

Novel blue-emitting carboxyl-functionalized poly(arylene ether nitrile)s with excellent thermal and mechanical properties†

Cite this: *Polym. Chem.*, 2014, 5, 3673Hailong Tang,^{ab} Zejun Pu,^a Xu Huang,^a Junji Wei,^a Xiaobo Liu^{*a} and Zhiqun Lin^{*b}

A series of novel carboxyl-functionalized poly(arylene ether nitrile)s (CPAENs) were synthesized via nucleophilic substitution polycondensation reactions of 2,6-dichlorobenzonitrile with carboxyl-functionalized phenolphthalin and diphenol compounds, using *N*-methyl-2-pyrrolidone (NMP) as solvent in the presence of anhydrous potassium carbonate. The resulting CPAENs exhibited high glass transition temperatures ranging from 181 °C to 251 °C, and were thermally stable up to 400 °C under either nitrogen or air atmospheres. The incorporation of phenolphthalin-units into the polymer chain imparted an improved solubility of CPAENs in organic solvents, such as NMP, *N,N*-dimethylformamide, and tetrahydrofuran. The CPAENs were amorphous and can be readily cast into transparent films with a tensile strength of 75.1–104.7 MPa and a tensile modulus of 2.6–3.2 GPa. All CPAENs displayed a highly intense UV absorption in the wavelength range of 280–330 nm and a characteristic blue-emitting fluorescence under the UV irradiation.

Received 29th December 2013

Accepted 19th February 2014

DOI: 10.1039/c3py01782f

www.rsc.org/polymers

Introduction

Poly(arylene ether)s such as poly(arylene ether sulfone)s, poly(arylene ether ketone)s, poly(arylene ether nitrile)s, poly(phenylene oxide) and poly(phenylene sulfide) have garnered considerable attention as they are an intriguing class of engineering thermoplastics possessing excellent chemical and thermal properties for a broad spectrum of applications. The aromatic constituent in poly(arylene ether)s contributes to high thermal stability and good mechanical properties of poly(arylene ether)s, and the ether linkages facilitate the polymer processing while maintaining its thermal stability. Notably, many different kinds of poly(arylene ether)s have found the widespread applications in electronics, energy, and automotive and aerospace industries.^{1–6} Among them, poly(ether ether ketone) (Victrex® PEEK, ICI, UK)⁷ and poly(arylene ether nitrile) (PEN-ID300®, Idemitsu, Japan)⁸ have been commercialized and recognized as high-performance engineering thermoplastics due to their good mechanical properties, and high chemical and thermal resistance.

It is noteworthy that poly(arylene ether nitrile)s (PAENs) are an important new class of high-performance engineering thermoplastics that exhibit outstanding mechanical properties, high thermal stability, excellent radiation resistance, and good chemical inertia and dielectric properties.^{9–13} Unlike many other poly(arylene ether)s, PAENs have strongly polar nitrile groups pendent on aromatic rings, which most probably promotes their adhesion to many substrates *via* the interaction with other polar groups on the substrate. PAENs can also serve as a potential site for the polymer crosslinking *via* trimerization of the nitrile groups to form thermally stable *sym*-triazines.^{14,15} These eminent performances make PAENs attractive candidates as matrices in advanced composites in aerospace industries.¹⁶ Nevertheless, owing to premature crystallization from organic solvents, the PAENs have the poor solubility, thus posing challenges in their synthesis, processing and widespread applications.¹⁷

To this end, in recent years the functionalization of PAENs has received much attention to broaden the applications of PAEN-based materials. One effective strategy involves the incorporation of pendant functional groups, such as sulfonic acid groups, carboxyl groups, *etc.* This can be realized by either postsynthesis chemical modification of the polymer chains^{18,19} or direct synthesis using functionalized monomers.²⁰ Recently, the sulfonated derivatives of PAENs have been reported. For example, a series of copoly(aryl ether ether nitrile)s containing sulfonic acid groups¹³ and copoly(aryl ether nitrile)s containing a naphthalene structure with sulfonic acid groups^{12,16} were synthesized as proton conducting membrane materials for fuel cells. The sulfonated PAENs as high-performance polymer electrolyte membranes for fuel cells were also reported.^{21–23}

^aHigh Temperature Resistant Polymers and Composites Key Laboratory of Sichuan Province, School of Microelectronics and Solid-State Electronics, University of Electronic Science and Technology of China, Chengdu 610054, P. R. China. E-mail: liuxb@uestc.edu.cn; Fax: +86 28-83207326; Tel: +86 28-83207326

^bSchool of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA. E-mail: zhiqun.lin@mse.gatech.edu; Tel: +1 404-385-4404

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3py01782f

The polymer functionalization with carboxyl groups has long been of interest as the carboxyl-functionalized polymers not only improve their solubility, but also enable some new additional properties, such as the adsorption of heavy metal ions,^{24,25} the preparation of composites by coordination with inorganic ions,^{26,27} etc. Furthermore, many derivatives with other functional groups can be readily obtained by reacting with carboxyl groups in carboxyl-functionalized polymers.²⁸ To date, polyimide, polyaryletherketone, polycarbonate and aromatic polyester with pendant carboxyl groups have been developed.^{28–31} In sharp contrast, to the best of our knowledge, there is little work on the functionalization of PAENs with carboxyl groups.

Herein, we report a series of novel carboxyl-functionalized poly(arylene ether nitrile)s (CPAENs) by the direct synthesis using carboxyl-functionalized monomer, and systematically explore their structure–property relationships, including thermal stability, solubility, mechanical and fluorescence properties for potential use in high-performance fuel cells, optical devices, and membranes for gas and solvent separation.

