

# Synthesis and properties of a series of cyanate resins based on phenolphthalein and its derivatives

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## ARTICLE INFO

### Article history:

Received 17 September 2008

Received in revised form

15 November 2008

Accepted 2 December 2008

Available online 9 December 2008

### Keywords:

Synthesis

Cyanate resin

Phenolphthalein

## ABSTRACT

Two new cyanate monomers simultaneously containing phthalide group and different alkyl substituents on the phenylene rings (o-PCY and t-PCY) and the Phenolphthalein-based cyanate (p-PCY) were successfully synthesized by the reaction of o-cresolphthalein, thymolphthalein and phenolphthalein with cyanogen bromide in the presence of triethylamine, respectively. Their chemical structures were confirmed by means of FTIR, NMR and elemental analysis methods. All these monomers owned sufficiently wide processing temperature windows and could be readily cured without the addition of catalyst. The dynamic mechanical analysis (DMA) results showed that the introduction of phthalide structure into the polycyanurate network could effectively improve the thermal properties of the cyanate ester (CE) resin. Especially, the  $T_g$  values of the fully cured p-PCY, o-PCY and t-PCY resins are 362 °C, 328 °C and 298 °C, respectively, which are apparently higher than that of most bisphenol-based cyanate resins reported in the literatures (190–290 °C). The thermal and thermo-oxidative properties as well as the water absorptions of the cured products were compared with those of the bisphenol A cyanate resin (BACY), and the structure–property relationships were explained according to the chemical structures and crosslinking densities of the formed polymer networks. The high- $T_g$  thermosetting materials thus prepared are expected to expand the usage of CEs to areas where higher temperature requirements are encountered.

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## 1. Introduction

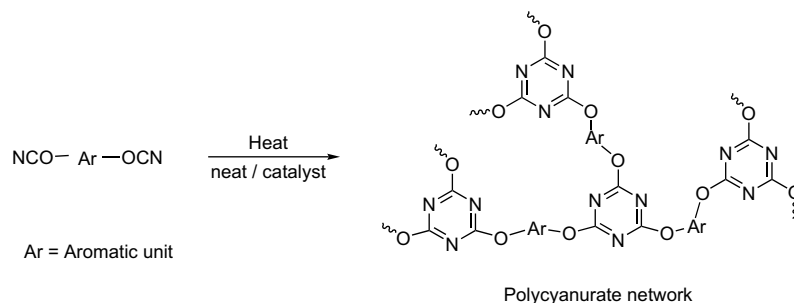
The development of polymer matrix resins possessing both high performance and easy processability has become the major driving force for the advanced lightweight composite materials. Cyanate ester resins (CEs) receive considerable attention due to their high heat-resistance, excellent dimensional stability, low moisture absorption and good compatibility with carbon fibre reinforcements. As shown in Scheme 1, cyanate ester monomers usually undergo thermal polycyclotrimerization to give polycyanurates, i.e., sym-triazine rings linked by aryl ether linkages, resulting in a uniformly cross-linked structure. The cured CE resins thus obtained have both the good processability of epoxy resins and thermal stability of bismaleimides (BMIs) as well as high fracture toughness than the epoxy and BMI counterparts [1–4]. The above features make them potentially strong competitors to polyimides in the aerospace industry [5–10].

Bisphenol A dicyanate (BACY) is a commercial CE monomer, and has been widely used in a variety of fields. However, the search to achieve further improvements in performance and reduction in cost is never ending. Over the past decade, many new cyanate monomers emerged, including phosphorus-containing dicyanates [11,12], silicon-containing dicyanates [13,14], aromatic ether and ketone-containing dicyanates [15,16], 2,7-dihydroxynaphthalene dicyanate [17], etc. However, most of them have the glass transition temperatures ( $T_g$ s) in the range from 190 to 290 °C, which are lower than BMIs (300–350 °C) [18–20].  $T_g$  is a key parameter for high-temperature thermosetting polymer materials. Many physical properties such as mechanical stiffness and creep resistance of the polymer composite materials rapidly deteriorate when the using temperature is over  $T_g$  [21]. For this reason, the materials based on CE resins usually have limited service temperatures around 135–250 °C. In order to achieve the higher service temperature (250–350 °C), the development of new CE resins with significantly enhanced  $T_g$  is becoming urgent to meet some application requirements.

Phenolphthalein is an inexpensive industry materials, and has been used as aromatic bisphenol monomer for preparing thermoplastics and thermosetting engineering resins, including

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**Scheme 1.** Diagram of triazine network formation of cyanate monomer.

polycarbonates [22–25], polyesters [26], poly(ether ketone)s and poly(ether sulfone)s [27–30], epoxy resins [31–33] and benzoxazine resins [34]. These polymers generally exhibit excellent mechanical strength, thermal stability and high glass transition temperature. In the early 1970s, Pankratov et al. disclosed the synthesis of a cyanate monomer via reaction of phenolphthalein with cyanogen chloride [35,36]. After cured, the cyanate resin exhibited high heat distortion temperature of 385 °C and initial thermal decomposition temperature of 405 °C. Since then, very few studies concerning cyanate ester resins containing phthalide structure have appeared in the literature.

Because of the existence of phthalide group, in addition to the excellent mechanical strength and thermal stability [37], the distorted stereo-configuration usually endows the phenolphthalein-based polymers with some special properties. For example, polyaryletherketone (PEK-C) and polyarylethersulfone (PES-C), which were derived from phenolphthalein with bis(4-fluorophenyl)ketone and bis(4-fluorophenyl)ketone, respectively, exhibit very good solubility in the common organic solvents. Moreover, the large free volume leads to PEK-C and PES-C high gas permeability coefficients compared to the other bisphenol-based polymers [27–29].

