

Soluble and Thermally Stable Copoly(Phenyl-s-triazine)s Containing both Diphenylfluorene and Phthalazinone Units in the Backbone

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Abstract A series of novel copoly(phenyl-s-triazine)s were prepared by solution polycondensation of 2,4-bis(4-fluorophenyl)-6-phenyl-1,3,5-s-triazine (BFPT) with 9,9-bis(4-hydroxyphenyl)fluorene (BHF) and 4-(4-hydroxyphenyl)(2H)-phthalazin-1-one (HHPZ) to investigate the effects of bulky diphenylfluorene units on solubility as well as thermal and mechanical properties. The synthetic procedure was efficiently optimized, resulting in high M_n up to 4.3×10^4 g/mol in GPC. Moreover, the introduction of diphenylfluorene moieties in the main chains leads to the outstanding modification in the solubility of the copolymers in common organic solvents, such as chloroform, chlorobenzene (CB) and *N*-methylpyrrolidone (NMP). Simultaneously, the copolymers exhibit remarkable dimensional stability as evidenced by DMA, and maintain excellent thermal properties with glass transition temperatures (T_g s) ranging from 307 °C to 340 °C, 5% mass-loss temperatures lying between 525 °C and 551 °C, and char yields at 800 °C higher than 55% in N₂. Their solubility increases with the increase of diphenylfluorene content in the polymer backbone, and the thermal properties just decrease slightly. The films obtained via solution casting technology possess commendable mechanical properties, even at elevated temperatures.

Keywords: Poly(phenyl-s-triazine)s Diphenylfluorene Phthalazinone Solubility Thermal stability

Introduction

Poly(arylene ether)s (PAEs) is one of the most important classes of high-performance polymers that have attracted much attention in recent years. These materials can be used as structural materials in automotive, aerospace, microelectronic industries [1-6] and polymer electrolyte membrane fuel cells [7-11] for possessing a combination of interesting properties, such as excellent mechanical strength per unit weight, highly thermal stability and good insulating properties.

In the research of PAEs, the PAEs bearing rigid phenyl-s-triazine rings (PAEPs) in the main chain are particularly valuable as thin membranes for fuel cells [12,13] and matrix resins for advanced composites [14,15], especially at elevated temperature applications, due to the merits brought by the high resonance energy of the phenyl-s-triazine units. Simultaneously, the high electron affinity and structural symmetry of the phenyl-s-triazine units in favor of electron injection and transport encouraged the researchers to explore their application in electroluminescent devices [16-18]. However, the plane-structural characteristic of phenyl-s-triazine units, in general, has limited solubility in common organic solvents, even with the incorporation of flexible ether linkages [18]. Additionally, gels always take place in the later stage of their polymerization. Thus, the high molecular

weights of poly(aryl ether phenyl-s-triazine)s were hardly attained.

As known, most high performance polymers composed of rigid rod-like main chain are extremely difficult to be dissolved in normal organic solvents or hardly to be melt processed due to their highly rigid molecular structure. Modifying the solubility of the polymers is a more feasible alternative than enhancing the fusion processing property [19]. Introducing flexible linkages [20] or polar pendent groups [21-24] into the polymer backbone is a commonly synthetic strategy for improving the solubility of PAEs. Tigelaar D M and cooperators [12] reported the effects of flexible sulfone bonds and pendant groups bonding to phenyl of the phenyl-s-triazine ring in poly(arylene ether sulfone)s on solubility. The results showed that the polymers with more bulky branching groups like diphenylamine group displayed better solubility, for instance in NMP, allowing formation of high molecular weight polymers, unfortunately, with sacrificing the thermal properties of PAEs.

Incorporating heterocyclic structure into the main chain has been proved to be an effective approach to promote the comprehensive properties of PAEs, especially mechanical properties and thermal stability with improving the solubility for some kinds of polymers with the large bulky heterocyclic structure in polymer backbone. Considerable research has been focused towards developing soluble PAEs with novel heterocyclic structures for broadening the applications of PAEs. Lu and coworkers [25] investigated the solubility of the poly(arylene ether)s derived from two kinds of biphenols, the rigid symmetric 2,5-bis(4-hydroxy-4-biphenyl)-1,3,4-oxadiazole (named as biphenol 3) and unsymmetrical 2,2'-bis(2-hydroxyphenyl)-p-quaterphenyl (named as biphenol 4). Poly(arylene ether) homopolymers prepared from biphenol 4 could be soluble in common organic solvents, while the homopolymers prepared from biphenol 3 were completely insoluble. A series of polymers containing phenyl-phthalazinone segments have been established in Hay and our group in the past few years. [26-29]. Phthalazinone-containing polymers have good solubility in some organic solvents like *N,N*-dimethyl acetamide (DMAc), chloroform, *N*-methyl pyrrolidone (NMP), owing to the twist non-coplanar special structure of the phthalazinone moieties in the polymers to hinder the close packing of the polymers chains, enlarge the average intermolecular distance of the polymers and enable solvent molecules to diffuse easily into the polymer chains [29]. Yu etc then explored the homopolymers containing phthalazinone and phenyl-s-triazine ring in the main chain of the polymer. Unfortunately, no high molecular weight polymer was obtained due to precipitation during polymerization [30]. This suggested that the huge rigid plane of phenyl-s-triazine ring weakened the role of phthalazinone segment.

Diphenylfluorene is a bulky moiety. Bae and coworkers [31] estimated its approximate molecular size via semiempirical molecular orbital calculation. The plane of the hydroxyphenyl units runs vertically rather than horizontally to the fluorene plane in 3D (Scheme 1). As a result, the polymers containing diphenylfluorene units were generally soluble in most of solvents [32-34], while maintaining the thermal stabilities [35]. To the best of our knowledge, there is little research on introducing diphenylfluorene moieties into the backbone of poly(aryl ether phenyl-s-triazine)s.

In this paper, we describe the synthesis of novel polymeric phenyl-s-triazines containing diphenylfluorene and phthalazinone moieties. The effects of the introduction of diphenylfluorene moieties on the solubility, thermal and mechanical properties as well as crystallinity of the copolymers were investigated in details. Additionally, several factors that would affect the molecular weight of the polymers were also discussed.

Experimental

Materials

2-Phenyl-4,6-bis(4-fluorophenyl)-1,3,5-triazine (BFPT) was synthesized according to the procedure reported previously [18]. The product was recrystallized from toluene, and white long thin needle crystal was obtained and ground before used; m.p.: 260.2-260.8 °C; purity: 99 wt%. The product was confirmed by MALDI-TOF/MS (M+ Calcd. as C₂₁H₁₃N₂F₂ 345.1078): m/z=345.1067(M+).

4-(4-Hydroxyphenyl)(2H)-phthalazin-1-one (HHPZ) was prepared as white powder by the method reported [36]. m.p.: 310.0-310.8 °C; yield: 90 wt%; purity: 99 wt%; MALDI-TOF/MS. (M+ Calcd. as C₁₄H₁₀O₂N₂ 238.0742): m/z =238.0750 (M+).

9,9-Bis(4-hydroxyphenyl)fluorene (BHF) was purchased from Suqian ever-galaxy pharma & Chem Co., Ltd. and used without further purification. Purity: 99.6 wt%.

