Synthesis and Characterization of Novel Aromatic Poly(ester amide)s Containing Pendant Trifluoromethylphenoxy Groups

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ABSTRACT: A new diamine monomer, 1,4-bis(4-aminophenoxycarbonyl)-2-(4-trifluoromethylphenoxy)benzene containing the trifluoromethyl and ester groups, was prepared from 2-(4-trifluoromethylphenoxy)terephthalyol chloride and 4-nitrophenol in two steps. Then, a series of novel aromatic poly(ester amide)s containing pendant trifluoromethylphenoxy groups with inherent viscosities of 0.51–1.14 dL/g have been prepared by low-temperature solution polycondensation from this diamine with various aromatic diacid chlorides. All the poly(ester amide)s are amorphous and readily soluble in many organic solvents such as *N,N*-dimethylacetamide (DMAC) and dimethyl sulfoxide. Tough and flexible polymer films cast from DMAc solutions have tensile strengths of 89–114 MPa, elongations at break of 5.8–8.8%, and initial moduli of 2.2–3.2 GPa. These poly(ester amide)s show glass transition temperatures between 166 and 256°C, 10% weight loss temperatures ranging from 395 to 445°C, and char yields higher of 46–56% at 800°C in nitrogen, and also exhibit low dielectric constants ranging from 3.31 to 3.52 (1 MHz), and high transparency with an ultraviolet–visible absorption cut-off wavelength in the 362–380 nm range.

Key words: fluorinated aromatic poly(ester amide); pendant trifluoromethylphenoxy group; 1,4-bis(4-aminophenoxycarbonyl)-2-(4-trifluoromethylphenoxy)benzene; low-temperature solution polycondensation

INTRODUCTION

Aromatic polyamides are one of the most important classes of high-performance polymeric materials because of their excellent mechanical property, thermal and oxidative stability, chemical resistance, and low flammability.[1] However, their limited solubility in organic solvents, high melting or softening temperatures by high stiffness and intermolecular hydrogen bonding between amide groups lead to difficult to process, thus limiting their applications.[2] Therefore, considerable efforts have been focused on improving their solubility and processability through structural modification. Several approaches have been employed to improve the processability of the polyamides including the incorporation of ester[3–8] or other flexible linkages,[9–11] bulky pendant[12–14] or cardo groups,[15–17] as well as noncoplanar[18–20] or unsymmetrical structures[21–23] into polymer backbones. In recent years, much attention has been devoted to the preparation of fluorine-containing polyamides because of their low dielectric constants, low moisture absorptions, and high thermal stability by introduction of flexible fluorinated groups such as trifluoromethyl substituents in the aromatic rings and hexafluoroisopropylidene moieties into polyamide backbones.[24–29] The introduction of ester groups and bulky unsymmetrical trifluoromethylphenoxy structures into the macromolecular chains of polyamides is expected to provide polymers with good performance characteristics, good solubility, high thermal stability, and good optical and dielectric properties. In this article we report the synthesis of a series of new organosoluble aromatic poly(ester amide)s with pendant trifluoromethylphenoxy groups, which derived from a novel unsymmetrical aromatic diamine monomer, 1,4-bis(4-aminophenoxycarbonyl)-2-(4-trifluoromethylphenoxy)benzene with various aromatic diacid chlorides by low-temperature solution polycondensation. The solubility, crystallinity, thermal stability, and mechanical property as well as optical and dielectric behaviors of these new fluorine-containing poly(ester amide)s were investigated.

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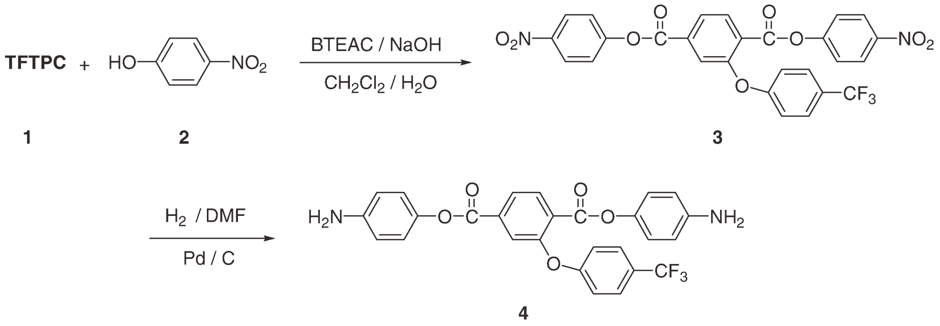


Scheme 1 Synthetic route to fluorine-containing bis(ester amine) **4**.

