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Soluble and curable poly(phthalazinone ether amide)s with terminal cyano groups and their crosslinking to heat resistant resin

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ABSTRACT

Soluble and curable aromatic polyamides have great potential use as processable and heat-resistant polymeric materials. In this study, a novel series of soluble aromatic polyamides (CN-PPAs) containing phthalazinone moiety and crosslinkable terminal cyano groups were synthesized by polycondensation of 1,2-dihydro-2-(4-carboxyphenyl)-4-[4-(4-carboxyphenoxyl)phenyl]-phthalazinone (DHPZ-DC) with calculated 4,4′-oxydianiline (ODA), followed by end-capping with 4-cyanobenzoic acid (CBA). Thermal crosslinking of CN-PPAs, catalyzed by zinc chloride, was then performed in the presence of terephthalonitrile (TPH) via heating either their films or powders up to 300–340 °C. The uncured synthesized polymers have good solubility while the cured samples become insoluble in common organic solvents. Spectra and elemental analysis measurements demonstrate cyclization reaction of terminal cyano groups to form s-triazine rings. The presence of TPH and $ZnCl_2$ is effective in promoting thermal crosslinking and s-triazine forming reaction of the CN-PPAs under normal pressure. The resulting cured samples exhibit no T_g up to 400 °C by DSC and have excellent thermal stability. This kind of cyano-terminated poly (phthalazinone ether amide) may be a good candidate as matrix for high performance polymeric materials.

1. Introduction

Full aromatic polyamides have been used in applications demanding service at elevated temperatures, because of their good balance of chemical, mechanical and physical properties [1]. Nevertheless, they have extremely high melt temperatures and poor solubility, due to their rod-like structures, strong intermolecular hydrogen bonding between the chains or semi-crystallinity [2]. Thus, the utilities of these materials as resins in laminating, molding, or coating applications often suffer from considerable processing and handling problems, because of their insolubility in organic solvents and infusibility before the decomposition. For example, the commercially available Kevlar® (DuPont) can only be spun from the highly corrosive concentrated sulfuric acid solution [3].

To tackle these problems, many efforts have been devoted to the improvement of their solubility or melt processability via structural modification of the polyamide chains [4]. Among of them, an effective approach to improve solubility or processability of polyamides is the incorporation of flexible ether linkages, and kink, non-coplanar or non-linear moieties into the main chains [5]. In this way, our laboratory have prepared organically soluble poly(ether amide)s containing phthalazinone segments in the main chain via the polycondensation of unsymmetrical heterocyclic diamines or diacids containing phthalazinone moieties [6]. The obtained amorphous polyamides possess improved solubility, since the kink, non-coplanar phthalazinone structure in the polymer parent chain disorders the packing of the intermolecular chain. And such materials show acceptable thermal properties with glass transition temperatures ranging from 291 to 340 °C. In addition, we have also reported the lyotropic liquid crystalline behavior of copolyamides containing phthalazinone moieties and ether linkages recently [7]. And the applications of these polymers such as dry–wet spinning of fibers or the preparation of films, membranes and coatings from their LC solutions are studied currently under way.

Another part of our current work focuses on the preparation of soluble and curable poly(phthalazinone ether amide)s, which can be processed in their organic solutions and thermally crosslinked to generate high performance thermosetting resins. Such materials are supposed to possess an attractive combination of excellent thermal stability, good chemical resistance and superior flame resistance due to the formation of crosslinked networks. For their good comprehensive properties, the resultant polymers may be

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used as base materials for high temperature adhesive, coating or composite matrix in a wide range of applications. It is well accepted that a good approach to obtain curable polymers is the introduction of curable groups such as styryl, cyano and phenyl ethynyl into the polymer chains [8–10]. As a typical and potent crosslinkable group, cyano is often used owing to its easy introduction to the polymer chains as pendent or terminal group and its trimerization to form s-triazine ring-based thermosetting possessing excellent thermal stability [11,12]. Furthermore, the curing of the cyano-containing polymers can be proceeded in the absence of catalyst, without evolution of any volatiles. Additionally, the introduction of cyano group into the polymers can not only appear to promote adhesion of the polymer to many substrates [13], but also endow their polymers with excellent thermal and chemical resistance, mechanical strength, flame retardancy, and molding workability even without being crosslinked [14], compared to commercially available thermoplastic resins such as polyethylene, polyphenylene oxide, polycarbonate, polyesters, etc. As reported, the s-triazine formed by the trimerization of cyano groups is usually extremely difficult, most likely due to the low content of cyano groups [15] and the high reaction activation energy of the trimerization [11]. However, there are also some reports concerning the crosslinking of cyano-modified polymers by formation of s-triazine rings, and certain aromatic polymers containing pendant [12,15] or terminal cyano groups [16–18] have been thermally converted to insoluble products. For instance, Haddad has described the crosslinking of poly(phenylene sulfide)s containing the pendant cyano groups to give insoluble products possessing excellent thermal stability [15]. Cyano-terminated polymers, such as polyethers, polysulfones, and polyketones were also thermally crosslinked effectively, possibly by the trimerization of cyano groups to triazines [16]. Hsu has published the synthesis of s-triazine-containing crosslinked polymers via the trimerization of aromatic nitrile-modified (terminated or appended) prepolymers or oligomers containing imide, benzimidazole, imidazopyrrolone or quinoxaline, and other condensation type polymers. The resulting thermosetting polymers are very useful in applications requiring high thermo-oxidative properties and high performance structural properties at elevated temperatures [17]. Believing that crosslinking of cyano groups would be promoted by increasing their concentration, Keller and his coworkers have synthesized aromatic diether-linked phthalonitrile resin from resorcinol, bisphenol or bisphenol A based biphthalonitrile monomers in the presence of amine, which could cure at elevated temperatures to form s-triazine ring-containing thermosetting polymers, leading to excellent thermo-oxidative properties and good chemical resistance [18].

To broaden the applications of the polyamides in structural applications, herein we report a kind of soluble and curable poly(ether amide)s containing phthalazinone moieties and terminal cyano groups (simplified as CN-PPAs) in the main chain. We have attempted their curing at decreased temperatures and under normal pressure by the introduction of terephthalonitrile and zinc chloride. Their crosslinking behaviors have been investigated in detail and properties of both linear and crosslinked polymers have been also studied.