Experimental section

Materials

N-Methyl-2-pyrrolidinone (NMP), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), chloroform (CHCl₃), toluene, sodium hydroxide (NaOH), anhydrous potassium carbonate (K₂CO₃), and zinc powder were purchased from Tianjin Bodi Chemical Holding Co., Ltd. 2,6-Dichlorobenzonitrile (DCBN) was obtained from Yangzhou Tianchen Fine Chemical Co., Ltd. Phenolphthalein (PP), resorcinol (RS), hydroquinone (HQ), and bisphenol A (BPA) were supplied by Chengdu Haihong Chemical Co., Ltd. All the materials were used without further purification unless otherwise stated.

Synthesis of a carboxyl-functionalized monomer

A typical procedure for synthesis of a carboxyl-functionalized monomer is illustrated in Scheme 1. Phenolphthalein (50 g, 0.16 mol), sodium hydroxide (75 g, 1.88 mol), and zinc powder

(32.5 g, 0.50 mol) were added into 1.2 L of water. The mixture (a purple solution) was kept at a fixed temperature of 60 °C under continuous stirring until the purple disappeared completely. The mixture was then filtered to remove zinc. Subsequently, dilute hydrochloric acid was poured into the filtered colorless solution until a white precipitate was completely formed. The white solid was then isolated by filtering the mixture, and rinsed repeatedly with deionized water until a neutral pH was reached. The carboxyl-functionalized monomer, phenolphthalin (PPL), was obtained after drying in a vacuum oven at 100 °C for 48 h and characterized.

Yield: 90.5%; mp 234 °C (by DSC); ¹H NMR (300 MHz, DMSO-*d*₆): δ (ppm) = 6.39 (s, 1H, CH), 6.64–6.79 (m, 8H, 2C₆H₄OH), 6.96–7.73 (m, 4H, C₆H₄COOH), 9.24 (s, 2H, OH), 12.81 (s, 1H, COOH); FTIR (KBr): ν (cm^{−1}) = 1693 (C=O), 1599, 1571, 1510 (phenyl), 2954 (CH), 3620 (OH) (Fig. S1 and S2†).

Synthesis of carboxyl-functionalized poly(arylene ether nitrile)s

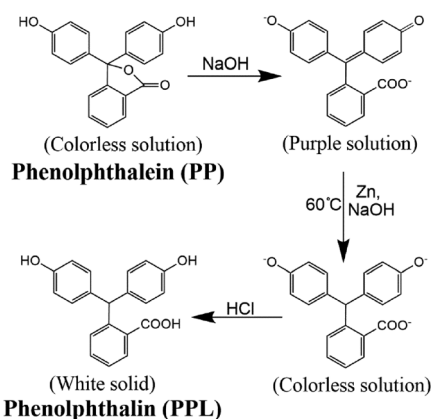
In a typical synthesis procedure, DCBN (22.0 g, 128 mmol), PPL (20.5 g, 64 mmol), HQ (7.05 g, 64 mmol), anhydrous K₂CO₃ (35.4 g, 256 mmol), NMP (85 mL), and toluene (35 mL) were added into a 250 mL three-neck round bottom flask equipped with a Dean–Stark trap, condenser, mechanical stirrer, and thermometer. The system was heated to 140–160 °C to remove water from the reaction by azeotropic distillation with toluene for 3 h. Toluene was then removed by distillation and the temperature was gradually raised to 190–200 °C. The system was kept stirring for about 5 h until its viscosity did not increase any more. Afterwards, the reaction mixture was poured into ethanol to precipitate the copolymer. The precipitate was then acidified by dilute hydrochloric acid after crushing. Finally, the collected copolymer was washed five times with boiling water and dried in a vacuum oven at 130 °C for 12 h to produce a white solid (yield: 83.7%). The other CPAEN copolymers were also synthesized using the similar procedure noted above.

In order to yield a series of carboxyl-functionalized poly(arylene ether nitrile) (CPAEN) copolymers with various structures and properties, different phenolic compounds were employed as the first diphenol monomer (M₁), including resorcinol, hydroquinone, bisphenol A and phenolphthalein, and phenolphthalin as the second diphenol monomer (M₂). The copolymers are denoted by CPAEN(M₁/M₂). It is important to note that the mole fractions of two diphenol monomers (*x*, *y*) can be adjusted freely, and all the copolymers were fixed at *x* = *y* = 50% in this study.

Characterizations

Relative molecular weights and molecular weight distributions of copolymers were determined by gel permeation chromatography (GPC) measurements, which were performed on a Waters 1515 GPC system with a Waters 2414 refractive index detector, using THF as an eluent and polystyrene as the standard.

Fourier transform infrared (FTIR) spectra in reflection mode were recorded on a Nicolet Nexus 670 FTIR spectrometer. Film samples of ca. 20 μm thickness were used for the test, which were vacuum-dried at 100 °C for 12 h prior to the measurement. The proton nuclear magnetic resonance (¹H NMR) spectra were



Scheme 1 Synthetic route to the carboxyl-functionalized monomer, phenolphthalin.

taken on a Bruker Avance DPX 300 spectrometer at 300 MHz, using deuterated dimethyl sulfoxide (DMSO- d_6) as the solvent, and tetramethylsilane (TMS) as an internal reference. Wide angle X-ray diffraction (WAXD) was performed at room temperature on an X'Pert PRO Alpha-1 diffractometer using Cu K α radiation.

