Synthesis, Polymerization, and Properties of the Allyl-Functional Phthalonitrile

Xingqiang Zou, Mingzhen Xu, Kun Jia, Xiaobo Liu

Research Branch of Functional Materials, Department of Applied Chemistry, Institute of Microelectronic and Solid State Electronic, High-Temperature Resistant Polymers and Composites Key Laboratory of Sichuan Province, University of Electronic Science and Technology of China, Chengdu 610054, People's Republic of China
Correspondence to: K. Jia (E-mail: jiakun@uestc.edu.cn) and X. B. Liu (E-mail: liuxb@uestc.edu.cn)

ABSTRACT: A novel bisphthalonitrile monomer containing allyl groups (DBPA-Ph) had been synthesized via the reaction of diallyl bisphenol A (DBPA) and 4-nitrophthalonitrile. The chemical structure of DBPA-Ph was confirmed by ^{1}HNMR, ^{13}CNMR, and FTIR spectroscopy. The curing behaviors and processability of DBPA-Ph were studied by differential scanning calorimetry (DSC) and dynamic rheological analysis. The monomer manifested a two-stage thermal polymerization pattern. The first stage was attributed to the polymerization of allyl groups and the second to the ring-form polymerization of cyano groups. The result of dynamic rheological analysis indicated the monomer had wide curing window and the self-catalyzed curing behavior. DBPA-Ph polymers were prepared from the thermal polymerization with short curing time, showing high glass transition temperature ($>350°C$) and attractive thermal decomposition temperature ($>430°C$). The outstanding glass transition temperature, desirable thermo-oxidative stabilities, good processability and sound process conditions could provide more applications to the DBPA-Ph polymers. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41203.

INTRODUCTION

In the past decades, a series of high-temperature resistance polymers, such as polyimides,[1,2] polypyrazole,[3] and polyphthalonitriles,[4] had been thoroughly researched, owing to their exceptional properties such as wonderful mechanical properties, excellent thermal and thermo-oxidative stabilities, high char yield, superior moisture resistance, and flame resistance.[5–13] Phthalocyanine, the thermosetting polymers obtained from phthalonitrile, had been applied in wide areas such as marine, aerospace and electronic fields due to their excellent properties above mentioned.[7,14,15] In these areas, phthalocyanine resins were expected to replace the application of metallic materials because of the requirement for reducing weight and enhancing performance.[1] In fact, the raw phthalonitrile monomers presented extremely slow curing reaction, which only occurs at high temperature or long cure time (>100 h at 280°C). Moreover the rigorous processing conditions and narrow process window had also tremendously limited the application of the high-performance polymer.[16] For example, 2, 2-bis[4-(3,4-dicyanophenoxy)phenyl]propane (BAPh), one of the most typical composition of phthalonitrile resins, had a high melting point (range between 194–200°C) and a narrow curing window (55.8°C).[11] In addition, 4, 4′-bis(3,4-dicyanophenoxy) biphenyl (BPh) was the first phthalonitrile-based, high-temperature

resistant resin reported,[13] the polymerization of BPh started immediately after monomer melted (231–233°C) which resulted in a narrow processing window (~20°C). Furthermore, the reactivity of BAPh monomer was lower than BPh and 2, 2-bis [4-(3, 4-dicyanophenoxy) phenyl] hexafluoropropane (6FPh) in the presence of curing additive, leading to the difficulties of the processability and wide application.[17] Therefore, new phthalonitrile based monomer need to be designed to improve the reactivity and processability of polymer.

Many efforts had been invested in order to improve the processability of phthalonitrile-based resins.[4,7] Various methods such as, the design of phthalonitrile-based monomer involving other polymerizable moieties, the introduction of various kinds of catalyst, copolymerization with various thermosetting/thermoplastic resins, alloy and blending have been employed to improve the properties of phthalocyanine-based resin systems. In our previous work, different materials, such as phthalonitrile/epoxy,[18] phthalonitrile/phenolic,[19] phthalonitrile/PEN,[20] phthalonitrile/curing additive,[21] phthalonitrile/biphenyl ethernitrile,[21,22] had been designed and studied. However, the polymer systems obtained by blending or copolymerization with various kinds of thermosetting resins showed limited improvement onto the overall properties of resulted polymers.
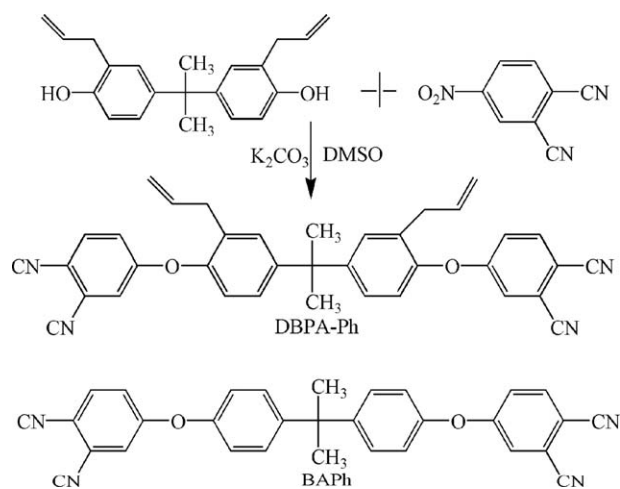
Scheme 1. Synthesis and structure of DBPA-Ph monomer.

