High-Optical Transparency and Low-Dielectric Constant of New Organosoluble Polyamides Containing Trifluoromethyl and Xanthene Groups

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ABSTRACT: A series of fluorinated polyamides was prepared directly by low-temperature polycondensation of a new cardo diacid chloride, 9,9-bis[4-(4-chloroformylphenoxy)phenyl]xanthene (BCPX), with various diamines containing trifluoromethyl substituents in *N,N*-dimethylacetamide (DMAc). Almost all polyamides showed excellent solubility in amide-type solvents such as DMAc and could also be dissolved in pyridine, *m*-cresol, and tetrahydrofuran. These polymers had inherent viscosities between 0.77 and 1.31 dL g^{-1}, and their weight-average molecular weights and number-average molecular weights were in the range of 69,000–102,000 and 41,000–59,000, respectively. The resulting polymers showed glass transition temperatures between 240–258°C and 10% weight loss temperatures ranging from 484°C to 517°C and 410°C to 456°C in nitrogen and air, respectively, and char yields at 800°C in nitrogen higher than 55%. All polymers were amorphous and could be cast into transparent, light-colored, and flexible films with tensile strengths of 81–100 MPa, elongations at break of 8–12%, and tensile modulus of 1.6–2.1 GPa. These polymers had low-dielectric constants of 3.34–3.65 (100 kHz), low-moisture absorption in the range of 0.76–1.91%, and high transparency with an ultraviolet–visible absorption cut-off wavelength in the 322–340 nm range. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2959–2968, 2010

Key words: fluorinated polyamide; 9,9-bis[4-(4-chloroformylphenoxy)phenyl]; xanthene; synthesis; property

INTRODUCTION

Aromatic polyamides with excellent balance of thermal and mechanical properties are a useful class of high-performance materials for advanced technologies.[1] Despite their outstanding properties, the infusibility and limited solubility of aromatic polyamides restrict their areas of application. Therefore, much research effort has been directed at improving their processability and solubility by structural modification without compromising their other desired properties. One of the most common approaches to increase solubility is the introduction of flexible linkages in the polymer backbone and/or bulky pendent groups along the main chain.[2–8] Introducing pendent loops into the polymer backbone is a successful approach for improving the processability of aromatic polyamide without an extreme loss of their outstanding properties.[9] It has been reported that incorporating cardo groups such as fluorene,[10] phthalide,[11] phthalimidine,[12] cyclododecylidene,[13] adamantine,[14] tricyclo [5.2.1.0^{2,6}]decane,[15] norbornane,[16] and *tert*-butylcyclohexylidene[17] groups into the backbone of polyamides provides polymers with greater solubility, enhanced rigidity, and better mechanical and thermal properties. Furthermore, it is well known that the incorporation of trifluoromethyl substituents into polymers reduces the dielectric constant because of the low-electronic polarizability of the C—F bond and the increase in the fractional free volume.[4,18–24] Very recent studies have also indicated that fluorinated aromatic polyamides containing cardo groups[25–27] are soluble, high-temperature polymeric materials with low-moisture uptake, a low-dielectric constant, and high-optical transparency. In our recent study, the bulky xanthene cardo group has been incorporated into the poly(aryl ether ketone)s[28] and polyamides[29] to improve their processability. As part of our continuing efforts in developing tractable, high-performance polymers containing xanthene units, this work describes the synthesis of a new diacid chloride, 9,9-bis[4-(4-chloroformylphenoxy)phenyl]xanthene (**BCPX**), and its use in the preparation of soluble cardo fluorine-containing polyamides by the reaction of the **BCPX** with aromatic

diamines bearing trifluoromethyl groups. The solubility, tensile property, crystallinity, thermal property, moisture absorption, dielectric constant, and optical transparency of all the obtained polymers were investigated and compared with unsubstituted derivatives, and tried to qualify the effect of the trifluoromethyl groups, xanthene and ether linkages.

EXPERIMENTAL

Materials

4-Fluorobenzonitrile, 2-chloro-5-nitrobenzotrifluoride, thionyl chloride, and anhydrous potassium carbonate were used as received. Commercially obtained N,N'-dimethylacetamide (DMAc) and pyridine (Py) were purified by distillation under reduced pressure from calcium hydride and stored over 4 Å molecular sieves before use. 9,9-Bis[4-(4-carboxyphenoxy)phenyl]xanthene (BCAPX)[29] was prepared by the nucleophilic fluoro displacement of 4-fluorobenzonitrile with the potassium phenolate of 9,9-bis(4-hydroxyphenyl)xanthene (BHPX)[28] followed by hydrolysis. Aromatic diamines with trifluoromethyl substituents such as 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (3a, m.p. 132–133°C),[20] 1,2-bis(4-amino-2-trifluoromethylphenoxy)benzene (3b, m.p. 116–117°C),[30] 4,4'-bis(4-amino-2-trifluoromethylphenoxy)biphenyl (3c, m.p. 155–156°C),[31] 4,4'-bis(4-amino-2-trifluoromethylphenoxy)diphenylsulfone (3d, m.p. 158–159°C), 2,2-[4-(4-amino-2-trifluoromethylphenoxy)phenyl]propane (3e, m.p. 131–132°C),[32] and 2,2-[4-(4-amino-2-trifluoromethylphenoxy)phenyl]hexafluoropropane (3f, m.p. 65–66°C)[33] were prepared by the aromatic nucleophilic substitution reaction of 2-chloro-5-nitrobenzotrifluoride with the corresponding bisphenol precursors in the presence of potassium carbonate, giving the dinitro compounds, followed by reduction with hydrazine as reducing agent and palladium on active carbon as catalyst.

