

## Synthesis, Curing and Properties of Poly(phthalazine ether sulfone ketone) Copolymers Crosslinked by Click Chemistry\*

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**Abstract** Functionalized poly(phthalazinone ether sulfone ketone) was synthesized by successive chloromethylation and azidation, followed by curing reaction with the propargyl end-groups of various molecular weight crosslinking agents in the presence of Cu(I) catalyst *via* the azide-alkyne click reaction. The influences of the chain length of crosslinking agents on the poly(phthalazinone ether sulfone ketone) system were studied. FTIR and DSC tests demonstrated certain crosslinking by azide-alkyne reaction with the formation of triazole ring. DSC results showed that curing temperature shifted to lower temperatures considerably in the presence of Cu(I) catalyst. TGA showed cured polymers were of much higher thermal stability, including higher thermal decomposition temperatures and higher char-yielding properties. After being cured, the polymers became insoluble in organic solvents and the gel fraction of the cured polymers exceeded 71%. Wide-angle X-ray diffraction results indicated there was a short distance order in the poly(ether sulfone) (PES) main chain except for the azido methyl poly(phthalazinone ether sulfone ketone) and 4,4'-bis(2-propynyloxy) biphenyl (AMPPEBK-BP) system.

**Keywords:** Poly(arylene ether sulfone); Crosslinking; Click chemistry.

### INTRODUCTION

For the past decades, heat-resistant polymer matrix materials have become main structural materials of aviation and aerospace industries. Among these advanced materials, much attention is paid to low temperature molding materials with high performance. Those materials, including polyimide (PI)<sup>[1, 2]</sup>, poly(arylene ether) (PAE)<sup>[3, 4]</sup>, bismaleimides (BMI)<sup>[5, 6]</sup>, phenolic resin<sup>[7, 8]</sup>, epoxy<sup>[9, 10]</sup>, cyanate<sup>[11, 12]</sup>, benzoxazine<sup>[13, 14]</sup> and so on, possess good thermo-oxidative stability, excellent thermal and chemical resistance, and low cost, making them have a wide variety of applications in automobile, aerospace and electronic fields. Poly(arylene ether sulfone) (PES) is an important member of them and widely used as polymer membrane<sup>[15, 16]</sup>.

Recently, with the development of science and technology, more attention has been paid to heat-resistance polymer matrix materials, and the grade of heat-resistance polymer materials is put forward for higher requirements. Curing is an effective method to improve comprehensive performance of polymer materials. Use specific reactive groups, such as epoxy<sup>[17, 18]</sup>, amine<sup>[19, 20]</sup>, phenol<sup>[21, 22]</sup>, and carboxyl<sup>[23, 24]</sup> in the polymer is a widely accepted practice. Lin prepared side-chain phenol-functionalized polymer through a post-functionalization<sup>[25]</sup>. Phenol groups of the polymer as curing sites reacted with epoxy resins to prepare flame-retardant and high-performance thermosets. Acrylates with pendant carboxylic acid groups, prepared by Czech *et al.*, reacted with metal complexes to obtain acrylic self-adhesives with excellent properties<sup>[26]</sup>. Smitha *et al.* synthesized epoxy-functional precursor polymer containing propargyl and azide groups by conventional free radical polymerization and chemical transformation<sup>[27]</sup>. The polymers obtained were

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effectively crosslinked through “click” reaction of 1,3-dipolar cyclo addition. To the best of our knowledge, there has been limited studies on introduction of alkynyl and azide groups into aromatic chains of poly(arylene ether sulfone) and on the investigation of the related curing process and properties of the final modified products.

Click chemistry is a powerful palette of bond forming reactions that has already been widely applied to the field of polymers and material synthesis. It enables one to achieve diverse building blocks in high yields and with no byproducts<sup>[28, 29]</sup>. Since azides and alkynes are readily attached to a variety of molecular scaffolds, Huisgen’s 1,3-dipolar cycloaddition of them offers an easy route to altering the cure mechanism of many polymer systems<sup>[30–32]</sup>.

In this article, we report the synthesis and characterization of click-curable poly(phthalazine ether sulfone ketone) and propargyl end-groups of PES oligomers systems. These polymers were subsequently crosslinked *via* click reaction. DSC and FTIR analysis demonstrated there existed certain crosslinking by azide-alkyne reaction with the formation of triazole ring. The cured polymers showed much higher thermal stability, including higher thermal decomposition temperatures and higher char-yielding properties. Thus, the resultant azide functional poly(phthalazinone ether sulfone ketone) and their crosslinked polymers may be used as base materials for high temperature adhesive, coating or composite matrix in a wide range of applications.

## EXPERIMENTAL

### Material and Reagents

poly(phthalazinone ether sulfone ketone) (PPESK) was obtained from Dalian Polymer New Material Company (China); chloromethyl ether was purchased from Shanghai Haiqu Chemical Company; biphenol and 4,4'-dichlorodiphenyl sulfone were purchased from commercial sources and purified by recrystallization from ethanol; propargyl bromide was purchased from Beijing Lideshi Chemical Company; analytical-grade anhydrous potassium carbonate ( $K_2CO_3$ ) was ground and dried in vacuum at 100 °C for 24 h before use. Sulfuric acid (98%), *N,N*-dimethylacetamide (DMAc), chloroform, dimethyl-sulfoxide, trimethylamine and *N*-methylpyrrolidone (NMP) were of analytical grade.

