

Highly organosoluble and transparent polyamides containing cyclohexane and trifluoromethyl moieties: Synthesis and characterization

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Abstract. New aromatic diamine with cyclohexane moiety substituted with trifluoromethyl group in the side chain, 4,4'-(cyclohexane-1,4-diylbis(oxy))bis(3-(trifluoromethyl)aniline) (**2**), was successfully synthesized through the Williamson reaction of 1,4-cyclohexanediol and 2-chloro-5-nitrobenzotrifluoride, to yield the intermediate dinitro compound **1**, followed by catalytic reduction with hydrazine and Pd/C to afford the diamine **2**. This diamine monomer leads to a series of organic-soluble polyamides (**4a–d**) when reacted with different commercially available aromatic diacids (**a–d**) via a direct polycondensation with triphenyl phosphite and pyridine. The resulting polymers had inherent viscosities ranging from 0.89 to 1.29 dl/g. All the polymers showed outstanding solubility and could be easily dissolved in amide-type polar aprotic solvents and even dissolved in less polar solvents. All the polymers formed transparent, strong, and flexible films with tensile strengths of 54–68 MPa, Young's moduli of 1.6–1.9 GPa, and elongations at break of 13.3–15.5%. These polyamide films have low dielectric constants of 2.15–2.88 at 1 MHz and low water absorptions of 1.96–2.84%. Wide-angle X-ray diffraction measurements revealed that these polyamides were amorphous in nature.

Keywords: polymer synthesis, molecular engineering, solubility, optical transparency, dielectric constant

1. Introduction

Commercial 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 [1–8]. However, these wholly aromatic polyamides usually shows poor solubility in common organic solvents and their extremely high melting temperatures, which lie above their decomposition temperatures, give rise to processing difficulties and so limit their applications. In order to overcome these drawbacks, considerable efforts have been made to modify their chemical structure to improve processability and solubility, so that to facility their use in a specific

field. There are various approaches for improvement of the solubility and processability of polyamides without sacrificing their high thermal stability and mechanical properties, such as, the incorporation of the flexible linkages (e.g. –O–, –SO₂–, etc.) [9, 10], cardo groups (such as cyclododecyldiene, pyrene, and naphthalene, etc.) [11–13], or molecular asymmetry (*ortho*, *meta* versus linkages) [14–16] into the backbone or addition of bulky side group (such as *tert*-butyl, norbornane units) [17–21]. For example, the bis(ether amine)s and its aromatic polymer with cyclohexane group was synthesized and showed solubility in organic and polar solvents [22, 23]. Moreover, it was also proved that polyamides with trifluoromethyl-sub-

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stituted benzene in the side chain could enhance the solubility, reduce dielectric constant and moisture absorption, and raise the optical transparency [24–30]. Therefore, this work is focused on the synthesis of a new CF₃-containing aromatic diamine **2** with cyclohexane moiety, and the preparation of fluorinated polyamides polycondensed with various diacids (**a–d**). The basic properties of the fluorinated polyamides were investigated.

2. Experimental section

2.1. Materials

1,4-cyclohexanediol (cis+trans, 98+%, from Alfa Aesar), 2-chloro-5-nitrobenzotrifluoride (98%, from ACROS), sodium hydride (60%, from Alfa Aesar) as well as 10% Pd/C (from MERCK) were used as received. Commercially obtained anhydrous calcium chloride (CaCl₂) was dried under vacuum at 180°C for 8 h. Reagent-grade aromatic dicarboxylic acids such as terephthalic acid (TPA), isophthalic acid (IPA), 4,4'-oxydibenzoic acid (OBA) and, 2,2-bis(4-carboxy-phenyl)hexafluoropropane (6FA) were purified by recrystallization. *N*-Methy-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.