Anhydrous potassium carbonate (Beijing Chemical Co., A.R.) was ground and dried in vacuum at 100 °C for 24 h before used. *N*-methyl pyrrolidone (NMP) (Tianjin Chemical Co., A.R.) was refluxed with CaH₂ for 2 h, and then vacuum distilled. The 125-127 °C boiling range fractions were collected, and stored over molecular sieves (type 4Å). Chloroform, *N,N*-dimethyl acetamide (DMAc), *N,N*-dimethyl formamide (DMF), pyridine and toluene were purchased from Tianjin Chemical Co., while alcohol and isopropanol were obtained from Damao Chemical Co. All of organic solvents and other chemicals were analytical grade and used as received.

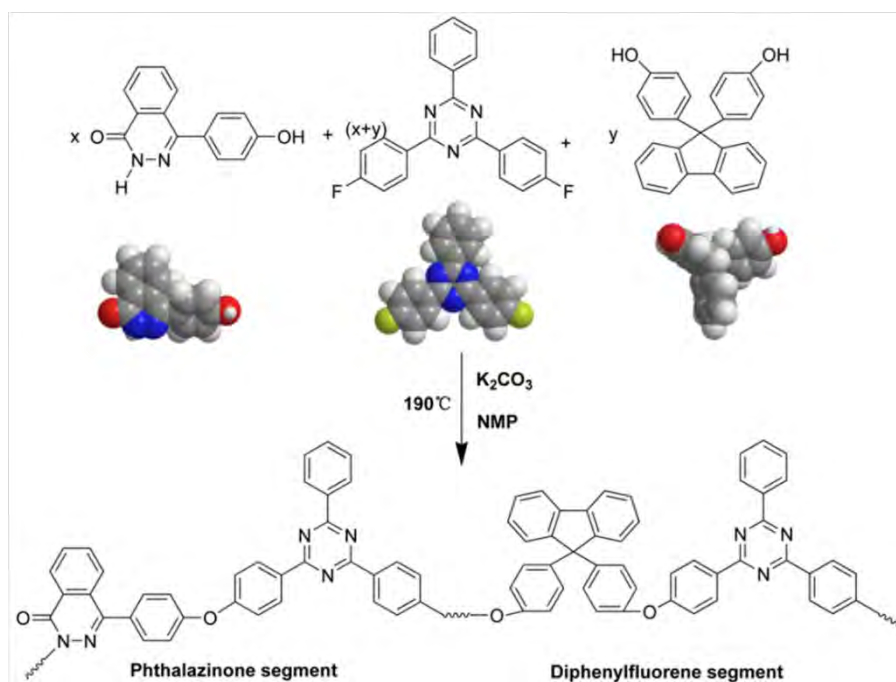
Characterization

Inherent viscosities (η_{inh}) of the polymers were measured using a Ubbelohde capillary viscometer at a concentration of 0.5 g dL⁻¹ in NMP at 25 °C. Fourier transform infrared (FT-IR) measurements were performed with a Thermo Nicolet Nexus 470 FT-IR spectrometer. ¹H-NMR (400 MHz), ¹H ¹H gCOSY NMR (400 MHz) and ¹³C-NMR (100 MHz) spectra were recorded with a Varian Unity Inova 400 spectrometer using CDCl₃ as a solvent and listed in parts per million downfield from tetramethylsilane (TMS). High performance liquid chromatogram (HPLC) was performed on a Hewlett-Packard (HP) 1100 liquid chromatography using a mixture of acetic acid (0.1 wt%) and methanol (v/v ¼ 90:10) as eluting solvent and a 2.0×150 mm Microbore column (Waters Spherisorb® S5 ODS2) as column. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) analyses were performed on a Micromass GC-TOF CA 156 MALDI-TOF/MS instrument. Elemental analyses were conducted on a Vario ELIII CHNOS Elementaranalysator from Elementaranalysesysteme GmbH for C, H and N determinations. Gel permeation chromatography (GPC) analyses were carried out on a HP 1090 HPLC instrument equipped with 5 mm Phenogel columns (linear, 4×500 Å) arranged in series with NMP as solvent calibrated with polystyrene standards. The glass transition temperatures (T_g s) were determined using a TA Q20 instrument at a heating rate of 10 °C/min under a nitrogen flow of 50 mL/min. The T_g values are reported from the second scan after first heating and quenching, and taken from the midpoint of the change in the slope of the baseline. Dynamic mechanical analysis (DMA) measurements were carried out on with a TA Q800 instrument at 1 Hz and heating rate of 3 °C/min under nitrogen atmosphere using a 40×6×0.02 mm³ film. In order to characterize the dynamic mechanical properties, mechanical damping tan δ , storage modulus E' and loss modulus E'' were all recorded. Thermal Gravimetric Analysis (TGA) was obtained from a TA Q500 instrument at a heating rate of 20 °C/min⁻¹ in N₂. Mechanical property measurements were determined using an Instron-5869 machine with a capacity of 100 N at a strain rate of 2 mm min⁻¹ on solution-cast film samples. Wide-angle X-ray diffraction (WAXD) was performed at room temperature on a Rigaku D/max 2400 automatic X-ray diffractometer with Ni-filtered Cu K α radiation (40 kV, 100

mA).

Polymerization

Herein the polymerization reaction of poly(aryl ether phenyl-s-triazine)s (Scheme 1) containing phthalazinone and diphenylfluorene moieties with the molar ratio of HHPZ and BHF as 1:1, named as PAEP5050, was selected to describe the general procedure of polymerization as follows. A 100mL round-bottomed flask was charged with HHPZ (1.9059g, 8.0mmol), BHF (2.8033g, 8.0mmol), BFPT (5.5254g, 16.0mmol), potassium carbonate (2.6536g, 19.2 mmol), 7.7mL of NMP (solid concentration is 1.3g/mL) and 15mL toluene. The reaction was carried out at 140-150 °C for 3h with Dean-Stark trap by rigorously stirring in order to remove the water produced in the phenolate formation by azeotroped with toluene. A nitrogen flow was maintained to protect the phenolate from oxidation. Then, the reaction temperature was elevated to 165 °C to eliminate excess toluene, followed by heating the resulting mixture to 190 °C and keeping for 7h until the viscosity of the reaction system had no obvious increase. A number of solvents were required to join to the system. Subsequently, the resultant viscous solution was slowly poured into hot distilled water with stirring to precipitate the polymer. The crude polymers were boiled several times with distilled water to remove solvent and inorganic salts. After dried in the vacuum oven, the polymers were dissolved in NMP, followed by filtering through a thin layer of celite. The polymer solution obtained was slowly poured into ethanol with stirring, in order to attain a kind of flocculent product. After filtered and rinsed with hot water, the purified polymer was dried at 120 °C under vacuum for 24h. The yield of PAEP5050 was 94%. IR (ATR, cm^{-1}): 2927(=C-H), 1675(C=O), 1592, 1519, 1496 (C=C or C=N), 1446, 1365 (C-N, triazine parts), 1416 (C-H, in-plane bending), 1301 (C-C), 1242, 1162 (C-O-C), 1016 (C-N, phthalazinone parts). $^1\text{H-NMR}$ (400MHz, CDCl_3 , ppm) δ : 8.87-8.76 (s, 1H), 8.76-8.53 (s, 26H), 8.05-7.94 (s, 1H), 7.83-7.69 (s, 8H), 7.69-7.59 (s, 1H), 7.59-7.45 (s, 13H), 7.45-7.38 (s, 6H), 7.38-7.31 (s, 6H), 7.31-7.25 (s, 6H), 7.25-7.12 (s, 14H), 7.12-6.99 (s, 16H), 6.99-6.86 (s, 14H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , ppm) δ : 171.37, 170.77, 161.23, 155.04, 154.72, 151.04, 141.47, 140.20, 139.92, 136.24, 132.54, 131.30, 130.99, 130.70, 129.78, 129.46, 128.83, 128.54, 127.91, 127.59, 126.07, 125.44, 120.52, 119.60, 119.29, 118.66, 118.05, 64.43. Elem. Anal. Calcd. for PAEP5050 ($\text{C}_{81}\text{H}_{50}\text{N}_8\text{O}_4$)_n (1199.31)_n: C, 81.12; H, 4.20; N 9.34%. Found: C, 79.38; H, 4.41; N, 9.39%.



