

# Preparation and Thermal Properties of Novel Phthalonitrile Oligomer Containing Biphenyl Ethernitrile/Bisphthalonitrile Blends

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**ABSTRACT:** A kind of novel  $n = 2$  phthalonitrile oligomer containing biphenyl ethernitrile (2PEN-BPh) had been firstly synthesized from 2,6-dichlorobenzonitrile, 4,4'-biphenol and 4-nitrophthalonitrile via solution reaction, and the 2PEN-BPh was characterized by FTIR,  $^1\text{H-NMR}$  spectra which exhibited that cyano groups and ethernitrile linkages existed in the backbone of 2PEN-BPh. The 2PEN-BPh oligomer was blended with bisphthalonitrile monomer, the curing reaction behaviors of the blends were studied by FTIR, DSC, and rheological analysis. The thermal and thermo-oxidative stabilities of the 2PEN-BPh/BPh

polymers were investigated by TGA, and the results showed that the completely cured polymers could achieve char yields up to 78% at 800°C in nitrogen, above 11% at 800°C in air. The whole research indicated that the 2PEN-BPh/BPh blends could efficiently improve the processability of BPh monomer without sacrificing other desirable high temperature properties. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 882–887, 2011

**Key words:** phthalonitrile oligomer; biphenyl ethernitrile; bisphthalonitrile; blends; thermal properties

## INTRODUCTION

In the past 30 years, considerable research had been expended on an attractive class of high-temperature resistant polymers based on phthalonitrile for their rigidity, outstanding thermal and thermo-oxidative stability, excellent mechanical properties, superior moisture resistance, and fire resistance.<sup>1–9</sup> Phthalonitrile resins were thermosetting polymers that were derived from phthalonitrile monomers. Initially, the polymerization of the neat phthalonitrile monomers was extremely sluggish and this procedure needed several days to obtain stable polymers.<sup>4,10,11</sup> Later some researchers found that the curing reaction could be promoted through the use of small amounts of curing additive, such as phenols,<sup>12</sup> organic amines,<sup>1</sup> strong organic acids,<sup>13</sup> strong organic acid/amine salts,<sup>14</sup> metals and their salts.<sup>15</sup> The fully cured phthalonitrile resins had a variety of applications in marine, aerospace, and microelectronic industries.<sup>16</sup> Bisphthalonitrile (BPh) was the first phthalonitrile-based high-temperature resin reported<sup>9,17</sup> and had been the most extensively studied phthalonitrile monomer.<sup>18</sup> Although bisphthalonitrile resins possessed many advantages, other disadvantages such as great rigidity,<sup>8</sup> low viscos-

ity,<sup>8,19</sup> and a small processing window ( $\sim 20\text{--}30^\circ\text{C}$ )<sup>8</sup> had kept these resins from being fully utilized for broad applications; meanwhile, these disadvantages also caused high cost and processing difficulties.<sup>8,19,20</sup>

In our laboratory, the previous investigations had demonstrated that incorporating flexible linkages into phthalonitrile terminals could enhance processability without sacrificing high temperature resistance,<sup>21</sup> thermal stability, and mechanical properties<sup>4</sup>; reactive side-groups incorporated could accelerate the curing rate as well.<sup>8,21</sup> Based on this idea, a kind of novel  $n = 2$  phthalonitrile oligomer containing biphenyl ethernitrile (2PEN-BPh) was firstly synthesized in this article; 2PEN-BPh had the flexibility which was introduced by the meta-catenated aromatic ether spacer.<sup>8</sup> The aromatic ether linkages possessed the linear backbone and the extra cyano functional groups in 2PEN-BPh could efficiently improve cross-link rate and high temperature resistance.<sup>21</sup> The novel 2PEN-BPh oligomer was blended with BPh monomer in the process of aromatic diamine as curing additive to achieve enhancing processability without sacrificing other desirable high temperature properties.

