

Aromatic Polyimides with Tertbutyl-substituted and Pendent Naphthalene Units: Synthesis and Soluble, Transparent Properties^{*}

Chan-juan Liu^{a,b}, Mei Mei^a, Xiang-lin Pei^a, Xiao-hua Huang^{a**} and Chun Wei^a

^a Key Laboratory of New Processing Technology for Nonferrous Metal & Materials, Ministry of Education, and School of Material Science and Engineering, Guilin University of Technology, Guilin 541004, China

^b Ministry of Education Key Laboratory for the Chemistry and Molecular Engineering of Medicinal Resources, School of Chemistry and Pharmaceutical Science, Guangxi Normal University, Guilin 541004, China

Abstract A novel non-coplanar aromatic diamine monomer, 3,3'-ditertbutyl-4,4'-diaminodiphenyl-4"-naphthylmethane (TAPN) was synthesized by a condensation reaction of 2-tertbutylaniline and 1-naphthaldehyde under catalyst hydrochloric acid. The structure of the monomer was confirmed by FTIR, NMR, elementary analysis and mass spectrometry. A series of aromatic polyimides (PIs) were synthesized *via* conventional one-step polycondensation from TAPN and various commercial aromatic dianhydrides. All of the PIs exhibit excellent solubility in common organic solvents, even in low boiling point solvents such as chloroform (CHCl₃), tetrahydrofuran (THF) and acetone. The PIs present outstanding thermal stability with the glass transition temperature (T_g) ranged from 299 °C to 350 °C, and the temperature at 10% weight loss ranged from 490 °C to 504 °C, and high optical transparency with the cutoff wavelengths of 306–356 nm. Moreover, the flexible and tough PI films have prominent mechanical properties with tensile strengths in the range of 77.6–90.5 MPa, tensile modulus in the range of 1.8–2.4 GPa and elongation at break in the range of 6.3%–9.5%, as well as lower dielectric constant (2.89–3.12 at 1 MHz) and lower moisture absorption (0.35%–0.66%).

Keywords: Polyimides; Solubility; Dielectric constant; Tertbutyl; Naphthyl.

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INTRODUCTION

Over the past five decades, polyimides (PIs) have attracted considerable attention as high performance polymers because of their outstanding comprehensive performance, such as good thermal stability, excellent mechanical and electrical properties, prominent chemical and radiation resistance, remarkable insulation properties and low water absorption. They have been widely used in the traditional fields of aerospace, automobile, microelectronics and optoelectronics device, microlens arrays, gas separation, coating materials and so on^[1–3]. However, traditional PIs present insolubility in most organic solvents and high melting temperature before their decomposition temperature due to the aromatic rigid chain characteristics and the strong inter-chain interactions. Furthermore, most of PIs exhibit strong color close to yellow or brown resulting from the inter-molecular charge transfer complex (CTC) between the aromatic structures in these polymers and intra-molecular CTC between

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^{**} Corresponding author: Xiao-hua Huang (黄孝华), E-mail: huangxiaohua@glut.edu.cn

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alternating electron donors and electron acceptors^[4].

In order to balance the thermal stability and the processability, great efforts have been devoted to overcome these drawbacks of PIs as mentioned above by chemical structure modification. So far, numerous considerable efforts have been made to develop solubility and processability of PIs by the introduction of flexible linkages^[5, 6], bulky substituents^[7–12], pendant loop groups^[13], non-coplanar and unsymmetrical structures^[14–18], and alicyclic moieties into the polymer backbones^[19–21]. Moreover, it is also an effective approach to develop the solubility and optical transparency of PIs by incorporation of fluorinated substituents, such as hexafluoroisopropylidene linkages^[22], perfluoroalkyl and pendent trifluoromethyl groups into the polymer structure^[23–25]. However, up to a certain extent, the high cost of the fluoride monomers limits their utility in various advanced technological applications. Among them, the introduction of bulky substituents, non-coplanar and unsymmetrical structures into polymer backbones is considered as an efficient way to develop the solubility and processability of PIs without sacrificing their thermal stability and mechanical properties. It is because the structure of PIs can interrupt the chain packing and weaken the polymer chain intermolecular interactions, and then improve the solubility and processability of PIs. Therefore, many new diamines and dianhydrides have been designed and synthesized to produce a series of soluble and processable PIs for various purposes and applications. Mousa Ghaemy *et al.*^[13] reported a series of PIs containing bulky-flexible triaryl pyridine pendent groups, and the PIs exhibited good solubility in various aprotic polar solvents and excellent thermal stability. Liaw *et al.*^[15] synthesized PIs with high optical transparency, good solubility and thermal properties derived from a novel diamine 4-(2-naphthyl)-2,6-bis(4-aminophenyl) pyridine containing pyridine heterocyclic group and naphthalene substituent.

In this study, a novel diamine 3,3'-ditertbutyl-4,4'-diaminodiphenyl-4"-naphthylmethane (TAPN) containing tertbutyl and naphthyl moieties was designed and synthesized, and then used to prepare non-coplanar PIs with five commercially available aromatic dianhydrides *via* one-step reaction. The CambridgeSoft Chem 3D structure of TAPN and its PI are presented in Fig. 1. As shown in the circle, the TAPN and its polymer have a special twisted non-planar steric structure in the polymer backbone under optimized energy state, and the non-planar steric structure reduces the strong inter- and intra-molecular interaction and tight stacking of the molecular chains effectively. In comparison with the previous research work, all of novel PIs are prepared by incorporation of the larger pendent groups and non-planar steric structures in the polymer chain. In this paper, we hope to provide a new approach to design and synthesize a series of organo-soluble PIs, and not sacrifice its other properties such as thermo-stability and mechanical properties. As a result, all of the obtained polymers exhibited excellent solubility in common polar solvents such as DMF, DMAc, NMP, DMSO, *m*-cresol, and even in low boiling point solvent such as CHCl₃, THF and acetone. Moreover, the thermal stability, optical transparency, mechanical properties, dielectric constant and moisture uptakes of the polymers were investigated.