Scheme 1 Synthesis of PAEPs via a step-growth solution polycondensation and 3D structural patterns of the monomers used.

Films preparation

All PAEPs films were readily prepared by casting techniques. A typical procedure was carried as follows. Purified copolymers (0.8-1.0 g) were dissolved in 10 mL NMP and evenly dispersed by stirring to give transparent solutions (8-10%, w/v). The films were cast from the solutions on glass plates and dried in an oven of 60 °C for 4 h, at 100 °C for two weeks under the well-ventilated environment. The resulting clear films were stripped from the substrates for WAXD and tensile tests.

Results and discussion

Polymer synthesis

PAEPs could be readily derived from a step-growth solution polycondensation of the BFPT, HHPZ and BHF. The fluorine in BFPT monomer towards the S_{NAr} reaction was activated by the electron withdrawing group *s*-triazine unit. NMP was chosen as the reaction solvent because it is a favorable reaction mediate for the synthesis of phenyl-*s*-triazine containing polymers with adequate solubility and reaction temperature. A one-step feed method was adopted, that is HHPZ, BHF and BFPT were added into reaction flask together. As commonly, the activated BFPT monomer in nucleophilic displacement reaction system might be denaturalized to 2,4-bis(4-hydroxyphenyl)-6-phenyl-1,3,5-*s*-triazine (BHPT) in alkali and microdose water environment [37]. Herein experiment was designed to examine whether denaturation of BFPT monomer occurred or not in our system. To a three-necked flask equipped with nitrogen inlet and condenser were added BFPT, K_2CO_3 , toluene and a drop of water. The mixture was heated to reflux for 4 h. The resulting solution was cooled down to room temperature. The product was collected by filter and then rinsed with distilled water for several times to remove the salt, followed by detected via TOF-MS instrument for the accurate mole mass. As Fig. 1 shows, only $m/z=345.1077$ peak belonging to BFPT ($m/z=345.34$) can be observed, whereas the molecular weight of BHPT ($m/z=341.36$) is absent. The results show that BFPT is stable during phenolate-forming process. Accordingly, one-step feed method is feasible.

The favorable reacting temperature was also investigated. According to the previous reports [38], high reaction temperature like exceeding 180 °C could suppress the different reactivity of O-H group and N-H group in HHPZ monomer. Thus, the reaction temperature was selected as 190 °C and 200 °C to investigate its effect on the reaction procedure via monitoring the increase of the molecular weight of the polymer for each one-hour interval using GPC instrument. The GPC results were shown in Fig. 2. As shown in Fig. 2, the molecular weights of the polymers rise rapidly at initial step of the reaction. After 3 hours, the chain increasing rate for 200 °C system slows down obviously with only M_n of 29,600 obtained finally. Simultaneously, the higher M_n of 38,400 at 190 °C for 7 hours means the rational reaction condition for the preparation of our PAEPs. The inherent viscosities (η_{inh}) of

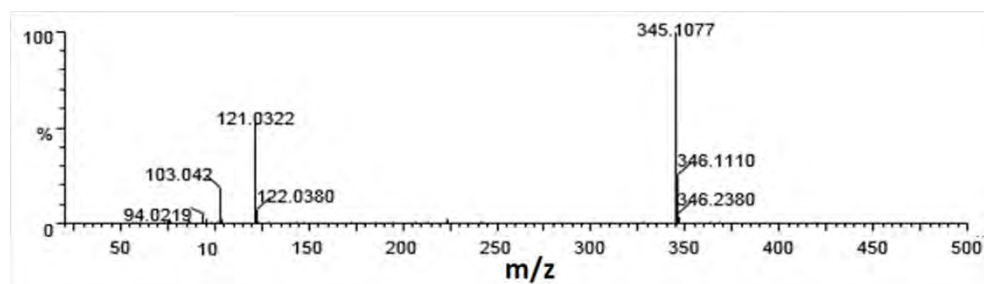


Fig. 1 TOF-MS spectra of BFPT treated by a simulated phenoxide-forming process.

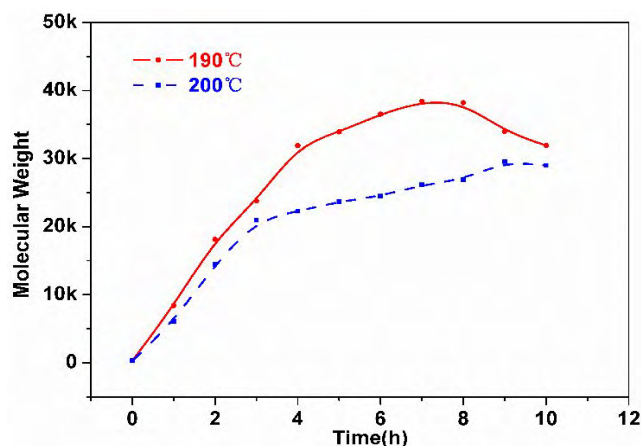


Fig. 2 Graph of molecular weight of PAEP5050 versus time reacting at 190 °C and 200 °C, respectively.

PAEP7525-PAEP0100 in NMP range from 0.60 to 1.17 dL/g, and increase with diphenylfluorene contents increase in the backbone, indicating that BHF is more active than HHPZ in nucleophilic substitute reaction. The synthetic details along with polymeric results for PAEPs are summarized in Table1.

Table 1 Synthetic condition, inherent viscosity and molar masses of PAEPs.

Polymer	Composition HHPZ/BHF	Reaction time(h)	η_{inh} (dL/g) ^a	M_n^b	PD ^b	Yield(%)
PAEP1000	100/0	5.0	1.35 ^c	- ^d	- ^d	90
PAEP7525	75/25	7.0	0.60	22,800	2.7	93
PAEP5050	50/50	7.0	0.67	38,400	2.7	94
PAEP2575	25/75	7.0	0.91	38,600	3.4	95
PAEP0100	0/100	6.0	1.17	43,000	2.2	95

^a Inherent viscosity of PAEPs was determined at a concentration of 0.5 g/dL in NMP at 25 °C.

^b Number-average molar mass (M_n) and polydispersity (PD) of PAEPs was measured by GPC in NMP calibrated with polystyrene standards.

^c Inherent viscosity of PAEP1000 was determined at a concentration of 0.5 g/dL in concentrated sulfuric at 25°C.

^d Number-average molar mass and polydispersity of PAEP1000 could not be detected by GPC.