## EXPERIMENTAL

### Materials

Toluene, *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidinone (NMP), dimethyl sulfoxide (DMSO),

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and anhydrous potassium carbonate were obtained from Tianjin BODI chemicals. 4,4'-Biphenol and 2,6-dichlorobenzonitrile were purchased from Beijing Yangcun Co. and Yangzhou Tianchen chemicals Co. of Jiangsu, respectively. 4-Nitrophthalonitrile (99 %) was obtained from Alpha chemicals (Dezhou) Co. 2,6-Bis(4-diaminobenzoyl)benzonitrile (BDB) as curing additive was synthesized from 2,6-dichlorobenzonitrile and 4-aminophenol according to the Ref. 22. 4,4'-Bis(3,4-dicyanophenoxy) biphenyl (BPh) was prepared according to the references with minor modification.<sup>17,18</sup> All the materials were reagent-grade and were used without further purification.

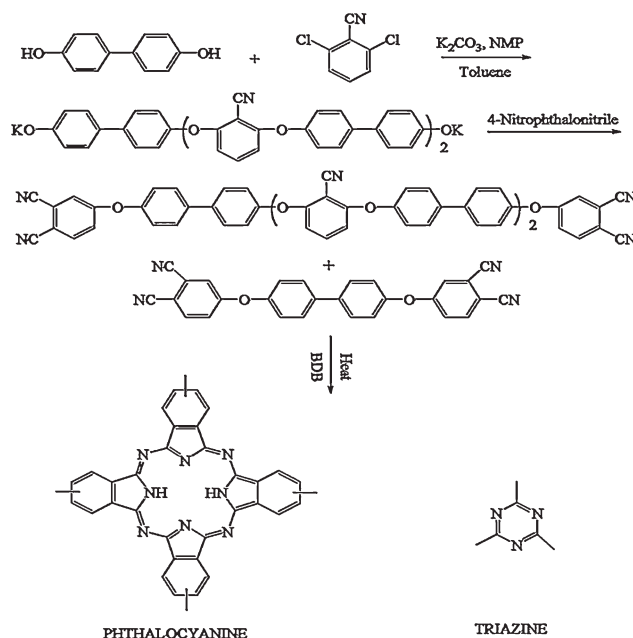
### Measurements

The FTIR spectra were recorded on NICOLET MX-1E Fourier Transform Infrared spectrometer in KBr pellets between 4000 and 400  $\text{cm}^{-1}$  in air.  $^1\text{H-NMR}$  spectra were obtained using a Bruker AV400 nuclear magnetic resonance (NMR) spectrometer at a proton frequency of 400 MHz and using  $\text{DMSO-d}_6$  as solvent. The thermal curing behaviors of the oligomer were measured by TA Instruments Modulated DSC-Q100 with a heating rate of 20°C/min and a nitrogen flow rate of 50 mL/min. The thermal decompositions of the polymers were determined by TA Instruments Q50 thermogravimetric analyzer with a heating rate of 20°C/min in nitrogen or air. The rheological behaviors of curing process were performed by TA Instruments Rheometer AR-G2 at low strain values (0.5%) and with a frequency of 1 Hz at different temperatures in air.

### Synthesis

#### Synthesis of the $n = 2$ phthalonitrile oligomer

The  $n = 2$  phthalonitrile oligomer containing biphenyl etheritrile (2PEN-BPh) was firstly synthesized via the reaction of 4,4'-biphenol, 2,6-dichlorobenzonitrile, and 4-nitrophthalonitrile. The typical procedure of the synthesis of 2PEN-BPh was as follows<sup>19</sup>: A 500 mL three-necked round-bottom flask equipped with a mechanical stirrer and refluxing, 4,4'-biphenol and 2,6-dichlorobenzonitrile with a molar ratio of 2 : 1<sup>19</sup> were taken and then anhydrous potassium carbonate, toluene, and NMP were added. The reaction mixture was refluxed at 160°C for 3h.<sup>23</sup> Then toluene was removed by distillation, and the system was cooled to room temperature. After cooling, 4-nitrophthalonitrile was added into the system, and the system was heated to 80–90°C and maintained for another 5 h.<sup>10</sup> Then the product was collected by filtration to remove anhydrous potassium carbonate; the filtrate was poured into 0.1 mol/L HCl solution with deionized water. The