Keeping the above suggestions in mind, the present work was undertaken to incorporate different alkyl substituents onto the phenylene rings of phenolphthalein-based cyanate esters by respective reaction of *o*-cresolphthalein, thymolphthalein and phenolphthalein with cyanogen bromide in the presence of triethylamine. The introduction of bulky alkyl groups could further twist the molecular structure of phenolphthalein-based cyanate monomer, and the cured product thus obtained was expected to have significantly increased free volume. This paper was mainly focused on their synthesis and structural characterization as well as the dynamic mechanical analyses, thermal and thermo-oxidative properties and water absorption rate of the cured products. The studies on the characterization of high free volume and even the possible three-dimensional network microporous structure,

mechanical properties, such as fracture toughness and impact strength, strain–stress behavior and their relationship with chemical structures are still in progress, and will be published subsequently in the second paper.

## 2. Experimental section

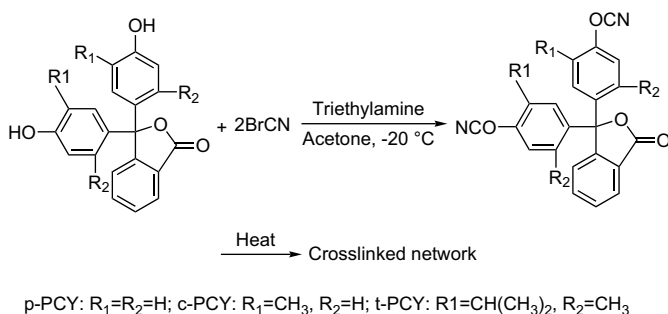
### 2.1. Materials

Cyanogen bromide was purchased from J&K-Chemical Co., Ltd. Phenolphthalein, *o*-cresolphthalein and thymolphthalein were purchased from Shanghai Chemical Reagent Co. and used without further purification. Bisphenol A dicyanate (BACY) was supplied by Shanghai Huifeng Technical & Business Co., Ltd. Acetone and triethylamine were purified by distillation under reduced pressure over calcium hydride. The other solvents were of reagent grade and were used as received.

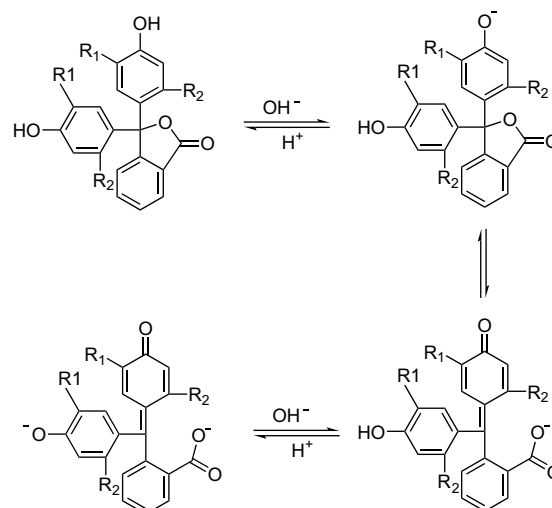
### 2.2. Measurements

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet-20DXB IR spectrophotometer. 64 scans were signal averaged with a resolution of 2 cm<sup>-1</sup> at room temperature. Samples were prepared by dispersing the complexes in KBr and compressing the mixtures to form disks.

<sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded on 400-MHz Varian INOVA NMR spectrometer, with the tetramethylsilane as an internal reference.



**Scheme 2.** General synthesis of dicyanate monomers and thermosets.



**Scheme 3.** Illustration of phenolphthalein acid–base equilibria.

**Table 1**

Elemental analysis results for phenolphthalein and its derivatives-based CE monomers.

Monomers	Molecular formula	Calculated values	Found values
p-PCY	C <sub>22</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub>	C: 71.74%, H: 3.28%, N: 7.61%	C: 72.01%, H: 3.29%, N: 7.58%
o-PCY	C <sub>24</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub>	C: 72.72%, H: 4.07%, N: 7.07%	C: 72.94%, H: 4.08%, N: 7.05%
t-PCY	C <sub>30</sub> H <sub>28</sub> N <sub>2</sub> O <sub>4</sub>	C: 74.98%, H: 5.87%, N: 5.86%	C: 75.17%, H: 5.87%, N: 5.81%

Elemental analyses were determined with an Elementar Vario EL III elemental analyzer.

TGA was performed on a NETZSCH TG 209 thermal analyzer both in purified nitrogen and air atmosphere, and all samples (around 10 mg) were heated from 25 to 700 °C at a rate of 10 °C/min, under the gas flow rates of 60 ml/min.

Differential scanning calorimetry (DSC) measurements were conducted with an NETZSCH DSC 204 instrument. The calorimeter was calibrated with indium metal as a standard. About 10–14 mg samples were used at a heating rate of 10 °C/min under a flow of nitrogen (20 ml/min).

Dynamic mechanical analysis (DMA) was performed with a PerkinElmer 7 series thermal analysis system at a frequency of 1 Hz and a heating rate of 5 °C/min under a nitrogen atmosphere. The samples were cut to dimensions of 16 mm × 3 mm × 1 mm prior to test. The tests were carried out in the three-point bending mode with the frequency 1 Hz. The strain amplitude was set at 10 μm and static force was always 10% more than the dynamic in order to ensure good contact between sample and probe.

The water absorption rates were measured as follows: the sample (1.5 × 1.5 × 1.0 cm<sup>3</sup>) was dried *in vacuo* at 120 °C until constant weight. Then the dried sample was immersed in a jar full of boiling deionized water for different times. After being wiped

with a dry cloth, it was weighed on a balance to obtain the percentage of absorbed water.