Polymer characterization

Several sets of tests including FT-IR, NMR and elemental analysis were carried out to investigate the chemical structure of the copolymers obtained. As Fig. 3 depicts, the peaks belonging to all easily discernible bands as well as to vibrations at certain characteristic positions were recorded and discussed according to the FT-IR spectra. All PAEPs exhibit a characteristic absorption band for C=N stretching at 1590 cm^{-1} and 1520 cm^{-1} due to skeletal stretching vibrations and in-plane vibrations of the s-triazine rings. The band in the region 1360-1380 cm^{-1} is caused by C-N stretching and the band appearing at 1660-1680 cm^{-1} belongs to the lactam C=O stretching, both of which convince the existence of phthalazinone groups. A strong band stretching at around 1240 cm^{-1} appears by virtue of Ph-O-Ph linkages. The absorption peak at 1167 cm^{-1} belongs to skeletal vibrations of C-C bonds. Furthermore, 1660-1680 cm^{-1} bands attributed to phthalazinone moieties are weakening gradually, while the absorption of C-C bonds are strengthening from top to bottom. The results are consistent with the increasing nature of the content of phthalazinone units born in the polymer backbone.

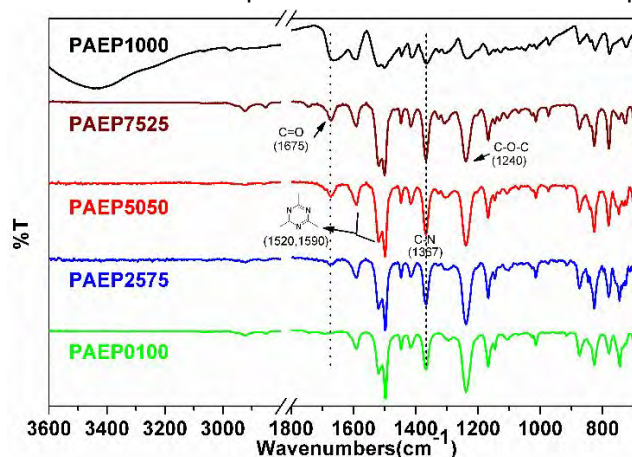
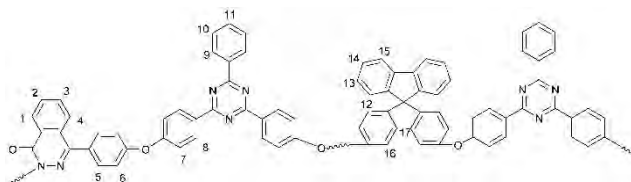


Fig. 3 FT-IR spectra of PAEPs.



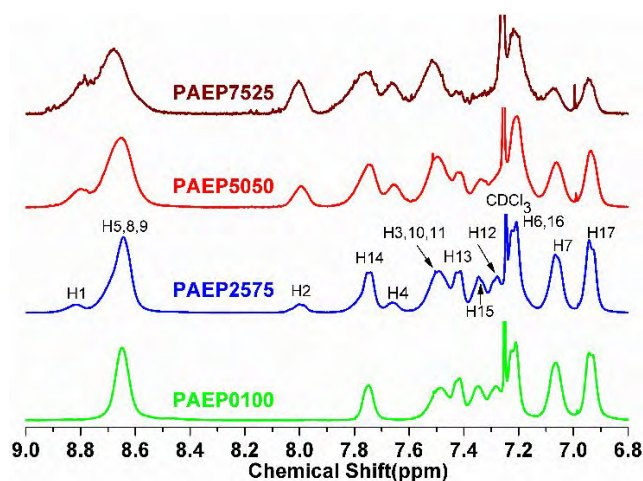


Fig. 4 ^1H NMR spectra (CDCl_3) of PAEPs, with assignments.

^1H -NMR and ^{13}C -NMR spectra were conducted to confirm the chemical structure of PAEPs samples. As evident from the ^1H -NMR spectra (Fig. 4), a multiplet at $\delta=6.80\text{--}9.0$ is caused by the presence of aromatic protons. However, the chemical shift assignment of each category of relative hydrogen protons is somewhat inconvenient. Thus, H-H gCOSY NMR test of PAEP2575 was carried out as a representative example in Fig. 5. The characteristic single peak shifting at downfield 8.77 ppm, which can always be adopted to fix up the other atom as the reference signals, is diagnostic for the presence of *ortho*-hydrogen (H-1) of lactam in phthalazinone. The hydrogen protons of phenyl-*s*-triazine in the main chain of polymers could be identified by signals at 8.51-8.75, 7.02-7.10 and 7.46-7.60 ppm, respectively. Shifting of the hydrogen protons (H-8, H-9) ortho to *s*-triazine rings appears at high frequencies due to the deshielding current effect of the strong electron-withdrawing *s*-triazine groups. H5, 8, 9 are shifting at nearly the same field, because they are in similar chemical environment for being adjacent to the C=N bond. The signals at 7.25-7.40 and 7.70-7.80 ppm are ascribed to the aromatic hydrogen protons (H-12, 15, 13, 14) bonding to diphenylfluorene groups. All the chemical shift peaks agree sufficiently well with the expected structure of PAEP2575 as indicated in Fig. 5. Additionally, the integration dimensions of characteristic peaks of H-12, 13, 14 and 15 decrease, while that of H-1, H-2 and H-4 increase with the increasing molar ratios of phthalazinone moieties contained in polymer backbone according to Fig. 4.

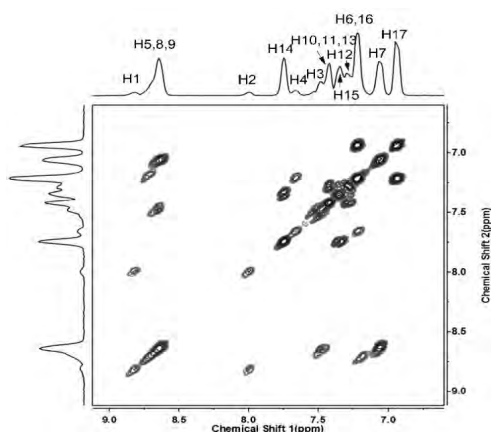


Fig. 5 H-H gCOSY spectra (CDCl_3) of PAEP2575, with assignments.

¹³C-NMR spectra were also used to convince further evidence for the chemical structure of PAEPs samples. In a representative ¹³C-NMR spectrum of PAEP2575, the signal of an alkyl carbon atom connected to four benzene rings in diphenylfluorene moiety appears upfield at 64.43 ppm, indicating the existence of fluorene structures. The signals at 171.42 and 170.74 ppm are assigned to the carbon protons of the s-triazine units owing to the deshielding current effect of s-triazine. Based on the analysis above, the spectral features of the synthesized PAEPs are consistent with their proposed structures.

Polymer solubility

Table 2 Solubility of PAEPs.

Polymer ^a	Solubility ^b														
	NMP ^c	CB	C ₂ H ₂ Cl ₄	CHCl ₃	Py	THF	Sf	To	DMAc	CH ₂ Cl ₂	DMSO	DMF	Acetone	IP	H ₂ SO ₄
PAEP1000	+-	-	+-	-	-	-	-	-	-	-	-	-	-	-	++
PAEP7525	+	+-	+-	+-	-	-	-	-	+-	+-	-	-	-	-	++
PAEP5050	++	+-	+	+	+-	+-	+-	-	+-	+-	-	-	-	-	++
PAEP2575	++	++	++	++	+	+-	+	+-	+-	+-	-	-	-	-	++
PAEP0100	++	++	++	++	+	+	+	+-	+-	+-	-	-	-	-	++

^a The solubility of PAEPs was tested with 0.04g of the polymers in 1mL of solvent

^b Solubility: ++: soluble in room temperature; +: soluble on heating; +/-: partially soluble on heating; -: insoluble.