**Figure 1** The preparation of 2PEN-BPh oligomer and 2PEN-BPh/BPh polymers.

resulting precipitate was collected by filtration and washed with deionized water until the filtrate was neutral and dried at 80°C under vacuum. The crude product was further purified by recrystallization. The purified product 2PEN-BPh was obtained as shown in Figure 1. The typical FTIR characteristic data: 2230  $\text{cm}^{-1}$  (stretch,  $-\text{CN}$ ), 1246, 1208  $\text{cm}^{-1}$  (stretch,  $\text{Ar}-\text{O}-\text{Ar}$ ), 832, 782, 729  $\text{cm}^{-1}$  (bend, benzene);  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 8.13 ppm, 7.87–7.88 ppm, 7.82–7.84 ppm, 7.60–7.64 ppm, 7.44–7.47 ppm, 7.20–7.36 ppm, 6.65–6.80 ppm. All the resonances were assigned to the H of benzene.

#### Preparation of phthalonitrile blends, prepolymers, and polymers

Phthalonitrile blends were prepared by mixing predetermined concentration of 2PEN-BPh and BPh in powered form under ambient conditions. The compositions of the physical mixtures were 75 : 25, 50 : 50, and 25 : 75 in which the numbers represented the weight percentages of 2PEN-BPh oligomer and BPh monomer, respectively. 2PEN-BPh/BPh prepolymers and prepolymer of the 2PEN-BPh were prepared in air by adding 5 mol % BDB curing additive to each melt at 250–260°C,<sup>19</sup> stirring vigorously for about 15 min, the reaction between the diamine and the phthalonitrile end groups was quenched by rapidly cooling the melt to room temperature.<sup>19</sup> The prepolymers were pulverized for use in viscosity studies.

**TABLE I**  
The Curing Schedule of the Prepolymers and Polymers

Sample	Time and temperature
b	250°C and 4 h; 280°C and 4 h
c	250°C and 4 h; 280°C and 4 h; 300°C and 4 h; 325°C and 4 h
d	250°C and 4 h; 280°C and 4 h; 300°C and 4 h; 325°C and 4 h; 350°C and 4 h; 375°C and 8 h

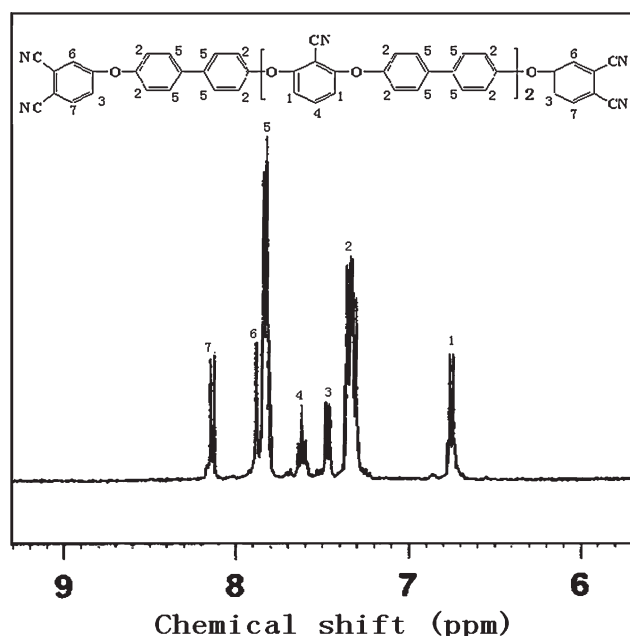
The 2PEN-BPh/BPh polymers were prepared by heating the phthalonitrile blends with 5 mol % BDB curing additive in air-circulation oven in sequence at elevated temperatures. The detailed polymerization procedures<sup>10</sup> of the prepolymers and polymers were described in Table I.

