

Synthesis and Properties of Phthalazinone-based Poly(ether imide)s End-capped with Phthalonitrile Moiety

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Abstract

A series novel of soluble and curable phthalonitrile-terminated poly(phthalazinone ether imide)s were prepared by polycondensation of phthalazinone-based diamine with different aromatic dianhydrides, followed by the end-capping of 4-(3-aminophenoxy)phthalonitrile. The crosslinking reactions were performed under normal pressure to form the heterocyclic s-triazine rings-containing thermosetting polymers in the presence of 4,4'-diaminodiphenylsulfone. The uncured polyimides showed good solubility in the common aprotic solvents, such as chloroform, pyridine, *m*-cresol and *N*-methyl-2-pyrrolidone, while the cured samples became insoluble in all solvents. DSC, FT-IR, and elemental analysis were used to confirm the formation of s-triazine rings-containing networks during the cure process. The glass transition temperatures (T_g s) of the uncured polymers were in the region of 200-256 °C, and the decomposition temperatures for 5% weight loss ($T_{d5\%}$) and 10% weight loss ($T_{d10\%}$) were greater than 516 °C and 545 °C, respectively. For the formation of the heterocyclic s-triazine rings during the crosslinking reactions, there were no glass transition temperatures of all cured samples were detected from 100 to 350 °C, and the decomposition temperatures for $T_{d5\%}$ and $T_{d10\%}$ were in the range of 510-540 °C and 543-567 °C, respectively, which were higher than the uncured counterparts. This kind of soluble and curable poly(ether imide)s may have many potential applications for high performance polymeric materials.

Key Words: Polyimide; Phthalazinone; Phthalonitrile, Aryl-s-triazine, Heat-resistant

1. Introduction

During the past 30 years, a lot of research efforts have been expended on the development of high temperature polymers based on polyimides.^[1] Polyimides are well known for their utilities in the aerospace and electronic industries in the forms of films and moldings for their excellent thermo-oxidative stability, balanced mechanical and electric properties.^[2-4] Other utilities of these polymers such as adhesives, gas separation membranes, composite matrices, coatings and foams are also rapidly increasing.^[5,6] However, conventional aromatic polyimides are difficult to fabricate into final products because of their high softening temperatures associated with insolubility in commercially available solvents.^[7-8] To tackle these problems, many efforts have been devoted to the structural modification such as the introduction of bulky pendant groups,^[9] flexible alkyl side chains,^[10] and

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hyperbranched or dendritic architectures into the polymer main chains.^[11]

In our laboratory, a series of poly(phthalazinone ether imide)s derived from the polycondensation of phthalazinone-containing diamine or dianhydride have been synthesized.^[12] The resultant poly(ether imide)s possess good thermal stability and improved solubility in polar aprotic solvents relative to conventional polyimides because of the incorporation of the crank, twisted and non-coplanar phthalazinone moiety which disorders the close packing of the intermolecular chains. To further broaden the applications of the poly(ether imide)s without sacrificing the improved solubility, our research interest has recently been focused on the preparation of soluble and curable poly(ether imide)s which can be fabricated in their organic solution or their melt and thermally crosslinked to high performance thermosetting resins. The cured poly(ether imide)s possess an attractive combination of excellent thermal stability, good chemical resistance and superior flame resistance because of the formation of crosslinked networks. It is a valuable approach to obtain the curable poly(ether imide)s by introducing of curable groups such as styryl, cyano and ethynyl into the polymer chains.^[13-15] Among these groups, the cyano group is often used, because it can be introduced into the polymer chains as pendant or terminal group easily and form heterocyclic s-triazine ring-based thermosets which possess excellent thermal stability.^[16,17] The introduction of cyano group into the polymers can not only appear to promote the adhesion of polymers to many substrates,^[18] but also endow the polymers with excellent thermal properties, chemical resistance, mechanical strength, flame retardancy and molding workability.^[19] For the low content of cyano groups^[20] and the high reaction activation energy of the trimerization,^[16] the crosslinking reaction of cyano groups to form the s-triazine rings is usually extremely difficult. For example, the aromatic nitrile compounds or cyano-containing polymers are usually trimerized to s-triazine rings at a temperature in the range of 200-500 °C under a pressure of 30-50,000 atmospheres with or without catalyst system.^[21] But the aromatic diether-linked phthalonitrile resin derived from resorcinol, 4,4'-dihydroxydiphenyl or bisphenol A can be cured under normal pressure in the presence of a nucleophilic compound such as an organic amine to form s-triazine rings-containing thermosetting polymers, which possess excellent thermo-oxidative properties and good chemical resistance.^[22-24]

