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Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Synthesis and properties of novel soluble fluorinated polyamides containing pyridine and sulfone moieties

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ARTICLE INFO

Article history:

Received 20 March 2013

Received in revised form 11 May 2013

Accepted 23 May 2013

Available online 20 June 2013

Keywords:

Fluorinated polyamide

Pyridine structure

4-Trifluoromethylphenyl pendant

Sulfone linkage

Soluble

ABSTRACT

A new diamine containing pyridine and trifluoromethylphenyl groups, 4-(4-trifluoromethylphenyl)-2,6-bis(4-aminophenyl)pyridine, was synthesized and used in the preparation of the fluorinated polyamides containing pyridine and sulfone moieties with inherent viscosities of 0.70–1.06 dL g⁻¹ by the low temperature polycondensation with 4,4'-sulfonyl dibenzoyl chloride, 4,4'-[sulfonyl bis(4-phenyleneoxy)]dibenzoyl chloride, 3,3'-[sulfonyl bis(4-phenyleneoxy)]dibenzoyl chloride and 4,4'-[sulfonyl bis(2,6-dimethyl-1,4-phenyleneoxy)]dibenzoyl chloride in *N,N*-dimethylacetamide (DMAc) solution containing pyridine, respectively. All the polymers are amorphous and readily soluble in organic solvents such as DMAc, *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylformamide, dimethyl sulfoxide, pyridine (Py), and tetrahydrofuran at room temperature. The resulting polymers showed glass transition temperatures between 280 and 318 °C and 10% weight loss temperatures ranging from 485 °C to 516 °C, and char yields at 800 °C higher than 50% in nitrogen. All polymers could be casted into transparent, flexible and strong films from DMAc solutions with tensile strengths of 72–81 MPa, elongations at break of 12–15%, and tensile moduli of 1.8–2.1 GPa. These polymers had low dielectric constants of 3.40–3.51 (1 MHz), low moisture absorption in the range of 1.08–1.28%, and high transparency with an ultraviolet–visible absorption cut-off wavelength in the 374–382 nm range.

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1. Introduction

It is well known that aromatic polyamides are characterized as highly thermally stable polymers because of their combination of excellent thermal, mechanical and chemical properties [1–6]. However, most of them have high melting or softening temperature and are insoluble in most of organic solvents partly because of the strong interchain interaction. These properties make them generally intractable or difficult to process, thus limiting their applications. To overcome these limitations, structural modification of the polymer backbones, such as the introduction of flexible bonds (e.g., –O–, –SO₂–, etc.) [7–9], bulky pendant [10–13] or cardo groups [14–16], unsymmetrical [17–19] or non-coplanar

structures [20–23], have been used to modify the polymer properties by the design and preparation of new monomers. Among these approaches, introduction of fluorine groups into the backbone or side chain of polyamides has been considered as one of the most effective methods and attracted more and more attention from both academia and industry because the introduction of fluorine groups can provide not only enhanced solubility but also other merits such as good thermal oxidative stability, good electrical insulating and dielectric properties, low water uptake and so on [24–29]. In recent years, there have been some reports concerning the incorporation of pyridine and its derivatives into polymeric frameworks [30–33]. The rigidity based on the symmetry and aromaticity of the pyridine ring would contribute to the thermal and chemical stability, retention of mechanical property of the resulting polymer at elevated temperature, and the polarizability resulting from the nitrogen atom in pyridine ring would be suitable to improve their solubilities in organic solvents. Although polyamides based on 4-aryl-2,6-bis(4-aminophenyl)pyridines such as 4-(4-methylphenyl)-2,6-bis(4-aminophenyl)pyridine and 4-phenyl-2,6-bis(4-aminophenyl)pyridine have been previously reported [30], to our knowledge, little attention has been paid to the preparation of fluorinated polyamide from diamine monomer bearing pyridine and trifluoromethyl groups. In a continuation of our studies on easily processable high-temperature fluorinated

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polyamides [16,27,28], we herein report several organosoluble aromatic polyamides containing pyridine moieties and 4-trifluoromethylphenyl substituents, along with flexible sulfone or sulfone ether linkages in the polymer main chains, based on a novel aromatic diamine monomer, 4-(4-trifluoromethylphenyl)-2,6-bis(4-aminophenyl)pyridine. The incorporation of the rigid pyridine heterocyclic ring units, bulky 4-trifluoromethylphenyl pendant groups and flexible sulfone linkages into the polymer backbone would be resulted in great benefits for improving polymer solubility and electrical and dielectric performance while maintaining thermal stability. In addition to the solubility, thermal, mechanical, optical and electric properties, the water uptakes of the obtained fluorinated poly(pyridine sulfone amide)s are also studied in this article.