### 2.3. Syntheses of cyanate ester monomers

All the monomers were synthesized by reacting the corresponding bisphenols with BrCN in the presence of triethylamine at low temperature, using acetone as solvent. The resultant compounds were identified by FTIR, NMR, elemental analysis and melting measurement methods. The detailed synthesis of p-PCY is described here as an example below. Other cyanate compounds were prepared in the similar procedures.

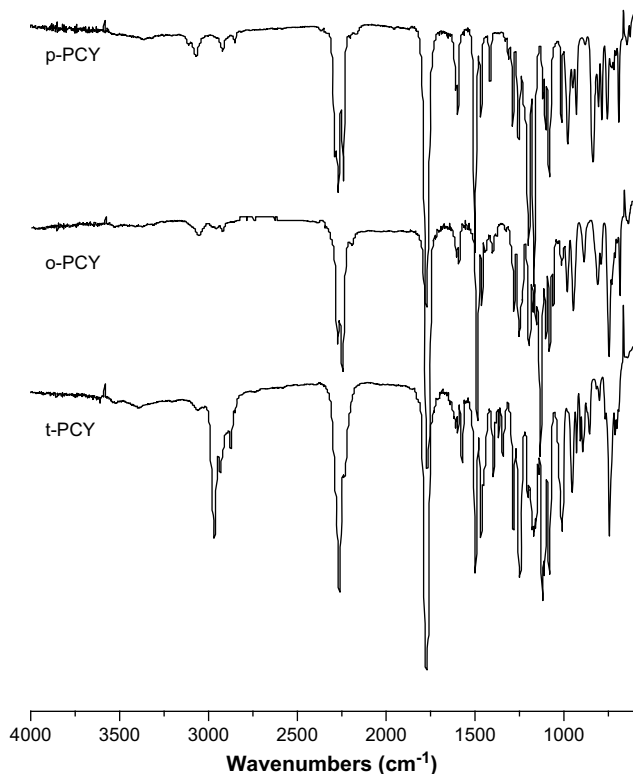


Fig. 1. FTIR spectra of phenolphthalein and its derivatives-based CE monomers.

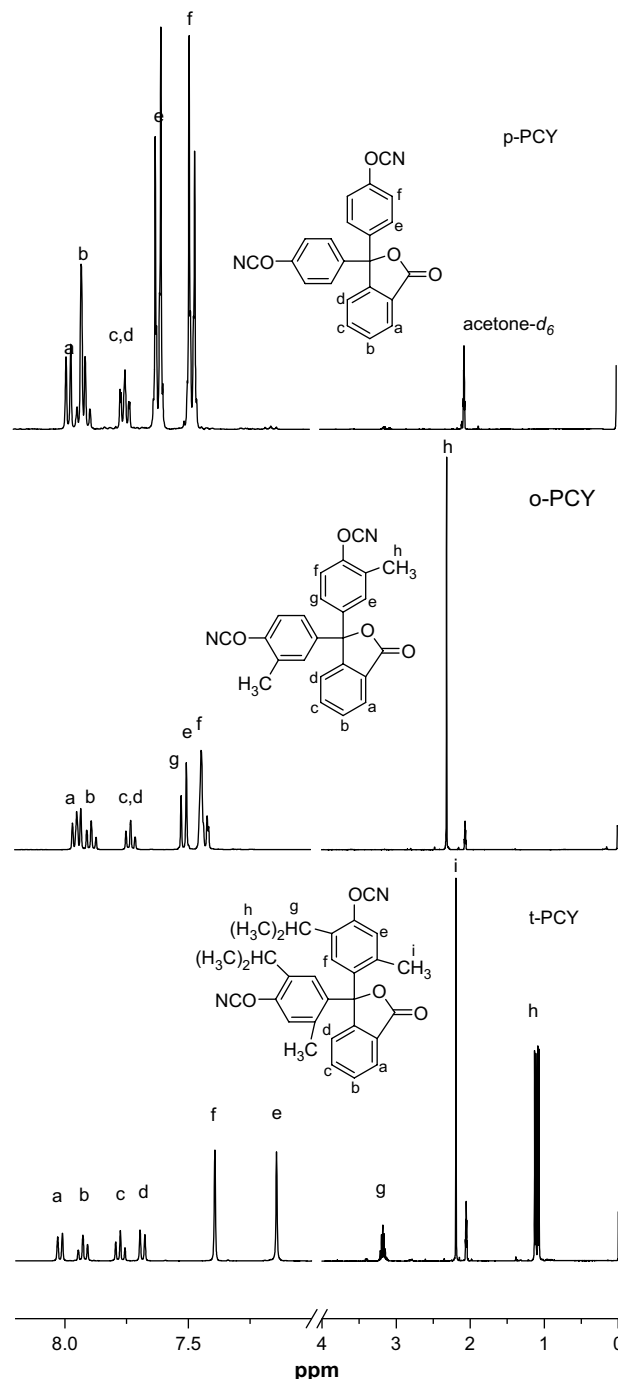


Fig. 2. <sup>1</sup>H NMR spectra of phenolphthalein and its derivatives-based CE monomers.