2. Experimental

2.1. Materials

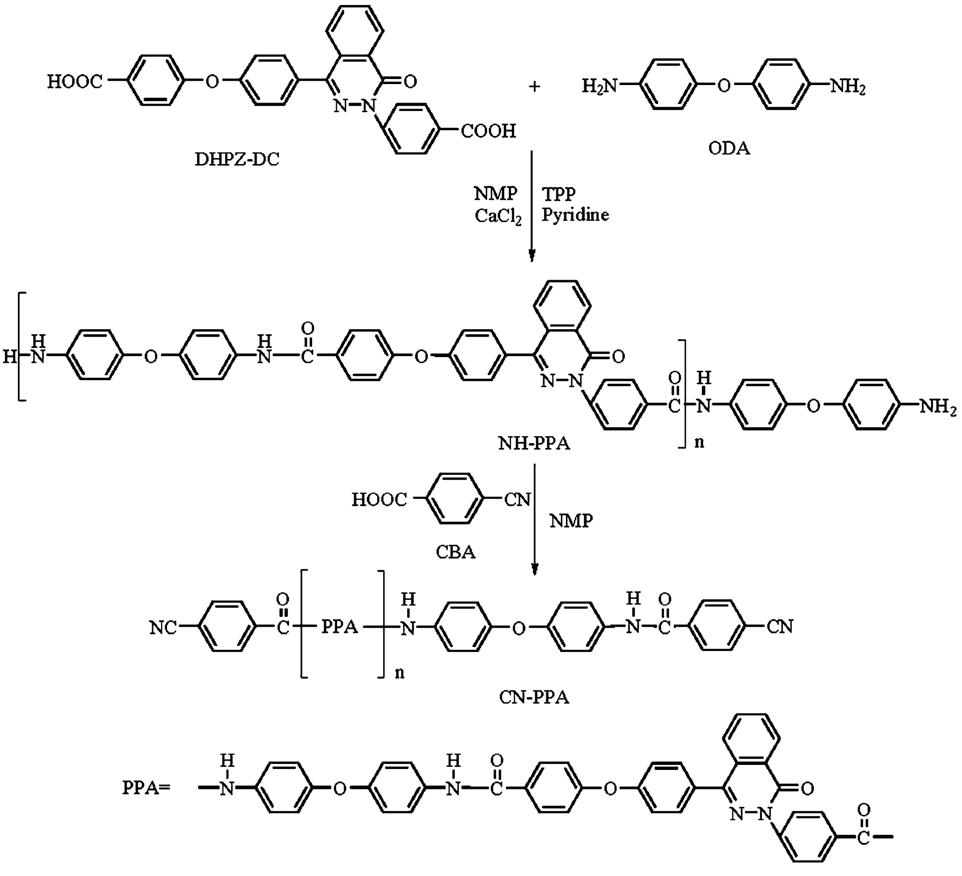
4,4′-Oxydianiline (ODA) was recrystallized from ethanol. *p*-Phenylenediamine was purified by vacuum sublimation. 4-Cyanobenzoic acid (CBA) and terephthalonitrile (TPH) were purchased from Aldrich–Sigma, and used as-received. Anhydrous zinc chloride was refluxed and distilled over thionyl chloride and later toluene to remove water, and dried for 24 h at 180 °C under vacuum. *N*-Methyl-pyrrolidone (NMP) was distilled under reduced pressure over CaH_2. Pyridine (Py) was refluxed over KOH pellets and distilled. Triphenyl phosphite (TPP) was distilled under vacuum. Anhydrous calcium chloride ($CaCl_2$) was dried for 4 h at 180 °C under vacuum just before use. 1,2-Dihydro-2-(4-carboxyphenyl)-4-[4-(4-carboxyphenoxyl)phenyl]-phthalazinone (DHPZ-DC) was synthesized according to the procedure reported previously [19]. The product was obtained as white powder; m.p.: 313 °C; yield: 99 wt% (weight percent). Unless otherwise specified, all other solvents and reagents were purchased from Beijing Chemical Co. and used as-received.

2.2. Characterization methods

Inherent viscosities (η_{inh}) of the polymers were measured by Ubbelohde capillary viscometer at 25 °C. Infrared measurements were performed on a Thermo Nicolet Nexus 470 Fourier transform infrared (FT-IR) spectrometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained with a Brucker spectrometer at an operating temperature of 25 °C using DMSO-d_6 as solvents. Gel permeation chromatography (GPC) analysis was carried out on a HP 1090 HPLC instrument equipped with 5 μm Phenogel columns (linear, 4 × 500 Å) arranged in series with tetrahydrofurfuran as solvent and a UV detector at 254 nm. And the values were calibrated versus polystyrene standard. 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 a nitrogen atmosphere at a heating rate of 20 °C/min from 100 to 800 °C. Decomposition temperature (T_d) in nitrogen was taken as the temperature 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 flowing nitrogen. The glass transition temperature (T_g) was determined with a Mettler DSC822 differential scanning calorimetry (DSC) in flowing nitrogen at a heating rate of 10 °C/min from 100 to 400 °C. The T_g value was taken at the inflection point and T_{cure} was recorded at the exothermal peak of DSC curves from DSC measurements. The limiting oxygen index (LOI) of samples was determined on an SH5706 oxygen index apparatus (Guangzhou Sunhe Co. Ltd., P.R. China) according to ASTM Test Method D 2863. Isothermal scan was performed at 350 °C over a 24 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 V, 100 mA).

2.3. Polymer synthesis

The preparation of oligomeric CN-PPA3 was given as a typical example: A 100 mL three-necked round-bottomed flask, fitted with nitrogen gas inlet tube, a stirrer and a condenser, was charged with a mixture of DHPZ-DC (0.478 g, 1.0 mmol), ODA (0.200 g, 0.9 mmol), $CaCl_2$ (0.48 g, 4.3 mmol), TPP (2.0 mmol), NMP (3 mL) and Py (1 mL). The mixture was stirred and refluxed under N_2 atmosphere at 110 °C for 3 h, and then cooled to room temperature. CBA (0.324 g, 0.22 mmol) was added into the reaction mixture and heated to 110 °C for another 1 h. After cooling, the reaction solution was poured into a mixture of methanol and water (60 mL, Volume ratio = 1:1) and the precipitated polymer was washed thoroughly with hot water and methanol. Then the white polymers were



Scheme 1. Synthetic route of CN-PPAs.

extracted with acetone for 12 h and dried under vacuum overnight at 100 °C. The yield was 99.6 wt%. Selected data of CN-PPA3: IR (KBr, cm^{-1}): 3307 (N–H), 3062, 3033 (=C–H), 2225 (C≡N), 1667 (C=O), 1599, 1528 (C=C/C=N), 1499, 1407, 1311, 1242 (C–O), 846. ^1H NMR (400 MHz, DMSO-d_6, ppm) δ: 10.51 (s, N–H), 10.27 (s, N–H), 10.40 (s, N–H), 8.48–8.49 (d, Ar–H), 6.90–8.22 (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 CN-PPA3 $(C_{97}H_{63}N_{10}O_{12})_n$: C, 74.65; H, 4.07; N, 8.98%. Found: C, 72.93; H, 4.03; N, 8.67%.

