New Soluble Cyano-Containing Poly(arylene ether) Copolymers Bearing Pendant Xanthene Groups

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ABSTRACT: Homopolymers and copolymers of poly-(arylene ether nitrile) (PAEN)-bearing pendant xanthene groups were prepared by the nucleophilic substitution reaction of 2,6-difluorobenzonitrile with 9,9-bis(4-hydroxy-phenyl)xanthene (BHPX) and with various molar proportions of BHPX to hydroquinone (100/0 to 40/60) with *N*-methyl-2-pyrrolidone (NMP) as a solvent in the presence of anhydrous potassium carbonate. These polymers had inherent viscosities between 0.61 and 1.08 dL/g, and their weight-average molecular weights and number-average molecular weights were in the ranges 34,200–40,800 and 17,800–20,200, respectively. All of the PAENs were amorphous and were soluble in dipolar aprotic solvents, including NMP, *N,N*-dimethylformamide, and *N,N*-di-methylacetamide and even in tetrahydrofuran and chloro-form at room temperature. The resulting polymers showed glass-transition temperatures (T_g's) between 220 and 257°C, and the T_g values of the copolymers were found to increase with increasing BHPX unit content in the polymer. Thermogravimetric studies showed that all of the polymers were stable up to 422°C with 10% weight loss temperatures ranging from 467 to 483°C and char yields of 54–64% at 700°C in nitrogen. All of the new PAENs could be cast into transparent, strong, and flexible films with tensile strengths of 106–123 MPa, elongations at break of 13–17%, and tensile moduli of 3.2–3.7 GPa. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 2788–2793, 2011

Key words: high performance polymers; polyethers; polymer synthesis and characterization

INTRODUCTION

Poly(arylene ether)s have attracted considerable attention because of their excellent properties, including good thermooxidative stability, high glass-transition temperature (T_g), and excellent mechanical strength.[1–5] Among this class of high-performance engineering thermoplastics, poly(arylene ether nitrile)s (PAENs) are well known as a class of semi-crystalline polymers with pendant nitrile groups.[6–8] It has been proposed that the introduction of the nitrile groups may promote adhesion with other materials and present a potential crosslinking site.[7] Such materials are currently gaining wide acceptance for their use as structural coatings for electrical devices or matrix resins for advanced composites because of their combination of excellent heat and chemical resistance, mechanical strength, flame retardancy, and molding workability. For instance,

the first commercialized product of PAENs was identified as a matrix resin for carbon reinforcement.[9] However, their poor solubilities, because of premature crystallization from organic solvent mediums, hamper their syntheses, processing, and widespread application. Additionally, their relatively low glass transitions result in a decrease in modulus and hardly qualify the composites for use at the elevated temperatures that are frequently encountered in aerospace, industrial, and automotive applications. To overcome these limitations, organic soluble and thermally stable PAENs have been developed in recent years by the structural modification of polymer backbones, with a view to improving their processability and, hence, broadening their applications, especially as adhesives, coatings, and membranes. These approaches include the incorporation of alkyl pendant groups,[10,11] flexible linkages,[12–15] or noncoplanar units[16] into the polymer backbones by the design and preparation of new monomers. Recently, our laboratory prepared xanthene-based cardo poly-(arylene ether ketone)s[17] and polyamides[18] with enhanced solubility, processability, good mechanical strength, and excellent thermal properties with a T_g above 210°C. To the best of our knowledge, although PAENs containing phthalide cardo groups in the polymeric chain were previously documented,[7] PAENs bearing xanthene cardo groups in the main chains have not been reported. As part of an

ongoing project dealing with the development of processable and heat-resistant polymeric materials, we report here the synthesis of homopolymers and copolymers of PAEN containing xanthene cardo groups derived from 9,9-bis(4-hydroxyphenyl)xanthene (BHPX or **1**), 2,6-difluorobenzonitrile (DFBN), and hydroquinone (HQ) by a nucleophilic substitution reaction. Their structure–property relationships were also investigated.

EXPERIMENTAL

Materials

9,9-Bis(4-hydroxyphenyl)xanthene BHPX was prepared using our recent method.[17] High-purity 2,6-difluorobenzonitrile (Sigma-Aldrich, USA) and hydroquinone HQ (Shanghai Chemical Reagent Co., Shanghai, China) were used as received. Anhydrous K_2CO_3 (Beijing Chemical Reagent Co., Beijing, China) was dried *in vacuum* at 100°C before use. *N*-methyl-2-pyrrolidone (NMP) (Shanghai Chemical Reagent Co., Shanghai, China) was refluxed with calcium hydride, distilled under reduced pressure, and stored over a 4-Å molecular sieve prior to use. The other reagents and solvents were obtained from commercial sources and used as received.

