DE GRUYTER Sci Eng Compos Mater 2016; 23(6): 579–588

Zhiran Chen, Yajie Lei, Hailong Tang and Xiaobo Liu*

Effect of polyarylene ether nitrile on the curing behaviors and properties of bisphthalonitrile

DOI 10.1515/secm-2013-0235
Received September 24, 2013; accepted July 22, 2014; previously published online October 14, 2016

Abstract: The 2,2-bis[4-(3,4)-dicyanophenoxy phenyl]-propane (BAPh)/polyarylene ether nitrile (PEN-OH) prepolymers and polymers were prepared by heat polymerization. Firstly, BAPh/PEN-OH systems were characterized using differential scanning calorimetry, dynamic rheological analysis, and thermal gravimetric analysis. The results revealed that the polymerization reaction can be controlled by various concentrations of PEN-OH and postcuring temperatures, and BAPh/PEN-OH prepolymers had low curing temperatures (229.3–300.4°C), large processing windows (~106.5°C) with low melt viscosities, and excellent thermal stabilities. Then, the polymerization reaction and surface structures of BAPh/PEN-OH systems were investigated using Fourier transform infrared and scanning electron microscopy, respectively. The interpenetrating polymer networks were found in BAPh/PEN-OH polymers, suggesting that the addition of PEN-OH can not only promote the curing behaviors of BAPh but also increase the toughness of the polymers. The flexure strength and modulus of BAPh/PEN-OH polymers increased with the introduction of PEN-OH. The dielectric properties of BAPh/PEN-OH polymers were investigated, which had little dependence on the frequency. BAPh/PEN-OH systems can be used as a good candidate for high-performance polymeric materials.

Keywords: bisphthalonitrile; mechanical properties; polyarylene ether nitrile; polymerization; thermal properties.

1 Introduction

Thermosets, such as epoxy and phthalonitriles, are known for their dimensional stability and stiffness [1–3]. In the past 30 years, a series of high-performance phthalonitrile polymers have been reported by Keller's group [4–6]. As a kind of thermosetting resin, phthalonitriles have been widely used for marine [7], aerospace [8], and microelectronic [9] industries. The heterocyclic ring structures and high level of aromatic characters make phthalonitrile polymers exhibit high-temperature-resistant properties. More importantly, the phthalonitrile thermosetting polymers derived from phthalonitrile monomers exhibit many attractive properties, such as high glass temperatures (T_gs), excellent mechanical properties, outstanding thermal stabilities, and good moisture resistance, which make it receive increasing attention from industries and academia [10–13]. However, the brittleness, poor impact resistance, and big internal stress have limited their wide applications [14]. Previous investigations demonstrated that there are mainly two ways to decrease the brittleness and improve the processabilities of phthalonitriles: the chemical method is to incorporate the flexible linkages into phthalonitrile terminals. The chemical structure of the cross-linked polymer network can be changed, and the formation of plastic deformation into nonuniform structure can lead to the toughening of phthalonitriles [15]. The physical method is to mix the toughener with thermosets directly. Compared with the former method, the latter is more easily to be carried out and cost-effective [16]. Therefore, the physical method is going to be used in the following experiment.

A toughener, such as a rubber elastomer, has been added into the thermosets to conquer the weakness of phthalonitriles, but it can decrease the modulus and thermal stabilities at the same time [16]. It is severely important to choose the right toughener. Engineering thermoplastics have been widely used in high-performance fields for their high thermal stability, outstanding mechanical strength, excellent chemical, and fire resistance. Polyarylene ether nitrile (PEN), a kind of engineering thermoplastic, exhibits outstanding electrical isolation and excellent toughness [17–20]. The existence

---

***Corresponding author: Xiaobo Liu,** Research Branch of Functional Materials, Institute of Microelectronic and Solid State Electronic, University of Electronic Science and Technology of China, Chengdu 610054, P.R. China, e-mail: liuxb@uestc.edu.cn
Zhiran Chen, Yajie Lei and Hailong Tang: Research Branch of Functional Materials, Institute of Microelectronic and Solid State Electronic, University of Electronic Science and Technology of China, Chengdu 610054, P.R. China

of -CN makes PEN to have the potential power of being cross-linkable. Compared with other engineering thermoplastics such as PEEK, PEN possesses good processing performance. The thermoset-thermoplastic interpenetrating polymer network (IPN) materials exhibit synergistic properties. In addition, the other properties of IPN materials are more outstanding than the single component [21]. IPN, as a new kind of blend modification technology, exhibits characteristic properties, such as synergistic effect, interface interpenetrating, and forced mutual capacitance. Thus, its chemical blends and interpenetrating network have attracted much attention and considerable research [22–24].

In this article, to modify the intrinsic brittleness of bisphthalonitriles, IPN was tested as an effective method. Therefore, a kind of PEN end-capped with hydroxyl groups (PEN-OH) was used as a toughener. A series of novel 2,2-bis[4-(3,4)-dicyanophenoxy phenyl]propane (BAPh)/PEN-OH prepolymers and polymers were prepared without sacrificing other desirable high-performance properties of bisphthalonitriles. The curing behaviors and thermal properties were evaluated using differential scanning calorimetry (DSC), dynamic rheological analysis (DRA), and thermal gravimetric analysis (TGA). Fourier transform infrared (FTIR) was used to investigate the polymerization reaction of BAPh/PEN-OH systems, and the fracture surfaces of BAPh/PEN-OH polymers were investigated using scanning electron microscopy (SEM). In addition, the mechanical and dielectric properties of the BAPh/BPA polymers were investigated in this paper.

2 Materials and methods

2.1 Materials

4,4′-Diaminodiphenyl sulfone (DDS) and *N*-methyl-2-pyrrolidone (NMP) were obtained from Tianjin BODI Chemicals (Tianjin, China). BAPh (T_m=194–200°C) and PEN-OH were synthesized in our lab [25, 26]. All materials were used without further purification. The chemical structures of BAPh, PEN-OH, and heterocyclic rings are shown in Figure 1.

2.2 Synthesis of PEN-OH

Biphenyl (30.5 g, 0.1696 mol), 1,4-benzenediol (4.4 g, 0.0400 mol), 2,6-dichlorobenzonitrile (34.4 g, 0.2000 mol), 25 ml methylbenzene, and 75 ml NMP were added into a 250 ml three-neck flask. K_2CO_3 (33 g) was added in several portions during the course of the reaction. The mixtures were heated at 190°C–200°C for 4 h. After cooling to room temperature, the viscous product mixture was poured into 500 ml of dilute HCl solution to remove K_2CO_3 and boiled in water four times. Then, the white product was dissolved in NMP and heated at 190°C–200°C for 30 min, and the viscous liquid was slowly poured into deionized water, boiled several times, and vacuum dried. PEN-OH can be obtained according to the above procedure.