Monomer synthesis

9,9-Bis[4-(4-chloroformylphenoxy)phenyl]xanthene (2, BCPX)

A mixture of 9,9-bis[4-(4-carboxyphenoxy)phenyl]xanthene (1, BCAPX) (36.40 g, 0.06 mol), thionyl chloride (150 mL), and two drops of N,N-dimethylformamide (DMF) was refluxed for 4 h under stirring. Then, the mixture was vacuum distilled to remove the residue thionyl chloride and cooled to 0–4°C. The white precipitate was afforded and collected by filtration. The crude product was purified by recrystallization from anhydrous petroleum ether to furnish BCPX (32.8 g, yield 85%). m.p. 167°C (by DSC with heating rate of 20°C min^{-1}). ^{1}H-NMR

(CDCl$_3$) δ = 8.09 (dd, J = 6.8, 6.8 Hz, 4 H), 7.31 (t, J = 8.4 Hz, 2 H), 7.22 (d, J = 8.0 Hz, 2 H), 7.11 (t, J = 7.6 Hz, 2 H), 7.06–7.02 (m, 8 H), 6.95–6.92 (m, 6 H). ^{13}C-NMR (CDCl$_3$) δ = 167.09, 163.70, 153.42, 152.47, 142.55, 133.94, 131.76, 129.84, 129.75, 128.33, 127.33, 123.71, 119.76, 117.44, 116.77, 53.61. FTIR (KBr): ν_{max} = 1765 (C=O stretching), and 1249 (C—O—C stretching). MS (EI, 70 eV) m/z: 642 (M$^+$, 14.8), 607 (100). Elem. Anal. calcd. for C$_{39}$H$_{24}$Cl$_2$O$_5$ (643.52 g mol^{-1}): C, 72.79%; H, 3.76%. Found: C, 72.56%; H, 3.68%.

Polymer synthesis

A representative polymerization procedure under nitrogen atmosphere for synthesis of polyamide (4a) is described as follows. In a three-necked flask, a solution of 2.1417 g (5.0 mmol) of diamine (3a) and pyridine (0.8 mL) in 20.0 mL of DMAc was cooled in a dry ice bath. To this solution, 3.2176 g (5.0 mmol) of BCPX (2) was added all at once with stirring. The mixture was stirred in nitrogen at room temperature for 12 h to yield a viscous polyamide solution. The viscous solution was precipitated in excess ethanol. The precipitate was collected and washed thoroughly with methanol and dried at 100°C in a vacuum oven for 6 h to give (4a) (4.84 g, yield 97%). The other polyamides were also prepared following a similar procedure by the polymerization of equimolar amounts of BCPX and the corresponding aromatic diamines.

Preparation of the polyamide films

A solution of polymer was made by dissolving about 0.5 g of the polyamide sample in 5 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 overnight in an oven at 120°C for the slow release of the solvent. The polyamide film was released from the glass substrate and further dried *in vacuo* at 150°C for 10 h, and then used for its corresponding properties analyzes.

Measurements

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on Bruker Avance 400 MHz spectrometer in dimethyl sulfoxide-d_6 (DMSO-d_6) or chloroform (CDCl$_3$). FTIR spectra of the monomer and polymers in KBr pellets were determined on a PerkinElmer SP One FTIR spectrophotometer. Microanalyses were performed with a Carlo Erba 1106 Elemental Analyzer. Mass spectra (EI, 70eV) were recorded on a HP5989B mass spectrometer. The glass transition temperatures (T_gs) were performed on a PerkinElmer DSC-7 instrument at a heating rate
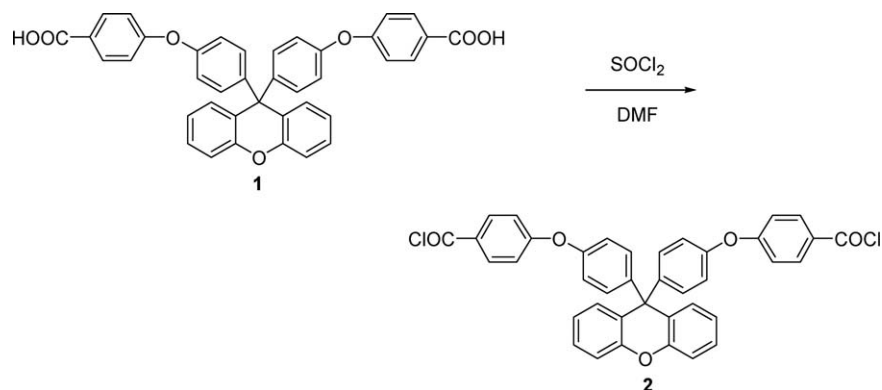
Scheme 1 Synthesis of the dicarboxylic acid chloride (**2, BCPX**).

of 20°C/min under nitrogen protection. The second scan was immediately initiated after the sample was cooled to room temperature. The T_g values were reported from the second scan after the first heating and quenching, and taken from the midpoint of the change in the slope of the baseline. Thermogravimetric analysis (TGA) was carried out on ∼ 6–8 mg film samples with a PerkinElmer Pyris 1 TGA in nitrogen or air (120 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 powders with a Rigaku Geiger Flex D-Max III X-ray diffractometer, using Ni-filtered CuK$_\alpha$ radiation (operating at 40 kV and 15 mA); the scanning rate was 2°/min over a range of $2\theta = 5$–40°). Molecular weights were determined by a gel permeation chromatography (GPC) with polystyrene calibration using a Waters 510 HPLC equipped with 5-µm Styragel HR–2 and HR–4 columns (7.8 mm i.d. × 300 mm) connected in series and a UV detector at 254 nm using tetrahydrofuran as eluent. The inherent viscosities were measured at 0.5 g dL^{-1} concentration in DMAc with an Ubbelohde viscometer at 30°C, in which the polyamides were pretreated by drying in oven at 120°C for 1 h to remove the adsorbed moisture. The mechanical properties were measured on an Instron 1122 testing instrument with a 5-kg load cell at a crosshead speed of 5 mm/min on film specimens ∼ 0.05 mm thick and 0.5 cm wide with 6 cm long, and an average of at least four individual determinations was used. Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on a Shimadzu UV-1601 UV–vis spectrophotometer. Dielectric constants were measured using a dielectric analyzer (TA Instruments DEA 2970).