## RESULTS AND DISCUSSION

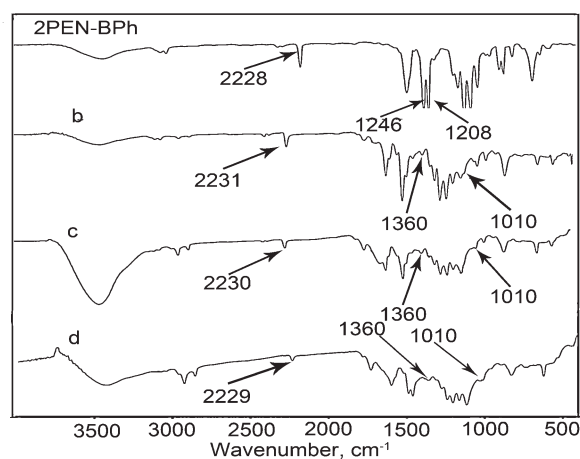
### NMR and FTIR spectra

The structure of the 2PEN-BPh oligomer shown in Figure 1 was verified by <sup>1</sup>H-NMR spectra (Fig. 2). In <sup>1</sup>H-NMR, the prominent resonances at 6.65–8.13 ppm in the aromatic frequency correspond to the hydrogen in the benzene ring. The ratio of the integral area of resonance at 7.44–7.47 ppm and resonances at 7.60–7.64 ppm should be 1. The calculated ratio was 1.1, and it was approach to the theoretical value.<sup>21</sup> Thus, it indicated that the target compound 2PEN-BPh was obtained.

The FTIR spectra provided more insight into the structure characterization. Figure 3 showed the FTIR spectra of 2PEN-BPh oligomer, 50 : 50 2PEN-BPh/



**Figure 2** <sup>1</sup>H-NMR spectra of 2PEN-BPh oligomer in DMSO-d<sub>6</sub>.



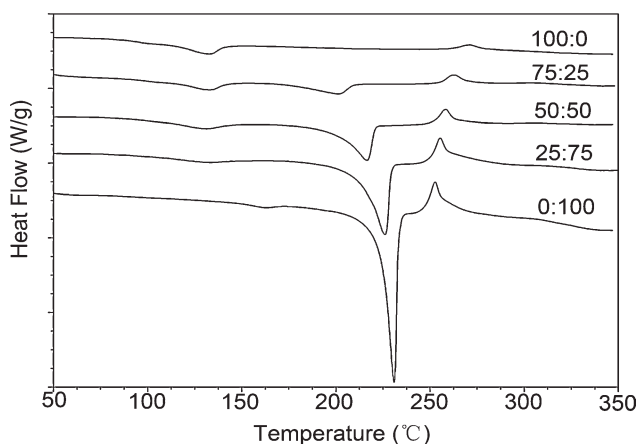
**Figure 3** FTIR spectra of 2PEN-BPh, (b and c) 50 : 50 2PEN-BPh/BPh prepolymers, (d) 50 : 50 2PEN-BPh/BPh polymer.