Polymer synthesis

According to the procedure described earlier,[7] a representative polymerization procedure under a nitrogen atmosphere for the synthesis of PAEN copolymer (**4d**) is described as follows. To a 250-mL, three-necked, round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet with a thermometer, and a Dean–Stark trap with a condenser were added BHPX (9.1604 g, 0.025 mol), HQ (2.7528 g, 0.025 mol), DFBN (6.9552 g, 0.050 mol), anhydrous K_2CO_3 (8.28 g, 0.06 mol), NMP (100 mL), and toluene (50 mL). The reaction mixture was heated to reflux, and water was removed by azeotropic distillation with toluene. Then, the toluene was removed by distillation, and the reaction mixture was heated at 190–200°C and stirred at this temperature under nitrogen for 4 h. After cooling, the viscous solution was poured into a methanol–water solution, and the precipitated polymer was collected by filtration and then pulverized into a powder with a blender. The polymer powder was washed successively with boiling water and methanol. After filtration, the white polymer (**4d**) was dried at 120°C *in vacuo* overnight.

Measurements

^{1}H-NMR (400 MHz) spectra were recorded on Bruker AVANCE 400 MHz spectrometer (Bruker, Kleve, Germany) in $CDCl_3$. The FTIR spectra of the monomer and polymers in KBr pellets were obtained on a Perkin-Elmer SP One FT-IR spectrophotometer (California, USA). Microanalyses were performed with a Carlo Erba 1106 Elemental Analyzer (Italy). Differential scanning calorimetry (DSC) analyses were performed on a Perkin Elmer Pyris 1 DSC (California, USA) at a scanning rate of 20°C/min from 50 to 400°C in flowing nitrogen (20 mL/min). glass-transition temperatures The (T_g's) were read at the midpoint of the transition in the heat capacity and were taken from the second heating scan after quick cooling from 400°C at a cooling rate of 200°C/min. Thermogravimetric analysis (TGA) was carried out on approximately 6–8 mg film samples with a Perkin-Elmer Pyris 1 TGA (California, USA) in nitrogen (40 mL/min) at a heating rate of 10°C/min from 50 to 700°C. Wide-angle X-ray diffraction patterns were recorded at room temperature (ca.25°C) on a Shimadzu XRD-6000 X-ray diffractometer (Kyoto, Japan) (operating at 40 kV and 30 mA) with graphite-mono-chromatized CuK_α radiation (λ = 1.5418 Å); the scanning rate was 2°/min over a range of 2 θ = 5–50°. The molecular weights were determined by gel permeation chromatography (GPC) with polystyrene calibration using a Waters 510 high performance liquid chromatography (HPLC) (Waters Associates Co., Ltd., USA) 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 (η_{inh} = ln η_r/c, where η_r and c are intrinsic viscosity and concentration, respectively) were measured at 0.5 g/dL concentration in of DMAc with an Ubbelohde viscometer (Shanghai, China) 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 mechanical properties of the polymer films (cast from chloroform solutions onto the glass plates and followed by heated at around 120°C *in vacuo*) were measured on an Instron 1122 testing instrument (Instron Co., UK) with a 5-kg load cell at a crosshead speed of 2 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.

