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Synthesis and characterization of novel polyamides derived from 1,4-bis((4-amino-2-(trifluoromethyl)phenoxy)methyl)cyclohexane and aromatic dicarboxylic acids

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Abstract A new aromatic diamine with a trifluoromethyl pendent group, 1,4-bis((4-amino-2-(trifluoromethyl)phenoxy)methyl)cyclohexane, was successfully synthesized in two steps from 1,4-cyclohexanedimethanol and 2-chloro-5-nitrobenzotrifluoride as starting materials. And the newly obtained diamine with various aromatic dicarboxylic acids, including isophthalic acid (IPA), 2,2-bis(4-carboxy-phenyl)hexafluoropropane (6FA) and 4,4′-oxydibenzoic acid (OBA), were polymerized, respectively via the usual Yamazaki reaction to prepare a series of fluorinated polyamides. The resulting polymers had inherent viscosities ranging from 1.85 to 2.36 dL/g. All the polymers showed outstanding solubility and could be easily dissolved in amide-type polar aprotic solvents [e.g., *N*-methyl-2-pyrrolidone (NMP), DMAc, and DMF] and even dissolved in less polar solvents (e.g., pyridine, and tetrahydrofuran). These polymers could also be easily be cast into transparent, tough and flexible films with tensile strengths of 76.5–82.3 MPa, Young's moduli of 1.64–1.85 GPa, and elongations at break of 10–12%. In addition, these polyamides films exhibited low dielectric constants of 2.37–2.53 at 100 MHz, low water absorptions in the range of 1.54–2.13%, and high transparency with an ultraviolet–visible absorption cut-off wavelength in the 326–333 nm range. Furthermore these polyamides still retained good thermal stability. These combined outstanding features make these obtained polyamides competitive for advanced microelectronic applications.

Keywords Polyamides · Solubility · Synthesis · Dielectric constant

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Introduction

Wholly aromatic polyamides have been well known for their high temperature stability, excellent mechanical strength and good chemical resistance, which qualify them as high-performance polymeric materials [1–3]. At the same time, aromatic polyamides like other aromatic and heterocyclic polymers are quite intractable to process because they are usually infusible and insoluble in organic solvents. For instance, purely aromatic polyisophthalamides are soluble only in a few aprotic polar solvents containing dissolved inorganic salts. The highly regular and rigid polymer backbones and the formation of intermolecular hydrogen bonding of these polyamides are generally responsible for the difficulty of processing. Moreover, the high moisture absorptions of aromatic polyamides, compared with other polymer materials, have resulted in obvious negative effect on their mechanical properties as well as electrical insulating and dielectric performance. Therefore, many efforts have been made to improve their solubility and dielectric properties without much impairing their thermal stability and mechanical properties. The successful approaches employed for those purpose include: introduction of flexible bonds [4, 5], cardo groups [6, 7], unsymmetrical [8–10] and alicyclic units [11, 12] into the macromolecular backbone. These structural modifications could disturb regularity of chain packing, thus provide better solubility.

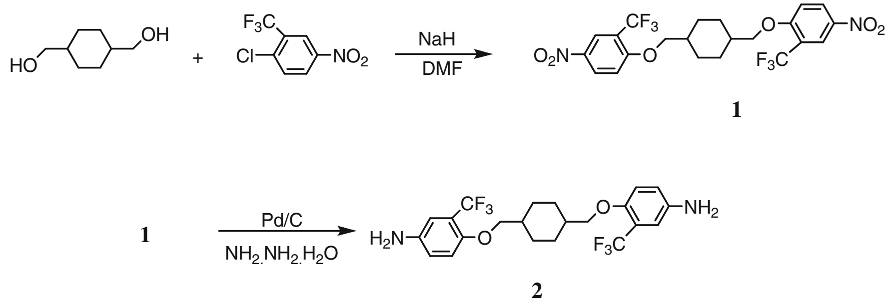
Recently, considerable attention has been devoted to the fluorinated aromatic polymers, including fluorinated polyimides [13–15], polyamides [16–22], poly(aryl ether)s [23–25] and so on. It was found that the incorporation of fluorinated groups into polymer backbones resulted in great benefits for promoting polymer solubility as well as electrical and dielectric performance, which might be attributed to the small dipole and the low polarizability of the C–F bond as well as the increase in free volume [26–28].