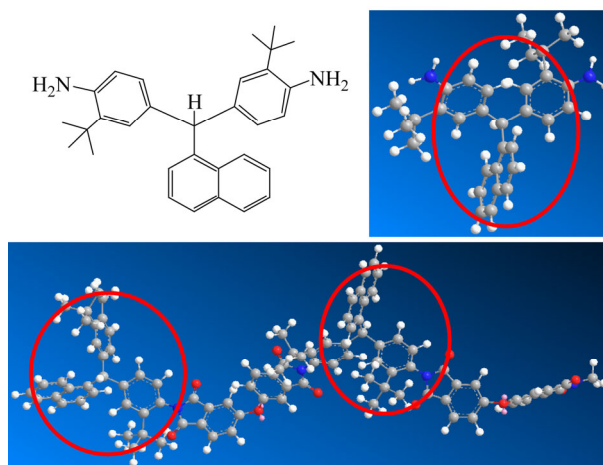


Fig. 1 3D structure of TAPN and its polyimide

EXPERIMENTAL

Materials

2-Tertbutylaniline (Shanghai DEMO Medical Tech Co., Ltd) and 1-naphthaldehyde (Shanghai Darui Chemical Co., Ltd) were used as received. Pyromellitic dianhydride (PMDA) (Shanghai Guoyao Chemical Co., Ltd), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), 4,4'-oxydiphthalic anhydride (ODPA) (Changzhou Linchuan Chemical Co., Ltd), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and (4,4'-hexafluoroisopropylidene)-diphthalic anhydride (6FDA) (Tokyo Chemical Industry Co., Ltd) were recrystallized from acetic anhydride and then dried in vacuum at 120 °C overnight before use. *N,N*-Dimethyl formamide (DMF) and *m*-cresol (Shanghai Guoyao Chemical Co., Ltd) were purified by vacuum distillation over calcium hydride prior to use. All other solvents were analytical-grade and used without further purification.

Preparation of Monomer

3,3'-Ditertbutyl-4,4'-diaminodiphenyl-4''-naphthylmethane (TAPN)

A 250 mL three-necked round-bottomed flask equipped with a dropping funnel, a reflux condenser and a nitrogen inlet was charged with 2-tertbutylaniline (20.00 g, 0.13 mol) and heated to 120 °C under nitrogen atmosphere. Then a mixture of 1-naphthaldehyde (8.12 g, 0.052 mol) and 3 mL (12 mol/L) of hydrochloric acid was added dropwise through the funnel over 1 h. The reaction mixture was stirred for another 10 h at 155 °C. After the reaction mixture was cooled to 70 °C, it was added into 30 mL (10 wt%) aqueous solution of sodium hydroxide to obtain the resulting suspension. The mixture was extracted three times with dichloromethane, then washed three times with deionized water and dried over anhydrous MgSO₄. After filtration, the solvent was distilled to obtain brown powders, then the pure monomer was obtained by column chromatography on silica gel (ethyl acetate:hexane (*V/V*) = 6:1) to obtain light yellow solid power (17.03 g, yield 75%); m.p. 40.2 °C (by DSC at a scan rate of 5 K/min). ¹H-NMR (δ, DMSO): 8.15 (d, 1H, *J* = 7.2 Hz), 7.90 (d, 1H, *J* = 7.6 Hz), 7.75 (s, 1H, *J* = 8.0 Hz), 7.45 (m, 3H, *J* = 19.6 Hz), 6.98 (d, 1H, *J* = 7.2 Hz), 6.90 (s, 2H), 6.65 (d, 2H, *J* = 7.6 Hz), 6.56 (d, 2H, *J* = 8.0 Hz), 5.99 (s, 1H), 4.61 (s, 4H, —NH₂), 1.24 (s, 18H, —CH₃); ¹³C-NMR (δ, DMSO): 144.54, 142.74, 134.21, 132.59, 132.39, 132.22, 129.11, 127.89, 127.59, 127.02, 126.43, 125.96, 125.87, 125.14, 117.60, 51.94, 34.62, 29.99. FTIR (KBr, cm⁻¹): 3386–3454 cm⁻¹ (—NH₂), 2963–2869 cm⁻¹ (C—H), 1618, 1466, 1245, 787; MS (*m/z*): 437.3 ([M + H]⁺).

Preparation of Polyimides

General one-step procedure for the preparation of PIs is described in Scheme 2. A typical example of PI-ODPA was polymerized as follows. A 50 mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet and a reflux condenser was charged with TAPN (1.0475 g, 2.40 mmol), ODPA (0.7442 g, 2.40 mmol), 16 mL of *m*-cresol and about 5 drops of isoquinoline. The mixture was stirred at room temperature for about 1 h until the reaction mixture to form a transparent solution under nitrogen atmosphere. Then the reaction mixture was heated gradually to reflux and maintained for 18 h. The water formed during the imidization was removed steadily by the stream of nitrogen. The reaction mixture was cooled, poured slowly into ethanol to form a fiber-like precipitate. The polymer was collected by filtration, washed thoroughly with hot ethanol and dried at 150 °C under vacuum overnight. The pure PI-ODPA was obtained by re-precipitating at least twice. The PIs of PI-PMDA, PI-BPDA, PI-BTDA and PI-6FDA were synthesized by the same procedures as adopted for the synthesis of PI-ODPA.