2. Results and discussion

2.1. Monomer synthesis

As shown in Scheme 1, the new aromatic diamine monomer, 4-(4-trifluoromethylphenyl)-2,6-bis(4-aminophenyl)pyridine (**2**) was prepared by a two-step synthetic route. Firstly, the dinitro compound (**1**) containing pyridine heterocyclic and 4-trifluoromethylphenyl pendant group, was synthesized via a modified Chichibabin pyridine synthesis [34] from 4-trifluoromethylbenzaldehyde and 4'-nitroacetophenone in the presence of ammonium acetate. The diamine **2** was then obtained by catalytic hydrogenation of the dinitro compound **1** using hydrazine hydrate and Pd/C catalyst in refluxing ethanol.

The structures of **1** and **2** were confirmed by elemental analysis, FTIR and ^1H NMR spectroscopy. In the FTIR spectrum of the dinitro compound **1** (Fig. 1A), representative absorptions appearing around 1522 and 1350 cm^{-1} were due to symmetric and asymmetric stretching of nitro groups which disappeared after reduction. The FTIR spectrum of diamine monomer **2** (Fig. 1B) showed the characteristic bonds of amino groups at 3445 and 3358 cm^{-1} (N–H stretching) and the characteristic absorption of trifluoromethyl group at 1164 cm^{-1} , respectively. In addition, the absorption band appeared at 1621 cm^{-1} was the characteristic one of pyridine ring. In the ^1H NMR spectrum of diamine **2** (Fig. 2), the signals of aromatic protons appeared in the range of 6.77–8.04 ppm, and the characteristic resonance signal at 3.86 ppm is due to the amino group. The assignments of each proton agreed well with the proposed molecular structure of diamine monomer **2**.

2.2. Polymer synthesis

The low-temperature solution polycondensation technique was used for the synthesis of the several fluorinated polyamides containing pyridine and sulfone moieties as depicted in Scheme 2. The polyamides **4a–4d** were prepared in a one-step pathway by the direct polycondensation reaction of 1 equiv. of **2** with 1 equiv.

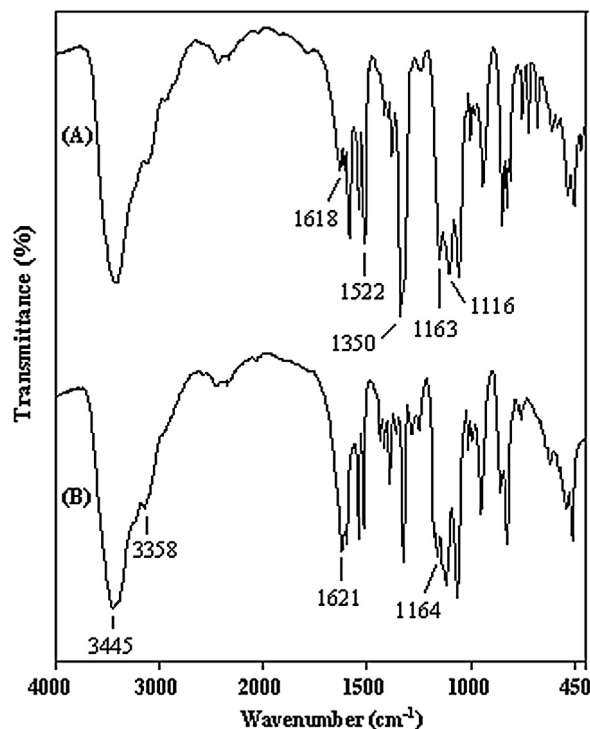
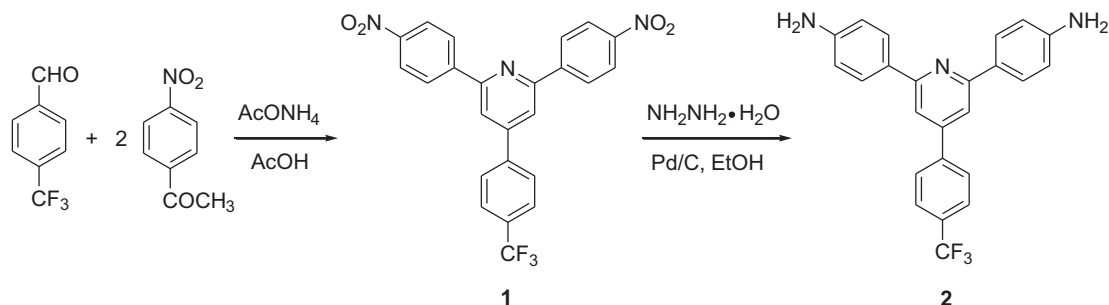


Fig. 1. FTIR spectra of the dinitro compound **1** (A) and the diamine **2** (B).

of the diacyl chloride (**3**) in DMAc solution containing a trace of pyridine cooled by an external ice–acetone bath. The reaction temperature was maintained at -10 to 0 $^{\circ}\text{C}$ in the initial 5 h. In order to obtain maximum molecular weight, the reaction was then allowed to proceed overnight at room temperature. All polymerizations proceeded homogeneously throughout the reaction, and highly viscous solutions were obtained. The polyamides **4a–4d** with inherent viscosities ranging from 0.70 to 1.06 dL g^{-1} (Table 1) were isolated as tough fibers in nearly quantitative yields, and could be solution-cast into films, indicating their high molecular weights.