2.2. Monomer synthesis

2.2.1. Synthesis of 1,4-bis(4-nitro-2-(trifluoromethyl)phenoxy)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, N₂ inlet, and dropping funnel. A mixture of 1,4-cyclohexanediol (6.5 g, 0.056 mol) and *N,N*-dimethylformamide (50 ml) was added dropwise through the dropping funnel at 0°C. After stirring at 0°C for 2 hours, the mixture of 2-chloro-5-nitrobenzotrifluoride (25.9 g, 0.115 mol) and *N,N*-dimethylformamide (50 ml) was then added dropwise, and the reaction mixture was stirred at 5°C for 20 hours. Then the mixture was poured into 300 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, light yellow crystals (20.07 g, 72.5%). The properties of the product were found to be as follow. Melting point: 247–248°C [differential scanning calorimetry (DSC) at a scanning rate of 10°C/min]. FT-IR (KBr): 1518, 1333 (C–NO₂ stretching); 1286, 1211, 1140, 1117 cm⁻¹ (C–O and C–F stretching). ¹HNMR (CDCl₃, δ): 8.56 (d, *J* = 2.57 Hz, 2H, H₁), 8.45 (dd, *J*₁ = 9.18 Hz, *J*₂ = 2.65 Hz, 2H, H₂), 7.14 (d, *J* = 9.24 Hz, 2H, H₃), 4.96 (s, 2H, H₄), 2.15 (m, 2H, H₅), 2.03 (m, 4H, H₆). Elemental analysis (C₂₀H₁₆F₆N₂O₆): Calcd. C, 48.59%; H, 3.26%; N, 5.67%. Found C, 49.01%; H, 3.45%; N, 5.94%.

2.2.2. Synthesis of 4,4'-(cyclohexane-1,4-diylbis(oxy))bis(3-(trifluoromethyl)aniline) (**2**)

The purified dinitro compound **1** (14.8 g, 0.03 mol), 0.3 g of 10% Pd/C and 100 ml ethanol were taken into a three-necked flask 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 filtered hot to remove Pd/C and the obtained solution was concentrated. Then the precipitated white solid was filtered and washed with ethanol to yield white crystals (11.1 g, 85.1%).

The properties of the crystals were found to be as follows. Melting point: 156–157°C (differential scanning calorimetry (DSC) at a scan rate of 10°C/min). FT-IR (KBr): 3460, 3436, 3357, (N–H stretching); 1259, 1236, 1217, 1146 cm⁻¹ (C–O and C–F stretching). ¹HNMR (DMSO-*d*₆, δ): 7.02 (d, *J* = 8.83 Hz, 2H, H₁), 6.83 (d, *J* = 2.70 Hz, 2H, H₂), 6.78 (dd, *J*₁ = 8.74 Hz, *J*₂ = 2.59 Hz, 2H, H₃), 5.15 (brs, 4H, –NH₂), 4.45 (s, 2H, H₄) 1.93 (d, *J* = 8.29 Hz, 4H, H₅), 1.58 (m, 4H, H₆). Elemental analysis (C₂₀H₂₀F₆N₂O₂): Calcd. C, 55.30%; H, 4.64%; N, 6.45%; Found C, 55.92%; H, 4.98%; N, 6.74%.

2.3. Polymer synthesis

A generally synthetic procedure for the polyamides was described as follows: A mixture of (0.6516 g, 1.5 mmol) of diamine **2**, 4,4'-oxydibenzoic acid ©

(0.3875 g, 1.5 mmol), 0.45 g of calcium chloride, 1.8 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. The resultant solution of the polymer was poured slowly into 400 ml of stirred methanol giving rise to a tough, fiber-like 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** (1.03 g, 95%). FT-IR (film): 3305 cm⁻¹ (N–H stretching), 1653 cm⁻¹ (C=O stretching), 1246 cm⁻¹ (C–O stretching), 1137, 1171 cm⁻¹ (C–F stretching). ¹HNMR (DMSO-*d*₆, δ): 10.34 (s, 2H, H₇), 8.12 (s, 2H, H₁), 8.06 (d, *J* = 8.44, 4H, H₉), 7.97 (d, *J* = 7.24, 2H, H₂), 7.37 (d, *J* = 9.24, 2H, H₃), 7.23 (d, *J* = 8.00, 4H, H₈), 4.79 (s, 2H, H₄), 1.99 (m, 4H, H₅), 1.74 (d, 4H, *J* = 3.20, H₆).