For these, we designed and synthesized a novel series of soluble and curable phthalonitrile-terminated poly(phthalazinone ether imide)s with well controlled molecular weights. The crosslinking reactions of these poly(ether imide)s were performed under normal pressure in the presence of 4,4'-diaminodiphenylsulfone at elevated temperatures to form the s-triazine rings-containing thermosetting polyimides. The crosslinking reactions were investigated as well as the solubility and thermal properties of both the cured and uncured polymers.

2. Experimental

2.1. Instruments

Inherent viscosities of the uncured poly(phthalazinone ether imide)s were measured by Ubbelohde capillary viscometer at 25 °C. Infrared measurements were performed on a Thermo Nicolet Nexus 470 Fourier transform infrared spectroscopy (FT-IR). ¹H NMR (400 MHz) spectra were obtained with a Bruker spectrometer at an operating temperature of 25 °C. Elemental analysis was measured on a Vario ELIII CHNOS Elementaranalysator from Elementaranalysesysteme GmbH. 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). Thermogravimetric analysis (TGA)

and derivative thermogravimetric analysis (DTG) for the uncured and cured polymers were performed on a Mettler TGA/SDTA851 thermogravimetric analysis instrument under nitrogen atmosphere at a heating rate of 20 °C/min from 100 to 800 °C. The 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. The glass transition temperatures (T_g s) 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 °C. High performance liquid chromatogram (HPLC) was performed on a Hewlett-Packard (HP) 1100 liquid chromatograph with a UV detector at 254 nm and a 2.0 × 150 mm Microbore column (Waters Spherisorb[®] S5 ODS2) as column.