BPh prepolymers and polymer obtained by the polymerization procedure described in the previous section. Cyano absorption peak was at around 2231  $\text{cm}^{-1}$  and the absorption peak at 1246  $\text{cm}^{-1}$  was contributed to the aromatic ether group, the peaks at 832, 782, and 729  $\text{cm}^{-1}$  were assigned to benzene rings. The peak at 2230  $\text{cm}^{-1}$  shuttled down obviously which indicated the reaction between the 2PEN-BPh oligomer and BPh monomer. On the other hand, new absorption peaks at 1010 and 1360  $\text{cm}^{-1}$  were observed which indicated the formation of phthalocyanine ring<sup>24</sup> and triazine ring<sup>24</sup> during the polymerization of the cyano groups. The NH stretching and bending vibrations were observed at about 1010  $\text{cm}^{-1}$  in phthalocyanine ring.<sup>25</sup> There were also bands at 1360  $\text{cm}^{-1}$  indicating the stretching vibration of triazine ring.<sup>24</sup> The peaks at 2230, 1010, and 1360  $\text{cm}^{-1}$  all changed with the curing temperature. The characterization of these thermally activated reactions showed the polymerization had occurred and the new characteristic peaks changed along with the temperature, suggesting the increase of the polymerization extent of the polymers. Based on these results, the curing polymerization of 2PEN-BPh/BPh followed thermally activated addition polymerization mechanisms via the phthalocyanine ring and triazine ring-formation of cyano groups, as shown in Figure 1.

### Curing behaviors of 2PEN-BPh/BPh blends

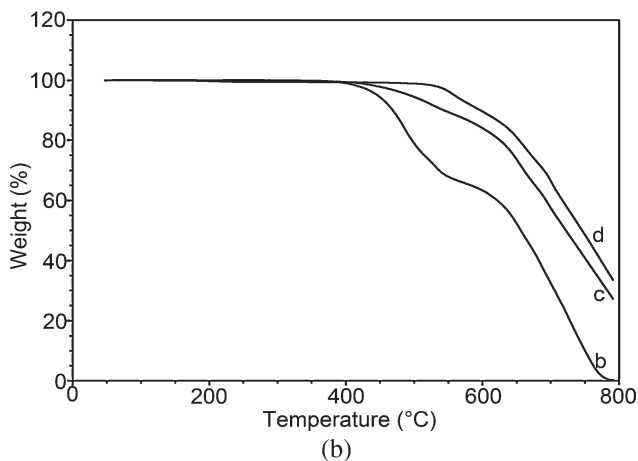
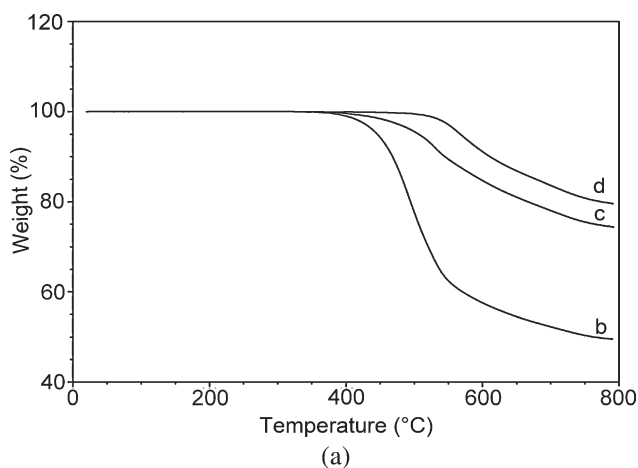
The curing behaviors of 2PEN-BPh/BPh blends were studied by DSC, TGA, and dynamic rheology, as shown in Figures 4–9.

DSC curves generated by heating the blends with 5 mol % BDB as curing additive were plotted in Figure 4. Pure BPh monomer and 2PEN-BPh oligomer with BDB each exhibited a characteristic melting