EXPERIMENTAL

Materials

2-(4-Trifluoromethylphenoxy)terephthalyol chloride (TFTPC) (**1**)[29] was prepared according to our reported procedures. Isophthaloyl chloride (**5a**) was purified by distillation *in vacuo*. Other aromatic diacid chlorides such as 1,4-bis(4-chloroformylphenoxy)benzene (**5b**), 1,3-bis(4-chloroformylphenoxy)-benzene (**5c**), 1,2-bis(4-chloroformylphenoxy)benzene (**5d**), and 4,4′-bis(3-chloroformylphenoxy)diphenylsulfone (**5e**) and bis(4-chloroformylphenyl)phenylphosphine oxide (**5f**) were prepared by the reaction of the corresponding aromatic dicarboxylic acids with thionyl chloride in the presence of a few drops of *N*,*N*-dimethylformamide (DMF) as a catalyst, and then purified from dry hexane. 4-Nitrophenol, benzyltriethylammonium chloride (BTEAC), and other commercial reagents were used as received. DMAc, DMF, and pyridine were purified by distillation under reduced pressure over calcium hydride prior to use.

Characterization

^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE 400 MHz spectrometer in dimethyl sulfoxide-d_6 (DMSO-d_6) or chloroform ($CDCl_3$) 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 FTIR spectrophotometer. Elemental analysis was performed with a Carlo Erba 1106 Elemental Analyzer. Melting points were determined on X_4 melting point apparatus and were uncorrected, unless otherwise specified. Differential scanning calorimetry (DSC) analysis was performed on a Perkin Elmer Pyris 1 DSC at a scanning rate of 20°C/min from 50 to 350°C in flowing nitrogen (20 mL/min). Thermogravimetric analysis (TGA) was carried out on $\sim$ 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. Wide-angle X-ray diffraction patterns were recorded on a Shimadzu XRD-6000 X-ray diffractometer (operating at 40 kV and 30 mA) with graphite-monochromatized CuK_α radiation (λ = 1.5418 Å) at room temperature (ca. 25°C); the scanning rate was 2°/min over a range of 2θ = 5°–40°). The inherent viscosities were measured at 0.5 g/dL concentration in DMAc with an Ubbelohde viscometer at 30°C, in which the poly(ester amide)s were pretreated by drying in an oven at 120°C for 1 h to remove the adsorbed moisture. 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 about 0.05 mm thick), and an average

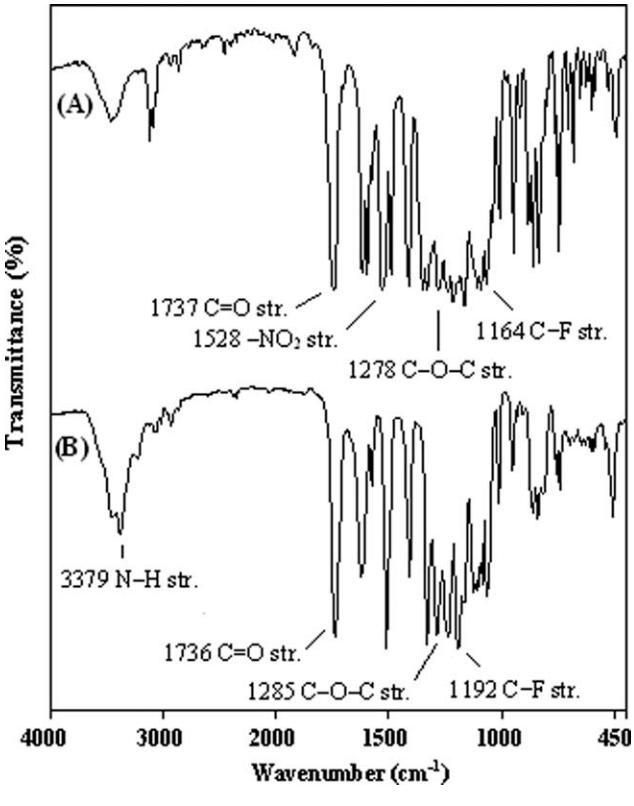
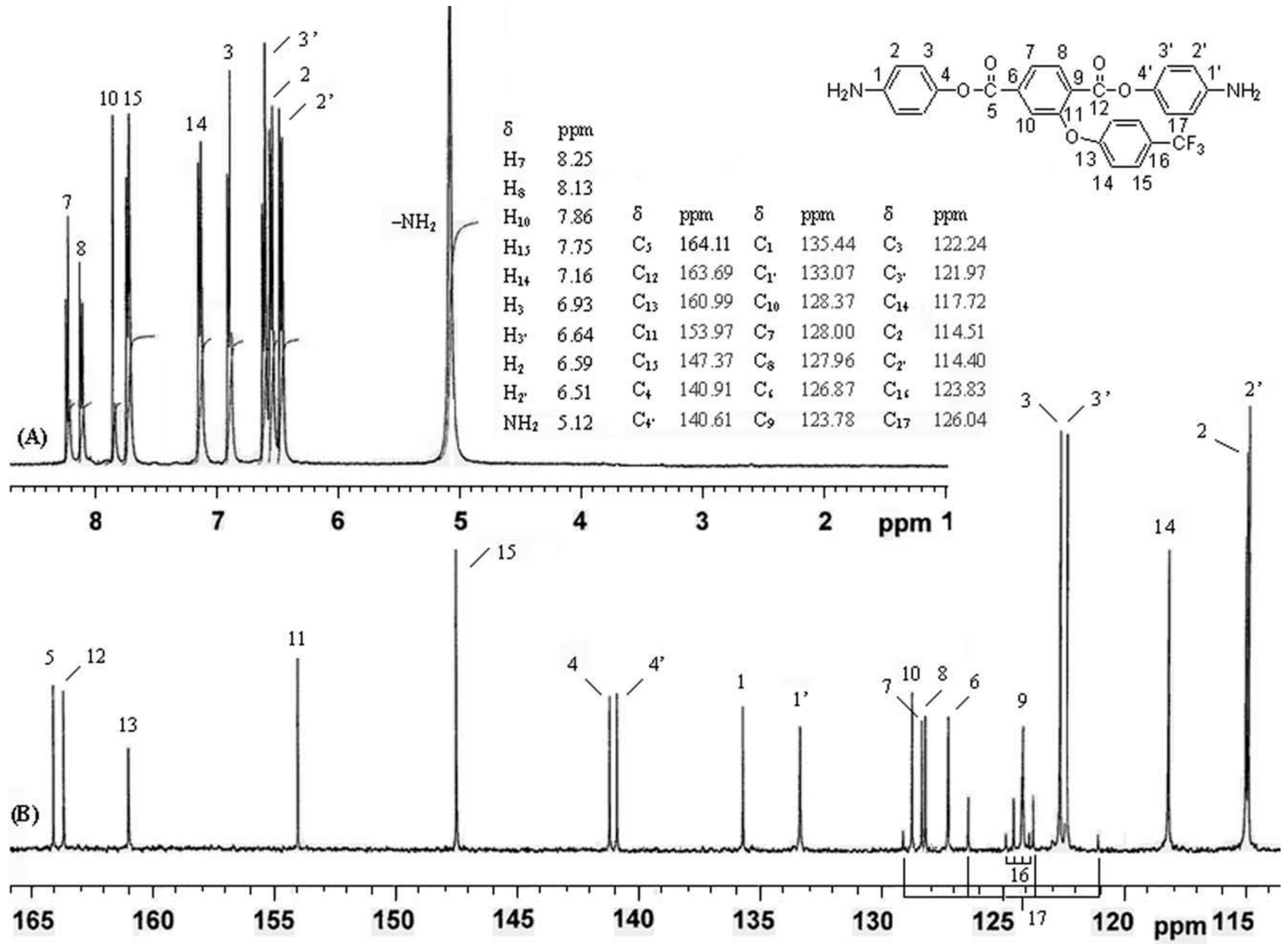