^c NMP: N-methylpyrrolidone; CB: chlorobenzene; THF: tetrahydrofuran; Sf: sulfolane; Py: pyridine; To: toluene; DMAc: N,N-dimethyl acetamide; DMSO: dimethylsulfoxide; DMF: N,N-dimethyl formamide; IP: isopropanol.

The solubility of the resulting copolymers was measured by dissolving 0.04g of the polymers in 1 mL solvent (4%, w/v), as shown in Table 2. The polymers exhibit reasonable solubility in several aprotic solvents at ambient temperature, such as NMP, chlorobenzene, C₂H₂Cl₄ and chloroform, when the fraction of diphenylfluorene segments in polymer backbone is higher than 50 percent. Whereas PAEP1000 is hardly soluble in any solvents due to the strengthening charge transfer interaction between phenyl-s-triazine rings and aromatic rings which hampers small solvent molecules to diffuse into them. Compared to reported PAEPs [18,39], our PAEPs could be soluble in chloroform. However, in poly(aryl 1,3,5-triazine)s system, this function of introducing the crank, twisted non-coplanar phthalazinone moieties into polymer backbone is weakened because of the large conjugated system. Herein, diphenylfluorene segments possessing bulky volume in space were incorporated into polymer backbone for increasing the free volume of polymer chains to a higher degree. The increasing steric congestion between macromolecular chains makes solvent molecules diffuse into more easily, eventually resulting in a visible modification of the solubility. The desirable solubility behavior of PAEPs will undoubtedly facilitate the synthetic process of polymers under milder conditions and broaden the application of the polymers in coating and film fields.

Polymer thermal property

The glass transition temperatures (T_g) of the polymers listed in Table 3 were detected by differential scanning calorimetry (DSC, Fig. 6) and dynamic mechanical analysis (DMA, Fig. 7, 8). In DSC analysis, the specimen was heated at a rate of 10 °C/min from 25 °C to 400 °C, then quenched back to 25 °C, and the spectrum was recorded with the same heating rate in the second heating cycle. As Fig. 6 depicts, a clear glass transition is found at 307, 312, 324, 328 and 340 °C for PAEP0100-PAEP1000, respectively. The DSC curves display only a single distinct T_g and no obvious trace of crystalline is detected, suggesting the amorphous stack of polymer chains. Fig. 6 also shows that the T_g values of the copolymers decrease with the diphenylfluorene contents increase in polymer backbone. The introduction of diphenylfluorene units enlarges the intermolecular free volume, which causes the polymer chains much easier to move, and finally leads to a decrease in T_g value. Moreover, the T_g s of all the polymers surpass 307 °C, higher than (60-70 °C) those of reported phenyl-1,3,5,-triazine polymers (T_g =240-255 °C), implying the outstanding thermal properties of the copolymers.

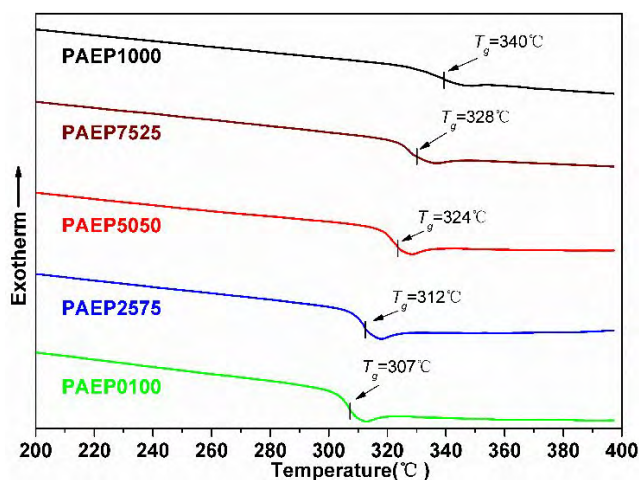


Fig. 6 DSC traces of PAEPs.

The glass transition temperatures of polymers were also detected on thin film samples by dynamic mechanical analysis (DMA), which described the transition via detecting relaxation of molecular motion (Fig. 7, 8). As shown in Fig. 7, a distinct decrease in E' trace occurring at 25-130 °C are associated with the secondary relaxations, which are probably caused by rearrangement and orientation of polymer main chains. For some favorable aspects, these transitions would lead to reduce or eliminate internal stresses though sub- T_g annealing during fabrication. It also makes us believe that the motions of individual units or small segments indeed happen in the molecular backbones, and the interspace between polymer chains actually exists, which is spacious enough for macromolecule to move inside. After that change, a steady creep of the modulus is observed before 260 °C caused by the orientation of macromolecular chains at high temperatures. Then E' value begins to decrease sharply, which means the catastrophic deterioration of the mechanical properties of the film samples. In Fig. 8, the maximum $\tan \delta$ values of the films represent the appearance of the glass transition at 328 °C, 337 °C, 348 °C, 360 °C for PAEP 0100-PAEP7525, respectively, indicating that the copolymers possess commendable dimensional stability at elevated temperature.

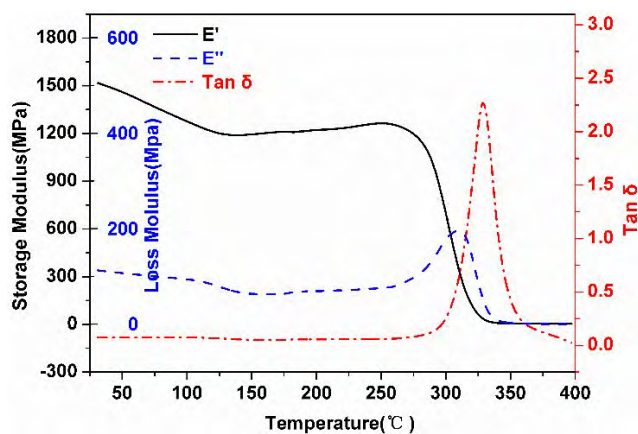


Fig. 7 DMA traces of PAEP0100 film.

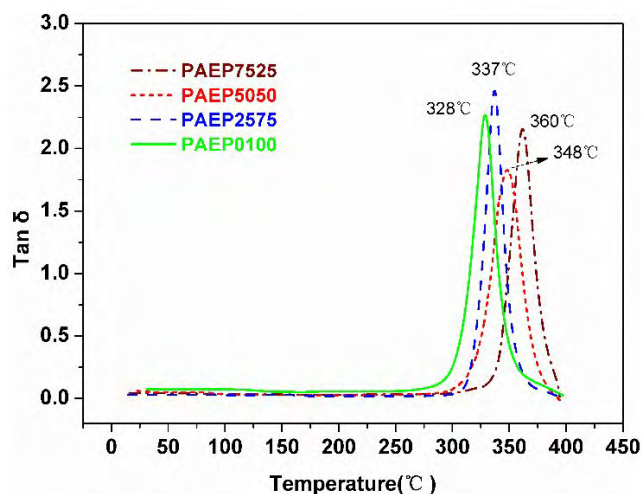
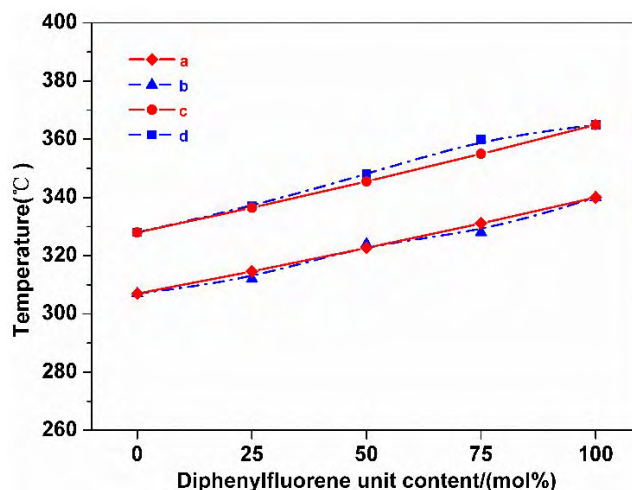


Fig. 8 Tan δ traces of PAEP films.