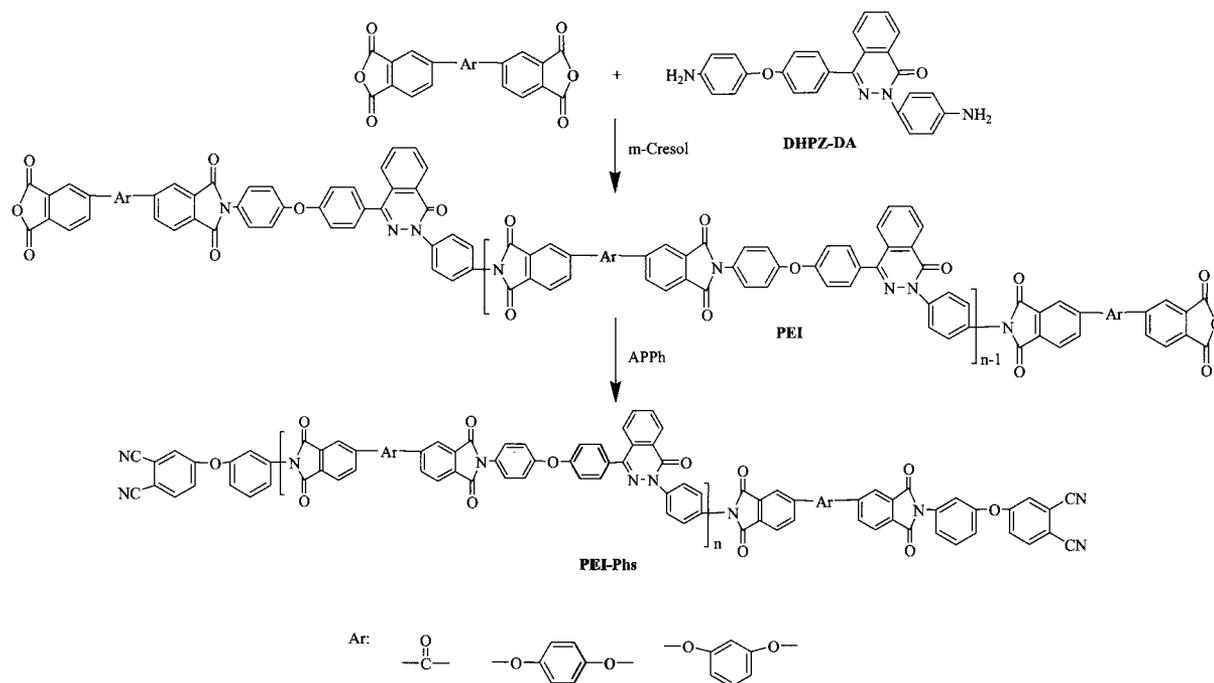
2.2. Materials

Dimethyl sulfoxide (DMSO) and *m*-cresol were purified by distillation under reduced pressure over calcium hydride and then stored over 4 Å molecular sieves before used. Anhydrous potassium carbonate (K₂CO₃) was ground and dried in vacuum at 100 °C for 24 h before use. 4-Nitrophthalonitrile was purchased from Aldrich-Sigma and used as received. 4-(3-Aminophenoxy)phthalonitrile was synthesized according to the modified procedure disclosed in reference.^[25] 1,2-Dihydro-2-(4-aminophenyl)-4-[4-(4-(aminophenoxy)phenyl)](2*H*)phthalazin-1-one (DHPZDA) was synthesized according to the procedure reported previously.^[26] Unless otherwise specified, all other solvents and reagents were purchased from Tianjin Fine Chemical Industry Co., Ltd., PR China and used without any further treatment.

2.3. Polymer synthesis

All the phthalonitrile-terminated poly(phthalazinone ether imide)s were synthesized by a one-pot, two-step reaction of bis(ether anhydride)s with the unsymmetrical phthalazinone-based diamine and 4-(3-aminophenoxy)phthalonitrile in the presence of isoquinoline as catalyst for imidization. The poly(ether imide)s derived from 1,4-bis(3,4-dicarboxyphenoxy)benzene dianhydride (HAD), 1,3-bis(3,4-dicarboxyphenoxy)benzene dianhydride (RDA) and 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BDA) were simplified as HPEI-Phs, RPEI-Phs and BPBI-Phs, respectively. The *n* in the simplified name of polymers represents as the degree of polymerization. All the poly(ether imide)s were synthesized in a similar procedure as shown in Scheme 1, and hence only the preparation of HPEI-Ph(5) is given as a typical example as follows: 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 HDA (1.448 g, 3.60 mmol), DHPZDA (1.261 g, 3.00 mmol), *m*-cresol (10 mL), and isoquinoline (catalyst, several drops). The mixture was stirred at room temperature for about 3 h till the mixture became clear. The reaction was continued at 180 °C for 16 h. After cooling to room temperature, APPh (0.242 g, 1.30 mmol) was added in one portion with stirring. Then the reaction mixture was stirred at room temperature for 3 h and at 180 °C for 12 h. The product mixture was poured into 300 mL methanol with vigorous stirring to precipitate the polymer. The white solid was collected by filtration and extracted by a Soxhlet extractor with methanol for 24 h in order to remove the residual *m*-cresol thoroughly. The dried polymer was further purified by dissolving in NMP and filtered through a thin layer of celite. Then the filtrate was slowly poured into a mixture of distilled water and ethanol (volume ratio 4: 1) with vigorous stirring, and the resulting product of HPEI-Ph(5) was collected by filtration and dried in vacuum at 100 °C for 24 h. The yield was 98.6 wt%. Selected data of HPEI-Ph(5): IR (KBr,