2.3 Preparation of BAPh/PEN-OH prepolymers and polymers

BAPh/PEN-OH prepolymers were obtained by heat polymerization. BAPh monomer and PEN-OH were melted at 200°C in the electric thermostat oil bath. When both BAPh monomer and PEN-OH were melted, 2% DDS (the weight DDS is 2% by weight of BAPh) was added to the mixture to get a homogeneous BAPh/PEN-OH liquid after stirring for 20 min. The blackish green liquid was rapidly cooled to room temperature for use in FTIR, DSC, and DRA studies. The weight ratios of PEN-OH contents were 0%, 5%, 10%, and 15%. In addition, BAPh/PEN-OH prepolymers were heated for another 10 min until dark green liquid appeared and then poured into a preheated polytetrafluoroethylene mold; the cavity dimensions were 65×15×5 mm. The samples were cured in the oven by the procedure as follows: 200°C for 4 h, 240°C for 4 h, 280°C for 4 h, and 300°C for 4 h. BAPh/PEN-OH polymers were removed from the molds and cooled gradually to room temperature.

2.4 Characterizations

The FTIR spectra of BAPh/BPA mixtures and polymers were recorded on NICOLET MX-1E FTIR spectrometer (MA, USA) in KBr pellets between 4000 and 400 cm^{-1} in air. DSC analysis was investigated using TA Instruments Modulated DSC-Q100 (DE, USA) with a heating rate of 10°C/min and a nitrogen flow rate of 50 ml/min. DRA was investigated using TA Instruments Rheometer AR-G2 (DE, USA) with 25 mm diameter parallel plates at a frequency of 1.0 Hz. TGA was investigated using TA Instruments TGA Q50 (DE, USA) with a heating rate of 20°C/min under nitrogen or air with a purge of 40 ml/min. The mechanical properties of the composite laminates were investigated using a SANS CMT 6104 Series Desktop Electromechanical Universal Testing

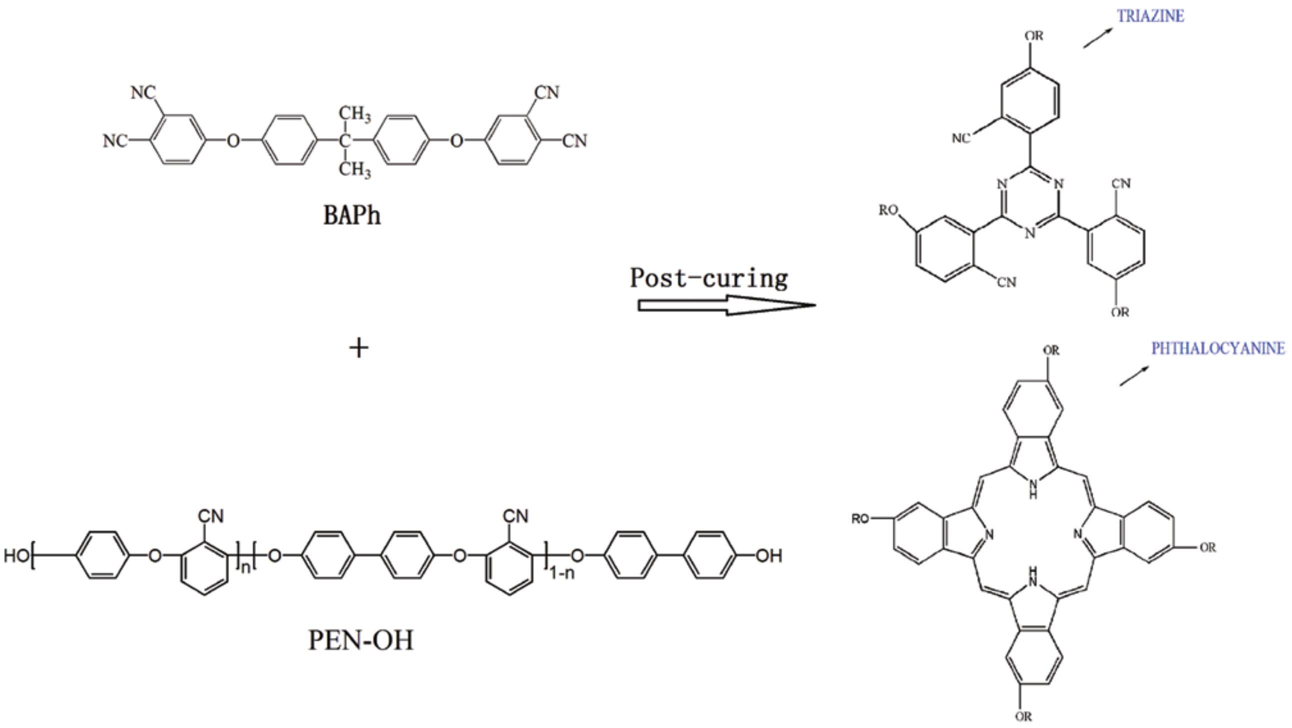

Figure 1: Chemical structures of BAPh, PEN-OH, and heterocyclic rings.

Machine (Guangdong, China). The composite laminates were cut into strips of about 80 mm in length and 15 mm in width, and three strips were needed to gain an average value. The dielectric properties were tested using a TH 2819A Precision LCRmeter (Tong hui Electronic Co., Ltd., Shanghai, China). The microstructures of the composite laminates were investigated using SEM (JEOL TSM-5900LV, Japan).

3 Results and discussion

3.1 FTIR characterization of PEN-OH and 10% BAPh/PEN-OH systems

Typical IR characteristic data: 2231 cm^{-1} (-CN), 3290, 1010 cm^{-1} (phthalocyanine ring), 1360, 1520 cm^{-1} (triazine ring), 1630 to 1670 cm^{-1} (C=N band in isoindole ring), and 3300–3500 cm^{-1} (phenolic hydroxyl group).