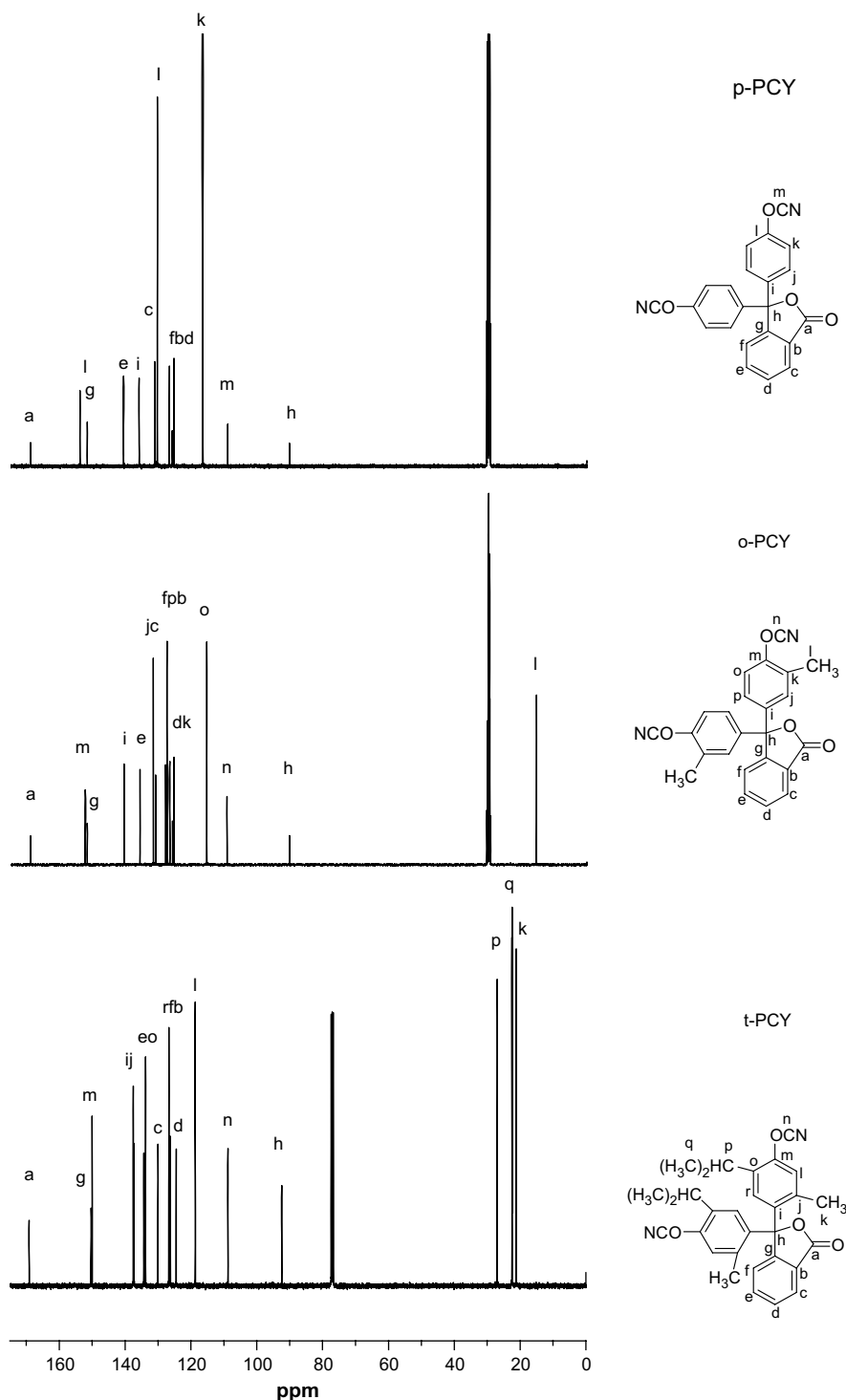


Fig. 3. <sup>13</sup>C NMR spectra of phenolphthalein and its derivatives-based CE monomers.

To a 200 ml three-necked flask was charged 40 ml of dried acetone, and the system was cooled to  $-10\text{ }^{\circ}\text{C}$ . Then BrCN (2.595 g, 24.5 mmol) and phenolphthalein (3.387 g, 10.6 mmol) were dissolved in acetone. Under the nitrogen atmosphere, to the above solution, triethylamine (2.186 g, 21.6 mmol) in acetone (20 ml) was added slowly over a period of 1 h. After addition was completed, the reaction temperature was increased to  $5\text{ }^{\circ}\text{C}$ , and the reaction was allowed to proceed at this temperature for another 2 h. Then, the mixture was filtered, and the filtrate was evaporated to dryness. The solid residue was dissolved in 50 ml of dichloromethane and

washed with deionized water three times ( $3 \times 50\text{ ml}$ ). The organic layer was dried over  $\text{MgSO}_4$ , filtered and concentrated by rotary evaporation under reduced pressure to about 20 ml. The solution was placed in a refrigerator overnight. An off-white crystalline solid was obtained. Yield: 81%.

#### 2.4. Preparations of the cyanurate networks

The PCY monomers were melted and degassed under reduced pressure to remove any volatiles or entrapped air, and were then

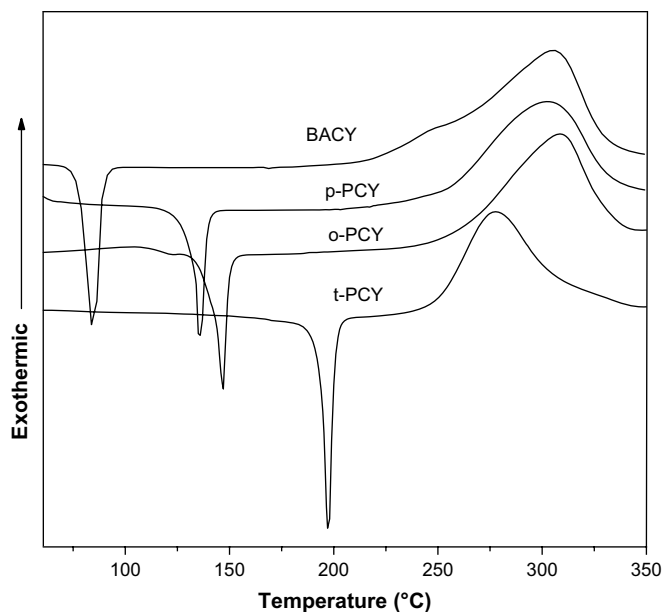


Fig. 4. DSC traces of p-PCY, o-PCY, t-PCY and BACY monomers.

poured directly into preheated (100°C) molds and thermally cured in an air convection oven. The cure schedule was set as: 200 °C/1 h, 250 °C/2 h and 280 °C/4 h. In order to conduct an effective property comparison, BACY was also cured under the completely same condition as above. All curing processes were carried out without the addition of catalyst. The cured resins were ejected from the molds, which were cut and polished according to the dimension requirements for the property measurements.