cm⁻¹): 3065 (arom. C-H), 2225 (C≡N), 1777 (asym, C=O), 1723 (sym, C=O), 1673 (lactam C=O), 1441-1600 (arom. C=C); 1374 (C-N), 1240 (C-O-C), 1100 and 720 (imide ring deformation). ¹H NMR (400 MHz, H₂SO₄-d₂, ppm) δ: 9.40 (s, Ar-H), 9.03 (s, Ar-H), 8.56 (s, Ar-H), 8.46-8.39 (m, Ar-H), 8.24-8.22 (m, H3 and H4), 8.11-7.88 (m, Ar-H), 7.80 (s, H2). Elem. Anal. Calcd for HPEI-Ph(5) ((C₄₈H₂₆N₄O₈)₅(C₅₀H₂₄N₆O₈)): C, 72.50; H, 3.10; N, 8.63%. Found: C, 72.94; H, 3.20; N, 9.02%.



Scheme 1. Synthetic route of phthalonitrile-terminated poly(phthalazinone ether imide)s

2.4. Thermal crosslinking

Thermal crosslinking reactions of the poly(ether imide)s end-capped with phthalonitrile were performed in an analogous procedure by heating the polymers mixed with 4,4'-diaminodiphenylsulfone (DDS, 2 wt% relative to the polymers) as curing agent under nitrogen atmosphere. A typical thermal crosslinking procedure of HPEI-Ph(5) was carried out as follows: the composition of HPEI-Ph(5) (2.00 g), and DDS (0.04 g) was thoroughly mixed in powdered form under ambient conditions. The composition was then heated to 250 °C for 2 h, 280 °C for 4 h, 320 °C for 10 h, and 350 °C for 10 h in the protection of nitrogen to afford the crosslinked polymer (cured HPEI-Ph(5)). Then the cured dark black product was well ground and washed with water for six times. The product was then extracted in Soxhlet equipment with chloroform for 48 h to remove the uncured polymer and residual DDS. Finally the product was dried under vacuum at 100 °C overnight for DSC and TGA studies.

2.5. Gel content

The gel contents of the cured poly(ether imide)s were determined through Soxhlet extraction using chloroform as solvent. The cured polymers were refluxed for at least 48 h, until the samples attained a constant weight. The residues after extraction were taken as the gel components, and the gel contents were calculated according to the following equation (1):

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

where W_1 and W_2 were the weights of the cured polymers before and after refluxed in chloroform for 48 h, respectively.

3. Results and discussion

3.1. Polymer synthesis and structural characterization

All the poly(ether imide)s end-capped with phthalonitrile were synthesized by a two-step, one-pot reaction of bis(ether anhydride)s including HDA, RDA and BDA with unsymmetrical phthalazinone-containing diamine (DHPZDA), followed by the end-capping of 4-(3-aminophenoxy)phthalonitrile (APPh) in the presence of isoquinoline as catalyst. The first stage was the polymerization reaction of excess dianhydride with diamine, and the second stage was the end capping reaction of the surplus anhydride with 4-(3-aminophenoxy)phthalonitrile. The molecular weights of poly(ether imide)s were controlled in the first stage by varying the molar ratio of the excess dianhydride to diamine. The polymerization reaction was performed by a one-step solution polymerization in the presence of *m*-cresol as solvent and isoquinoline as catalyst for imidization.

FT-IR, ^1H NMR and elemental analysis were used to confirm the structures of resultant poly(ether imide)s. The FT-IR spectra reveal the characteristic peaks of poly(ether imide)s at about 1774 cm^{-1} (asym C=O), 1720 cm^{-1} (sym C=O), 1370 cm^{-1} (C-N), 1240 cm^{-1} (C-O-C), and $1100, 720\text{ cm}^{-1}$ (imide ring deformation). The characteristic stretching band of cyano group appearing at 2230 cm^{-1} , whose intensity decreases with the increasing of molecular weight of polymers, means that the different contents of cyano groups have been introduced into the end of the main chain successfully during the synthesis process. The absorption band at 1664 cm^{-1} is contributed to the stretch of the lactam C=O of the phthalazinone moiety. All the absorption bands correlate sufficiently well with the expected chemical structures of the target products. In the ^1H NMR spectra of BPEI-Phs (Figure 1), the single peak shifting downfield at about 9.40 ppm is attributed to the typical H1 signal of the phthalazinone, which is always used as the reference signal to assign the other protons.^[27] The chemical shifts for H2, H3 and H4 of terminal phthalonitrile appear downfield at 7.81 ppm and 8.27-8.21 ppm, respectively. With the increasing of molecular weight, the integral intensities of H2 and H3, H4 decrease normalized compared to that of H1, so the molecular weights of the uncured polymers can be easily determined using ^1H NMR. In the ^1H NMR analysis, the molecular weights were calculated from the ratio of the area peaks H1 to those of H2, H3 and H4, since these area peaks can be well distinguished in the ^1H NMR spectra. The number *n* in polymer codes, which represents as the degree of polymerization, was calculated using the following equation (2):