In other way, based on the T_g s of the homopolymers distinguished from the feed ratio of the different monomers, the T_g s of copolymers could be predicted according to Fox equation{Fox, 1956 #4737}[40] as follow:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (1)$$

Where T_g is the glass transition temperature of the copolymer, W_1 , W_2 is the weight fraction of one single monomer to total diphenols, respectively. T_{g1} , T_{g2} is the glass transition temperature of the corresponding homopolymers, respectively. The T_g s determined both by DSC and DMA coincide with that calculated by Fox equation (Fig. 9), which illustrates the structures of these copolymers are consistent with design from another point of view. However, PAEP1000 couldn't be detected by DMA due to its poor film-forming property. Thus, we adopted the T_g measured by DSC plus 25 °C as substitute.



- a: calculated T_g values according to FOX equation determined by DSC;
 b: tested T_g values determined by DSC
 c: calculated T_g values according to FOX equation determined by DMA;
 d: tested T_g values determined by DMA

Fig. 9 Correlation between T_g value of PAEPs and the diphenylfluorene content (mol% relative to the total diphenols).

The thermal stabilities of the polymers were evaluated using thermogravimetric analysis (TGA) as shown in Fig. 10. In order to make a clear comparison, the temperature of each significant stage such as 5% weight loss, char residue at 800 °C as a function of monomer fraction is listed in Table 3. The polymers are stable before 500 °C under nitrogen atmosphere. They retain 95% weight at 499-580 °C and 90% weight at 538-590 °C in N₂, respectively. PAEP0100 containing no fraction of phthalazinone reveals a superior performance of thermal stability with the weight retention at 95% higher than 580 °C, indicating that its alkyl structural character adjacent to four benzene rings doesn't draw back the temperature of decomposition. The excellent thermal stabilities of these polymers are confirmed by the high char residues as well. The char yields of all polymers obtained are greater than 55%, suggesting that phenyl-s-triazine units endow PAEPs with a more stable polymer backbone. The 5% mass loss temperatures decrease and the C_y values at 800 °C increase with the increase of the fraction of phthalazinone units in the main chain. The nitrogen atoms of phthalazinone and phenyl-s-triazine units lead to high C_y values. Likewise, the evidence that two kinds of peaks appear in DTG curves indicates two different degradation mechanisms.

Table 3 Thermal properties of the PAEPs.

Polymer	$T_g/^\circ\text{C}^{a,b}$	$T_g/^\circ\text{C}^{c,d}$	$T_d/^\circ\text{C}^e$	$T_{5\%}/^\circ\text{C}^f$	$T_{10\%}/^\circ\text{C}^f$	$T_{\max}/^\circ\text{C}^g$	$\text{C}_y(\%)^h$
PAEP1000	340(365)	-	499	498	538	541,633	56.7
PAEP7525	328(360)	331(355)	501	531	558	537,591	62.5
PAEP5050	324(348)	323(346)	507	539	563	543,591	57.3
PAEP2575	312(337)	315(337)	511	563	582	547,598	56.5
PAEP0100	307(328)	-	531	580	592	601	55.3

^a Glass transition temperature was measured by DSC and the reflection point was taken as T_g .

^b Glass transition temperature in the parentheses was measured by DMA and the peak point of $\tan \delta$ was taken as T_g .

^c Glass transition temperature was calculated according to FOX equation measured by DSC.

^d Glass transition temperature in the parentheses was calculated according to FOX equation measured by DMA

^e Temperature for initial decomposition was recorded on TGA at the heating rate of 20 °C /min inr N₂ and the onset

temperature was taken as T_d

^f Temperature for 5%, 10% weight loss was recorded on TGA at the heating rate of 20 °C/min in N₂.

^g Temperature for the maximum decomposition was recorded on TGA at the heating rate of 20 °C/min in N₂.

^h Char yield at 800 °C was recorded on TGA at the heating rate of 20 °C/min in N₂.

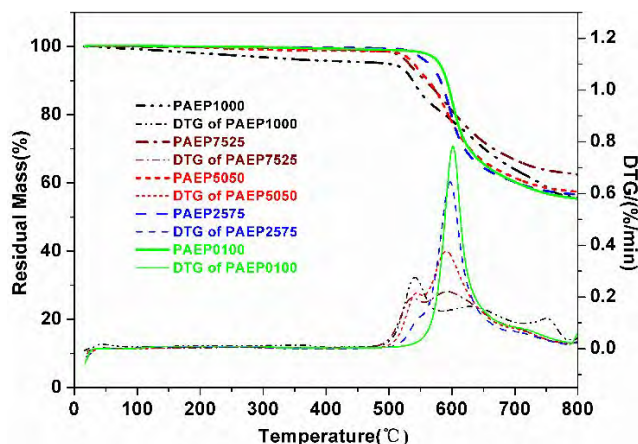


Fig. 10 TGA and DTG thermograms of the PAEPs.

Polymer mechanical property

The mechanical properties of PAEP7525 to PAEP0100 films were tested by tensile measurement at the stretching speed of 2 mm/min, as shown in Table 4. The samples have tensile stress at maximum load of 73-112 MPa, tensile moduli of 1.8-2.4 GPa, and elongation at break of 6% to 8% at room temperature, respectively. Furthermore, film samples were treated in oven under air atmosphere at 150 °C and 250 °C for 4 h, respectively, followed by investigating their residual mechanical properties. As evidenced in Table 4, all the film specimens treated at 150 °C for 4 h exhibit better tensile strength than no heat treated samples, probably because of the rearrangement and orientation of polymer main chains at elevated temperature. Thus, treating the PAEPs at 150 °C is preferable to orientate polymer chains to eliminate the residual stress for our polymers. However, when treated at 250 °C, their tensile strengths exhibit a slightly decrease. These results agree well with the DMA analysis which showed the decrease of E' value at near 250 °C. Tensile modulus and elongation at break abide the same trend after heated at elevated temperatures. The results indicate that the PAEPs materials have good mechanical properties, especially at elevated temperatures, indicating their excellent thermal stabilities.

Table 4 Mechanical properties of PAEPs^a.

Polymer	Tensile Strength/MPa			Elongation at break (%)			Tensile Modulus/GPa		
	A	B	C	A	B	C	A	B	C
PAEP7525	84	89	53	6	8	4	2.0	2.2	1.9
PAEP5050	73	84	64	6	6	6	1.8	2.0	1.6
PAEP2575	106	118	110	8	9	8	2.1	2.8	2.1
PAEP0100	112	130	112	8	8	6	2.4	2.4	2.3

^a Key: A: original samples before thermal degradation; B: samples thermally degraded at approximately 150 °C for 4 h; C: samples thermally degraded at approximately 250 °C for 4 h.

