

Synthesis and Characterization of Cross-Linkable Poly(phthalazinone ether ketone)s

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ABSTRACT: A novel class of crosslinkable poly(phthalazinone ether ketone)s with relative high molecular-weight and good solubility were successfully synthesized by the copolymerization of bisphthalazinone containing monomer, 3,3'-diallyl-4,4'-dihydroxybiphenyl and 4,4'-difluorobenzophenone. The synthesized polymers with inherent viscosities in the range of 0.42 to 0.75 dL/g can form flexible and transparent membranes by casting from their solution. The crosslinking reaction of these polymers can be carried out by thermally curing of the virgin polymers in or without the presence of crosslinking agent. The experimental results demonstrated that the crosslinking

reaction also occurred to some extent during the polymerization. The crosslinked polymers exhibited equivalent glass transition temperature (T_g) at lower crosslinking density, and showed higher T_g than virgin polymers at higher crosslinking density. The crosslinked high-temperature polymer can be used as the base material for high temperature adhesive, coating, enamel material, and composite matrices. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1821–1827, 2007

Key words: polyaromatics; high performance polymer; crosslinking; crosslinking agent

INTRODUCTION

Poly(arylene ether)s (PAEs) are a class of high performance polymers that have attracted much attention as structural materials in automobile and electronic industries because of their excellent mechanical strength per unit weight, highly thermal stability, chemical resistance, and good insulating properties.¹ However, a large number of PAEs have extremely high glass transition temperature and poor solubility in organic solvents, thus making them difficult to process. In this respect, considerable research effort has been devoted to develop new polymers containing heterocyclic moieties because of their good solubility in common organic solvents, outstanding mechanical strength and high thermooxidative stability. Since then many kinds of heterocyclic polymers, such as poly(ether imide)s,² poly(aryl ether phenylquinoxaline)s,³ and poly(aryl ether benzoxazole)s,⁴

have been synthesized by nucleophilic aromatic substitution reactions.

In 1993, Hay and coworker first described the polymerization of 1,2-dihydro-4-(4-hydroxyphenyl)-1(2H)-phthalazinone **1** with activated dihalo compounds, such as bis(4-fluorophenyl) sulfone, to synthesize poly((1,2-dihydro-*l*-oxo(2H)-phthalazine-2,4-diyl)-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenylene) **2**. The phthalazinone **1** behaves like a biphenol to give a polymer with N—C linkages (Scheme 1).⁵ The polymerization has been confirmed to proceed via a novel N—C coupling reaction as evidenced by spectroscopic studies.^{6,7} Thereafter, many phthalazinone-containing high-performance polymers, such as poly(phthalazinone ether)s,^{8–13} polyamides, and polyimides¹⁴ with good solubility and excellent thermal stability have been reported. The poly(phthalazinone ether)s, represented by poly(phthalazinone ether ketone)s and poly(phthalazinone ether sulfone)s, are a new class of PAEs with excellent thermooxidative stability, high glass transition temperature (T_g), good solubility, and outstanding mechanical properties.

The introduction of the rigid unsymmetrical phenyl phthalazinone moiety into the polymer backbone gives good solubility and high rigidity to the polymer backbone. Similarly, the compounds with two phthalazinone groups should react like bisphenols in nucleophilic aromatic substitution reactions. The resulting polymers would be expected to be thermally stable at high temperatures since similar poly-

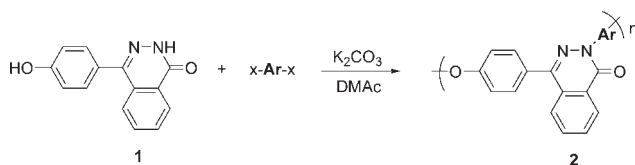
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Scheme 1 Synthesis of poly(phthalazine ether).

mers have been previously synthesized via an alternative route.^{13–15}

In this work, a crosslinkable PAE has been synthesized by copolymerizing monomer bisphthalazinone with 3,3'-diallyl-4,4'-dihydroxybiphenyl and 4,4'-difluorobenzophenone. These polymers are soluble in chlorinated solvents such as chloroform and dipolar solvents such as *N*-methyl-pyrrolidone. The double containing polymers can be crosslinked by heat, electron rays, and crosslinking agent to form a polymer network without any elimination component that tends to the formation of microcavities, voids, and pinholes.^{16–19} The crosslinkable polymers show potential application in the fields of aerospace and electronics industries.

