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Synthesis, characterization, and crosslinking of soluble cyano-containing poly(arylene ether)s bearing phthalazinone moiety

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ABSTRACT

A novel series of phthalazinone-based poly(arylene ether nitrile)s bearing terminal cyano groups via N–C linkages (PPEN-DCs) were synthesized by a simple solution polycondensation of 4-(4-hydroxylphenyl)(2*H*)-phthalazin-1-one (HPPZ) with calculated 2,6-difluorobenzonitrile (DFBN), followed by the termination of 4-chlorobenzonitrile (CBN). The M_ns of oligomeric PPEN-DCs, which are in the range of 1600–6200, can be well-controlled by adjusting reactant ratio. The incorporation of phthalazinone into the polymer chain results in an improvement in the solubility and glass transition temperatures (T_gs). The amorphous PPEN-DCs were thermally crosslinked to afford insoluble products in the presence of terephthalonitrile and zinc chloride. The pendant cyano groups in the polymer chain hardly undergo any crosslinking or cyclization, while the terminal cyano groups with nitrogen-bridged phthalazinone in the *para*-substitution are much more reactive in s-triazine forming reaction and effectively promote certain crosslinking under normal pressure. T_gs of the oligomers, which range from 245 to 269 °C, could be further increased at least by 94 °C upon thermal curing. The crosslinked samples exhibit excellent thermal stability and absorb less than 2.7 wt% water after exposure to an aqueous environment for extended periods. This kind of cyano-terminated poly(arylene ether nitrile)s may be a good candidate as matrix resins for high-performance polymeric materials.

1. Introduction

Due to the outstanding comprehensive properties, poly(arylene ether)s are the most commonly used materials in transportation, aerospace, electrical and electronic fields etc, with utilities as matrix resins for advanced composites, high-temperature membranes or structural coatings [1]. Among this category of high-performance thermoplastics, poly(arylene ether nitrile)s (PAENs) are well-known as a class of semi-crystalline polymer with pendant cyano groups [2–4]. Such materials always possess an attracting balance of heat and chemical resistance, mechanical strength, flame retardancy and molding workability, which makes them one of the leading candidates for use as structural coating for electrical devices or matrix resin for advanced composites. For example, the first commercialized product of PAENs, which was developed by Idemitsu with trade name PEN®, has been identified as excellent matrix resins for carbon reinforcement [5]. Nevertheless, the poor solubility of PAENs, owing to premature crystallization from organic solvent mediums, hampers their syntheses, processing and widespread application, especially of high-molecular weight materials. In addition, PAENs have relatively low glass transitions (PEN®, $T_g = 148$ °C) compared to other commercially available polymers (e.g., A-300® PES), which results in a decrease of modulus and hardly qualifies composites for use at elevated temperatures that frequently encounters in aerospace, industrial and automotive applications. These problems have initiated a search for soluble and thermally stable PAENs by using structural modification of polymer chain in recent years [6–9], with a view to improving processability and hence broadening their applications, especially as adhesives, coatings and membranes. In summary, the research efforts evolve the incorporation of flexible linkages [6], alkyl pendant groups [7], kink groups [8] or non-coplanar units [9] into the polymer backbones.

Recently, our laboratory has prepared phthalazinone-based PAENs which were disclosed with reasonable solubility in selected aprotic polar solvents [10]. This kind of polymer also shows high mechanical strengths and good thermal properties with glass transition temperature at 295 °C. Additionally, we have developed

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new series of organosoluble poly(arylene ether nitrile sulfone) and poly(arylene ether nitrile ketone) containing phthalazinone segments in the main chain [11–13]. These polymers can be easily cast into tough and creasable films, and their applications such as proton exchange membrane and high-temperature coating are studied currently under way. Therefore, the heterocyclic phthalazinone has been proved to be a high efficiency unit for improving solubility and raising glass transitions of PAENs.

Crosslinking is another effective approach for enhancing the glass transitions, and it is frequently assumed to heighten thermal stability of polymer systems [14,15]. As a typical and potent crosslinkable group, cyano is often utilized owing to its easy introduction to the polymer chain as pendant or terminal group and its trimerization to afford high-temperature s-triazine resins [16–22]. Furthermore, the crosslinking of the cyano-containing polymers can be proceded in the absence of catalyst without the liberation of any volatile byproducts. Up to now, the terminal cyano group has been utilized successfully to crosslink a variety of polymers including polyethers, polysulfones, polyketones, polyamides and polyimides [18–21]. Our group has recently described the crosslinking of poly(arylene ether amide)s to give insoluble products with excellent thermal stability, most possibly by the cyclization of activated terminal cyano groups [20]. Believing that the crosslinking of cyano groups would be further promoted by increasing their concentration and activated by the strong *ortho*-substituted electron-withdrawing groups, Keller's research group has synthesized aromatic diether-linked phthalonitrile resins that could cure at elevated temperatures to form s-triazine thermosets [21,22]. Although cyclization reaction of the pendant cyano groups is usually extremely difficult owing to the great steric hindrance of polymer long chains in the *ortho*-substitutions, there are also some reports involving the crosslinking of polymers with pendant cyano groups [8,16]. For example, cyano-appended poly(phenylene sulfide)s have been crosslinked to afford thermosets by the trimerization of cyano group [16].

As part of an ongoing project dealing with the development of processable and heat-resistant polymeric materials, we disclose a new kind of soluble and crosslinkable poly(phthalazinone ether nitrile)s (simplified as PPEN-DCs) in this article. The introduction of pendant cyano groups into the chain aims to increase the cyano concentration while the incorporation of the activated terminal cyano groups aims to promote some cyclization and crosslinking. We have attempted their curing at decreased temperatures under normal pressure by the charge of terephthalonitrile and zinc chloride into the curing system. The curing reactivity of pendant and terminal cyano groups has been compared, and the structure–property relationships of both linear and crosslinked polymers have been also studied.

2. Experimental

2.1. Materials

4-(4-Hydroxylphenyl)(2*H*)-phthalazin-1-one (HPPZ) was prepared as white powders by the method reported in ref [23]. M.p.: 310.0–310.8 °C; yield: 90 wt%; the product was confirmed by MALDI-TOF/MS. GC/MS (M + calcd. as $C_{14}H_{10}O_2N_2$ 238.0742): $m/z = 238.0750$ (M+).

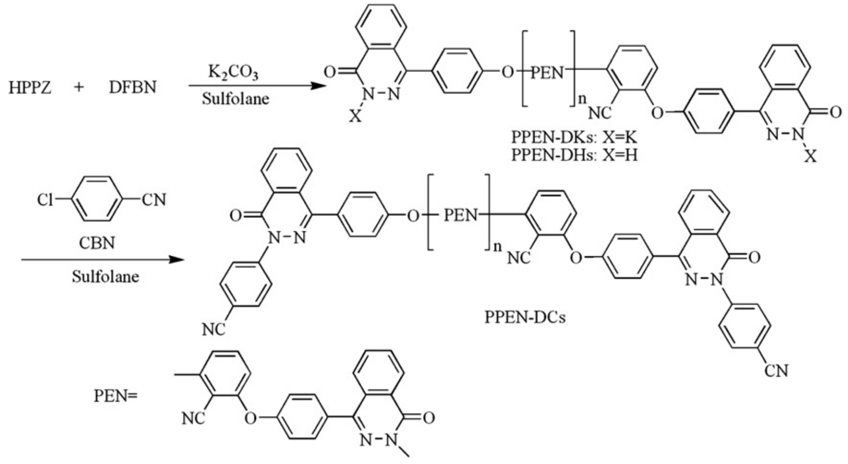
Anhydrous potassium carbonate (K_2CO_3) was ground and dried in vacuum at 100 °C for 24 h before use. 4-Chlorobenzonitrile (CBN) were purified by recrystallization from aqueous ethanol and dried in a vacuum oven for 24 h. 2,6-Difluorobenzonitrile (DFBN) and terephthalonitrile (TPh) were purchased from Aldrich–Sigma and used as received. Zinc chloride was refluxed and distilled over thionyl chloride to remove water, and then excess thionyl chloride was azeotropically distilled with toluene. After the removal of thionyl chloride and toluene, anhydrous zinc chloride was obtained after being dried at 180 °C for 24 h under vacuum. Sulfolane (Beijing Chemical Co., A.R.) was dried and vacuum distilled over sodium hydroxide pellets (Beijing Chemical Co., A.R.), then the middle fractions were collected and stored over molecular sieves (type 4 Å) before use. Toluene was distilled over calcium hydride under reduced pressure. Unless otherwise specified, all other solvents and reagents were obtained from commercial sources and used without further purification.