On the contrary, the molecular design of novel monomer would be an effective method to improve the processability of phthalonitrile-based polymer. For instance, two new monomers of 3-aminobenxyl-o-phthalonitrile (3-APN)[23] and phthalonitrile containing benzoxazine (BA-ph)[24] had been prepared and studied in our lab previously. Results confirmed that the 3-APN presents low melting temperature (175°C) and polymerizing temperature (239°C), while BA-ph can thermally polymerized at low temperature (210–240°C). Therefore, the previous research indeed demonstrated that the introduction of new radicals would have a great impact on the properties of phthalonitrile-based resins.

In this paper, the allyl groups were introduced to the phthalonitrile for their excellent curing behavior. It was expected that the polymerization of allyl group would improve the density of cross-linkage network and toughness of the phthalonitrile-based polymer.[25] Specifically, allyl functional phthalonitrile monomers were designed and prepared via diallyl bisphenol A and 4-nitrophthalicnitrile. The composition, structure, and the polymerization was extensively studied by ^{1}HNMR, ^{13}CNMR, DSC, FTIR, and TGA.

EXPERIMENTAL

Materials

Diallyl bisphenol A (DBPA, AR) was obtained from Yan Tai Heng Nuo Chemical Technology, China. 4-Nitrophthalonitrile (4-NPh, 99%) was obtained from Alpha chemicals (Dezhou), China. Dimethyl sulfoxide (DMSO) and potassium carbonate (AR) were obtained from Tianjin BODI chemicals. All the starting solvents were used without further purification.

Synthesis of Allyl-Functional Phthalonitrile Monomer (DBPA-Ph)

The phthalonitrile monomer containing allyl group (DBPA-Ph) was firstly synthesized based on the reaction of diallyl bisphenol A and 4-nitrophthalonitrile. The main synthesis procedure was shown as followed: Diallyl bisphenol A and catalyst (potassium carbonate) were firstly added into the DMSO solvent in a 1000 mL three-necked round-bottom flask equipped with a mechanical stirrer and refluxing. Then, the mixture was gradually heated to 60°C for 5 h. Next, 4-Nitrophthalonitrile was

added into the solution, and the temperature remained constant for another 3 h. Then, the reaction mixture was filtrated and the filtration was poured to water to precipitate the DBPA-Ph monomer with vigorously stirring, the products was separated and washed several times by distilled water and then dried at 100°C over night. The detailed reaction process and the structure of DBPA-Ph monomer was shown in Scheme 1.

Preparation of DBPA-Ph Polymers

The DBPA-Ph polymers were prepared by thermally activated polymerization of the DBPA-Ph monomer in air-circulation oven in sequence at elevated temperatures. The detailed polymerization procedures were accompanied by applying a cure cycle as 260°C/4 h, 280°C/4 h, 300°C/4 h, 320°C/4 h, 340°C/4 h, 360°C/4 h. The cured DBPA-Ph polymers were sanded to a thickness of 2 mm for the Dynamic mechanical measurements (DMA). Meanwhile, the cured DBPA-Ph polymers were physically pulverized under ambient condition for thermal gravimetric analysis (TGA).

Measurements

Nuclear magnetic resonance spectrometer (^{1}HNMR) spectra were taken on an AV400 nuclear magnetic resonance spectrometer (Bruker, Germany) with a proton frequency of 300 MHz and the solvent was $CDCl_3$. Fourier Transform Infrared (FTIR) spectra were recorded with FTIR8400S Fourier Transform Infrared spectrometer (Shimadzu, Japan) in KBr pellets between 4000 and 500 cm^{-1} in air. Differential scanning calorimetric analysis was performed by Modulated DSC-Q100 (TA Instruments, USA) at a heating rate of 10°C/min and a nitrogen flow rate of 50 mL/min. Viscosity studies and curing process of the DBPA-Ph were conducted using Rheometer AR-G2 (TA Instruments, USA) with a heating rate of 5°C/min and a frequency of 1Hz from 50 to 300°C in air. The samples (0.5–1 g) were melted between 25 mm diameter parallel plates with the gap of 1000 μm and shear rate of 1 Hz. Dynamic mechanical analysis (DMA) in a three-point-blending mode was performed on QDMA-800 dynamic mechanical analyzer (TA Instruments, USA) to determine the glass transition temperature (T_g). The storage modulus and tan delta (tan δ) were investigated at a frequency of 1 Hz and amplitude of 20 μm, and the samples (dimensions 30 mm × 10 mm × 2 mm) were heated from 50 to 400°C at a temperature ramp of 3°C/min. Thermogravimetry (TGA) and Differential presentation of integral TGA (DTA) were performed on a TGA Q50 (TA Instruments, USA) with a heating rate of 20°C/min (under nitrogen or air) and a purge of 40 mL/min from 100 to 800°C.

RESULTS AND DISCUSSION

Characterization of the Structure of DBPA-Ph Monomer

The DBPA-Ph monomer had been synthesized via substitution reaction of 4-nitrophthalonitrile and diallyl bisphenol A in the presence of K_2CO_3 in the N,N-dimethylformamide (DMSO) solvent (Scheme 1). The monomer structures were characterized by ^{1}HNMR, ^{13}CNMR, and FTIR spectroscopy. The relevant data were listed as follows.