Polymer crystallinity

The wide-angle X-ray diffraction (WAXD) was utilized to character the crystallinity of the polymers on thin film at room temperature showed in Fig.11. The crystalline pattern can be accurately predicted by measuring intensities at 2θ values. According to this procedure, the dispersion peak from 10° to 33° is associated with the amorphous nature of the copolymers obtained. The areas at 22.5° , 24.2° , 26.8° and 29.6° are measured as crystalline diffraction. The crystallizing field [41] was calculated less than 5% (PAEP1000-PAEP0100 for 1.1%, 1.7%, 2.4%, 1.9% and 2.6%, respectively). It is noteworthy that the peak value at $2\theta=29.6^\circ$ vanishes in the curves of PAEP7525-PAEP0100, indicating that the partial crystallinity is attributed to the phthalazinone segments. The peak value at $2\theta=22.5^\circ$, 24.2° , 26.8° might be caused by diphenylfluorene segments. No obvious distinction of intensities is detected, suggesting that the sizes of crystallinity regions don't depend on the content of construction units. The presence of bulky moieties hampers the crystallization process and disrupts the planarity and symmetry of polymer chains, finally leading to the amorphous or micro-crystalline nature. What interested us more was that crystallization indeed occurred in polymer internals. The mechanism of crystallization will be researched and discussed elsewhere.

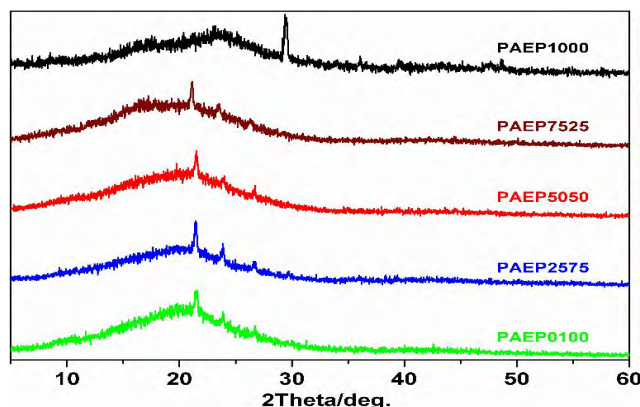


Fig. 11 WAXD diffractograms of PAEPs.

Conclusions

A series of novel organosoluble and thermally stable poly(phthalazinone ether 1,3,5-triazine)s were prepared by the polymerization reaction of BFPT with BHF and HHPZ. The obtained random copolymers were characterized by FT-IR and NMR for convincing their accurate structure. Diphenylfluorene units in polymer main chain have brought about an improvement on solubility while maintaining desirable thermal properties. The copolymers with more than 50% content of diphenylfluorene augments could be dissolved in chloroform and NMP at room temperature. Thus, they could be readily processed from solution to derive flexible transparent films. Their films have commendable mechanical properties at both room and elevated temperatures. All the polymers possess excellent thermal properties with high T_g s, decomposition temperatures and C_y values in comparison with previously reported analogues. All polymers display amorphous nature with a typical pattern of micro-crystallinity as evidenced by WAXD. Combining all the above merits suggests a good application of the resulting PAEPs for processable and heat-resistant structural materials.

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References

1. Colquhoun HM, Hodge P, Paoloni FoPV, McGrail PT, Cross P (2009) Reversible, nondegradative conversion of crystalline aromatic poly(ether ketone)s into organo-soluble poly(ether dithioketal)s. *Macromolecules* 42 (6):1955-1963. doi:10.1021/ma8023377
2. Liu HY, Shen Y, Song Y, Nan CW, Lin YH, Yang XP (2011) Carbon nanotube array/polymer core/shell structured composites with high dielectric permittivity, low dielectric loss, and large energy density. *Adv Mater* 23 (43):5104-5108. doi:10.1002/adma.201102079
3. Shao SY, Ding JQ, Ye TL, Xie ZY, Wang LX, Jing XB, Wang FS (2011) A novel, bipolar polymeric host for highly efficient blue electrophosphorescence: A non-conjugated poly(aryl ether) containing triphenylphosphine oxide units in the electron-transporting main chain and carbazole units in hole-transporting side chains. *Adv Mater* 23 (31):3570-3574. doi:10.1002/adma.201101074
4. Mir AA, Matsumura S, Hlil AR, Hay AS (2011) Synthesis and properties of polymers containing 2h-benzimidazol-2-one moieties: Polymerization via N-C coupling reactions. *ACS Macro Lett* 1 (1):194-197. doi:10.1021/mz200138v
5. Lin CH, Wang YR, Feng YR, Wang MW, Juang TY (2013) An approach of modifying poly(aryl ether ketone) to phenol-containing poly(aryl ether) and its application in preparing high-performance epoxy thermosets. *Polymer* 54 (6):1612-1620. doi:http://dx.doi.org/10.1016/j.polymer.2013.01.034
6. Tang HL, Pu ZJ, Huang X, Wei JJ, Liu XB, Lin ZQ (2014) Novel blue-emitting carboxyl-functionalized poly(arylene ether nitrile)s with excellent thermal and mechanical properties. *Polym Chem.* doi:10.1039/C3PY01782F
7. Tian SH, Shu D, Wang SJ, Xiao M, Meng YZ (2007) Poly(arylene ether)s with sulfonic acid groups on the backbone and pendant for proton exchange membranes used in pemfc applications. *Fuel Cells* 7 (3):232-237. doi:10.1002/fuce.200600005
8. Li N, Hwang DS, Lee SY, Liu Y-L, Lee YM, Guiver MD (2011) Densely sulfophenylated segmented copoly(arylene ether sulfone) proton exchange membranes. *Macromolecules* 44 (12):4901-4910. doi:10.1021/ma200937w
9. Li NW, Zhang Q, Wang CY, Lee YM, Guiver MD (2012) Phenyltrimethylammonium functionalized polysulfone anion exchange membranes†. *Macromolecules* 45 (5):2411-2419. doi:10.1021/ma202681z
10. Chen D, Hickner MA (2013) Ion clustering in quaternary ammonium functionalized benzylmethyl containing poly(arylene ether ketone)s. *Macromolecules* 46 (23):9270-9278. doi:10.1021/ma401620m
11. Chen P, Chen XB, An ZW (2012) Covalently and ionically crosslinked sulfonated poly(arylene ether ketone)s as proton exchange membranes. *Polym Bull* 68 (5):1369-1386. doi:10.1007/s00289-011-0638-1
12. Tigelaar DM, Palker AE, Jackson CM, Anderson KM, Wainright J, Savinell RF (2009) Synthesis and properties of novel proton-conducting aromatic poly(ether sulfone)s that contain triazine groups. *Macromolecules* 42 (6):1888-1896. doi:10.1021/ma802553w
13. Tigelaar DM, Palker AE, He R, Scheiman DA, Petek T, Savinell R, Yoonessi M (2011) Synthesis and properties of sulfonated and unsulfonated poly(arylene ether triazine)s with pendant diphenylamine groups for fuel cell applications. *J Membr Sci* 369 (1-2):455-465. doi:10.1016/j.memsci.2010.12.018
14. Tong LF, Pu ZJ, Chen ZR, Huang X, Liu XB (2014) Effect of nanosilica on the thermal, mechanical, and dielectric properties of polyarylene ether nitriles terminated with phthalonitrile. *Polym Composite* 35 (2):344-350. doi:10.1002/pc.22667
15. Xu MZ, Liu MD, Dong SH, Liu XB (2013) Design of low temperature self-cured phthalonitrile-based polymers