$$\frac{n}{6} = \frac{I_{H1}}{I_{H2} + I_{H3} + I_{H4}} \quad (2)$$

where I_{H1} , I_{H2} , I_{H3} and I_{H4} represent as the integration of characteristic peak areas for H1, H2, H3 and H4, respectively. The calculated results are listed in Table 1.

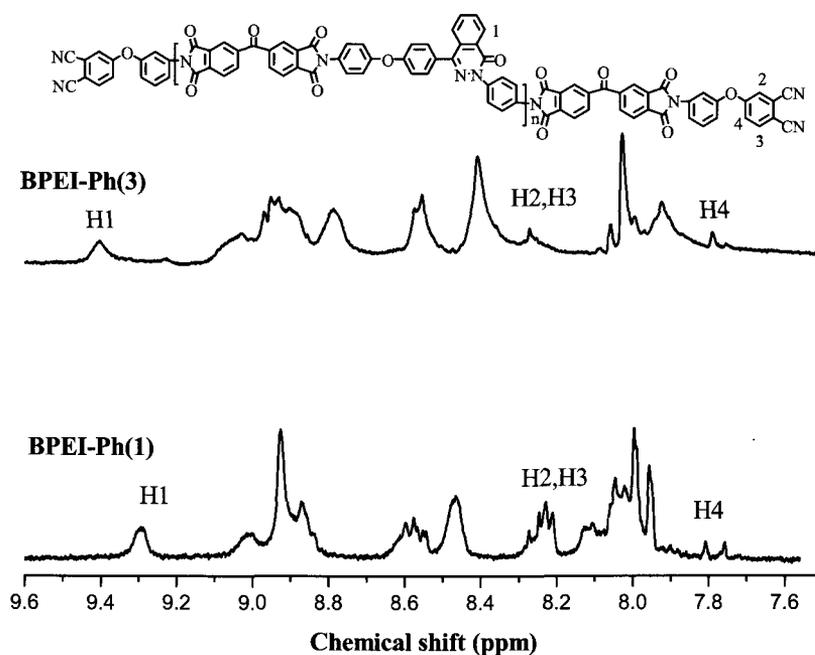


Figure 1. ^1H NMR spectra of BPEI-Ph(1) and BPEI-Ph(3)

Table 1 Synthetic data of BPEI-Phs.

Polymer	Molar ratio			η_{inh} (dL/g) ^a	n^b	Yield (%)	Color
	HDA	DHPZ-DA	APPPh				
BPEI-Ph(1)	2.00	1.00	2.20	0.10	1	1.67	98.0
BPEI-Ph(3)	4.00	3.00	2.20	0.12	3	3.26	98.6
BPEI-Ph(5)	6.00	5.00	2.20	0.16	5	4.82	99.1

^a Measured in NMP at 25 °C at a concentration of 0.5 g/dL.

^b The degree of polymerization calculated by ^1H NMR using equation (2).

The values determined by the ^1H NMR analysis are found to be close to the theoretic values calculated by the reactant ratio, indicating that the molecular weights could be well controlled by varying the reactant ratio. From the studies of FT-IR, ^1H NMR and elemental analysis, the target polymers with well-controlled molecular weights were successfully synthesized by varying the reactant ratio.