The FTIR spectrum of PEN-OH is shown in Figure 2A, with the characteristic stretching band at 2231 cm^{-1} (-CN) and 3440 cm^{-1} (-OH), which offer support for the structure of PEN-OH containing the functional group of -CN and -OH. The FTIR spectra of 10% BAPh/PEN-OH prepolymers and polymers are shown in Figure 2B. The characteristic peaks of phthalocyanine ring at 1010 cm^{-1} [27], stretching vibration in triazine ring at 1360 cm^{-1} [28], and C=N bond in isoindole ring at 1660 cm^{-1} [29] were clearly found in BAPh/PEN-OH prepolymers, suggesting that the polymerization between -CN groups in BAPh and -OH group in PEN-OH had happened. Their high level of heterocyclic ring structure can make BAPh/PEN-OH polymers exhibit high-temperature-resistant properties, and the detailed reaction mechanism between -CN and -OH has been given in our previous study [30]. With increasing postcuring temperature, the characteristic peaks of isoindole ring disappeared and the stretching vibration of triazine ring at 1520 cm^{-1} appeared on the FTIR spectrogram, because the isoindole ring can completely react with -CN to form phthalocyanine ring and triazine ring. Based on these results, PEN-OH can be used as a kind of thermoplastic to effectively react with BAPh. However, the hydroxyl group at 3300–3500 cm^{-1} can still be found in the BAPh/PEN-OH polymer, which means that only a part of PEN-OH had reacted with BAPh. Because PEN-OH had large molecular and long main chains, some -OH may be embedded in the main chains of PEN-OH and there will be a decrease of active H atoms. The unreacted PEN-OH and BAPh can make up the thermoset-thermoplastic IPN materials and exhibit synergistic properties. Thus, further investigations about the curing behaviors, mechanical properties, thermal stabilities, and inner structures of BAPh/PEN-OH systems were carried out.

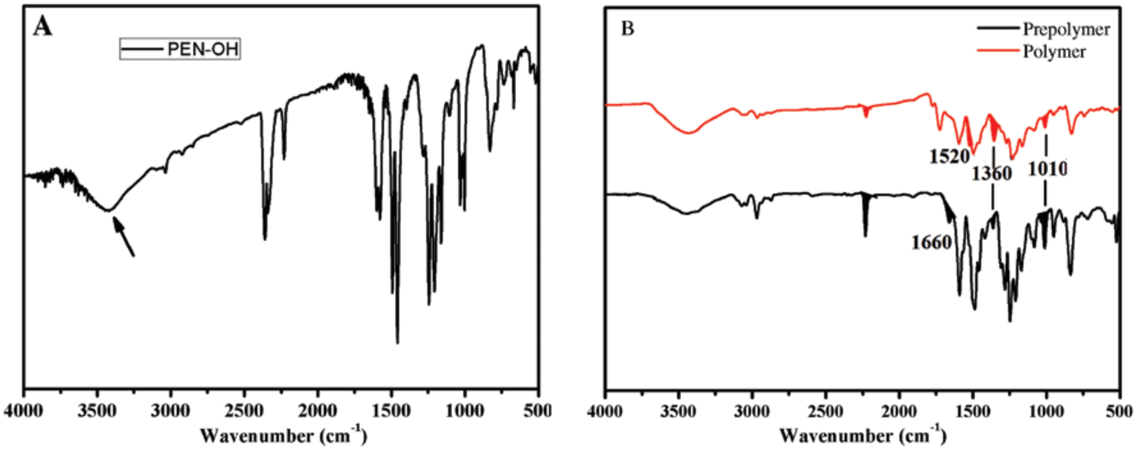

Figure 2: FTIR curves of PEN-OH (A) and 10% BAPh/PEN-OH (B) systems.

3.2 Curing behaviors of BAPh/PEN-OH prepolymers

Figure 3 shows the DSC curves of BAPh/PEN-OH prepolymers with various PEN-OH contents. Two melt peaks (at 171.9°C and 194.7°C) and no characteristic curing peak can be seen on the curve of BAPh/PEN-OH prepolymer with 0% PEN-OH; the two melt peaks were attributed to the melting temperature of DDS and BAPh, respectively. However, with the introduction of PEN-OH, 5%, 10%, and 15% BAPh/PEN-OH prepolymers each exhibited a single melt peak at 193.9°C, 192.1°C, and 190.1°C, respectively. The one endothermic peak suggested that BAPh/PEN-OH systems exhibited no phase separation. With the contents of PEN-OH increased from 5% to 15%, the peak temperature of the exothermic peak ranged from 300.4°C to 229.3°C and the corresponding exothermic heat flow (ΔH_{curing}) ranged from 1.3 to 24.7 J/g, the thermal properties of these polymers were summarized in Table 1 as well. The decreased exothermic peak and ΔH_{curing} referred to the occurrence of polymerization reaction between the -OH group in PEN-OH and the -CN group in BAPh and the easy formation of heterocyclic rings in Figure 2 [31]. PEN-OH can efficiently improve the cross-link rate for BAPh/PEN-OH systems [32]. In addition, the endothermic and exothermic peaks both shifted to lower temperatures with the content of PEN-OH increased to 10%. This is because, with more content of PEN-OH, the polymerization rate of BAPh became faster and the polymerization reaction was more complete. However, when the PEN-OH contents increased from 10% to 15%, the curing temperature shifted to higher temperature. The main reason might be that 15% BAPh/PEN-OH prepolymers contained more PEN-OH and a part of -OH functional group was wounded inside the PEN-OH main chain, so the content of effective -OH decreased. Therefore, too much contents of PEN-OH will decrease the polymerization reaction of BAPh. To better understand the curing reaction between BAPh and PEN-OH, the rheological measurements on BAPh/PEN-OH prepolymers was conducted.

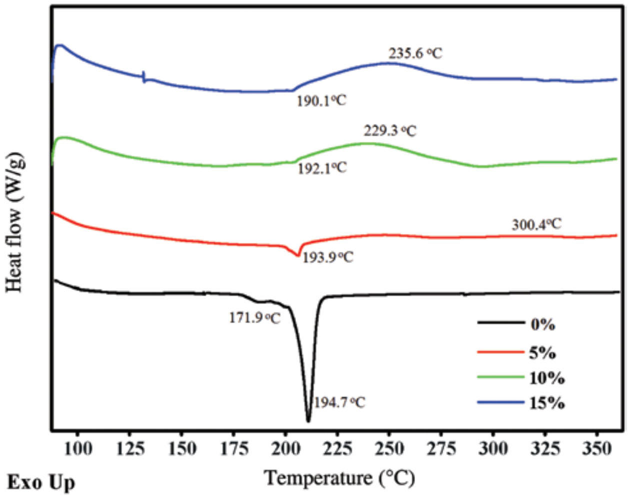

Figure 3: DSC curves of BAPh/PEN-OH prepolymers with various PEN-OH contents.

Table 1: Thermal properties of BAPh/PEN-OH prepolymers with various PEN-OH contents.