As part of the efforts to develop the high-performance polymers containing fluorine substituents, the present article describes the successful synthesis of a novel CF_3-substituted bis(ether amine), 1,4-bis((4-amino-2-(trifluoromethyl)phenoxy)methyl)cyclohexane (diamine **2**, as shown in Scheme 1), and its use for the preparation of soluble polyamides by the Yamazaki reaction when various aromatic dicarboxylic acids were employed. The present bulky CF_3 groups might decrease polymer interchain interactions such as hydrogen bonding and generally disturb the coplanarity of aromatic units so that to reduce packing efficiency and crystallinity. Thus the enhanced solubility, optical transparency and dielectric constants, moisture absorption, as well as thermal and physical properties could be expected from these fluorinated polyamides.

Experimental

Materials

1,4-Cyclohexanedimethanol (CHDM, Alfa), 2-chloro-5-nitrobenzotrifluoride (ACROS), sodium hydride (60%, Alfa) as well as 10% Pd/C (MERCK) were used



Scheme 1 Synthesis of diamine **2**

as received. Commercially obtained anhydrous calcium chloride ($CaCl_2$) was dried under vacuum at 180 °C for 8 h. Reagent-grade aromatic dicarboxylic acids such as isophthalic acid (IPA), 2,2-bis(4-carboxy-phenyl)hexafluoropropane (6FA) and 4,4′-oxydibenzoic acid (OBA), were purified by recrystallization. *N*-Methyl-2-pyrrolidone (NMP), Pyridine (Py), *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF) and Triphenyl phosphite (TPP) all from Alfa were purified by distillation under reduced pressure over calcium hydride. All other chemicals and solvents were reagent-grade and used without further purification unless otherwise noted.

Measurements

^{1}HNMR spectra were performed on a Bruker AV400 instrument with dimethyl sulfoxide (DMSO-d_6) or $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal standard. FT-IR spectra were recorded on a Nicolet Magna 470 spectrometer. Ultraviolet-visible (UV–vis) spectra of the polymer films ($\sim$15 μm thickness) were recorded on a Lambda 35(Perkin Elmer) spectrophotometer at room temperature. Elemental analysis was carried out on a Carlo Erba1106 system. Differential scanning calorimetry (DSC) analysis was carried out on a PE Diamond DSC instrument at a heating rate of 10 °C/min in nitrogen atmosphere. Glass transition temperatures (T_g) were read at the middle of the transition in the heat capacity from the second heating scan. Thermogravimetric analysis (TGA) of the samples was measured on a Netzsch TG 209F1 instrument at a heating rate of 20 °C min^{-1} in nitrogen atmosphere, and T_{10} is reported as the temperatures where 10% weight losses was observed. Inherent viscosities ($\eta_{inh} = \ln\eta_r/c$) were measured at a concentration of 0.5 g/dL in DMAc at 30 °C with an Ubbelohde viscometer. Mechanical properties of the films were investigated with an AGS-500ND tensile tester at a crosshead speed of 5 mm/min. An average of at least five individual specimens was used for each sample. Wide-angle X-ray diffraction (WAXD) patterns were obtained at room temperature with film specimens about 50 μm thick on a Rigaku D/MAX 2500 powder diffractometer with a scanning speed of 4°/min, and the patterns were recorded in the 2θ range of 5–40°. The dielectric constants were measured on a HP4291B at a frequency region of 1 MHz–1.1 GHz and 25 °C. The equilibrium water uptake was determined by the weighing of the changes in vacuum-dried film specimens before and after immersion in deionized water at 25 °C for 3 days.

Monomer synthesis

*Synthesis of 1,4-bis((4-nitro-2-(trifluoromethyl)phenoxy)methyl)cyclohexane (**1**)*

NaH (6.4 g, 0.16 mol) was firstly placed into a 250 mL, three-necked round-bottom flask equipped with a mechanical stirrer, N_2 inlet, and dropping funnel. A mixture of 1,4-cyclohexanedimethanol (8.0 g, 0.056 mol) and DMF (50 mL) was added dropwise through the dropping funnel at 0 °C. After stirring at 0 °C for 2 h, the mixture of 2-chloro-5-nitrobenzotrifluoride (25.9 g, 0.115 mol) and DMF (50 mL) was then added dropwise, and the reaction mixture was stirred at 10 °C overnight. Then the mixture was poured into 400 mL distilled water. Some yellow solids precipitated out which were filtered and washed with ethanol for several times. The crude product obtained was recrystallized from DMF/ethanol to give fine, white crystals **1**(22.3 g, 76.3%).