Figure 1 FTIR spectra of (A) dinitro-diester **3** and (B) bis(ester-amine) **4**.



δ	ppm
H_7	8.25
H_8	8.13
H_{10}	7.86
H_{15}	7.75
H_{14}	7.16
H_3	6.93
$H_{3'}$	6.64
H_2	6.59
$H_{2'}$	6.51
NH_2	5.12

δ	ppm	δ	ppm	δ	ppm
C_5	164.11	C_1	135.44	C_3	122.24
C_{12}	163.69	$C_{1'}$	133.07	$C_{3'}$	121.97
C_{13}	160.99	C_{10}	128.37	C_{14}	117.72
C_{11}	153.97	C_7	128.00	C_2	114.51
C_{15}	147.37	C_8	127.96	$C_{2'}$	114.40
C_4	140.91	C_6	126.87	C_{16}	123.83
$C_{4'}$	140.61	C_9	123.78	C_{17}	126.04

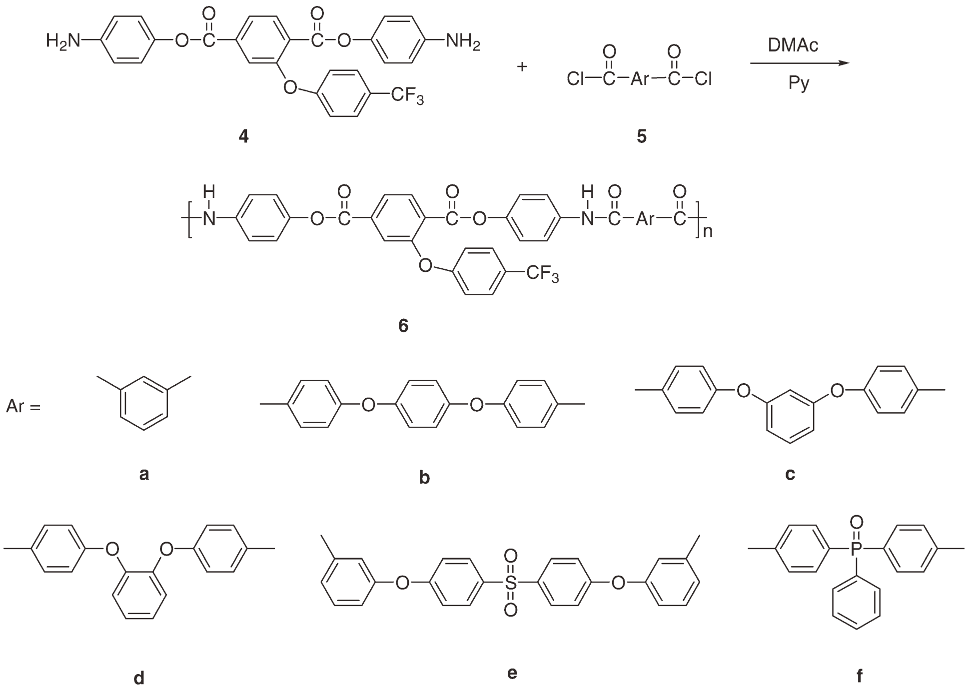
Figure 2 ^{1}H NMR (A) and ^{13}C NMR (B) spectra of bis(ester amine) **4** in DMSO-d_6.