Differential scanning calorimetry (DSC) measurements were conducted on a TA Instruments DSC Q100 module. Samples were placed in aluminum pans under nitrogen and heated from 30 °C to 300 °C at a heating rate of 10 °C min⁻¹. In order to remove any previous thermal histories, all samples were initially heated from room temperature to 300 °C, and then cooled to 30 °C with a rate of 20 °C min⁻¹. Thermogravimetric analyses (TGA) were carried out on a TA Instruments TGA Q50 module under flowing nitrogen or air, from room temperature to 800 °C at a heating rate of 20 °C min⁻¹. All samples were kept at 100 °C for 30 min in the TGA apparatus to avoid the effect of ambient humidity prior to the measurement.

Mechanical properties of the copolymer films were measured on a SANS CMT6104 series desktop electromechanical universal testing machine with a cross-head speed of 5 mm min⁻¹. The results were reported as the average value for five samples (size: 10 mm × 100 mm).

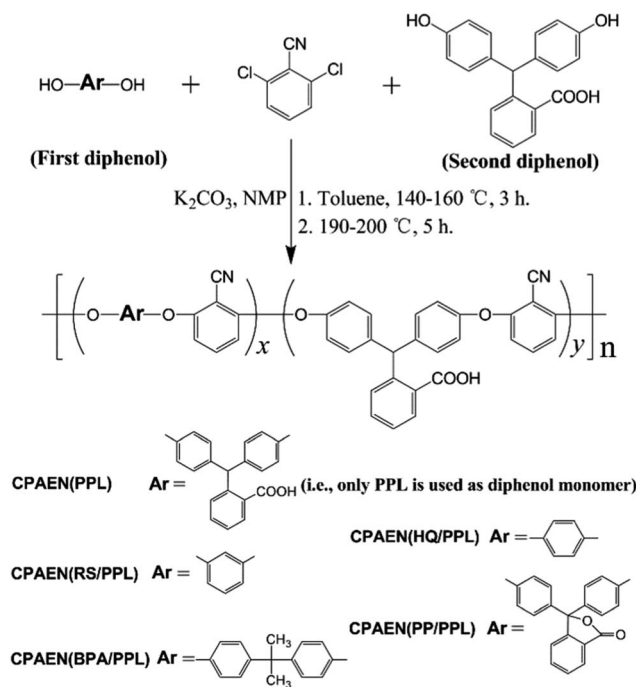
Ultraviolet-visible (UV-vis) absorption spectra were recorded using a Shimadzu 3100 UV-vis-near-IR spectrophotometer. Fluorescence emission spectra in NMP were measured using a Hitachi F-7000 FL spectrophotometer at a polymer concentration of 1.5 mg mL⁻¹.

Results and discussions

Synthesis and characterization of carboxyl-functionalized poly(arylene ether nitrile) copolymers

A set of carboxyl-functionalized poly(arylene ether nitrile) (CPAEN) copolymers were synthesized by the nucleophilic substitution polycondensation reactions of 2,6-dichlorobenzonitrile and phenolphthalein with various diphenol monomers (*i.e.*, first diphenol) using anhydrous potassium carbonate as a catalyst in NMP, as depicted in Scheme 2. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of as-synthesized polymers determined by GPC are shown in Table 1. Their polydispersity index ($PDI = M_w/M_n$) is also summarized in Table 1.

The FTIR spectra of CPAENs are shown in Fig. 1. Two sharp and strong absorption bands observed at 1500 cm⁻¹ and 1460 cm⁻¹ can be attributed to the skeleton vibration of benzene rings. The other two weak bands at 1600 cm⁻¹ and 1580 cm⁻¹ were also associated with the absorption of benzene rings. Moreover, a characteristic ether band at 1243 cm⁻¹ was seen, which is due to the phenylene ether stretching vibrations.³² These observations indicated the formation of aryl ether (Ar–O–Ar) *via* nucleophilic polycondensation reaction. The peak at 1718 cm⁻¹ corresponded to the C=O absorption of the free carboxyl groups,²⁹ and the absorption band at 2231 cm⁻¹ was assigned to the symmetrical stretching vibration of nitrile groups (–CN). They are all the characteristic absorption of PAENs and evidenced in all CPAENs. The characteristic absorption bands of CPAEN(RS/PPL) and



Scheme 2 Schematic synthesis procedure of carboxyl-functionalized poly(arylene ether nitrile)s (CPAENs), where x and y are the mole fractions of the first diphenol monomer and phenolphthalein in the feed, respectively.

Table 1 Molecular weights of carboxyl-functionalized poly(arylene ether nitrile)s (CPAENs)

Polymer	M_w^a (g mol ⁻¹)	M_n^a (g mol ⁻¹)	PDI^b
CPAEN(PPL)	19 230	11 470	1.68
CPAEN(RS/PPL)	11 360	5850	1.94
CPAEN(HQ/PPL)	65 580	46 180	1.42
CPAEN(BPA/PPL)	76 970	51 680	1.49
CPAEN(PP/PPL)	55 970	34 170	1.64

^a Determined by GPC *vs.* polystyrene standards in THF. ^b Polydispersity index, $PDI = M_w/M_n$.