### Measurements

Fourier-transform infrared (FTIR) spectra of the compounds were tested on a Fourier transform infrared spectrometer (Thermo Nicolet Nexus 470) using KBr pellet or film.  $^1H$ -NMR (400 MHz) was done with a Varian Unity Inova 400 spectrometer at operating temperature of 25 °C using  $CDCl_3$  as solvent and were listed in parts per million down field from tetramethylsilane (TMS). Gel permeation chromatography (GPC) analysis was carried out with chloroform as eluent on a PL GPC-50 instrument equipped with 5  $\mu m$  PLgel Mixed C columns (heated to 40 °C) arranged in series with a RI detector. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a TA 2000 thermal analyzer.  $T_g$  of the polymer was obtained with DSC instrument at a heating rate of 10  $K \cdot min^{-1}$  in  $N_2$ . TGA measurement was conducted at a heating rate of 20  $K \cdot min^{-1}$  in  $N_2$  atmosphere. Wide-angle X-ray diffraction (WAXD) was performed at room temperature on a Rigaku D/max 2400 automatic X-ray diffractometer with Ni-filtered Cu  $K\alpha$  radiation (40 V, 100 mA). SAXS measurement was carried out on A Seifert ID 3000 X-ray generator operating at 55 kV and 40 mA provided Cu  $K\alpha$  radiation with a wavelength of  $\lambda = 0.1524$  nm.

### Synthesis of Chloromethyl Poly(phthalazinone ether sulfone ketone) (CMPPEK) (P1)

A three-necked round-bottom flask of 250 mL, equipped with an mechanical stirrer, was charged with 100 mL of concentrated sulfuric acid and 10 g of PPESK at room temperature, the flask was cooled to 0 °C in an ice bath after PPESK was dissolved, then appropriate amount of chloromethyl ether was added to the solution, and the reaction was allowed to proceed for 10 h at 0 °C. The end solution was precipitated in water, the white rod-like polymer was obtained, which was filtered, washed with deionized water several times until pH = 7, and dried under vacuum at 90 °C for 24 h.

FTIR: 2959  $cm^{-1}$  ( $-CH_2-$ ), 1668  $cm^{-1}$  ( $-C=O$ ), 1242  $cm^{-1}$  ( $C-O-C$ ).  $^1H$ -NMR (400 MHz,  $CDCl_3$ ,  $\delta$ ): 8.53–7.19 ( $C_6H_5$ ), 4.75 ( $-CH_2Cl$ ). GPC:  $M_n = 38800$   $g \cdot mol^{-1}$ ,  $M_w/M_n = 3.3$ .

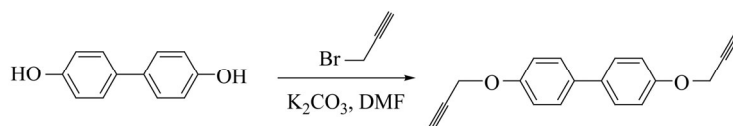
### Synthesis of Azido Methyl Poly(phthalazinone ether sulfone ketone) (AMPPESK) (P2)

CMPPESK (1.0 g) as prepared above was dissolved in 10 mL of DMAC in a 50 mL three-necked round-bottom flask. Sodium azide was carefully added to the solution, the polymer solution was slowly raised to 70 °C. After stirring for 30 h, the mixture was precipitated into ethanol. The product was filtered, washed with distilled water and ethyl ether, and then vacuum-dried at room temperature for 24 h. After filtered and dried, the polymer was purified by filtering its chloroform (CH<sub>3</sub>Cl) solution through a thin layer of Celite before precipitating it into sufficient ethanol. The white powder was collected by filtration and then treated thoroughly with boiling water and methanol, and then drying at 50 °C under vacuum for 24 h.

FTIR: 2960 cm<sup>-1</sup> (—CH<sub>2</sub>—), 2103 cm<sup>-1</sup> (—CH<sub>2</sub>N<sub>3</sub>), 1665 cm<sup>-1</sup> (—C=O), 1240 cm<sup>-1</sup> (C—O—C); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.53–7.19 (C<sub>6</sub>H<sub>5</sub>), 4.53 (—CH<sub>2</sub>N<sub>3</sub>), GPC:  $M_n = 35200 \text{ g} \cdot \text{mol}^{-1}$ ,  $M_w/M_n = 3.1$

### Synthesis of Curing Agent 4,4'-Bis(2-propynyloxy)biphenyl (BP) (3)

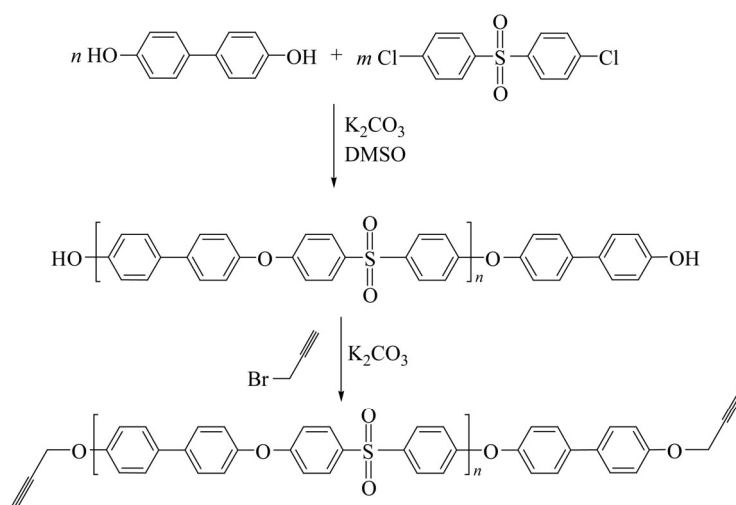
A round bottom flask of 200 mL, equipped with a mechanical stirrer, condenser and N<sub>2</sub> inlet, was charged with biphenol (1.86 g), potassium carbonate (1.932 g) and 22 mL of DMF. Propargyl bromide was then dropped into the flask over 10 min. The reaction was stirred for 48 h at room temperature (Scheme 1). The resulting mixture was poured into deionized water (pH = 3), the white power was filtered and recrystallized in toluene with a yield of 67%. Mass spectrum (*m/e*): 262.1; FTIR: 3277 cm<sup>-1</sup> (≡C—H), 2919 cm<sup>-1</sup> (—CH<sub>2</sub>—), 2130 cm<sup>-1</sup> (—C≡C—), 1240 cm<sup>-1</sup> (—C—O—C—); <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.50 (C<sub>6</sub>H<sub>4</sub>), 7.02 (C<sub>6</sub>H<sub>4</sub>), 4.72 (O—CH<sub>2</sub>—), 2.53 (≡C—H).