- for advanced glass fiber composite laminates. *J Mater Sci* 48 (23):8108-8116. doi:10.1007/s10853-013-7623-z
16. Ren SJ, Fang Q, Lei K, Fu HT, Chen XY, Du JP, Cao AM (2005) New pi-conjugated polymers containing 1,3,5-triazine units in the main chain: Synthesis and optical and electrochemical properties of the polymers. *Macromol Rapid Comm* 26 (12):998-1001. doi:10.1002/marc.200500139
 17. Ren SJ, Fang Q, Yu F, Bu DS (2005) Synthesis and optical and electrochemical properties of new pi-conjugated 1,3,5-triazine-containing polymers. *J Polym Sci Pol Chem* 43 (24):6554-6561. doi:10.1002/pola.21091
 18. Matsuo S (1994) Synthesis and properties of poly(arylene ether phenyl-s-triazine)s. *J Polym Sci Pol Chem* 32 (11):2093~2098. doi:10.1002/pola.1994.080321111
 19. Huang B, Cheng SJ, Xi Q, Cai MZ (2012) Synthesis and characterization of novel copolymers of poly(ether ketone ketone) and poly(ether ketone sulfone imide). *Polym Bull* 69 (6):661-673. doi:10.1007/s00289-012-0753-7
 20. Yu GP, Liu C, Zhou HX, Wang JY, Lin EC, Jian XG (2009) Synthesis and characterization of soluble copoly(arylene ether sulfone phenyl-s-triazine)s containing phthalazinone moieties in the main chain. *Polymer* 50 (19):4520~4528. doi:10.1016/j.polymer.2009.07.030
 21. Mohanty AD, Lee YB, Zhu L, Hickner MA, Bae C (2014) Anion exchange fuel cell membranes prepared from C-H borylation and suzuki coupling reactions. *Macromolecules* 47 (6):1973-1980. doi:10.1021/ma500125t
 22. Wu CS, Lee SL, Chen Y (2011) Bipolar copoly(aryl ether) containing distyrylbenzene, triphenylamine, and 1,2,4-triazole moieties: Synthesis and optoelectronic properties. *J Polym Sci Pol Chem* 49 (14):3099-3108. doi:10.1002/pola.24747
 23. Li HB, Jackson AB, Kirk NJ, Mauritz KA, Storey RF (2011) Poly(arylene ether sulfone) statistical copolymers bearing perfluoroalkylsulfonic acid moieties. *Macromolecules* 44 (4):694-702. doi:10.1021/ma102717d
 24. Wang JH, Li SH, Zhang SB (2010) Novel hydroxide-conducting polyelectrolyte composed of an poly(arylene ether sulfone) containing pendant quaternary guanidinium groups for alkaline fuel cell applications. *Macromolecules* 43 (8):3890-3896. doi:10.1021/ma100260a
 25. Lu JP, Miyatake K, Hlil AR, Hay AS (2001) Novel soluble and fluorescent poly(arylene ether)s containing p-quaterphenyl, 2,5-bis(4-phenylphenyl)oxadiazole, or 2,5-bis(4-phenylphenyl)triazole groups. *Macromolecules* 34 (17):5860-5867. doi:10.1021/ma0103977
 26. Wang JY, Wang MJ, Liu C, Zhou HX, Jian XG (2013) Synthesis of poly(arylene ether nitrile ketone)s bearing phthalazinone moiety and their properties. *Polym Bull* 70:1467-1481. doi:10.1007/s00289-012-0866-z
 27. Li XP, Liu C, Zhang SH, Zong LS, Jian XG (2013) Functionalized 4-phenyl phthalazinone-based polybenzimidazoles for high-temperature pemfc. *J Membr Sci* 442:160-167. doi:10.1016/j.memsci.2013.04.044
 28. Chen DY, Wang SJ, Xiao M, Meng YZ, Hay AS (2011) Novel polyaromatic ionomers with large hydrophilic domain and long hydrophobic chain targeting at highly proton conductive and stable membranes. *J Mater Chem* 21:12068-12077. doi:10.1039/c1jm10950b
 29. Xiao LH, Liu C, Liao GX, Zhang YA, Jian XG (2010) Synthesis and characterization of novel copoly(aryl ether sulfone) containing phthalazinone and biphenyl moieties. *High Perform Polym* 22 (3):274-285. doi:10.1177/0954008308092057
 30. Yu GP, Liu C, Wang JY, Xu J, Jian XG (2010) Synthesis and characterization of poly(arylene ether s-triazine)s containing alkyl-, aryl- and chloro-substituted phthalazinone moieties in the main chain. *Polym Int* 59 (9):1233-1239. doi:10.1002/pi.2853
 31. Bae B, Miyatake K, Watanabe M (2009) Effect of the hydrophobic component on the properties of

- sulfonated poly(arylene ether sulfone)s. *Macromolecules* 42 (6):1873-1880. doi:10.1021/ma8026518
32. Hsiao SH, Yang CP, Lin WL (1999) Synthesis and characterization of new diphenylfluorene - based aromatic polyamides derived from 9,9 - bis [4 - (4 - carboxy - phenoxy) phenyl] fluorene. *Macromol Chem Phys* 200 (6):1428-1433. doi:10.1002/(SICI)1521-3935(19990601)200:61428::AID-MACP1428>3.0.CO;2-J
 33. Huang WY, Huang SY (2010) Sterically encumbered fluorene-based poly(arylene ether)s containing spiro-annulated substituents on the main chain. *Macromolecules* 43 (24):10355~10365. doi:10.1021/ma102093t
 34. Tian SH, Meng YZ, Hay AS (2009) Membranes from poly(aryl ether)-based ionomers containing randomly distributed nanoclusters of 6 or 12 sulfonic acid groups. *Macromolecules* 42 (4):1153-1160. doi:10.1021/ma802456m
 35. Wang CY, Li NW, Shin DW, Lee SY, Kang NR, Lee YM, Guiver MD (2011) Fluorene-based poly(arylene ether sulfone)s containing clustered flexible pendant sulfonic acids as proton exchange membranes. *Macromolecules* 44 (18):7296-7306. doi:10.1021/ma2015968
 36. Jian XG, Meng YZ, Zheng HB (1995) Polyether ketones containing diazanaphthalene structures and preparing processes therefor. CN Patent CN1098097A,
 37. Bunnett JF, Zahler RE (1951) Aromatic nucleophilic substitution reactions. *Chem Rev* 49:273-412
 38. Zhou HX, Liu C, Wang JY, Jian XG (2012) Synthesis and characterization of phthalazinone-based poly(aryl ether ketone) derived from 4,4'-dichlorobenzophenone. *Polym Advan Technol* 23:742-747. doi:10.1002/pat.1950
 39. Fink R, Frenz C, Thelakkat M, Schmidt HW (1997) Synthesis and characterization of aromatic poly(1,3,5-triazine-ether)s for electroluminescent devices. *Macromolecules* 30 (26):8177~8181. doi:10.1021/ma970528x
 40. Fox TG (1956) Influence of diluent and of copolymer composition on the glass temperature of a polymer system. *B Am Phys Soc* 1 (1):123-129
 41. Aggarwal SL, Tilley GP (1955) Determination of crystallinity in polyethylene by x - ray diffractometer. *J Polym Sci* 18 (87):17-26