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A novel soluble polyamide containing xanthene structure and trifluoromethylphenoxy pendent

Zhen Zhong Huang, Xue Mei Wan, Hai Bo Xiao, Shou Ri Sheng *, Cai Sheng Song

College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, China

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Abstract

A novel polyamide containing xanthene structure and trifluoromethylphenoxy pendent was prepared from 9,9-bis[4-(4-aminophenoxy)phenyl]xanthene, a novel diamine with 2-(4-trifluoromethylphenoxy)terephthaloyl chloride, by the low temperature polycondensation. This new polyamide with the inherent viscosity of 0.95 dL/g was amorphous and readily soluble in polar solvents such as DMAc, *m*-cresol, etc. This polyamide showed the glass transition temperature (T_g) of 236 °C, decomposition temperature (T_d) at 5% weight loss of 455 °C and char yield of 56% at 800 °C in N_2. Transparent, flexible, and tough film of the polymer cast from DMAc solution exhibited tensile strength of 93 MPa, elongation at break of 14%, initial moduli of 2.2 GPa. The electric properties such as the dielectric constant of 3.03 (1 MHz) and surface resistance (2.78×10^{14} Ω), and the moisture uptake of 1.36% were also described.

Keywords: Polyamide; Xanthene cardo group; Trifluoromethylphenoxy pendent; Soluble

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Aromatic polyamides are well known as high-performance polymers because of their combination of excellent thermal, mechanical, and chemical properties [1]. Despite their outstanding properties, the infusibility and limited solubility of aromatic polyamides restrict their areas of application. Therefore, numerous attempts have been made to improve their processability. Introducing cardo groups such as fluorene [2] and *tert*-butylcyclohexylidene [3] is a successful approach for improving the processability of aromatic polyamides without an extreme loss of their outstanding properties. Additionally, it was found that the incorporation of flexible fluorinated groups into polyamide backbones resulted in great benefits for improving polymer solubility as well as electrical and dielectric properties [4,5]. To our knowledge, the incorporation of trifluoromethylphenoxy pendent and xanthene cardo group into the polyamide backbone has not been reported. In this paper, a new monomer diamine, 9,9-bis[4-(4-aminophenoxy)phenyl]xanthene (BAPX), as shown in Scheme 1, and a novel soluble polyamide containing xanthene cardo group and trifluoromethylphenoxy pendent (Scheme 2) was prepared and characterized, and its thermal and mechanical properties as well as electrical and dielectric behavior were also investigated.

9,9-Bis(4-hydroxyphenyl)xanthene **1** [6] and 2-(4-trifluoromethylphenoxy)terephthaloyl chloride (TFFPC) [7] were synthesized according to our reported method. The intermediate 9,9-bis[4-(4-nitrophenoxy)phenyl]xanthene **2**

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* Corresponding author.

E-mail address: shengsr@jxnu.edu.cn (S.R. Sheng).

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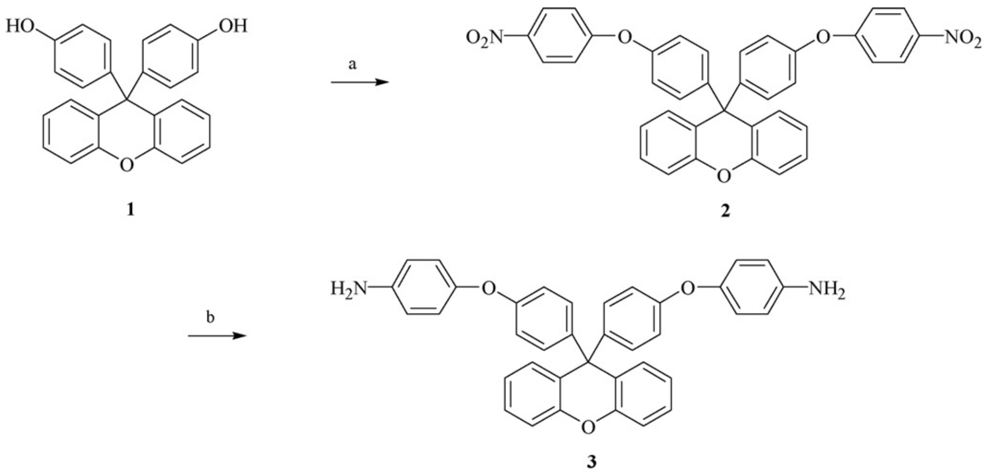
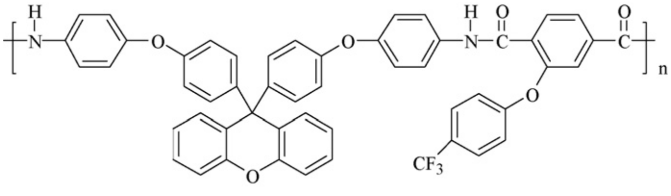