PI-PMDA

The PI-PMDA was prepared from the diamine (TAPN) and PMDA. The yield was 93%. ¹H-NMR (400 MHz, DMSO, δ): 8.474 (s, 2H, ArH), 8.45–8.43 (d, H, ArH), 8.29–8.26 (d, H, ArH), 7.97–7.95 (d, H, ArH), 7.88–8.40 (t, H, ArH), 7.50–7.47 (t, 2H, ArH), 7.45–7.43 (d, 2H, ArH), 7.35–7.33 (d, 2H, ArH), 7.19–7.17 (d, 2H, ArH), 7.07 (s, H, ArH), 6.68 (s, H, CH), 1.14 (s, 18H, CH₃). FTIR (KBr, cm⁻¹): 3030–2870 (alkyl), 1779 and 1724 (C=O, imide, stretching vibration), 1371 (C—N), 732 (C=O, imide, bending vibration). Elemental analysis calculated for (C₄₇H₃₈N₂O₅)_n: C, 79.59%; N, 4.53%. Found: C, 79.66%; N, 4.50%.

PI-BPDA

The PI-BPDA was prepared from the diamine (TAPN) and BPDA. The yield was 95%. ¹H-NMR (400 MHz, DMSO, δ): 8.40 (s, 2H, ArH), 8.34–8.32 (d, 2H, ArH), 8.27–8.25 (d, H, ArH), 8.07–8.05 (m, 2H, ArH), 7.94–7.92 (d, H, ArH), 7.84–7.82 (d, H, ArH), 7.51–7.48 (m, 3H, ArH), 7.42–7.40 (d, 2H, ArH), 7.26 (s, 2H, ArH), 7.13–7.11 (d, 2H, ArH), 7.07–7.06 (d, H, ArH), 6.64 (s, H, CH), 1.12 (s, 18H, CH₃); FTIR (KBr, cm⁻¹): 3031–2871 (alkyl), 1779 and 1724 (C=O, imide, stretching vibration), 1371 (C–N), 732 (C=O, imide, bending vibration). Elemental analysis calculated for (C₄₇H₃₈N₂O₅)_n: C, 81.24%; N, 4.03%. Found: C, 81.33%; N, 4.00%.

PI-ODPA

The PI-ODPA was prepared from the diamine (TAPN) and ODPA. The yield was 91%. ¹H-NMR (400 MHz, DMSO, δ): 8.26–8.24 (d, H, ArH), 8.04–8.02 (d, 2H, ArH), 7.95–7.93 (d, H, ArH), 7.85–7.83 (d, H, ArH), 7.67–7.63 (m, 4H, ArH), 7.52–7.48 (m, 3H, ArH), 7.39–7.37 (s, 2H, ArH), 7.23 (s, 2H, ArH), 7.11–7.05 (m, 3H, ArH), 6.62 (s, H, CH), 1.11 (s, 18H, CH₃). FTIR (KBr, cm⁻¹): 3030–2870 (alkyl), 1779 and 1720 (C=O, imide, stretching vibration), 1371 (C–N), 730 (C=O, imide, bending vibration). Elemental analysis calculated for (C₄₇H₃₈N₂O₅)_n: C, 79.42%; N, 3.94%. Found: C, 79.31%; N, 3.98%.

PI-BTDA

The PI-BTDA was prepared from the diamine (TAPN) and BTDA. The yield was 90%. ¹H-NMR (400 MHz, DMSO, δ): 8.27–8.24 (m, 3H, ArH), 8.20 (s, 2H, ArH), 8.18–8.16 (d, H, ArH), 7.94–7.92 (d, H, ArH), 7.85–7.83 (d, H, ArH), 7.52–7.48 (m, 4H, ArH), 7.43–7.41 (d, 2H, ArH), 7.29 (s, 2H, ArH), 7.15–7.13 (d, 2H, ArH), 7.07–7.05 (d, H, ArH), 6.65 (s, H, CH), 1.12 (s, 18H, CH₃). FTIR (KBr, cm⁻¹): 3031–2871 (alkyl), 1779 and 1724 (C=O, imide, stretching vibration), 1371 (C–N), 732 (C=O, imide, bending vibration). Elemental analysis calculated for (C₄₇H₃₈N₂O₅)_n: C, 79.76%; N, 3.88%. Found: C, 79.84%; N, 3.90%.

PI-6FDA

The PI-6FDA was prepared from the diamine (TAPN) and 6FDA. The yield was 91%. ¹H-NMR (400 MHz, DMSO, δ): 8.25–8.23 (d, H, ArH), 8.13–8.11 (d, 2H, ArH), 7.93–7.90 (m, 3H, ArH), 7.84–7.80 (m, 3H, ArH), 7.50–7.46 (m, 3H, ArH), 7.37–7.35 (d, 2H, ArH), 7.29 (s, 2H, ArH), 7.12–7.09 (m, 3H, ArH), 6.62 (s, H, CH), 1.10 (s, 18H, CH₃). FTIR (KBr, cm⁻¹): 3030–2870 (alkyl), 1779 and 1720 (C=O, imide, stretching vibration), 1371 (C–N), 732 (C=O, imide, bending vibration). Elemental analysis calculated for (C₄₇H₃₈N₂O₅)_n: C, 71.08%; N, 3.32%. Found: C, 70.93%; N, 3.38%.

Preparation of Membranes

The flexible and tough PI films were prepared by the traditional method of solution casting. First, the obtained PIs were dissolved in DMF with a concentration of approximate 2 wt% or 10 wt%. Then the homogeneous solution was cast onto a dust-free glass plate and then heated at 60 °C for 12 h. When most of the DMF was evaporated, the PI films were heated under vacuum at 100 °C for 4 h, and 150 °C for another 6 h to remove the residual solvent. Finally, the films were peeled off from the glass substrates by immersing in warm deionized water, and further dried in a vacuum oven at 180 °C for 12 h. The films with thickness about 50–70 μ m were used for thermal properties, mechanical strength, dielectric constant and water absorption characterization, and the films with thickness of about 10–15 μ m were used for FTIR and optical performance analysis.