of at least three replicas was used. Dielectric constants were determined by the parallel plate capacitor method using a dielectric analyzer (TA instruments DEA 2970) on thin films at frequency of 1 MHz. Gold electrodes were vacuum deposited on both surfaces of dried films, followed by measuring at 25°C in a sealed chamber maintained in nitrogen. Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on a Shimadzu UV–1601 UV–vis spectrophotometer.

Preparation of monomer

Synthesis of 1,4-bis(4-nitrophenoxycarbonyl)-2-(4-trifluoromethylphenoxy)benzene (3)

Dinitro-diester **3** was prepared from the condensation of 4-nitrophenol with TFTPC (**1**). 4-Nitrophenol **2** (6.95 g, 0.05 mol) was dissolved in 48 mL of 1.0*M* aqueous sodium hydroxide in a 250 mL three-necked round-bottomed flask equipped with a mechanical stirrer. After the mixture was stirred for 1 h at room temperature, BTEAC (0.1 g) was then added to the reaction mixture, and the stirring was continued for another 30 min. The solution of TFTPC (0.023 mol, 8.35 g) in 50 mL of dichloromethane was added to the reaction mixture and the mixture was stirred vigorously at room temperature for 1.5 h. After that, the organic phase was washed with aqueous sodium hydroxide and water (each of 3 × 10 mL), dried over anhydrous $MgSO_4$, and then the solvent was removed. The crude product was purified by recrystallization from DMF to give 12.05 g (92.2% yield) of pure dinitro-diester **3** as light yellowish needles. Mp: 166°C (DSC peak temperature, 10°C/min). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38–8.29 (m, 5 H), 8.21 (dd, *J* = 1.6, 8.0 Hz, 1 H), 7.97 (s, 1 H), 7.67 (d, *J* = 8.8 Hz, 2 H), 7.46 (dd, *J* = 4.8, 7.2 Hz, 2 H), 7.28 (dd, *J* = 4.8, 6.8 Hz, 2 H), 7.13 (d, *J* = 8.4 Hz, 2 H). ^{13}CNMR (100 MHz, $CDCl_3$): δ = 162.40, 161.85, 159.80, 155.49, 155.03, 154.90, 145.75, 145.64, 134.72, 133.10, 127.64, 127.03, 126.26, 125.43, 125.34, 125.27, 123.59, 122.57, 122.49, 122.32, 117.53. Elem. Anal. Calcd for $C_{27}H_{15}F_3N_2O_9$ (568.42 g/mol): C, 57.05%; H, 2.66%; N, 4.93%. Found: C, 56.90%; H, 2.82%; N, 4.86%. FTIR (KBr): ν_{max} = 1737 (C=O),



Scheme 2 Syntheses of fluorinated poly(ester amide)s **6a–6f**.

1528, 1348 (NO_2), 1278, 1093 (C—O—C), 1164, 1109 (C—F) cm^{-1}.

Synthesis of 1,4-bis(4-aminophenoxycarbonyl)-2-(4-trifluoromethylphenoxy)benzene (4)

Bis(ester amine) **4** was synthesized by the catalytic hydrogenation of dinitro-diester **3** according to a modification of Hsiao's method.[7] A mixture of dinitro-diester **3** (5.68 g, 0.01 mol) and 0.4 g of 10% Pd/C in 100 mL of DMF was stirred at 40°C under a hydrogen atmosphere until the theoretical amount of hydrogen was consumed. The time taken to reach this stage was about 2 days. The solution was filtered to remove the catalyst, and the obtained filtrate was poured into 500 mL of stirring water, giving rise to a white precipitate. The crude product was then filtered, washed with water, dried, and recrystallized from anhydrous ethanol to give 4.45 g (87.6% yield) of white crystals bis(ester amine) **4**. Mp: 67°C (DSC peak temperature, 10°C/min). ^1H NMR (400 MHz, DMSO-d_6): δ = 8.25 (d, J = 8.0 Hz, 1 H), 8.13 (d, J = 8.0 Hz, 1 H), 7.86 (s, 1 H), 7.75 (d, J = 8.4 Hz, 2 H), 7.16 (d, J = 8.4 Hz, 2 H), 6.93 (d, J = 8.4 Hz, 2 H), 6.64 (d, J = 8.8 Hz, 2 H), 6.59 (d, J = 8.8 Hz, 2 H), 6.51 (d, J = 8.4 Hz, 2 H), 5.12 (s, NH_2, 4 H). ^{13}CNMR (DMSO-d_6, 100 MHz): δ = 164.11, 163.69, 160.99, 153.97, 147.37, 140.91, 140.61, 135.44, 133.07, 128.37, 128.00, 127.96, 126.87, 126.04 (q, $^1J_{C\text{-}F}$ = 271 Hz, C^{17}), 123.83 (q, $^2J_{C\text{-}F}$ = 34 Hz, C^{16}), 123.78, 122.24, 121.97, 117.72, 114.51, 114.40. Elem. Anal. Calcd for $C_{27}H_{19}F_3N_2O_5$ (508.45 g/mol): C, 63.78%; H, 3.77%; N, 5.51%. Found: C, 63.51%; H, 3.98%; N, 5.33%. FT-IR (KBr): ν_{max} = 3442, 3379 (NH_2), 1736 (C=O), 1285, 1083 (C—O—C), 1192, 1121 (C—F) cm^{-1}.