The characteristics of compound **1** are as follows. Melting point: 176–177 °C (DSC at a scan rate of 10 °C/min). FT-IR (KBr): 3,093 (Ar–H stretching); 2,927, 2,856 (C–H stretching); 1,526, 1,366 (C–NO_2 stretching); 1,290, 1,119 cm^{-1} (C–O and C–F stretching). ^{1}HNMR ($CDCl_3$, δ): 8.51 (d, $J = 2.72$ Hz, 2H, H_1), 8.42(dd, $J_1 = 9.12$ Hz, $J_2 = 2.76$ Hz, 2H, H_2), 7.08 (d, $J = 9.21$ Hz, 2H, H_3), 4.02 (d, $J = 5.88$ Hz, 4H, H_4), 1.99 (t, $J = 9.40$ Hz, 4H, H_6), 1.91 (d, $J = 2.56$ Hz, 2H, H_5), 1.26 (m, $J = 7.01$ Hz, 4H, H_7). Elemental analysis ($C_{22}H_{20}F_6N_2O_6$): calcd. C, 50.58%; H, 3.86%; N, 5.36%; found C, 50.71%; H, 3.95%; N, 5.54%.

*Synthesis of 1,4-bis((4-amino-2-(trifluoromethyl)phenoxy)methyl)cyclohexane (**2**)*

The purified dinitro compound **1** (15.7 g, 0.03 mol), 0.3 g of 10% Pd/C and 100 mL ethanol were mixed in a three-necked flask firstly, and hydrazine monohydrate (15 mL) was added dropwise over a period of 30 min at 80 °C. Upon completing addition, the mixture was heated at the reflux temperature for another 3 h. The reaction solution was then hot filtered to remove Pd/C and the obtained solution was concentrated. Then the precipitated white solid was filtered and washed with ethanol to yield silvery white crystals **2** (14.2 g, 90.4%). The properties of the crystals **2** were found below. Melting point: 173–174 °C (DSC at a scan rate of 10 °C/min). FT-IR (KBr): 3,429, 3,209 (N–H stretching); 3,029 (Ar–H stretching); 2,914, 2,853 (C–H stretching); 1,283, 1,259, 1,237, 1,115 cm^{-1} (C–O and C–F stretching). ^{1}NHMR (DMSO-d_6, δ): 6.92 (d, $J = 8.80$ Hz, 2H, H_1), 6.82 (d, $J = 2.72$ Hz, 2H, H_3), 6.77 (dd, $J_1 = 8.72$ Hz, $J_2 = 2.68$ Hz, 2H, H_2), 4.98 (s, 4H, –NH_2). 3.74 (d, $J = 6.08$ Hz, 4H, H_4), 1.85 (d, $J = 9.13$ Hz, 4H, H_6), 1.66 (brs, 2H, H_5), 1.09 (m, $J = 6.27$ Hz, 4H, H_7). Elemental analysis ($C_{22}H_{24}F_6N_2O_2$): calcd. C, 57.14%; H, 5.23%; N, 6.06%; found C, 57.71%; H, 5.48%; N, 6.24%.

Polymer synthesis

As a typical example, **4c** was prepared as follows: a mixture of (0.6936 g, 1.5 mmol) of diamine **2**, 6FA (0.5883 g, 1.5 mmol), 0.3 g of $CaCl_2$, 2.5 ml of TPP, 1.0 ml of pyridine, and 6 ml of NMP was heated in nitrogen with stirring at 120 °C for 3 h. As the polycondensation proceeded, the reaction mixture became viscous gradually implying the formation of polyamide **4c**. The resultant solution was poured slowly into 400 ml of stirred methanol giving rise to a tough, fibrous polymer precipitate. The precipitate was collected, washed with hot ethanol for three times and dried at 160 °C under vacuum for 6 h to give **4c** (1.21 g, 95%). The FT-IR absorption bands of **4c** film were found at 3,296 cm^{-1}(N–H stretching), 3,078 (Ar–H stretching), 2,926, 2,862 (C–H stretching), 1,668 cm^{-1} (C=O stretching), 1,255 cm^{-1} (C–O stretching), and 1,137 cm^{-1} (C–F stretching). ^{1}HNMR (DMSO-d_6, δ): 10.49 (m, 2H, H_8), 8.07 (t, $J = 9.40$, 6H, $H_{1,9}$), 7.97 (d, $J = 8.96$, 2H, H_2), 7.52 (d, $J = 6.40$, 4H, H_{10}), 7.26 (d, $J = 8.24$, 2H, H_3), 3.93 (s, 4H, H_4). 1.93 (m, 4H, H_6), 1.83 (s, 2H, H_5), 1.16 (s, 4H, H_7).