Scheme 1. Synthetic route to BAPX: (a) 4-$ClC_6H_4NO_2$, K_2CO_3, DMF, 160 °C, 8 h; (b) $NH_2NH_2{\cdot}H_2O$, Pd/C, reflux, 12 h.



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Scheme 2. The structure of novel fluorinated polyamide with xanthene cardo group.

[8] was obtained from the nucleophilic chloro displacement of 4-chloronitrobenzene with the potassium phenolate of **1** in DMF. BAPX **3** [9] was prepared by catalytic hydrogenation of the dinitro compound **2** using hydrazine hydrate and Pd/C catalyst in refluxing ethanol. The intermediate and monomer structures were confirmed by FTIR, NMR and elemental analyses. The polyamide **4** was obtained in a one-step pathway by the low-temperature solution polycondensation reaction of TFFPC with BAPX in DMAc solution containing a trace of pyridine cooled by an external ice–acetone bath. The reaction temperature was maintained at –10 to 0 °C in the initial 5 h. In order to obtain maximum molecular weight, the reaction was then allowed to proceed overnight at room temperature. The new polyamide **4** with inherent viscosity of 0.95 dL/g, exhibited characteristic IR absorption bands (Fig. 1) of the amide group around 3370 cm^{-1} (N–H stretching), 1633 cm^{-1} (C=O stretching), and 1120 cm^{-1} (C–F stretching), along with the characteristic absorption bands of aryl ether stretching near 1219 cm^{-1}, demonstrating the formation of amide linkages. The polymerization results and the thermal properties of polymers are summarized in Table 1. No endothermic peak above its T_g was observed in DSC scan, which may be attributed to the amorphous structure, further confirmed by WAXD analysis.

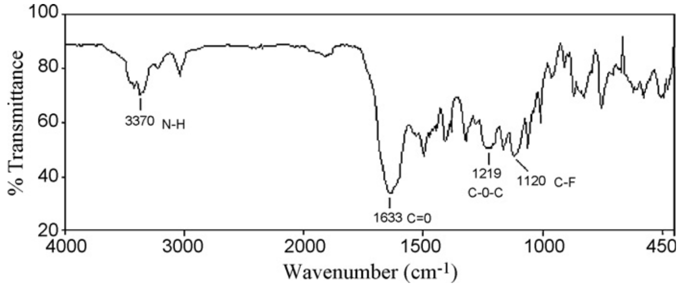

Fig. 1. IR spectrum of polyamide **4**.

Table 1
The polymerization and thermal properties of polyamide **4**.

Yield (%)	η_{inh}[a] (dL/g)	T_g[b] (°C)	T_{d5}[c] (°C)	T_{d10}[d] (°C)	R_w[e] (%)
97	0.95	236	455	480	56

[a] Detected in DMAc with a concentration of 0.5 g/dL at 30 °C.
[b] Detected by DSC at a heating rate of 10 °C/min in N_2.
[c] 5% weight loss temperature. (Determined by TGA at a scan rate of 20 °C/min in N_2)
[d] 10% weight loss temperature. (Determined by TGA at a scan rate of 20 °C/min in N_2)
[e] Residual weight (%) when heated to 800 °C (Determined by TGA at a scan rate of 20 °C/min in N_2).