ω (PEN-OH) wt (%)	$T_{melt\,1}$ (°C)	$T_{melt\,2}$ (°C)	T_{top} (°C)	ΔH_{curing} (J/g)
0	171.9	194.7	–	–
5	–	193.9	300.4	1.3
10	–	192.1	229.3	21.9
15	–	190.1	235.6	24.7

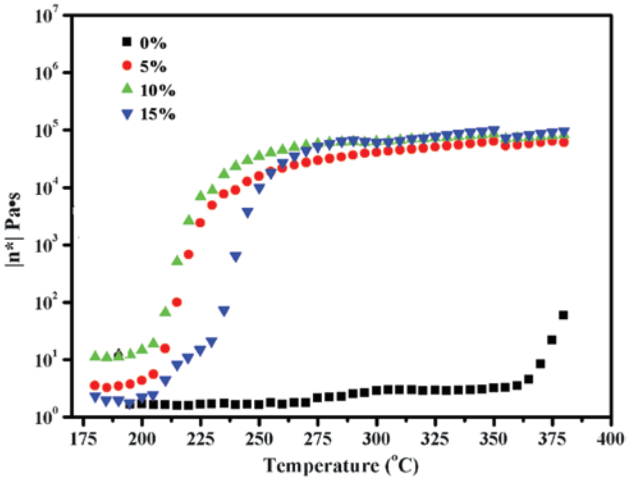

Figure 4: Temperature vs. viscosity curves of BAPh/PEN-OH prepolymers with various PEN-OH contents.

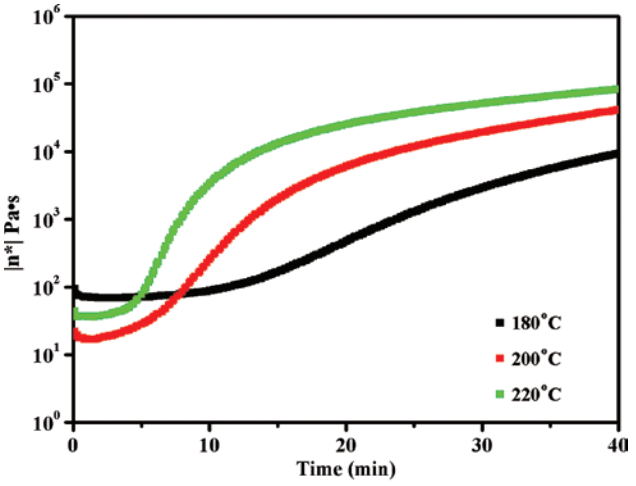

Figure 5: Time vs. viscosity curves with 10% BAPh/PEN-OH prepolymers at various temperatures.

To determine the processability of a material, the rheological behavior is an important factor. Figure 4 shows the temperature vs. viscosity curves of BAPh/PEN-OH prepolymers with various PEN-OH contents. When the temperature increased from 175°C to 225°C, the initial melt viscosity slightly increased and was between 1 and 10 Pa s. The 0%, 5%, 10%, and 15% BAPh/PEN-OH prepolymers displayed an abrupt complex viscosity increase at 360°C, 215°C, 213°C, and 237°C, respectively. Compared with 0% BAPh/PEN-OH prepolymers, the temperatures of abruptly increased complex viscosities for other BAPh/PEN-OH prepolymers were much lower, suggesting that PEN-OH can effectively speed up the curing reaction of BAPh [21]. The findings were consistent with the above curing temperature of the DSC results. More importantly, the relatively lower complex viscosity of BAPh/PEN-OH prepolymers at moderate temperatures can be a promise for good processability. In Figure 4, the polymerization rate of BAPh/PEN-OH prepolymers can be controlled by various contents of PEN-OH. To select the premium content of PEN-OH is seriously important for material processing. Among the four kinds of BAPh/PEN-OH prepolymers, the viscosity of 10% BAPh/PEN-OH prepolymers exhibited the fastest rate at the lowest curing temperature, which was therefore selected as the premium content to investigate the influence of various temperatures on complex viscosities.

It is necessary to control the polymerization rate for the fabrication of the composites, and before gelation occurs, the melt needs to be impregnated completely. Figure 5 shows the time vs. viscosity curves with 10% PEN-OH content of BAPh/PEN-OH prepolymers at various temperatures. The 10% BAPh/PEN-OH prepolymers investigated at 180°C, 200°C, and 220°C exhibited an abrupt increase in viscosity at 15, 10, and 5 min, respectively. The higher the postcuring temperature is, the more active are the molecular chains of BAPh/PEN-OH, the faster is the polymerization reaction of BAPh/PEN-OH processes, and the viscosity increases, but lesser time is needed. The time for an abrupt viscosity increase at 220°C was too short for a full reaction to be completed, suggesting that the polymerization reaction was carried out too fast. An increase at 180°C was too long to be cost-effective, suggesting that the polymerization reaction was carried out rather slowly. The time vs. viscosity curves of 10% BAPh/PEN-OH prepolymer at 200°C had the lowest initial complex viscosity at relatively high temperature, which promises good wetting

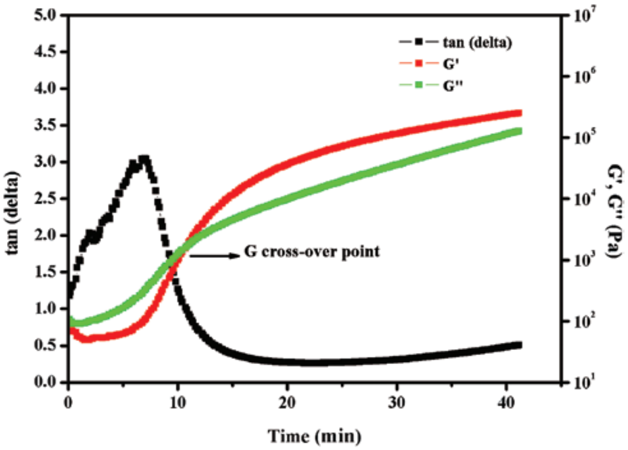

Figure 6: Time vs. viscosity curves with 10% BAPh/PEN-OH prepolymers at 200°C.

of fibers and proves to be useful for processability [33]. Therefore, 200°C was the proper initial postcuring temperature for BAPh/PEN-OH prepolymers. Higher curing temperature can make the rate of complex viscosity increase faster, which means that the polymerization reaction of BAPh/PEN-OH systems can be accelerated by higher curing temperature.

Figure 6 shows the time vs. viscosity curves with 10% PEN-OH content of BAPh/PEN-OH prepolymers at 200°C. The storage modulus (G′) and loss modulus (G″) were referred to as the solid state and viscosity flow state of the samples, respectively. With longer processing time, both G′ and G″ increased. The storage modulus increased quickly from 6 to 12 min and the loss modulus increased at the same time, and the corresponding BAPh/PEN-OH prepolymers were transferred from flow state to solid state, which means that the cross-link network structures started to form. According to the rheological theory, the gelation time (G crossover point) was observed at 12 min [34], suggesting that the prepolymers underwent gelation transition. The sharp peak of the tan δ was 8 min, indicating that BAPh can be polymerized with PEN-OH under a certain temperature. The curve of tan δ underwent an increase first to reach a maximum then decreased. This can also be better demonstrated as that BAPh/PEN-OH systems were transferred from flow state to solid state during the postcuring reaction. Thus, the rheological measurements revealed that the curing rate of BAPh/PEN-OH systems can be easily controlled by varying the contents of PEN-OH and different curing temperatures. These rheological behaviors of BAPh/PEN-OH prepolymers are useful to the process and application.