Scheme 1 Synthetic route of curing agent 4,4'-bis(2-propynyloxy) biphenyl

### Synthesis of the Propargyl End-groups of PES Oligomer with Different Molecular Weight (4,5)

Poly(aryl ether sulfone)s with terminated propargyl groups were synthesized *via* a nucleophilic aromatic substitution (S<sub>N</sub>Ar) as illustrated in Scheme 2. PES with 1000 molecular weight (4) and PES oligomer with 3000 molecular weight (5) were prepared with the similar procedure. Therefore, only the preparation of PES (5) with 3000 molecular weight was depicted as a typical example. A 100 mL three-necked flask, equipped with a mechanical stirrer, an nitrogen inlet, Deane-Stark trap and condenser, was charged with biphenol (4.9549 g,



Scheme 2 Synthetic route of propargyl end-groups of PES oligomer

0.0266 mol), 4,4'-dichlorodiphenyl sulfone (5.7192 g, 0.02 mol),  $K_2CO_3$  (4.4097 g, 0.0319 mol), 10 mL of DMSO, and 25 mL of toluene. The reaction mixture was heated to 135 °C under vigorously stirring until no more water was formed by azeotropic distillation. Toluene was then removed slowly as the reaction mixture was heated to 160 °C. The reaction temperature was maintained at 160 °C for 4 h. The mixture was then cooled to room temperature. 3-Bromo-1-propyne (3.2 g, 0.0268 mol) was slowly dropped into the three-necked flask. After addition, this mixture was heated to 60 °C for 24 h. The product was slowly poured into a solution of sufficient boiling water under vigorous stirring. The resulting precipitate was filtrated and washed with hot water twice to give a dark-yellow precipitate. The obtained polymer was Soxhlet-extracted with acetone for 48 h. The product was dried at 60 °C under vacuum for 48 h. Yield: 95.4%.

FTIR: 3295  $cm^{-1}$  ( $-C\equiv C-H$ ), 3062  $cm^{-1}$  ( $C_6H_5$ ), 2958  $cm^{-1}$  ( $-CH_2-$ ), 2116  $cm^{-1}$  ( $-C\equiv C-$ ), 1294  $cm^{-1}$  ( $-S=O$ ), 1243  $cm^{-1}$  ( $C-O-C$ );  $^1H$ -NMR (400 MHz,  $CDCl_3$ ,  $\delta$ ): 7.98–6.89 (Ar-H), 4.89 ( $-CH_2-C\equiv C-$ ), 3.64 ( $-C\equiv C-H$ ).

### Crosslink of AMPPEK and Curing Agents via Click Reaction

The azide containing polymer was reacted, at 60 °C for 20 h, with different propargyl functional curing agents in equal molar ratios in the presence of 0.3 wt% of CuI as catalyst. The mixing was done by dissolving both the polymers together, along with the catalyst, in dimethylacetamide followed by casting the mixture as a thin film. The thermal cross-linking behaviors of the films were then performed by heating the polymer films at 150 °C for 4 h. The cured product was characterized by FTIR, DSC and TGA. Crosslinking density of the film was determined by swelling.

### Gel Fraction

Gel fraction of the powdered crosslinked sample was determined through Soxhlet extraction, using *N,N*-dimethyl acetamide (DMAc) as the 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 fraction was calculated according to Eq. (1):

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

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

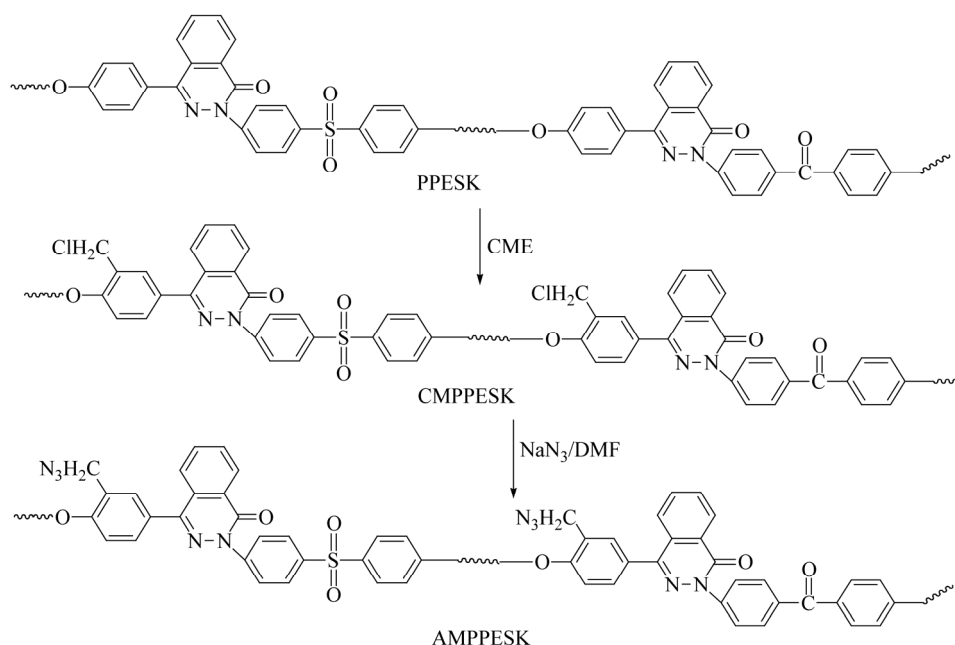
## RESULTS AND DISCUSSION

### Characterization of AMPPEK

Azido functionalized poly(phthalazone ether sulfone) was synthesized from poly(phthalazone ether sulfone) by reaction with chloromethyl ether at 0 °C for 9 h, subsequently by nucleophilic substitution with sodium azide (Scheme 3).