### 3. Results and discussion

The PCY cyanate monomers are synthesized according to the Grigat and Pütter methods by reacting the bisphenol compounds with cyanogen bromide in the presence of triethylamine (see Scheme 2) [38], where the bisphenols used here are phenolphthalein, and its derivatives o-cresolphthalein and thymolphthalein. The compounds containing phthalide ring are the well known acid–base indicator, and the coloured species of deprotonated phenolphthalein is the result of delocalization of the phenolate anion through the formation of the quinone structure and the ring-opened carboxylic acid anion (as shown in Scheme 3) [39]. Thus, in our study, the weak organic base (triethylamine) was slowly added to the system, and no acid–base colour change was observed, indicating that the phthalide structures of the monomers did not change in this reaction system. This result is identified by the elemental analyses (Table 1), narrow melting temperature range, FTIR and <sup>1</sup>H NMR spectra results.

**Table 2**  
DSC cure characteristics of p-PCY, o-PCY, t-PCY and BACY monomers.

Monomers	$M_p$ (°C)	$T_i^a$ (°C)	$T_p^b$ (°C)	$T_f^c$ (°C)	Processing windows (°C)	$\Delta H$ (J/g)
p-PCY	135.6	252.5	302.2	330.7	116.9	377.4
o-PCY	146.8	259.0	308.2	333.6	112.2	308.7
t-PCY	199.3	268.8	287.8	346.4	69.5	328.5
BACY	84.7	253.6	306.3	331.5	168.9	429.7

<sup>a</sup> The temperature corresponding to the onset of curing.

<sup>b</sup> The temperature corresponding to the maximum in the thermogram.

<sup>c</sup> The temperature corresponding to the end of the reaction.

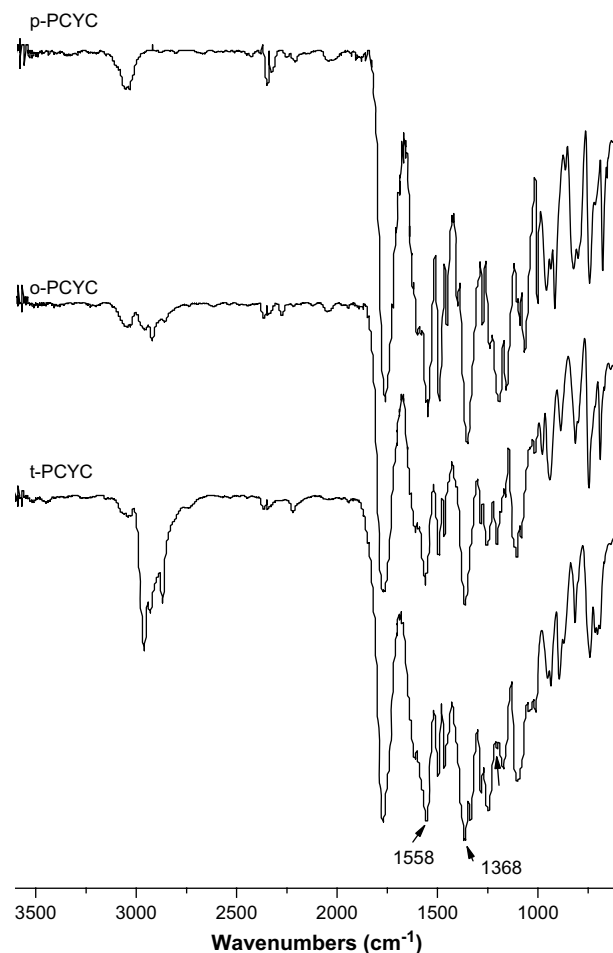


Fig. 5. FTIR spectra of cured resins.

The FTIR spectra of PCYs are shown in Fig. 1. The absence of the OH peak at around 3400 cm<sup>-1</sup> and the appearance of new peaks at around 2270 and 2240 cm<sup>-1</sup>, characteristic of the –OCN group, confirming the formation of the cyanate ester. The absorption band at 1773 cm<sup>-1</sup> is attributed to carbonyl of lactone group. Characteristic bands at 3060 cm<sup>-1</sup> and 1500 cm<sup>-1</sup> are corresponded to aromatic C–H stretching and aromatic C–C stretching, respectively.

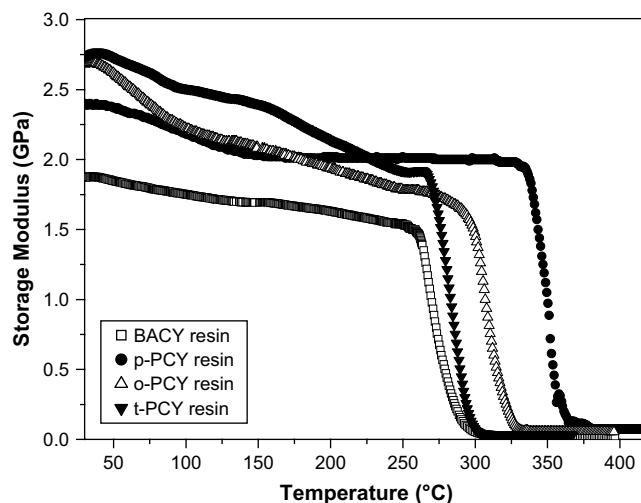


Fig. 6. Storage modulus for various cured resins.