As shown in Table 1, the viscosity of these polymers was in the order: **4a** > **4b** > **4c** > **4d**. This might be attributed to the presence of the more flexible ether groups in the main chains (polymers **4b** and **4c**), which decreased the intermolecular hydrogen bonding. Further, attachment of methyl substituents on the benzene ring (polymer **4d**) led to increased packing distance, introduction of lateral disorder, and decreased polar forces; thus polymer **4d** showed a lower viscosity.

Structural features of these polymers were characterized by FTIR and NMR spectroscopy. A typical FTIR spectrum for the polymer **4b** is displayed in Fig. 3. The FTIR spectra of all polymers showed the characteristic absorptions of the amide group at



Scheme 1. Synthetic route to new diamine monomer **2**.

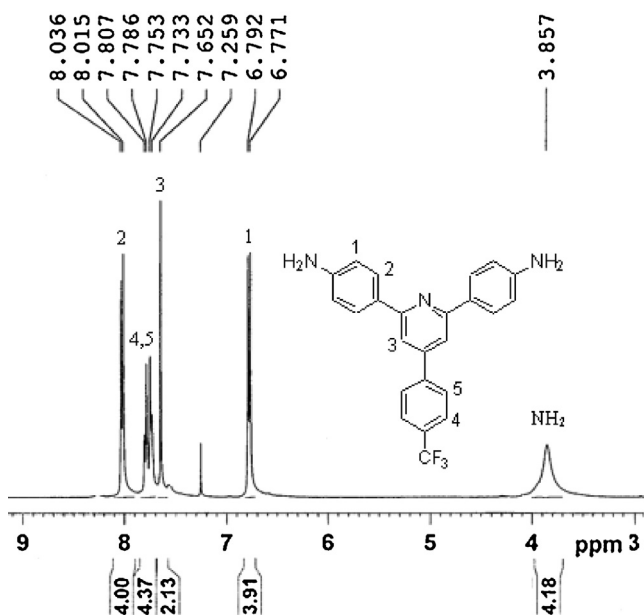


Fig. 2. ^1H NMR spectrum of the diamine monomer **2**.

around $3310\text{--}3300\text{ cm}^{-1}$ (N–H stretching), $1685\text{--}1668\text{ cm}^{-1}$ (amide C=O stretching) and $1500\text{--}1550\text{ cm}^{-1}$ (combined N–H band and C–N stretching). The polymers also exhibited characteristic absorptions of sulfone stretching at around $1150\text{--}1160\text{ cm}^{-1}$, along with the characteristic absorption bands of C–F stretching at around $1128\text{--}1132\text{ cm}^{-1}$. In addition, the formation of the amide group was also confirmed by the resonance signals of amide protons at around $\delta 10.40\text{--}10.35$ in the ^1H NMR spectra and amide carbons at around $\delta 167\text{--}169$ in the ^{13}C NMR spectra.