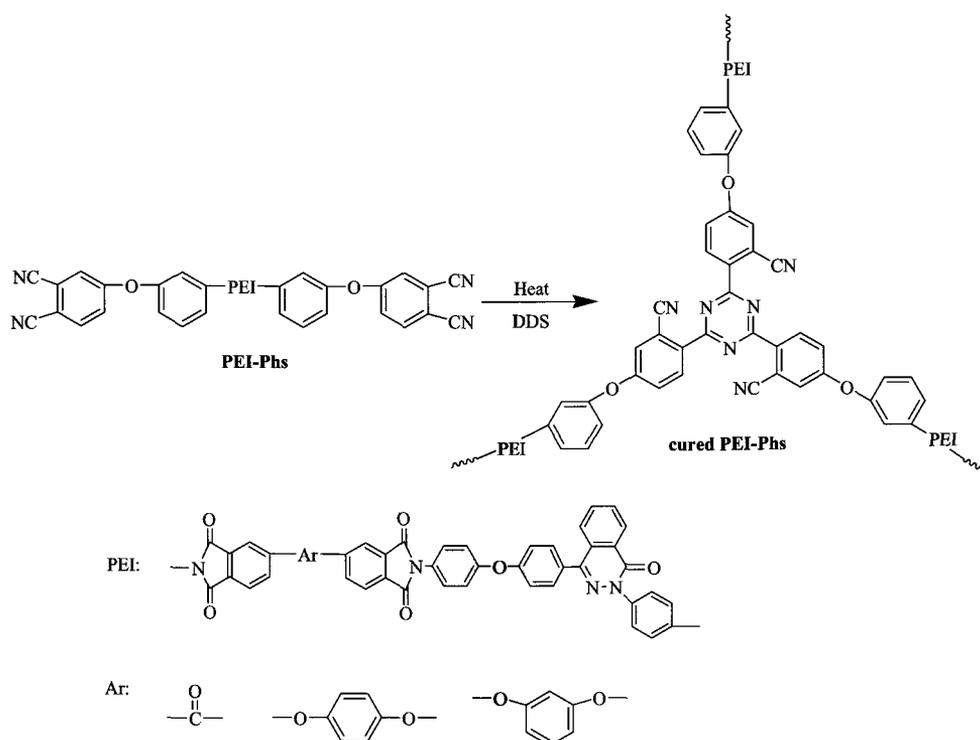
The crystallinity of the uncured poly(ether imide)s was evaluated by wide-angle X-ray diffraction experiments. No obvious diffraction peak is observed in all cases of the films of the synthesized poly(ether imide)s. It may be due to the incorporation of the crank, twisted and non-coplanar phthalazinone moiety into the polymer main chain, which disorders the close packing of the intermolecular chain.

3.2. Thermal crosslinking

The neat polymerization of phthalonitrile oligmer without active hydrogen atoms to form the s-triazine ring-containing thermosetting polymers is also extremely difficult and requires several days of continuous heating at 260-290 °C before the viscosity increases. But the cure time and temperature can be greatly reduced in the presence of a nucleophilic compound such as an organic amine.^[22] In this

paper, all the crosslinking reactions of the poly(ether imide)s end-capped with phthalonitrile were performed under normal pressure in the presence of 4,4'-diaminodiphenylsulfone (DDS, 2 wt% relative to the polymers) at elevated temperatures, as shown in Scheme 2.

The thermal crosslinking reaction of poly(ether imide)s mixed with 4,4'-diaminodiphenylsulfone (DDS) was investigated by DSC thermal analysis at a heating rate of 10 °C/min from 100 to 350 °C under nitrogen. On the DSC curves, the obvious intense and wide exothermic peaks can be clearly observed at about 250 °C resulting from the trimerization of cyano groups. The glass transition temperature (T_g) is approximate to the cure temperature. The heat released due to the trimerization of cyano group may be higher than that of endothermic event for the glass transition. Therefore, it is reasonable that no glass transition temperature (T_g) but only the cure temperature was detected from the DSC study. It is clearly observed that there is no intense endothermic inflection from 100-350 °C for cured polyimides, implying that certain thermal crosslinking reaction occurred. It may be due to the formation of the heterocyclic s-triazine networks which decrease the flexibility of polymer backbone.