Results and discussion

Monomers synthesis and characterization

The CF_3-containing diamine **2** was prepared in two steps as shown in Scheme 1. Firstly, the intermediate dinitro compound **1** was synthesized by the Williamson reaction between 2-chloro-5-nitrobenzotrifluoride and 1,4-cyclohexanedimethanol (CHDM) in the presence of sodium hydride in anhydrous DMF. Secondly, the novel diamine **2** was obtained by the catalytic reduction of **1** with hydrazine hydrate and Pd/C catalyst in refluxing ethanol. The FT-IR spectra of dinitro compound **1** and diamine **2** are showed in Fig. 1. The nitro groups compound **1** gave two characteristic bands at 1,526 and 1,366 cm^{-1} (–NO_2 asymmetric and symmetric stretching). After reduction, the characteristic absorptions of the nitro group disappeared, and the amino group showed the typical of N–H stretching bands in 3,429 and 3,209 cm^{-1}. Figure 2 illustrate the ^{1}HNMR spectra of dinitro compound **1** and diamine **2**, respectively. From the ^{1}HNMR spectra **1** and **2**, the absorption signals of aromatic and cyclohexane protons of **1** appeared in the region of 7.09–8.51 and 1.26–2.17 ppm, respectively; and those of **2** shifted to a higher field between 6.75–6.94 and 1.09–1.86 ppm, respectively. The protons H_1 of **1** resonated at the farthest downfield due to the inductive effect of electron withdrawing –NO_2 and –CF_3 groups. And the protons H_3 and H_4 oriented to the electron donating property of ether group shifted to the upfield. After reduction, the H_1 and H_2 of **2** shifted to the upfield because of the electron-donating property of the amino group.

Synthesis of polyamides

A series of fluorinated polyamides **4a–c** were prepared through the polycondensations of diamine **2** with various aromatic dicarboxylic acids **a–c** based on the

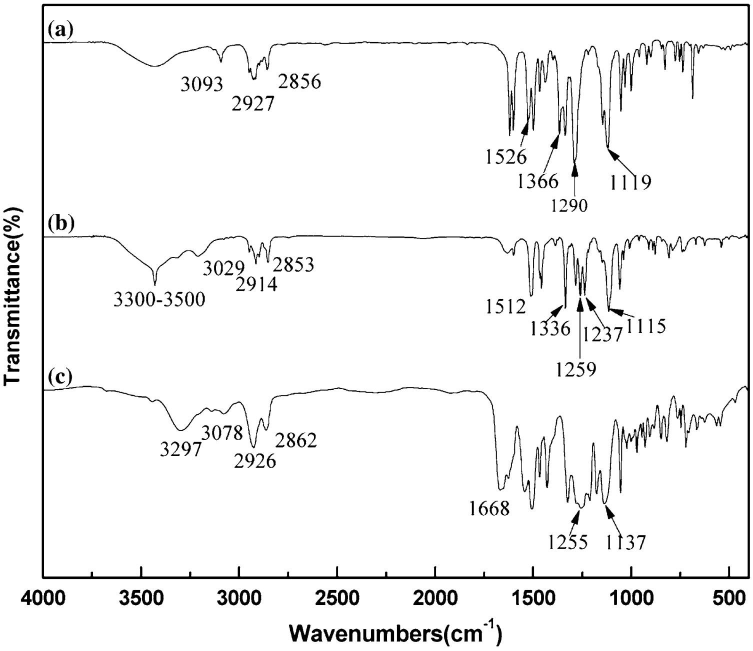


Fig. 1 FT-IR spectra of dinitro **1** (**a**), diamine **2** (**b**) and **4c** (**c**)