EXPERIMENTAL

Materials

2-(4-chlorophenyl) benzoic acid (Taixin SUUMY Fine Chemical Co., Jiang Su, China) was purified by recrystallization from ethanol. 4,4'-Dihydroxybiphenyl, allylbromide and 4,4'-difluorobenzophenone **3** (DFBP) were purchased from Aldrich Chemical Co. and used as received. Highly pure 1,1'-(methylene-di-4,1-phenylene)bismaleimide (BMI) was kindly provided by the Northwest Research Institute of Chemical Industry (Shan Xi, China). Reagent-grade hydrazine monohydrate, methanol, *N,N'*-dimethylacetamide (DMAc), *N*-methyl-pyrrolidone (NMP), toluene, methanol, chloroform, and anhydrous potassium carbonate were obtained from commercial sources (Guangzhou, China) and used without further purification. NMP was dried over 4 Å molecule sieves and toluene was dried over sodium wire prior to use.

Instrumentation and measurement

The ¹H NMR spectra was recorded on a Bruker NMR instrument (model DRX 400 MHz) using CDCl₃ as a solvent; chemical shifts were given in ppm against tetramethylsilane as an internal standard. Elemental analyses were performed on an Elementar elemental analyzer (model Varios EL). Melting points were taken on a XT4A melting point apparatus. The glass transition temperatures (*T*_gs) were determined on a NETZSCH 200 PC DSC instrument at a heating rate of 10°C/min under nitrogen protec-

tion. Thermal stability was analyzed using a Seiko TG analyzer (TGA/dynamic thermal analysis, model SSC-5200) under a nitrogen atmosphere (200 mL/min) at temperature range of 70–600°C. The heating rate was 20°C/min. Inherent viscosity was determined for a solution of 0.5 g/dL in chloroform at 30°C with a calibrated Ubbelohde viscometer.

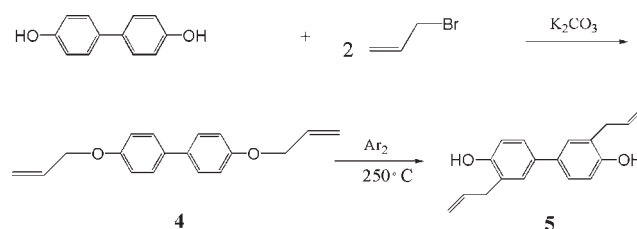
The gel content of the crosslinked samples was determined according to ASTM D2765 method using a Soxhlet extractor, using chloroform as solvent. Samples were refluxed in chloroform for at least 48 h, until the sample attained a constant weight. The residue after extraction was taken as the gel component, and the gel content was calculated according to the following equation.

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

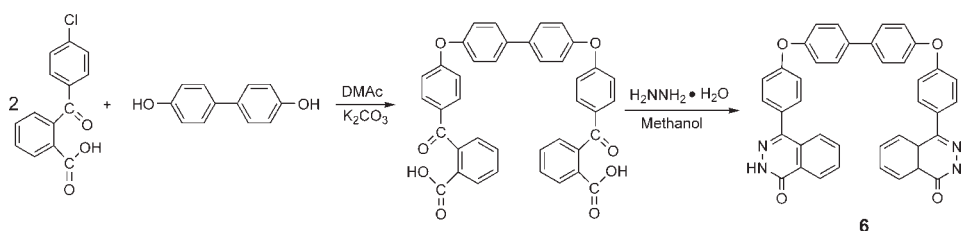
Where *W*₁ and *W*₂ are the weights of the samples before and after refluxed in DMAc for 48 h.

Preparation of 3,3'-diallyl-4,4'-dihydroxybiphenyl **5**²⁰

4,4'-Dihydroxybiphenyl (9.31 g, 50 mmol), anhydrous K₂CO₃ (7.60 g, 55 mmol), DMAc (20 mL), and toluene (20 mL) were charged into a 50 mL three-necked round-bottom flask equipped with a Dean-stark trap, a condenser, nitrogen inlet/outlet, and a magnetic stirrer. The reaction is depicted as Scheme 2. Nitrogen was purged through the reaction mixture with stirring for 15 min, and then the mixture was heated to 150°C and kept at this temperature for 3 h. After the produced water was azeotroped off with toluene, the temperature was cooled to 110°C and the Dean-stark trap was removed. Allylbromide (14.52 g, 120 mmol) was added to the reaction mixture. After 8 h, cold water was added and the precipitated powders were collected, washed for several times with boiling 95% ethanol, finally filtered, and dried in oven to give monomer **4** (m.p. 154°C, yield 92%). Following the Claisen rearrangement procedure, the monomer **4** was kept at 240°C under argon for 30 min, thus obtaining monomer **5**, which was crystallized by cooling at room temperature, then puri-



Scheme 2 Synthesis of 3,3'-diallyl-4,4'-dihydroxybiphenyl (monomer **5**).