2.4. Measurements

¹HNMR spectra were performed on a Bruker AV400 instrument with dimethyl sulfoxide (DMSO-*d*₆) or CDCl₃ 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 (~10 μm thickness) were recorded on a Lambda 35 (Perkin Elmer) spectrophotometer at room temperature. Elemental analysis was carried out on a Carlo Erba 1106 system. Differential scanning calorimetry (DSC) analysis was performed 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 polymer samples was measured on a Netzsch TG 209F1 instrument at a heating rate of 20°C/min 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. Wide-angle X-ray diffraction (WAXD) was conducted on a Rigaku D/Max-2550PC X-ray dif-

fraction with Cu/K_{α1} radiation, operated at 40 kV and 300 mA. The dielectric constants (round shape samples, *D* = 15 mm) 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 three days.

3. Results and discussion

3.1. Monomers synthesis and characterization

The new CF₃-substituted bis (ether amine) **2** was prepared in a two-step reaction process as shown in Figure 1. The first step is the Williamson reaction of 2-chloro-5-nitrobenzotrifluoride with 1,4-cyclohexanediol in anhydrous DMF in the presence of sodium hydride. The target diamine **2** was obtained by the catalytic reduction of **1** with hydrazine hydrate and Pd/C catalyst in refluxing ethanol. The structure of the dinitro compound **1** and the diamine monomer **2** were investigated by elemental analysis as well as FT-IR and ¹HNMR spectroscopy. The FT-IR spectra of dinitro compound **1** and diamine **2** are showed in Figure 2. The nitro groups in compound **1** gave two characteristic bands at 1518 and 1333 cm⁻¹ (–NO₂ asymmetric and symmetric stretching). After reduction, the characteristic absorptions of the nitro group disappeared, and the amino group occurred at bands in 3300–3500 cm⁻¹ showing typical of N–H stretching. Figure 3 illustrates the ¹HNMR spectra of dinitro compound **1** and diamine **2** respectively. From the ¹HNMR spectra **1** and **2**, the absorption signals