2.2. Characterization methods

Infrared measurements were performed on a Thermo Nicolet Nexus 470 Fourier transform infrared (FT-IR) spectrometer. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained with a Bruker spectrometer at an operating temperature of 25 °C using DMSO-d_6 or $CDCl_3$ as solvents and the data were listed in parts per million downfield from tetramethylsilane (TMS). Inherent viscosities (η_{inh}) of the polymers were measured by Ubbelohde capillary viscometer at 25 °C. Gel permeation chromatography (GPC) analysis was carried out on an HP 1090 HPLC instrument equipped with 5 μm Phenogel columns (linear, 4 × 500 Å) arranged in series with chloroform as solvent and a UV detector at 254 nm. And the values were calibrated versus polystyrene standard. 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. Elemental analysis was measured on a Vario ELIII CHNOS Elementaranalysator from Elementaranalysesyteme GmbH. Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) of the polymers were performed on a Mettler TGA/SDTA851 thermogravimetric analysis instrument in the nitrogen atmosphere at a heating rate of 20 °C/min from 100 to 800 °C. Decomposition temperatures (T_ds) in nitrogen were taken as the temperatures of 5% and 10% weight loss. Temperature for the maximum weight loss rate (T_{max}) in nitrogen was also measured at a heating rate of 20 °C/min. Char yield (C_y) was calculated as the percentage of solid residue after heating from 100 to 800 °C in a flowing nitrogen atmosphere. Glass transition temperature (T_g) and curing temperature (T_c) were determined with a Mettler DSC822 differential scanning calorimetry (DSC) in flowing nitrogen at a heating rate of 10 °C/min from 100 to 400 or 450 °C. The T_g value was taken at the inflection point and T_c was recorded at the exothermal peak of DSC curves. Isothermal scan (ISO-TGA) was performed at 350 °C over a 48 h period in air or nitrogen atmosphere on the Mettler TGA/SDTA851 thermogravimetric analysis instrument. 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 Ka radiation (40 kV, 100 mA).

2.3. Synthesis of PPEN-DHs and PPEN-DCs

The oligomeric PPEN-DCs were synthesized via a nucleophilic aromatic substitution (S_NAr), as depicted in Scheme 1. The numbers of the sample name indicated the molar percentages of terminal cyano groups relative to phthalazinone moieties. For example, the resultant oligomers in the reaction starting from 100 fractions of HPPZ and 67 fractions of CBC could be labeled as PPEN-DC67. All PPEN-DCs were prepared in the similar procedures. Therefore, only the preparation of PPEN-DC67 was depicted and given as a typical example. A 100 mL three-necked round-bottomed flask was equipped with a mechanical stirrer, a nitrogen gas inlet tube and a Dean–Stark trap. The flask was charged with a mixture of HPPZ (2.38 g, 10.0 mmol), DFBN (0.92 g, 6.7 mmol) and K_2CO_3 (1.66 g, 12.0 mmol), and then rinsed with 5 mL sulfolane and 30 mL



Scheme 1. Synthetic route of PPEN-DHs and PPEN-DCs.

toluene. The mixture was stirred and heated to the reflux temperature (140–150 °C) for 6 h to dehydrate the system. After the produced water was azeotroped off completely with toluene, the reaction mixture was heated to 180 °C for another 6 h. A small amount of reaction mixture was taken out prior to the termination reaction and it was slowly poured into a solution of sufficient boiling water containing a few drops of concentrated hydrochloric acid under vigorous stirring. The produced pale yellow precipitate (PPEN-DH67) was rinsed thoroughly with water and then vacuum-dried overnight at 100 °C. After cooling to room temperature, the residual reaction mixture was charged with an excess amount of CBN (1.01 g, 7.4 mmol). Subsequently, it was step-wisely heated to 190 °C and maintained at this temperature for 4 h. The resulting solution was poured into a large amount of hot water and the precipitated products were washed thoroughly with hot water. The pale yellow products were then extracted with acetone for 12 h and vacuum-dried overnight at 100 °C. The yield of PPEN-DC67 was 95 wt%.

Selected data of PPEN-DH67: FT-IR (KBr, cm^{-1}): 3423 (N–H), 3021 (=C–H), 2237 (C≡N), 1671 (C=O), 1509, 1575, 1504 (C=C), 1465, 1336, 1256 (Ph–O), 1231, 1176, 839. ^1H NMR (400 MHz, DMSO-d_6, ppm) δ: 12.93 (s, Ar–H), 8.38 (s, Ar–H), 7.84–7.98 (m, Ar–H), 7.62–7.79 (m, Ar–H), 7.36–7.45 (m, Ar–H), 6.79–6.94 (m, Ar–H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ: 164.71, 164.55, 162.02, 159.07, 158.51, 158.08, 157.63, 156.79, 154.65, 152.60, 150.52, 146.66, 146.08, 144.20, 134.74, 134.44, 133.75, 131.94, 130.06, 127.18, 126.28, 122.10, 119.92, 119.19, 118.71, 118.25. Elem. Anal. Calcd. for PPEN-DH67 $(C_{56}H_{32}N_8O_6)_n$ $(912.90)_n$: C, 73.68; H, 3.53; N, 12.27%. Found: C, 72.45; H, 3.61; N, 12.17%. Selected data of PPEN-DC67: FT-IR (KBr, cm^{-1}): 3017 (=C–H), 2232 (C≡N), 1675 (C=O), 1601, 1578, 1508 (C=C), 1462, 1330, 1261 (Ph–O), 1214, 1166, 859. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.62 (s, Ar–H), 7.82–7.88 (m, Ar–H), 7.69–7.79 (m, Ar–H), 7.55–7.76 (m, Ar–H), 7.43–7.54 (m, Ar–H), 7.28–7.42 (m, Ar–H), 6.89–6.80 (m, Ar–H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 164.71, 164.55, 162.02, 159.07, 158.51, 158.08, 157.63, 156.79, 154.65, 152.60, 150.52, 146.66, 146.08, 144.20, 134.74, 134.44, 133.75, 131.94, 130.06, 127.18, 126.28, 122.10, 119.92, 119.19, 118.71, 118.25. Elem. Anal. Calcd. for PPEN-DC67 $(C_{70}H_{38}N_{10}O_6)_n$ $(1115.11)_n$: C, 75.40; H, 3.43; N, 12.56%. Found: C, 74.86; H, 3.51; N, 12.52%.

2.4. Crosslinking of PPEN-DCs to CPPEN-DCs

Thermally activated crosslinking reactions of the oligomeric PPEN-DCs were performed by heating their oligomer powders with $ZnCl_2$ (1.9 wt%) and TPh (2.9 wt%) in nitrogen atmosphere. The resultant crosslinked samples were simplified as CPPEN-DCs. A typical crosslinking procedure of PPEN-DC67 was given as an example and it was carried as follows. A mixture of PPEN-DC67 (1.00 g), TPh (0.03 g) and $ZnCl_2$ (0.02 g) was pulverized and evenly dispersed by vigorous stirring. The mixture was crosslinked via heating in a sealed test tube at 250 °C for 2 h, 280 °C for 4 h, 300 °C for 12 h, 320 °C for 6 h and 350 °C for 4 h under nitrogen atmosphere. Once the samples were readily cooled, the resultant black products were well ground and washed thoroughly in water, and extracted in Soxhlet equipment with alcohol. The obtained powdered CPPEN-DC67 was dried under vacuum overnight at 120 °C and used for DSC and TGA studies. Selected data of CPPEN-DC67: FT-IR (KBr, cm^{-1}): 3017 (=C–H), 1677 (C=O), 1601, 1578, 1508 (C=C/C=N), 1462, 1361 (C–N), 1323, 1251 (Ph–O), 1169, 851. Elem. Anal. Calcd. for CPPEN-DC67 $(C_{70}H_{38}N_{10}O_6)_n$ $(1115.11)_n$: C, 75.40; H, 3.43; N, 12.56%. Found: C, 74.06; H, 3.32; N, 12.50%.