2.4. Thermal crosslinking

The thermal crosslinking reaction of the oligomeric CN-PPAs was performed by heating either the oligomer powders or their films using $ZnCl_2$ as catalyst (1.9 wt% relative to the polymer) and TPH as curing agent (2.9 wt% relative to the polymer) in nitrogen atmosphere.

A typical thermal crosslinking procedure of the CN-PPA3 powders was carried as follows. A mixture of CN-PPA3 (1.00 g), TPH (0.03 g) and $ZnCl_2$ (0.02 g) was pulverized and evenly dispersed by vigorous stirring. Then the mixture was cured via heating in a test tube at 260 °C for 2 h, 300 °C for 2 h, 320 °C for 2 h and at 340 °C for 42 h under nitrogen atmosphere to afford crosslinked samples. Once the samples were readily cooled, the resultant dark black products were well ground and washed with water, and extracted in Soxhlet equipment with alcohol. The obtained powdered cured CN-PPA3 was dried under vacuum overnight at 120 °C and used for the thermal crosslinking studies.

All CN-PPAs films were thermally crosslinked in a similar procedure. Herein, a typical procedure of the thermal crosslinking of the CN-PPA3 film was given as an example. A mixture of CN-PPA3 (1.00 g), TPH (0.03 g) and $ZnCl_2$ (0.02 g) was dissolved in 10 mL NMP and evenly dispersed by vigorous stirring to obtain a transparent solution (10%, w/v). The film was cast from the solution on glass plates in an oven of 70 °C. Then the film was semidried in the oven and further dried in a vacuum oven at 120 °C for 12 h. The obtained film was cured in a vacuum oven under the same thermal treatment cycle of CN-PPA3 powders under nitrogen atmosphere. The resultant dark cured film was stripped from the substrates (0.04 mm in thickness) and used for solubility and WAXD tests.

Both the powdered CN-PPA1 and its film in the presence of TPH and $ZnCl_2$ were cured at 260 °C for 2 h, 300 °C for 46 h under nitrogen atmosphere to afford crosslinked samples. Both the

Table 1
Synthetic data of CN-PPAs.

Polymer	Molar ratio			M_n				η_{inh} (dL/g)[d]	Yield (%)	Color
	A	*B*	*C*	M_n[a]	M_n[b]	M_n[c]	PD[c]			
CN-PPA1	3.0	2.0	2.2	1743	2070	1200	1.37	0.15	98.3	[e]
CN-PPA2	4.0	3.0	2.2	2385	3140	1900	1.68	0.16	99.2	White
CN-PPA3	10.0	9.0	2.2	6241	7010	5300	1.40	0.23	99.6	White

[a] Calculated number-average molecular weight from the molar reactant ratio of ODA (*A*), DHPZ-DC (*B*) and CBA (*C*).

[b] Determined by ^1H NMR analysis assuming two cyano end groups according to Eq. (2).

[c] Determined number-average molecular weight and polydispersities by GPC calibrated with polystyrene standards.

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

[e] Pale yellow.

Table 2
Elemental data of the CN-PPAs and cured CN-PPAs.

Polymer	Elemental analysis						
	Formula	Calc.			Found		
		C	H	N	C	H	N
CN-PPA1	$(C_{108}H_{70}N_{12}O_{13})_n$	74.39	4.05	9.64	72.18	3.99	9.09
Cured CN-PPA1					72.54	3.86	9.16
CN-PPA2	$(C_{74}H_{48}N_8O_9)_n$	74.49	4.05	9.39	72.74	4.01	8.83
Cured CN-PPA2					72.93	3.94	8.91
CN-PPA3	$(C_{97}H_{63}N_{10}O_{12})_n$	74.65	4.07	8.98	72.93	4.03	8.67
Cured CN-PPA3					73.12	3.98	8.73

powdered CN-PPA2 and its film in the presence of TPH and $ZnCl_2$ were cured at 260 °C for 2 h, 300 °C for 2 h, 320 °C for 44 h under nitrogen atmosphere to afford crosslinked samples.

2.5. Gel content

The gel content of the powdered crosslinked sample was determined through Soxhlet extraction, using *N*,*N*-dimethyl acetamide (DMAc) as solvent. Samples were refluxed in DMAc 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 calculated according to Eq. (1). Gel content:

$$\text{Gel content}(\%) = \frac{W_1}{W_2} \times 100 \tag{1}$$

where W_1 and W_2 are the weights of the samples before and after refluxed in DMAc for 48 h, respectively.

3. Results and discussion

3.1. Polymer synthesis

The oligomeric CN-PPAs with different crosslinkable cyano group content were synthesized by a direct polycondensation method via the Yamazaki–Higashi phosphorylation route of ODA with various content of DHPZ-DC and CBA in the presence of $CaCl_2$ [20]. According to the previous reports [19,21], the DHPZ-DC has demonstrated a good reactivity in the phosphorylation polycondensation reaction and hence always acts as a novel starting material for the preparation of high molecular weight poly(phthalazinone ether amide)s. As shown in Scheme 1, the polymerization of excess ODA with DHPZ-DC produced aniline-terminated intermediate NH–PPAs, and then the NH–PPAs intermediate was readily converted to cyano-terminated polyamides with the charge of CBA into the reaction mixture. All polymerizations homogeneously proceeded in transparent solutions throughout the reaction and the oligomeric CN-PPAs were successfully obtained almost quantitative yields with inherent viscosities (η_{inh}) in the range of 0.15–0.23 dL/g (Table 1). All CN-PPAs were obtained as white powders except that CN-PPA1 was pale yellow.