^{1}HNMR (400 MHz, DMSO-d_6) δ (ppm): 1.69 (-CH$_3$), 3.22 (-CH$_2$-), 4.94 (=CH$_2$), 5.58 (-CH=), 7.07–8.06 (benzene ring).
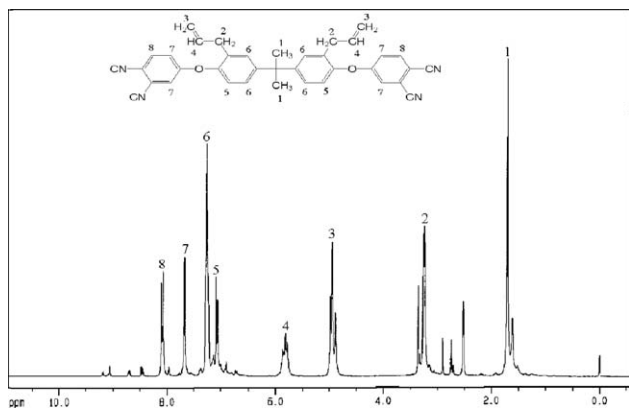
Figure 1. ^{1}HNMR spectra of DBPA-Ph monomer.

^{13}CNMR (400 MHz, CDCl$_3$) δ (ppm): 31.80 (-CH$_2$-), 35.15 (-CH$_3$), 116.07 (=CH$_2$), 117.38 (-CN), 132.56 (-CH=), 150.9 (C$_{14}$), 162.74 (C$_{15}$).

FTIR (solid state, KBr, cm^{-1}): 2967 cm^{-1} (-CH$_3$), 3082 cm^{-1} (=C-H), 2230 cm^{-1} (-CN), 1248 cm^{-1} (stretch, Ar—O—Ar), 1638 cm^{-1} and 838 cm^{-1} (-CH=CH$_2$), 1410 cm^{-1} (C=C-CH$_2$), 997 cm^{-1} (out of plane bending vibration of olefinic C—H), 1487 cm^{-1} (-C=C-, Ar).

^{1}HNMR spectrum was shown in Figure 1, ^{13}CNMR spectrum was shown in Figure 2 and FTIR spectra were depicted in Figure 3.

In ^{1}HNMR spectrum, the salient resonance appearing at 1.69 ppm was the peak of methyl proton in the linkage. The resonance at 3.22 ppm was the hydrogen in methylene. The resonance of the hydrogen in ethenyl was at 4.92 ppm and 5.80 ppm. The resonance at 7.07–8.06 ppm was the hydrogen in benzene ring. The calculated ratio of the integral area of resonance at integral area of resonance at 7.04–7.07ppm and resonance at 8.06–8.09ppm was 1.2, which was quite close to the theoretical value of 1.0. Consequently, the data were found to be in good agreement with the proposed structure. Furthermore, the structure of the DBPA-Ph monomer was confirmed by using ^{13}CNMR (Figure 2). The characteristic resonance of –CN was
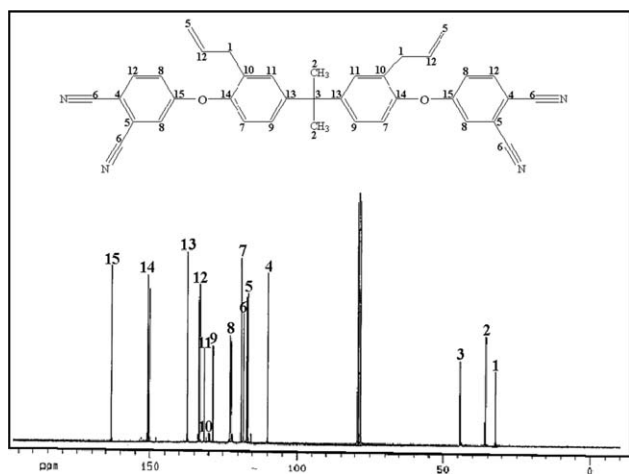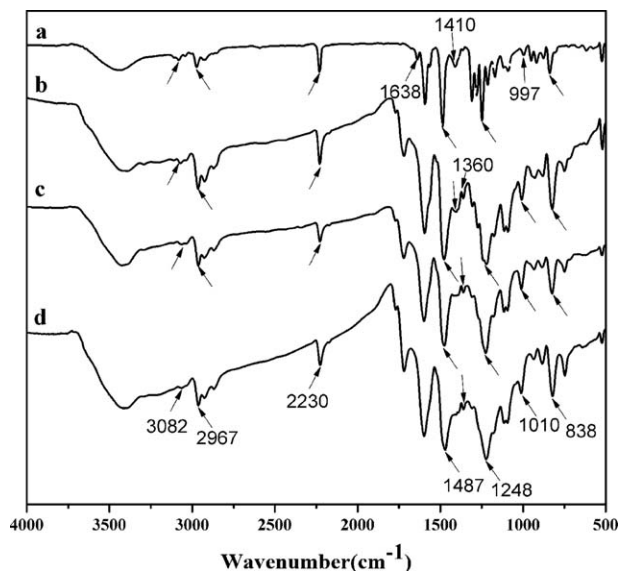

Figure 3. FTIR spectra of DBPA-Ph monomer and polymers: (a) DBPA-Ph monomer; (b) the polymer being cured at 280°C; (c) the polymer being cured at 320°C; (d) the polymer cured at 340°C.

the peak at 117.38ppm, the peak at 35.15 ppm was the characteristic resonance of –CH$_3$. The data was in agreement with the calculated data. In FTIR spectra [Figure 3(a)], the appearance of absorption bonds at 1248 cm^{-1} (stretch, Ar—O—Ar) revealed the reaction between diallyl bisphenol A and 4-Nitrophthalonitrile indeed had happened. The absorption peak at 2230 cm^{-1} was assigned to the stretching vibrations of cyano group (-CN).[6,11] The characteristic band of C=C-CH$_2$ group appeared at 1420 cm^{-1}. The characteristic absorption bands in Figure 3(a) demonstrated the DBPA-Ph monomer was obtained, and the structure of DBPA-Ph was shown in Scheme 1.