2.5. Long-term water absorption study

CPPEN-DC films were prepared by heating film samples of PPEN-DCs mixing with $ZnCl_2$ (1.9 wt%) and TPh (2.9 wt%) under the above heating cycles. The resulting dark films were cut to dimensions of approximately 10 mm × 13 mm × 0.04 mm. It was immersed at 25 °C in distilled water for 30 days. The films were removed from the water, sponged up, and weighed periodically to determine the amount of water absorbed.

3. Results and discussion

3.1. Synthesis of PPEN-DHs and PPEN-DCs

PPEN-DC oligomers with different terminal cyano content were successfully synthesized by the aromatic nucleophilic displacement polymerization of HPPZ with various molar ratios of DFBN and CBN (Scheme 1). Both O–H and lactam N–H of the bisphenol-like HPPZ, which are acidic, have demonstrated a good reactivity in the nucleophilic displacement reaction and hence HPPZ always acts as a novel starting material for the preparation of high-molecular weight polymers [10,13]. In this study, the polymerizations of excess HPPZ with activated dihalogenated monomers were accomplished by using a weak base and an azeotropic solvent. Anhydrous potassium carbonate as a base was used to covert the bisphenol-like monomer into the more reactive phenolate anions and aza-nitrogen anions. And this reaction was promoted in the presence of a minimal amount of toluene to allow azeotropic distillation of the water formed as a byproduct. Subsequently, these anions reacted with dihalogenated monomers to produce aza-nitrogen anions terminated intermediates or phenolate anions terminated intermediates. Considering higher acidity of N–H than O–H group, and the moderate reaction temperature, the phenolate anions produced should demonstrate much higher reactivity relative to the aza-nitrogen anions and as a result the substitution reaction of the former is much faster than the latter. Therefore, it was most possible to generate the aza-nitrogen anion terminated intermediates rather than the phenolate anion terminated intermediates in this step. These intermediates were readily converted to oligomers with N–H ends (PPEN-DHs) in the presence of an acid. Meantime, phthalazinone-based poly(arylene ether nitrile)s bearing terminal cyano groups through N–C linkages (PPEN-DCs) were facilely obtained by the displacement reactions of these aza-nitrogen anions terminated intermediates with the terminal agent (CBN). In all cases, an excess amount of CBN was used to ensure complete termination of the oligomers. All polymerizations homogeneously proceeded in transparent solutions throughout the reactions. PPEN-DCs were successfully obtained in essentially quantitative yields (exceeding 95%) with inherent viscosities (η_{inh}) in the range of 0.10–0.22 dL/g (Table 1). According to the GPC results, the number–average molecular weights (M_ns) and polydispersities (PDs) are in the range of 1600–6200 and 2.57–3.38 using polystyrene standards, respectively. PPEN-DC10 and PPEN-DC20 were white fibrous solid, whereas the other oligomers were obtained as pale yellow powders.

For comparison, phthalazinone-based poly(arylene ether nitrile) without terminal cyano groups (simplified as PPEN) was also prepared in a similar procedure as for the oligomers. The synthesized polymer (PPEN1) has an inherent viscosity (η_{inh}) of 0.71 dL/g and its M_n detected by GPC is 18 700 (Table 1), indicating the formation of a high-molecular weight polymer. The intrinsic viscosity (η_{inh}) of the resulting polymer (PPEN2) reaches a maximum (1.02 dL/g) when the polycondensation time was prolonged to 12 h, and the maximum M_n is 27,500.

3.2. Characterization of PPEN-DHs and PPEN-DCs

The chemical structure of the oligomers synthesized was characterized using instrumental techniques including IR, NMR and elemental analysis. FT-IR spectra of several representative oligomers are illustrated in Fig. 1. PPEN-DH67 shows a characteristic stretching band appearing at 3444 cm^{-1}, suggesting the presence of lactam N–H in the oligomer chain ends, prior to the termination reaction. In cases of PPEN-DCs, disappearance of absorptions in the range of 3200–3500 cm^{-1} indicates the complete conversion of O–H and N–H groups. The characteristic stretching band of both pendant and terminal cyano groups appears at around 2237 cm^{-1}, whose intensity decreases with the increasing molecular weight, indicating that varying content of cyano group has been introduced into the main chain successfully during the reaction. The absorption band of lactam C=O in phthalazinone appears at 1670 cm^{-1} and the band for Ph–O–Ph linkages at around 1240 cm^{-1}, which correlate sufficiently well with the expected structure of the target oligomers.

A comparison of ^{1}H NMR spectra of two representative samples, PPEN-DH67 and PPEN-DC67, is shown in Fig. 2. The characteristic peaks shifting downfield at around 8.55 ppm, which can always used as the reference signal to assign the other protons, is diagnostic of the typical H-1 signal of phthalazinone moiety. For PPEN-DH67, the presence of lactam N–H ends is identified by signals at 12.91 ppm, which provides powerful evidence for identifying the

Table 1
Synthetic data of PPEN and PPEN-DCs.

Polymer	A/B/C	M_n					η_{inh} (dL g^{-1})[e]	Yield (%)
		M_n[a]	M_n[b]	M_n[c]	M_n[d]	PD[d]		
PPEN1	100/100/0	–	–	–	18,700	2.70	0.71	96
PPEN2	100/100/0	–	–	–	27,500	2.93	1.02	96
PPEN-DC10	100/95/10	6849	7220	7010	6400	3.38	0.22	97
PPEN-DC20	100/90/20	3374	3320	3180	3100	3.14	0.19	96
PPEN-DC50	100/75/50	1453	1420	1610	1400	3.10	0.12	95
PPEN-DC67	100/67/67	1115	1100	1260	1000	2.97	0.10	95
PPEN-DC100	100/50/100	779	830	950	700	2.87	0.10	97

[a] Calculated number-average molecular weight from the molar reactant ratio of HPPZ (A), DFBN (B) and CBN (C).

[b] Estimated by FT-IR analysis assuming two cyano end groups according to Formula I.

[c] Determined by ^{1}H NMR analysis assuming two cyano end groups according to Formula II.

[d] Determined number–average molecular weight and polydispersities by GPC using chloroform as eluting solvent calibrated with polystyrene standards.

[e] Measured in chloroform at 25 °C at a concentration of 0.5 g/dL.

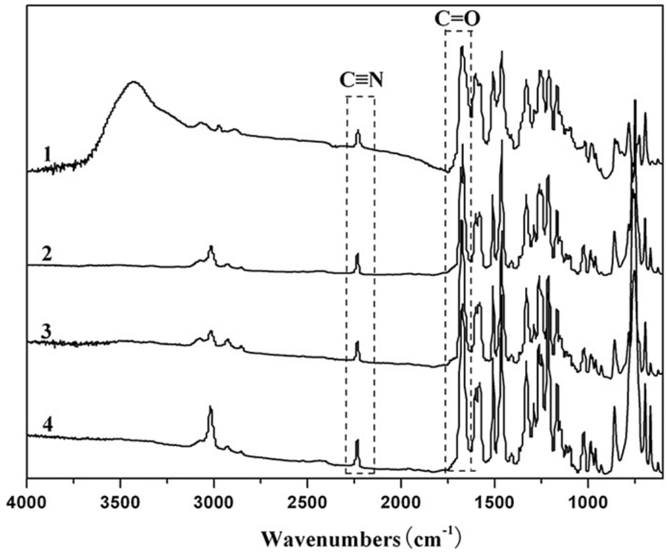


Fig. 1. IR spectra of PPEN-DH67 (1) and PPEN-DCs (2: PPEN-DC10; 3: PPEN-DC50; 4: PPEN-DC67).