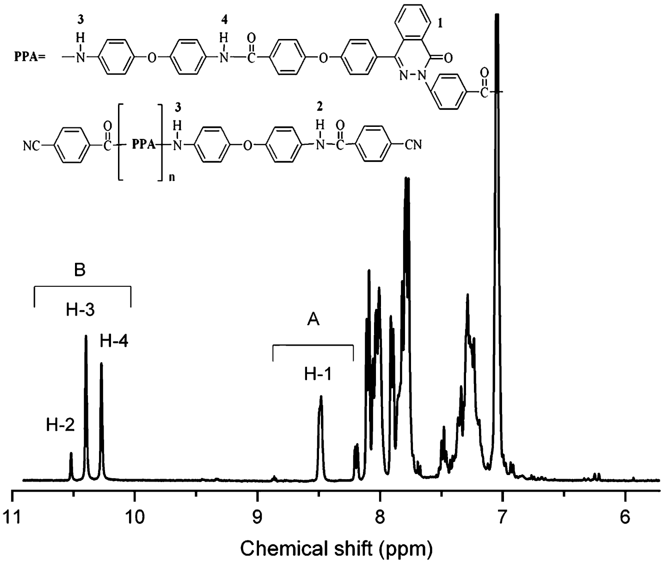


Fig. 2. Partial ^1H NMR spectra of CN-PPA3 (in DMSO-d_6).

3.2. Structural characterization

The structure of the resulting CN-PPAs oligomers was characterized by FT-IR, NMR and elemental analysis. The tested values by the element analysis are in reasonable agreement with the theoretical calculated values of CN-PPAs (Table 2). IR spectra of CN-PPAs in Fig. 1 reveal the weak, broad peaks in the range of 3305–3321 cm^{-1} for the secondary amine of polyamides. The

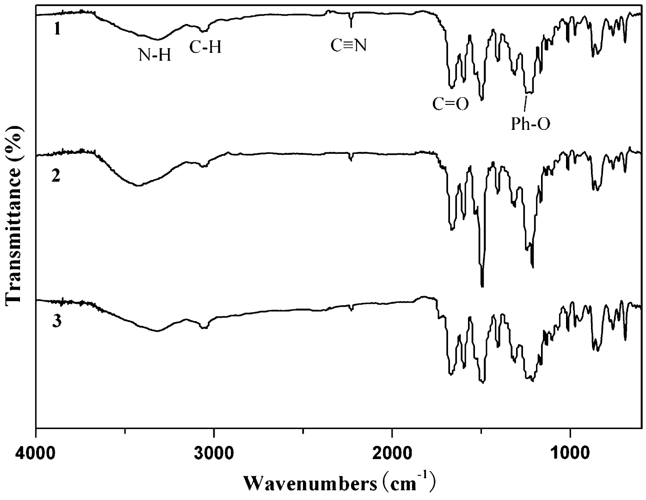


Fig. 1. FTIR spectrum of CN-PPAs (1 CN-PPA1; 2: CN-PPA2; 3: CN-PPA3).

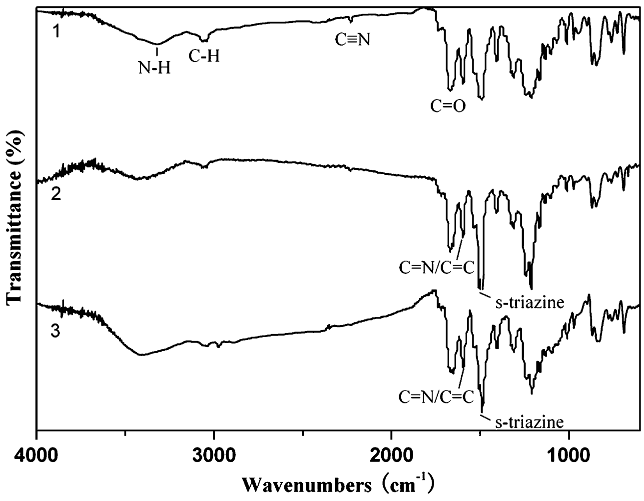


Fig. 3. FTIR spectrum of the CN-PPA3 mixing with TPH and $ZnCl_2$ (1: before cured; 2: after cured at 320 °C; 3: after cured at 340 °C).

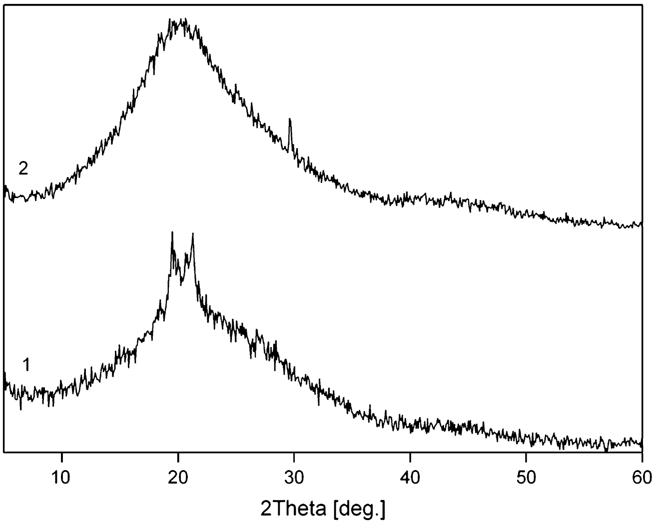


Fig. 4. WAXD diffractograms of CN-PPA3 (1) and cured CN-PPA3 (2).

characteristic stretching band of nitrile group appearing at 2225 cm^{-1}, whose intensity decreases with the increase of molecular weight of polymers, indicates that the different content of cyano group has been introduced into the end of the main chain successfully during the reaction. The absorption bands for amide C═O or the lactam C═O appear at 1664 cm^{-1} and the bands for Ph–O–Ph stretch appear at 1245 cm^{-1}, which correlate well with the expected chemical structure of the target product. Fig. 2 shows a representative partial ^1H NMR spectrum of CN-PPA3. The single peak splitting and shifting downfield at 8.48 and 8.49 ppm is attributed to the typical H-1 signal of the phthalazinone, which is always used as the reference signal to assign the other atoms. The chemical shifts for H-2, H-3 and H-4 appear downfield at 10.51, 10.40 and 10.27 ppm, respectively. The H-3 signals from the –NHCO– groups of the main chain of CN-PPAs appear at high frequencies due to the deshielding ring current effect of the adjacent benzene rings that are attached to phthalazinone segments through C–N linkage. The downfielding H-2 signal of the terminal –NHCO– group is owing to the impact of strong electron-withdrawing *para*-cyano-substituted benzene ring. ^{13}C NMR spectra in DMSO-d_6 of CN-PPAs are also found to be well according with the chemical structures of the polymers.