Characterization

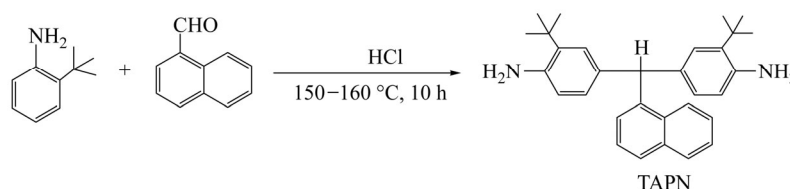
Fourier transform infrared (FTIR) measurements were performed on a Thermo Nexus 470 FTIR spectrometer. ¹H- and ¹³C-NMR were recorded using an Avance III 400 apparatus with deuterated dimethylsulfoxide (DMSO-d₆) as solvents. UV-Visible spectra were studied on a UV-3600 UV-Visible spectrophotometer. Thermogravimetric analysis (TGA) was carried out on a TGA Q500 analyzer in nitrogen with a heating rate of 10 K/min. Differential scanning calorimetry (DSC) was performed on a DSC-204 phoenix thermal analyzer in a nitrogen atmosphere at a heating rate of 20 K/min. The mechanical properties of the films were measured using a CMT-4104 (SANS, Shenzhen, China) tensile tester with a load cell of 5 Kg at a crosshead speed of 2 mm/min at

room temperature, and the size of each film sample was approximately 50 mm × 10 mm × 0.05 mm. Elemental analysis was measured by a Perkin-Elmer model 2400 II instrument. Mass spectrometry was run on an Elementar Vario EL III/Isoprime apparatus. The molecular weight and molecular weight distribution were measured with a Waters 1515 gel permeation chromatography (GPC) analyzer relative to polystyrene standards using DMF as the eluent with LiBr salt added. Dielectric constant was determined by the parallel plate capacitor method using a dielectric analyzer (Agilent 4294A) with thin films. Gold electrodes were vacuum deposited on both surfaces of films, and these films were tested in a dry chamber at different frequencies. The water absorption was determined by weighing the change of PI films before and after being immersed in distilled water at 25 °C for 72 h.

RESULTS AND DISCUSSION

Monomer Synthesis

The novel diamino monomer, 3,3'-ditertbutyl-4,4'-diaminodiphenyl-4"-naphthylmethane (TAPN) was prepared from commercially available 2-tertbutylaniline and 1-naphthaldehyde catalyzed by hydrochloric acid. The reaction sequence is shown in Scheme 1. It should be noted that the critical condition of this reaction must be performed under completely oxygen-free atmosphere. The obtained crude product TAPN was purified by silica gel chromatography and pure enough for polymerization with commercial aromatic dianhydride monomers to prepare PIs.



Scheme 1 Synthesis of diamine monomer TAPN

The chemical structures of the novel aromatic diamine (TAPN) were identified by FTIR, ¹H- and ¹³C-NMR, elemental analysis and MS spectrometry. The FTIR spectrum of TAPN showed amino group characteristic bands at 3454 and 3386 cm⁻¹ (stretching vibration) and typical C—H stretching absorption peaks at 2963 and 2869 cm⁻¹. The structure of diamine was also confirmed by high-resolution NMR spectra. As shown in Fig. 2(a), in the ¹H-NMR spectroscopy, the signal in $\delta = 4.61$ was ascribed to the protons of primary amine (—NH₂), the signals in the range of $\delta = 8.15$ – 6.56 were attributed to the protons of the aromatic rings, and the characteristic resonance signals at $\delta = 5.99$ and 1.24 corresponded to alkyl (—CH—) and alkyl (—CH₃) groups, respectively. The ¹³C-NMR spectrum of the monomer TAPN is shown in Fig. 2(b). The ¹³C-NMR spectrum exhibited 18 peaks for aromatic carbons of TAPN, and assignments of each carbon are given in the figure, and the spectrum agrees well with the proposed molecular structure. Furthermore, the results of the elemental analysis and MS spectrometry are in good agreement with the calculated results. The geometric structure of TAPN illustrated in Fig. 1 was optimized by CambridgeSoft Chem 3D Ultra. Because of the introduction of tertbutyl and naphthyl groups, the novel amine monomer could keep a large twist of non-coplanar structure and dihedral angle between aromatic phenyl rings to get the minimum energy of conformation. This non-coplanar structure is helpful to endow PIs with some outstanding properties.

Polymer Synthesis

Usually, aromatic polyimide is synthesized from aromatic diamine and aromatic dianhydride by a two-step method or a one-step method condensation polymerization. The two-step method synthetic techniques for PIs generally consist of the formation of the poly(amic acid) (PAA) precursor followed by a thermal or chemical imidization to give PI. The one-step homogeneous solution polymerization technique is another normal method for the PIs, which must be soluble in organic solvents at elevated polymerization temperature. As shown in

Scheme 2, the new PIs were synthesized from novel diamine TAPN and commercially available dianhydrides, such as PMDA, BPDA, ODPA, BTDA and 6FDA *via* a one-step method in *m*-cresol using isoquinoline as catalyst. The whole polymerization process maintained homogeneously throughout the reaction and afforded clear, viscous polymer solutions. The pure fibrous PIs were obtained by precipitation in an excess of ethanol and re-precipitated at least twice.