phosphorylation method first reported by Yamazaki [29] for the synthesis of polyamides, as shown in Scheme 2. All the polycondensations proceeded homogenously in solution without precipitates even at the end of polymerization, indicating the good solubility of obtained polyamides in the NMP. Polymers with inherent viscosities of ranged from 1.85 to 2.36 dL/g (Table 1) were obtained, implying high molecular weights of these polyamides **4a**–**c**. Structure features of these polyamides were verified by elemental analysis, FT-IR and ^{1}HNMR spectroscopies. The results of the elemental analyses listed in Table 1 were almost in good agreement with the calculated values of the proposed structures except carbon percentage, which usually was attributed to the very aromatic nature of these polyamides, which commonly leave a small coal residue in the standard conditions of microanalysis. They all exhibited characteristic absorption bands of amide group around 3,300 cm^{-1} (N–H stretching), 1,660 cm^{-1} (C=O stretching), 1,250 cm^{-1} (C–O–C stretching), and 1,130 cm^{-1} (C–F stretching). And the absorptions at around 2,925 and 2,860 cm^{-1} present in the IR spectra should be assigned to the CH_2 and CH vibration of alicyclic units. The formation of amide groups was verified by the resonance signals of amide protons at δ10.49 in the ^{1}HNMR spectrum (Fig. 3).

Properties of obtained polyamides

The WAXD patterns of polyamides **4a**–**c** (Fig. 4) indicated that all of these polyamides were predominately amorphous, which are generally in accordance with

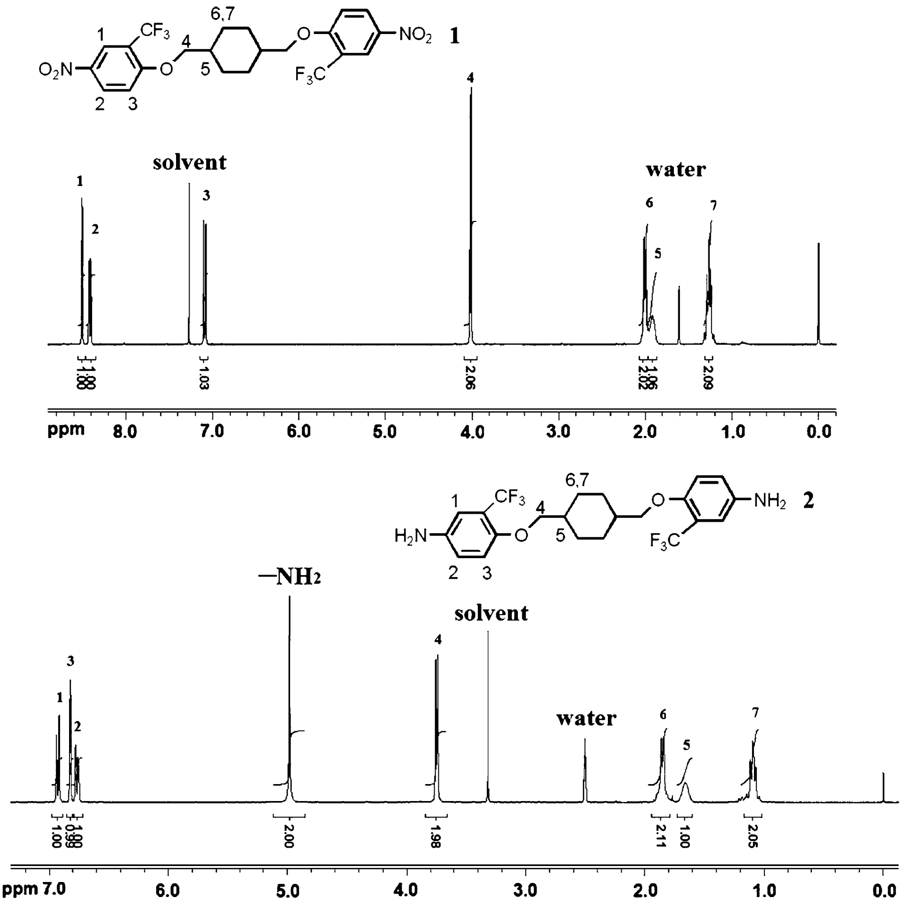
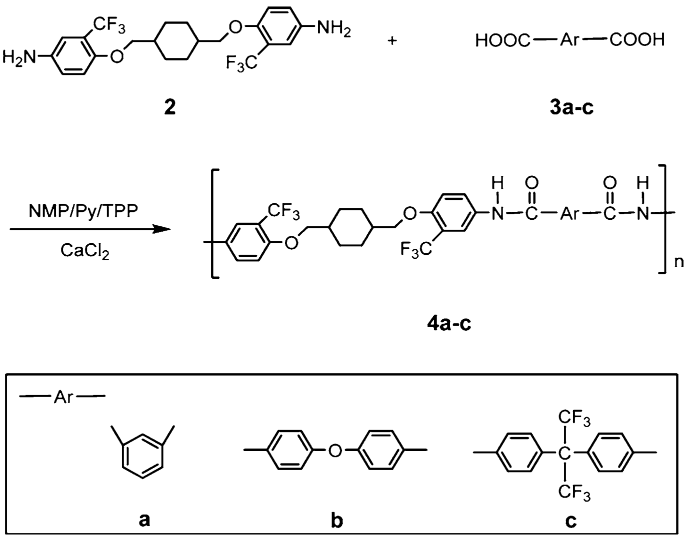