Scheme 3 Preparation of bisphthalazinone 6.

fied by crystallization from boiling heptane. (yield 76%); m.p.: 82–83°C.

$^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ (ppm) 3.45 (m, 3H), 4.99 (m, 2H), 5.13–5.25 (m, 1H), 5.97–6.14 (m, 1H), 6.87 (m, 2H), 7.25–7.31 (m, 4H). ($\text{C}_{18}\text{H}_{18}\text{O}_2$) (266.33); Calcd C, 81.17; H, 6.81; O, 12.01; Found C, 80.94, H, 6.84; O, 12.21.

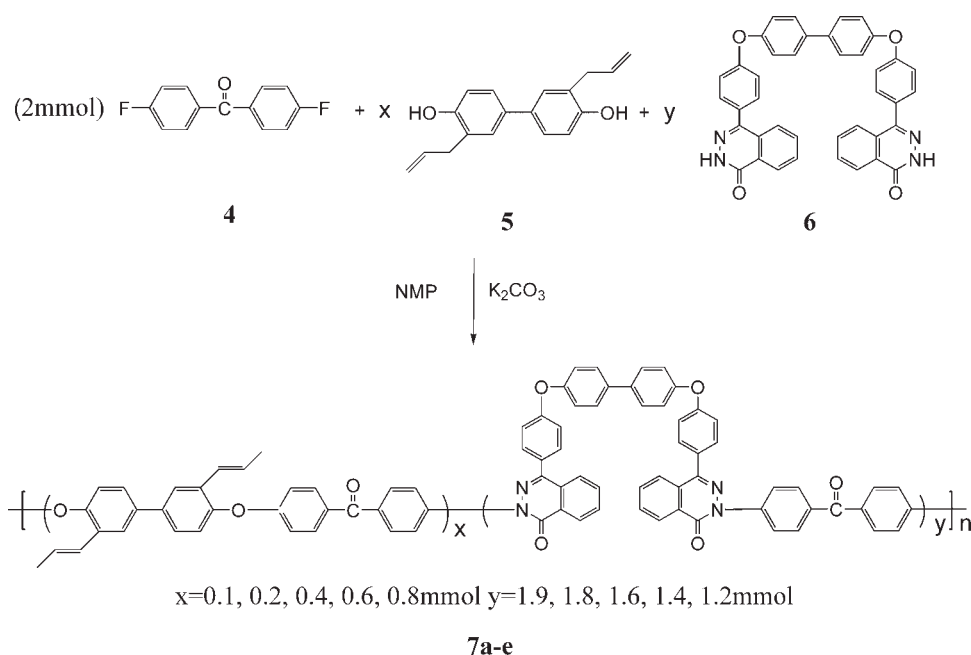
Preparation of bisphthalazinone 6 containing biphenyl moiety

Bisphthalazinone 6 was synthesized according to previous work¹⁴ in a two-step sequence as depicted in Scheme 3. The nucleophilic substitution reaction of 2-(4-chlorobenzoyl) benzoic acid with 4,4'-dihydroxybiphenyl gave dicarboxylic acid, which was converted to bisphthalazinone 6 by refluxing with hydrazine monohydrate in methanol via the ring-closure reaction (yield 91%). m.p.: 358–360.

$^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ (ppm): 7.20–7.23 (m, 8H), 7.63 (d, 4H), 7.73–7.75 (m, 6H), 7.88–7.92 (m, 4H), 8.33 (m, 2H), 12.85 (s, 2H).