Scheme 2. Thermal crosslinking reactions of phthalonitrile-terminated poly(phthalazinone ether imide)s

The FT-IR and elemental analysis were used to confirm the structures of the cured polyimides. In the FT-IR spectral analysis, the intensity of the characteristic stretching band of cyano at 2230 cm^{-1} decreases dramatically after cured. It can be found that the absorption band at 1600-1500 cm^{-1} attributed to the C=C and the C=N stretches obviously increases, meaning that the polytriazine reaction of the cyano groups occurred. Additionally, there is no obvious change on the other characteristic absorptions including 1774 (asym C=O), 1720 (sym C=O) 1370 (C-N), 1240 (C-O-C), 1100 and 720 cm^{-1} (imide ring deformation), suggesting that no decomposition occurred during the curing process at elevated temperatures. From the elemental analysis data, the tested values of carbon, nitrogen and hydrogen contents for the cured samples are very close to those of the uncured samples. It is a helpful evidence for

that no decomposition or carbonization happened during the curing process. The data from FT-IR and elemental analysis identify that the crosslinked polymers results from the polytriazine of cyano groups, rather than the decomposition or carbonization.

3.3. Solubility

The solubility of the uncured poly(ether imide)s and the cured poly(ether imide)s was tested in common organic solvents by dissolving 0.04 g of the polymers in 1 mL solvent (4%, w/v). The uncured polymers are soluble in several common polar aprotic solvents such as chloroform, pyridine, *m*-cresol and *N*-methyl-2-pyrrolidone. The good solubility may result from two aspects. The first is the incorporation of crank, twisted and non-coplanar phthalazinone moiety into the polymer main chain, which disorders the close packing of the intermolecular chain. The other possible explanation for the improved solubility is the introducing of flexible ether linkages into the main chain. The cured polymers are insoluble in all polar aprotic solvents and even in 98% H₂SO₄. The good chemical resistance may be due to the formation of the heterocyclic s-triazine networks during the crosslinking reaction of the cyano groups. The speciality that the uncured polymers show good solubility in the common aprotic solvents while the cured samples become insoluble in all solvents makes them be fabricated in their organic solutions and thermally crosslinked to high performance thermosetting resins.

3.4. Thermal properties

The thermal properties of both the uncured and cured poly(ether imide)s were evaluated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG). As outlined in Table 2, the glass transition temperature (T_g) values of the uncured polymers are at the range of 200-256 °C. There is no intense endothermic inflection up to 350 °C for the glass transition of all the cured polymers due to the formation the heterocyclic s-triazine networks.

TGA and DTG were used to study the thermal stability of both the uncured and cured polymers. The decomposition temperatures were detected by the TGA thermal analysis under nitrogen atmosphere at a heating rate of 20 °C/min from 100 to 800 °C. There is no significant weight loss before 400 °C in nitrogen for both the cured and uncured samples. The decomposition temperatures of the uncured polymers for 5% weight loss ($T_{d5\%}$) and 10% weight loss ($T_{d10\%}$) are in the range of 504-516 °C and 523-545 °C, respectively. And the decomposition temperatures of the uncured polymers for $T_{d5\%}$ and $T_{d10\%}$ are in the range of 510-540 °C and 543-567 °C, respectively, which are higher than those of the uncured counterparts. The values of carbonized residue (C_y) at 800 °C of the uncured and cured polymers were recorded in the range of 50-71% and 63-74%, respectively. The reason for higher $T_{d5\%}$, $T_{d10\%}$ and C_y of the cured polymers than the uncured ones is due to the formation of the heterocyclic s-triazine networks which possess excellent thermal stability. It can be found that the decomposition temperatures of the uncured polymers for both $T_{d5\%}$ and $T_{d10\%}$ increase with the increasing molecular weights from the TGA data as outlined in Table 2. On the contrary, the decomposition temperatures of the cured poly(ether imide)s for both $T_{d5\%}$ and $T_{d10\%}$ decrease with the increasing molecular weights. The reason may be that with the increasing molecular weights of the uncured polymers, the concentration of the heterocyclic s-triazine rings decreases, which is significantly affected by the relative concentration of cyano groups. So it is reasonable that the decomposition temperatures of the cured polymers for both $T_{d5\%}$ and $T_{d10\%}$ decrease with the increasing of the molecular weights of the