Fig. 2 The ^{1}HMNR spectra of dinitro **1** and diamine **2**

anticipation. In addition, these polymers with similar structure containing –CF_3 groups are amorphous [30–33]. The solubility of the fluorinated polyamides is summarized in Table 2. It could be seen that all the newly synthesized polyamides showed excellent solubility in aprotic polar solvents such as NMP, DMAc and DMF, and even soluble in less polar solvents like pyridine, m-cresol and DMSO at room temperature. Their good solubility and amorphous nature may be apparently due to the presence of the pendent trifluoromethyl groups and ether links in macromolecular chains, which might disrupt the interaction of polymer chains by enlarging the distance between polymer chains, thereby leading to a decrease in crystallinity and an increase in solubility. Meanwhile, the introduction of 1,4-dimethyl-cyclohexane groups at the macromolecular chain, could further decrease the packing density and improve the solubility. Among these polyamides, **4c** exhibited better solubility owing to the more flexible ether linkages in the macromolecular backbone and more –CF_3 pendant groups. The excellent solubility



Scheme 2 Synthesis of the polyamides

Table 1 Inherent viscosity and elemental analysis of polyamides

Polyamides		Elemental analysis (%) of polyamides				
Code	η_{inh}^{a} (dL/g)	Formula (formula weight)		C	H	N
4a	2.26	$(C_{32}H_{32}F_6N_2O_4)_n$	Calcd	61.73	5.18	4.50
		$(622.60)_n$	Found	60.41	5.02	4.58
4b	2.36	$(C_{38}H_{36}F_6N_2O_5)_n$	Calcd	63.86	5.08	3.92
		$(714.69)_n$	Found	61.57	5.31	3.82
4c	1.85	$(C_{41}H_{36}F_{12}N_2O_4)_n$	Calcd	58.02	4.28	3.30
		$(848.72)_n$	Found	57.18	4.19	3.23

[a] Measured at a concentration of 0.5 g dL^{-1}in DMAc at 30 °C

could make these polyamides easy to be processed and benefit their practical applications.

As mentioned above, the obtained polyamides are soluble in several solvents. Thus it is easy to prepare polyamides films by casting of their solutions. These produced films were subjected to tensile tests and their mechanical properties were listed in Table 3. **4a–c** showed good tensile performance with tensile strengths, Young modulus and elongation at break in the range of 76.5–82.3 MPa, 1.64–1.85 GPa and 10–12%, respectively. These results indicated that the incorporation of the $-CF_3$ groups and ether links into the structure of polyamides not only improved solubility but also retained the good mechanical properties, which are desirable for practical applications. The optical performance of the polyamides films displays in Table 3, and the UV–Vis spectra of these films, about 20 μm thick, are shown in Fig. 5. It could be seen from Table 3 that these polyamides films exhibited high