Synthesis of PAEs 7a–e

The typical procedure for the synthesis of Poly(arylene ether)s (PAEs) 7a–e is as follows (Scheme 4): 4,4'-difluorobenzophenone (2 mmol) monomer 3, 3,3'-diallyl-4,4'-dihydroxybiphenyl monomer 5 and bisphthalazinone monomer 6 (2 mmol), anhydrous potassium carbonate (2.5 mmol), and 8 mL of NMP and 9 mL of toluene were added into a 25-mL three-neck flask equipped with a Dean-Stark trap, a nitrogen inlet/outlet, a condenser, and a magnetic stirrer. The proportion of the monomer 5 and the monomer 6 were 0.05, 0.1, 0.2, 0.3, 0.4 and 0.95, 0.9, 0.8, 0.7, 0.6, respectively. The mixture was refluxed for 3 h at 140°C to azeotrope off the formed water with toluene. After distilling off the excess toluene, the temperature was slowly raised to 165°C and maintained at this temperature for 10 h. Before cooling down 5 mL NMP was added to dilute the reaction mixture. The resulting viscous polymer solution was poured into the mixture of methanol/water (1 : 1 v/v) to precipitate out the polymer. The precipitates were filtered off and washed with water.



$x=0.1, 0.2, 0.4, 0.6, 0.8\text{mmol}$ $y=1.9, 1.8, 1.6, 1.4, 1.2\text{mmol}$

7a–e

Scheme 4 Synthesis of poly(phthalazinone ether ketone)s.

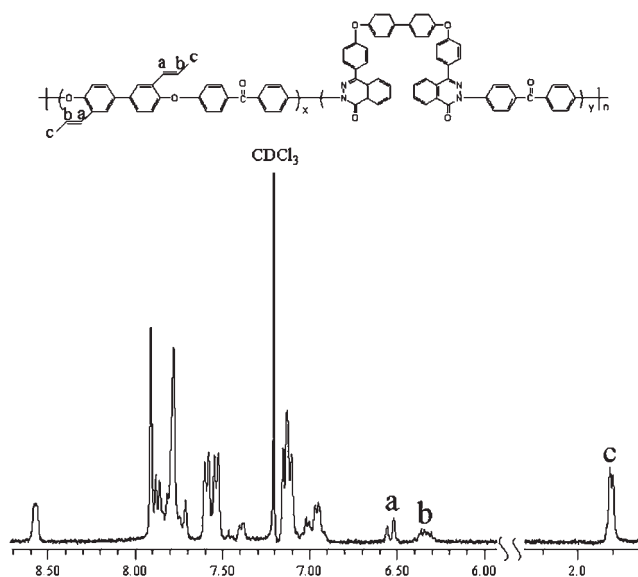


Figure 1 ^1H NMR spectrum of polymer 7e.

The recovered polymers were dried at 110°C under vacuum for 24 h.

Thermal curing of the PAEs

Two classes of film samples prepared were subjected to thermal curing. One was prepared by casting their 10% solutions in chloroform (Sample 1); the other was prepared by casting 10% solutions together with electron deficient crosslinking agent BMI (Sample 2). The amount of BMI was 0.6 stoichiometric ratio to the amount of propenyl groups on the backbone of the PAEs. Both were dried at room temperature for 24 h and then at 80°C for 24 h under vacuum. The final thickness of the samples was about 100 μm .

RESULTS AND DISCUSSION

Synthesis of PAEs 7a–e

The PAEs 7a–e with different crosslinkable group content were synthesized by aromatic nucleophilic polycondensation of monomer 4 (2 mmol) with vari-

ous content of monomer 5 (0.1, 0.2, 0.4, 0.6, 0.8 mmol) and monomer 6 (1.9, 1.8, 1.6, 1.4, 1.2 mmol), respectively, (Scheme 4). The ^1H NMR spectrum of PAE 7e was shown in Figure 1. Comparing ^1H NMR data of bisphenol 5 with Figure 1, we can find that ally group of 3,3'-diallyl-4,4'-dihydroxybiphenyl was rearranged into propenyl group due to that the potassium carbonate in the reaction mixture acted as the base-catalyze of isomerization of allyl group to propenyl group.^{21,22} The rearrangement arose from the stable structure. The double bond containing PAEs could be easily thermally crosslinked. The synthesized and uncross-linked polymers were soluble in chlorinated solvents such as chloroform and dipolar solvents such as NMP. Therefore, they could cast from solution to form flexible and transparent membranes. The crosslinking density could be readily controlled by adjusting the ratio of bisphenol 5 to monomer 6. Relative high molecular-weight PAEs with inherent viscosities ranging from 0.42 to 0.75 dL/g (Table I) were readily obtained. It should be noted that some crosslinking reaction occurred during the polymerization when DMSO was used as solvent, resulting insoluble product. Presumably, this was due to the strong acidic and electron withdrawing nature of DMSO, which could initiate unsaturated propenyl groups to crosslink.