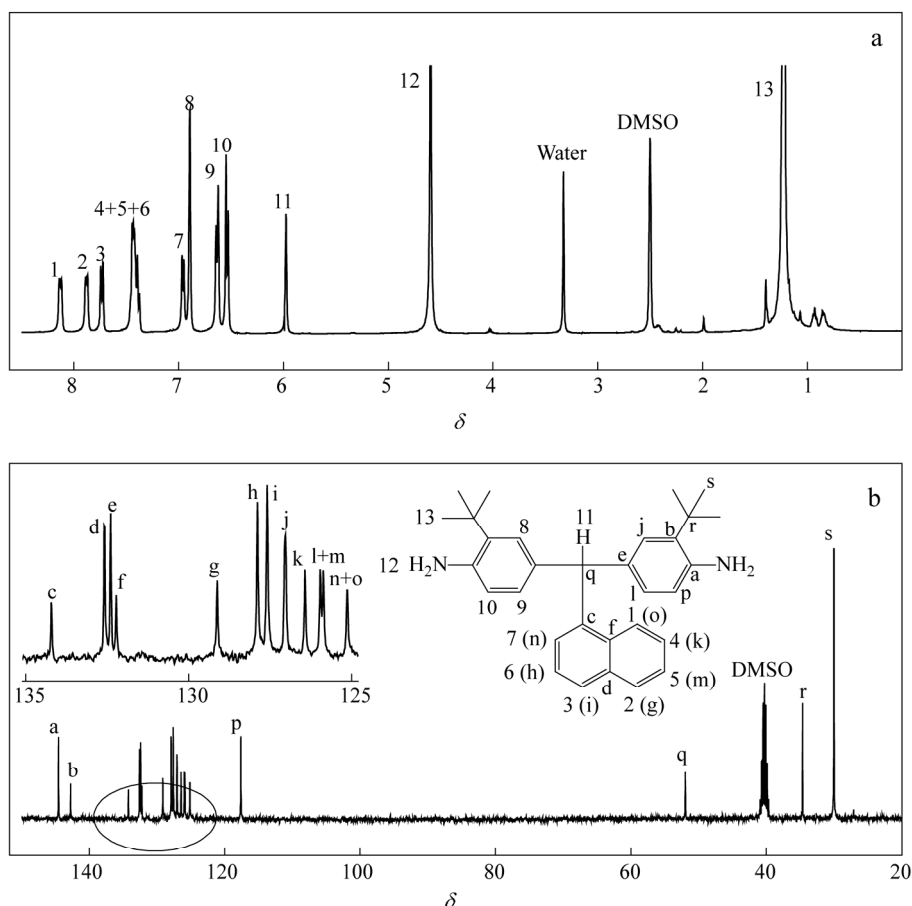
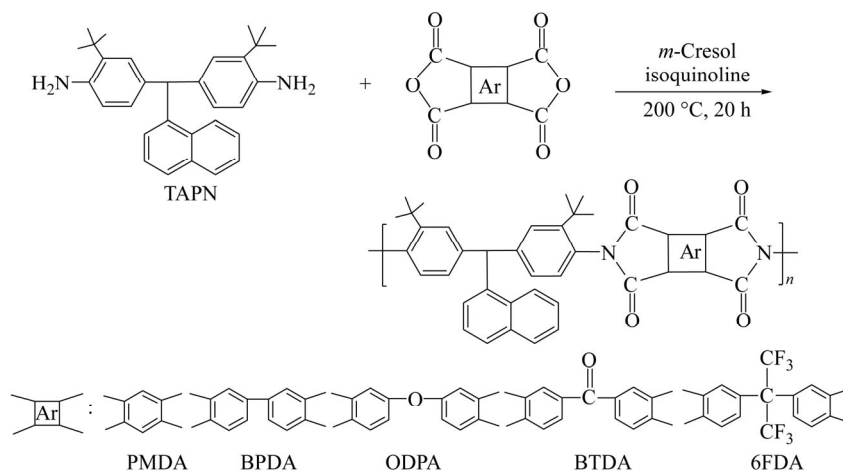


Fig. 2 ^1H -NMR (a) and ^{13}C -NMR (b) spectra of diamine TAPN



Scheme 2 Synthesis of polyimide

GPC analysis was performed to determine the molecular weights and molecular weight distributions of the PIs. GPC traces of the PIs are included in supplementary material (Fig. 1S), and GPC chromatographs of all PIs showed unimodal peaks. As summarized in Table 1, the obtained PIs have relatively high molecular weight and narrow molecular weight distribution. The values of molecular weight and molecular weight distribution were in the range of 4.5×10^4 – 5.3×10^4 (weight average molecular weight) and 1.5–1.6, respectively. It is also in accordance with the fact that the tough and flexible films could be cast through solvent evaporation from polymer solutions. The structures of the PIs were confirmed by FTIR and $^1\text{H-NMR}$. The FTIR spectrum of PIs is shown in Fig. 3. The characteristic imide absorption bands of PI around 1779, 1720, 1371 and 730 cm^{-1} were observed, and the characteristic alkyl absorption bands around 3030 and 2870 cm^{-1} were also identified. The typical $^1\text{H-NMR}$ of PI-ODPA is shown in Fig. 4, and the assignments of each proton are in accordance with the proposed polymer structure. Furthermore, the elemental analysis results of the polymers are also outlined in Table 1, and the measured results are in good agreement with the theoretically calculated values of the expected structures.

Table 1. GPC data and elemental analyses of the polyimides

Polymer	GPC data ^a			Elemental analysis (%)			
	$M_n \times 10^4$	$M_w \times 10^4$	M_w/M_n	Formula		C	N
PI-PMDA	3.0	4.5	1.5	$(\text{C}_{41}\text{H}_{34}\text{N}_2\text{O}_4)_n$	Calcd	79.59	4.53
				$(618.72)_n$	Found	79.66	4.50
PI-BPDA	3.5	5.3	1.5	$(\text{C}_{47}\text{H}_{38}\text{N}_2\text{O}_4)_n$	Calcd	81.24	4.03
				$(694.82)_n$	Found	81.33	4.00
PI-ODPA	3.3	5.2	1.5	$(\text{C}_{47}\text{H}_{38}\text{N}_2\text{O}_5)_n$	Calcd	79.42	3.94
				$(710.82)_n$	Found	79.31	3.98
PI-BTDA	3.3	5.2	1.6	$(\text{C}_{48}\text{H}_{38}\text{N}_2\text{O}_5)_n$	Calcd	79.76	3.88
				$(722.83)_n$	Found	79.84	3.90
PI-6FDA	2.9	4.7	1.6	$(\text{C}_{50}\text{H}_{38}\text{F}_6\text{N}_2\text{O}_4)_n$	Calcd	71.08	3.32
				$(844.84)_n$	Found	70.93	3.38