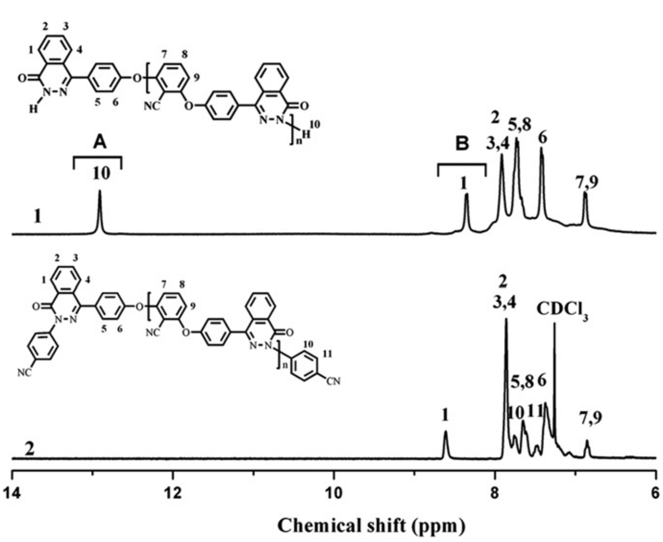


Fig. 2. ^{1}H NMR spectra of PPEN-DH67 (1) and PPEN-DC67 (2).

formation of the aza-nitrogen anion terminated intermediates in the polymerization. In addition, no signal for the hydrogen protons of O–H is observed in the ^{1}H NMR spectrum, suggesting the absence of O–H ends in the PPEN-DH chains and confirming the IR analysis. ^{13}C NMR spectra of PPEN-DHs and PPEN-DCs are also found to be in good accordance with the proposed chemical structure of the corresponding oligomers. The tested values by the element analysis are in reasonable agreement with the theoretical values, which also provides helpful evidence for identifying the chemical structure of the oligomers (see the Experimental Section 2.3 for details).

Molecular weights of PPEN-DCs were determined by IR and ^{1}H NMR spectroscopy technologies, respectively. Based on Beer–Lambert's law, the absorbance of carbon–nitrogen triple bond (2232 cm^{-1}) as a function of cyano content, for specific samples were measured. The number *n* in the oligomeric PPEN-DCs codes, which represents as the degree of polymerization, was calculated by the ratio of absorbance of carbon–nitrogen triple bond in sample spectrum to absorbance in PPEN spectrum, normalized to the lactam carbonyl bands at 1771 cm^{-1}, expressed as follows:

$$\frac{A_{[\mathrm{C}\equiv\mathrm{N}]_n}}{A_{[\mathrm{C}=\mathrm{O}]_n}} = \frac{(n+2)}{(n+1)} \times \frac{A_{[\mathrm{C}\equiv\mathrm{N}]_0}}{A_{[\mathrm{C}=\mathrm{O}]_0}} \tag{1}$$

where $A_{[\mathrm{C}\equiv\mathrm{N}]n}$ and $A_{[\mathrm{C}=\mathrm{O}]n}$ represent as the absorbance of carbon–nitrogen triple bond and lactam carbonyl in PPEN-DCs, respectively. $A_{[\mathrm{C}\equiv\mathrm{N}]0}$ and $A_{[\mathrm{C}=\mathrm{O}]0}$ represent as the absorbance of carbon–nitrogen triple bond and lactam carbonyl in high-molecular weight PPENs, respectively.

In case of the NMR analysis, the degree of polymerization was calculated from the ratio of the area peaks A to that of B (Fig. 2, curve 2), since these area peaks were well distinguished in the ^{1}H NMR spectra of PPEN-DHs. The number *n* in the PPEN-DHs codes could be calculated using the following equation:

$$\frac{2}{n+1} = \frac{I_{\mathrm{H\text{-}10}}}{I_{\mathrm{H\text{-}1}}} \tag{2}$$

where $I_{\mathrm{H\text{-}1}}$ and $I_{\mathrm{H\text{-}10}}$ represent as the integration of characteristic peak for H-1 and H-10, respectively. It is apparent that the number *n* in the PPEN-DCs codes is the same as that in the PPEN-DHs codes. Therefore, the molecular weights of PPEN-DCs could be easily calculated from the number *n*, and the obtained results are listed in Table 1, along with those estimated by IR analysis.

The average molecular weights of PPEN-DCs are dependant on molar ratios of HPPZ and DFBN used in the initial polycondensation, as shown by M_{n}s. According to GPC results, polydispersities of oligomers increase with increasing molecular weights. The tested M_{n}s of the oligomers through either spectral analyses or GPC are very close to the theoretical values calculated from the reactant ratio, indicating that the molecular weights could be well-controlled by adjusting reactant ratio (Table 1).

3.3. *Solubility of PPEN-DCs and PPEN*

The solubility behavior of the obtained oligomers was studied in various organic solvents by dissolving 0.04 g of samples in 1 mL solvent (4%, w/v) at different temperatures. The oligomeric PPEN-DCs are readily soluble in several common solvents such as chloroform, *N*,*N*′-dimethylacetamide (DMAc), *N*,*N*∼-dimethylformamide (DMF) and *N*-methyl-pyrrolidone (NMP) at room temperature. All PPEN-DCs can be easily cast into transparent films through their solutions. For this reason, the oligomers synthesized can possibly be used in applications other than those of the known PEN® and other conventional PAENs, such as membrane and coating applications. The incorporation of crank and twisted non-coplanar phthalazinone into the polymer main chain, which disorders the packing of the intermolecular chain, and hence makes the oligomers organically soluble.

3.4. *Thermal activated crosslinking of PPEN-DCs*

Trimerization of aromatic nitriles was firstly disclosed by Kunz who attempted to obtain s-triazine derivatives and polymers in chlorosulphonic acid about 80 years ago [24]. However, useful polymeric materials were hardly obtained due to the presence of strong toxic and corrosive catalyst. Since then, there have been thousands of s-triazine derivatives or s-triazine polymeric materials derived from aromatic nitriles or cyano-containing oligomers in the catalysis of common acids [25,26]. In summary, these reactions are usually conducted at high-temperatures (200–500 °C) under super-high pressures (3000–50000 atm) [25]. These harsh reaction conditions extremely hamper the preparation and widespread applications of such materials as composite matrix resins, coatings or adhesives, especially for the large volume of bulky equipments. The cyclization of the cyano groups is facilitated by the presence of high-performance catalyst and can be accomplished under much milder reaction conditions [16–20]. For example, the cyano-terminated aromatic polyimide was crosslinked to s-triazine thermosets by heating with *p*-toluenesulfonic acid monohydrate at 200–350 °C under 30–60 atm [19]. The modest trimerization of aromatic nitrile compounds or cyano-containing polymers can be achieved through the charge of a Lewis acid catalyst or its mixtures under normal pressure. For example, the cyclization of the pendant cyano groups in poly(phenylene sulfide)s was conducted at 290–300 °C under atmosphere pressure in the presence of $\mathrm{ZnCl_2}$ [16]. Another successful example was the polymerization of 4,4′-biphenyl-carbonitrile which affords s-triazine polymers under the same conditions described above [17]. In a similar way, the polymerization of terephthalonitrile (TPh) was successfully conducted to generate poly(phenyl-s-triazine)s in our lab. The addition of anhydrous zinc chloride as a catalyst to these reactions was found to be an effective approach in lowering activation energy, thereby reducing the reaction temperature and pressure. In addition, the trimerization of cyano groups can be usually activated by the presence of strong electron-withdrawing groups, such as cyano, nitro or carbonyl in the *ortho*- or *para*-substitutions. Considering the above factors, in a preliminary publication we have also designed a series of oligomeric poly(arylene ether amide)s in which the terminal cyano groups are activated by the *para*-substituted carbonyl groups [20]. This kind of oligomer was crosslinked effectively in the presence of TPh and $\mathrm{ZnCl_2}$ to form s-triazine polymers. The charge of a small quantity of TPh, which increases the concentration of activated cyano groups significantly, was proved to favorite the trimerization statistically.