Thermally activated crosslinking of PAEs

The thermal curing of virgin PAEs 7a–e (Sample 1) and the PAEs with BMI (Sample 2) were studied *in situ* using DSC thermal analysis (first heating run, $10^\circ\text{C}/\text{min}$), as shown in Figures 2 and 3, respectively. In Figure 2, there is no obvious exothermic event relate to the crosslinking reaction of propenyl groups besides PAE the 7e. This means that virgin PAEs are hard to undergo thermal curing until higher propenyl group content reached 40 mol %. This can be explained by the rigid backbone of PAEs that makes PAE segments difficult to move. The crosslinking reaction can only occur in case that propenyl group content is higher than 40 mol % by thermal heating. In this case, high

TABLE I
Properties of PAEs

Polymer	Yield (%)	η^a (dL/g)	T_g^b ($^\circ\text{C}$)	T_g^c ($^\circ\text{C}$)	TGA (5%) ^d	TGA (5%) ^e	Gel content (%) ^d	Gel content (%) ^e
7a	93	0.56	278	270	501	479	2.6	11.6
7b	97	0.58	272	271	478	469	3.8	65.2
7c	95	0.75	266	276	452	444	12.1	91.7
7d	97	0.42	237	257	451	442	20.5	94.9
7e	98	0.50	247	256	425	401	62.7	96.6

^a η was measured at a concentration of 0.5 g/dL in chloroform at 30°C .

^b Obtained from Figure 4.

^c Obtained from Figure 5.

^d Virgin PAEs (sample 1).

^e PAEs in the presence of BMI (sample 2).

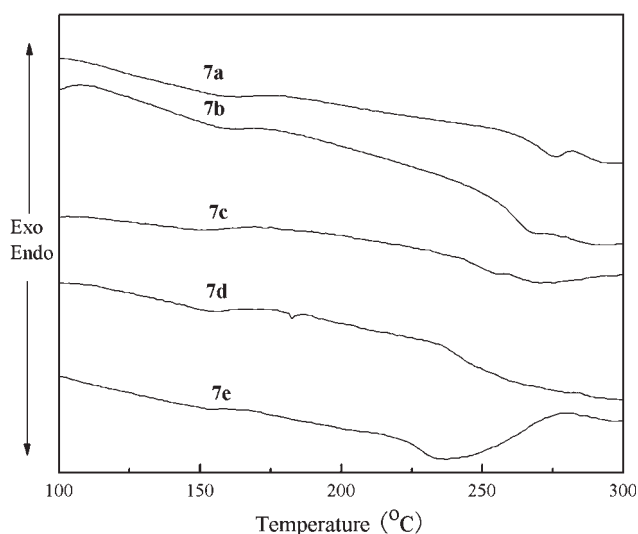


Figure 2 DSC traces of the thermal curing of the virgin PAEs 7a–e (Sample 1).

crosslinking density may lead to a brittle material with the deterioration in mechanical properties. Furthermore, thermal stability also decreased with increasing crosslinking density as shown in Figure 6. This behavior was resulted from the incorporation of sp^3 hybrid moieties of bisphenol 5. In case BMI was added, an exothermic event related to the crosslinking reaction of the propenyl groups with BMI was observed in Figure 3. BMI contains two electron deficient olefin groups comprising adjacent electron withdrawing group makes it easy to react with the propenyl. Moreover the BMI melt (m.p.: 156–158°C) at crosslinking temperature exhibits highly moving ability and acts as a plasticizer to promote the translation of PAEs. All the above factors facilitate the crosslinking reaction extensively occurred. The crosslinking reaction takes place via Ene