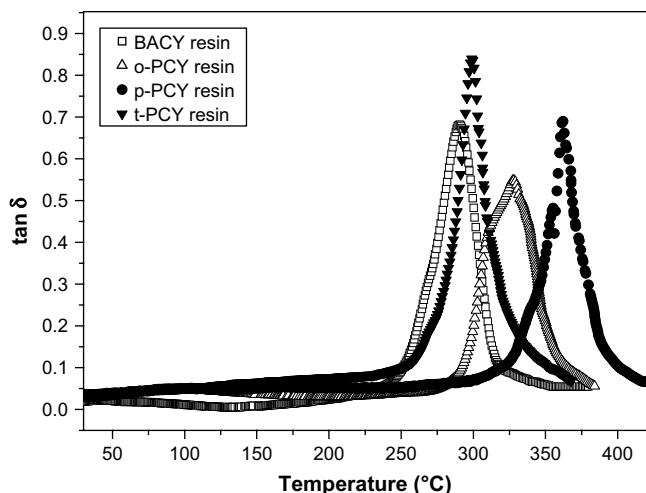


Fig. 7. Damping factors ( $\tan \delta$ ) for various cured resins.

The FTIR spectra of cyanate esters c-PCY and t-PCY show absorption bands at  $2960\text{ cm}^{-1}$  and  $2870\text{ cm}^{-1}$  due to the presence of methyl and isopropyl groups.

Fig. 2 illustrates the  $^1\text{H}$  NMR spectra of PCYs with the assignment of all the protons. The complete disappearance of the phenolic protons around 9.7 ppm and the downfield shifts of the aromatic protons ortho to the cyanate functional group indicate the conversion of the bisphenols to the cyanate ester monomers. Fig. 3 shows the  $^{13}\text{C}$  NMR spectra of PCYs. The characteristic signals of OCN group in cyanate ester are found at 108.7 ppm. The peak at 169.1 ppm corresponding to carbonyl group of lactone group further confirms that the phthalide structure was well maintained.

Cyanate ester monomers were polymerized by a cyclotrimerization reaction to create a uniformly cross-linked polytriazine network, and no secondary reactions took place [40,41]. It is known that pure cyanate ester monomer did not undergo polymerization even at high temperature. Therefore, the reaction is believed to be catalyzed by trace amount of residual hydrogen-donating impurities such as phenol or moisture, etc. The reactions can also be catalyzed by transition-metal complexes. In our case, in order to study the properties of the neat resins, no transition metals salts, which could later diminish many of thermal, adhesive, and electrical characteristics of the networks, were applied in the system.

Fig. 4 shows dynamic scanning thermograms (DSC) obtained from different PCY cyanate esters at a heating rate of  $10^\circ\text{C}/\text{min}$ . A sharp melting endotherm and a broad curing exotherm peak are observed in each curve. The results are presented in Table 2. As expected, the temperatures corresponding to the onset of curing exotherms ( $T_i$ ) are in the order of t-PCY ( $T_i = 268.8^\circ\text{C}$ ) > o-PCY ( $T_i = 259.0^\circ\text{C}$ ) > p-PCY ( $T_i = 252.5^\circ\text{C}$ ), indicating that the chemical reactivities of the cyanate ester monomers decreased caused by the

Table 3  
DMA measurement results of the cured resins.

Resins	$T_g$ ( $^\circ\text{C}$ )	Storage modulus (GPa)		$\rho$ ( $10^{-3}$ mol/cm $^3$ )	$\tan \delta^c$
		Glassy region <sup>a</sup>	Rubbery region <sup>b</sup>		
p-PCY	362	2.39	0.074	4.33	0.69
o-PCY	328	2.69	0.057	3.51	0.55
t-PCY	298	2.73	0.033	2.13	0.83
BACY	289	1.87	0.024	1.71	0.68

<sup>a</sup> Storage modulus at  $30^\circ\text{C}$ .

<sup>b</sup> Storage modulus at  $T_g + 50^\circ\text{C}$ .

<sup>c</sup> Maximum value of  $\tan \delta$ .

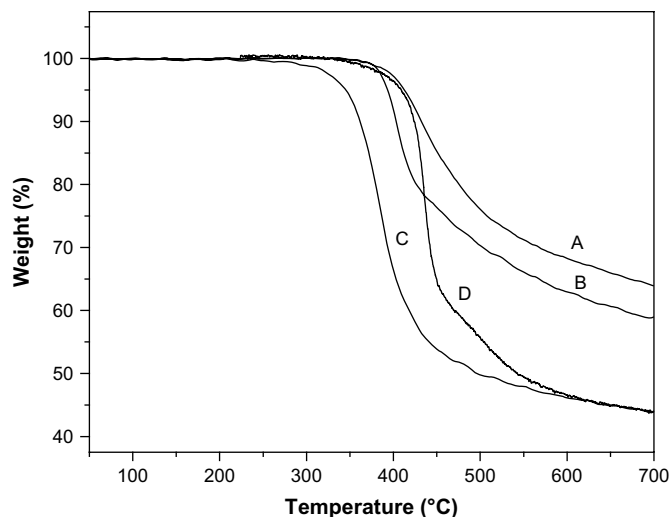


Fig. 8. Dynamic TGA behavior ( $10^\circ\text{C}/\text{min}$ ) for various cured resins in  $\text{N}_2$  (A) p-PCY resin; (B) o-PCY resin; (C) t-PCY resin; (D) BACY resin.