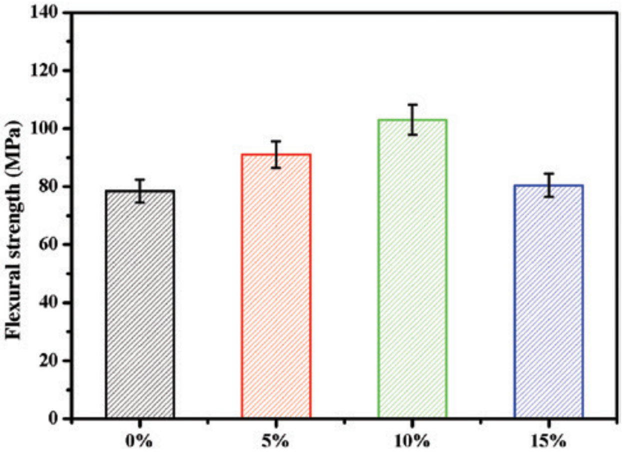

Figure 7: Flexure strength of BAPh/PEN-OH polymers cured at 300°C.

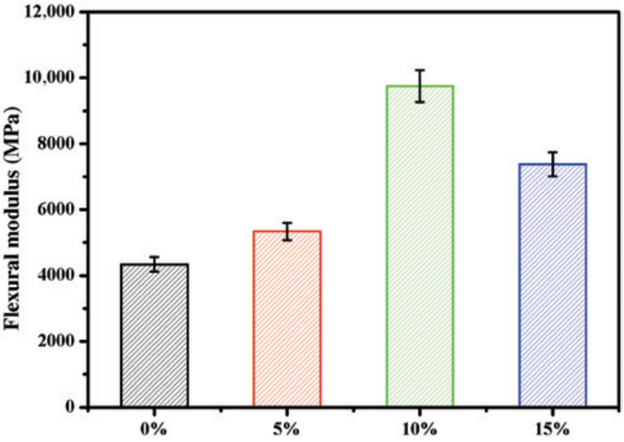

Figure 8: Flexure modulus of BAPh/PEN-OH polymers cured at 300°C.

3.3 Mechanical properties of BAPh/PEN-OH polymers

The flexure strength and modulus of BAPh/PEN-OH polymers maximum cured at 300°C are shown in Figures 7 and 8, respectively. The flexure strength of 0%, 5%, 10%, and 15% BAPh/PEN-OH polymers were 78.5, 91.0, 103.2, and 80.4 MPa, respectively, whereas the flexure modulus of 0%, 5%, 10%, and 15% BAPh/PEN-OH polymers were 4338.7, 5338.6, 9746.9, and 7377.4 MPa, respectively. With increasing PEN-OH contents, the flexure strength and modulus of the polymers both increased to a maximum point and then decreased, indicating that the mechanical properties of BAPh/PEN-OH polymers can be affected by various contents of PEN-OH. When the contents of PEN-OH increased to 10%, the flexure strength and modulus increased to 103.2 and 9746.9 MPa, respectively. The mechanical properties exhibited a decrease as the concentration of PEN-OH increased to 15%. Except for a part of PEN-OH that participated in the polymerization reaction with -CN, the BAPh network offered a rigid frame, and other flexible PEN-OH chains, BAPh, and heterocyclic rings wound around the framework of each other. Therefore, with the introduction of PEN-OH, the mechanical properties of BAPh/PEN-OH polymers can be raised. However, too much contents of PEN-OH could decrease the mechanical properties, because -OH functional groups were wounded in the PEN-OH main chain, making the effective -OH decrease and the polymerization reaction of BAPh/PEN-OH prepolymers become incomplete. Although the mechanical properties of 15% BAPh/PEN-OH polymers exhibited a slight decrease, the flexure strength and modulus of 15% BAPh/PEN-OH polymers were still higher than 0% BAPh/PEN-OH polymers. Therefore, the introduction of PEN-OH can effectively modify the intrinsic brittleness of

BAPh. Bisphthalonitriles/PEN polymers exhibited flexure strength and modulus at 94.8 and 3675.7 MPa when cured at 250°C for 4 h, 280°C for 4 h, 300°C for 4 h, 350°C for 6 h, and 380°C for 2 h [14]. Thus, the mechanical properties had improved with the introduction of PEN-OH. The results of this investigation demonstrated that the suitable content of PEN-OH showed an excellent balance of the desirable properties of BAPh/PEN-OH polymers with an improvement in ambient mechanical properties.

3.4 Thermal stabilities of BAPh/PEN-OH polymers

The thermal and thermal-oxidative stabilities of BAPh/PEN-OH polymers were evaluated by TGA. The temperature of 5% weight loss ($T_{5\%}$) and the retention of weight at 800°C in nitrogen and air atmosphere are summarized in Table 2. When heated in nitrogen atmosphere, 0%, 5%, 10%, and 5% BAPh/PEN-OH polymers started to lose weight at temperatures ($T_{5\%}$) of 484.1°C, 486.1°C, 487.2°C, and 487.2°C, respectively, and the retention of weight at 800°C was in the range of 68.5%–72.7%. In contrast, in air atmosphere, the $T_{5\%}$ of BAPh/PEN-OH polymers were 484.6°C, 487.1°C, 490.6°C, and 486.7°C, respectively, and the retention of weight at 800°C was in the range of 24.9%–44.6%. The $T_{5\%}$ and the retention of weight at 800°C was somewhat higher in air atmosphere than in nitrogen atmosphere. Based on these data, various contents of PEN-OH had little effect on the thermal and thermal-oxidative stabilities of BAPh/PEN-OH polymers. Taking the mechanical properties and thermal and thermal-oxidative stabilities of BAPh/PEN-OH polymers into consideration, the introduction of PEN-OH can improve the toughness of BAPh without sacrificing the high performance of BAPh. The good thermal stabilities are due to the flexible PEN-OH chains, BAPh, and heterocyclic rings wounded around the framework of each other. Thus, their thermal stabilities were not largely affected. More importantly, the polymerization reaction between nitrile groups on the BAPh and the hydroxyl groups of PEN-OH had occurred, and the formation of heterocyclic ring in FTIR results indicated high-temperature-resistant properties.