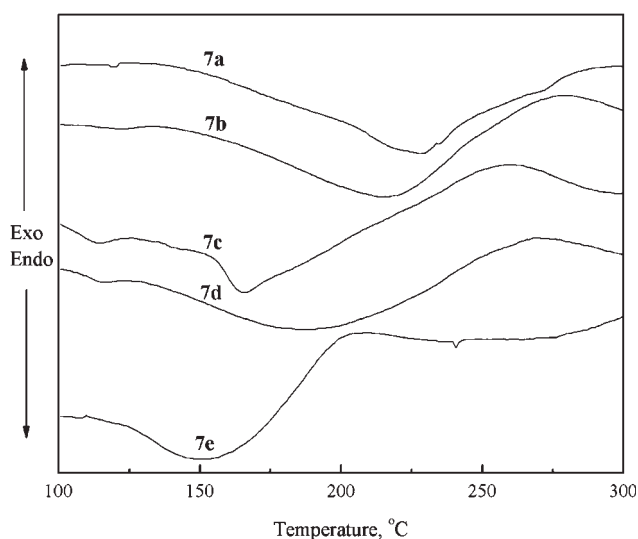


Figure 3 DSC traces of the thermal curing of PAEs 7a–e in the presence of BMI (Sample 2).

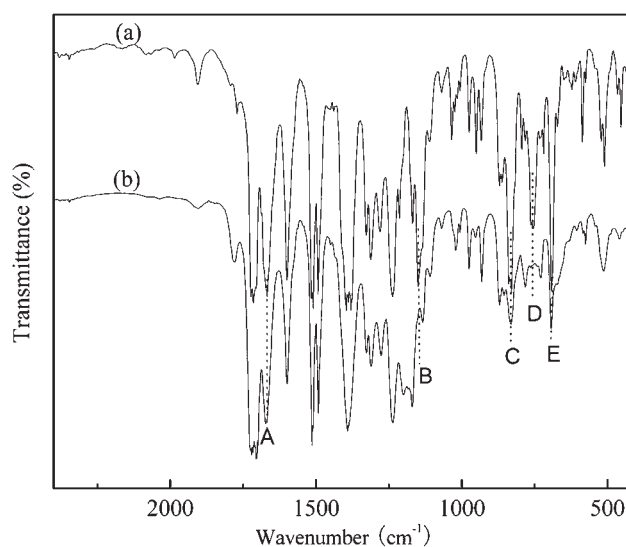


Figure 4 FTIR spectra of 7e with BMI before (a) and after (b) thermal curing.

or Ene and Diels–Alder reactions. As shown in Figure 3, the endothermic events of 7c, 7d, 7e are attributed to the endothermic phase transition of the unreacted BMIs dispersed within the cast films of PAEs.

The FTIR spectra of 7e containing BMI were recorded before and after subjecting to curing at a programmed temperature profile from 150 to 300°C for 1 h under vacuum (Fig. 4). Prior to curing, the absorption peaks at 1672 cm^{-1} (A) was raised from the C=C stretch of maleimide and propenyl groups. The peaks at 1141 cm^{-1} (B) was due to the ether group and a doublet at 679 and 693 cm^{-1} (E) was due to the bending mode of =C–H of maleimide. The peak at 831 cm^{-1} (C) came from =C–H out-of-plane deformations of maleimide, and the peaks at 752 cm^{-1} (D) were caused

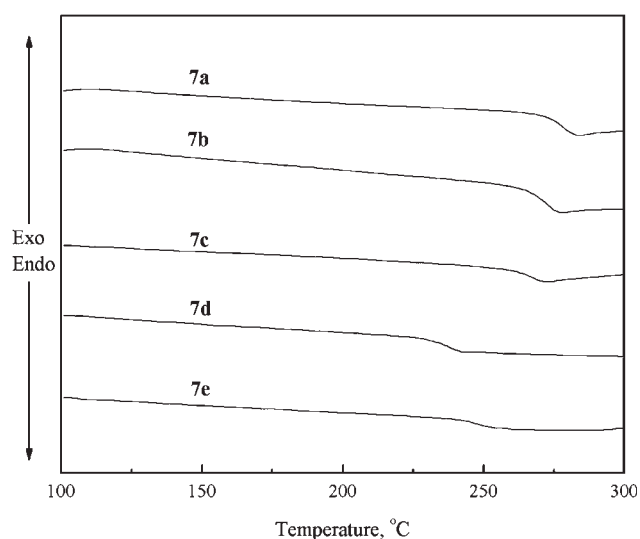


Figure 5 DSC traces of the virgin PAEs 7a–e (Sample 1) after thermal curing.