RESULTS AND DISCUSSION

Monomer synthesis

The original bis(ether carboxylic acid) (**1, BCAPX**)[29] was obtained in good yield and high purity from the nucleophilic fluoro displacement of 4-fluorobenzonitrile with the potassium phenolate of 9,9-bis(4-hydroxyphenyl)xanthene (**BHPX**), followed by alkaline hydrolysis. As shown in Scheme 1, treatment of **BCAPX** with thionyl chloride in the presence of a trace amount of DMF afforded 9,9-bis[4-(4-chloroformylphenoxy)phenyl]xanthene (**2, BCPX**). The structure of **BCPX** was confirmed by elemental analysis, FTIR, and NMR spectroscopy.

Figure 1 showed the ^{1}H-NMR and ^{13}C-NMR spectra of **BCPX** in CDCl$_3$ solution, respectively. Assignments to all protons and carbons are given in the figure. In the ^{1}H-NMR spectrum, the aromatic protons (H[14]) ortho to the chlorocarbonyl groups and those (H[2], H[3], and H[4]) on the xanthene unit were clearly distinguished, whereas the aromatic protons (H[10] and H[13]) ortho to the ether groups, those (H[9]) ortho to the xanthene unit, and those (H[1]) on the xanthene unit were overlapped. However, all carbon nuclei in **BCPX** gave well-separated peaks in the ^{13}C-NMR spectrum. The resonance of carbonyl carbon occurred at the farthest downfield (δ 167.09).

Polymer synthesis

The direct low-temperature solution polycondensation of the new cardo diacid chloride **BCPX** (**2**) with structurally different aromatic diamines with trifluoromethyl groups **3a–3f** in DMAc resulted in the fluoro- and xanthene-containing polyamides **4a–4f** as shown in Scheme 2. All polymerization reactions proceeded homogeneously throughout the reaction and gave highly viscous polymer solutions. Seen from Table I, the obtained polyamides with inherent viscosities between 0.77 and 1.31 dL g^{-1} exhibited weight-averaged molecular weights (M_w) in the range of 69,000–102,000 and number-average molecular weights (M_n) in the range of 41,000–59,000, relative to standard polystyrene, respectively. The polydispersity index (PDI) of these polymers was in the range of 1.65–1.80. The molecular weight of the
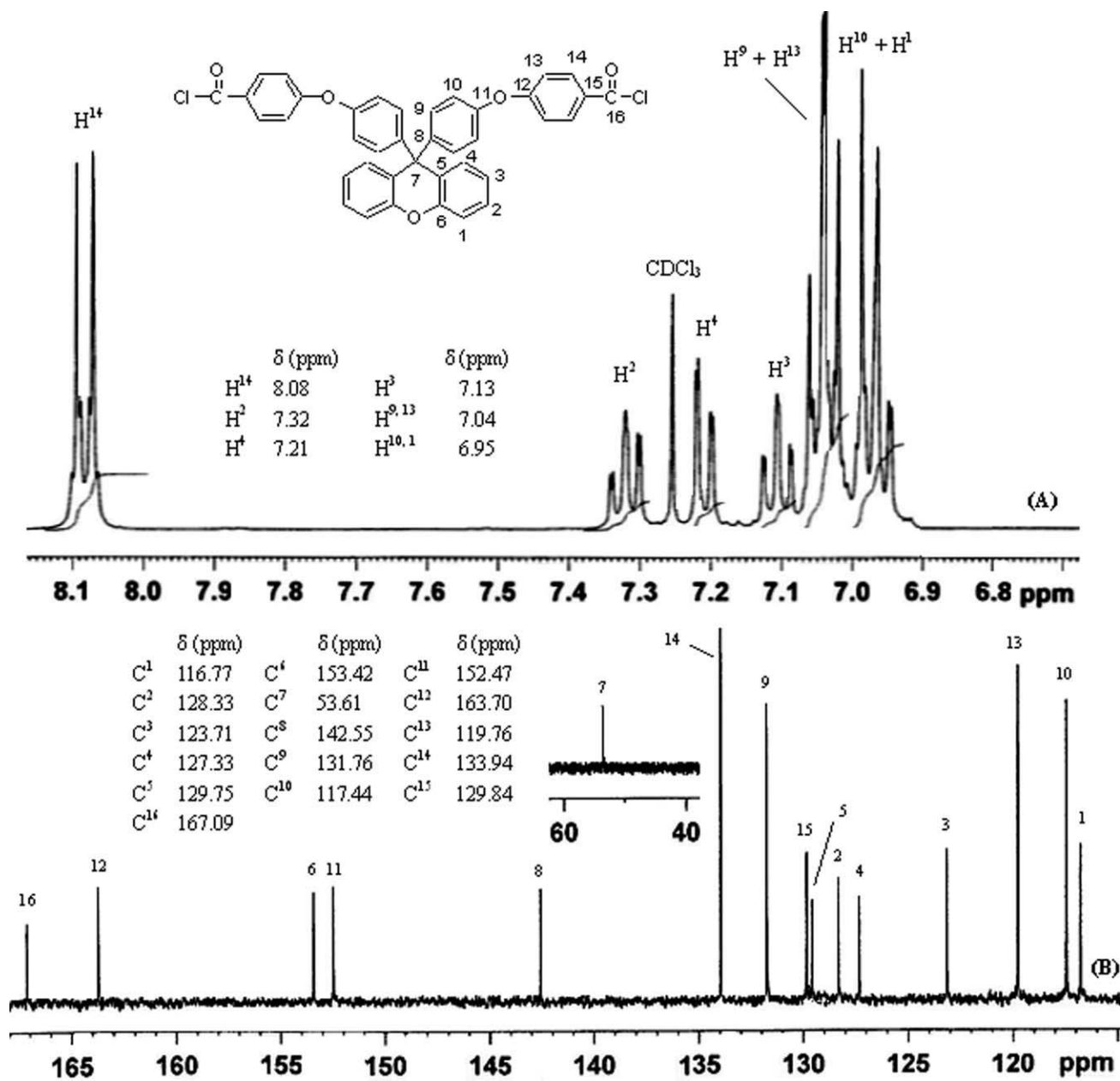
Figure 1 The NMR spectra of **BCPX** (**2**) in CDCl₃ solution.

polymers was high enough to obtain flexible and tough polymer films by casting from their DMAc solutions.