RESULTS AND DISCUSSION

Polymer synthesis

As shown in Scheme 1, PAEN with pendant xanthene cardo groups (**4a**) was prepared by the reaction of BHPX with DFBN in NMP in the presence of potassium carbonate. Accordingly, the PAEN copolymers (**4b–4e**) were synthesized by the variation of the molar ratio of BHPX to HQ. The feed ratios and some physical properties of these
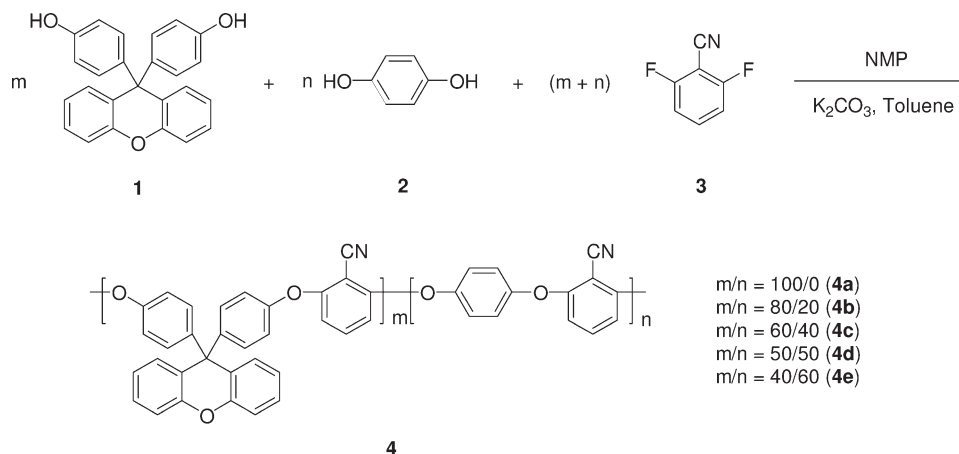
Scheme 1 Synthetic route to xanthene-containing PAENs.

polymers are given in Table I. These PAENs were obtained in almost quantitative yields, with η_{inh}'s in the range 0.61–1.08 dL/g. As shown in Table I, the η_{inh}'s of the copolymers increased with increasing BHPX content in the polymeric chain; this indicated the higher reactivity of BHPX toward the electrophilic substrate. This might have been due to the presence of electron-donor diphenylmethyl groups in xanthene, which enhanced the nucleophilicity of BHPX. Moreover, the GPC data obtained for the resulting PAENs indicated that the weight-average molecular weights (M_w's) and number-average molecular weights (M_n's) were in the ranges 34,200–40,800 and 17,800–20,200, respectively, relative to the polystyrene standards; this indicated that all of the polymers had sufficiently high molecular weights to permit the casting of tough and flexible films.

The formation of PAENs was characterized with instrumental techniques, including IR, NMR, and elemental analysis. A typical FTIR spectrum for PAEN **4b** is shown in Figure 1. The FTIR spectra of all of the polymers showed characteristic absorptions of the symmetrical stretching of the nitrile group near 2231

cm^{-1} and aryl ether stretching around 1240–1252 cm^{-1}. The ^{1}H-NMR spectrum of the representative sample PAEN **4d** is presented in Figure 2, in which the absorption signals of aromatic protons appeared in the range $\delta = 7.34$–6.87 ppm. The ^{1}H-NMR spectrum was in good accordance with the proposed chemical structure of the corresponding polymer **4d.** The results of elemental analyses are also reported in Table I and indicate that the observed values were in reasonable agreement with theoretical values and confirmed the proposed structures.

Thermal properties

The thermal properties of all of the PAENs evaluated by DSC and TGA are summarized in Table II. The samples were first heated to 400°C and then quenched rapidly to room temperature to give predominantly amorphous samples so that the T_g's of all of the polymers could be easily revealed in the second DSC scans. None of the polymers showed melting endotherms from T_g to 400°C on their DSC curves; this supported the amorphous nature of

TABLE I
Synthetic Data and Some Physical Properties of the PAENs

Polymer	DFBN/BHPX/HQ molar ratio[a]	Yield (%)	η_{inh} (dL/g)[b]	M_w[c]	M_n[c]	PDI[d]	Elemental analysis (%)[e]		
							C	H	N
4a	100/100/0	97	1.08	40,800	20,200	2.02	82.33 (82.57)	4.24 (4.11)	2.95 (3.01)
4b	100/80/20	96	0.79	37,900	18,500	2.05	81.52 (81.77)	4.22 (4.04)	3.48 (3.38)
4c	100/60/40	98	0.72	35,400	18,000	1.97	80.65 (80.74)	4.15 (3.94)	3.75 (3.86)
4d	100/50/50	98	0.66	35,500	18,300	1.94	79.96 (80.11)	4.08 (3.88)	4.23 (4.15)
4e	100/40/60	96	0.61	34,200	17,800	1.92	79.15 (79.37)	4.01 (3.82)	4.35 (4.49)