Polymer synthesis

The synthesis of poly(ester amide) **6a** is described here as an example to illustrate the general synthetic route to produce the present poly(ester amide)s. In a three-necked flask, a solution of 2.5423 g (5.0 mmol) of bis(ester amine) **4** and pyridine (0.8 mL) in 20 mL of DMAc was cooled to –10°C in an ice–acetone bath. After that, 1.0151 g (5.0 mmol) of isophthaloyl chloride **5a** was added all at once with stirring. The mixture was stirred at –10°C for 1 h and then at room temperature under nitrogen for 10 h to yield a highly viscous poly(ester amide) solution. The viscous solution was precipitated in 300 mL of stirred methanol, and the stringy, fiber-like precipitate was collected by filtration, washed thoroughly with methanol and hot water, and dried at 100°C in a vacuum oven for 6 h to give 3.10 g (97%) of poly(ester amide) **6a**. Other poly(ester amide)s were synthesized in similar method.

Preparation of the polymer films

A solution of polymer was made by dissolving about 1.0 g of the poly(ester amide) in 10 mL of DMAc to afford an ~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.

TABLE I
Inherent Viscosities and Elemental Analyses of the Poly(ester amide)s

Polymer	η_{inh} (dL g^{-1})^a	Formula of the repeat unit (molecular weight)	C (%)		H (%)		N (%)	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
6a	0.63	$C_{35}H_{21}F_3N_2O_7$ (638.55)	68.83	67.45	3.31	3.67	4.39	4.20
6b	1.14	$C_{47}H_{29}F_3N_2O_9$ (822.75)	68.61	67.55	3.55	3.79	3.40	3.30
6c	0.70	$C_{47}H_{29}F_3N_2O_9$ (822.75)	68.61	67.48	3.55	3.77	3.40	3.27
6d	0.65	$C_{47}H_{29}F_3N_2O_9$ (822.75)	68.61	67.50	3.55	3.82	3.40	3.28
6e	0.96	$C_{53}H_{33}F_3N_2O_{11}S$(962.91)	66.11	65.76	3.45	3.77	2.91	2.69
6f	0.51	$C_{47}H_{30}F_3N_2O_8P$ (838.73)	67.31	66.12	3.61	3.94	3.34	3.21

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

The poly(ester amide) film was released from the glass substrate and further dried *in vacuo* at 150°C for 10 h, and then used for its X-ray diffraction measurement, tensile test, thermal analysis, and optical property measurement.

RESULTS AND DISCUSSION

Synthesis of monomer

To further develop soluble and processable poly(ester amide)s without too much sacrificing thermal stability, a novel bis(ester amine) monomer bearing pendant trifluoromethylphenoxy group as nonsymmetrical structure was designed and prepared in two steps.

As shown in Scheme 1, nucleophilic condensation reaction of TFTPC (**1**) with 4-nitrophenol **2** in the presence of aqueous sodium hydroxide and BTEAC at room temperature afforded dinitro-diester **3**, which was then converted the corresponding bis(ester amine) **4** through hydrogen Pd/C-catalyzed reduction reaction. Elemental, IR, and NMR analyses were used to confirm the structures of compounds **3** and **4**. The elemental analysis data of the dinitro and diamino compounds were generally in agreement with the calculated values for the expected structures. Figure 1 compared the FTIR spectra of dinitro-diester **3** and bis(ester amine) **4**. The characteristic absorption bands at 1528 and 1349 cm^{-1} signed to the asymmetric and symmetric stretching of the nitro groups in dinitro-diester **3** disappeared in the FTIR spectrum (**B**) of bis(ester amine) **4**, and the characteristic bands of the amino groups at 3442 and 3379 cm^{-1} (N—H stretching) were observed. In addition, the ^{1}H NMR and ^{13}C NMR spectra of bis(ester amine) **4** were also shown in Figure 2. Because the pendant trifluoromethylphenoxy group made the structure of **4** unsymmetrical, signals of $H_{2,\ 3}$ and $H_{2',\ 3'}$ appeared at different regions of the ^{1}H NMR spectrum (**A**). The ^{13}C NMR spectrum (**B**) of bis(ester amine) **4** showed 17 signals as a result of the overlap of C^2 and $C^{2'}$. Additionally, the C^{16} and C^{17} showed clear quartet absorptions at 123–124 and 121–129 ppm, respectively, probably because of the $^2J_{C–F}$ and $^3J_{C–F}$ coupling of the carbons with fluorine atoms in the diamine. These results clearly confirmed that bis(ester amine) **4** prepared herein was consistent with its proposed structure.