Each step of the functionalization process was monitored by FTIR and  $^1H$ -NMR spectroscopy. As shown in Fig. 1, the absorption peaks at around 2959 and 2853  $cm^{-1}$  were attributed to the stretching vibration of  $-CH_2Cl$ . After substitution, characteristic absorption of azido groups was seen at around 2103  $cm^{-1}$  in the resulting polymer.

The azido substitution was further confirmed by  $^1H$ -NMR spectroscopy. The degree of chloromethylation was found to be 10 mol% as determined from the integration ratio of  $CH_2$  protons at  $\delta = 4.75$  to that of the typical H-1 signal of phenyl ring adjacent to the carbonyl group of phthalazinone moiety, appearing at around  $\delta = 8.63$ . Compared with PPEK and CMPPEK, a new peak, different from PPEK, was observed at around  $\delta = 4.75$ , which was assigned to the protons of chloromethyl groups. After treatment with sodium azide, the signals corresponding to methylene protons shifted from  $\delta = 4.75$  to 4.53, indicating successful azidation (Fig. 2).



**Scheme 3** Synthetic route of chloromethyl and azido methyl modified polymers

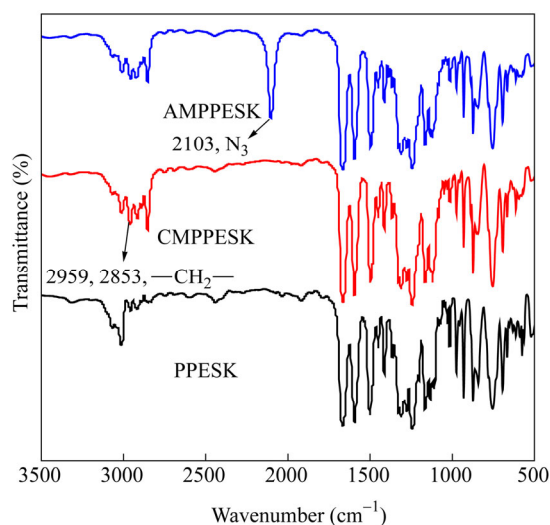


**Fig. 1** FTIR spectra of PPESK, CMPPEK and AMPPEK

GPC analysis of the polymers revealed that the molecular weight and molecular weight distribution of PPESK did not significantly change in the functionalization process (Table 1).

**Table 1.** The conversion of chemical transformations and the molecular-weight characteristics of the PPESK at various stages

| Polymer | Conversion <sup>a</sup> (%) | $M_n^b$ | $M_w/M_n$ | $\eta_{inh}^c$ (g·dL <sup>-1</sup> ) | Yield (%) |
|---------|-----------------------------|---------|-----------|--------------------------------------|-----------|
| PPESK   | —                           | 36620   | 2.96      | 0.44                                 | —         |
| CMPPEK  | 80                          | 38800   | 3.3       | 0.48                                 | 96        |
| AMPPEK  | 100                         | 35200   | 3.1       | 0.42                                 | 94        |

<sup>a</sup> Determined from <sup>1</sup>H-NMR analysis; <sup>b</sup> Number-average molecular weight and dispersity ( $M_w/M_n$ ) determined by GPC using chloroform as eluting solvent at 40 °C with polystyrene standards;

<sup>c</sup> Measured in CHCl<sub>3</sub> at 25 °C at a concentration of 0.5 g·dL<sup>-1</sup>