[a] On the basis of 0.050 mol of DFBN.
[b] Measured at a polymer concentration of 0.5 g/dL in DMAc at 30°C.
[c] Determined by GPC with THF as an eluent calibrated with polystyrene standards.
[d] The polydispersity index (PDI) was obtained by M_w/M_n.
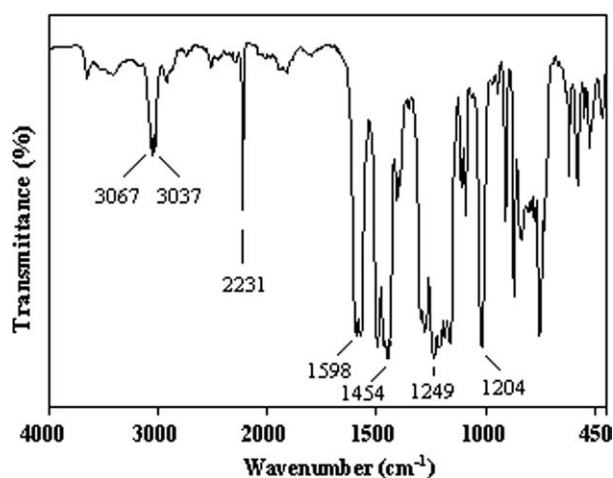[e] Theoretical percentages are in parentheses.

Figure 1 FTIR spectrum of PAEN **4b.**

TABLE II
Thermal Properties of the PAENs

Polymer	T_g (°C)[a]	T_{d0} (°C)[b]	T_{d5} (°C)[c]	T_{d10} (°C)[d]	R_w (%)[e]
4a	257	427	447	467	62
4b	237	422	462	477	64
4c	230	424	456	468	62
4d	226	428	463	474	61
4e	220	435	471	483	54
4f[f]	182[g]	490[h]	535[g]	—[i]	51[h]

[a] T_g based on the second heating trace of DSC measurements.
[b] T_{d0}, initial decomposition temperature, measured by TGA in N_2.
[c] T_{d5}, temperature at 5% weight loss, measured by TGA in N_2.
[d] T_{d10}, temperature at 10% weight loss, measured by TGA in N_2.
[e] R_w, residual weight percentage, heated to 700°C in N_2.
[f] Derived from DFBN with HQ.
[g] Reported in ref. 7.
[h] Reported in ref. 11.
[i] Not reported.

these PAENs. Figure 3 illustrates several typical DSC thermograms of polymers **4a, 4b,** and **4e.** The T_g values of all of the polymers, as shown in Table II, were recorded in the range 220–257°C. Furthermore, the T_g's of the PAEN copolymers increased with increasing BHPX content in the polymers; this was attributed to the gradual increase of the bulky pendant xanthene groups in the copolymer backbones, which efficiently inhibited the polymer backbone's free rotation.

The thermal degradation behavior of all of the polymers was studied by TGA, and the results are reported in Table II. A typical TGA curve for PAEN copolymer **4b** in nitrogen is presented in Figure 4. As observed, the BHPX content in the copolymers did not much affect the thermal stability of the copolymers. The temperatures at 5 and 10% weight loss in nitrogen were in the ranges 447–471 and 467–483°C, respectively. Moreover, all of the polymers were sta-
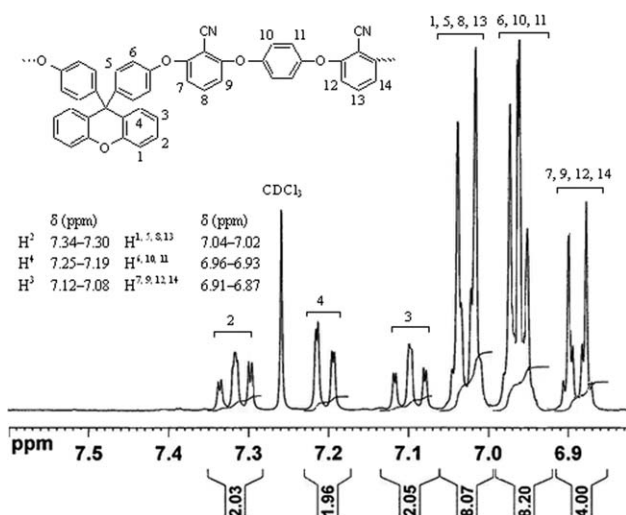
ble up to 422°C and gave a char yields of 54–64% at 700°C in a nitrogen atmosphere. There was a large window between T_g and the decomposition temperature for each of the PAENs; this could be advantageous in the processing of these polymers.