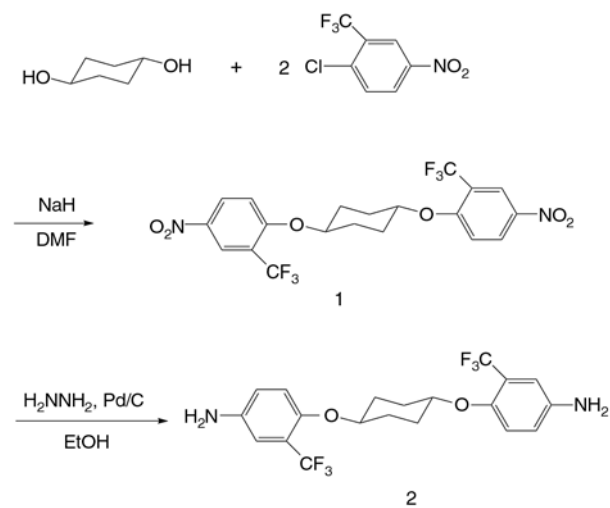


Figure 1. Synthetic route to the diamine monomer **2**

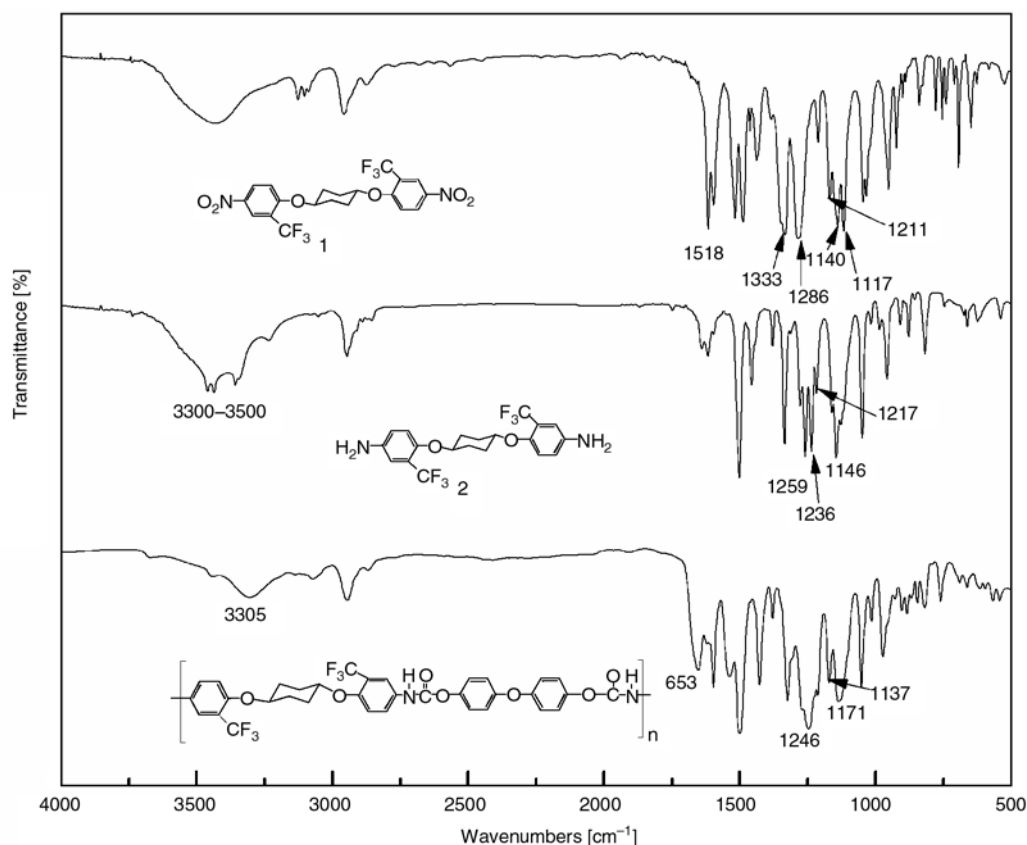


Figure 2. FT-IR spectra of dinitro **1**, diamine **2** and polyamide **4c**

of aromatic and cyclohexane protons of **1** appeared in the region of 7.14–8.56 and 2.03–4.96 ppm respectively; and those of **2** shifted to a higher field between 6.78–7.02 and 1.58–4.45 ppm respectively. The protons H₁ of **1** resonated at the farthest downfield, which is due to the inductive effect of electron withdrawing of –NO₂ and –CF₃ groups. And the protons H₃ and H₄ affected by the electron donating behavior of ether group shifted to the upfield. After reduction, the H₁ and H₂ of **2** shifted to the upfield because of the electron-donating property of the amino group.

3.2. Polymer synthesis

Polyamides were prepared by Yamazaki-Higashi phosphorylation polyamidation technique [31]. Diamine **2** was polymerized with four different aromatic dicarboxylic acids-TPA, IPA, OBA, and 6FA to produce polyamides **a**, **b**, **c**, and **d**, respectively (Figure 4). The inherent viscosities (Table 1) of the polyamides are in the range of 0.89–1.29 dl/g. The structures of polyamides were confirmed by elemental analysis, FT-IR and ¹HNMR spectroscopies. The results of the elemental analyses (Table 1) were almost in good agreement with the calculated values of the proposed structures.

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	0.90	(C ₃₀ H ₂₈ F ₆ N ₂ O ₄) _n (594.54) _n	Calcd	60.60	4.75	4.71
			Found	59.71	4.68	4.77
4b	0.89	(C ₃₀ H ₂₈ F ₆ N ₂ O ₄) _n (594.54) _n	Calcd	60.60	4.75	4.71
			Found	59.57	4.62	4.74
4c	1.29	(C ₃₆ H ₃₂ F ₆ N ₂ O ₅) _n (686.64) _n	Calcd	62.97	4.70	4.08
			Found	62.04	4.63	4.01
4d	1.18	(C ₃₉ H ₃₂ F ₁₂ N ₂ O ₄) _n (820.66) _n	Calcd	57.08	3.93	3.41
			Found	55.72	3.87	3.35