steric hindrance of the substituent group at the ortho-position of the aromatic ring to the  $-\text{OCN}$  group. Cyanate esters p-PCY and o-PCY display a large processing window (temperature range between a melting temperature and onset temperature of the polymerization exotherm) typically greater than  $110^\circ\text{C}$ . The relatively narrow processing window of t-PCY than o-PCY and p-PCY is due to its high melting point of  $199^\circ\text{C}$ . As shown in Fig. 5, the disappearance of the cyanate absorption at  $2270$  and  $2240\text{ cm}^{-1}$  of the cured products suggests that the conversions of cyanate groups to the triazine rings are almost complete. The characteristic absorption of triazine can be found at  $1586\text{ cm}^{-1}$  and  $1360\text{ cm}^{-1}$ .

Dynamic mechanical analysis (DMA) is a useful tool for determining the stiffness and mechanical damping of a cyclically deformed material as a function of temperature. Figs. 6 and 7 show the temperature dependences of the storage modulus ( $G'$ ) and loss tangent ( $\tan \delta$ ) for p-PCY, o-PCY, t-PCY and BACY resins. The sharp drop in  $G'$  curve and the peak of  $\tan \delta$  plot are indicative of the physical transitions in polymers. Although the transition

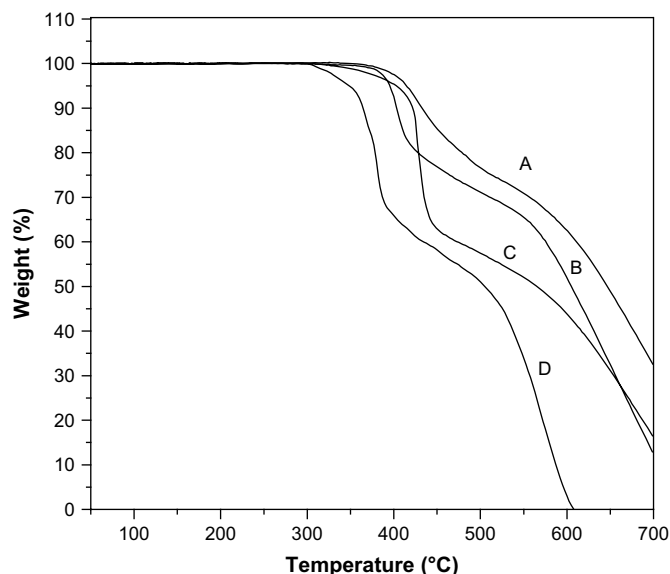


Fig. 9. Dynamic TGA behavior ( $10^\circ\text{C}/\text{min}$ ) for various cured resins in air. (A) p-PCY resin; (B) o-PCY resin; (C) t-PCY resin; (D) BACY resin.



**Table 4**  
TGA results of various cured resins.

Resins	Nitrogen atmosphere				Air atmosphere			
	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{20\%}$ (°C)	RW (%)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{20\%}$ (°C)	RW (%)
p-PCY	414.6	432.6	475.2	64.1	415.2	433.0	480.0	33.0
o-PCY	394.0	404.1	427.5	58.8	395.3	404.0	427.5	13.4
t-PCY	345.1	362.6	380.1	43.8	347.5	365.0	378.4	0
BACY	409.1	424.4	434.6	44.0	402.5	422.3	429.0	16.9

$T_{5\%}$ ,  $T_{10\%}$  and  $T_{20\%}$  refer to the temperature with weight loss of 5%, 10% and 20%, respectively; RW refers to the residual weight percentage at 700 °C.

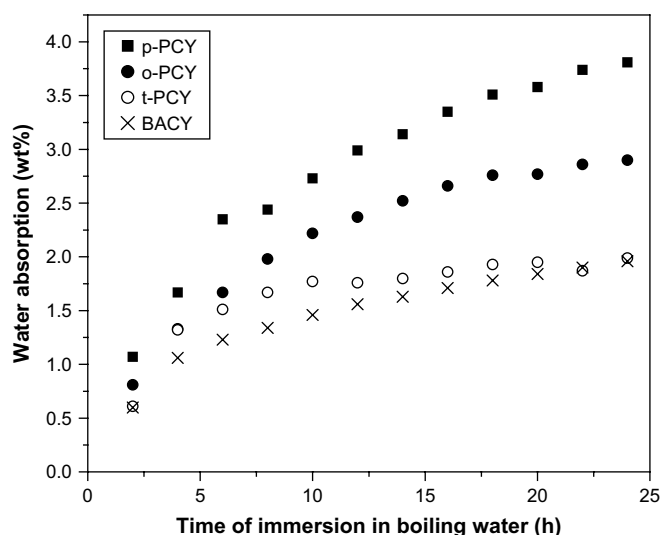
temperatures could be taken at the maximum rate of turndown of the storage modulus  $G'$ , the peak temperature of  $\tan \delta$  is assumed to be  $T_g$  in this article.

The crosslinking density of polymer network ( $\rho$ ) is determined according to the rubber elasticity theory as follows [42].

$$\rho = G' / 3RT$$

where  $G'$  is the storage modulus at  $T_g + 50$  °C,  $R$  is the gas constant,  $T$  is the absolute temperature at  $T_g + 50$  °C. The  $T_g$ s, storage modulus at both below and above  $T_g$ , and crosslinking density results are summarized in Table 3.