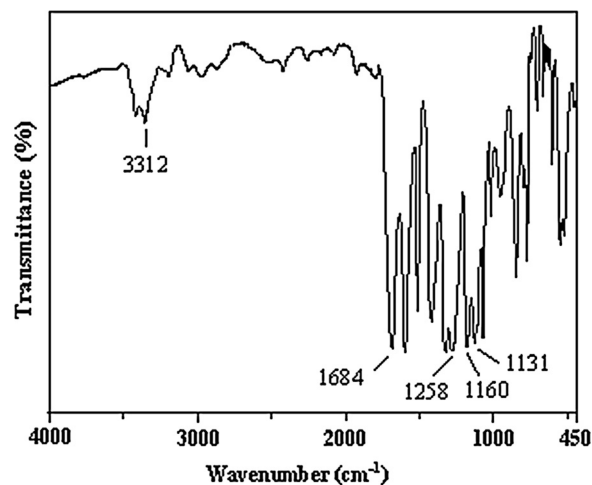
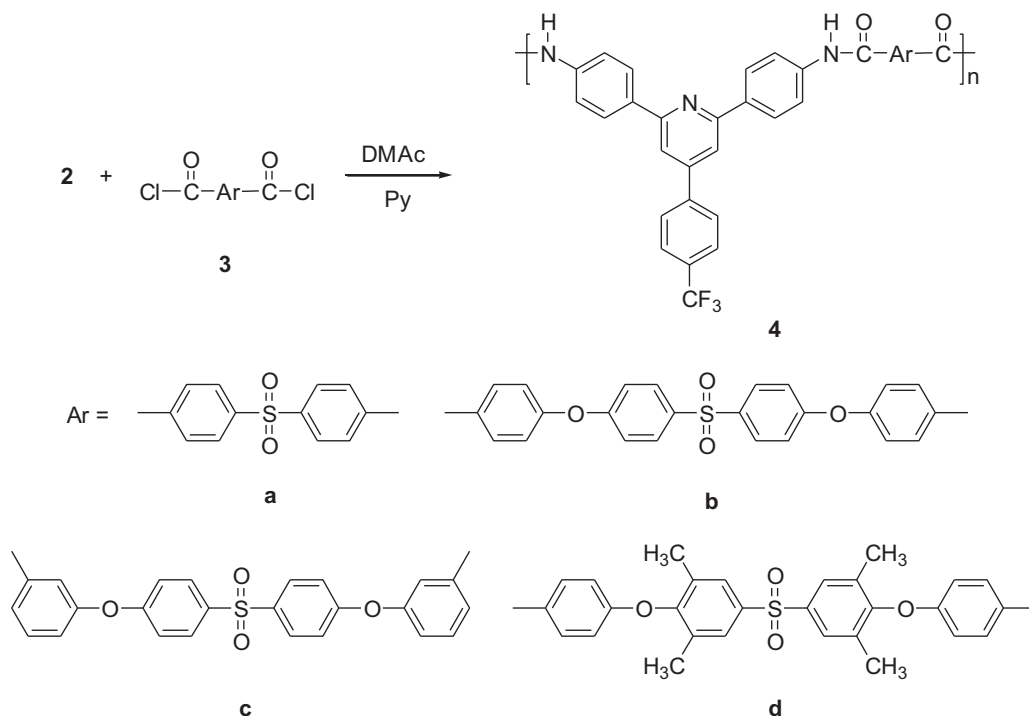


Fig. 3. FTIR spectrum of the polymer **4b**.

2.3. Thermal stabilities

DSC and TGA were used to evaluate the thermal properties of these polymers, and the results are summarized in Table 2. Their so-called amorphous characters were supported by no melting peaks (T_m) detected by DSC (Fig. 4). Polymers **4a–4d** showed the glass-transition temperature (T_g) values in the range of $280\text{--}318\text{ }^\circ\text{C}$. As can be seen from Table 2, polymer **4a** had a higher T_g than the corresponding analogs of **4b** and **4c**. This result was very reasonable and might be attributed to the fact that the insertion of flexible ether linkages in the polymer backbone, which increased the conformational freedom of the polymer chain and tended to decrease T_g . In general, the introduction of less symmetrical *m*-phenylene unit led to a decreased T_g . As expected, the polymer **4c** showed a lower T_g value than **4b** with symmetric orientation of the *p*-phenylene unit in its backbone. Notably, the polyamide **4d**



Scheme 2. Synthesis of the fluorinated poly(pyridine sulfone amide)s **4a–4d**.

Table 1
Inherent viscosities, elemental analysis and water uptakes of the polymers (4a–4b).

Polymer	$\eta_{inh}(dLg^{-1})^a$	Formula (molecular weight)	Elemental analysis			Water uptake (%) ^b	
			Calcd	Found	Corr. ^c		
4a	1.06	$(C_{38}H_{24}N_3F_3SO_4)_n$ (675.69) _n	Calcd	67.55	3.58	6.22	1.08
			Found	66.78	3.72	6.01	
			Corr. ^c	67.50	3.68	6.07	
4b	0.78	$(C_{50}H_{32}N_3F_3SO_6)_n$ (859.88) _n	Calcd	69.84	3.75	4.89	1.13
			Found	68.80	3.92	4.77	
			Corr. ^c	69.58	3.88	4.82	
4c	0.75	$(C_{50}H_{32}N_3F_3SO_6)_n$ (859.88) _n	Calcd	69.84	3.75	4.89	1.15
			Found	68.78	3.95	4.80	
			Corr. ^c	69.57	3.90	4.86	
4d	0.70	$(C_{54}H_{40}N_3F_3SO_6)_n$ (915.99) _n	Calcd	70.81	4.40	4.59	1.28
			Found	69.67	4.70	4.39	
			Corr. ^c	70.56	4.63	4.45	