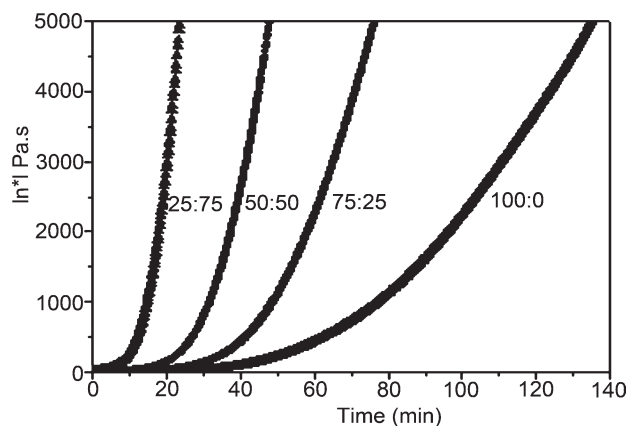


**Figure 4** DSC curves of the BPh monomer (0 : 100), the 2PEN-BPh oligomer (100 : 0), and the 2PEN-BPh/BPh blends with 5 mol % BDB.

transition and a polymerization exotherm.<sup>8</sup> The peaks of their melting transitions ( $T_{\text{melt}}$ ) occurred at 231°C, 133°C, and the polymerization exotherm ( $T_{\text{top}}$ ) appeared at 253°C, 271°C, respectively. For



**Figure 5** TGA curves of the 50 : 50 2PEN-BPh/BPh prepolymers and polymer with 5 mol % BDB in (a) nitrogen and (b) air.



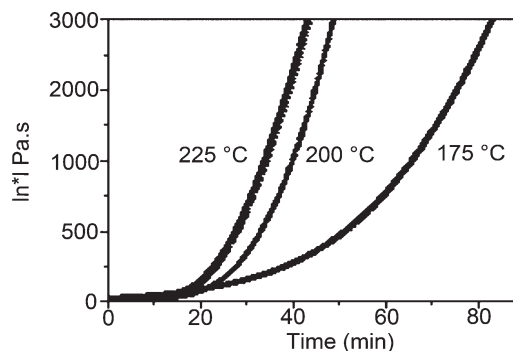
**Figure 6** Time sweep viscosity curves of 2PEN-BPh/BPh prepolymers with different weight ratio of 2PEN-BPh at 200°C.

comparison, curves generated from blends of BPh monomer and 2PEN-BPh oligomer with BDB were included in the Figure 4.<sup>8</sup> The endothermic ( $T_{\text{melt}}$ ) and exothermic ( $T_{\text{top}}$ ) transitions of the blends were centered at 201–225°C and 255–263°C, respectively.

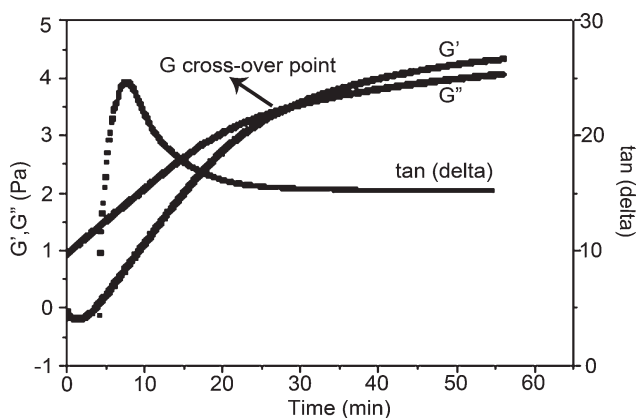
The DSC results showed that 2PEN-BPh possessed a large processing window ( $T_{\text{window}} \sim 139^\circ\text{C}$ ) and could cross-link at high temperature, so the processing window was much wider than BPh, as presented in Table II.

The DSC data of the 2PEN-BPh/BPh blends in Figure 4 showed that with the weight percentages of 2PEN-BPh in the blends increased, the temperature of the polymerization exotherm of 2PEN-BPh/BPh blends moved to higher temperatures from 253°C to 271°C, while the exothermic heat flows ( $H_{\text{curing}}$ ) decreased from 31.43 J/g to 5.89 J/g. These results indicated that when the weight percentage of 2PEN-BPh increased, the concentration of cyano groups in curing system decreased, so the density of crosslink units decreased, the polymerization reaction became more and more difficult.