The  $G'$ - $T$  curve offers a valuable insight into the stiffness of the sample as a function of temperature, and the storage modulus  $G'$  is roughly equal to the elastic modulus for a single, rapid stress and reversible deformation [43]. Fig. 6 clearly shows that the initial modulus  $G'$  of polymers decrease in the order: t-PCY (2.73 GPa) > o-PCY (2.69 GPa) > p-PCY (2.39 GPa) > BACY (1.87 GPa). The values of the cured cyanate esters containing phthalide structure are higher than that of BACY, and the rigidity of the samples is observed to increase with the introduction of the alkyl substituent groups to the same aromatic ring of the -OCN functionality. This may be attributed to the restricted molecular mobility in main chain arising from the rigid phthalide skeleton and alkyl substituents. A very important point to note is that, the storage modulus of cured p-PCY resin almost keeps constant in a wide range of temperature between 142 and 330 °C, while the values of other samples decrease with the temperature. The results show that the p-PCY resin will own good thermo-mechanical stability in potential high-temperature application.



**Fig. 10.** The variation of water absorptions with time for cured products in boiling water.

In Fig. 7, all the polymer samples studied show a relaxation peak, which is analogous to the glass transition temperature. The values of  $T_g$  follow the order: p-PCY (362 °C) > o-PCY (328 °C) > t-PCY (298 °C), which are apparently higher than most bisphenol-based cyanate ester resins (190–290 °C). There are three possible major factors that affect the glass transition temperature of these cyanate esters. Firstly, the incorporation of bulky phthalide structure into the cross-linked network of cyanate ester leads to a decrease in segment motion, which serves to increase the  $T_g$ . Secondly, because of the presence of lactone group in the backbone of the networks, the dipole–dipole interaction between the polymer chains is also advantageous for the improvement of  $T_g$ . Thirdly, the steric hindrance of the substituent groups at the ortho-position of the aromatic ring of the -OCN group may decrease the overall cross-link density of the resin per unit volume, as demonstrated by the relative apparent cross-link densities listed in Table 3.

The thermal and oxidative stabilities of the cured cyanate ester resins are examined by TGA analyses (see Figs. 8 and 9). The thermal decomposition temperatures at different weight loss percentage and char yield at 700 °C are listed in Table 4. Cyanate ester resins are well known for their good thermal stability due to their aromatic ring and triazine ring. As expected, the phenolphthalein cyanate ester p-PCY has 5% decomposition temperature ( $T_{5\%}$ ) of 414 °C and char yield of 64% under nitrogen atmosphere, exhibiting higher thermal stability than the commercial BACY resin, which shows a  $T_{5\%}$  of 409 °C and an overall char yield of 44%. Of interest is the observation that the  $T_{5\%}$  of BACY resin in air is lower than that in  $N_2$ , whereas that of p-PCY in air is even higher than that in  $N_2$ , indicating that the thermal-oxidative stability of dicyanate ester resin has been enhanced due to the introduction of the phthalide structure into resin networks, which characteristic is of significance in the practical high-temperature application. On the other hand, the presence of the alkyl substituent groups on the same aromatic ring of the -OCN functionality obviously decreases the thermal stability of the phenolphthalein cyanate ester. For example, t-PCY resin containing isopropyl and methyl substituents exhibits  $T_{5\%}$  of 347 °C and an overall char yield of 43% under  $N_2$  atmosphere, probably due to its lowest crosslinking density in the polycyanurate network among the three resins. However, in spite of the relatively lower thermal stability of t-PCY resin, we are interested in its other physical properties, such as the low density, high free volume and even the possible microporous structure, as well as the hydrogen storage ability. The further investigations are being carried out in our laboratory.

Fig. 10 shows the water absorption curves of the cured cyanate ester resins in boiling water as a function of immersion time. It can be seen that the water absorption of p-PCY and o-PCY in boiling water is higher than that of the pure BACY, but the water absorption of t-PCY maintains at a low level. Moreover, after a rapid uptake, the continuing water absorption process of t-PCY is even slower than that of BACY. Because of the polar lactone groups in the network, the water absorption rates for phenolphthalein-based cyanate ester resin are higher than BACY. On the contrary, the introduction of non-polar alkyl substituent groups to the phenolphthalein-based cyanate ester resin is favourable to reduce the water absorption of cyanate ester resin.

#### 4. Conclusions

A series of cyanate ester monomers, having phthalide structure, were successfully prepared from phenolphthalein and its derivatives as bisphenols with cyanogens bromide. The thermal curings of these monomers give the corresponding network polymers by converting cyanate ester group to a cyanurate heterocycle linkage. Compared with the commercial BACY resin, the phenolphthalein-based

resins exhibit significantly improved storage modulus and glass transition temperatures. Among these, the p-PCY resin shows good thermo-mechanical stability in a wide range of temperatures (between 142 and 330 °C). More importantly,  $T_g$  value of the p-PCY resin is above 360 °C, which is remarkably higher than that of most bisphenol-based CE resin systems (190–290 °C). The p-PCY resin shows similar thermal stability but improved thermo-oxidative stability performance compared to BACY resin. The thermal stability of resins decreased with the introduction of alkyl substituent groups into the structures, but they still maintain  $T_{5\%}$  decomposition temperature above 340 °C. These novel phenolphthalein-based cyanate ester resins with enhanced thermal properties are expected to use for polymer-matrix systems with service temperature ranging between 250 and 300 °C, which are currently occupied by polyimides.

### Acknowledgements

The financial support from the National Natural Science Foundation of China (Nos. 50673014, 20874007), the Program for New Century Excellent Talents in University of China (Grant No. NCET-06-0280), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry (Grant No. 2005-546), and the Supporting Program for Optoelectronic Materials of Dalian University of Technology is gratefully acknowledged.

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