. It is well known that polyimides containing aromatic groups or trifluoromethyl groups usually exhibit high thermal stability.[7,12,19] However, polyimides with aromatic heterocyclic groups or linear alkyls often display relatively low thermal stability.[17] Here, we compared the decomposition temperatures at 5% weight loss ($T_{5\%}$) of all PIs. The PI-1 derived from PMDA with only one benzene ring exhibited the lowest $T_{5\%}$ value, while PI-4 derived from BPDA with biphenyl in the polymer chains showed the highest $T_{5\%}$ value. In addition, PI-2 with trifluoromethyl groups, PI-3 with flexible ether group and PI-5 with carbonyl group possessed lower $T_{5\%}$ values than PI-4.

The T_gs of PI-(1-5) were characterized *via* DSC in nitrogen. The DSC thermograms were derived from the second heating curves obtained in DSC plots, as shown in Figure 6 (right). The corresponding T_g values are illustrated in Table 4. The T_g values of all the PIs ranged from 245 to 295 °C. As expected, the different T_g values mainly depended on the different dianhydride components, with the order of PI-1 > PI-4 > PI-2 > PI-5 > PI-3, which was consistent with the rigidity of the dianhydride monomer PMDA> BPDA> 6FDA> BTDA> ODPA.[39] It was observed that the T_g of PI-1 derived from PMDA was the highest (295 °C) among all PIs, which could be attributed to its most rigid structure. The PI-3 derived from ODPA possessed the lowest T_g value (245 °C) due to the flexible ether linkage in the polymer chain. Moreover, PI-4 with biphenyl in the polymer chains exhibited the second highest T_g value. Compared to PI-5 with carbonyl group, trifluoromethyl groups of PI-2 could limit the movement of polyimide chains and increase the T_g value.

Table 4. TGA and DSC data of all the PIs

PIs	T_g^a (°C)	$T_{10\%}^b$ (°C)	$T_{5\%}^c$ (°C)
PI-1	295	545	500
PI-2	268	546	524
PI-3	245	562	526
PI-4	271	562	541
PI-5	257	550	528

$^a T_g$: glass transition temperature, evaluated by DSC; $^b T_{10\%}$: temperature at 10% weight loss, evaluated by TGA; $^c T_{5\%}$: temperature at 5% weight loss, evaluated by TGA.

3.6. Mechanical properties

The mechanical properties of the resulting PI films were measured by tensile testing at room temperature. There are many factors influencing the mechanical properties of polyimides, such as the chemical structure, molecular weight, preparation procedure and film preparation, *etc*. In fact, therefore, no clear rule can be discerned for the mechanical properties of the polyimides. In general, however, flat and uniform polyimide films with high molecular weights and rigid structures tend to exhibit high tensile strength and tensile modulus.[3,15] In addition, polyimides with flexible linkage units or noncoplanar and asymmetrical structures in the main chain tend to usually possess higher value of elongation at break.[40,41]

In Table 5, it can be observed that the tensile strength of the PIs containing CF_3 groups and imidazole structure ranges from 30.1 to 52.8 MPa, together with modulus values of 1.0 to 1.7 GPa. Compared to general polyimides with the elongation at break ranging from 2 to 15%, PI-(1-5) synthesized in this work showed low elongation at break (< 6.1%), which could be contributed to the rigid structures of all PIs.[3] The data for the PI-3 prepared by ODPA were not successfully obtained through the tensile test. Among all aforementioned factors, here, the chemical structure of the polyimides seemed to play important roles

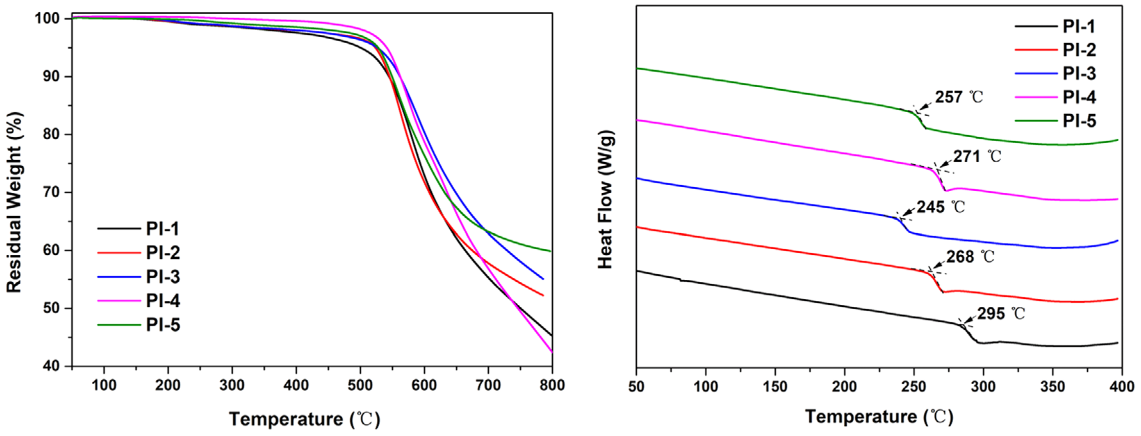


Figure 6. TGA curves (left) and DSC thermograms (right) of all the PIs.