3.5 Dielectric properties of BAPh/PEN-OH polymers

The influence of frequency on the dielectric constant of BAPh/PEN-OH polymers is shown in Figure 9A, with

Table 2: Thermal and thermal-oxidative properties of BAPh/PEN-OH polymers with various proportions.

ω (PEN-OH) wt (%)	**Nitrogen**		**Air**	
	$T_{5\%}$ (°C)	**Retention of weight (%) at 800°C**	**$T_{5\%}$ (°C)**	**Retention of weight (%) at 800°C**
0	484.1	72.1	484.6	40.5
5	486.1	72.7	487.1	44.6
10	487.2	71.5	490.6	34.1
15	487.2	68.5	486.7	24.9

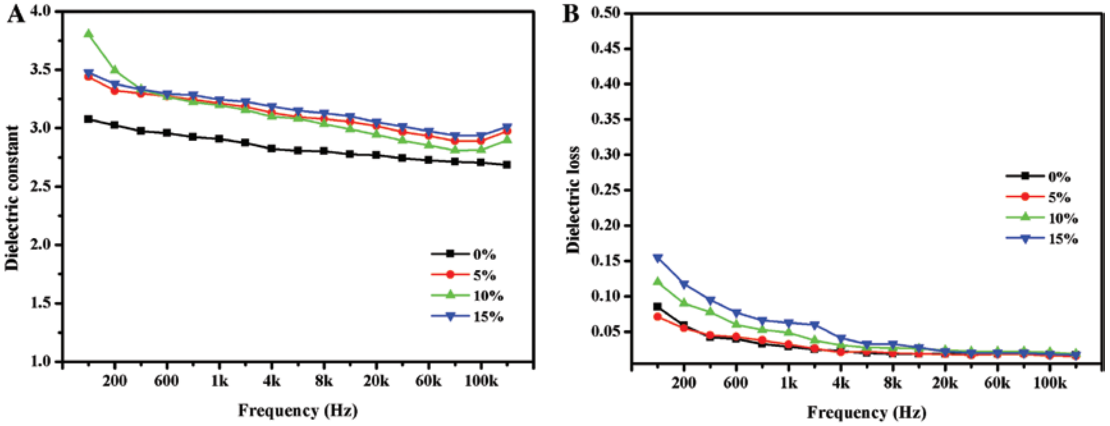

Figure 9: Influence of frequency on the (A) dielectric constant of BAPh/PEN-OH polymers and (B) dielectric loss of BAPh/PEN-OH polymers.

PEN-OH increasing from 0% to 15%. The dielectric constant ranged from 2.7 to 3.5. Compared with 0% PEN-OH BAPh/PEN-OH polymers, the addition of PEN-OH can increase the dielectric constant to some degree. However, the dielectric constant showed little dependence on various contents of PEN-OH. The dielectric constant of the pure PEN-OH was approximately 4.0. The decreased dielectric constant for BAPh/PEN-OH polymers may be attributed to the occurrence of polymerization reaction and the formation of nonpolar phthalocyanine ring and triazine ring as symmetrical structures. As the frequency increased from 100 to 200 kHz, the dielectric constant of BAPh/PEN-OH prepolymers exhibited little change. The influence of frequency on the dielectric loss of BAPh/PEN-OH polymers is shown in Figure 9B. The dielectric loss of BAPh/PEN-OH polymers ranged from 0.017 to 0.08. The dielectric loss of all BAPh/PEN-OH polymers decreased fast when the frequency ranged from 100 to 4 kHz; it had a tendency to remain the same as the frequency increased. Furthermore, the low-frequency zone had strong influence on the dielectric loss of BAPh/PEN-OH polymers, whereas the high-frequency zone had weak influence. Thus, the dielectric loss of BAPh/PEN-OH polymer exhibited little dependence on frequency.

3.6 Fracture morphology of BAPh/PEN-OH polymers

After the flexural tests, SEM micrographs were performed on fractured surface of 0%, 10%, and 15% BAPh/PEN-OH polymers, as shown in Figure 10A–C, respectively. In Figure 10A, the fracture was relatively flat. The cracks had central and straight extension directions, suggesting that 0% BAPh/PEN-OH polymers had a typical brittle fracture. However, with the introduction of PEN-OH (the ductile fracture in Figure 10B), the fracture strips were changed from straight lines to branch shapes and the fracture surfaces became rougher. In Figure 10C, the boundaries of