CPAEN(HQ/PPL) different from other CPAENs were observed at 1130 cm⁻¹ (Fig. 1b) and 1191 cm⁻¹ (Fig. 1c), respectively, which can be attributed to the skeletal vibrations of the phenoxy group in RS-units and HQ-units, respectively.³³ The characteristic absorption band of CPAEN(BPA/PPL) was found at 2969 cm⁻¹ (Fig. 1d), corresponding to the stretching vibration of C–H in methyl groups. A sharp and strong characteristic absorption band at 1770 cm⁻¹ was obtained in CPAEN(PP/PPL) (Fig. 1e), arising from the stretching vibration of C=O of lactone rings in phenolphthalein.³⁴

The structural properties of CPAENs were also studied by liquid phase ¹H NMR spectroscopy with DMSO- d_6 as the solvent. As examples, the typical ¹H NMR spectra of CPAEN(PPL) and CPAEN(BPA/PPL) are shown in Fig. 2a and b, respectively. A characteristic peak at $\delta = 12.98$ ppm represented the carboxyl proton in the PPL-unit, and the proton attached to the tertiary carbon of the PPL-unit was identified at 6.71 ppm,

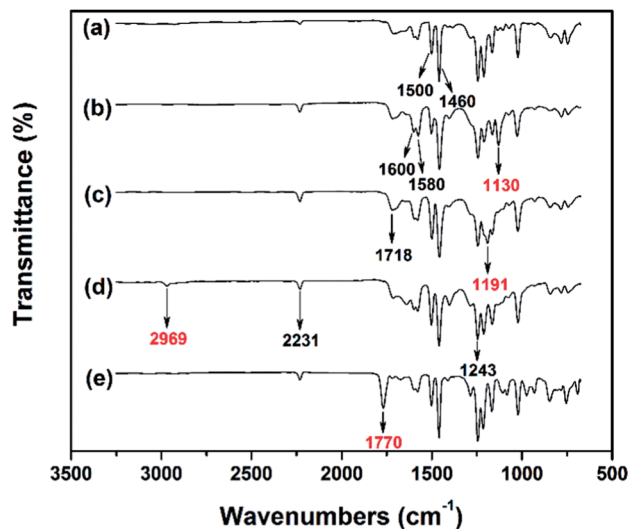


Fig. 1 FTIR spectra of carboxyl-functionalized poly(arylene ether nitrile)s: (a) CPAEN(PPL), (b) CPAEN(RS/PPL), (c) CPAEN(HQ/PPL), (d) CPAEN(BPA/PPL), and (e) CPAEN(PP/PPL).

which suggested that the copolymers had the structure of PAENs with a pendant carboxyl functional group. The chemical shift at $\delta = 6.54\text{--}7.83$ ppm can be assigned to the protons on phenyl rings. An intense characteristic peak at $\delta = 1.67$ ppm resulted from the methyl protons in the BPA-unit. Furthermore, the intensity of the distinct signal of six methyl protons in the BPA-unit is 5.31 (*i.e.*, peak c in Fig. 2b), and the intensity of the proton attached to the tertiary carbon of the PPL-unit is 0.92 (*i.e.*, peak i in Fig. 2b). Therefore, the ratio of the BPA-unit to the PPL-unit in CPAEN(BPA/PPL) can be estimated to be 0.49 to 0.51, which is in good agreement with the feed ratio.

Thermal properties

Thermally induced phase transition behavior of CPAENs was examined by DSC over two heating cycles under a nitrogen atmosphere (Fig. 3). The glass transition temperatures (T_g s) of CPAENs were found to be in the range of 181–251 °C, which are much higher than that of the commercial PEN-ID300® ($T_g = 148$ °C).¹⁷ Furthermore, the T_g s progressively increased from CPAEN(RS/PPL), CPAEN(HQ/PPL), CPAEN(BPA/PPL), CPAEN(PPL) to CPAEN(PP/PPL), depending primarily on the rigidity and flexibility of structural units and their contents in the copolymers. Clearly, the CPAEN(PP/PPL) showed the highest T_g (251 °C) due to the presence of PP-units, which have a higher rigidity than other structural units due to the lactone ring structure. In comparison, the PPL-units carry a relatively lower rigidity than PP-units due to the internal rotation of benzoyloxy hanging on the tertiary carbon and flexible side groups (*i.e.*, carboxyl group). This resulted in a lower T_g of CPAEN(PPL) (237 °C) than that of CPAEN(PP/PPL). The T_g of CPAEN(HQ/PPL) (202 °C) is slightly higher than that of CPAEN(RS/PPL) (181 °C) because of the greater symmetry of the HQ-unit than the RS-unit.³³ Furthermore, according to the previous reports,^{10,33} the T_g s of PAEN(RS), PAEN(HQ), PAEN(BPA) and PAEN(PP) without the addition of PPL-units are 145 °C, 175 °C, 178 °C and