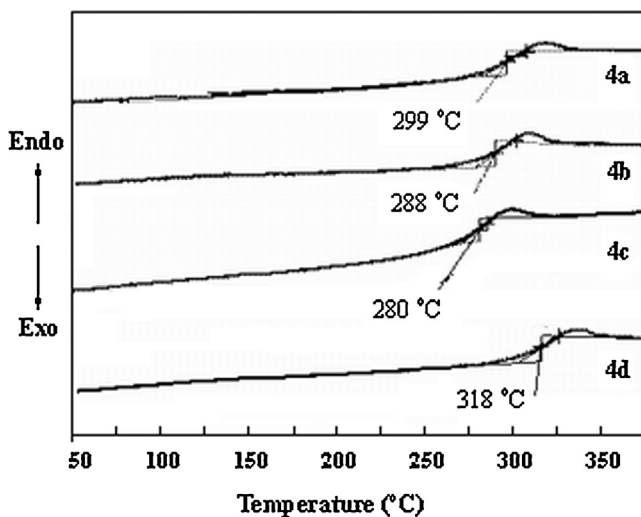
^a Measured in NMP at a concentration of 0.5 g dL⁻¹ at 30 °C.^b Water uptake (%) = 100 × (W – W₀)/W₀; W: weight of polymer sample after standing at room temperature; W₀: weight of polymer sample after being dried in vacuum at 100 °C.^c Corrected value = found value × (100 + moisture intake %) for C and N; corrected value = found value × (100 – moisture intake %) for H.**Table 2**
Thermal properties of the polymers (4a–4b).

Polymer	T_g (°C) ^a	T_{d0} (°C) ^b	T_{d5} (°C) ^c	T_{d10} (°C) ^d	R_w (%) ^e
4a	299	433	445	516	55
4b	288	420	435	502	53
4c	280	422	432	510	54
4d	318	413	425	485	52

^a Determined by the second heating trace of DSC measurements.^b Initial decomposition temperature by TGA in nitrogen.^c Temperature for 5% weight loss by TGA in nitrogen.^d Temperature for 10% weight loss by TGA in nitrogen.^e Residual weight (%) when heated to 800 °C in nitrogen.

exhibited the highest T_g of 318 °C in this series of polymers. This was attributed to the attachment of methyl substituents to the backbone, which restricted the internal rotation, thus generally leading to the increase of T_g value.

As shown in Table 2, all the polymers exhibited good thermal stability without significant weight loss up to temperature of approximately 413 °C under nitrogen atmosphere. Their temperatures at 5 and 10% weight loss were in the range of 425–445 and

**Fig. 4.** DSC thermograms of the polymers 4a–4d.

485–516 °C respectively, and the char yields for all polymers were more than 50% at 800 °C under nitrogen atmosphere.

2.4. Solubilities

The solubility was qualitatively determined by the dissolution of 1.0 g of polymer sample in 9.0 g of solvent (10 wt.%), and the results are summarized in Table 3. As shown in Table 3, all the prepared polyamides are readily soluble in polar solvents such as NMP, DMF, DMAc and DMSO, and even in less polar solvents like Py, THF, and *m*-cresol at room temperature or on heating at 60 °C. Compared with the conventional aromatic polyamides, the present new polyamides have good solubilities, which resulted from the introduction of polar pyridine units and polar bulky sulfone groups in the polymer chains, as well as the bulky 4-trifluoromethylphenyl pendant groups. The bulky pendant groups increased the chain distance, inhibited the chain packing, and decreased the interaction of the polymer chains. Consequently, the solvents molecules were able to penetrate easily to solubilize the polymer chains. Additionally, the presence of polar pyridine and sulfone groups in the main chains also contributed effectively in the solubility of these polyamides by interacting with the polar functional group in the solvent molecule. The excellent solubility made these polyamides to be potential candidates for practical applications in spin-on and casting processes.

2.5. Crystal and mechanical properties

All polyamides were characterized by WAXD studies in the film form. As expected, all the polyamides displayed a nearly completely amorphous pattern (Fig. 5). This could be attributed

Table 3
Solubilities of the polymers (4a–4b).^a

Polymer	NMP	DMAc	DMF	DMSO	Py	THF	<i>m</i> -Cresol	CHCl ₃	MeOH
4a	++	++	++	++	++	+	++	–	–
4b	++	++	++	++	++	++	++	–	–
4c	++	++	++	++	++	++	++	–	–
4d	++	++	++	++	++	++	++	+	–

^a ++ = soluble at room temperature; + = soluble on heating 60 °C; – = insoluble even on heating.NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethylsulfoxide; THF: tetrahydrofuran; Py: pyridine.