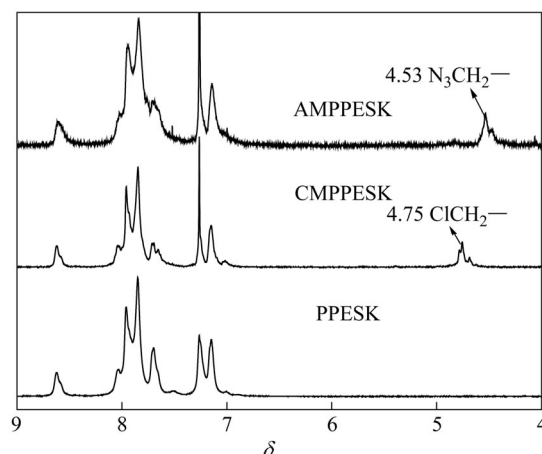
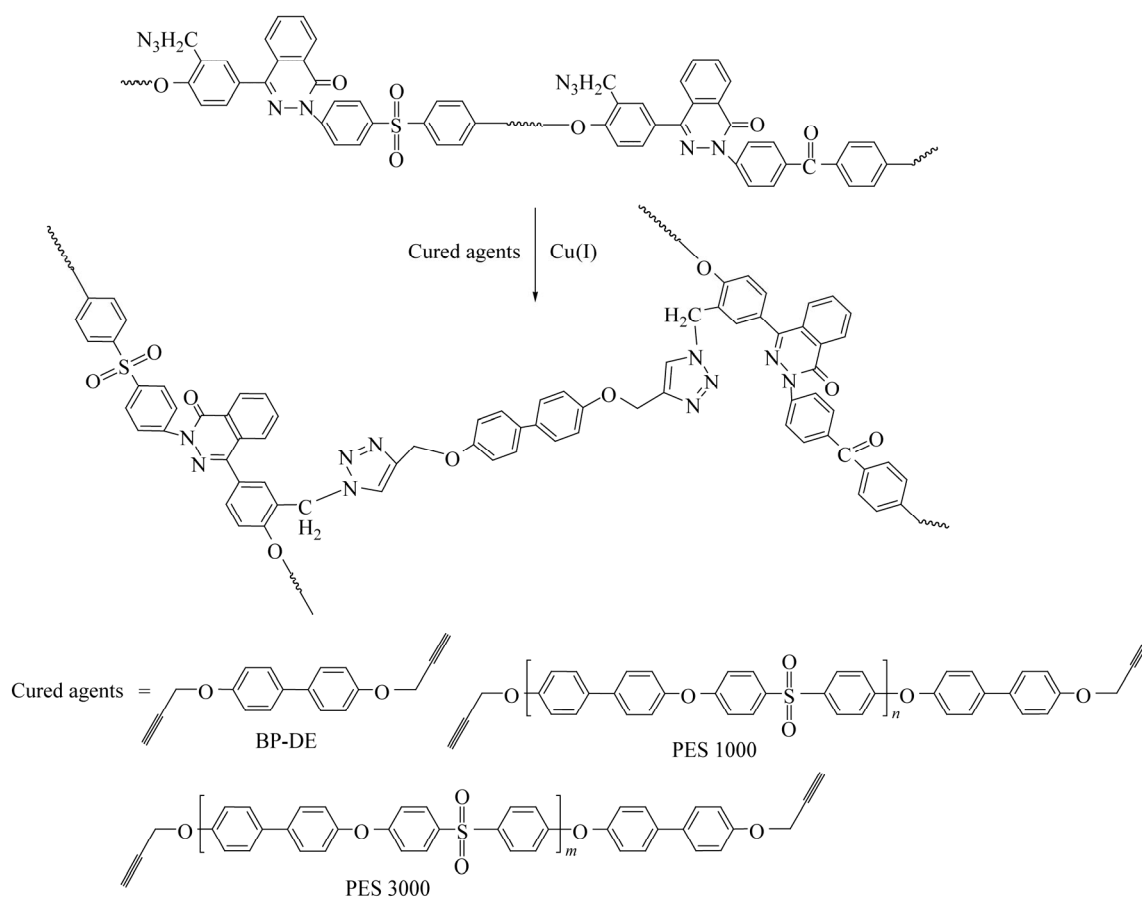


Fig. 2  $^1\text{H}$ -NMR spectra of PPESK, CMPESK and AMPPESK

### Cure Reaction of AMPPESK and Curing Agents

AMPPESK and curing agents were coupled *via* the click reaction (Scheme 3) utilizing the reaction between the azide and propargyl groups to form 1,2,3-triazole ring. The cure reaction of AMPPESK-curing agents systems was monitored using FTIR and DSC (Scheme 4).



Scheme 4 Crosslinking *via* click reaction of AMPPESK and curing agents

FTIR was employed to study the curing reactions of AMPPESK-BP. The characteristic peak at  $3277\text{ cm}^{-1}$  was the absorption of  $\text{—C}\equiv\text{H}$  stretching vibrations (BP) and the peak at  $2103\text{ cm}^{-1}$  attributed to the absorption of azides groups, respectively. The intensity of the three absorption peaks at  $3277$ ,  $2103$ , and  $2130\text{ cm}^{-1}$  decreased gradually during the curing process of AMPPESK-BP resin. After curing at  $150\text{ }^{\circ}\text{C}$  for 4 h, the azide and propargyl groups disappeared and new peaks appeared at  $1371$  and  $1488\text{ cm}^{-1}$  because of  $\text{N}=\text{N}$  in triazole rings as shown in Fig. 3.

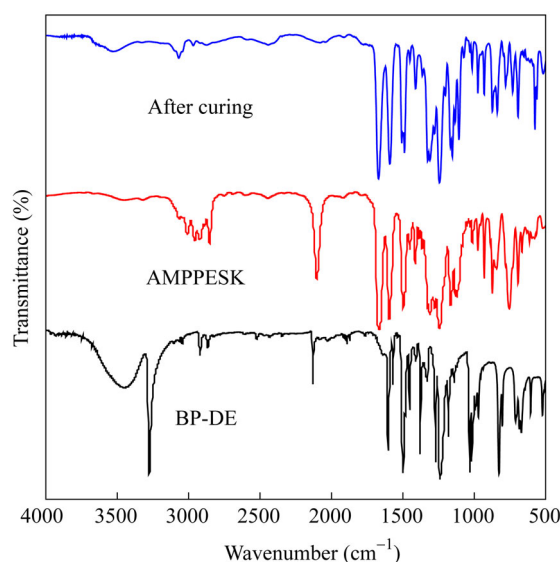


**Fig. 3** FTIR spectra of AMPPESK and curing agents

#### *The Properties of Curing Systems*

The curing reactions of AMPPESK-BP were studied by DSC using blend of azide and ethynyl group at equal moles. The nonisothermal DSC showed two exotherms for both catalyzed and uncatalyzed cases as shown in Fig. 4. The first exotherm was attributed to the click cure reaction. Since complete reaction of all the azide groups and ethynyl groups cannot take place during the dynamic ramping of temperature. The second exotherm was attributed to the residual azide groups decompose and thermal crosslinking of ethynyl groups at higher temperature. These were manifested as a second exotherm at around  $250\text{ }^{\circ}\text{C}$ . Compared with the uncatalyzed DSC curves of AMPPESK-BP system, the first exotherm peak shifted to considerably lower temperature owing to the reduced activation energy by the catalyst, while the second peak shifted only marginally.