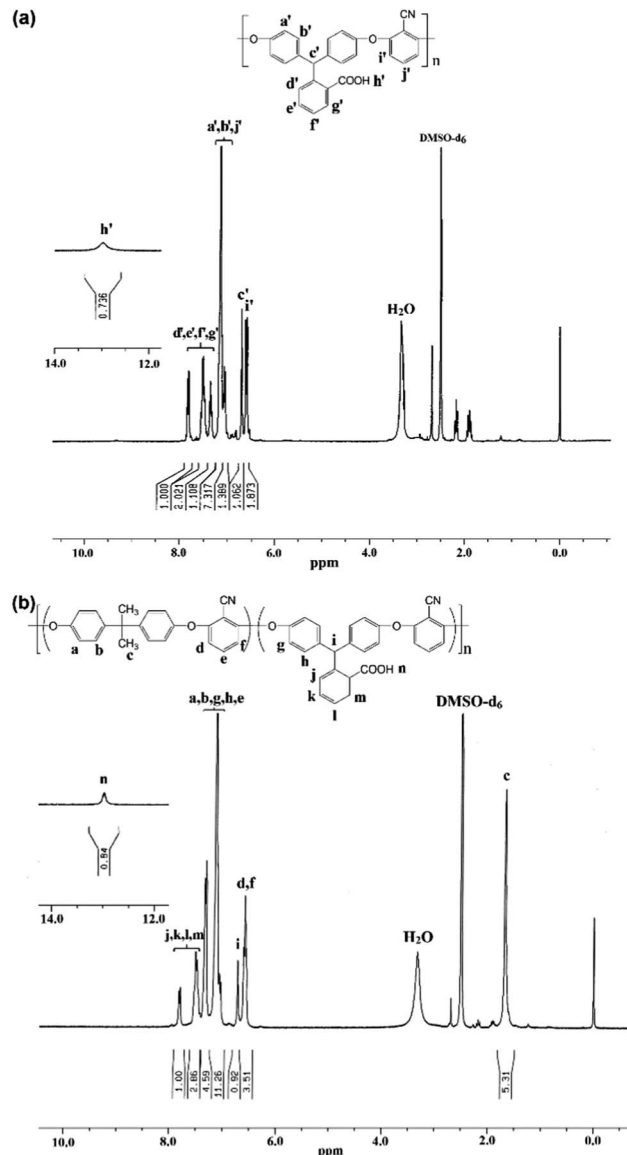


Fig. 2 ^1H NMR spectra of (a) CPAEN(PPL) and (b) CPAEN(BPA/PPL).

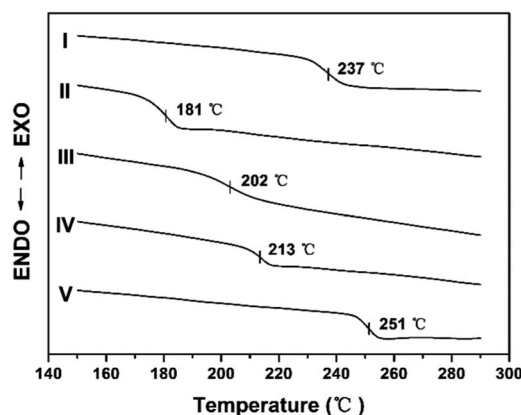


Fig. 3 DSC curves of carboxyl-functionalized poly(arylene ether nitrile)s (CPAENs). I: CPAEN(PPL); II: CPAEN(RS/PPL); III: CPAEN(HQ/PPL); IV: CPAEN(BPA/PPL) and V: CPAEN(PP/PPL).

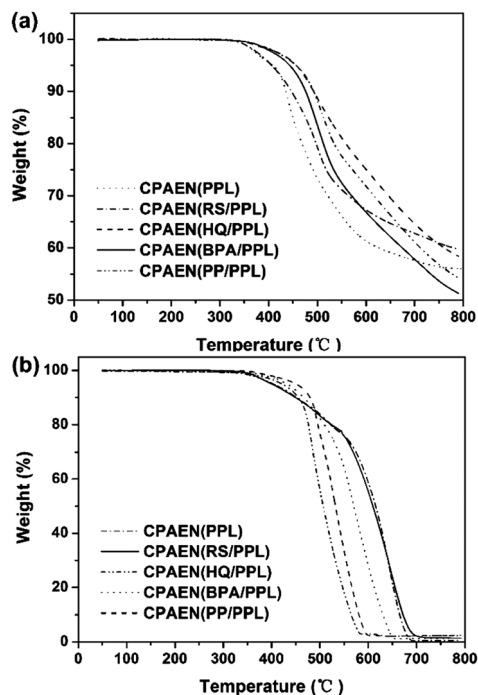


Fig. 4 TGA curves of carboxyl-functionalized poly(arylene ether nitrile)s (CPAENs) under (a) nitrogen and (b) air atmospheres, respectively.

260 °C, respectively. This signified that the incorporation of PPL-units into the polymers increased their T_g s, except CPAEN(PP/PPL), which can be rationalized on the basis of rigidity of the triphenylmethane structure of the PPL-unit.

The thermal stabilities of CPAENs were evaluated by TGA under both nitrogen and air atmospheres (Fig. 4). As summarized in Table 2, the decomposition temperatures at 5% weight loss ($T_{5\%}$) under nitrogen and air atmospheres were in the range of 407–457 °C and 400–450 °C, respectively. For 10% weight loss ($T_{10\%}$), the decomposition temperatures under nitrogen and air atmospheres ranged from 435 °C to 493 °C and from 449 °C to 480 °C, respectively. The char yields (CYs) at 800 °C under nitrogen for CPAENs were in the range of 51–59 wt%. The high char yield of these copolymers under nitrogen can be ascribed to their high aromatic contents. Taken together, these results indicated that all CPAENs possessed excellent thermal stabilities.

Table 2 Thermal stability of carboxyl-functionalized poly(arylene ether nitrile)s (CPAENs)

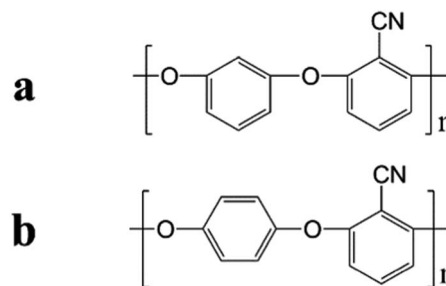
Polymer	In nitrogen			In air	
	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	CY ^a (%)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)
CPAEN(PPL)	408	435	56	403	451
CPAEN(RS/PPL)	407	448	59	400	449
CPAEN(HQ/PPL)	450	489	58	422	456
CPAEN(BPA/PPL)	444	476	51	432	466
CPAEN(PP/PPL)	457	493	54	450	480

^a Char yield at 800 °C in the nitrogen atmosphere.