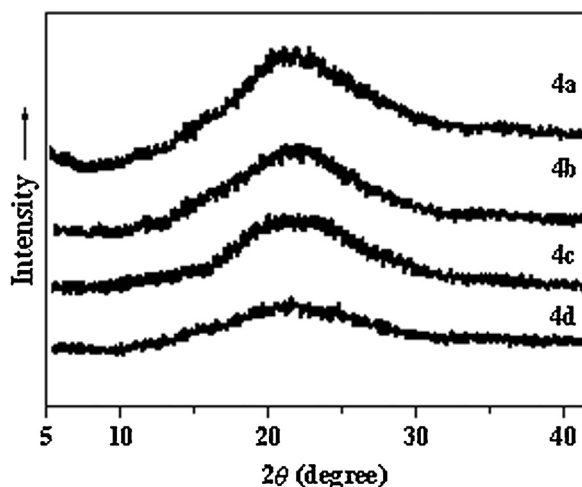


Fig. 5. Wide-angle X-ray diffractograms of the polymers 4a–4d.

Table 4
Mechanical properties of the polymers 4a–4d.

Polymer	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
4a	81	13	2.1
4b	78	15	1.9
4c	75	14	1.9
4d	72	12	1.8

to the combined effects of the bulky 4-trifluoromethylphenyl pendant groups and flexible sulfone linkages in the polymer backbones, which produced wider separation of polymer chains, weakening intermolecular hydrogen bonding, lowering chain packing efficiency with a gain of free volume, thus resulting in a decrease in crystallinity. The amorphous structure of these polyamides was also reflected in their excellent solubility and good film forming ability.

All polymer films with highly transparent, flexible and strong characteristics were easily formed via the casting of polymer solutions in DMAc. The mechanical properties of these polyamide films are listed in Table 4. The values of the tensile strength varied in the range of 72–81 MPa, the elongation at break varied in the range of 12–15%, and the initial modulus varied in the range of 1.8–2.1 GPa. All the polyamides possessed good mechanical properties, which suggested that these new polyamides could be considered as engineering plastics and photoelectric materials.

2.6. Optical and dielectric properties

The optical properties of these polymer films with approximately 50 μm thickness were evaluated by UV–vis spectroscopy, and the typical UV–vis spectrum of polymer 4b is presented in Fig. 6. The transparency of the polymers was evaluated at the

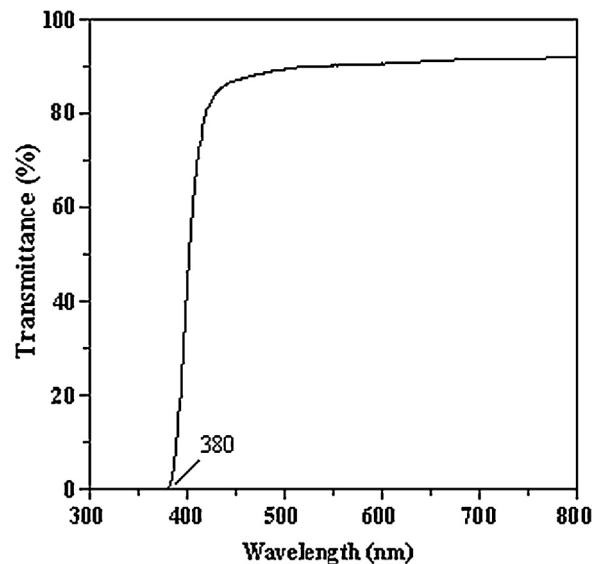


Fig. 6. Transmission UV–vis absorption spectrum of the polymer 4b.

Table 5
Optical transparency and dielectric constants of the polymers 4a–4d.

Polymer	λ_{cut} (nm) ^a	Transparency (%)			$\lambda_{80\% \text{ trans.}}$ ^b (nm)	D_c ^c (1 MHz)
		500 (nm)	600 (nm)	700 (nm)		
4a	382	88	90	90	430	3.44
4b	380	88	90	91	423	3.51
4c	378	87	89	91	423	3.48
4d	374	84	88	91	421	3.40

^a λ_{cut} = cutoff wavelength.

^b $\lambda_{80\% \text{ trans.}}$ = 80% transmission wavelength.

^c D_c = Dielectric constant.

wavelengths from 200 to 800 nm, and the UV data at several wavelengths were also reported in Table 5. As shown in Table 5, the cut-off wavelengths of these polymers ranged from 374 to 382 nm and the 80% transmission wavelength ranged from 425 to 431 nm. The higher optical transparency of the resulting polymers was mainly possible due to the presence of the pendant 4-trifluoromethylphenyl substituents in the polymer backbone.