For comparison, the thermal behavior data of PAEN **4f** (T_g = 182°C), derived from DFBN with HQ,[7,11] are also listed in Table II. As shown in Table II, the T_g of this homopolymer **4a** (257°C) was higher than that of **4f** (182°C) because of the presence of the more rigid and bulky structure in the polymer chain (**4a**). As expected, the introduction of the bulky
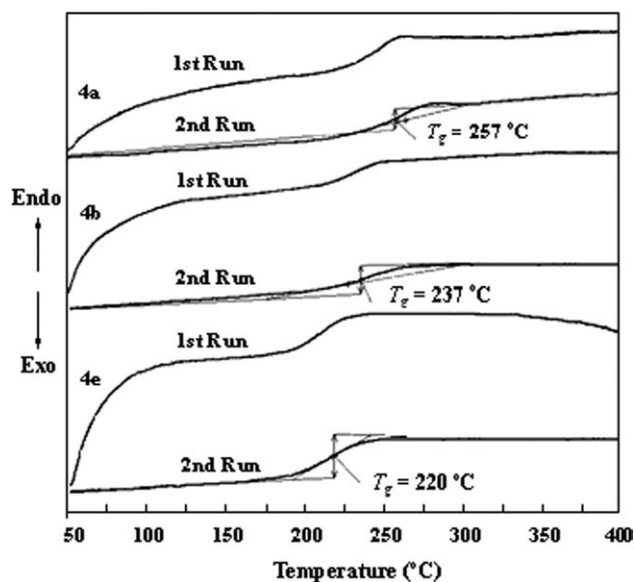

Figure 2 ¹H-NMR spectrum of PAEN **4d.**

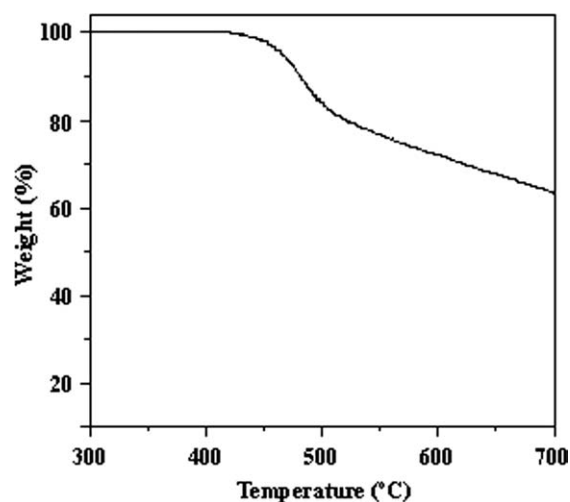**Figure 3** DSC thermograms of PAENs **4a, 4b,** and **4e.**

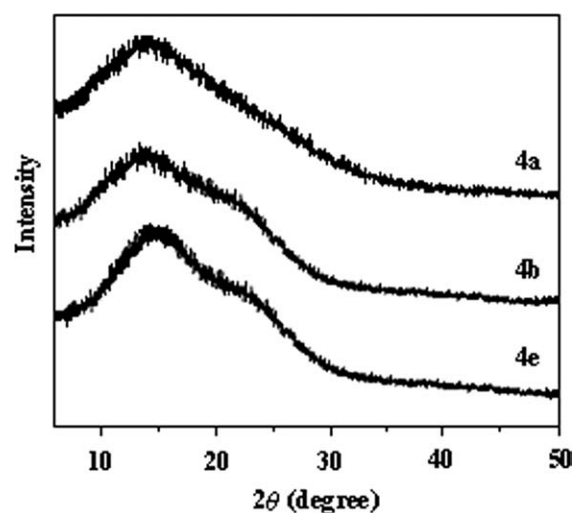**Figure 4** Typical TGA curve of PAEN **4b** in N$_2$.

Figure 5 WAXD patterns of PAENs **4a, 4b,** and **4e.**

xanthene pendant groups into the polymer chains apparently enhanced the T_g values of the PAEN copolymers. However, all of the homopolymers and copolymers of PAEN had relatively lower decomposition temperature (T_{d0}) than the corresponding analogue **4f;** this might have been a result of poor packing and weaker chain–chain interactions because of the presence of the bulky xanthene pendant groups.