Curing Behaviors of DBPA-Ph Monomer

The DSC thermograms in the temperature range from 50 to 380°C at the heating rate of 10°C/min of DBPA-Ph monomer and DBPA were shown in Figure 4. The self-promoted curing behaviors of the DBPA-Ph monomers were studied and the
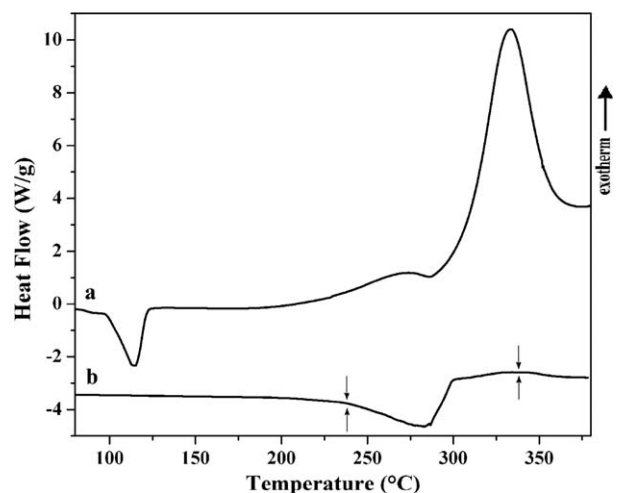

Figure 2. ^{12}CNMR spectra of DBPA-Ph monomer.

Figure 4. DSC curves of (a) DBPA-Ph monomer; (b) DBPA.

Table I. Thermal Properties of DBPA-Ph Monomer

Sample	T_{melt}	T_{top1}	T_{top2}	$\Delta H_{curing1}$	$\Delta H_{curing2}$
DBPA-Ph	122°C	270°C	332°C	7.3 J/g	266.9 J/g
DBPA	–	202°C	335°C	4.5 J/g	24.1 J/g

main results were listed in Table I, including temperature of melting point (T_{melt}), exothermal peak temperature (T_{top}), and heat of polymerization (ΔH_{curing}). In the curves shown in Figure 4(a), only one endothermic peak (range between 100 and 123°C) was observed, indicating the product was purified and the melting temperature of DBPA-Ph monomer was at 122°C. Compared with the melting temperature of BAPh (range between 194 and 200°C), the melting temperature of DBPA-Ph reduced significantly (at least 72°C). The lower melting temperature was advantageous to the polymer processing as a wider processing window would be obtained for this kind of alyll functionalized phthalonitrile polymer. Besides, in comparison with BAPh monomer, two polymerization peaks were observed in Figure 4(a). The wide, short polymerization peak around 270°C was followed by a much intense and sharper polymerization peak around 332°C. It was reported that the polymerization of allyl groups appeared above 200°C.[26] Thus, it can be speculated that the first exothermic peak was attributed to the polymerization of allyl moieties and the second to the ring-forming polymerization of cyano groups.

The polymerization of DBPA-Ph system was also monitored by FTIR. The IR spectra of DABA-Ph polymers with various cure temperature were depicted in Figure 3. It could be seen that, with increasing the curing temperature, the intensity of the characteristic absorption bands for =C–H bond of the allyl moiety at 3082 cm^{-1} reduced significantly. The characteristic absorption bands for –CH=CH$_2$ bond of the allyl moiety at 1638 cm^{-1} and 1410 cm^{-1} disappeared gradually. The results
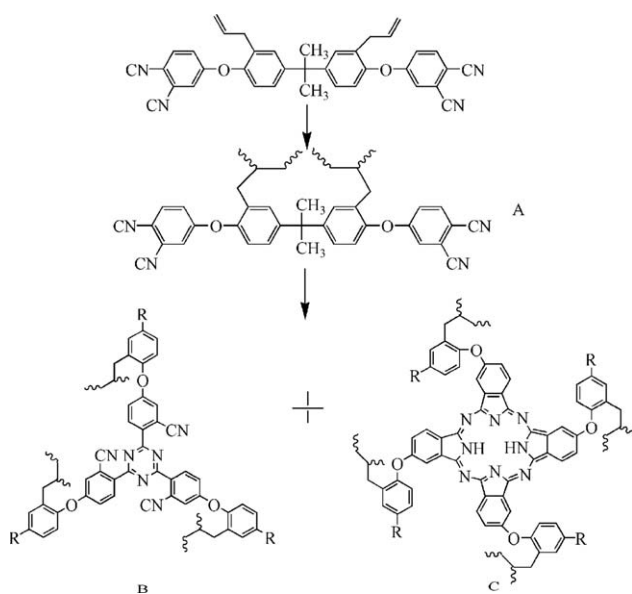
indicated that the allyl groups have been involved to a great extent in the polymerization. With increasing curing temperature, active groups were consumed and the polymerization degree became higher and higher gradually. New absorption bands at 1010 and 1360 cm^{-1} was observed which indicated the formation of phthalocyanine [Scheme 2(C)] and triazine [Scheme 2(B)] rings among cyano groups. Meanwhile, with increasing the curing temperature, the intensities of the characteristic absorption bands at 1010 and 1360 cm^{-1} increased. Based on the results of DSC and FTIR, it was considered that the addition polymerization of allyl moiety at low temperature (Figure 4) produced the active hydrogen, the product as Scheme 2(A) shown. Furthermore, the active hydrogen catalyzed the polymerization of phthalonitrile to generate the phthalocyanine and triazine rings found in FTIR spectra, the possible mechanism for the self-catalyzed DBPA-Ph monomer was shown in Scheme 2.[22,26]