The electrical insulating properties of these polyamide films were evaluated on the basis of the dielectric constants, measured by the parallel plate capacitor method using a dielectric analyzer. As can be seen from Table 5, these polyamides showed lower dielectric constants in the range of 3.40–3.51 (1 MHz) than commercial Nylatron (ca. 3.7 at 1 MHz). Furthermore, the present poly(sulfone amide)s exhibited lower dielectric constants than that of an analog without the trifluoromethyl groups (4.46–5.10 at 1 Hz–100 kHz) (Fig. 7) [35]. The low dielectric constants of these new polyamides could be attributed to the presence of bulky 4-trifluoromethylphenyl pendant groups, which led to efficient

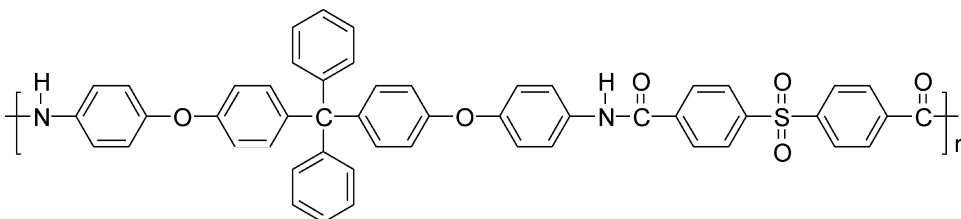


Fig. 7. Chemical structure of the non-fluorinated poly(sulfone amide).

chain packing and increased free volume in the polymer backbone. In addition, the strong electronegativity of fluorine and associated low polarizability of the C–F bonds resulted in decrease in the dielectric constants.

3. Conclusions

A series of the fluorinated polyamides containing pyridine and sulfone moieties were synthesized from a new diamine, 4-(4-trifluoromethylphenyl)-2,6-bis(4-aminophenyl)pyridine with aromatic diacyl chloride by the low temperature polycondensation technique. All the polymers had good solubility in many organic solvents and could be casted into strong and flexible films. The obtained fluorinated polyamides also exhibited high thermal stability, good mechanical properties, excellent optical properties, low dielectric constants and lower water uptake. These characteristics indicated that these new polyamides could be considered as new candidates for processable high-performance engineering plastic and photoelectric materials.

4. Experimental

4.1. Materials

4-Trifluoromethylbenzaldehyde, 4'-nitroacetophenone, ammonium acetate, glacial acetic acid, hydrazine monohydrate, and 10% palladium on activated carbon (10%, Pd/C) were used as received from commercial sources. DMAc and Py were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieve prior to use. 4,4'-Sulfonyl dibenzoyl chloride (**4a**) and 4,4'-[sulfonyl bis(2,6-dimethyl-1,4-phenyleneoxy)]dibenzoyl chloride (**4d**) were prepared by the reaction of their corresponding acids with thionyl chloride in the presence of a catalytic amount of DMF and were purified by crystallization from toluene/*n*-hexane according to the published method [36]. 4,4'-[Sulfonyl bis(*p*-phenyleneoxy)]dibenzoyl chloride (**4b**) and 3,3'-[sulfonyl bis(*p*-phenyleneoxy)]dibenzoyl chloride (**4c**) were prepared using procedures similar to those described in the literature [37].

4.2. Measurements

¹H and ¹³C NMR spectra were recorded on Bruker AVANCE 400 MHz spectrometer in dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) or chloroform (CDCl₃) as a solvent, with tetramethylsilane (TMS) as internal standard. FTIR spectra of the monomer and polymers in KBr pellets were obtained on a Perkin-Elmer SP One FT-IR spectrophotometer. Elemental analysis was performed with a Carlo Erba 1106 Elemental Analyzer. Differential scanning calorimetry (DSC) analysis was performed on a Perkin-Elmer Pyris 1 DSC at a scanning rate of 10 °C/min from 50 to 350 °C in flowing nitrogen (20 mL/min). Thermogravimetric analysis (TGA) was carried out on approximately 6–8 mg film samples with a Perkin Elmer Pyris 1 TGA in nitrogen (40 mL/min) at a heating rate of 10 °C/min from 50 to 800 °C. Wide-angle X-ray diffraction patterns were recorded at room temperature (ca. 25 °C) on a Shimadzu XRD-6000 X-ray diffractometer (operating at 40 kV and 30 mA) with graphite-monochromatized Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$); the scanning rate was 2°/min over a range of $2\theta = 5\text{--}40^\circ$. The inherent viscosities were measured at 0.5 g dL⁻¹ concentration in NMP with an Ubbelohde viscometer at 30 °C, in which the polymers were pretreated by drying in oven at 120 °C for 1 h to remove the adsorbed moisture. The water uptake was measured by the weighing of the changes in the samples (50 mm × 50 mm × 0.05 mm) before and after immersion in water at 25 °C for 24 h. The mechanical properties of the polymer

films were measured on an Instron 1122 testing instrument with a 5 kg load cell at a crosshead speed of 5 mm/min on strips (0.5 cm wide, 6 cm long, and ca. 0.05 mm thick), and an average of at least three replicas was used. The dielectric constants were measured at 25 °C and a frequency of 1 MHz using a dielectric analyzer (TA Instruments DEA 2970). Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on a Shimadzu UV–1601 UV–vis spectrophotometer.