In this case, cyano groups were introduced into the polymer chains as both pendant groups and terminal groups, with an eye to increasing the crosslinkable group concentration significantly. Facile cyclization reaction of the terminal cyano groups in PPEN-DCs may occur in the presence of TPh and $\mathrm{ZnCl_2}$, since the nitrogen-bridged phthalazinone is a strong electron-withdrawing group similar to conventional activating groups (e.g., carbonyl, sulfone, etc) [27]. The electronic effect of the nitrogen-bridged phthalazinone can be evaluated by ^{1}H NMR, as the deshielding of the protons *ortho* to a substituent is indicative of an electron-withdrawing group. ^{1}H NMR analysis of PPEN-DC67 shows that the peaks of protons (H-10) in the benzonitrile moiety moved downfield dramatically due to the strong electron-withdrawing effect of the *ortho*-oriented nitrogen-bridged phthalazinone moiety (Fig. 2, curve 2). In addition, a comparison of the ^{1}H NMR data of PPEN-DC67 and 4-formylbenzonitrile shows the deshielding of the aromatic protons *ortho* to the nitrogen-bridged phthalazinone ($\delta = 7.8$) verse the aromatic protons *ortho* to a carbonyl group ($\delta = 8.0$), more conventional activating groups, to be only a little smaller with respect to electron affinity. Herein we attempted to present the crosslinking of either pendant cyano groups or terminal cyano groups that was supposed to be conducted at moderate temperatures under normal pressure.

Crosslinking of PPEN and PPEN-DHs with or without the presence of TPh and $ZnCl_2$ was investigated to demonstrate the feasibility of the cyclization of pendant cyano groups to s-triazine. IR spectra experiments were conducted to monitor the structure change of the samples before or after thermal treatment. PPEN mixing with $ZnCl_2$ (1.9 wt%) and TPh (2.9 wt%) was thermally treated under nitrogen atmosphere in a similar procedure as for the preparation of CPPEN-DCs, and the resulting sample was labeled as CPPEN. Neat PPEN samples after thermal treatment under nitrogen and air atmosphere were simplified as PPEN-N_2 and PPEN-Air, respectively. A comparison of IR spectra of these samples is demonstrated in Fig. 3. Of primary interest is the absorption band at 2225 cm^{-1} associating with the stretch of $C\equiv N$, since it gives useful information on the chemical structure change during the crosslinking process. Compared to that of original PPEN, IR spectra of PPEN-N_2 and CPPEN are basically the same. For PPEN-air, the Ar–O–Ar absorption at 1225 cm^{-1} almost disappears, and the absorptions at 1610 and 1513 cm^{-1} for C–H of phenyl rings significantly decrease in their intensity, implying the occurrence of some chain rupture or dehydrogenation during the thermal treatment process under air atmosphere. However, it gives no change in intensity or location of the absorption band attributed to the $C\equiv N$ stretch, suggesting that the chemical structure change would not be attributed to the reactions of cyano groups. Similar experimental results are also exhibited by PPEN-DH67 samples after thermal heating cycles with or without the presence of TPh and $ZnCl_2$. In comparison with IR spectra of these samples, in which the intensity of the $C\equiv N$ absorption keeps almost constantly, we conclude that the pendant cyano groups hardly undergo any reactions under these conditions, even in the presence of TPh and $ZnCl_2$. DSC traces were also performed on PPEN, PPEN-N_2, PPEN-air and CPPEN (Fig. 4). There is no obvious exothermic event relate to the reaction of cyano groups in the DSC runs of PPEN or CPPEN. Additionally, the T_g values of PPEN-N_2 and CPPEN detected by DSC are very close to that of neat PPEN. These phenomena indicated that no crosslinking of the pendant cyano groups occurred with or without the presence of TPh and $ZnCl_2$, confirming the IR analysis. This may be explained by the fact that the great steric hindrance of long polymer chains in the *ortho*-substitutions makes cyano groups hard to move and reduces their collision probability, thereby making the crosslinking kinetically unfavorable. The detected T_g value of PPEN-air is a little higher than that of PPEN, possibly due to the emergence of certain crosslinking under air atmosphere. Therefore, the cyano crosslinking of PPEN-DCs should be performed under the protection of an inert atmosphere to avoid other unexpected reactions.

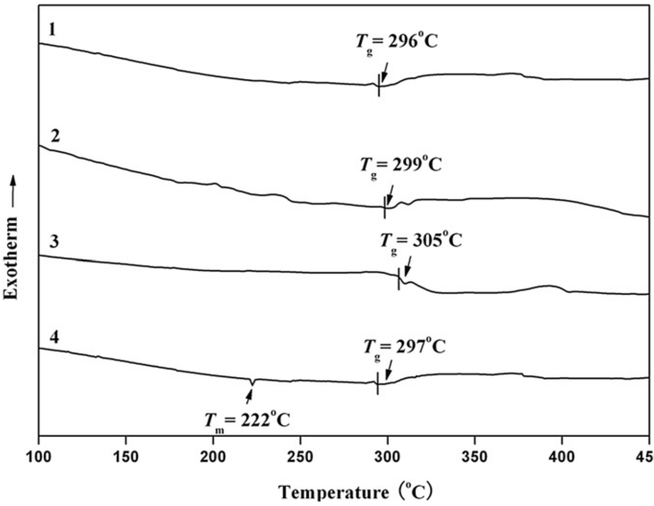


Fig. 4. DSC traces of PPEN before/after thermal treatment (1: PPEN; 2: PPEN-N_2; 3: PPEN-air; 4: CPPEN).

The crosslinking of PPEN-DCs was monitored *in situ* by using IR spectra on KBr pellets. Fig. 5 shows IR spectra of a representative PPEN-DC67 mixing with TPh and $ZnCl_2$ after cumulative curing at each temperature for 6 h under nitrogen atmosphere. Since the pendant cyano groups are not reactive enough to polymerize to s-triazines, the crosslinkable groups in curing system include the terminal cyano of oligomers and the cyano groups of TPH both of

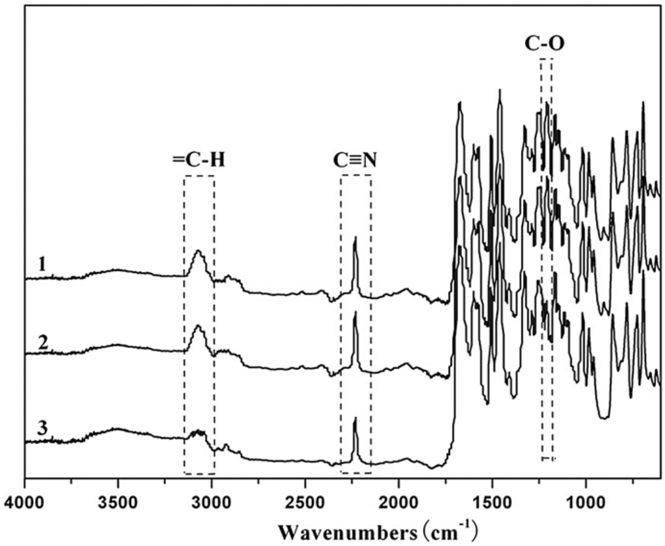


Fig. 3. IR spectra of PPEN before/after thermal treatment (1: PPEN-N_2; 2: CPPEN; 3: PPEN-air).

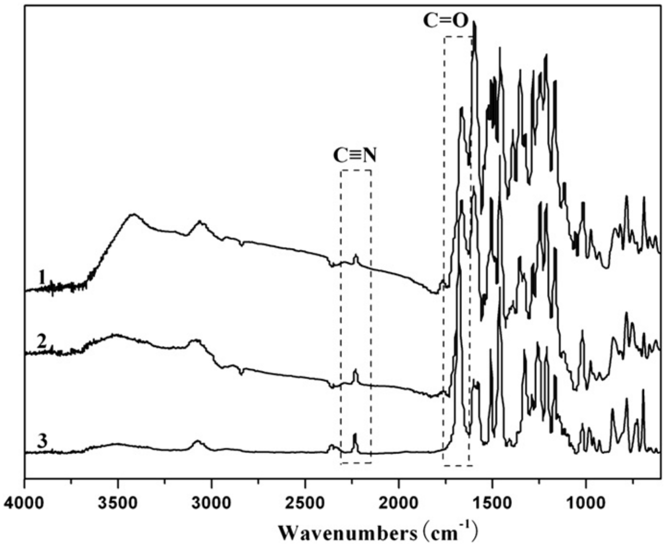


Fig. 5. IR spectra of PPEN-DC67 mixing with TPh and $ZnCl_2$ after crosslinked at different temperatures (1: 310 °C; 2: 330 °C; 3: 350 °C).