Table 5. Mechanical properties of the PIs

PIs	Film thickness (μm)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
PI-1	35	49.4 ± 1.3	1.7 ± 0.04	5.1 ± 0.2
PI-2	40	45.0 ± 1.6	1.2 ± 0.02	4.7 ± 0.1
PI-3	40	-	-	-
PI-4	30	30.1 ± 2.6	1.2 ± 0.03	3.5 ± 0.2
PI-5	42	52.8 ± 1.9	1.0 ± 0.02	6.1 ± 0.4

in influencing the mechanical properties.[3] Since there are two flexible ether linkages in the diamine unit, ODPA with one ether linkage between two benzene rings in the dianhydride unit may significantly reduce the rigidity of the PI-3, which may lead to the difficulty in the tensile test.[42] PI-1 and PI-5 exhibited the best mechanical properties, which were mainly due to their rigid skeletal structures and relatively high molecular weights.[43] It was reported that PI with higher molecular weight exhibited higher tensile strength and tensile modulus.[42]

3.7. Optical properties

In general, the optical properties of PI films are mainly affected by the chemical structures, synthesis routes and imidization methods, and film preparation process. Here we used a low-temperature two-step method *via* chemical imidization to inhibit the influence of high temperatures. As for chemical structures, the intra- and inter-chain donor-acceptor charge transfer interactions can create a new absorption band in the visible light region, resulting in deep color and low transparency of polyimides.[15]

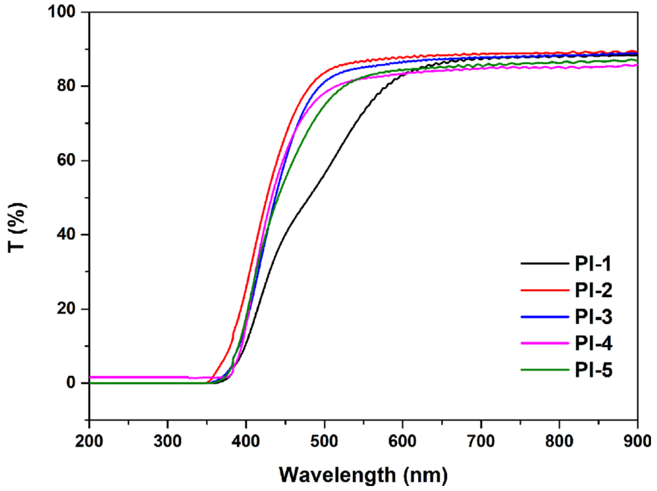


Figure 7. UV-Vis spectra of the PI films (Thickness: 21-26 μm).

The optical properties of the resulting PI films were measured using a UV-Vis spectrometer. The UV-Vis spectra are displayed in Figure 7, and the related data are listed in Table 6. All the resulting PI films exhibited transmittances over 74% in the visible light region ranging from 400 to 760 nm, with a cut-off wavelength between 301 and 352 nm, though they are partially colored. The yellowness index (YI) of the PI films were in the range of 17.3-45.5, with the order in accordance with that of the optical transparency. Among PI-(1-5), PI-2, derived from 6FDA, showed the best optical transparency and lightest color due to the presence of CF_3 groups in 6FDA, which was considerably effective in inhibiting CTC formation between polymer chains through steric hindrance. Moreover, PI-1, derived from PMDA, possessed the deepest color and the lowest average transmittance (74%) owing to its rigid backbone, although it still surpassed that of Kapton (69%).[13] For PI-3, the introduction of the flexible ether group as an electron-donating group in the dianhydride unit can weaken the interchain CT interactions and improve the optical transparency.[15] For PI-4 with biphenyl in the polymer chains and PI-5 with the carbonyl group, they showed generally better optical transparency and the lower YI values that of a typical commercial polyimide such as Upilex-S (YI=46.0 with a thickness of 15 μm).[7] Generally, the transparency of PI-(1-5) derived from the novel diamine **3** with CF_3 groups and the imidazole unit was enhanced due to the decreased interchain interaction and CTC formation.

4. Conclusions

In this work, a novel diamine containing CF_3 groups and an imidazole unit was successfully synthesized *via* three steps, and a series of PIs were prepared through a low-temperature two-step polycondensation process *via* chemical imidization. All of the obtained PIs exhibited outstanding solubility in various organic solvents, including high-boiling point solvents, such as NMP, DMAc, DMSO, and *m*-cresol, as well as low-boiling point solvents, including $CHCl_3$ and THF. The PI films exhibited T_g> 245 °C, $T_{5\%}$> 500 °C, water absorption rates in a range of 0.78%

Table 6. Optical properties of the PIs

PIs	Film thickness (μm)	T_{vis}[a] (%)	T_{450}[b] (%)	T_{400}[c] (%)	λ_0[d] (nm)	YI[e]
PI-1	26	74	40	11	352	45.5
PI-2	23	83	67	26	326	17.3
PI-3	21	81	60	16	324	23.3
PI-4	22	79	62	16	301	31.9
PI-5	21	78	55	18	336	34.1

[a]The average transmittance in the visible light range (400 - 760 nm). [b]Transmittance at 450 nm. [c]Transmittance at 400 nm. [d]UV cut-off wavelength. [e]Yellowness index.

to 1.98%, and transmittances of $T_{vis} > 74\%$ in the visible light region ranging from 400 to 760 nm. The tensile strength of the PI films is in the range of 30.1 to 52.8 MPa, while the tensile modulus ranges from 1.0 to 1.7 GPa, while the toughness of the PI films should be more improved. Summarily, introducing CF_3 groups and imidazole units into polymer chains is an effective way to enhance the solubility and transparency of the PI films without significantly reducing the inherent thermal stability.

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