FTIR, NMR, and elemental analysis confirmed the chemical structures of these polyamides. They showed characteristic FTIR absorption bands of the amide group around 3310 (N—H stretching), 1654 (C=O stretching), 1540 cm⁻¹ (N—H bending), and 1137 cm⁻¹ (C—F stretching), along with the characteristic absorption bands of aryl ether stretching near 1250 cm⁻¹. Additionally, all chemical structures of the polyamides were also confirmed by ¹H-NMR and ¹³C-NMR spectra in DMSO-d_6 solution with amide proton chemical shifts at δ 10.39–10.56 ppm, am-

ide carbons chemical shifts at δ 164.68–164.89, respectively. A typical ¹H-NMR spectrum of the polyamide (**4d**) was depicted in Figure 2.

The results of elemental analysis were also listed in II, which showed that the polymers had slight moisture absorptions ranging from 0.76% to 1.91% because of their amide groups.[34] The observed values were corrected by the elimination of the amount of absorbed water, and the corrected values were almost in good agreement with the calculated ones. Generally, fluorine substitution almost resulted in lower water absorption. Seen from Table II, the polyamides **4f** showed the lowest value for water absorption, which might be attributed to the presence of
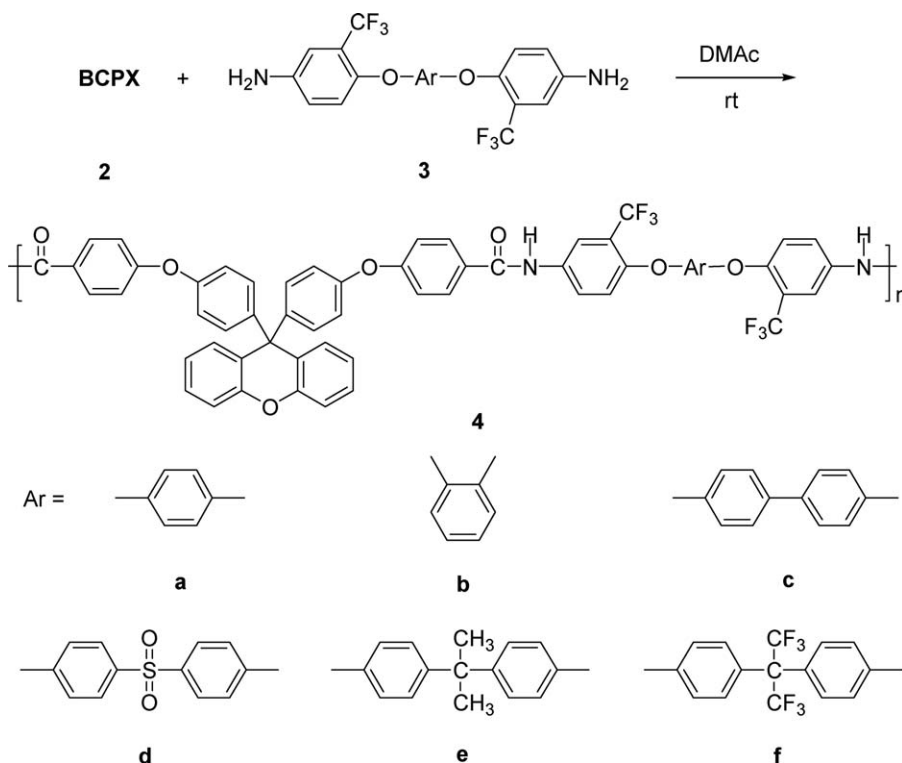
Scheme 2 Synthesis of the synthesis of polyamides (4a–4f).

hydrophobic trifluoromethyl and hexafluoroisopropylidene substitution in the polymer backbones.

Thermal properties

The thermal properties of all the polyamides were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The results are summarized in Table III. Quenching from an elevated temperature of about 400°C to room temperature in air gave predominantly amorphous samples so that the glass transition temperatures (T_g) of all the polymers could be easily revealed in the subsequent DSC scans. It was found that there was no melting peak (T_m) detected in DSC and the absence of peak in DSC supported the generally amorphous nature of the polymer.

The T_g values of these polyamides were in the range of 240–258°C, which followed the decreasing order of the chain flexibility and steric hindrance of the polymer backbones. As observed, polyamide 4d, containing a sulfone group, exhibited a higher T_g value (258°C) because of its higher polar interactions between sulfonyl groups in the main chain.[35] On the other hand, the insertion of rigid biphenyl and p-phenyl units increased T_g (e.g., polyamides 4a and 4c), whereas an m-phenyl unit (polyamides 4b, 241°C) lowered T_g; which was probably due to the change in the packing density of the polymer aggregation and the rigidity of the polymer chains.

The thermal properties of the polyamide (4a′) without trifluoromethyl substituents[29] (Scheme 3) was also listed in Table III. Polyamide 4a, incorporated with trifluoromethyl groups, exhibited a T_g of 247°C, which was lower than that of 4a′ analog (272°C). This might be a result of a significant reduction in the density of hydrogen bonding between chains, and the introduction of trifluoromethyl group apparently renders the molecular structure in the polymer chain more asymmetric.[36]

The thermal behavior of all the polymers was evaluated by TGA. All TGA curves for these resulting polyamides showed one-step weight-loss behaviors, indicating that the side groups of the polymers

TABLE I
Inherent Viscosity and GPC Data of the Polyamides

Polymer	η_{inh} (dL g^{-1})[a]	M_w (g/mol)[b]	M_n (g/mol)[b]	PDI[c]
4a	1.31	102,000	59,000	1.73
4b	0.77	69,000	41,000	1.68
4c	1.22	—[d]	—[d]	—[d]
4d	1.00	83,000	46,000	1.80
4e	1.24	90,000	54,000	1.67
4f	0.87	71,000	43,000	1.65