Table 3 Solubility of carboxyl-functionalized poly(arylene ether nitrile)s (CPAENs)^{a,b}

Polymer	NMP	DMF	DMAc	DMSO	THF	CHCl ₃	Toluene
CPAEN(PPL)	++	++	++	++	++	–	–
CPAEN(RS/PPL)	++	++	++	++	++	–	–
CPAEN(HQ/PPL)	++	++	++	++	+	–	–
CPAEN(BPA/PPL)	++	++	++	++	+	–	–
CPAEN(PP/PPL)	++	++	++	++	+	–	–
Ref. 33	+–	–	–	–	–	–	–

^a Solubility was tested with a 20 mg polymer in 1 mL of solvent. ^b The symbols denote the follow meanings: ++, fully soluble at room temperature; +, fully soluble on boiling temperature; +–, partially soluble on boiling temperature and –, insoluble on boiling temperature.



Scheme 3 Structures of reference PAENs in ref. 33.

Solubility

The solubility of CPAENs in common organic solvents is summarized in Table 3. Obviously, all CPAENs were readily dissolved in strong polar aprotic solvents, such as NMP, DMF, DMAc, DMSO at room temperature. Even in intermediate polar solvents, for example THF, CPAENs also showed good solubility. We note that according to the measurements performed by ourselves as well as described in the literature,³³ the PAEN consisting of RS-units (a in Scheme 3) and PAEN containing HQ-units (b in Scheme 3) showed very poor solubility in commonly used organic solvents. They were found to be only partially soluble in NMP at boiling temperature. This suggested that the incorporation of PPL-units into the polymer chain markedly improved the solubility of polymers, which may be attributed to the following two aspects: (1) the pendant benzoyloxy groups in PPL-units prevent the polymer chains from closely packing, thereby allowing the solvent molecules to diffuse into the polymer chains; and (2) the introduction of strong polar groups (*i.e.*, carboxyl groups) improve the solubility of the polymers in polar solvents, based on the solubility principle of “like dissolves like”; consequently, the CPAENs have poor solubility (even insoluble) in nonpolar or weakly polar solvents, such as CHCl₃ and toluene.

Crystallization and mechanical properties

The crystallization behaviors of CPAENs were investigated by means of wide-angle X-ray diffraction (WAXD) at room temperature. As evidenced in Fig. 5, the WAXD diffractograms displayed almost completely amorphous diffraction patterns,

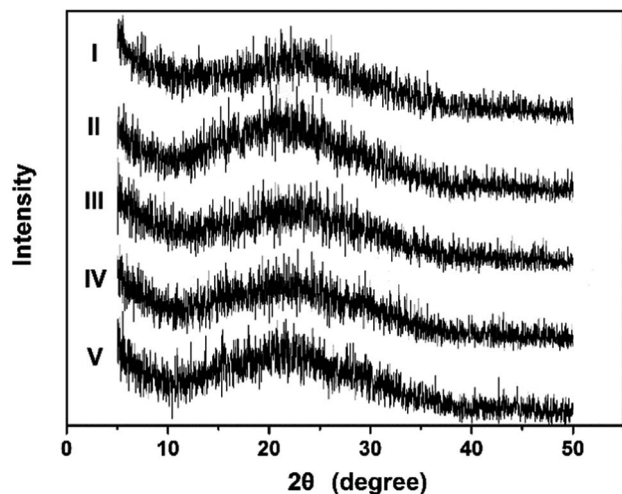


Fig. 5 WAXD diffractograms of carboxyl-functionalized poly(arylene ether nitrile)s (CPAENs). I: CPAEN(PPL); II: CPAEN(RS/PPL); III: CPAEN(HQ/PPL); IV: CPAEN(BPA/PPL) and V: CPAEN(PP/PPL).

Table 4 Mechanical properties of carboxyl-functionalized poly(arylene ether nitrile)s (CPAENs)

Polymer	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)	Film state
CPAEN(PPL)	75.1	3.5	2.6	Flexible
CPAEN(RS/PPL)	— ^a	— ^a	— ^a	Brittle
CPAEN(HQ/PPL)	99.3	5.9	2.8	Flexible
CPAEN(BPA/PPL)	83.1	4.4	2.9	Flexible
CPAEN(PP/PPL)	104.7	5.0	3.2	Flexible

^a The polymer film is too brittle to be measured.

which is consistent with the DSC studies where all CPAENs did not show any melting and crystallization peaks (Fig. 3). The amorphous nature can be ascribed primarily to the introduction of the PPL-units that produced a wider separation of polymer chains, thereby lowering chain packing efficiency with a gain of free volume. It is worth noting that the amorphous structure of all CPAENs was also reflected in their good solubility (Table 3).