The polyamide was readily soluble (3.0%, w/v) in DMAc, NMP, DMF, DMSO, *m*-cressol, and even in pyridine at room temperature, attributable to the presence of xanthene cardo group, trifluoromethylphenoxy pendent and flexible ether linkages, but insoluble in THF and $CHCl_3$. Thin film (120 × 5 mm) cast from its DMAc solution was tested for mechanical properties in Instron instrument at 25 °C. The film had tensile strength of 93 MPa, elongation at break of 14%, and tensile modulus of 2.2 GPa. The electric properties of the polyamide film were also measured. The electric properties such as the volume resistance, surface resistance and dielectric strength were $2.35 \times 10^{15}\ \Omega$ cm, $2.78 \times 10^{14}\ \Omega$ and 94 kV/mm, respectively. Moreover, the dielectric constant at 1 MHz was 3.03 and the moisture uptake of the polyamide was 1.36%.

The thermal and mechanical properties of the new resulting polyamide were compared with those of the fluorinated fluorene-containing polyamides [4]. In addition, this new fluorinated polyamide exhibited lower dielectric constant than those of the fluorinated polyamides without cardo groups in the main [7], which may be speculated that this polyamide containing xanthene cardo structures have higher bulk density resulting in larger free volume.

In conclusion, a novel diamine was synthesized, characterized, and polymerized with TFFPC to afford a novel fluorinated polyamide with xanthene structure. The introduction of xanthene cardo group, trifluoromethylphenoxy pendent and flexible ether linkages into the polyamide backbone resulted in dramatic changes in its properties, especially in the improvement of solubility and lowering of the moisture uptake. This new fluorinated polyamide exhibited good thermal stability, as well as good mechanical, electrical and dielectric properties.

Acknowledgments

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[8] Mp 263–264 °C; IR (KBr): 1515, 1344 cm^{-1} (N=O stretch), 1248 cm^{-1} (C—O—C stretch); ^1H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, 4H, J = 8.6 Hz), 7.31 (t, 2H, J = 8.0 Hz), 7.20 (d, 2H, J = 8.0 Hz), 7.09 (t, 2H, J = 7.6 Hz), 7.07–7.03 (m, 8H), 6.99–6.94 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.38, 152.67, 151.48, 148.50, 142.25, 141.92, 129.74, 129.45, 128.31, 125.94, 123.12, 119.97, 117.25, 116.70, 53.51. Anal. Calcd. for $C_{37}H_{24}N_2O_7$: C, 73.02; H, 3.97; N, 4.60. Found: C, 73.12; H, 3.90; N, 4.70.
[9] Mp 209–211 °C; IR (KBr): 3370, 3042 cm^{-1} (N—H stretch), 1236 cm^{-1} (C—O—C stretch); ^1H NMR (400 MHz, $CDCl_3$): δ 7.25 (t, 2H, J = 7.6 Hz), 7.13 (d, 2H, J = 8.0 Hz), 7.02 (t, 2H, J = 8.8 Hz), 6.92 (d, 2H, J = 8.0 Hz), 6.87–6.81 (m, 8H), 6.77 (d, 4H, J = 8.0 Hz), 6.65 (d, 4H, J = 8.0 Hz), 3.53 (br s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.47, 152.62, 148.26, 142.78, 139.38, 131.07, 130.54, 130.03, 127.80, 122.82, 121.32, 116.41, 116.20, 116.14, 53.20; Anal. Calcd. for $C_{37}H_{28}N_2O_3$: C, 81.00; H, 5.14; N, 5.11. Found: C, 81.14; H, 5.23; N, 5.20.