Processabilities of DBPA-Ph

The polymerization behaviors of DBPA-Ph system were confirmed by the time sweep curves of the rheological tests, shown in Figure 5. As can be seen, in the DBPA-Ph system, the storage modulus (G') decreased at first, indicating that DBPA-Ph had been transferred from solid state to liquid state, then the G' increased sharply from 80 min, DBPA-Ph transferred from viscosity flow state to solid state. At the same time, the loss modulus (G'') also increased. Based on the principle of classical rheological theory, the gelation time (determined from the crossover point of G' and G'') was observed at 67 min and 82 min, which corresponded to the addition polymerization of allyl moiety and ring-forming of cyano groups, respectively.[14] The tan δ curve exhibited one peak from 65 min to 80 min, which meant that the DBPA-Ph could polymerize well under certain curing temperature (range between 250 and 275°C), which were consistent with the DSC observations.

To further determine the processing temperature and time for DBPA-Ph, the complex viscosity ($\eta^\star$) changes of DBPA-Ph were measured as a function of time at several temperatures, shown in Figure 6. It could be seen that the $\eta^\star$ at different

Scheme 2. Possible polymerization reaction of DBPA-Ph monomer.
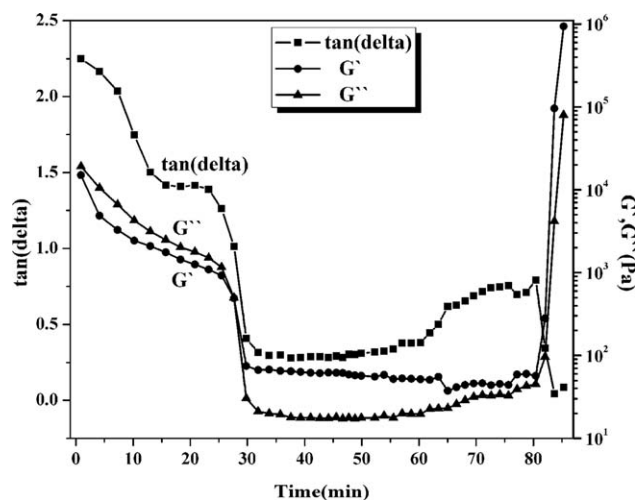
Figure 5. Storage modulus (G') and loss modulus (G'') curves of DBPA-Ph.
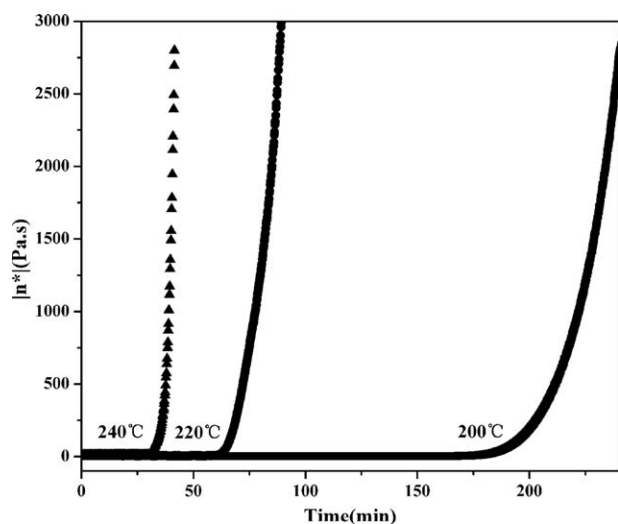
Figure 6. Complex viscosity as a function of time for the DBPA-Ph at various temperatures.

temperatures were relatively low and stable before the final curing reaction occurred. However, after the curing reaction started, the $\eta^{\star}$ increased dramatically and the increased viscosity meant the higher polymerization degree. Nevertheless, the time for dramatic $\eta^{\star}$ increase was varied with the different temperatures. Namely, the $\eta^{\star}$ increase of DBPA-Ph at 200°C took a very long time (173 min), indicating that the reaction was carried out slowly. On the contrary, the $\eta^{\star}$ increase of DBPA-Ph at 240°C took a rather short time (31 min), revealing that curing reaction was carried out very fast. Meanwhile, the $\eta^{\star}$ increase of DBPA-Ph at 220°C took place at a relatively proper time (60 min). Thus, 220°C was chosen as a proper processing temperature for DBPA-Ph. On the one hand, these results manifested that the $\eta^{\star}$ of the DBPA-Ph processed faster with the increase of processing temperature. On the other hand, these results revealed that processing temperature could accelerate the polymerization reaction of DBPA-Ph. From Figure 6, the processing time and polymerization rate of DBPA-Ph systems could be easily controlled by varying the processing temperature and the
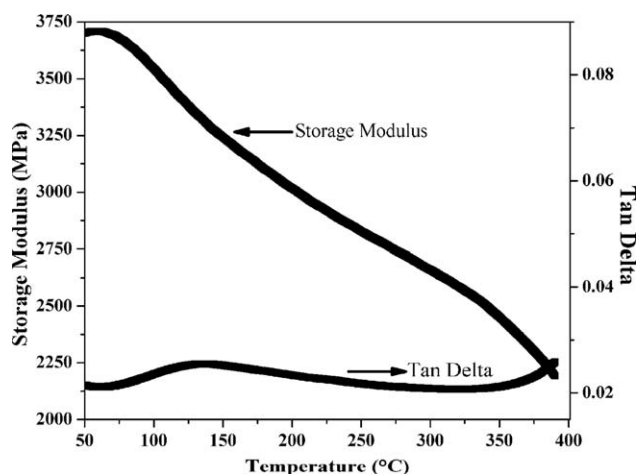
optimized processing temperature for DBPA-Ph was about 220°C. The result provided the possibility of processing of DBPA-Ph at low temperature.