Synthesis of polymer

The direct low-temperature solution polycondensation of bis(ester amine) **4** with structurally different

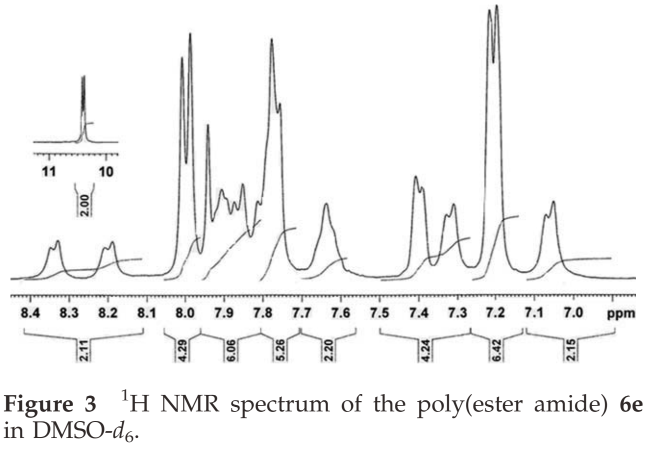


Figure 3 ^{1}H NMR spectrum of the poly(ester amide) **6e** in DMSO-d_6.

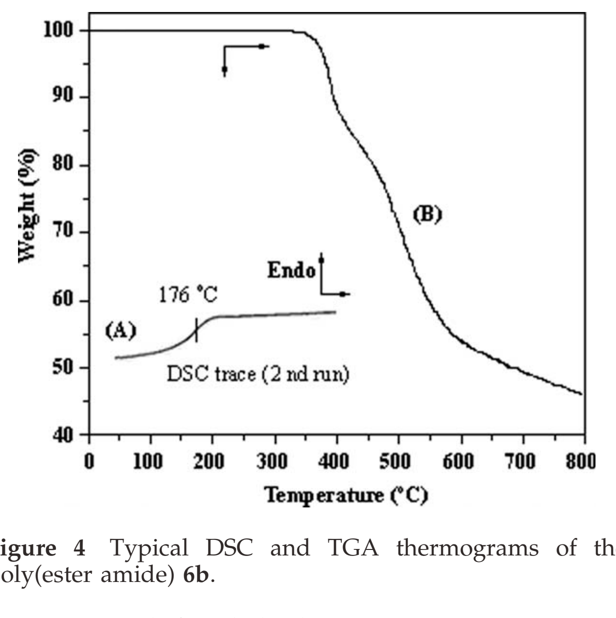


Figure 4 Typical DSC and TGA thermograms of the poly(ester amide) **6b**.

TABLE II
Thermal Properties of the Poly(ester amide)s

Polymer	T_g (°C)[a]	T_{d5} (°C)[b]	T_{d10} (°C)[c]	R_w (%)[d]
6a	256	376	412	51
6b	176	382	395	46
6c	166	384	425	54
6d	175	378	418	52
6e	191	378	406	47
6f	233	381	445	56

[a] Glass-transition temperature from the second heating trace of DSC measurements.
[b] 5% weight-loss temperatures in nitrogen.
[c] 10% weight-loss temperatures in nitrogen.
[d] Residual weight (%) when heated to 800°C in nitrogen.

aromatic diacid chlorides **5** in DMAc resulted in the fluoro-containing poly(ester amide)s **6a–6f** as shown in Scheme 2. All polymerizations proceeded homogeneously throughout the reaction, and the solutions became highly viscous, indicative of the formation of high molecular weights. These poly(ester amide)s were obtained in almost quantitative yields with inherent viscosities of 0.51–1.14 dL/g (Table I). All the polymers had sufficiently high molecular weights to permit the casting of tough and flexible films.

Structural features of the fluorinated poly(ester amide)s were verified by FTIR spectra and elemental analyses. These new polymers showed the characteristic absorptions of the amide groups at around 3263–3324 cm^{-1} (N—H stretching), 1648–1675 cm^{-1} (amide C=O stretching), and 1531–1550 cm^{-1} (N=H bending). All poly(ester amide)s also exhibited strong characteristic absorption bands at around 1737–1740 cm^{-1} (ester C=O stretching) and 1231–1285, 1066–1108 cm^{-1} (asymmetrical and symmetrical C—O—C stretching) because of the ester groups, along with the characteristic absorption bands of C—F stretching at around 1166–1195 cm^{-1}. Figure 3 depicted the typical ^{1}H NMR spectrum of the poly(ester amide) **6e**, in which the resonances for all the aromatic protons in the range of δ 8.35–7.05 ppm and the resonance peaks the of amide linkages appearing in 10.40 ppm were clearly assigned in good agreement with its structure. In addition, the results of the elemental analyses of all poly(ester amide)s were also listed in Table I. The elemental analysis values were generally in agreement with the calculated values for the corresponding recurring units.