Due to the good solubility in common organic solvents and high molecular weight, all CPAENs can be easily cast into transparent, tough and flexible films from NMP solution, except CPAEN(RS/PPL) which had low molecular weight. Their tensile properties, including tensile strength, elongation at break and tensile modulus, determined from the stress-strain curves are summarized in Table 4. The tensile strength and the elongation at break were in the range of 75.1–104.7 MPa and 3.5–5.9%, respectively. As compared to the analogous poly(arylene ether nitrile)s without PPL-units,^{35,36} the obtained CPAENs exhibited relatively lower tensile properties. This may be due to the presence of the bulky pendant benzoyloxy groups in PPL units, which increases the distance of polymer chains and reduces the intermolecular interactions. Moreover, the CPAEN(PP/PPL) exhibited the best tensile properties with a tensile strength of

104.7 MPa and a tensile modulus of 3.2 GPa, which was due most likely to the rigidity, contributed by the PP-unit.

Optical properties

The optical properties of CPAENs in NMP solutions were explored by UV-vis absorption and fluorescence emission spectroscopies. As shown in Fig. 6a, owing to the high aromatic content, all CPAENs exhibited a highly intense UV absorption band in the wavelength region of 280–330 nm, with an absorption maxima at approximately 315 nm, which can be attributed to the $\pi \rightarrow \pi^*$ electronic transition of aromatic rings.³⁷ The fluorescence emission spectra of CPAENs due to the short lifetime of the excited state are shown in Fig. 6b. The CPAENs exhibited a characteristic emission band in the solution state, with the emission maxima at 425 nm for CPAEN(PPL), 415 nm for CPAEN(BPA/PPL) and 427 nm for other three CPAENs. This may be ascribed to the fact that the triphenylmethane structure can be transformed into a stable triphenylmethyl radical, which is delocalized over the surrounding three benzene rings.^{38,39} A slight blue shift (10–12

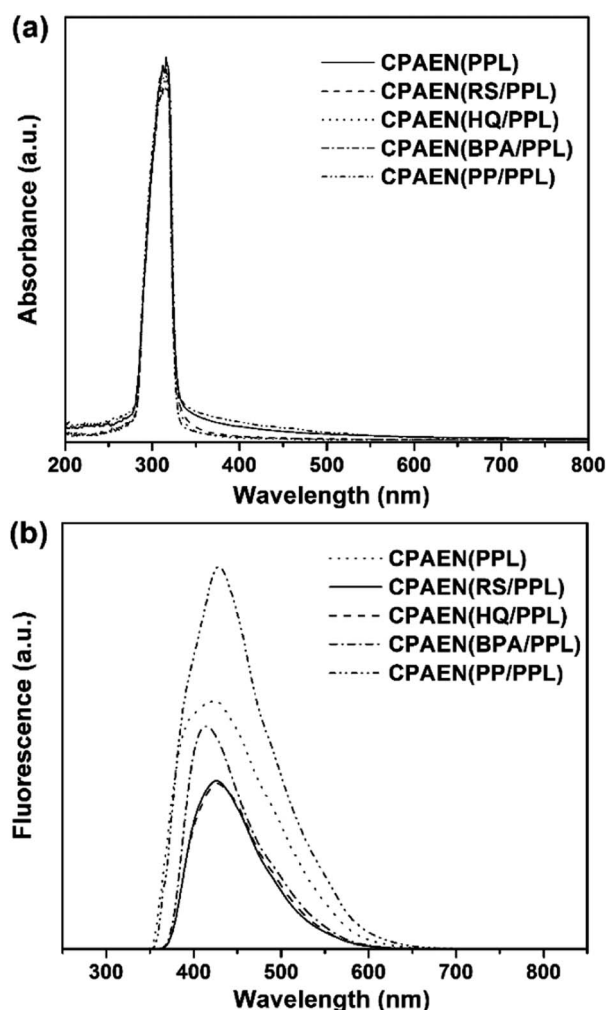


Fig. 6 (a) UV-vis absorption, and (b) fluorescence emission spectra of carboxyl-functionalized poly(arylene ether nitrile)s (CPAENs).

nm) was observed for CPAEN(BPA/PPL) as compared with other CPAENs. The CPAEN solutions were colorless and transparent under visible light, and emitted blue fluorescence under the UV irradiation at 365 nm (Fig. S3†).

Conclusions

In summary, a class of novel carboxyl-functionalized poly(arylene ether nitrile)s (CPAENs) with different structures have been successfully synthesized by the nucleophilic substitution polycondensation reactions by employing a carboxyl-functionalized monomer. Quite intriguingly, the incorporation of PPL-units into the polymers not only greatly improved their solubility, but also markedly raised their glass transition temperatures. All CPAENs were amorphous and exhibited excellent thermal and mechanical properties. They displayed a highly intense UV absorption and possessed a blue fluorescence under the UV irradiation. These remarkable characteristics suggested that the CPAENs can be considered not only as new promising candidates for processable high-performance engineering plastics, but also as potential functional materials. The CPAENs may also be exploited as reactive polymers to yield a large variety of functional derivatives possessing other additional properties by their reacting carboxyl groups in CPAENs. Further investigations on the functionalization of CPAENs are currently underway.

Acknowledgements

We gratefully acknowledge funding support from the 863 National Major Program of High Technology of China (2012AA03A212) and National Natural Science Foundation of China (no. 51173021, no. 51373028).