[a] Measured in DMAc at a concentration of 0.5 g dL^{-1} at 30°C.
[b] Measured by GPC in THF, polystyrene was used as standard.
[c] The polydispersity index (PDI) was obtained by M_w/M_n.
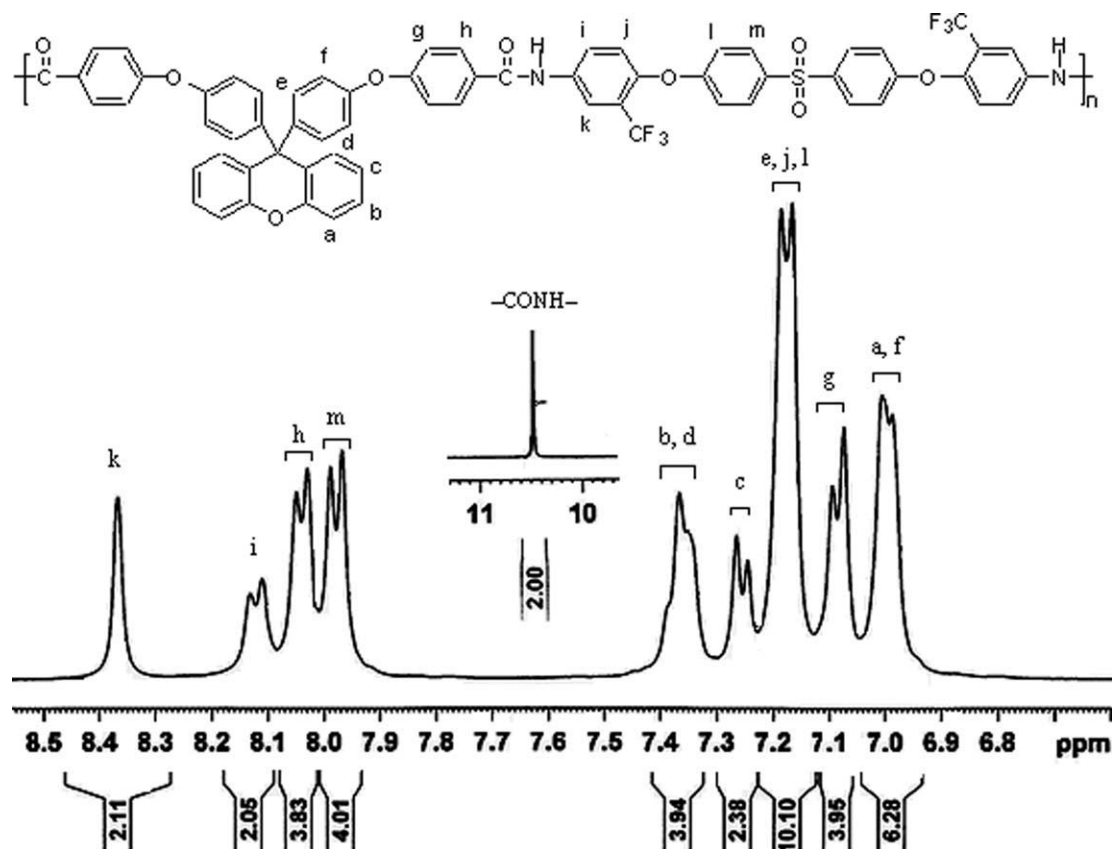[d] Polymer was partially soluble in THF.

Figure 2 The ^{1}H-NMR spectrum of the polyamide (**4d**) in DMSO-d_6 solution.

were thermally degraded together with the main-chain parts. Typical TGA curves for polyamide **4f** both in nitrogen and air atmospheres were presented in Figure 3. The temperatures at 5% and 10% weight loss (T_5 and T_{10}, respectively) in nitrogen and air atmospheres were read from the original TGA

TABLE II
Elemental Analysis and Moisture Uptake of the Polyamides

Polymer	Formula (formula weight)		Elemental analysis (%)			Moisture uptake (%)[a]
			C	H	N	
4a	$(C_{59}H_{36}F_6N_2O_7)_n$ (998.93)$_n$	Calcd.	70.94	3.63	2.80	1.38
		Found	69.06	3.78	2.62	
		Corr.[b]	70.01	3.73	2.66	
4b	$(C_{59}H_{36}F_6N_2O_7)_n$ (998.93)$_n$	Calcd.	70.94	3.63	2.80	1.39
		Found	69.11	3.81	2.65	
		Corr.[b]	70.07	3.76	2.69	
4c	$(C_{65}H_{40}F_6N_2O_7)_n$ (1075.03)$_n$	Calcd.	72.62	3.75	2.61	1.08
		Found	71.26	3.89	2.42	
		Corr.[b]	72.03	3.85	2.45	
4d	$(C_{65}H_{40}F_6N_2O_9S)_n$ (1139.09)$_n$	Calcd.	68.54	3.54	2.46	1.91
		Found	66.68	3.75	2.27	
		Corr.[b]	67.95	3.68	2.31	
4e	$(C_{68}H_{46}F_6N_2O_7)_n$ (1117.11)$_n$	Calcd.	73.11	4.15	2.51	1.13
		Found	71.97	4.09	2.42	
		Corr.[b]	72.78	4.04	2.45	
4f	$(C_{68}H_{40}F_{12}N_2O_7)_n$ (1225.05)$_n$	Calcd.	66.67	3.29	2.29	0.76
		Found	65.53	3.55	2.17	
		Corr.[b]	66.03	3.52	2.19	

[a] Moisture uptake (%) = $100 \times (W - W_0)/W_0$, where W is the weight of polymer sample after standing at room temperature for 3 days and W_0 is the weight of polymer sample after being dried in vacuum at 100°C for 10 h.
[b] Corrected value = found value × (100% ± moisture uptake %) where "+" for C and N, "−" for H.