Solubility

The solubility behavior of the obtained PAENs was tested in various organic solvents by the dissolution of 0.03 g of the samples in 1 mL of solvent (3%, w/v) at different temperatures (Table III). All of the polymers readily dissolved in dipolar aprotic solvents such as NMP, *N,N*-dimethylformamide (DMF), and DMAc and some common organic solvents, such as THF and chloroform, at room temperature. Except for PAEN copolymer **4e,** the other

polymers were also soluble in dichloromethane and 1,2-dichloroethane (DCE). In contrast, as shown in Table III, PAEN **4f,** without xanthene units,[7,11] was insoluble in common organic solvents, including dipolar aprotic solvents, such as dimethyl sulfoxide (DMSO), DMF, NMP, and DMAc, at room temperature. Obviously, the good solubilities of the homopolymers and copolymers of PAEN were attributed to the combined effects of the nitrile and xanthene pendant groups and flexible ether linkages in the polymer backbones, which prevented close chain packing and allowed the solvent molecules to diffuse into the polymer chains.

Crystal and mechanical properties

The obtained PAENs with 100–40% BHPX contents in their main chains were characterized by WAXD studies and displayed almost completely amorphous diffraction patterns. The results were consistent with

TABLE III
Solubilities of the PAENs[a]

Polymer	Solvent								
	DMF	DMAc	NMP	DMSO	THF	CHCl$_3$	CH$_2$Cl$_2$	DCE	MeOH
4a	+ +	+ +	+ +	+ −	+ +	+ +	+ +	+ +	− −
4b	+ +	+ +	+ +	+ −	+ +	+ +	+ +	+ +	− −
4c	+ +	+ +	+ +	+ −	+ +	+ +	+ +	+ +	− −
4d	+ +	+ +	+ +	+ −	+ +	+ +	+ +	+ +	− −
4e	+ +	+ +	+ −	− −	+ +	+ +	+	+	− −
4f[b]	−[c]	−[c]	−[c]	−[c]	−[c]	−[c]	−[c]	−[c]	−[c]

[a] The symbols represent the following: + + = soluble at room temperature; + = soluble on heating at 60°C; + − = partially soluble; − = insoluble at room temperature; − − = insoluble even on heating.
[b] Derived from DFBN with HQ.
[c] Reported in refs. 7 and 11.

TABLE IV
Mechanical Properties of the PAENs

Polymer	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
4a	106	15	3.7
4b	112	14	3.5
4c	115	17	3.2
4d	120	13	3.3
4e	123	16	3.6
4f[a]	150[b]	35[b]	3.9[b]

[a] Derived from DFBN with HQ.
[b] Reported in ref. 7.

the DSC studies, where all of the polymers failed to show melt crystallization temperatures. The WAXD patterns of PAENs **4a**, **4b**, and **4e** are presented in Figure 5. The amorphous nature was mainly ascribed to the introduction of the BHPX moiety, which produced a wider separation of polymer chains and lowered the chain packing efficiency with a gain of free volume; this resulted in a decrease in the crystallinity. In addition, the amorphous structure of these PAENs also reflected in their excellent solubilities.

Transparent, strong, and flexible films for all of PAENs were obtained via the casting of their solutions in chloroform. The mechanical properties of these polymer films are summarized in Table IV. The polymer films had tensile strengths of 106–123 MPa, elongations at break of 13–17%, and tensile moduli of 3.2–3.7 GPa. Compared to the analogous PAEN **4f** without xanthene units,[7,11] the obtained homopolymers and copolymers of PAEN exhibited relative lower tensile properties. Furthermore, the tensile strengths of PAEN copolymers decreased with increasing BHPX content in the copolymers; this was probably due to the presence of bulky xanthene pendant groups, which increased the distance of polymeric chains and reduced their intramolecular interactions. However, the elongations at break and tensile moduli of these copolymers revealed no significant difference with different molar ratios of BHPX to HQ. In addition, although the incorporation of bulky xanthene pendant groups decreased the polymeric chain–chain interactions to some extent, the pendent nitrile groups afforded the polymer chains interaction forces. Therefore, the resulting homopolymers and copolymers of PAEN still exhibited excellent mechanical properties and can be considered new engineering high-performance plastics.

CONCLUSIONS

A new series of soluble PAENs bearing pendant xanthene groups with high molecular weights were synthesized by the nucleophilic displacement reaction of DFBN with BHPX or with various molar proportions of BHPX to HQ (100/0 to 40/60) in NMP and with potassium carbonate as a catalyst. All of the polymers were amorphous and exhibited good mechanical and thermal properties. The incorporation of BHPX into the copolymers not only increased the T_g's but also evidently improved the solubility of the polymers. These characteristics indicated that these xanthene-containing PAENs could be considered not only as new candidates for processable high-performance engineering plastics but also as a functional materials.

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