^aMeasured at a concentration of 0.5 g/dl in DMAc at 30°C

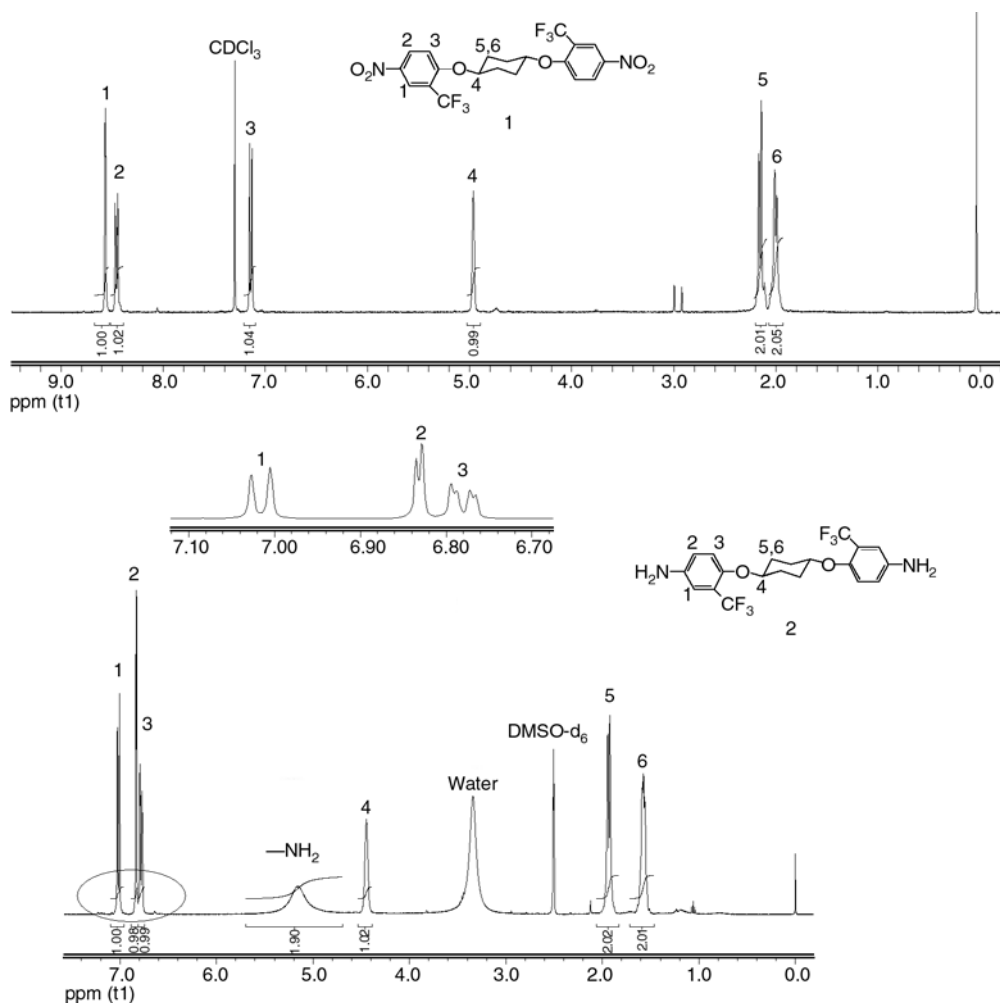


Figure 3. The ¹H NMR spectra of dinitro **1** and diamine **2**

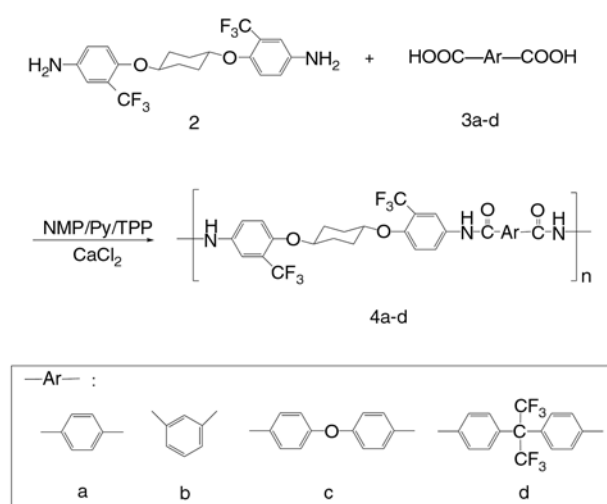


Figure 4. Synthesis of the fluorinated polyamides

The FT-IR spectra of the polyamides showed the characteristic absorptions around 3300 cm⁻¹ and 1658 cm⁻¹, which are characteristic of N–H stretching and carbonyl stretching(C=O), respectively. A strong absorption band was observed around

1250 cm⁻¹ due to the C–O–C linkage. In addition, the strong C–F absorptions between 1000 and 1200 cm⁻¹ are also found in all of the polymers. All protons in **4b** are identified as number, and their integral values are in good agreement with the anticipated proton numbers. Furthermore the formation of amide groups was verified by ¹H NMR, the resonance signals of amide protons appeared at δ10.34. Generally, the protons *ortho*-to the –CF₃ group (H₁) appear at the farthest downfield in the spectra due to the effect of the electron-withdrawing –CF₃ group. In Figure 5, the protons in the cyclohexane (H₄, H₅, H₆) all show absorptions at the farthest upfield area.