^a Relative to polystyrene standards, using DMF as the eluent

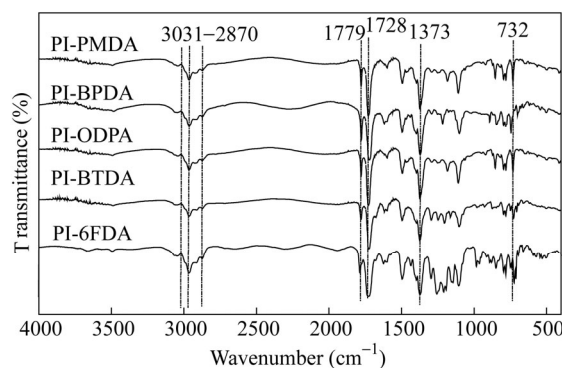


Fig. 3 FTIR spectra of polyimide

Solubility of the Polyimides

In general, aromatic PIs exhibit poor solubility in organic solvents due to the inherent molecular feature of aromatic PI, such as molecular stiffness, high polarity and high intermolecular interactions. However, there are many ways to increase the solubility of PIs by introducing the flexible linkages, bulky side group or molecular asymmetry structure into the backbone. These above approaches would be helpful to decrease the polymer chain intermolecular interaction, chain close packing, and charge transfer complex (CTC) effect.

The solubility behavior of the obtained PIs was investigated in different organic solvents by dissolving 10 mg polymer in 1 mL solvent at room temperature or on heating, and the results are listed in Table 2. Almost all the PIs exhibited good solubility in polar aprotic solvents and less polar solvents, such as DMF, DMAc,

DMSO, NMP, *m*-cresol at room temperature. Excellent solubility was also studied for PIs in low-boiling-point solvents such as CHCl_3 , THF and acetone. The good solubility of these polymers should be the result of introduction of bulky side group tertbutyl and bulky pendant naphthyl group in the polymer backbone, which reduce the polymer inter- and intra-chain interactions and disturb the co-planarity of the aromatic units to decrease the chain close packing efficiency and crystallinity. The PI-6FDA was soluble at room temperature in acetone. The PI-PMDA was soluble only under heating, while the PI-BPDA, PI-ODPA and PI-BTDA were partially soluble on heating. Among all the PIs, PI-6FDA shows the best solubility due to the presence of bulky pendent $-\text{C}(\text{CF}_3)_2-$ group in the backbone which led to the increased chain distance and decreased chain interaction, thereby increasing the solvent molecule penetrate easily and leading to enhancement of solubility. The PI-PMDA is soluble on heating in the acetone which may be due to the relatively low molecular weight. The solubility of the PIs in low boiling organic solvents such as THF, CDCl_3 and acetone is very useful for processing films at relatively low processing temperatures, and these soluble PIs may have the application prospects as coating materials for advanced microelectronics manufacturing, flexible displays, flexible printed circuit board (FPCP) and flexible organic solar cells and so on^[26–30].

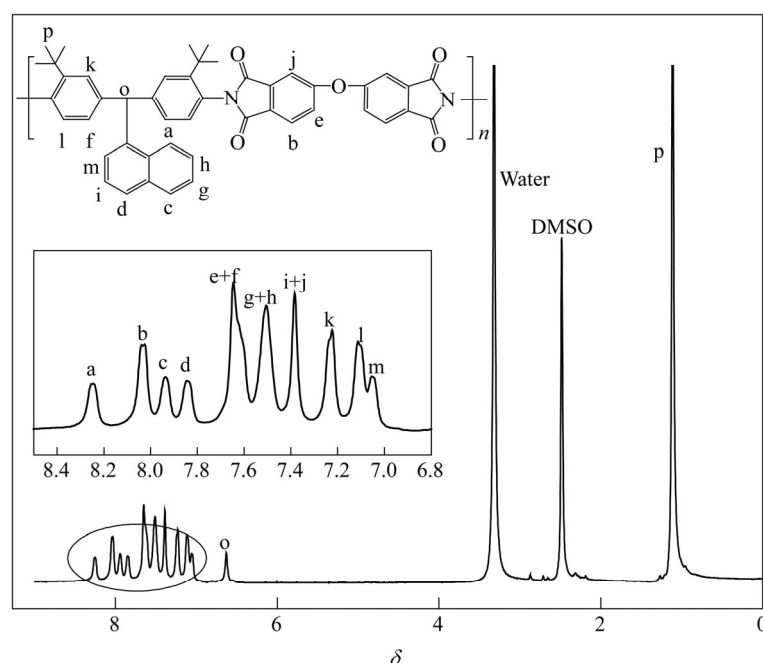


Fig. 4 ^1H -NMR spectra of polyimide PI-ODPA

Table 2. Solubility of polyimides

Polymer	Solvent								
	DMF	DMAc	DMSO	NMP	<i>m</i> -Cresol	CHCl_3	THF	Acetone	<i>n</i> -Hexane
PI-PMDA	++	++	++	++	++	++	++	+h	–
PI-BPDA	++	++	++	++	++	++	++	–h	–
PI-ODPA	++	++	++	++	++	++	++	–h	–
PI-BTDA	++	++	++	++	++	++	++	–h	–
PI-6FDA	++	++	++	++	++	++	++	++	–

^a Solubility was tested with a polymer concentration of 10 mg/mL in solvent with stirring. ++ = soluble at room temperature; +h = soluble on heating; –h = partially soluble on heating; – = insoluble. ^b DMF, *N,N*-dimethylformamide; DMAc, *N,N*-dimethyl acetamide; DMSO, dimethyl sulfoxide; NMP, *N*-methyl-2-pyrrolidone; CHCl_3 , Chloroform; THF, tetrahydrofuran.