Molecular weights of CN-PPAs were determined by ^1H NMR (in DMSO-d_6) and GPC (THF eluent), respectively. In the case of the NMR analysis, the molecular weight was calculated from the ratio of the area peaks A to that of B (as shown in Fig. 2), since these area peaks were well distinguished in the ^1H NMR spectra. The number *n* in the CN-PPAs codes, which represents as the degree of polymerization, could be calculated using the following equation:

$$\frac{n}{2n+2} = \frac{I_{\text{H-1}}}{I_{\text{H-2}} + I_{\text{H-3}} + I_{\text{H-4}}} \tag{2}$$

where $I_{\text{H-1}}$, $I_{\text{H-2}}$, $I_{\text{H-3}}$ and $I_{\text{H-4}}$ represent as the integration of characteristic peak for H-1, H-2, H-3 and H-4, respectively. The calculated results are listed in Table 1.

Table 3
Solubility of the CN-PPAs and cured CN-PPAs.

Polymer	Solubility[a]						
	NMP	DMAc	*m*-Cresol	$CHCl_3$	THF	DMSO	Py
CN-PPAs	++	++	–	–	++	++	–
Cured CN-PPAs	–	–	–	–	–	–	–

[a] Solubility ++: soluble in room temperature +: soluble on heating –:insoluble.

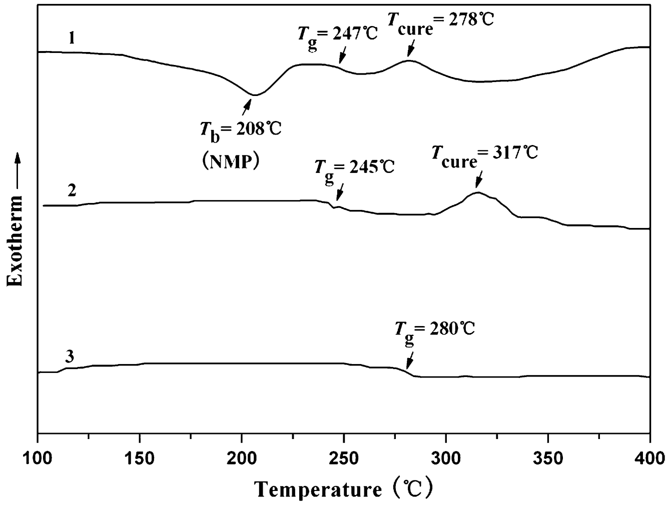


Fig. 5. DSC curves of CN-PPAs mixing with TPH and $ZnCl_2$ (first run, 1: CN-PPA1; 2: CN-PPA2; 3: CN-PPA3).

According to the GPC results, the number-average molecular weight and polydispersity of the resulting CN-PPAs are in the range of 1200–5300 and 1.37–1.68 with polystyrene standards, respectively.

The molecular weight values determined by GPC are a little lower than those calculated by the ^1H NMR analysis (Table 1). It is reasonable considering the fact that the former as a relative molecular weight determination method gives a number-average molecular weight value, whereas the latter is an absolute molecular weight determination method and gives a maximum molecular weight value. Moreover, the calculated M_n*s* of the resulting polymers through ^1H NMR analysis or GPC are found to be close to the theoretically values calculated by the reactant ratio, which indicates that the molecular weight could be well controlled by the reactant ratio (Table 1).

3.3. Crosslinking behavior

Traditionally, the aromatic nitrile compounds or cyano-containing polymers were usually trimerized to s-triazine rings at a temperature in the range of 200–500 °C under a pressure of 30–

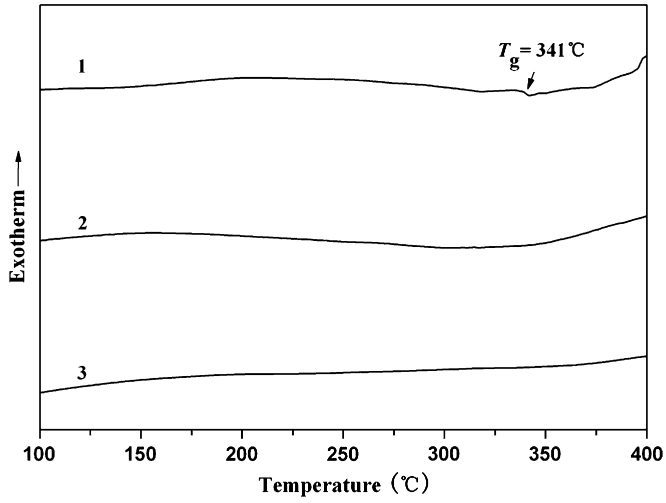


Fig. 6. DSC curves of CN-PPAs mixing with TPH and $ZnCl_2$ (second run, 1: CN-PPA1; 2: CN-PPA2; 3: CN-PPA3).

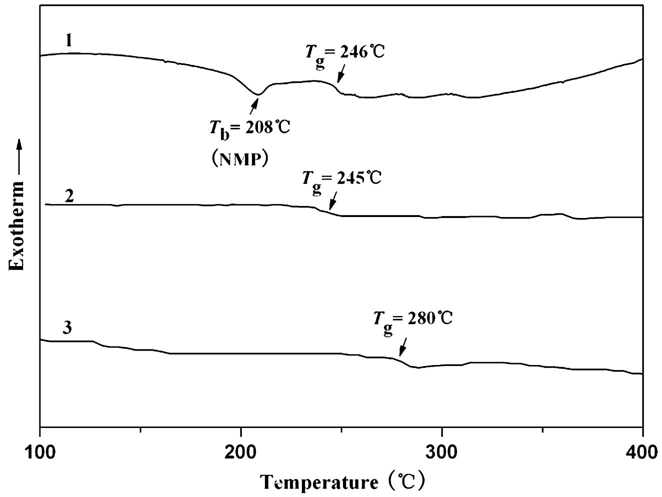
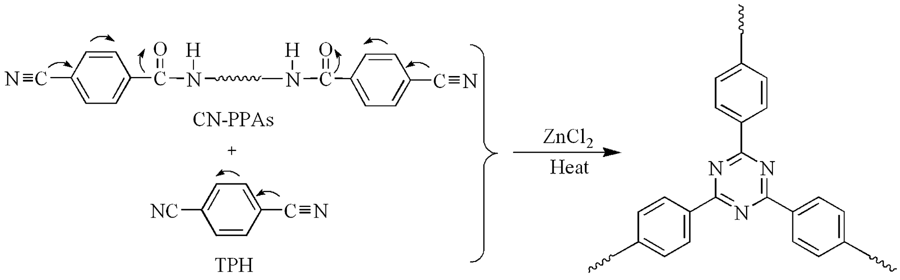


Fig. 7. DSC curves of neat CN-PPAs (first run, 1: CN-PPA1; 2: CN-PPA2; 3: CN-PPA3).