which are activated by the strong electron-withdrawing substituent in the *para*-orientation. For PPEN-DC67, the calculated activated cyano content is 69 mol percents relative to the total cyano groups in the curing system. After curing at 310 °C, the intensity of nitrile absorption is about 89% of the origin intensity, while it is around 74% of the origin intensity after curing at 330 °C, normalized to the lactam carbonyl bands at 1671 cm^{-1}. The intensity of nitrile absorption of sample after curing at 350 °C decreases by 33% relative to the origin sample, suggesting the near completeness of the crosslinking reaction. Instead, the intensity of both the absorption at 1602 cm^{-1} attributed to C=N and the absorption at 1495 cm^{-1} attributed to C–N increases significantly in the spectra of the crosslinked samples, indicative of the formation of s-triazine. Besides these characteristic absorptions, the other absorptions such as C=O stretch (lactam carbonyl), C–H stretch (benzene ring) and Ph–O–Ph stretch (ether linkage) demonstrate no obvious change in their intensities and locations after the cumulative curing. These data from IR identify that certain crosslinking reactions have taken place through the cyclization of activated cyano groups, and no obvious decomposition or carbonization have occurred during the curing processes. Crosslinking studies of PPEN-DCs were also achieved by DSC analysis up to 400 °C in the presence of TPh and $ZnCl_2$ under nitrogen. Typical first DSC traces on several representative samples are presented in Fig. 6, and the second DSC runs were also performed under nitrogen after quenching at the end of the first scan (10 °C/min, not shown). For this study, homogeneous mixtures of PPEN-DCs with TPh and $ZnCl_2$ were obtained by thoroughly stirring the powdered materials at room temperature. As specified in Tables 2 and 3, the blended mixtures show small exothermic peaks ranged from 298 to 316 °C corresponding to thermally induced reaction of cyano groups after an endotherm during the first DSC run. The exothermic center moves to the region of higher temperatures with the increasing molecular weight, dependent of the exact blend composition. Additionally, the exothermic peaks observed in the first scan disappear in the second DSC scan. These results also clearly indicate the occurrence of certain thermally activated crosslinking of the oligomers in the presence of TPh and $ZnCl_2$. The apparent endothermic events in the first DSC run are attributed to glass transitions (T_gs, 245–269 °C) of uncured PPEN-DCs, while the glass transitions advances to higher temperatures in the second DSC run. These phenomena may be ascribed to the partly crosslinking of the mixtures which was progressing in the DSC sample cell during the heating run.

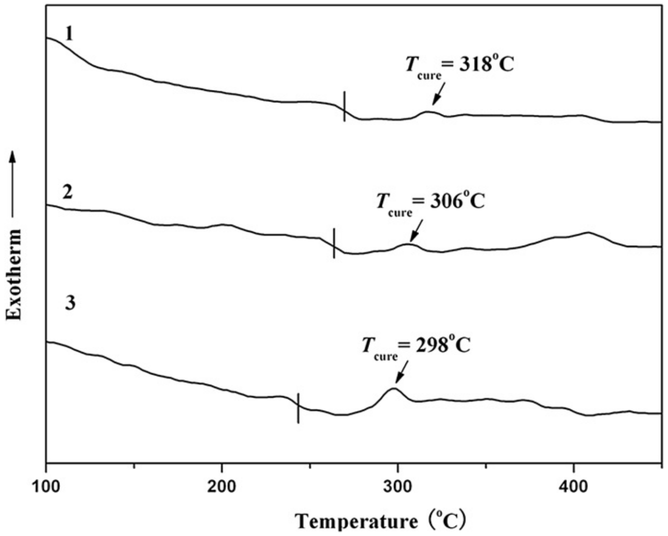


Fig. 6. DSC traces of PPEN-DCs mixing with TPh and $ZnCl_2$ (1: PPEN-DC10; 2: PPEN-DC50; 3: PPEN-DC67).

Table 2
Gel content, long-term water absorption and isothermal data of the samples.

Polymer	Gel content	Water uptake[a]	Rates (wt%/h)[b]		Rates (wt%/h)[c]	
	(%)	(%)	N_2	Air	N_2	Air
CPPEN-DC10	62	2.7	0.016	0.323	0.011	0.271
CPPEN-DC20	69	2.5	0.019	0.353	0.009	0.252
CPPEN-DC50	72	2.5	0.025	0.365	0.007	0.240
CPPEN-DC67	86	2.4	0.026	0.368	0.007	0.239
CPPEN-DC100	92	2.2	0.031	0.391	0.005	0.214

[a] The maximum amount of water absorption over the course of 30 days at 25 °C.
[b] Weight loss rates of isothermal aging of oligomeric PPEN-DCs were determined at 371 °C with a nitrogen or air flow of 50 mL/min over 24 h by isothermal scan.
[c] Weight loss rates of isothermal aging of CPPEN-DCs were determined at 371 °C with a nitrogen or air flow of 50 mL/min over 24 h by isothermal scan.

Testing gel content of crosslinked polymers is a commonly used method to evaluate curing degree. Solubility experiments indicate that CPPEN-DCs become insoluble in the organic solvents, in which the oligomeric PPEN-DCs can readily dissolve. Therefore, the intense difference in solubility makes it possible to determine the gel content of the crosslinked samples simply by using Soxhelt extraction. The gel content was determined by using chloroform as an extracting solvent according to ASTM D2765 method. Samples were refluxed in chloroform for at least 48 h, until the sample attained a constant weight. The residue after extraction was taken as the gel component, and the gel content was then calculated according to the following equation (Formula (3)).

$$\text{Gel content}: \ \text{Gel content}(\%) = \frac{W_1}{W_2} \times 100 \tag{3}$$

where W_1 and W_2 are the weights of the samples after and before refluxed in chloroform, respectively. As shown in Table 2, the gel contents of CPPENs are in the range of 62–92%. It is well accepted that the crosslinking degree of a crosslinked sample depends on a number of factors. The main factors involve the concentration of crosslinkable groups, the curing cycles, the catalyst type and content, the mobility of curing agent, oligomer reaction sites, etc. In this case, the different crosslinking extents, which are reflected in gel content value, may be mainly due to the difference in the mobility of the reaction sites and their concentration. The mobility of the terminal cyano groups and their concentration decrease with an increase in the molecular weight of the oligomers, and hence the gel content of the corresponding crosslinked samples decreases. For example, PPEN-DC100 has the lowest molecular weight and softening temperature among the samples investigated, and in turn the highest gel content is exhibited by its crosslinked sample.

Table 3
Thermal properties of PPEN and PPEN-DCs.

Polymer	T_g[a] (°C)	T_c[a] (°C)	$T_{5\%}$[b] (°C)	$T_{10\%}$[b] (°C)	T_{max}[c] (°C)	C_y[d] (%)
PPEN	296	–	516	527	516	69
PPEN-DC10	269	318	488	519	516	65
PPEN-DC20	254	310	480	518	517	64
PPEN-DC50	249	306	476	510	518	62
PPEN-DC67	247	305	463	501	518	61
PPEN-DC100	245	298	459	491	517	60

[a] Glass transition temperature (T_g) and curing temperature (T_c) tested by DSC in nitrogen, 10 °C/min.
[b] Temperature for 5% weight loss and 10% weight loss tested by TGA in nitrogen, 20 °C/min.
[c] Temperature for the maximum tested by DTG in nitrogen, 20 °C/min.
[d] Char yield calculated as the percentage of solid residue after heating from 100 to 800 °C by TGA in nitrogen, 20 °C/min.

Therefore, both the terminal cyano concentration and mobility are crucial factors for the crosslinking of oligomers. This can be explained by the fact that both good mobility of oligomer chain ends and high crosslinkable group concentration favorite the crosslinking and cyclization statistically and kinetically. The formation of the insoluble polymers and high gel content values suggests that the activated cyano groups in the curing systems are thermally reacted with each other by the curing.

Our experimental results demonstrate that certain thermal crosslinking reaction of cyano groups occurred, resulting in crosslinked networks containing s-triazine units. It is suggested, therefore, that the activated cyano groups were consumed in the crosslinking reaction forming three-dimensional polymers whereas the pendant cyano groups remained the same. However, it is still very hard to know the exact chemical structure of the produced networks since there are many optional structural formulas deriving from the cyclization of the activated cyano groups of PPEN-DCs or TPh. Referring to the literatures, the proposed crosslinking reaction process of PPEN-DCs and TPh catalyzed by zinc chloride is illustrated in Scheme 2, postulating that the reaction of the terminal cyano groups forms s-triazine rings via trimerization mechanism [17,20].