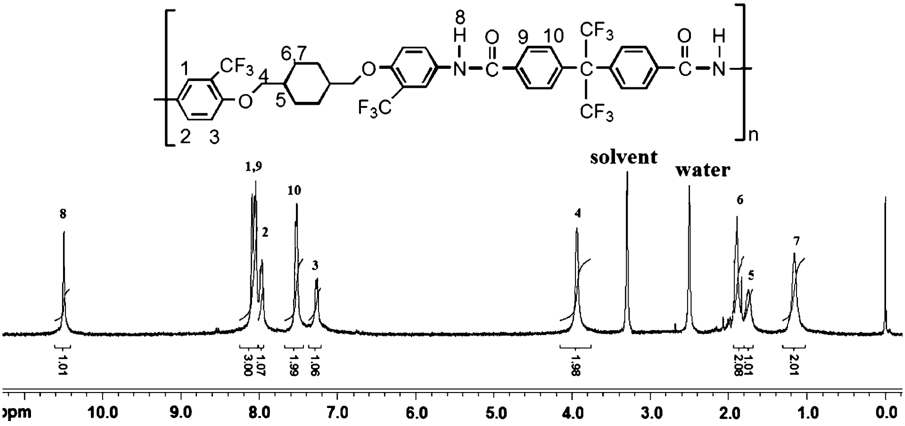


Fig. 3 The ^{1}HMNR spectrum of **4c** in DMSO-d_6

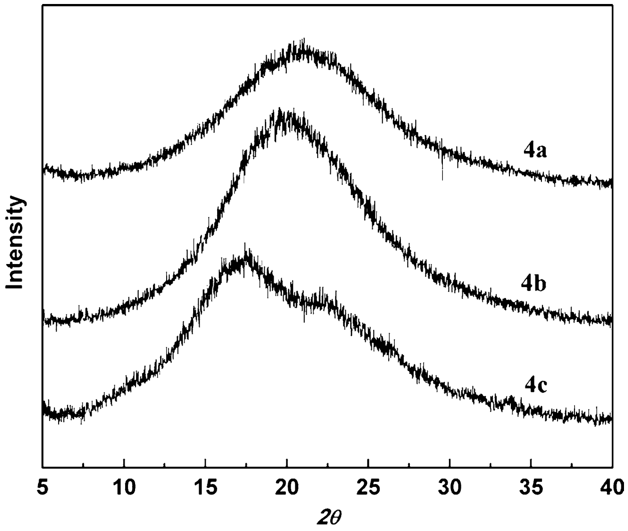


Fig. 4 Wide-angle X-ray diffractograms of polyamides

transparency, the UV cutoff wavelength ($\lambda_{\mathrm{cutoff}}$) was in the range of 326–333 nm, the transparency at 450 nm (T_{450}) was higher than 85%, except for **4b** with lower transparency 80%. This is because of little crystallinity measuring by wide-angle X-ray diffractograms as shown in Fig. 4. Thus, the introduction of bulky trifluoromethyl and 1,4-dimethyl-cyclohexane groups at the macromolecular chain, were effective to break the aromatic conjugation along the backbone and provide enhanced optical transparency.

The thermal properties of all polyamides are listed in Table 4. The T_g values of **4a–c** were in the range of 202–246 °C, depending on the structure of the dicarboxylic acids component. **4a** and **4c** exhibited the higher T_g value because of

Table 2 Solubility behavior of these polyamides

Polymer code[a]	Solvents								
	NMP	DMAc	DMF	DMSO	*m*-Cresol	THF	Py	$CHCl_3$	Toluene
4a	++	++	++	+−	+−	+−	+−	(S)	−
4b	++	++	++	+−	+−	+−	+−	(S)	−
4c	++	++	++	+−	+−	+−	+−	+−	−

[a] The qualitative solubility was tested with 10 mg samples in 1 mL of solvent; ++ soluble at room temperature, +− partial soluble on heating, − insoluble on heating

NMP N-Methyl-2-pyrrolidinone, *DMAc N*,*N*-dimethylacetamide, *DMF N*,*N*-dimethylformamide, *DMSO* dimethyl sulfoxide, *Py* pyridine, *THF* tetrahydrofuran, *S* swelling

Table 3 Molecular weights, mechanical and optical properties of polyamides films

Polymer code	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)	$\lambda_{\mathrm{cut\ off}}$ (nm)	T_{450} (%)
4a	76.5	1.85	12.1	333	88
4b	82.3	1.74	10.8	326	79
4c	77.8	1.64	10.2	332	86

the effect of the rigid macromolecular backbone, whereas **4b** derived from OBA exhibited a lower T_g because of the presence of a flexible ether linkage between the amide units.

The temperature of 10% weight loss (T_{10}) and a char yield for these polyamides were determined from original TGA thermograms and are also tabulated in Table 4. The T_{10} values of the polyamides stayed in the range of 408–414 °C in nitrogen and in the range of 385–405 °C in air, respectively. They left more than 40% residual weight at 800 °C in nitrogen. In comparison with some fluorinated poly(ether amide)s derived from trifluoromethyl-substituted bis(ether amine)s [34], **4b** (Fig. 6) showed equivalent T_g but lower stability, which were mainly due to the thermal stability of 1,4-dimethyl-cyclohexane lower than that of aromatic ring structural unit.