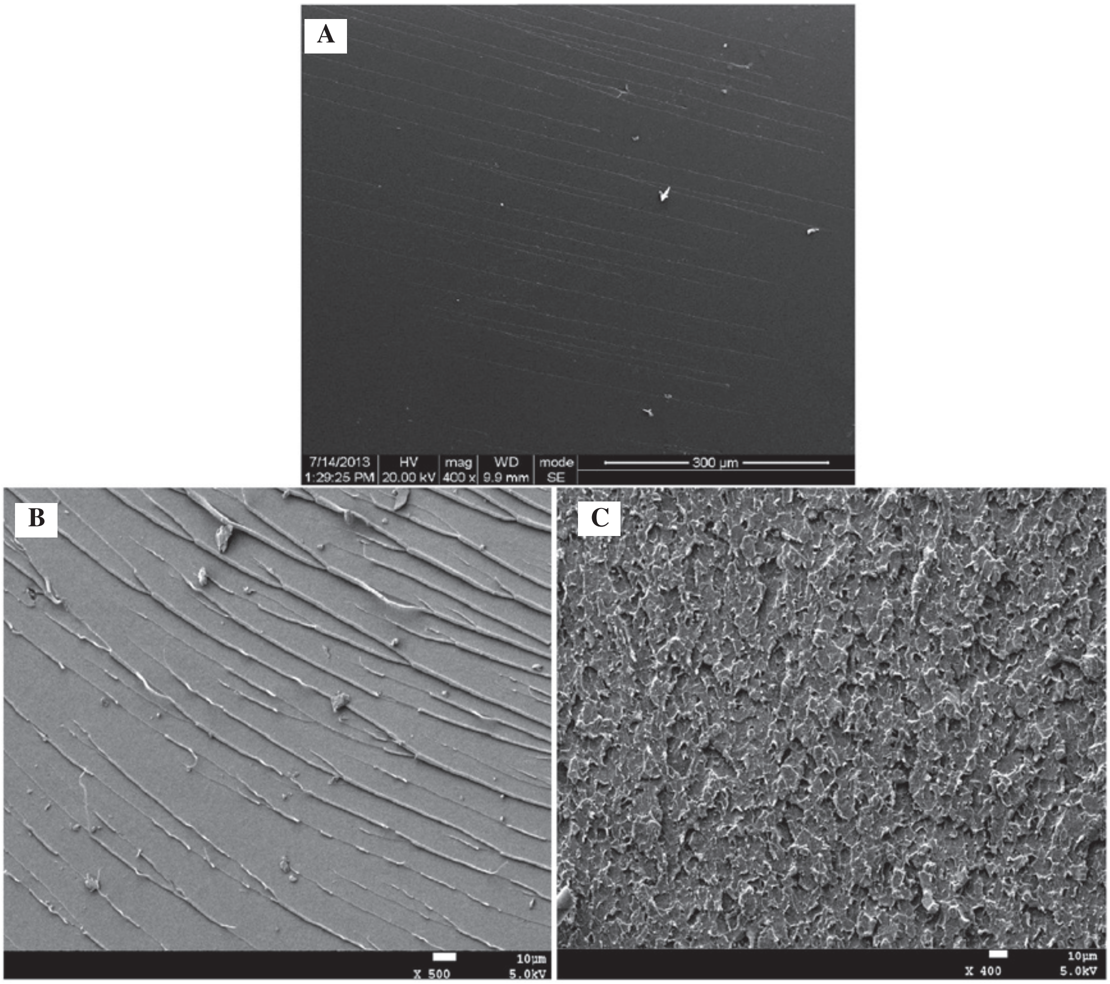

Figure 10: SEM micrographs of 0% (A), 10% (B), and 15% (C) BAPh/PEN-OH polymers.

fracture surfaces became blurred and the ductile fracture was more apparent. The chains of PEN-OH run through the entire network, demonstrating that the IPN structure might have been formed in the BAPh/PEN-OH polymers.

To further understand the inner structures of BAPh/PEN-OH polymers, 10% BAPh/PEN-OH polymers were heated in a three-neck round bottle flask with 100 ml NMP for 1 h. The polymers were treated in the oven at 200°C until no NMP was left on it. SEM micrographs were performed on fractured surface of 10% BAPh/PEN-OH polymers. The fracture morphology in BAPh/PEN-OH polymers played an important part in the mechanical performance. Figure 11A and C shows the direct fracture surface of 10% BAPh/PEN-OH polymers. The fracture strips had a tendency to disperse. The ductile fracture characteristic is shown in Figure 11A. More importantly, the obviously projecting segments in Figure 11A suggest that the addition of PEN-OH can largely increase the toughness and effectively absorb the external impact energy. In Figure 11B and D, the fracture surfaces of 10% BAPh/PEN-OH polymers treated with NMP and the unreacted PEN-OH in 10% BAPh/PEN-OH polymer had melted in the NMP solvent. As shown in Figure 11B, the projecting segments had disappeared, the fracture surface became rough, and the “island-like” shape could be easily found, suggesting the high degree of molecular chains interpenetrating.

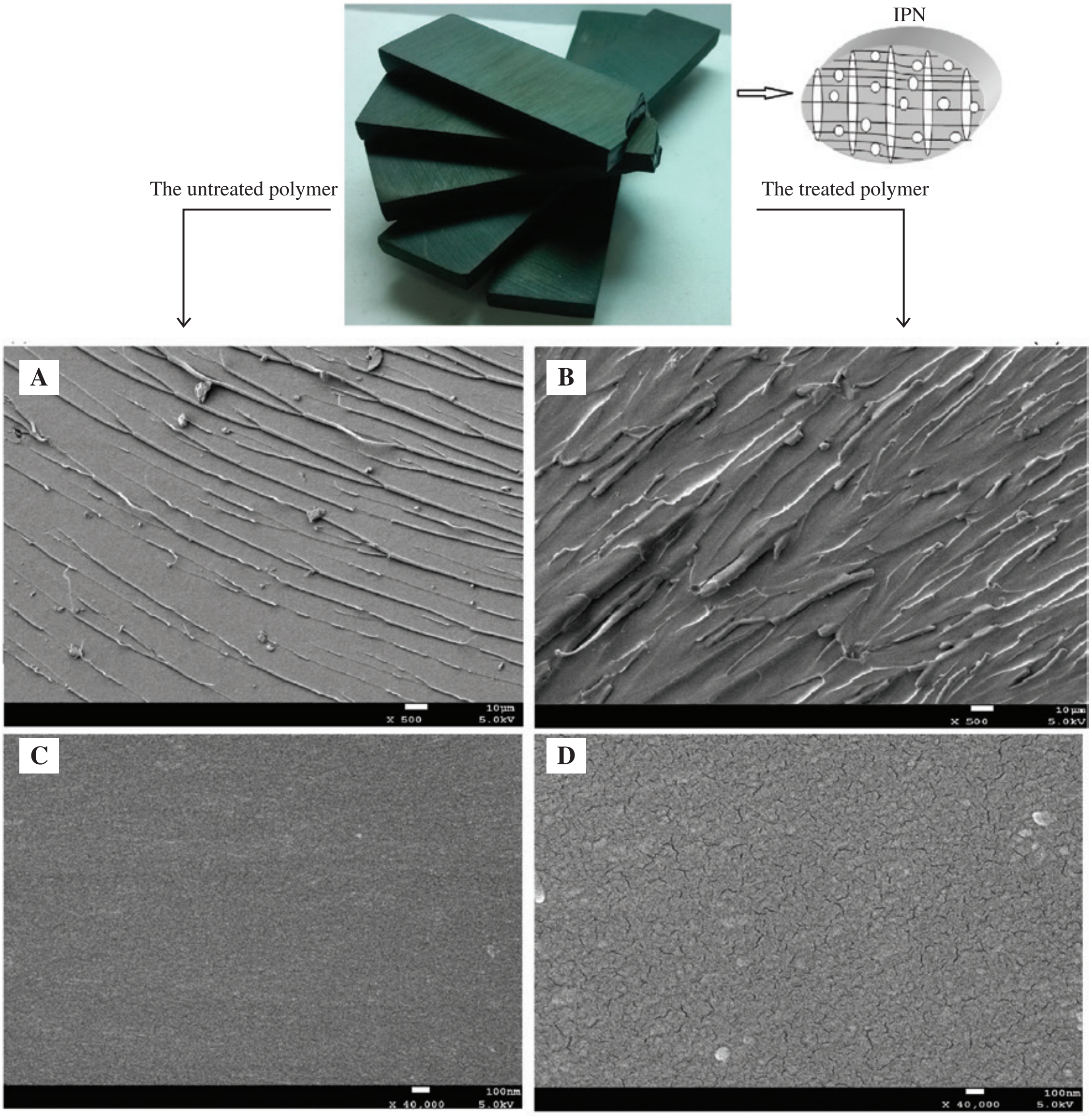

Figure 11: SEM micrographs of untreated BAPh/PEN-OH polymers at lower (A) and higher (C) magnification as well as BAPh/PEN-OH polymer treated with NMP at lower (B) and higher (D) magnification.