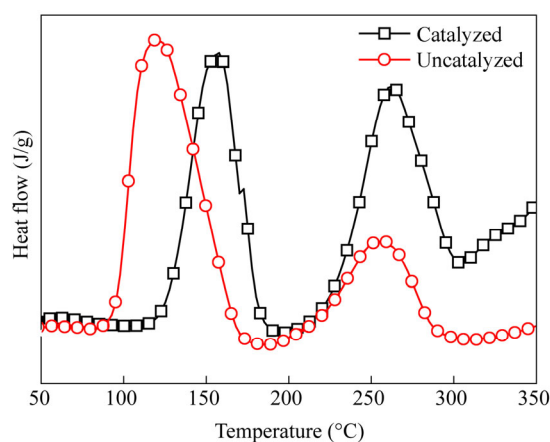


**Fig. 4** DSC curves of catalyzed and uncatalyzed cured reaction of AMPPESK-BP system

Accordingly, the enthalpy of the first exotherm was measured to be  $164 \text{ kJ}\cdot\text{mol}^{-1}$  for the uncatalyzed click cure reaction. In the presence of catalysis, due to the increases of click cure reaction, the enthalpy of the first exotherm peak was estimated as  $184 \text{ kJ}\cdot\text{mol}^{-1}$  and thus the second exotherm peak becomes less predominant in this case.

The thermal mechanical property was one of the most important properties for high-performance materials. In our study, the glass transition temperatures ( $T_g$ ) of polymers were also detected on thin film samples by dynamic mechanical analysis (DMA), which described the transition *via* detecting relaxation of molecular motion (Figs. 5 and 6). As shown in Fig. 5, the values of the storage modulus ( $E'$ ) for all curing system exceeded 2000 MPa under the glassy state.  $E'$  was mainly affected by the crosslinking density of cured resin, hence  $E'$  of AMPPESK-BP was the highest due to the highest crosslinking density. In addition, a slight decrease in  $E'$  occurring at 50–100 °C was associated with the secondary relaxations caused by rearrangement and orientation of polymer chains. Subsequently, a steady creep of the modulus was observed before 250 °C caused by the orientation of macromolecular chains at high temperatures. With the slow increase in temperature,  $E'$  began to decrease sharply, which indicated a catastrophic deterioration of the mechanical properties for the film samples.

In Fig. 6, the maximum of  $\tan\delta$  of the films, representing the appearance of the glass transition, decreased from 289 °C to 259 °C with increasing molecules weights of curing agents.  $\tan\delta$  is a measurement of damping, the relation between the elastic energy stored and the energy dissipated per cycle of vibration. The interface effects and adhesion degree have a slight influence on the modulus of composites, but they are very important factors for the damping behavior of composites. The rigidity and high crosslink density of the cured resins would enhance the internal friction resistance of molecular chain and increase the peak values of  $E''$  and  $\tan\delta$ . Hence, AMPPESK-BP possessed maximal glass transition value. The  $T_g$  of pristine polymer, however, was only 259 °C.

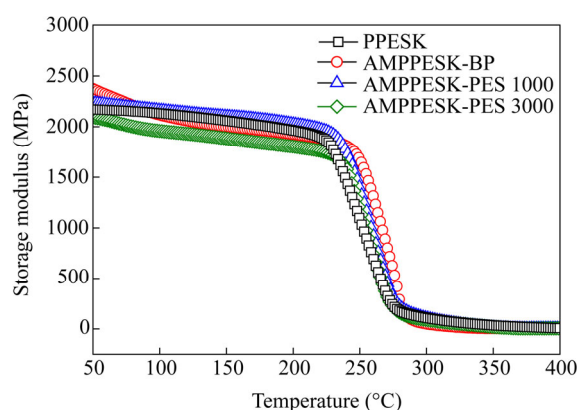


**Fig. 5** DMA curves of PPESK, AMPPESK-BP, AMPPESK-PES 1000 and AMPPESK-PES 3000

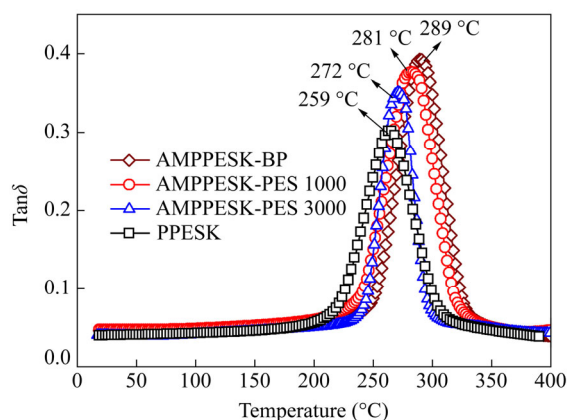


**Fig. 6**  $\tan\delta$  curves of PPESK, AMPPESK-BP, AMPPESK-PES 1000 and AMPPESK-PES 3000

Thermal decomposition behavior of the cured resins of AMPPESK with different cured agents blends were investigated by thermo gravimetric analysis (Fig. 7). The temperature of 5% weight loss ( $T_{d5\%}$ ), measured by TGA in nitrogen atmosphere at a heating rate of  $20\text{ K}\cdot\text{min}^{-1}$ , was used to describe the thermal stability of the resins. Compared with the  $T_{d5\%}$  of PPESK reported<sup>[33]</sup>, a major mass loss of the obtained polymers were observed at around  $400\text{ }^{\circ}\text{C}$  because of decomposition of triazole and methylene of cured resins. The  $T_{d5\%}$  of AMPPESK-BP system was  $456\text{ }^{\circ}\text{C}$  due of the increased aromatic content and cross-linking density. Compared with thermal stability of AMPPESK-PES 1000 system, the  $T_{d5\%}$  of AMPPESK-PES 3000 system was significantly reduced to  $369\text{ }^{\circ}\text{C}$  due to the incompletely cured reaction. Char residue at  $800\text{ }^{\circ}\text{C}$  for these three systems was found to be close to 78%.