Dynamic Mechanical Properties of DBPA-Ph Polymers

Dynamic mechanical studies were conducted to evaluate the changes in the sample modulus as a function of temperature and determinate the T_g of the polymers. From these studies, storage modulus plots generated on DBPA-Ph polymers versus temperature were presented in Figure 7.

As well known, one of the fundamental parameters to describe the polymer was glassy transition temperature (T_g). For temperature greater than T_g, the polymer was at rubbery state. As the polymer was at lower temperature than T_g, the polymer was at glass state.[27,28] The glass transition in amorphous polymers was accompanied with significant changes in their viscoelastic response. Thus the stress relaxation modulus commonly decreased by about three orders of magnitude in the vicinity of the T_g. Meanwhile, the tan δ exhibited maxima in the glass transition region.[28] In Figure 7, the modulus for DBPA-Ph polymer changed from 3700 MPa to 2173 MPa when heated from 50 to 400°C. Significant modulus changes were observed after 350°C. Meanwhile, T_g was obtained from the maximum of tan δ and there were two relaxation peaks observed in each plot. The tan δ band (100–150°C) of DBPA-Ph polymers was attributed to the movement of the oligomer shown in Scheme 2(A). On heating to 350°C, the value of the tan δ increased and the peak would occur above 350°C. Therefore, it was confirmed that the value of T_g is above 350°C. It was well known that the T_g of polymers depended on the rigidity of the molecular chains and the cross-linking degree.[29–34] For highly cross-linked systems, a semi empirical equation had been used for calculating cross-link density[26,27]

$$\text{Log}_{10}\,G' = 7 + 293 d_{\text{croos-link}} \qquad (1)$$

Where G' was the storage modulus of the cured polymer in the rubbery plateau region in dynes/cm^2 above T_g (i.e., $T_g + 40°C$),

Figure 7. Storage modulus (G') and damping factor (tan δ) as a function of temperature for DBPA-Ph polymer heated in nitrogen.
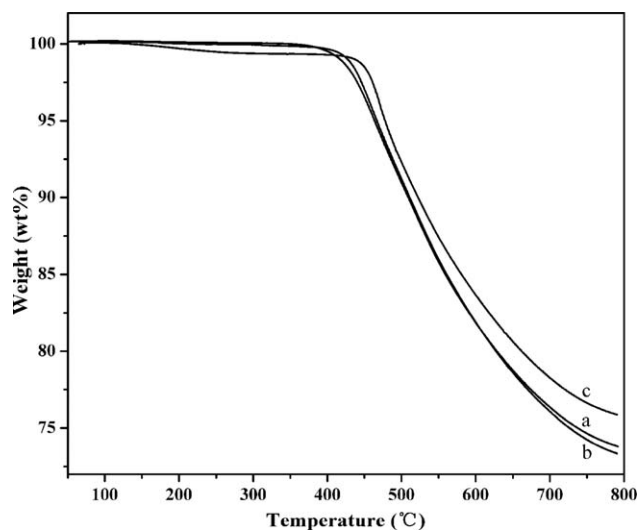

Figure 8. TGA curves of DBPA-Ph polymers being cured at various temperatures in nitrogen: (a) the polymer being cured at 280°C; (b) the polymer being cured at 320°C; (c) the polymer being cured at 340°C.

Table II. Thermal and Thermo-Oxidative Stabilities of DBPA-Ph Polymers

Samples	N$_2$			Air		
	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	Char yield at 800°C (%)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	Char yield at 800°C (%)
A	463.8	509.2	73.8	451.8	509.0	38.9
B	466.8	510.2	73.4	447.0	500.3	43.9
C	477.8	522.4	75.9	464.4	520.7	46.3

$d_{cross-link}$ was the cross-link density of the polymer. According to eq. (1), the cross-link density of DBPA-Ph polymer was 11389 mol/m^3. Thus, the outstanding T_g was mainly attributed to the high cross-linking degree of heterocyclization formed by cyano groups in the DBPA-Ph system, as well as the addition polymerization of allyl moieties. The polymerization of the active groups significantly increased the cross-linking degree and rigidity of the polymer, which greatly limited the motion of the molecular chains.