3.3. Polymer solubility

Table 2 summarizes the solubilities of the fluorinated polyamides. It can be seen that the obtained polyamides were soluble at a concentration of over 10% in the amide type solvents such as NMP,

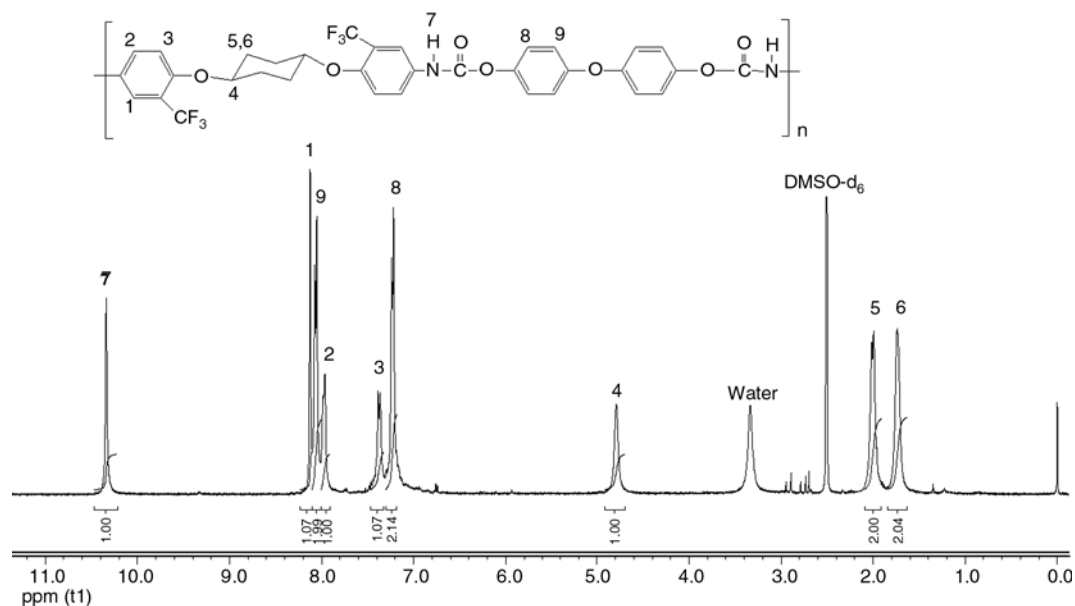


Figure 5. The ^1H NMR spectrum of **4c** in $\text{DMSO-}d_6$

Table 2. Solubility behavior of the polyamides

Polymers ^a	Solvents ^b							
	NMP	DMAc	DMF	Py	DMSO	THF	Cy	CH_2Cl_2
4a	+++	+++	+++	++	++	++	+	+
4b	+++	+++	+++	++	++	++	+	+
4c	+++	+++	+++	++	++	++	+	+
4d	+++	+++	+++	++	++	++	+	+

^a+++ , 100 mg sample dissolved in 1 ml solvent (10%); ++, soluble at 5%; +, soluble at 1%

^bAbbreviations: NMP – *N*-methyl-2-pyrrolidinone; DMAc – *N,N*-dimethylacetamide; DMF – *N,N*-dimethylformamide; DMSO – dimethyl sulfoxide; Py – pyridine; THF – tetrahydrofuran; Cy – Cyclohexanone

DMAc, and DMF, 5% in pyridine, DMSO and THF, and 1–5% in CH_2Cl_2 and cyclohexanone. 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 packing density and an increase in solubility. The excellent solubility could make these polyamides easy to be processed and benefit their practical applications.