3.5. Long-term water absorption capability of CPPEN-DCs

An important aspect of crosslinked networks is their water absorption capability. The water absorption capability of CPPEN-DCs was determined by using long-term water absorption experiments on film samples. Table 2 lists the maximum amount of water absorption at the ambient temperature over the course of 30 days for crosslinked samples after thermal heating runs. The maximum amounts of water absorption of CPPEN-DCs are ranging from 2.2 to 2.7 wt%. The water uptake value appears to decrease with the increasing crosslinking extent of the investigated samples. For the use of CPPEN-DCs in a high humidity or aqueous environment, the limited water absorption is a significant advantage over other high-temperature polymers.

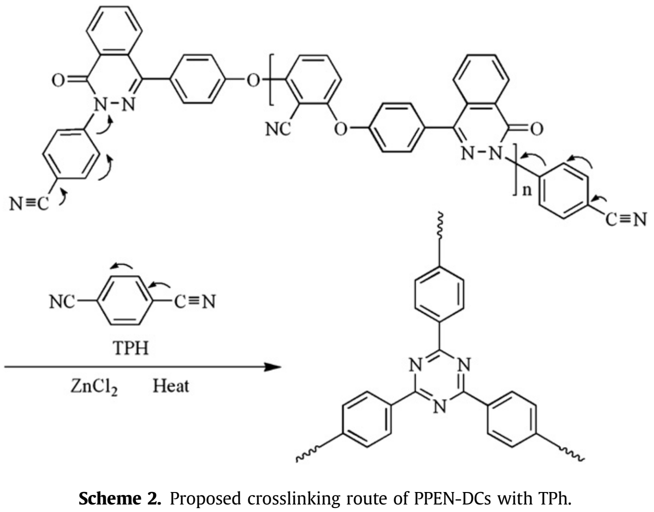
3.6. Thermal properties of PPEN-DCs and CPPEN-DCs

The thermal behavior of PPEN-DCs and their crosslinked samples was investigated by applying differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) measurements. As could be expected from the molecular structure, the resulting oligomers exhibit transitions in the region of high-temperatures exceeding 245 °C (taking as the midpoint of the change in slope of the baseline in DSC curve), indicative of good heat resistance (Table 3). It is apparent that the T_g values increase gradually with the molecular weight and is a function of molecular weight, which approximately fits the rule of common oligomers. For example, PPEN-DC10, whose has the highest number–average molecular weight (6400), determined by GPC, has the highest T_g among the samples investigated. The T_gs of oligomers can be predicted based on their molecular weight as presented in Table 3 using the following equation [28]:

$$T_g(\infty) - T_g = k \log[M_n(\infty) - M_n] \tag{4}$$

where k and M_n are characteristics of each polymer, and $M_n(\infty)$ defines a value above which T_g ceases to be molecular-weight dependent. T_g and M_n represent as the glass transition and the molecular weight of the oligomers, respectively. The relationship of $T_g(\infty)$–T_g verse $\log[M_n(\infty) - M_n]$ is plotted in Fig. 7. In the practical range of molecular weights (1600–6200), a good agreement of the T_g values of the oligomers with values predicted by Formula IV according to the M_n is also observed. Therefore, the T_gs of the oligomers can be tailored by varying the molar reactant ratio. In addition, another key feature is that the T_gs of PPEN-DCs are much higher than that of the known PEN® ($T_g = 148$ °C) [5], due to the introduction of the heterocyclic phthalazinone into the backbone which leads to an increase in polymer chain stiffness. These results demonstrate that the incorporation of rigid phthalazinone is an effective way to raise T_gs and improve the heat resistance of PAENs. Fig. 8 presents DSC traces (10 °C/min, first scan) of several typical crosslinked samples. The glass transitions of CPPEN-DCs, which are higher than 363 °C, are increased at least by 94 °C relative to their oligomers (Table 4). The increase in T_g values results from the thermally activated crosslinking that leaded to a three-dimensional structure and hence decreased the flexibility of polymer backbone. For CPPEN-DC67 and CPPEN-DC100, no evident endothermic events corresponding to glass transitions is observed in their DSC runs up to 450 °C, possibly due to their higher crosslinking extents than others.

TGA and DTG curves of PPEN-DC67 and its corresponding crosslinked sample, CPPEN-DC67, are illustrated as examples in Fig. 9. The oligomers show char yields (C_y) of 60–65%, when heated to 800 °C under nitrogen atmosphere, whereas the char yields of the samples crosslinked with TPH and $ZnCl_2$ are increased by 6% at



Scheme 2. Proposed crosslinking route of PPEN-DCs with TPh.

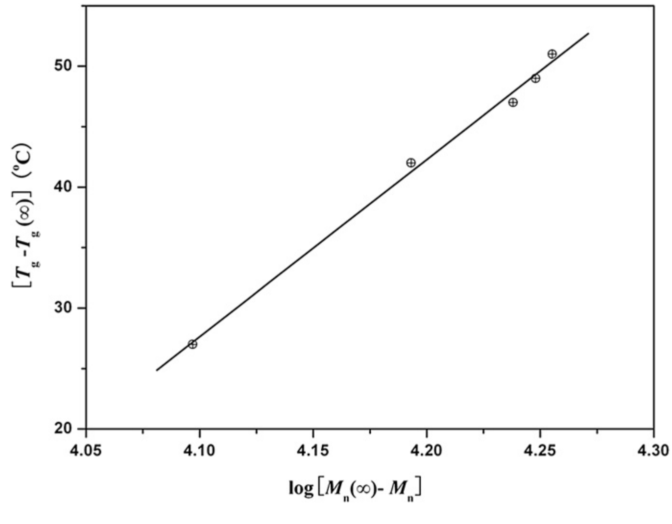


Fig. 7. Relationship of $T_g(\infty)$–T_g verse $\log[M_n(\infty) - M_n]$ of oligomeric PPEN-DCs.

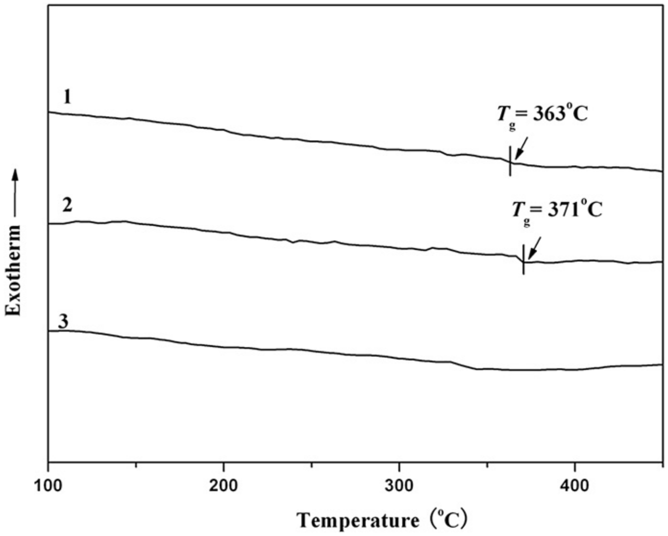


Fig. 8. DSC curves of CPPEN-DCs (1: CPPEN-DC10; 2: CPPEN-DC50; 3: CPPEN-DC67).