4.3. Monomer synthesis

4-(4-Trifluoromethylphenyl)-2,6-bis(4-nitrophenyl)pyridine (**1**): In a 500 mL, round-bottomed flask, a mixture of 4-trifluoromethylbenzaldehyde (12.2 g, 70 mmol), 4'-nitroacetophenone (23.1 g, 140 mmol), ammonium acetate (108 g, 1.40 mol) and glacial acetic acid (300 mL) was refluxed for 12 h. After completion of the reaction (monitored by TLC), the mixture was cooled to room temperature, the precipitated yellow solid was collected by filtration and washed with cold DMAc. The crude product was recrystallized from DMAc two times to afford the dinitro compound **1** (19.5 g, yield 60%) as yellow needles; mp 373 °C (by DSC). ¹H NMR (400 MHz, DMSO-*d*₆): $\delta = 8.61$ (d, $J = 7.6$ Hz, 4H), 8.38 (d, $J = 7.2$ Hz, 4H), 8.15 (d, $J = 8.4$ Hz, 2H), 8.04 (d, $J = 8.4$ Hz, 2H), 7.85 (s, 2H). Elem. Anal. Calcd for C₂₄H₁₄F₃N₃O₄ (465.39 g/mol): C, 61.94%; H, 3.03%; N, 9.03%. Found: C, 61.82%; H, 3.18%; N, 9.14%. FTIR (KBr): $\nu_{\text{max}} = 1522, 1350$ (–NO₂), 1618 (C=N), 1163, 1116 (C–F) cm⁻¹.

4-(4-Trifluoromethylphenyl)-2,6-bis(4-aminophenyl)pyridine (**2**): A mixture of the dinitro compound **1** (7.0 g, 15.0 mmol, 10% Pd/C (0.15 g), hydrazine monohydrate (7.5 mL), and ethanol (100 mL) was placed in a 250 mL of round-bottomed flask. The reaction was heating at 60 °C for 24 h and then removed the ethanol under reduce pressure. THF (50 mL) was then added to the mixture, filtered to remove Pd/C and removed the THF using rotation evaporator. The light yellow solid was purified by recrystallization from THF/ethanol (10/1, v/v) twice and dried under vacuum to furnish the diamine monomer **2** (5.0 g, yield 83%) as light yellow needles; mp 210 °C (by DSC). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.04\text{--}8.02$ (d, $J = 8.4$ Hz, 4H), 7.81–7.73 (m, 4H), 7.65 (s, 2H), 6.79–6.77 (d, $J = 8.4$ Hz, 4H), 3.86 (s, 4H). Elem. Anal. Calcd for C₂₄H₁₈F₃N₃ (405.42 g/mol): C, 71.11%; H, 4.48%; N, 10.37%. Found: C, 70.95%; H, 4.60%; N, 10.44%. FTIR (KBr): $\nu_{\text{max}} = 3445, 3358$ (N–H), 1621 (C=N), 1164 (CF) cm⁻¹.

4.4. Polymer synthesis

Preparation of polyamide **4b** is described as a typical procedure. A solution of 40 mL of DMAc containing Py (0.10 g) and 6.00 mmol of **2** (2.4325 g) in a 100 mL flask was cooled to –10 °C on a dry ice–acetone bath, and then 6.00 mmol of **3b** (3.1643 g) was added. The mixture was stirred at –10 to 0 °C for 5 h. The reaction was then continued overnight at room temperature. The resulting highly viscous polymer solution was poured slowly with stirring into 250 mL of methanol. The white fiberlike precipitate formed was washed repeatedly with methanol and hot water, collected by filtration, and dried at 120 °C under vacuum for 5 h to give polyamide **4b** (5.1 g, 98%). The inherent viscosity of **4b** was 0.78 dL g⁻¹, as measured at a concentration of 0.5 g dL⁻¹ in NMP at 30 °C. The FTIR spectrum exhibited characteristic absorptions at 3427 (N–H stretching), 1684 (C=O stretching), 1258 (C–O–C stretching), 1160 (–SO₂– stretching) and 1131 cm⁻¹ (C–F stretching). The other polyamides were also prepared using a similar procedure.

4.5. Preparation of the polymer films

A solution of polymer was made by dissolving the resulting polyamide (1.0 g) in DMAc (9 mL) to afford an approximate 10 wt.%

solution. The homogeneous solution was poured into a 9 cm diameter glass culture dish, which was placed in a 100 °C oven overnight for the slow release of the solvent, and further dried in vacuo at 150 °C for 10 h. The flexible polymer films were then stripped from the glass.

Acknowledgments

The financial support for this work provided by the National Natural Science Foundation of China (Nos. 21064003, 51163008) and the training Program for Science and Technology Leaders in Major Subjects of Jiangxi Province of China (No. 20113BCB22012) and the Natural Science Foundation of Jiangxi Province of China (No. 20114BAB203014) is gratefully acknowledged.

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