TABLE III
Thermal Properties of the Polyamides

Polymer	T_g (°C)[a]	T_{d5} (°C)[b]	T_{d5} (°C)[c]	T_{d10} (°C)[d]	T_{d10} (°C)[e]	R_w (%)[f]
4a	247	457	398	484	438	56
4b	241	464	397	486	435	55
4c	255	476	414	498	450	59
4d	258	469	408	488	441	55
4e	256	462	390	492	410	55
4f	240	476	413	517	456	62
4a'	272	480	421	508	494	57

[a] From the second heating trace of DSC measurements.
[b] 5% Weight loss temperatures measured by TGA in nitrogen.
[c] 5% Weight loss temperatures measured by TGA in air.
[d] 10% Weight loss temperatures measured by TGA in nitrogen.
[e] 10% Weight loss temperatures measured by TGA in air.
[f] Residual weight (%) when heated to 800°C in nitrogen.

thermograms and also reported in Table III. The 10% weight loss temperatures were in the range of 484–517°C and 410–456°C in nitrogen and air atmosphere, respectively. Moreover, the char yield of all these polymers at 800°C in nitrogen was above 55%. The TGA results implied that these polymers with trifluoromethyl and xanthene groups in the polymer backbone showed excellent thermal stability. Moreover, polyamide **4a** exhibited relatively lower T_d than the corresponding analog **4a'** without the trifluoromethyl substituents, which might be a result of poor packing and weaker chain–chain interactions because of the presence of the trifluoromethyl groups.

Solubilities

As expected, these new designed polyamides with xanthene units in the main chain as well as bulky trifluoromethyl side groups provided not only excellent thermal stability but also good solubility. The solubilities of the polyamides in various organic solvents at 3.0% (m/v) are presented in Table IV. All the polymers showed excellent solubility in polar solvents such as *N*-methyl-2-pyrrolidone, *N,N*-dimethylformamide, *N,N*-dimethylacetamide, dimethyl sulfoxide, pyridine, and *m*-cresol at room temperature or on heating at 60°C. They also could be dissoluble in tetrahydrofuran except polyamide **4c**, which derived from diacid chloride with more rigid
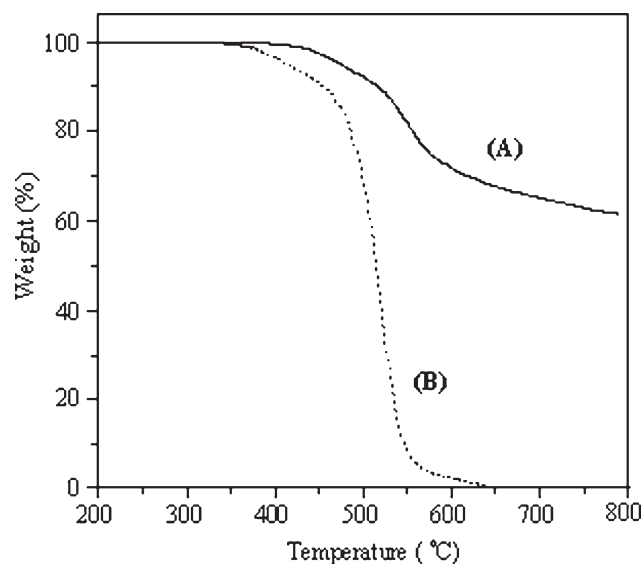

Figure 3 TG curves for the polyamide (**4f**) in nitrogen (A) and air (B).

4,4'-biphenyl structure. Moreover, polyamides **4f** can dissolve even in acetone. Obviously, the introduction of the bulky xanthene cardo unit, polyflexible ether linkages, and trifluoromethyl substituents into the polymer led to increase chain-packing distances and decreased intermolecular interactions; consequently, the solvent molecules could easily penetrate to solubilize the polymer.

For comparison, the solubility behavior of the corresponding non-fluorinated polyamide **4a'**[29] is also illustrated in Table IV. Polyamide **4a** is readily soluble in THF, which indicated that the incorporation of trifluoromethyl substituents into polymers might improve the solubility of the corresponding polyamide.

Mechanical and crystal properties

X-ray diffraction patterns confirmed that all polyamides were amorphous (Fig. 4). This can be attributed to the combined effects of the bulky xanthene groups in the polymer backbone, flexible ether linkages with trifluoromethyl substituents, which resulted in poor chain packing. The amorphous structure of these polyamides also reflected in their excellent solubility and good film forming ability.

Highly transparent flexible films for all polyamides were obtained via the casting of polymer
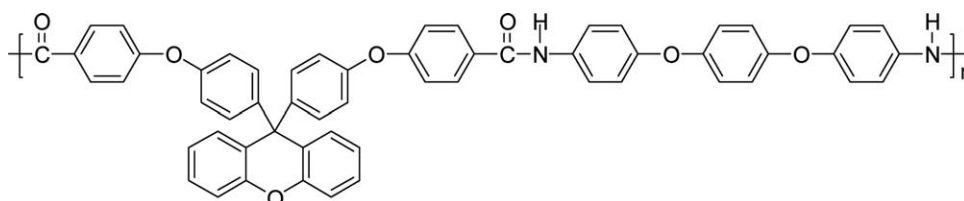
Scheme 3 Chemical structure of the polyamide (**4a'**) without trifluoromethyl groups.

TABLE IV
Solubility Behavior of the Polyamides in Various Organic Solvents[a]

Polymer	NMP	DMAc	DMF	DMSO	Py	m-Cresol	THF	Acetone	CHCl₃	MeOH
4a	++	++	++	++	++	+	++	–	–	–
4b	++	++	++	++	++	++	++	+–	–	–
4c	++	++	++	++	++	+	+–	–	–	–
4d	++	++	++	++	++	+	++	–	–	–
4e	++	++	++	++	++	++	++	+–	–	–
4f	++	++	++	++	++	++	++	++	–	–
4a′	++	++	++	++	++	+	–	–	–	–

[a] The symbols represent the following: ++ = soluble at room temperature, + = soluble on heating at 60°C, +– = partially soluble, – = insoluble even on heating; NMP, N-methyl-2-pyrrolidone; DMAc, N,N-dimethylacetamide; DMF, N,N-dimethylformamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran; Py, pyridine.

solutions in DMAc. The mechanical properties of the polyamide films are summarized in Table V. The values of the tensile strengths varied in the range of 81–100 MPa, elongations to break varied in the range of 8–12%, and tensile modulus varied in the range of 1.6–2.1 GPa, respectively. Polyamides **4a** and **4c** exhibited low elongations at breakage of 9% and 8%, respectively, due to the rigid biphenyl and p-phenyl units in polymer backbone. Good mechanical properties suggested that these polyamides could be considered as new engineering high-performance plastics.