TGA curves of the 50 : 50 2PEN-BPh/BPh prepolymers and polymer were shown in Figure 5(a,b),

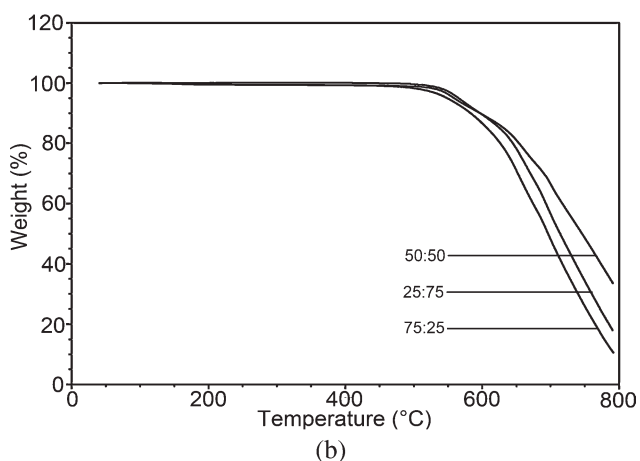
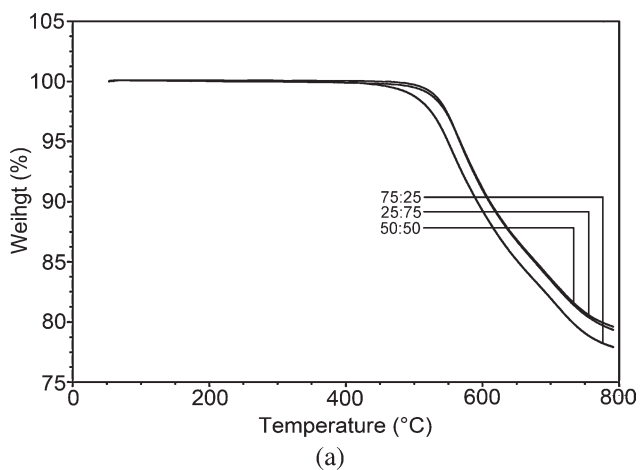


**Figure 7** Time sweep viscosity curves of 50 : 50 2PEN-BPh/BPh prepolymer at different temperatures.



**Figure 8** Time sweep curves of 50 : 50 2PEN-BPh/BPh prepolymer at 225°C.

and the letters b, c, and d refer to the curing schedules listed in Table I. The thermal and thermo-oxidative stabilities of the prepolymers and polymer increased with the curing temperature and time. This indicated that the extent of the curing reaction and cross-linking density increased with the curing temperature and time.



**Figure 9** TGA curves of 2PEN-BPh/BPh polymers with 5 mol % BDB in (a) nitrogen and (b) air.

**TABLE II**  
The Thermal Properties of BPh Monomer, 2PEN-BPh Oligomer, and 2PEN-BPh/BPh Blends

Sample	$T_{\text{melt}}$ (°C)	$T_{\text{top}}$ (°C)	$\Delta H_{\text{curing}}$ (J/g)	$T_{\text{window}}$ (°C)
100 : 0	133	271	5.89	139
75 : 25	201	263	8.34	62
50 : 50	216	258	13.83	43
25 : 75	225	255	30.12	31
0 : 100	231	253	31.43	22

The rheological behavior of a material was a key factor in determining its processability. Therefore, the variation of the melt viscosity of the blends was determined to study the effect of curing temperature and the concentration of 2PEN-BPh on the rheological behaviors of the 2PEN-BPh/BPh prepolymers under curing process of thermally activated polymerization, as presented in Figures 6–8.