Notes and references

- 1 P. Hergenrother, B. Jensen and S. Havens, *Polymer*, 1988, **29**, 358–369.
- 2 Y. Qi, J. Ding, M. Day, J. Jiang and C. L. Callender, *Chem. Mater.*, 2005, **17**, 676–682.
- 3 R. K. Nagarale, W. Shin and P. K. Singh, *Polym. Chem.*, 2010, **1**, 388–408.
- 4 T. J. Peckham and S. Holdcroft, *Adv. Mater.*, 2010, **22**, 4667–4690.
- 5 W. Wang, X. Lu, Z. Li, J. Lei, X. Liu, Z. Wang, H. Zhang and C. Wang, *Adv. Mater.*, 2011, **23**, 5109–5112.
- 6 L. Cheng, K. Han, K. Xu, M. R. Gadinski and Q. Wang, *Polym. Chem.*, 2013, **4**, 2436–2439.
- 7 A. Saxena, V. Rao and K. Ninan, *Eur. Polym. J.*, 2003, **39**, 57–61.
- 8 S. R. Sheng, W. Zhang, S. P. Huang, B. Wang and C. S. Song, *Polym. Adv. Technol.*, 2012, **23**, 441–446.
- 9 Y. Zhan, X. Yang, H. Guo, J. Yang, F. Meng and X. Liu, *J. Mater. Chem.*, 2012, **22**, 5602–5608.
- 10 H. Tang, J. Yang, J. Zhong, R. Zhao and X. Liu, *Mater. Lett.*, 2011, **65**, 2758–2761.
- 11 T. Takahashi, H. Kato, S. Ma, T. Sasaki and K. Sakurai, *Polymer*, 1995, **36**, 3803–3808.
- 12 Y. Gao, G. P. Robertson, D. S. Kim, M. D. Guiver, S. D. Mikhailenko, X. Li and S. Kaliaguine, *Macromolecules*, 2007, **40**, 1512–1520.
- 13 Y. Gao, G. P. Robertson, M. D. Guiver, S. D. Mikhailenko, X. Li and S. Kaliaguine, *Macromolecules*, 2005, **38**, 3237–3245.
- 14 H. Zhang, D. Wang, A. Li, X. Li and Z. Jiang, *J. Membr. Sci.*, 2005, **264**, 56–64.
- 15 H. Tang, X. Huang, X. Yang, J. Yang, R. Zhao and X. Liu, *Mater. Lett.*, 2012, **75**, 218–220.
- 16 Y. Gao, G. P. Robertson, M. D. Guiver, S. D. Mikhailenko, X. Li and S. Kaliaguine, *Polymer*, 2006, **47**, 808–816.
- 17 G. Yu, C. Liu, J. Wang, G. Li, Y. Han and X. Jian, *Polymer*, 2010, **51**, 100–109.
- 18 M. Tanaka, M. Koike, K. Miyatake and M. Watanabe, *Polym. Chem.*, 2011, **2**, 99–106.
- 19 Y. Chang, G. F. Brunello, J. Fuller, M. L. Disabb-Miller, M. E. Hawley, Y. S. Kim, M. A. Hickner, S. S. Jang and C. Bae, *Polym. Chem.*, 2013, **4**, 272–281.
- 20 D. W. Shin, S. Y. Lee, N. R. Kang, K. H. Lee, M. D. Guiver and Y. M. Lee, *Macromolecules*, 2013, **46**, 3452–3460.
- 21 D. S. Kim, Y. S. Kim, M. D. Guiver and B. S. Pivovar, *J. Membr. Sci.*, 2008, **321**, 199–208.
- 22 Y. S. Kim, D. S. Kim, B. J. Liu, M. D. Guiver and B. S. Pivovar, *J. Electrochem. Soc.*, 2008, **155**, B21–B26.
- 23 Y. Sakaguchi, S. Takase, K. Omote, Y. Asako and K. Kimura, *J. Macromol. Sci., Part A: Pure Appl. Chem.*, 2013, **50**, 879–884.
- 24 X. Zhao, G. Zhang, Q. Jia, C. Zhao, W. Zhou and W. Li, *Chem. Eng. J.*, 2011, **171**, 152–158.
- 25 D. Zeng, J. Cheng, S. Ren, J. Sun, H. Zhong, E. Xu, J. Du and Q. Fang, *React. Funct. Polym.*, 2008, **68**, 1715–1721.
- 26 D. Liu and Z. Wang, *Polymer*, 2008, **49**, 4960–4967.
- 27 D. Liu, Z. Wang, H. Yu and J. You, *Eur. Polym. J.*, 2009, **45**, 2260–2268.
- 28 C. Wang and S. Nakamura, *J. Polym. Sci., Part A: Polym. Chem.*, 1995, **33**, 2157–2163.
- 29 M. G. Zolotukhin, H. M. Colquhoun, L. G. Sestiaa, D. R. Rueda and D. Flot, *Macromolecules*, 2003, **36**, 4766–4771.
- 30 T. Fukushima, K. Hosokawa, T. Oyama, T. Iijima, M. Tomoi and H. Itatani, *J. Polym. Sci., Part A: Polym. Chem.*, 2001, **39**, 934–946.
- 31 T. F. Al-Azemi and K. S. Bisht, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**, 1267–1274.
- 32 Z. Li, F. Dong, L. Xu, S. Wang and X. Yu, *J. Membr. Sci.*, 2010, **351**, 50–57.
- 33 A. Saxena, R. Sadhana, V. Rao, M. Kanakavel and K. Ninan, *Polym. Bull.*, 2003, **50**, 219–226.
- 34 Z. Wang, T. Chen and J. Xu, *J. Appl. Polym. Sci.*, 1997, **63**, 1127–1135.
- 35 S. Matsuo, T. Murakami and R. Takasawa, *J. Polym. Sci., Part A: Polym. Chem.*, 1993, **31**, 3439–3446.
- 36 V. Lakshmana Rao, A. Saxena and K. Ninan, *J. Macromol. Sci., Polym. Rev.*, 2002, **42**, 513–540.
- 37 G. Venugopal, X. Quan, G. Johnson, F. Houlihan, E. Chin and O. Nalamasu, *Chem. Mater.*, 1995, **7**, 271–276.
- 38 M. Gomberg, *J. Am. Chem. Soc.*, 1900, **22**, 757–771.
- 39 M. Gomberg, *J. Am. Chem. Soc.*, 1901, **23**, 496–502.