Thermal Properties of the Polyimides

Thermal analysis exhibited that all of the PIs have prominent thermal stability, and the corresponding results are summarized in Table 3. As shown in Fig. 5, the thermo stability of the PIs was evaluated in nitrogen atmosphere. The $T_{5\%}$ and $T_{10\%}$ weight loss temperature of these polymers under nitrogen were in the range of 477–493 °C and 490–504 °C, respectively. The values of thermal onset decomposition temperature (T_d) were in the range of 475–488 °C. Furthermore, the char yield at 800 °C for the resulting PIs were in the range of 59%–66% in nitrogen.

Table 3. Thermal and optical properties of polyimides

Polymer	T_g^a (°C)	T_d^b (°C)	$T_{5\%}^c$ (°C)	$T_{10\%}^c$ (°C)	Char Yield ^d (%)	λ_{cutoff} (nm)	$\lambda_{80\%}$ (nm)
PI-PMDA	350	482	483	495	60	323	460
PI-BPDA	325	488	493	504	66	356	461
PI-ODPA	299	484	491	500	59	337	388
PI-BTDA	314	475	477	490	59	322	454
PI-6FPA	300	488	489	501	61	306	389

^a Glass transition temperature, obtained from DSC at a heating rate of 10 K/min in N₂;

^b Onset decomposition temperature, obtained from TGA at a heating rate of 10 K/min in N₂;

^c Temperature at 5% and 10% weight loss recorded by TGA at a heating rate of 10 K/min in N₂;

^d Char yield (wt%) at 800 °C in N₂

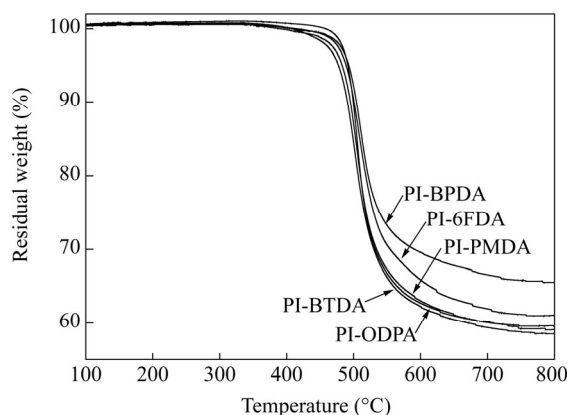


Fig. 5 TGA curves of polyimides

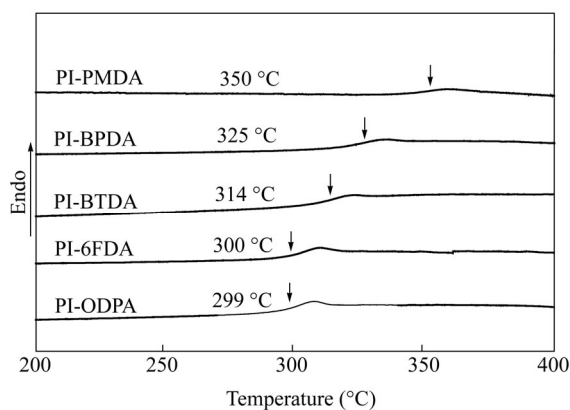


Fig. 6 DSC curves of polyimides

Typical DSC curves for PIs are described in Fig. 6. The glass-transition temperatures (T_g) of the PIs were in the range from 299 °C to 350 °C. In general, T_g is associated with the stiffness and conformation of polymer backbones. In this paper, on the one hand, the introduction of tertbutyl into the *ortho*-position of the imide nitrogen hindered the rotation of the two aromatic rings around the C–N bonds, which increased the polymer chain rigidity and T_g values^[31–33]. On the other hand, the presence of non-coplanar naphthyl moieties on the polymer backbone also improved the steric hindrance, thereby which led to relatively higher rigidity of the polymer chain. These PIs did not exhibit any melting or crystallization even up to 400 °C. The PI-PMDA derived from PMDA dianhydride showed the highest T_g . This may be the result of the incorporation of rigidity in the polymer backbone. Nevertheless, PI-ODPA originated from ODPA dianhydride presented the lowest T_g due to the introduction of flexible ether linkage moieties in the polymer structure. Consequently, the arrangement of the T_g of these polymers is in accordance with the increasing order of rigidity and polarity of the polymer chains.

Optical Properties of the Polyimides

The PIs with such optical properties have widely potential application in optoelectronic devices and microlens arrays. All of the PI films were characterized by UV-Vis spectra, and the optical data are listed in Table 3. As shown in Fig. 7, the PIs showed lower cutoff wavelength and higher optical transparency. The UV cutoff wavelengths (λ_{cutoff}) of the PI films were in the range of 306–356 nm, and the wavelengths of 80%

transmittance ($\lambda_{80\%}$) were in the range of 388–461 nm. As shown in Fig. 8, the optical transparency was also compared for the commercial Kapton and the obtained PI films in visible light, and these films about 45 μm in thickness were photographed against a special background to emphasize the optical transparency in visible light. It is obvious that the PI films displayed much lighter color than Kapton film. The PI films exhibited excellent optical properties due to the incorporation of the bulky pendant tertbutyl and non-coplanar naphthyl linkages in the polymer chains, which can loosen the conjugation effect and intermolecular CTC effect. In particular, PI-6FDA based on 6FDA dianhydride presented the highest light transmittance at 450 nm (84%) and the lowest cutoff wavelength (306 nm). PI-6FDA also showed almost colorless transparent as compared with other PI films in the visible light. Its excellent optical property is attributed to the flexible linkage of fluorinated bulky $-\text{C}(\text{CF}_3)_2-$, which could inhibit the formation of the CTC effectively between alternating electron donor (diamine) and electron acceptor (dianhydride) moieties^[34], and the $-\text{CF}_3$ group might reduce the chain-to-chain cohesive force owing to lower polarizability of the C–F bond. Moreover, PI-ODPA originated from ODPA presented lighter color in the visible light, and it is due to the presence of the flexible ether bridged linkages in the polymer backbone, which could inhibit the formation of the inter- and intra-molecular CTC effectively. Unexpectedly, PI-BPDA originated from BPDA also exhibited lighter color in the visible light, it may be attributed to the twist of biphenyl structures in the polymer chain, which could make polymer chains have the higher fractional free volume, and then reduce the molecular chain conjugation effect and restrict the formation of CTC.