50,000 atmospheres with or without catalyst system [22]. For instance, the cyano-terminated aromatic polyimide was crosslinked by heating with *p*-toluenesulfonic acid monohydrate at 200–350 °C and 30–60 atmospheres to form hard and dark cured samples [17]. The super high pressure extremely restricts the applications of these materials as composite matrix resin, coating or adhesives for the large volume of bulky equipment. The modest trimerization of aromatic nitrile compounds or cyano-containing polymers can be achieved under normal pressure through the charge of an acid catalyst or mixture of catalyst. For example, the cyclization of the pendent cyano groups in poly(phenylene sulfide)s has been achieved at 290–300 °C under atmosphere pressure in the presence of zinc chloride [15]. Another successful example is that s-triazine ring-based polymers have been prepared via the trimerization of 4,4′-biphenyl-carbonitrile in the catalysis of zinc chloride at 300 °C under normal pressure [11,23]. Similarly, the trimerization of terephthalonitrile (TPH) was successfully conducted at 300 °C in the presence of zinc chloride or without zinc chloride under normal atmosphere in our lab. The chemical structure of the resulting hard and dark black glassy products was identified to be aromatic poly(s-triazine). No endothermic inflections for the glass transitions was observed in the DSC run of the resulting polymers up to 400 °C, and TGA data revealed the decomposition temperature ($T_{10\%}$) under nitrogen was exceeding 570 °C. Additionally, the addition of anhydrous zinc chloride as a catalyst to TPH was found to be an effective approach in lowering the reaction activation energy, thereby decreasing the trimerization temperature and pressure. Moreover, as reported previously [23], 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. Thus, the terminal cyano groups of CN-PPAs activated by the electron-withdrawing carbonyl groups in the *para*-substitution possess enough reactivity to form the s-triazine. In order to increase the concentration of cyano groups in curing system, a small quantity of TPH was added to favorite the trimerization statistically. Zinc chloride was used as catalyst to decrease the curing temperature and pressure by lowering the reaction activation energy of the CN-PPAs curing system. Herein we presented the crosslinking of CN-PPAs most probably by the formation of s-triazine rings, which was conducted at a moderate temperature under normal pressure in the presence of TPH and $ZnCl_2$. The curing reaction is an exothermic process, and the oligomers may be sensitive to thermal degradation at elevated temperatures. Considering the above two factors, the thermal curing cycles were optimized on the basis of completing the curing at moderate temperatures and controlling the temperature of the reaction mixtures from approaching thermal degradation of CN-PPAs. Experiments were made on different curing cycles at different temperatures, to study the variations of gel content, changes of characteristic absorptions of FTIR spectra and element contents under different cure conditions. The optimized curing cycles could result in a cycle which produced the highest gel content with hardly any obvious decomposition or carbonization.

The thermal curing of oligomeric CN-PPAs mixing with TPH and $ZnCl_2$ was monitored using both FTIR spectra and elemental analysis. As illustrated in Fig. 3, the characteristic absorption at 2225 cm^{-1} associating with the stretch of C≡N decreases dramatically after CN-PPA3 was cured at 320 °C for 48 h, while it almost disappears after CN-PPA3 was cured at 340 °C for 48 h. Instead, the intensity of the absorption at 1495 cm^{-1} attributed to s-triazine ring obviously increases in the spectra of the cured samples. Additionally, there is no obvious change on the other characteristic absorptions including C═O and N–H stretch (amide), C–H and C═C stretch (benzene ring), and Ph–O–Ph stretch (ether linkage). As the absorption of both the C═C stretch of aromatic rings and the C═N stretch of s-triazine ring fall in approximately the same region, IR is somewhat less informative than usual in confirming the generating of s-triazine ring. Elemental analysis of both uncured CN-PPAs and the crosslinked powdered samples was conducted and also helpfully presented evidence for the identification of s-triazine forming reaction. Table 2 reveals that the carbon, nitrogen and hydrogen contents of the crosslinked samples are very close to those of uncured CN-PPAs, respectively. Further evidence for the crosslinking was supplied by the means of wide-angle X-ray diffraction on film samples, in which a comparison of the crystallinity was made between the linear and crosslinked samples. As shown in Fig. 4, two diffraction peaks appearing at $2\theta = 19.5°$ and $2\theta = 20.3°$ were observed in a representative WAXD pattern of uncured CN-PPA3, suggesting the existence of short-distance order in the main chain, whereas no obvious diffraction peak was observed in the case of the cured film. The crystallinity of the cured CN-PPAs films decreases dramatically, which suggests that some crosslinking occurs and formation of networks causes



Scheme 2. The proposed crosslinking routine of CN-PPAs with TPH.

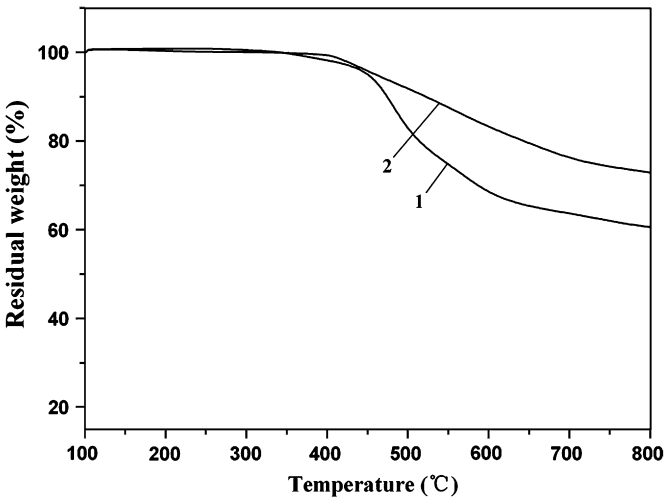


Fig. 8. TGA curves of CN-PPA1 (1) and cured CN-PPA1 (2).

the profound disturbance in the regularity of polymer chains. These data from IR, elemental analysis and WAXD identify that the crosslinked samples are the results of trimerization of cyano groups, and no obvious decomposition or carbonization occurs during the thermal curing.