Figures 6 and 7 showed that the viscosity of 2PEN-BPh oligomer and 2PEN-BPh/BPh prepolymers was low before the curing reaction occurred and then increased quickly after the curing reaction started.<sup>18</sup> As Figure 6 showed, all the blends exhibited sharp increase in viscosity when heated at 200°C. The influence of 2PEN-BPh content on the viscosity was evident. As the 2PEN-BPh content of the blends increased, the viscosity of the blends increased slower. This result was expected since the blends richer in 2PEN-BPh had the tendency to react or cure at a slower rate.<sup>18</sup> The rheological behaviors of the blends indicated that there was processing temperature advantage for these materials over that of the neat BPh. Figure 7 showed that the viscosity of 2PEN-BPh/BPh blends processed faster with the increase of curing temperature, which indicated that higher curing temperature could accelerate the crosslink reaction of 2PEN-BPh/BPh.

From the above results, the rate of the polymerization could be easily controlled by varying 2PEN-BPh concentration or the curing temperature.

From Figure 8, we could find that the storage modulus ( $G'$ ) increased quickly from 3 min to 40 min, it was observed that 50 : 50 2PEN-BPh/BPh prepolymer had been transferred from viscosity flow state to solid state and at the same time the loss modulus ( $G''$ ) also increased. Based on the principle of rheological theory, the gelation time (determined from the  $G'$  and  $G''$  crossover point)<sup>18</sup> was observed at 30 min. The delta curve exhibited one sharp peak at 7 min, which meant that 50 : 50 2PEN-BPh/BPh blend could polymerized with aromatic diamine under certain curing temperature. The rheological results of the prepolymer revealed that 2PEN-BPh/BPh blend possessed good processability.

TABLE III  
Thermal and Thermo-Oxidative Stabilities of 2PEN-BPh/BPh Polymers

Samples	N <sub>2</sub>			Air		
	T <sub>i</sub> (°C)	T <sub>5%</sub> (°C)	Char yield (%)	T <sub>i</sub> (°C)	T <sub>5%</sub> (°C)	Char yield (%)
75 : 25	493	549	78	459	5498	11
50 : 50	522	567	80	493	559	34
25 : 75	527	566	79	526	565	18

### Thermal properties of 2PEN-BPh/BPh resins

The thermal and thermo-oxidative stabilities of completely cured polymers were determined by TGA analysis. The results of these studies were presented in Figure 9(a,b), and the main results of these studies were summarized in Table III, in which the initial degradation temperature ( $T_i$ ), the temperatures at weight loss 5% ( $T_{5\%}$ ), and the char yields for the polymers heated to 800°C were displayed.

From Figure 9(a,b) and Table III, it was observed that the 50 : 50 2PEN-BPh/BPh polymer possessed the best thermal and thermo-oxidative stabilities. This was due to the 2PEN-BPh contained flexible linkages in its structure, while the rigidity of BPh was too great to form complete crosslinking structure. When 2PEN-BPh was blended with BPh at a ratio of 50 : 50, the system had the greatest extent of the polymerization reaction, crosslinking density tended to be higher, and the thermal stability of the 50 : 50 2PEN-BPh/BPh polymer tended to be better.

All of the 2PEN-BPh/BPh polymers exhibited thermal stability above 550°C, the initial decomposing temperatures ( $T_i$ ) were above 490°C, and the char yields at 800°C were above 78% in nitrogen. Also the polymers had good thermo-oxidative stabilities with the initial decomposing temperatures ( $T_i$ ) above 460°C and the char yield at 800°C above 11% in air.

### CONCLUSIONS

Phthalonitrile oligomer containing biphenyl ethernitrile (2PEN-BPh) had been firstly synthesized from 2,6-dichlorobenzonitrile, 4,4'-biphenol, and 4-nitrophthalonitrile via solution reaction. The 2PEN-BPh oligomer was blended with bisphthalonitrile monomer, and the curing reaction behaviors and the thermal properties of the blends were fully studied. The whole research indicated that the 2PEN-BPh/BPh

blends could efficiently improve the processability of BPh monomer without scarifying other desirable high temperature properties.

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