3.4. Mechanical and optical properties

All the obtained polyamides could be readily processed to flexible, creasable, and essentially col-

orless films by casting from solutions in DMAc. The tensile properties of the polyamides films are summarized in Table 3. Their tensile strengths, elongations at break, and initial moduli of polymer films were in the range of 54–68 MPa, 13.3–15.4%, and 1.6–1.9 GPa, respectively. The optical performances of these fluorinated polyimides films are also given in Table 3, and the UV-Vis spectra of these films, are shown in Figure 6. It can be seen from Table 3 that these fluorinated polyamides films exhibited good transparency, the UV cutoff wavelength ($\lambda_{\text{cut off}}$) was in the range of 338–357 nm, and the transparency at 450 nm (T_{450}) was higher than 84%. As expected, the introduction of bulky pendant groups effectively disrupt the dense packing of molecular chains and lead to low color and high optical transparent polymer films.

Table 3. Mechanical and optical properties of the polyamides films

Polymer code	Tensile strength [MPa]	Tensile modulus [GPa]	Elongation at break [%]	$\lambda_{\text{cut off}}$ [nm]	T_{450} [%]
4a	54	1.6	13.3	357	84
4b	64	1.9	14.1	339	87
4c	68	1.6	15.5	335	86
4d	58	1.7	15.4	338	87

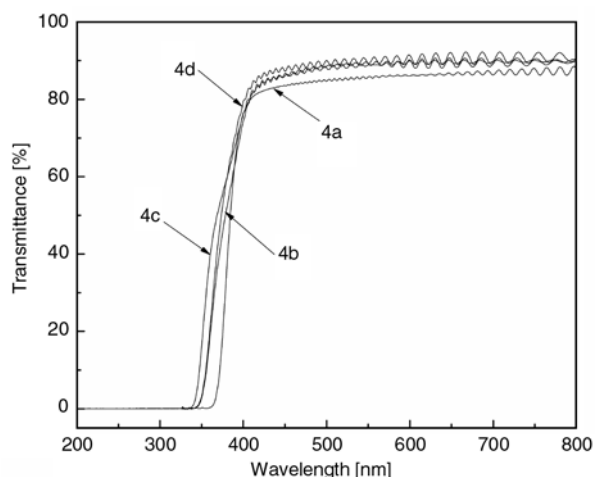


Figure 6. UV-visible spectra of the polyamide films

3.5. Thermal properties

The thermal properties of the polyamides were evaluated with TGA and DSC. The results are tabulated in Table 4. Owing to amorphous nature, the T_g values of all the polyamides could be easily identified in the DSC traces. The values for the polyamides were found to be in the range of 203–225°C, depending on the structure of the chain flexibility and the CF₃ hindrance of the polymer backbones Figure 7 presents typical TGA curves of

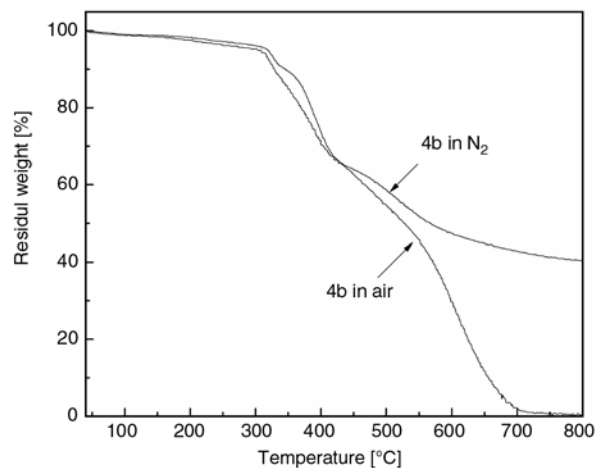


Figure 7. TGA curves of **3b** at a heating rate of 20°C/min

Table 4. Thermal properties of polyamides

Polymer code	T_g^a [°C]	T_d^b [°C]	T_{10}^c [°C]		Char yield ^d [%]
			In N ₂	In Air	
4a	219	330	340	330	40
4b	225	331	345	331	41
4c	213	321	356	335	40
4d	224	342	364	350	42

^aFrom DSC measurements conducted at a heating rate of 10°C/min

^bOnset decomposition temperature in TGA at a heating rate of 20°C/min in nitrogen atmosphere

^cTemperature at 10% weight loss (T_{10}) were determined by TGA in nitrogen atmosphere at a heating rate of 20°C/min