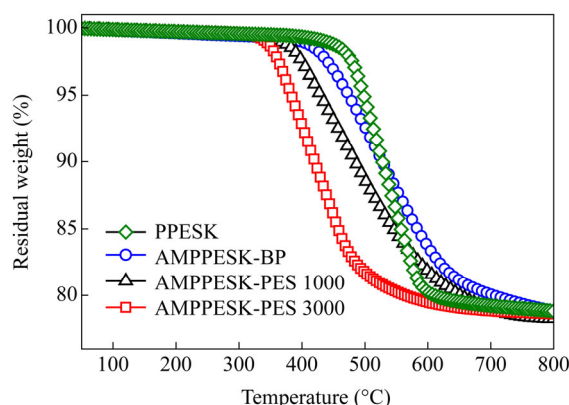


**Fig. 7** TGA curves of PPESK, AMPPESK-BP, AMPPESK-PES 1000 and AMPPESK-PES 3000

The solubility of the functional PPESKs, PES and cured polymers were also investigated, by dissolving  $0.04\text{ g}$  of the powered samples in  $1\text{ mL}$  of common organic solvent ( $0.04\text{ g/mL}$ ). The results were summarized in Table 2. PPESK, CMPESK and AMPPESK exhibited good solubility in polar organic solvents such as DMAc, DMSO, NMP and chloroform at room temperature, which may be owing to the incorporation of crank and twisted non-coplanar phthalazinone units into the polymer main chain. This incorporation contributed to disorders for the packing of the intermolecular chain and therefore made the synthesized polymers soluble. The propargyl end-groups of PES oligomers could hardly be dissolved in other common organic solvents like THF, toluene and acetone, even at elevated temperatures, due to the regular chains of PES oligomer. However, polymers *via* click cured reaction became insoluble in organic solvents, and were partially dissolved in concentrated sulfuric acid.

**Table 2.** Solubility of the functional PPESKs, PES and cured polymers at different solvents

| Sample        | Solubility at different solvents |     |      |      |     |                 |         |
|---------------|----------------------------------|-----|------|------|-----|-----------------|---------|
|               | Concentrated sulfuric acid       | NMP | DMAc | DMSO | THF | $\text{CHCl}_3$ | Toluene |
| PPESK         | ++                               | ++  | ±    | ++   | —   | ++              | —       |
| CMPESK        | ++                               | ++  | ++   | ++   | —   | ++              | —       |
| AMPPESK       | ++                               | ++  | ++   | ++   | —   | ++              | —       |
| PES 1000      | —                                | ++  | ++   | +    | —   | —               | —       |
| PES 3000      | —                                | ++  | ++   | +    | —   | —               | —       |
| Cured resin 1 | ±                                | —   | —    | —    | —   | —               | —       |
| Cured resin 2 | ±                                | —   | —    | —    | —   | —               | —       |
| Cured resin 3 | ±                                | —   | —    | —    | —   | —               | —       |

++: soluble at room temperature; +: soluble at heating; ±: partially soluble; —: insoluble

Determination of gel fraction in cured polymers was a direct method to evaluate the content of curing reaction. The gel fraction of the cured powder samples was tested by Soxhlet extraction. The gel fraction of the

cured AMPPESK-BP was 81%, they were only 75% and 71%, respectively, in AMPPESK-PES 1000 and AMPPESK-PES 3000. It is well accepted that the gel fraction 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.*). The differences of the gel fraction in these polymers may be due to the concentration difference of the terminal ethynyl groups in AMPPESK-cured agents. The concentration of terminal ethynyl groups in BP was much higher than the propargyl end-groups of PES oligomers. Thus, the gel fraction of cured AMPPESK-BP system was the highest among the investigated samples.

Crystallinity of cured polymers was investigated by WAXD on film samples at room temperature (Fig. 8). No sharp peak owing to crystalline nature was observed in WAXD patterns of cured AMPPESK-BP, demonstrating their amorphous nature. This was ascribed to the presence of the cranked, twisted non-coplanar of the phthalazinone moieties in the polymers. A diffraction peak appearing at  $2\theta = 20.86^\circ$  was observed in a typical active WAXD pattern of cured AMPPESK-PES 1000 and AMPPESK-PES 3000, suggesting the existence of crystallinity in these cured resins owing to short distance order in the PES main chains.