Optical and electrical insulating properties

The optical properties of these polyamide films could be evaluated from the cut-off wavelength observed in the transmission UV–vis absorption spectra and the results are listed in Table VI. The cut-off wavelengths ranged from 322 to 340 nm, indicating that all the polyamides were colorless and

had high transmittances. Polyamide **4f** exhibited the lowest cut-off wavelength (322 nm) because of the presence of two trifluoromethyl and hexfluoroiso-propylidene groups. Furthermore, all the polyamides exhibited high-optical transparency higher than 85% transmittance even at 400 nm. The good optical transparency of the resulting polymers may be resulted from two reasons. The incorporation of xanthene cardo group into the polymer chains restricted the molecular alignment, and therefore, disturbed effective charge–transfer-complex formation.[37] In addition, the extent of donor–acceptor complex formation could also be further reduced by the lowering of the degree of charge separation along the polymer chain through the introduction of electron-withdrawing trifluoromethyl groups into the substituted aromatic rings of the diamine. This reduced the charge build up on these aromatic rings resulting from electron donation by the adjacent nitrogen atoms and also removed extensive electronic conjugations.[38]

Comparing polyamide **4a** with **4a′** without trifluoromethyl groups,[29] as shown in Figure 5, polyamide **4a** exhibited a cut-off wavelength at 325 nm, 20 nm lower than that of polyamide **4a′** (345 nm), which was attributed to the presence of trifluoromethyl substituents in the polymer backbone.

The electrical insulating properties of these polymers were evaluated on the basis of the dielectric constants, measured by the parallel plate capacitor method using a dielectric analyzer. As shown in
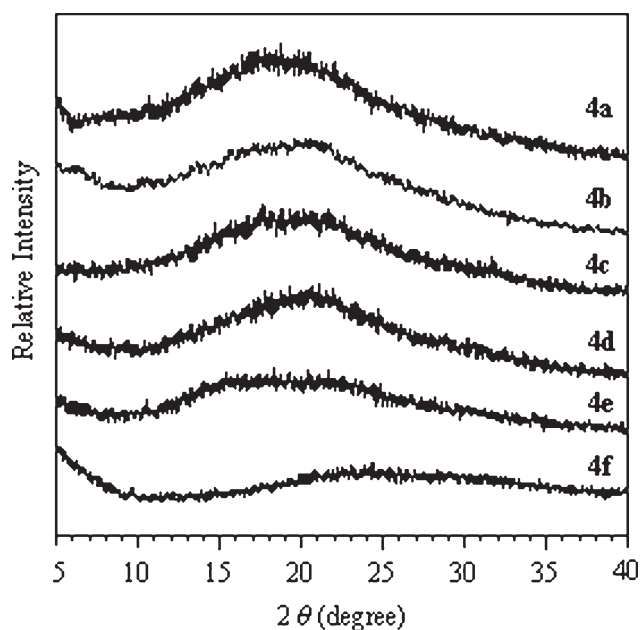

Figure 4 X-ray diffraction patterns of the polyamides.

TABLE V
Mechanical Properties of the Polyamide Films

Polymer	Tensile strength (MPa)	Elongation to break (%)	Tensile modulus (GPa)
4a	81	9	1.7
4b	96	10	1.9
4c	83	8	1.7
4d	100	10	2.1
4e	93	12	1.6
4f	92	12	1.6
4a′	90	21	2.2

TABLE VI
Optical Transparency and Dielectric Constants of the Polyamide Films

Polymer	Cut-off wavelength[a] (nm)	Transparency[b] (%)	Transparency[c] (%)	Thickness (μm)	Dielectric constant[d]
4a	325	86	90	65	3.52
4b	327	88	90	70	3.48
4c	340	85	89	66	3.61
4d	324	88	90	62	3.65
4e	327	88	90	64	3.43
4f	322	86	91	70	3.34
4a′	345	54	78	66	4.22

[a] The wavelength range of UV measurement was from 200 to 800 nm.
[b] Transparency at 400 nm.
[c] Transparency at 500 nm.
[d] Dielectric constants were obtained in the frequency of 100 kHz.

Table VI, The dielectric constants of these polyamide were in the range of 3.34–3.65 (100 kHz) and were lower than that of commercially available Nylatron (ca. 3.7 at 1 MHz). These results could be attributed to the small dipole and the low polarizability of the C—F bond as well as the increase in the free volume and also because of the lowering of the moisture absorption.[36] Additionally, the polyamides with bulky xanthene groups increase the free volume of polymer and further decrease the number of polarizable groups per unit volume, resulting in lower values for dielectric constant of atomic and dipolar.[39] In contrast, polyamide **4a** containing trifluoromethyl group had a lower dielectric constant (3.52 at 100 kHz) than that of the corresponding non-fluorinated polyamide **4a′** (4.22 at 100 kHz). Likewise, polyamide **4f** exhibited the lowest dielectric constant of 3.34 at 100 kHz because of higher free volume and hydrophobicity.
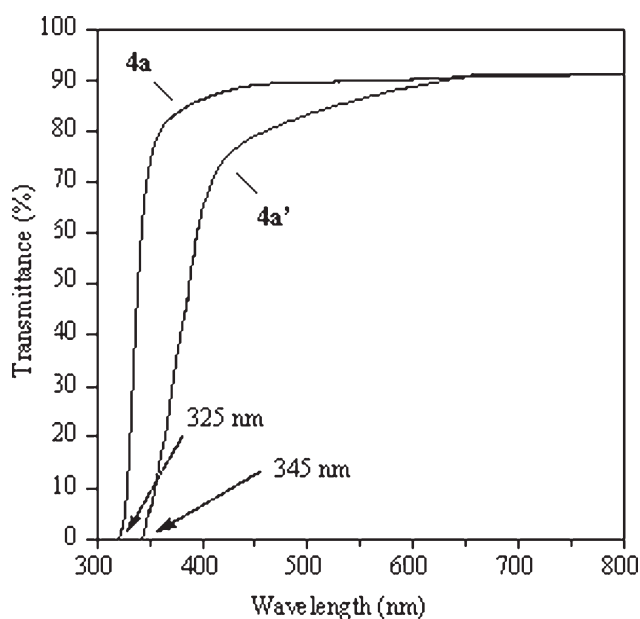

Figure 5 Transmission UV–vis absorption spectra of the polyamides (**4a**) and (**4a′**).