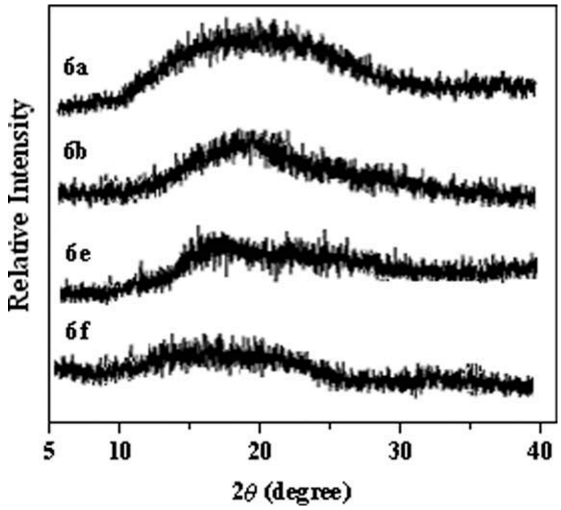


Figure 5 WAXD patterns of some poly(ester amide)s.

Thermal stabilities

The thermal behavior of the fluorine-containing poly(ester amide)s was evaluated by means of TGA and DSC, and the results were summarized in Table II. Typical DSC and TGA curves of a representative poly(ester amide) **6b** were illustrated in Figure 4. The influence of the residual solvent or the absorbed moisture and history of thermal annealing was sometimes observed in the first heating scan of DSC. Therefore, the poly(ester amide)s were first heated to ~350°C (heating rate = 20°C/min), and then

TABLE III
Solubility Behavior of the Poly(ester amide)s[a]

	Solvent[b]							
Polymer	NMP	DMAc	DMF	DMSO	Py	THF	*m*-Cresol	Cyclohexanone
6a	++	++	++	++	+h	–	–	+h
6b	++	+h	+h	+h	–	–	–	–
6c	++	++	++	++	+h	–	–	+h
6d	++	++	++	++	+h	–	–	+h
6e	++	++	++	++	++	–	+h	++
6f	++	++	++	++	+h	–	–	+h

[a] The symbols represent the following: ++, soluble at room temperature; +h, soluble on heating 100°C; –, insoluble even on heating.
[b] NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethylsulfoxide; THF, tetrahydrofuran; Py, pyridine.

TABLE IV
Mechanical Properties of the Poly(ester amide) Films

Polymer	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
6a	111	7.1	2.9
6b	114	6.7	3.2
6c	110	6.4	3.1
6d	95	5.8	3.0
6e	106	8.8	2.8
6f	89	6.7	2.2

rapidly quenched to room temperature (cooling rate = 200°C/min) to form predominantly amorphous samples, so that T_g values of all the polymers could be easily measured in the DSC charts of the subsequent heating trace. As observed, none of the polymers showed clear melting endotherms from T_g to 350°C on the DSC thermograms, which supported the amorphous nature of these poly(ester amide)s. The T_g values of these polymers were in the range of 166–256°C, following the decreasing order of chain flexibility (Table II). Poly(ester amide) **6a** exhibited the highest T_g value (256°C) in this series because of the effect of the rigid 1,3-biphenylene polymer backbone. However, the poly(ester amide)s **6b**, **6c**, and **6d** had relatively lower T_g values because of their more flexible ether components. Moreover, the T_g values of **6b**, **6c**, and **6d** were not noticeably influenced by constitutional isomerism of the recurring units. On the other hand, the introduction of sulfonyl or phenylphosphine oxide groups into the polymer backbones also raised T_g values of the corresponding polymers (**6e** and **6f**) significantly.

The 10% weight loss temperatures (T_{d10}) and the char yields at 800°C of these polymers in nitrogen, measured by TGA were also reported in Table II. As could be seen from Table II, all the polymers exhibited good thermal stability, and their 10% weight loss temperatures (T_{d10}) were in the range of 395–445°C, and 46–56% weights were retained even at 800°C. Among these polymers, poly(ester amide) **6f** with phenylphosphine oxide units in the main chains had the highest T_{d10} value (445°C) and char-yield (56%), showing its higher thermal stability than the other analogues.

Solubilities

The solubilities of these poly(ester amide)s in various organic solvents at 3.0% (mg/mL) were presented in Table III. Probably because of the presence of bulky pendant trifluoromethylphenoxy groups, all the polymers, except for poly(ester amide) **6b**, were readily soluble in polar solvents such as *N*-methyl-2-pyrrolidone, DMF, DMAc, and dimethyl sulfoxide at room temperature. Poly(ester amide) **6b** had poor solubility compared with other poly(ester amide)s because of its symmetrical and rigid backbone of *para*-phenylene moieties. It is worth mentioning that the two isomeric poly(ester amide)s **6c** and **6d**, containing *meta*- and *ortho*-phenylene rings, respectively, showed higher solubility than the corresponding isomeric poly(ester amide) **6b**. All in all, the good solubilities of these poly(ester amide)s made them potential candidates for practical applications in spin coating and casting processes.