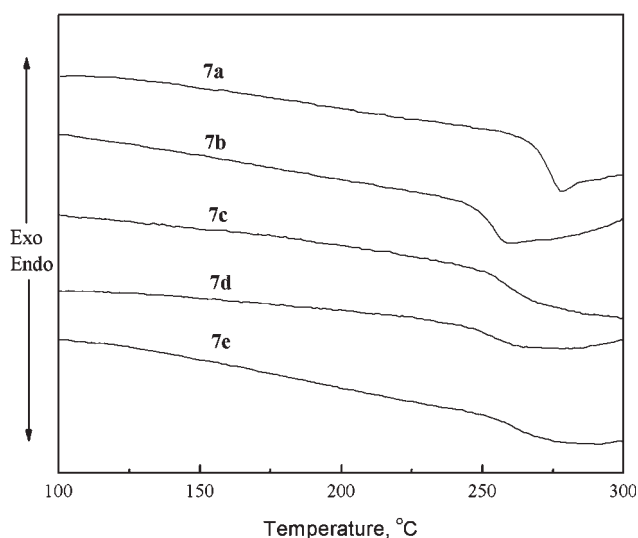


Figure 6 DSC traces of PAEs 7a–e in the presence of BMI (Sample 2) after thermal curing.

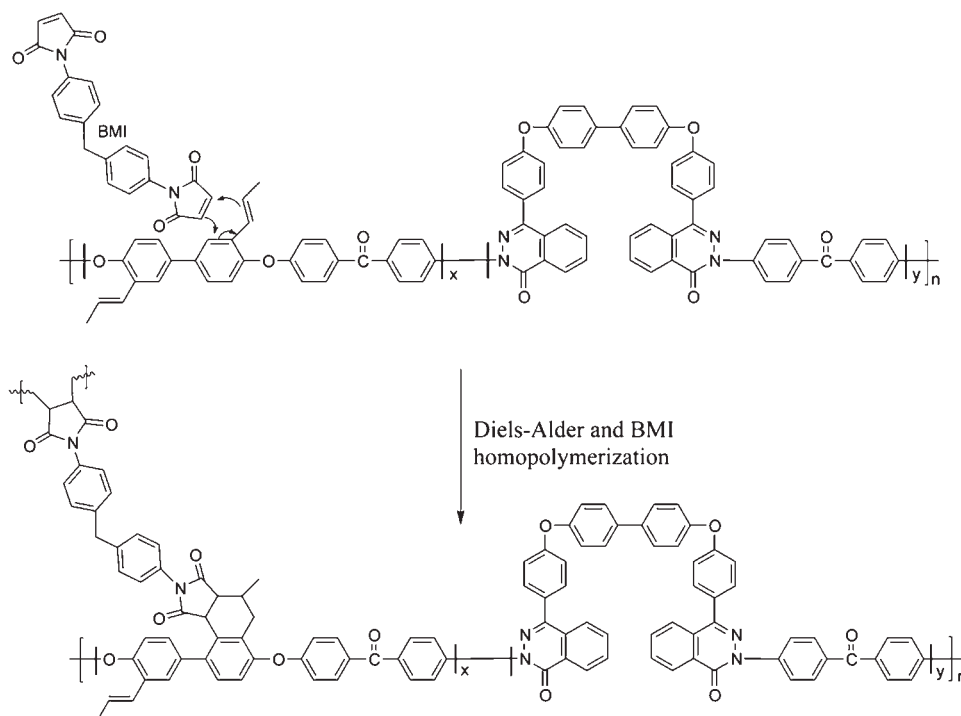
by the conjugated $=C-H$ group out-of-plane deformations for cis alkene of propenyl groups, respectively. The strength of above bends decreased or almost disappeared; demonstrating the occurrence of crosslinking reaction of Sample 2.

Thermal properties

Figures 5 and 6 shows the DSC (10/min under nitrogen, second scan) traces of Sample 1 and Sample 2. As shown in Figure 5, concerning the molecular

weight, the T_g of PAEs decreased with the increase of propenyl group content, indicating that the propenyl group can defect the chair sequence. Nevertheless, no obvious endothermic events associated with the melting of BMI and exothermic event associated with thermal curing are observed in Figure 6. This implies that the thermal crosslinking reaction has occurred, resulting in a crosslinked PAE. The proposed crosslinking process is illustrated in Scheme 5, presumably the reaction takes place via a Diels-Alder mechanism between the pendent propenyl group and the maleimide olefin²³. The glass transitions associated with the unreacted PAEs become more and more obscure in both Figures 5 and 6 (listed in Table I), showing that crosslinking content increased with increasing the amount of propenyl group. In case the propenyl group content was smaller than 10 mol %, T_g s of crosslinked PAEs were lower than those uncross-linked, whereas the situation was reverse. Presumably, the lower T_g resulted from the unreacted BMI that acted as a plasticizer for the PAEs. After crosslinked, the T_g s of PAEs showed higher than the virgin PAEs (Fig. 5).