The solubility tests of both powdered uncured and cured CN-PPAs were also conducted to investigate the crosslinking behavior. The solubility of the samples was tested in common organic solvents by dissolving 0.04 g of the powered samples in 1 mL solvent (4%, w/v), and the results are summarized in Table 3. The uncured CN-PPAs are soluble in several aprotic solvents such as DMAc, DMF, THF and NMP. The good solubility may be resulted from the incorporation of crank and twisted non-coplanar phthalazinone into the polymer main chain, which disorders the packing of the intermolecular chain and therefore makes the synthesized polymers organically soluble. As a result, it is easy to prepare films, coatings or fibers from the solutions of oligomeric CN-PPAs. Both the cured powders and cured films become insoluble in organic solvents. Testing gel content of cured polymers is a direct method to evaluate the content of curing reaction. Thus the gel content of the powdered cured samples was tested by Soxhlet extraction according to ASTM D2765 method. As shown in Table 5, the gel contents of the cured CN-PPA1, CN-PPA2 and CN-PPA3 are about 75%, 50% and 73%, respectively. It is well accepted that the gel content of a cured sample is insignificantly affected by a number of factors (e.g., the concentration of crosslinkable groups, the curing process, the catalyst type and content, the moving ability of curing agent, etc.). In this study, the differences of the gel content may be due to the different curing temperature and terminal cyano concentration of CN-PPAs. The terminal cyano concentration of CN-PPA1 is much higher than those of the other oligomers. Thus, the gel content of cured CN-PPA1 is highest among the investigated samples, although the highest curing temperature of CN-PPA1 is lower than those of the others. When CN-PPA3 was heated under the thermal cycle of 260 °C for 2 h, 300 °C for 2 h, 320 °C for 2 h and 340 °C for 42 h, its gel content is just a little lower than that of CN-PPA1 although it has the lowest terminal groups. This result indicates that both the terminal cyano concentration and curing temperature are crucial factors for the cyclization of cyano group. The gel contents for the cured samples are not as high as expected, probably ascribed to the difficulty for the trimerization of the terminal cyano groups during the formation of crosslinked network. The formation of the insoluble polymers and gel content results of cured samples suggest that the cyano groups in the curing systems are thermally reacted with each other by the curing.

The crosslinking process of powdered CN-PPAs mixing with TPH (2.9 wt% relative to the polymer) and $ZnCl_2$ (1.9 wt% relative to the polymer) under nitrogen was investigated by DSC thermal analysis, and the results of the first and second DSC runs (The second scan was performed after quenching at the end of the first scan, 10 °C/min under nitrogen) are represented in Figs. 5 and 6, respectively. As shown in Fig. 5, intense exotherms due to the crosslinking reaction of the cyano groups were observed at 278 °C and 317 °C in the first DSC scan of CN-PPA1 and CN-PPA2, respectively. The exothermic peaks observed in the first scan disappeared in the second DSC scan up to 400 °C (Fig. 6). In the case of CN-PPA3, no obvious exothermic peak related to the crosslinking reaction of the cyano groups was observed in the first and the second scan, which might be due to the relative low concentration of cyano group. Besides, there were obvious endothermic inflections for the glass transitions (T_g's, 245–280 °C) of all uncured CN-PPAs in the first DSC run (Fig. 5), while no obvious T_g was detected in the second DSC run (Fig. 6) except for curve **1** at 341 °C. These phenomena may be ascribed to the partly thermal crosslinking of the mixture of CN-PPAs, TPH and $ZnCl_2$, which occurred in the DSC sample cell during the heating run. To examine the effect of the addition of terephthalonitrile and zinc chloride on the curing of CN-PPAs, DSC traces of neat CN-PPAs powders without any additive were also performed in nitrogen atmosphere (first heating run, Fig. 7). There was no obvious exothermic event related to the crosslinking reaction of the cyano groups in both the first run and the second run (10 °C/min, not shown) of CN-PPAs. Moreover, the T_g values detected by the first DSC run were very close to those tested by the second run. These results indicated CN-PPAs can hardly undergo thermal crosslinking in the absence of TPH and $ZnCl_2$. This can be explained by the fact that the low content of cyano groups and the high reaction activation energy of trimerization make the crosslinking both statistically and kinetically unfavorable. The strong endotherm peak at 208 °C (curve **1** in both Figs. 5 and 7) was the boil point temperature (T_b) of the residual NMP in the CN-PPA1. Thus, the addition of TPH and $ZnCl_2$ to the curing system is found to be effective in decreasing the curing temperature and facilitating the thermal curing of CN-PPAs.

Although our experimental results demonstrated that certain thermal crosslinking reaction of cyano groups occurred, resulting in a crosslinked CN-PPAs, and their FT-IR spectra also gave the characteristic absorption of s-triazine ring, it was hardly to know their

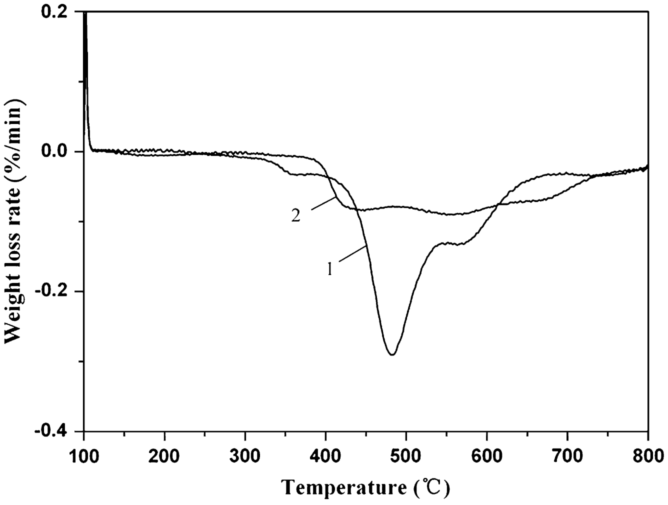


Fig. 9. DTG curves of CN-PPA1 (1) and cured CN-PPA1 (2).

exact chemical structures, because there are many possible structures deriving from the trimerization of the activated cyano groups of both CN-PPAs and TPH. Referring to the literatures, the proposed crosslinking reaction process of CN-PPAs and TPH catalyzed by zinc chloride is illustrated in Scheme 2, postulating that the reaction of the terminal cyano groups of both polymers and TPH form s-triazine rings via trimerization mechanism [11,15,24].

3.4. Thermal properties

Thermal properties of the uncured oligomers and cured samples were evaluated by DSC and TGA. As illustrated in Fig. 7, the glass transition temperature (T_g) values of uncured CN-PPAs (ranging from 245 to 280 °C) increase with the increasing molecular weight of the oligomers. CN-PPA3, whose number-average molecular weigh is 5300, determined by GPC, has the highest T_g (280 °C), which is in correspondence to a higher molecular weight and consequently a smaller number of end groups. The DSC traces (10 °C/min, first scan, not shown) were also performed to determine the T_g values of powdered cured CN-PPAs after the thermal treatment cycles. It was clearly observed there was no intense endothermic inflection up to 400 °C for the glass transitions of all crosslinked samples, implying that certain thermal crosslinking had occurred. No evidence of the glass transition for the cured samples up to 400 °C, results from the crosslinking that leaded to three-dimensional structure which decreased the flexibility of polymer backbone.

Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) under nitrogen atmosphere were applied to study the thermal behavior of both the oligomeric CN-PPAs and the powdered cured samples. TGA and DTG curves of a representative oligomeric CN-PPA1 with its cured powders are illustrated in Figs. 8 and 9, respectively. Thermal data from TGA and DTG (Table 4) indicated CN-PPAs and their cured samples possessed excellent thermal stability without significant weight loss till 440 °C in nitrogen. The decomposition temperature of CN-PPAs for 5% weight loss ($T_{5\%}$) and 10% weight loss ($T_{10\%}$) increases with the increasing molecular weights, whereas those of cured CN-PPAs decreases with the increasing molecular weights. In the case of cured polymers, both the $T_{5\%}$ values and the $T_{10\%}$ values show an increase at least by 10 °C and 45 °C relative to the corresponding uncured ones, respectively, thus being more thermally stable. The amounts of carbonized residue (C_y) of uncured CN-PPAs in the nitrogen atmosphere are around 60% weight at 800 °C (Table 4), confirming the high thermal stability of the phthalazinone-containing oligomeric polyamides. The C_y values of cured samples are recorded in the range of 67–75%, indicating an increase by at least seven percents after thermal crosslinking, 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 C_y values of cured CN-PPAs increase with the decreasing molecular weights of the corresponding oligomers, since the s-triazine content of cured samples is significantly affected by the relative concentration of cyano groups in the curing system. The DTG curves of CN-PPAs and their cured samples demonstrate that there are two decomposition stages at temperatures higher than 480 °C under nitrogen except the cured CN-PPA2 (Table 4). A common feature of the cured samples is that the weight loss stages are less apparent in their DTG curves (Fig. 9), suggesting that the thermal decompositions of the crosslinked samples are slowed down relative to that of CN-PPAs. The fire-retardant characteristics of both oligomeric CN-PPAs and their cured sample were evaluated by the limiting oxygen index (LOI). The cured samples give a LOI value ranging from 29 to 30 (Table 5), whereas those of uncured oligomeric CN-PPAs have LOI values of near 28, showing a little higher intrinsic fire-retardant characteristics after thermal crosslinking.

The thermal stabilities of both uncured CN-PPAs and powdered cured samples were also evaluated in isothermal aging experiments. The data (Table 5) from isothermal aging experiments indicates the uncured CN-PPAs show weight loss rates ranging from 0.007 to 0.013 wt%/h during isothermal aging at 350 °C under nitrogen atmosphere. The weight loss rates under air atmosphere (ranging from 0.314 to 0.431 wt%/h) are much higher than those under nitrogen atmosphere, which could be ascribed to the more obvious thermal degradation under such rigorous circumstances. These results demonstrate that the uncured CN-PPAs exhibit good thermal and oxidative stability, which is a vital factor for their process at elevated temperatures. The comparison of the weight loss rates under nitrogen and air atmosphere indicates the overall thermal and oxidative stability increase dramatically after thermal crosslinking. The main reason is the formation of s-triazine, which is known as a heterocyclic unit with high resonance energy and high decomposition activation energy. The cured CN-PPA1 was found to be most thermally stable in nitrogen and air atmosphere among the resultant samples, due to its highest concentration of cyano groups in the curing system, leading to the highest crosslinking density and s-triazine content.

Table 4
Thermal properties of the CN-PPAs and cured CN-PPAs.

Polymer	T_g[a] (°C)	T_{cure}[a] (°C)	$T_{5\%}$[b] (°C)	$T_{10\%}$[b] (°C)	T_{max}[c] (°C)	C_y[d] (%)
CN-PPA1	247	278	447	469	482,570	60
Cured CN-PPA1	–[e]	–[e]	464	531	468,572	75
CN-PPA2	245	317	450	473	482,569	61
Cured CN-PPA2	–[e]	–[e]	460	523	440,558,572[f]	73
CN-PPA3	280	–[e]	452	474	481,571	60
Cured CN-PPA3	–[e]	–[e]	463	519	469,567	67

[a] Glass transition temperature (T_g) and curing temperature (T_{cure}) tested by DSC at a heating rate of 10 °C/min in nitrogen.

[b] Temperature for 5% weight loss and 10% weight loss tested by TGA, at a heating rate of 20 °C/min in nitrogen.

[c] Temperature for the maximum tested by DTG, at a heating rate of 20 °C/min in nitrogen.

[d] Char yield calculated as the percentage of solid residue after heating from 100 to 800 °C by TGA, at a heating rate of 20 °C/min in nitrogen.

[e] Not detected.

[f] Three peaks in the DTG curves.

Table 5
Gel content, LOI and isothermal data of the CN-PPAs and cured CN-PPAs.

Polymer	Gel content (%)	LOI[a]	Rates (wt%/h)[b]	
			N_2	Air
CN-PPA1	–[c]	28	0.013	0.431
Cured CN-PPA1	75	30	0.005	0.314
CN-PPA2	–[c]	28	0.012	0.378
Cured CN-PPA2	50	29	0.007	0.314
CN-PPA3	–[c]	28	0.007	0.355
Cured CN-PPA3	73	29	0.005	0.321

[a] LOI represents limiting oxygen index.

[b] Weight loss rates of isothermal aging were determined at 350 °C with a nitrogen or air flow of 50 mL/min over 24 h by isothermal scan.

[c] Not detected.

4. Conclusion

Well-controlled molecular weights, oligomeric polyamides containing phthalazinone moieties, flexible ether linkages and terminal cyano groups have been successfully synthesized via Yamazaki–Higashi phosphorylation polycondensation. The resulting oligomers show good solubility in several aprotic solvents and can be proposally used as films, coatings, fibers or other applications. The presence of terephthalonitrile and zinc chloride is effective in promoting thermal crosslinking and s-triazine formation of the oligomer films or powders. DSC, FT-IR, TGA, DTG, elemental analysis and WAXD demonstrate certain crosslinking of terminal cyano groups and formation of s-triazine ring, rather than decomposition or carbonization occurring during thermal treatment cycles. Cured samples show much higher thermal stability, including higher thermal decomposition temperatures and higher char-yielding properties, compared to linear oligomers. Thus, the resultant phthalazinone-based poly(ether amide)s with terminal cyano groups and their crosslinked polymers may be used as base materials for high temperature adhesive, coating or composite matrix in a wide range of applications.

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