CONCLUSIONS

A series of highly organosoluble and optically transparent polyamides were synthesized by low-temperature polycondensation from 9,9-bis(4-chloroformylphenoxyphenyl)xanthene (BCPX) with diamines containing trifluoromethyl substituents. The obtained fluorine-containing polyamides exhibited amorphous nature, excellent optical properties, low-dielectric constants, good thermal stabilities, and mechanical properties, as well as excellent solubilities in most of the common organic solvents. These characteristics indicated that these xanthene-containing fluorinated polyamides could be considered as new candidates for processable high-performance engineering plastic and photoelectric materials.

References

1. Cassidy, P. E. Thermally Stable Polymers; Dekker: NY, 1980.
2. Liaw, D. J.; Liaw, B. Y. Macromol Symp 1997, 122, 343.
3. Yagci, H.; Mathias, L. J. Polym Prepr 1998, 39, 262.
4. Spiliopoulos, I. K.; Mikroyannidis, J. A.; Tsivgoulis, G. M. Macromolecules 1998, 31, 522.
5. Hsiao, S. H.; Yang, C. P.; Chen, S. H. Polymer 2000, 41, 6537.
6. Espeso, J. F.; Ferrero, E.; De La Campa, J. G.; Lozano, A. E.; De Abajo, J. J Polym Sci Part A: Polym Chem 2001, 39, 475.
7. Liou, G. S.; Hsiao, S. H. J Polym Sci Part A: Polym Chem 2002, 40, 1781.
8. Hsiao, S. H.; Lin, K. H. Polymer 2004, 45, 7877.
9. Korshak, V. V.; Vinogradova, S. V.; Vygodski, Y. S. J Macromol Sci Rev Macromol Chem 1974, C11, 45.
10. Yang, C. P.; Lin, J. H. J Polym Sci Part A: Polym Chem 1993, 31, 2153.
11. Yang, C. P.; Lin, J. H. J Polym Sci Part A: Polym Chem 1994, 32, 423.
12. Yang, C. P.; Lin, J. H. Polymer 1995, 36, 2607.
13. Liaw, D. J.; Liaw, B. Y. Polym Adv Technol 1998, 9, 740.
14. Liaw, D. J.; Liaw, B. Y.; Chung, C. Y. Acta Polym 1999, 50, 135.
15. Liaw, D. J.; Liaw, B. Y.; Chung, C. Y. Macromol Chem Phys 1999, 200, 1023.
16. Liaw, D. J.; Liaw, B. Y. J Polym Sci Part A: Polym Chem 1999, 37, 2791.
17. Liaw, D. J.; Liaw, B. Y.; Chung, C. Y. Macromol Chem Phys 2000, 201, 1887.
18. Liaw, D. J. J Polym Sci Part A: Polym Chem 2005, 43, 4559.

19. Ge, Z. Y.; Yang, S. Y.; Tao, Z. Q.; Liu, J. G.; Fan, L. Polymer 2004, 45, 3627.
20. Yang, C. P.; Chen, Y. P.; Woo, E. M. J Polym Sci Part A: Polym Chem 2004, 42, 3116.
21. Yang, C. P.; Su, Y. Y. Macromol Chem Phys 2005, 206, 1947.
22. Liaw, D. J.; Huang, C. C.; Chen, W. H. Polymer 2006, 47, 2337.
23. Maji, S.; Banerjee, S. J Appl Polym Sci 2008, 108, 1356.
24. Sheng, S. R.; Pei, X. L.; Liu, X. L.; Song, C. S. Eur Polym J 2009, 45, 230.
25. Yang, C. P.; Su, Y. Y.; Hsu, M. Y. Colloid Polym Sci 2006, 284, 990.
26. Liaw, D. J.; Huang, C. C.; Hu, C. K.; Lee, K. R.; Lai, J. Y. Polymer 2007, 48, 6571.
27. Maji, S.; Sen, S. K.; Dasgupta, B.; Chatterjee, S.; Banerjee, S. Polym Adv Technol 2009, 20, 384.
28. Sheng, S.-R.; Ge, W.-W.; Huang, Z.-Z.; Liu, X.-L.; Song, C.-S. J Appl Polym Sci 2009, 114, 570.
29. Sheng, S.-R.; Ma, C. X.; Jiang, J. W.; Huang, Z. Z.; Song, C. S. J Appl Polym Sci 2010, 116, 1650.
30. Yang, C. P.; Chen, R. S.; Chiang, H. C. Polym J 2003, 35, 662.
31. Yang, C. P.; Hsiao, S. H.; Hsu, M. F. J Polym Sci Part A: Polym Chem 2002, 40, 524.
32. Yang, C. P.; Chen, R. S.; Chen, K. H. J Appl Polym Sci 2005, 95, 922.
33. Yang, C. P.; Chen, R. S.; Chen, K. H. J Polym Sci Part A: Polym Chem 2003, 41, 922.
34. Liaw, D. J.; Liaw, B. Y. J Polym Sci Part A: Polym Chem 1998, 36, 2301.
35. Bruma, M.; Mercer, F.; Fitch, J.; Cassidy, P. J Appl Polym Sci 1995, 56, 527.
36. Hougham, G.; Tesoro, G.; Shaw, J. Macromolecules 1994, 27, 3642.
37. Devasahayam, S.; Hill, D. J. T.; Connell, J. W. Radiat Phys Chem 2001, 62, 189.
38. Varma, I. K.; Kumar, R.; Bhattacharyya, A. B. J Appl Polym Sci 1990, 40, 531.
39. Liaw, D. J.; Chang, F. C.; Leung, M. K.; Chou, M. Y.; Muellen, K. Macromolecules 2005, 38, 4024.