Thermal Properties of DBPA-Ph Polymers

The thermal decomposition of the DBPA-Ph polymers was also examined by TGA (Figure 8) both in inert (nitrogen) and air (20% oxygen) environments at a heating rate of 20°C/min and the main results were summarized in Table II, in which the temperatures at weight loss of 5% ($T_{5\%}$), 10% ($T_{10\%}$) and the retention of weight at 800°C (char yield at 800°C) were displayed. According to the Figure 8, in nitrogen atmosphere, the DBPA-Ph polymers after curing at 280, 320, and 340°C for 4 h started to degrade at temperature ($T_{5\%}$) of 436.8°C, 466.8°C, and 477.8°C, respectively. It was clear that the DBPA-Ph polymer cured after 340°C exhibited obviously enhanced thermal stability compared with other two samples cured at 280°C and 320°C, this is due to the phtahlocyanine forming reaction occurred above 332°C from the DSC results shown in Figure 6. And the thermo-oxidative stability of DBPA-Ph polymers in air atmosphere was similar with the thermal stability in nitrogen atmosphere within the margin of error. Meanwhile, the polymer being cured at 340°C was measured by TGA in nitrogen and air atmosphere, the difference was shown in Figure 9. According to the Figure 9, the $T_{5\%}$ and $T_{10\%}$ in nitrogen atmosphere were 477.8°C and 522.4°C, respectively, and the char yield at 800°C was 75.9%. In air atmosphere, $T_{5\%}$ and $T_{10\%}$ were 464.4°C and 520.7°C, respectively, and the char yield at 800°C was 46.3%. With a directly observation of Figure 9(A), the difference of the thermal and thermo-oxidative stabilities before heating the sample to 560°C was slight, while there was a large difference in the stability for the sample in the air and nitrogen atmosphere at higher temperature above 600°C. Thus the derivative TGA curves were used to elucidate the different decomposition behaviors in air and nitrogen [Figure 9(B)]. As noted in Figure 9, a main degradation step was observed in the nitrogen while two decomposition steps were detected in air. It could be seen in the curve a, there was a main degradation step which started at around 402°C and reached maximum at around 498°C. While for the curve b, the double-step thermal degradation was observed at around 456°C and 701°C, indicating that there were two major decomposition processes. In inter atmosphere, thermal chain scission was the main thermal degradation process. Nevertheless, in the presence of oxygen, there were not only thermal chain scission started at elevated temperature (>550°C), but also thermal oxidation at around 456°C. Above of all, the thermal cure could improve the thermal property of
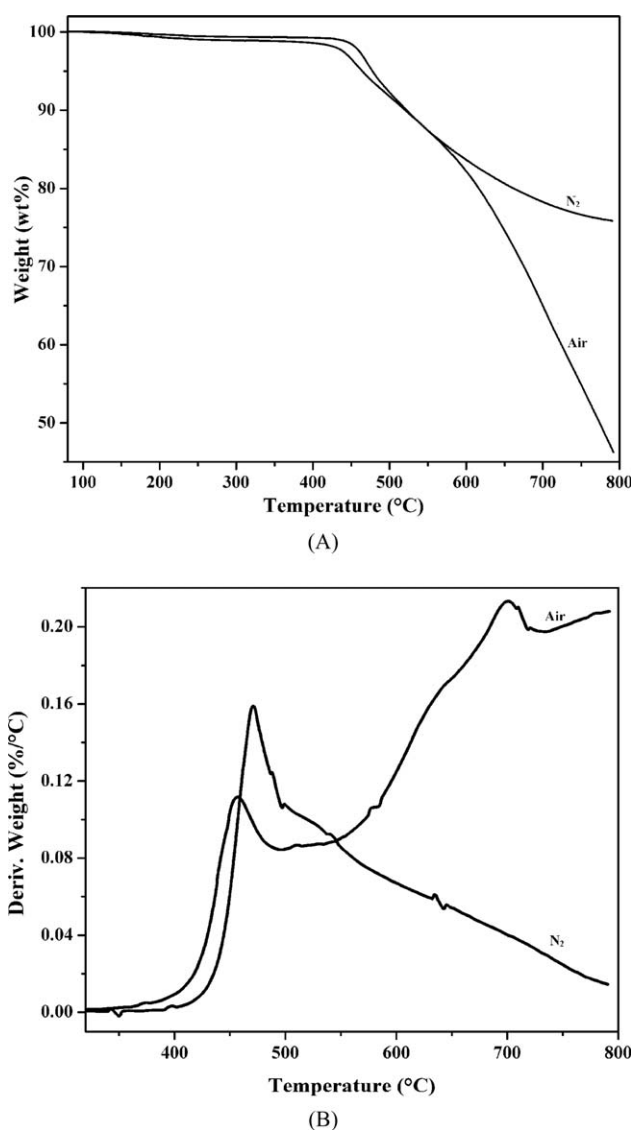

Figure 9. TGA (a) and DTA (b) curves of DBPA-Ph polymer being cured at 340°C.

DBPA-Ph monomer. However, the improvement with further curing at higher temperature was limited, as the degree of polymerization was low, and higher curing temperature would bring more decomposition.

CONCLUSIONS

A novel kind of phthalonitrile containing allyl (DBPA-Ph) had been successfully synthesized and investigated. The curing and rheological behaviors of the DBPA-Ph were studied. Results indicated that the DBPA-Ph has two stages polymerization: addition polymerization of allyl moiety at lower temperature ($\sim$270°C) and ring-forming polymerization of cyano groups at higher temperature ($\sim$332°C). Moreover, it also manifested that the viscosity and processability of the DBPA-Ph could be readily tuned by varying the process temperature and time. The DBPA-Ph polymers were obtained after certain curing procedure without using any other curing agents. Results demonstrated that the DBPA-Ph polymer exhibited outstanding glass transition temperature (T_g>350°C) and good thermal stability ($T_{5\%}$>430°C). Good processability and improved processing conditions, combined with the outstanding T_g as well as excellent thermal stabilities enable the as-prepared DBPA-Ph polymers to be used as a potential matrix for high performance polymer composites.