Crystal and mechanical properties

All the polymers were characterized by WAXD studies, and revealed almost completely amorphous diffraction patterns. Some selected WAXD patterns of poly(ester amide)s **6a**, **6b**, **6e**, and **6f** were shown in Figure 5. It is interesting to note that polymer **6a** derived from isophthaloyl chloride (**5a**) with relative more rigid 1,3-biphenyl structure also displayed nearly completely amorphous nature, which indicated that the incorporation of bulky pendant trifluoromethylphenoxy groups decreased the polymer crystallinity dramatically because it produced wider separation of polymer chains, weakening intermolecular hydrogen bonding, lowering of chain packing efficiency with a gain of free volume, thus resulting in a decrease in crystallinity. On the other hand, the amorphous nature of these polymers was also reflected in their good solubility and good film forming ability.

As mentioned earlier, all of the amorphous poly(ester amide)s could be cast into flexible and tough films from their DMAc solutions. These films were subjected to tensile test, and their tensile properties

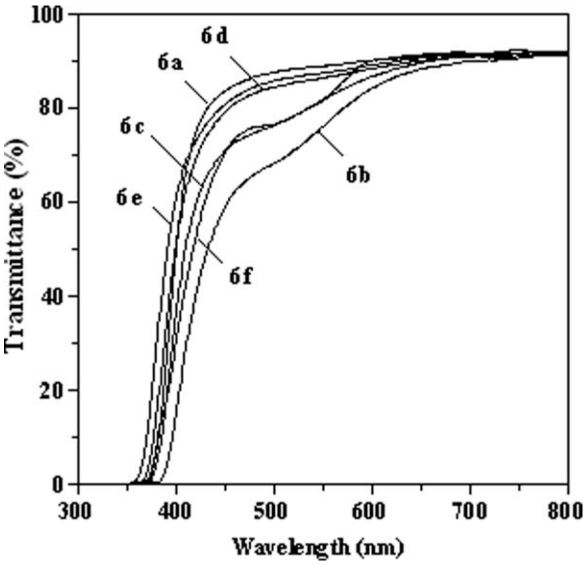


Figure 6 Transmission UV–vis absorption spectra of the poly(ester amide) films.

TABLE V
Optical Transparency and Dielectric Constants of the Poly(ester amide) Films

Polymer	Cut-off wavelength (nm)[a]	Transparency (%)				80% transmission wavelength (nm)	Dielectric constant[b]
		400 (nm)	500 (nm)	600 (nm)	700 (nm)		
6a	365	51	87	90	91	434	3.44
6b	380	16	68	84	90	574	3.36
6c	370	38	76	86	90	538	3.34
6d	362	52	84	88	90	456	3.31
6e	373	62	85	88	90	450	3.48
6f	366	24	74	88	91	564	3.52

[a] The wavelength range of UV measurement was from 200 to 800 nm.
[b] Dielectric constants were obtained in the frequency of 1 MHz.

were presented in Table IV. The polyamide films had tensile strengths of 89–114 MPa, elongations at break of 5.8–8.8%, and initial moduli of 2.2–3.2 GPa, qualifying them as strong and tough materials.

Optical and dielectric properties

The optical properties of these poly(ester amide) films with ∼50 μm thickness were evaluated by UV–vis spectroscopy, and their UV–vis spectra were displayed in Figure 6. The transparency of the polymers was evaluated at the wavelengths from 200 to 800 nm, and the UV data at several wavelengths were also reported in Table V. As shown in Table V, the cut-off wavelengths of these polymers ranged from 362 to 380 nm and the 80% transmission wavelength ranged from 434 to 574 nm. The higher optical transparency of the resulting polymers was main possible due to the presence of the pendant trifluoromethylphenoxy substituents in the polymer backbone. Additionally, poly(ester amide) **6d** with the lowest cut-off wavelength at 362 nm, which was lower than that of the other analogues, and might be attributed to the bulky *ortho*-phenylene rings in the diacid chloride, nonsymmetrical trifluoromethylphenoxy groups in the diamine units, which separated the chromophoric groups and interrupted the intramolecular conjugation.[19]

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. Seen from Table V, these polyamides showed lower dielectric constants in the range of 3.31–3.52 (1 MHz) than commercial Nylatron (ca. 3.7 at 1 MHz). The low dielectric constants could be attributed to the presence of bukyl pendant trifluoromethylphenoxy groups, which led to efficient 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 decreasing the dielectric constants.

CONCLUSIONS

A series of highly organosoluble and optically transparent fluorine-containing poly(ester amide)s were synthesized from a new diamine, 1,4-bis(4-aminophenoxycarbonyl)-2-(4-trifluoromethylphenoxy)benzene with aromatic dicarboxylic acid chlorides by low-temperature solution polycondensation technique. Because of the presence of the bulky trifluoromethylphenoxy in the polymer backbones, no crystallinity was observed for any of these polymers. Almost all the polymers had good solubility in many aprotic solvents and could be cast into strong and fiexible films. The obtained poly(ester amide)s also exhibited excellent optical properties, low dielectric constants, good thermal stability, and mechanical properties. These characteristics indicated that the present fluorinated poly(ester amide)s could be considered as new candidates for processable high-performance engineering plastic and photoelectric materials.

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