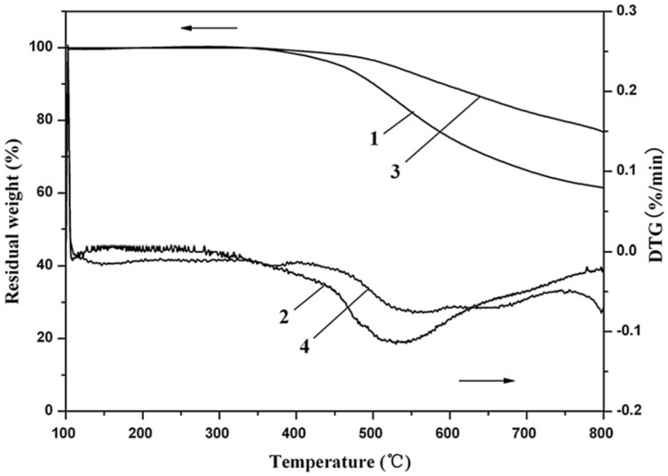


Fig. 9. TGA and DTG thermograms of PPEN-DC67 (1: TGA; 2: DTG) and CPPEN-DC67 (3: TGA; 4: DTG).

least. Among the samples investigated, CPPEN-DC100 exhibits the best thermal stability with a weight retention of about 78% at 800 °C. The increase in anaerobic char yields is most probably due to the formation of heterocyclic s-triazine groups that have higher char concentration than uncured cyano groups at the elevated temperatures. Additionally, the anaerobic C_y values of CPPEN-DC increase with the decreasing molecular weights of the corresponding oligomers, since the s-triazine content is significantly affected by the relative concentration of terminal cyano groups in the curing system. Thermal data from TGA indicate PPEN-DC and CPPEN-DC possesses excellent thermal stability without significant weight loss till 400 °C in nitrogen (Fig. 9). A study of PPEN-DCs shows that the oligomers commence to slowly lose weight at about 450 °C with catastrophic weight loss occurring between 500 and 550 °C. Therefore, the oligomers are stable indefinitely on room temperature storage or during thermal heating cycles. The crosslinked samples show much higher weight retentions at 550 °C, which is attributed to the greatly enhanced thermal stability after crosslinking. The decomposition temperatures of PPEN-DCs for 5% weight loss ($T_{5\%}$) and 10% weight loss ($T_{10\%}$) increase with the increasing molecular weights, whereas those of CPPEN-DCs decrease with the increasing molecular weights (Table 4). In the case of crosslinked polymers, the $T_{5\%}$ values and $T_{10\%}$ values show an increase at least by 27 °C and 47 °C relative to the uncured samples, respectively, and these values are much higher than those of analogous PPEN, thus being more thermally stable. The DTG curves of PPEN-DCs demonstrate one decomposition stage at around 517 °C, while the crosslinked samples exhibit two stages at temperatures higher than 549 °C under nitrogen (Fig. 9). It is very apparent that the thermal decompositions of the samples are slowed down after being crosslinked in the presence of TPH and $ZnCl_2$, as shown in the DTG curves.

Table 4
Thermal properties of CPPEN and CPPEN-DCs.

Polymer	T_g[a] (°C)	$T_{5\%}$[b] (°C)	$T_{10\%}$[b] (°C)	T_{max}[c] (°C)	C_y[d] (%)
CPPEN	296	518	528	516	69
CPPEN-DC10	363	515	566	547, 658[e]	71
CPPEN-DC20	368	519	579	552, 664[e]	73
CPPEN-DC50	371	520	581	549, 670[e]	74
CPPEN-DC67	–	525	591	551, 663[e]	77
CPPEN-DC100	–	528	599	553, 661[e]	78

[a] Glass transition temperature (T_g) tested by DSC in nitrogen, 10 °C/min.
[b] Temperature for 5% weight loss and 10% weight loss tested by TGA in nitrogen, 20 °C/min.
[c] Temperature for the maximum tested by DTG in nitrogen, 20 °C/min.
[d] Char yield calculated as the percentage of solid residue after heating from 100 to 800 °C by TGA in nitrogen, 20 °C/min.
[e] Two peaks in the DTG curves.

The thermal and oxidative stabilities of both PPEN-DCs and crosslinked samples were also evaluated in isothermal aging experiments by using ISO-TGA. The results (Table 2) from isothermal aging experiments indicate that the linear oligomers show weight loss rates ranging from 0.014 to 0.031 wt%/h during isothermal aging at 371 °C under nitrogen atmosphere. The weight loss rates under air atmosphere (ranging between 0.323 and 0.391 wt%/h) are much higher than those under nitrogen atmosphere, which could be ascribed to more obvious thermal degradation under such rigorous circumstances. These results demonstrate that the uncured PPEN-DCs exhibit good thermal and oxidative stability, which is a vital factor for their process and crosslinking at elevated temperatures. A comparison of the weight loss rates under nitrogen and air atmosphere indicates the overall thermal and oxidative stability increase significantly after thermal crosslinking. The main reason is the formation of s-triazine which is known as a heterocyclic unit with high resonance energy along the polymer chain and high decomposition activation energy. CPPEN-DC100 was found to be most thermally stable in nitrogen and air atmosphere, confirming the TGA and DTG analysis.

3.7. *Crystallinity of PPEN-DCs and CPPEN-DCs*

Crystallinity of the oligomeric PPEN-DCs and their crosslinked samples was investigated by means of wide-angle X-ray diffraction (WAXD) on powder samples at room temperature. The WAXD patterns of PPEN-DC67 and CPPEN-DC67 are illustrated in Fig. 10. The etherification chemistry of 2,6-dihalobenzonitrile with HPPZ gave the synthesized oligomers a symmetrical *m*-phenylene ether structure. This short-range ordering suggests that an X-ray diffraction spectrum could contain more information than just an amorphous reflection, despite the cranked, twisted non-coplanar nature of the phthalazinone moieties. Several sharp diffraction peaks appearing at $2\theta = 10–40°$ are observed in the WAXD patterns of the oligomers, implying the existence of short-distance order in the main chain, whereas no obvious diffraction peak is observed in cases of the corresponding crosslinked samples. A decrease in the

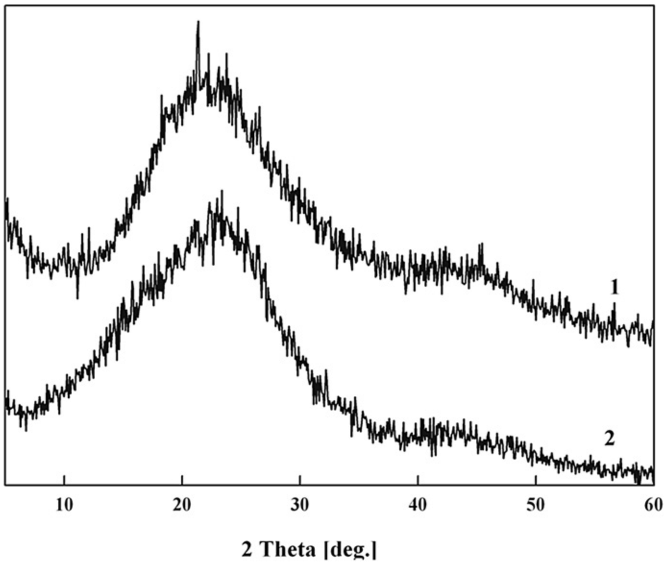


Fig. 10. WAXD diffractograms of PPEN-DC67 (1) and CPPEN-DC67 (2).

crystallinity of crosslinked samples relative to the oligomers may be attributed to the formation of networks that causes profound disturbance in the regularity of polymer chains, suggesting the occurrence of certain crosslinking. The calculated crystallinity degree of the oligomers is almost negligible, and therefore, they are amorphous. The amorphous nature could be mainly ascribed to the presence of the phthalazinone moiety that disrupts the planarity and symmetry of polymer chains.

4. Conclusion

A series of oligomeric phthalazinone-base poly(arylene ether nitrile)s with different terminal cyano contents have been successfully synthesized via nucleophilic substitution polycondensation from commercially available materials under milder reaction conditions. The incorporation of phthalazinone into the polymer chain is an effective way to improve the solubility, and raise T_gs of PAENs. The resulting oligomers can potentially be used as films, coatings, fibers or other applications. DSC, IR, TGA, DTG, ISO-TGA and WAXD results demonstrate the emergence of certain crosslinking of cyano groups in the presence of terephthalonitrile and zinc chloride after thermal treatment cycles. The pendant cyano groups are not reactive enough to cyclize while the terminal cyano groups demonstrate much higher reactivity in s-triazine forming reaction. Their interconnection with phthalazinone via N–C linkages promotes some crosslinking and cyclization under normal pressure. Crosslinked samples exhibit superior thermal and oxidative stability, compared to the linear oligomers, and shows limited water absorption. This kind of PPEN-DCs and their cross-linked networks may be considered as potential high-temperature materials in a wide range of applications.

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