ACKNOWLEDGMENTS

REFERENCES

1. Hergenrother, P. M. *High Perform. Polym.* **2003**, *15*, 13.

2. Kuroki, T.; Shibuya, M.; Toriida, S.; Tamai, S. *J. Polym. Sci. Part. A: Polym. Chem.* **2003**, *42*, 2395.

3. Ameduri, B.; Boutevin, B.; Malek, F. *J. Polym. Sci. Part A: Polym. Chem.* **1994**, *32*, 3161.

4. Keller, T. M. *Chem. Mater.* **1994**, *6*, 302.

5. Keller, T. M.; Price, T. R. *J. Macromol. Sci.-Chem.* **1982**, *A18*, 931.

6. Warzel, M. L.; Keller, T. M. *Polymer* **1993**, *34*, 663.

7. Sastri, S. B.; Armistead, J. P.; Keller, T. M. *Polym. Compos.* **1996**, *17*, 816.

8. Zhang, J. H.; Liu, X. H.; Wen, H. R.; Xie, M. L.; Cai, X. X. *Polym. Int.* **1997**, *42*, 363.

9. Sastri, S. B.; Keller, T. M. *J. Polym. Sci., Part. A: Polym. Chem.* **1998**, *36*, 1885.

10. Dominguez, D. D.; Jones, H. N.; Keller, T. M. *Polym. Compos.* **2004**, *25*, 554.

11. Laskoski, M.; Dominguez, D. D.; Keller, T. M. *J. Polym. Sci., Part. A: Polym. Chem.* **2005**, *43*, 4136.

12. Keller, T. M.; Dominguez, D. D. *Polymer* **2005**, *46*, 4614.

13. Dominguez, D. D.; Keller, T. M. *Polymer* **2007**, *48*, 91.

14. Brunovska, Z.; Lyon, R., Ishida, H. *Thermochim. Acta* **2000**, *357*, 195.

15. Keller, T. M. *J. Polym. Sci. Part. A: Polym. Chem.* **1988**, *26*, 3199.

16. Li, W. T.; Zuo, F.; Jia, K.; Liu, X. B. *Chin. Chem. Lett.* **2009**, *20*, 348.

17. Sastri, S. B.; Keller, T. M.; *J. Polym. Sci. Part. A: Polym. Chem.* **1999**, *37*, 2105.

18. Guo, H.; Zou, Y. k.; Chen, Z. R.; Zhang, J. D.; Zhan, Y. Q.; Yang, J.; Liu, X. B. *High Perform. Polym.* **2012**, *24*, 571.

19. Guo, H.; Lei, Y. J.; Zhao, X.; Yang, X. L.; Zhao, R.; Liu, X. B. *J. Appl. Polym. Sci.* **2012**, *125*, 649.

20. Lei, Y. J.; Zhao, R.; Yang, X. L.; Liu, X. B. *J. Appl. Polym. Sci.* **2013**, *127*, 3595.

21. Yang, X. L.; Zhang, J. D.; Lei, Y. J.; Zhong, J. C.; Liu, X. B. *J. Appl. Polym. Sci.* **2011**, *121*, 2331.

22. Yang, X. L.; Lei, Y. J.; Zhong, J. D.; Zhao, R.; Liu, X. B. *J. Appl. Polym. Sci.* **2011**, *119*, 882.

23. Guo, H.; Chen, Z. R.; Zhang, J. D.; Yang, X. L.; Zhao, R.; Liu, X. B. *J. Polym. Res.* **2012**, *19*, 9918.

24. Xu, M. Z.; Yang, X. L.; Zhao, R.; Liu, X. B. *J. Appl. Polym. Sci.* **2013**, *128*, 1176.

25. Andre, S.; Guida-Pietrasanta, F.; Rousseau, A.; Boutevin, B.; Caporiccio, G. *J. Polym. Sci., Part. A: Polym. Chem.* **2000**, *38*, 2993.

26. Kumar, K. S. S.; Reghunadhan Nair, C. P.; Radhakrishnan, T. S.; Ninan, K. N. *Eur. Polym. J.* **2007**, *43*, 2504.

27. Ward, I. M.; Hadley, D. W. John Wiley & Sons, Inc., **1993**; pp 72–95.

28. Montgomery, T. S.; William, J. M. John Wiley & Sons, Inc., **2005**; pp 130–133.

29. Chow, T. S. *Macromolecules* **1980**, *13*, 362.

30. Hancock, B. C.; Zografi, G. *Pharm. Res.* **1994**, *11*, 471.

31. Forrest, J. A.; Dalnoki-Veress, K.; Stevens, J. R.; Dutcher, J. R. *Phys, Rev. Lett.* **1996**, *7*, 2002.

32. Forrest, J. A.; Dalnoki-Veress, K.; Dutcher, J. R. *Phys. Rev. E* **1997**, *56*, 5705.

33. Aïssa, A.; Nour-Eddine, E. B. *eXPRESS Polym. Lett.* **2009**, *3*, 588.

34. Kimura, H.; Ohtsuka, K.; Matsumoto, A. *eXPRESS Polym. Lett.* **2011**, *5*, 1113.