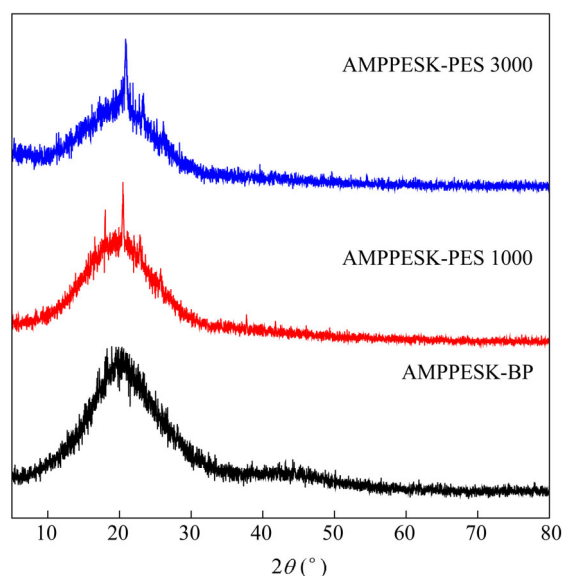


Fig. 8 WAXD patterns of cured polymers

SAXS spectra of the cured polymer membranes acquired at room temperature were shown in Fig. 9. It was seen that no ionic cluster peaks were observed for AMPPESK-BP and AMPPESK-PES 1000 membranes. There were two reasons for the absence of the ionic cluster peaks for the cured polymer membranes. One was that the twisted and unsymmetrical phthalazinone units disrupted the symmetry of polymer chains. Hence, no ionic clusters were formed. The other possibility was that the ionic clusters existed, but the electron density contrast between the clusters and PPESK polymer phase was too small to produce any pronounced SAXS peak. However, the figure of the AMPPESK-PES 3000 cured membranes showed a weak and broad peak with  $q$ -values of around  $2.7 \text{ nm}^{-1}$ . It could be attributed to the ionic clusters of PES 3000.

Morphologies of AMPPESK with various chain lengths of crosslinking agents were also studied by SEM (Fig. 10). Compared with the others, the surface of AMPPESK-BP membrane was very smooth. In Fig. 10(c), 'crack bifurcation' was obviously observed with increasing the molecular weight of the crosslinking agents, which suggested that the PES domain size increased with increased chain length of the crosslinking agents. Increasing the chain length of the cured agent caused the molecular weight of the crosslinkers to increase, so the amount of molecules in the same weight ratio of each sample decreased, and this resulted in lowering the crosslinking density. In addition, no phase separation was observed from Fig. 10, which implied that BP and PES were miscible with PPESK resin before curing.

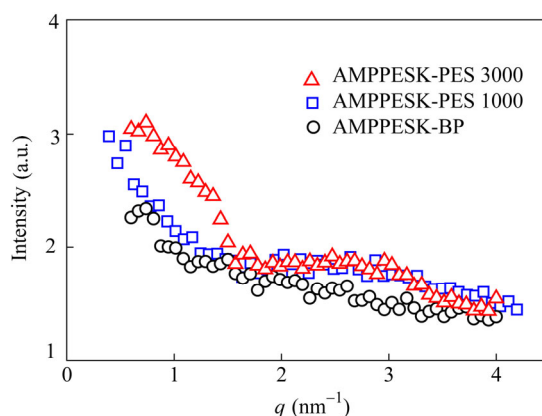


Fig. 9 SAXS data recorded on the cured polymer membranes

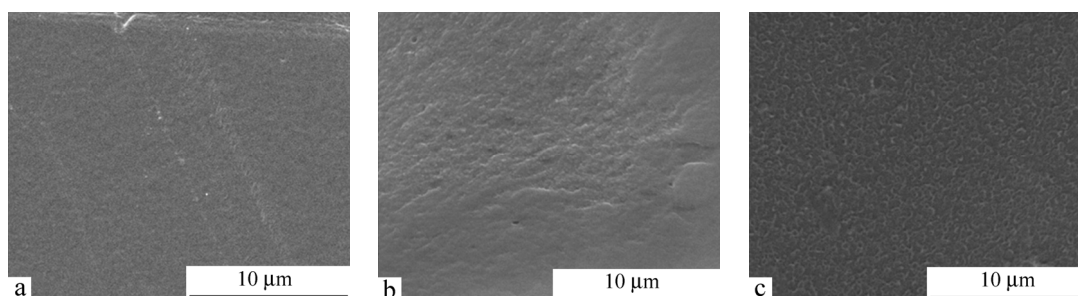


Fig. 10 Morphologies of AMPPESK with various chain lengths of crosslinking agents: (a) BP, (b) PES 1000 and (c) PES 3000

Mechanical properties of the polymers were measured on film samples, according to GB/T 1040-2006. Tough and nearly transparent films of the polymers were obtained. Mechanical properties of the AMPPESK and curing agents were determined at room temperature, the results were summarized in Table 3. The films had tensile strengths of 68–76 MPa, which indicated the good mechanical properties of the cured polymers. The elongation at break of these polymers was in the range of 11%–15%, and very close to each other. AMPPESK-BP had the highest tensile strength and modulus, whereas AMPPESK-PES 3000 has the lowest, which may be ascribed to the relatively lower crosslink density in the latter.

Table 3. Mechanical properties of the composites

| Sample           | Elongation at break (%) | Tensile strength <sup>a</sup> (MPa) | Tensile modulus (GPa) |
|------------------|-------------------------|-------------------------------------|-----------------------|
| AMPPESK-BP       | 12                      | 76                                  | 0.84                  |
| AMPPESK-PES 1000 | 15                      | 74                                  | 0.82                  |
| AMPPESK-PES 3000 | 11                      | 68                                  | 0.83                  |

<sup>a</sup> Measured on a film with dimension of 8 mm × 30 mm × 0.05 mm at room temperature

## CONCLUSIONS

Poly(phthalazinone ether sulfone ketone) with propargyl end-groups of PES oligomer system, curable at low temperature, was derived by anchoring clickable groups to the corresponding polymers. The anchored clickable groups enabled the polymer to undergo curing reaction through 1,3-dipolar cycloaddition reaction (Huisgen reaction) to form triazole network polymer. Azido groups were attached to poly(phthalazinone ether sulfone ketone) resin and propargyl groups were end-capped on the chains of PES oligomers. The presence of CuI was effective in promoting cure reaction and triazole formation of the oligomer films or powders. DSC and FTIR tests demonstrated certain crosslinking by the azide-alkyne reaction with the formation of triazole ring. Cured

polymers showed much higher thermal stability, including higher thermal decomposition temperatures and higher char-yielding properties. Thus, the resultant azido functional poly(phthalazinone ether sulfone ketone) 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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