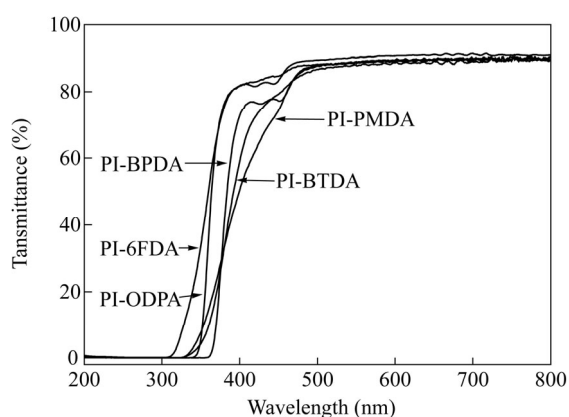


Fig. 7 UV-Vis spectra of PI films



Fig. 8 The profile images of PI films

Mechanical Properties of the Polyimides

All the PI films casting from DMF were transparent and flexible. The mechanical properties of the films were summarized in Table 4. The polymers exhibited good tensile strength in the range of 77.6–90.5 MPa, tensile modulus in the range of 1.8–2.4 GPa, and elongation at break in the range of 6.3%–9.5%, respectively. As shown in Table 4, PI-BPDA based on BPDA dianhydride presented the highest tensile strength, and it may be due to the inherent rigidity of the biphenyl units and relatively high molecular weight of the polymers. However, PI-6FDA derived from 6FDA dianhydride exhibited the lowest tensile strength, and the reasonable explanation is that the introduction of bulky trifluoromethyl groups damages the electronic conjugation and inhibits the formation of CTC in the polymer backbone, and then reduces the inter-chain interaction. PI-PMDA originated from PMDA dianhydride showed the least elongation at break because of containing the rigidity of the pyromellitic linkages in the polymer molecular structure.

Table 4. Mechanical properties of the polyimide films

Polymer	Film thickness	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (GPa)
PI-PMDA	55	79.8	6.3	1.9
PI-BPDA	62	90.5	7.8	2.4
PI-ODPA	58	86.3	8.5	2.1
PI-BTDA	65	84.7	8.1	2.1
PI-6FDA	70	77.6	9.5	1.8

Dielectric Constants and Water Absorption

It must be emphasized that lower dielectric constant is one of the most prospective characteristics in microelectronic fields. At present the polymers have been used widely as dielectric materials due to the ease of processing, flexibility and better resistance to chemical attack. Furthermore, polyimide dielectric materials have been attracted much attention in recent years. It is because of its excellent comprehensive performance, such as high T_g , high modulus and low dielectric constant as compared with other polymers^[35].

The dielectric constants and water absorption of PI films are summarized in Table 5. The PI films presented dielectric constants in the range of 3.03–3.31 at 1 kHz, 2.98–3.25 at 10 kHz and 2.89–3.12 at 1 MHz, respectively, which are lower than the commercial PI such as Kapton film (3.48 at 1 MHz). The low dielectric constants of the PIs are mainly attributed to the incorporation of bulky side group *tert*butyl and non-coplanar bulky pendant naphthyl group in the polymer backbones, which reduce polymer packing density and the intermolecular force, subsequently reducing the polymer dielectric constants. Moreover, PI-6FDA prepared from diamine TAPN and dianhydride 6FDA presented the lowest dielectric constant (2.89 at 1 MHz) due to the introduction of $-\text{CF}_3$ groups in the backbone of PI-6FDA. The strong electronegativity of fluorine atoms would result in very low C–F polarizability, which could endow the PIs with low dielectric constants. The moisture absorption of PIs also has a significant influence on the dielectric properties in microelectronic fields. It might be related to some factors including the chemical structures, the introduction of functional groups such as fluorinated groups, and the geometrical packing of the polymer chains. As shown in Table 5, all of the PIs presented low water absorption in the range of 0.35%–0.66%, which is due to the presence of hydrophobic bulky naphthyl pendants and *tert*butyl groups in the polymer backbone. In particular, PI-6FDA based on 6FDA dianhydride showed lower value of water uptake (0.35%) compared with other PIs, such as PI-PMDA (0.45%), PI-BPDA (0.40%), PI-ODPA (0.58%) and PI-BTDA (0.66%). It is mainly because of the introduction of the trifluoromethyl groups that restrain the moisture absorption on the surface of the fluorinated polymer.

Table 5. Dielectric properties and water absorption of polyimides films

Polymer	Film thickness (μm)	Dielectric constant			Water absorption (%)
		1 kHz	10 kHz	1 MHz	
PI-PMDA	56	3.31	3.25	3.12	0.45
PI-BPDA	65	3.17	3.14	2.99	0.40
PI-ODPA	70	3.20	3.13	3.02	0.58
PI-BTDA	60	3.25	3.20	3.10	0.66
PI-6FDA	58	3.03	2.98	2.89	0.35

CONCLUSIONS

A novel aromatic diamine monomer TAPN bearing *tert*butyl and naphthyl groups, was successfully synthesized and followed by polymerization with commercial aromatic dianhydrides to obtain a series of non-coplanar PIs. All of the PIs exhibited excellent solubility in common solvents such as DMF, DMAc, NMP, DMSO, *m*-cresol, CHCl_3 , THF and acetone. Furthermore, the PI films present remarkable thermo-stability, outstanding optical properties, prominent mechanical properties, low dielectric constant and low moisture absorption. These polymers could have potential applications for microelectronic and photoelectric devices, flexible solar cells, flexible displays and flexible printed circuit board.

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