The results of dielectric constants and moisture absorption were summarized in Table 5. **4c** showed lower dielectric constants 2.37 at 100 MHz than the others because of the higher fluorine content in the repeat unit. The decreased dielectric constants could be attributed to the presence of bulky CF_3 groups, which resulted in the strong electronegativity of fluorine results in very low polarizability of C–F bonds. In addition, the polymer also exhibited lower water absorptions (1.54−2.13%) due to the hydrophobic nature of the trifluoromethyl groups. The low water absorptions will guarantee stable dielectric performance of these polyamides.

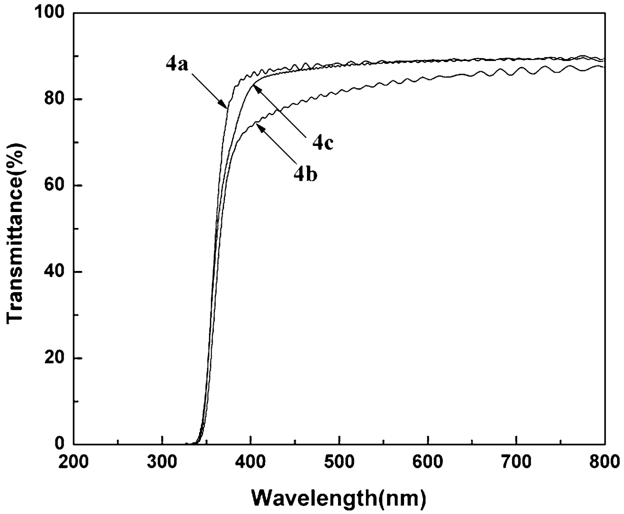


Fig. 5 UV–visible spectra of polyamide films

Table 4 Thermal properties of polyamides

Polymer code	T_g^a (°C)	T_{10}^b (°C)		Char yield^c (%)
		In N_2	In air	
4a	222	414	392	45
4b	202	412	405	40
4c	246	408	385	42

[a] From DSC measurements conducted at a heating rate of 10 °C min^{-1}

[b] Temperature at 10% weight loss (T_{10}) were determined by TGA in nitrogen atmosphere at a heating rate of 20 °C min^{-1}

[c] Residual weight (%) at 800 °C in nitrogen

Conclusions

A novel bis(ether amine) containing CF_3 and cyclohexane group monomer **2** was successfully synthesized by hydrazine hydrate reduction of the dinitro compound **1**, which was produced through the Williamson reaction of 1,4-cyclohexanedimethanol (CHDM) and 2-chloro-5-nitrobenzotrifluoride. A series of light-colored and organosoluble polyamides were prepared from diamine **2** with various aromatic dicarboxylic acids via the Yamazaki process. The obtained polyamides showed a good solubility in many solvents and they could be easily processed to flexible and tough films by casting of their solutions. These polyamides showed good mechanical properties, low dielectric constants and water absorption; moreover, they displayed high optical transparency and retained good thermal stability. Thus,

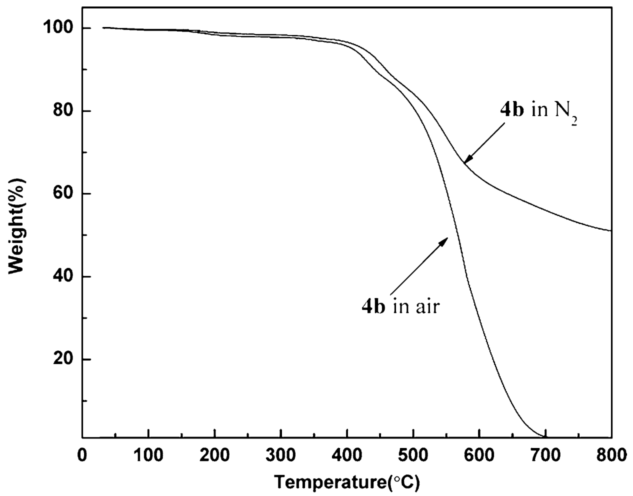


Fig. 6 TGA curve of polyamide **4b** with a heating rate of 20 °C/min

Table 5 Dielectric constant and water absorption of various polyamides films

Polymer code	Film thickness (μm)	Dielectric constant				Water absorption (%)
		1 MHz	10 MHz	100 MHz	1 GHz	
4a	73	2.77	2.57	2.53	2.49	2.13
4b	64	3.63	2.44	2.41	2.37	1.87
4c	60	2.60	2.41	2.37	2.34	1.54

these obtained polyamides possessed an eminent combination of several desired properties and could be used as potential high-temperature resistant materials for optical or microelectronic applications.

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