uncured polymers. The gel content testing is a direct method to evaluate the content of polymerization reaction. The gel contents for the cured HPEI-Ph(1), HPEI-Ph(5) and HPEI-Ph(11) are 98%, 95% and 93%, respectively, which were tested by Soxhlet extraction according to ASTM D2765 method. In this case, the difference of the gel contents is due to the different terminal phthalonitrile concentration. So the gel content of cured HPEI-Ph(1) is the highest among the investigated cured polymers. The gel content values of all the cured samples are listed in Table 2.

Table 2 Thermal properties of the uncured and cured polymers

Polymer	T_g^a (°C)	$T_{5\%}^b$ (°C)	$T_{10\%}^b$ (°C)	T_{max}^c (°C)	C_y^d (%)	Gel content ^e (%)
BPBI-Ph (1)	200	505	542	557	71	- ^f
BPBI-Ph (3)	236	512	542	560	66	-
BPBI-Ph (5)	249	516	544	580	67	-
HPEI-Ph(1)	221	504	523	548	56	-
HPEI-Ph(5)	243	509	536	560	51	-
HPEI-Ph(11)	256	514	539	567	65	-
RPEI-Ph(5)	214	505	533	550	50	-
RPEI-Ph(9)	237	510	537	557	52	-
RPEI-Ph(15)	251	512	545	563	58	-
Cured BPBI-Ph (1)	-	532	566	581	69	96
Cured BPBI-Ph (3)	-	530	567	575	74	93
Cured BPBI-Ph (5)	-	522	556	569	71	89
Cured HPEI-Ph(1)	-	540	567	594	63	98
Cured HPEI-Ph(5)	-	523	553	520	73	95
Cured HPEI-Ph(11)	-	518	549	577	66	93
Cured RPEI-Ph(5)	-	521	562	577	71	96
Cured RPEI-Ph(9)	-	510	555	567	76	93
Cured RPEI-Ph(15)	-	512	543	577	63	89

^a Glass transition temperature (T_g) 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 weight loss 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 Gel content tested by Soxhlet extraction according to ASTM D2765 method.

^f Not detected.

The maximum decomposition temperatures for both the uncured and cured polymers were tested by DTG under nitrogen atmosphere at a heating rate of 20 °C/min from 100 to 800 °C. The data from the DTG analysis also indicate that these poly(ether imide)s, for both the cured and uncured ones, possess excellent thermal stability. For the excellent thermal stability of the crosslinked polymers, they can be used as high performance polymeric materials in the aerospace and base materials for high temperature composite matrix in a wide range of applications.

4. Conclusion

A novel series of soluble and curable phthalonitrile-terminated poly(phthalazinone ether imide)s with well controlled molecular weights were successfully prepared by varying the reactant ratio. The crosslinking reactions could be performed under normal pressure at elevated temperatures to form the heterocyclic s-triazine rings-containing thermosetting polymers. The uncured polymers have good solubility in common aprotic solvents, while the cured samples became insoluble in all solvents. Both the uncured and cured polymers have good thermal stability from DSC, TGA and DTG studies. Due to the formation of the heterocyclic s-triazine networks, the cured samples exhibit more excellent thermal stability than the uncured counterparts. And the decomposition temperatures of the cured for $T_{d5\%}$ and $T_{d10\%}$ decrease with the increasing of the molecular weights, owing to the concentration of the heterocyclic s-triazine networks decreased with the increasing of the molecular weights of the uncured polymers. This kind of soluble and curable poly(ether imide)s, which can be fabricated in their organic solutions and thermally crosslinked at normal pressure to high performance thermosetting resins, may have wider applications for high performance polymeric materials than conventional poly(ether imide)s.

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