^dResidual weight [%] at 800°C in nitrogen

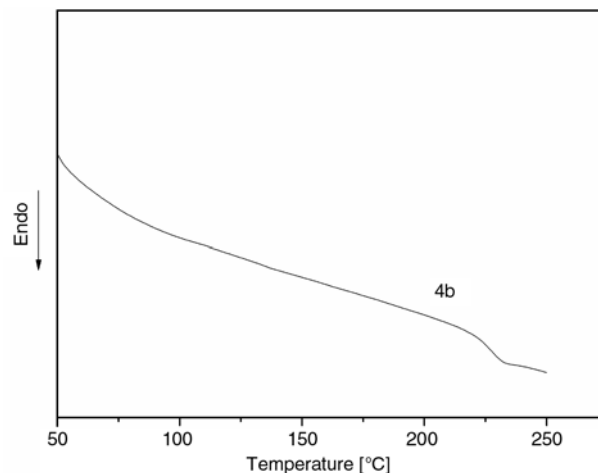


Figure 8. DSC curve of **4b** in air at a scanning rate of 20°C/min

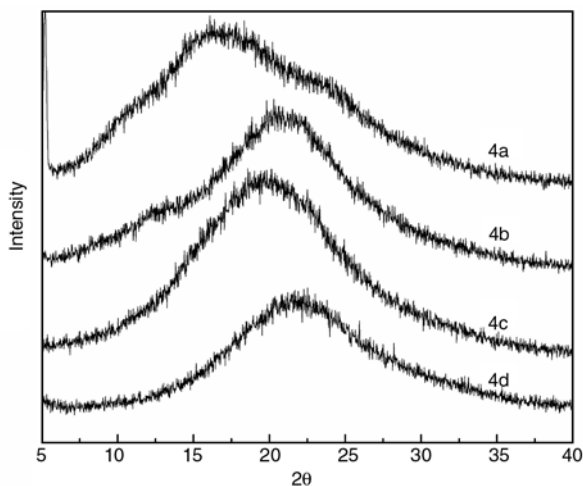
3b and the 10% weight loss temperature (T_{10}) as well as the anaerobic char yield at 800°C in nitrogen were also summarized in Table 4. All the polymers exhibited good thermal stability. Figure 8 shows the DSC curve of **4b** in air atmosphere. The T_{10} of the polyamides stayed between 330–364°C in nitrogen and 308–350°C in air, onset decomposition temperature in the range of 330–342°C, and the char yield of all the polyamides at 800°C were in the range of 40–42%. It implied that these polyamides with trifluoromethyl groups in the polymer backbone showed good thermal stability.

3.6. X-Ray diffraction of the polyamides

The WAXD studies of polyamides **4a–d** indicated that all of these polymers were essentially amorphous as showed in Figure 9. The obtained polymers displayed almost amorphous patterns in nature, this could be attributable to the presence of pendants which reduce attraction between molecules and hindrance macromolecular packing regularly. Generally, these polymers with similar struc-

Table 5. Dielectric constant and water absorption of various fluorinated polyamides films

Polymer code	Film thickness [μm]	Dielectric constant (dry)				Water absorption [%]
		1 MHz	10 MHz	100 MHz	1000 MHz	
4a	53	2.25	2.10	2.07	2.05	2.33
4b	63	2.88	2.82	2.78	2.75	2.57
4c	47	2.77	2.59	2.56	2.52	2.84
4d	54	2.15	2.03	2.00	1.97	1.96

**Figure 9.** Wide-angle X-ray diffraction patterns of the polyamides

ture containing $-\text{CF}_3$ groups are amorphous [32–35].

3.7. Dielectric constant and water absorption

Table 5 summarizes the results of dielectric constants and moisture absorption. **4d** showed lower dielectric constants of 2.15 at 1 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 (1.96–2.84%) due to the hydrophobic nature of the trifluoromethyl groups. The low water absorptions also ensured that these polyamides possess stable dielectric performance.

4. Conclusions

A series of new organosoluble alicyclic polyamides containing trifluoromethyl and cyclohexane groups were prepared by polycondensation. The obtained polyamides show an excellent solubility in many solvents and they could be easily processed to flex-

ible and tough films by casting of their solutions. These polyamides derived from diamine **2** exhibited amorphous nature, excellent optical properties, good mechanical properties, as well as good thermal stability. Moreover, these polyamides display low dielectric constants and water absorption; thus, 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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