The virgin PAEs 7a–e (Sample 1) and the PAEs with the presence of BMI (Sample 2) were both subjected to thermal curing at a programmed temperature from 150 to 300°C for 1 h under vacuum. The TGA thermograms under nitrogen atmosphere at a heating rate of 20°C/min of the resulted samples are depicted in Figures 7 and 8 and the gel content are listed in Table I. All of these samples exhibited a similar pattern of decomposition. The onset of



Scheme 5 The proposed crosslinking process of the PAEs with BMI.

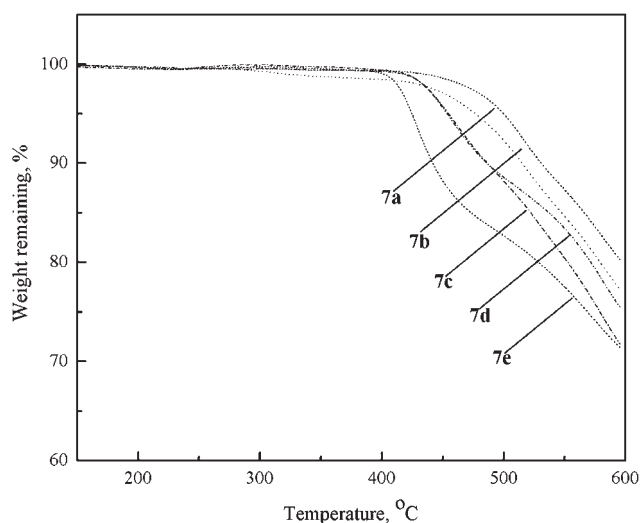


Figure 7 TGA thermogram curves for the virgin PAEs 7a–e (Sample 1).

decomposition temperature decreased with increasing propenyl group content. The crosslinking reaction showed no improvement in thermal stability of PAEs due to the presence of unreacted BMI. Moreover, the sp^3 carbon on hybrid propenyl groups can decrease the decomposition temperature of the crosslinked PAEs. The gel content listed in Table I demonstrated the well crosslinked structure of the PAEs.

CONCLUSIONS

A novel class of crosslinkable poly(phthalazinone ether ketone)s with relative high molecular-weight

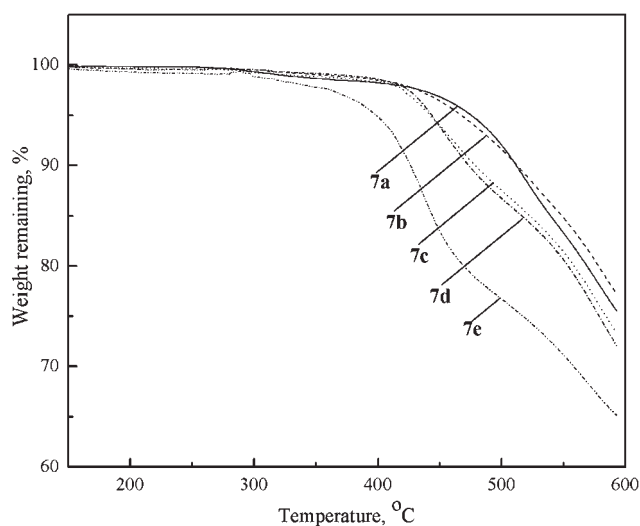


Figure 8 TGA thermogram curves for PAEs 7a–e in the presence of BMI (Sample 2).

and good solubility were successfully synthesized by copolymerization of bisphthalazinone monomer, 3,3'-diallyl-4,4'-dihydroxybiphenyl and 4,4'-difluorobenzophenone. The thermal curing of the synthesized polymers in the presence of BMI initiator was *in situ* investigated using differential scanning calorimetry. The experimental results showed that BMI is an efficient crosslinking agent for the synthesized polymers. The crosslinked polymers exhibited equivalent glass transition temperature (T_g) at lower crosslinking density, and showed higher T_g than virgin polymers at higher crosslinking density. Because of the easier crosslinking process, the synthesized high-temperature polymer can be used as the base material for high temperature adhesive, enamel coating and the matrix of composites.

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