Comparing the higher-magnification micrographs of Figure 11C and D, the fracture surface of Figure 11C was very smooth, suggesting good compatibility of BAPh/PEN-OH polymers. However, there existed a large amount of small gaps and these small gaps had a uniform distribution in Figure 11D. The small gaps were the unreacted PEN-OH, which had now been dissolved in the solvent of NMP. According to the FTIR and SEM results, phthalocyanine ring and triazine ring, the unreacted small molecules, and the PEN-OH chain wound up in each other to form the IPN structure (Figure 11). The addition of PEN-OH can increase the mechanical properties of BAPh/PEN-OH polymers. The SEM results were consistent with the curing behavior and mechanical findings.

4 Conclusions

A series of BAPh/PEN-OH prepolymers and polymers were prepared and characterized without sacrificing other desirable high-temperature properties of BAPh monomer. The curing behaviors and thermal properties of BAPh/PEN-OH systems were studied. The results indicate that BAPh/PEN-OH systems have good processability and excellent thermal stabilities. The curing behaviors can be controlled by various contents of PEN-OH and curing temperatures. The FTIR results show that the structures of BAPh/PEN-OH polymers are mainly phthalocyanine ring and triazine ring. The introduction of PEN-OH in the bisphthalonitriles can improve the flexure strength and flexure modulus to 103.2 and 9746.9 MPa, respectively. The dielectric properties of BAPh/PEN-OH polymers have little dependence on the frequency. The fracture morphology of the polymers was demonstrated by the SEM. The whole research indicates that the performances of BAPh/PEN-OH systems are the bases of industrial applications for the development of engineering materials.

Acknowledgments: The authors wish to thank the National Natural Science Foundation (No. 51173021) and “863” National Major Program of High Technology (No. 2012AA03A212) for financial support of this work.

References

[1] Zhang CH, Wei HG, Liu YY, Guo ZH. *High. Perform. Polym.* 2012, 8, 702–709.
[2] Guo H, Zhou YK, Cheng ZR, Zhang JD, Zhan YQ, Yang J, Liu XB. *High. Perform. Polym.* 2012, 24, 571–579.
[3] Zhang BX, Luo ZH, Zhou H, Liu F, Yu RL, Pan YX, Wang Y, Zhao T. *High. Perform. Polym.* 2012, 5, 398–404.
[4] Keller TM. *J. Polym. Sci. Part A Polym. Chem.* 1997, 26, 3199–3212.
[5] Sumner MJ, Sankarapandian M, McGrath JE, Riffle JS, Sorathia U. *Polymer* 2002, 43, 5069–5076.
[6] Dominguez DD, Keller TM. *J. Appl. Polym. Sci.* 2008, 110, 2504–2515.
[7] Sastri SB, Armistead JP, Keller TM. *Polym. Compos.* 1996, 17, 816–822.
[8] Brunovska Z, Lyon R, Ishida H. *Thermochim. Acta* 2000, 357, 195–203.
[9] Keller TM. *J. Polym. Sci. Part A Polym. Chem.* 1997, 26, 3199–3212.
[10] Sastri SB, Keller TM. *J. Polym. Sci. Part A Polym. Chem.* 1999, 37, 2105–2111.
[11] Cao GP, Chen WJ, Liu XB. *Polym. Degrad. Stabil.* 2008, 93, 739–744.
[12] Keller TM. *Chem. Mater.* 1993, 6, 302–305.
[13] Laskoski M, Keller TM, Qadri SB. *Polymer* 2007, 48, 7484–7489.
[14] Lei YJ, Zuo F, Zhao R, Liu XB. *J. Mater. Eng.* 2009, s2, 1001–4381.
[15] Yang XL, Zhang JD, Lei YJ, Zhong JC, Liu XB. *J. Appl. Polym. Sci.* 2011, 121, 2331–2337.
[16] Wirasate S, Dhumrongvaraporn S, Allen DJ, Ishida H. *J. Appl. Polym. Sci.* 1998, 7, 1299–1306.
[17] Huang X, Pu ZJ, Tong LF, Wang ZC, Liu XB. *J. Mater. Sci. Mater. Electron.* 2012, 23, 2089–2097.
[18] Tang HL, Yang J, Zhong JC, Zhao R, Liu XB. *Mater. Lett.* 2011, 65, 1703–1706.
[19] Li C, Gu Y, Liu XB, Zou YB, Tang AB. *Thin Solid Films* 2006, 515, 1872–1876.
[20] Wang JY, Wang MJ, Liu C, Zhou HX, Jian XG. *Polym. Bull.* 2013, 70, 1467–1481.
[21] Zhao X, Guo H, Lei YJ, Zhao R, Zhong JC, Liu XB. *J. Appl. Polym. Sci.* 2012, 6, 4873–4878.
[22] Frisch HL. *Polym. Int.* 1985, 2, 149–153.
[23] Lipatov YS. *Prog. Polym. Sci.* 2002, 9, 1721–1801.
[24] Jia LY, Zhang C, Du ZJ, Li CJ, Li HQ. *Polym. J.* 2007, 39, 593–597.
[25] Laskoski M, Dominguez DD, Keller TM. *ACS Symp. Ser.* 2005, 922, 378–388.
[26] Zhou YK, Yang J, Zhan YQ, Yang XL, Zhong JC, Zhao R, Liu XB. *J. Appl. Polym. Sci.* 2012, 5, 3829–3835.
[27] Du RH, Li WT, Liu XB. *Polym. Degrad. Stabil.* 2009, 12, 2178–2183.
[28] Keller TM. *Chem. Mater.* 1994, 6, 302–305.
[29] Seoudi R, El-Bahy GS, El Sayed ZA. *J. Mol. Struct.* 2005, 753, 119–126.
[30] Chen ZR, Guo H, Tang HL, Yang XL, Xu MZ, Liu XB. *J. Appl. Polym. Sci.* 2013, 129, 2621–2628.
[31] Guo H, Lei YJ, Zhao X, Yang XY, Zhao R, Liu XB. *J. Appl. Polym. Sci.* 2012, 125, 649–656.
[32] Keller TM, Griffith JR. *ACS Org. Coat. Plast. Chem. Prep.* 1980, 43, 804–807.
[33] Xu MZ, Yang XL, Zhao R, Liu XB. *J. Appl. Polym. Sci.* 2013, 2, 1176–1184.
[34] Laza JM, Vilas JL, Mijangos F, Rodriguez M, Leon LM. *J. Appl. Polym. Sci.* 2005, 98, 818–824.