A Novel Benzimidazole-Containing Phthalonitrile Monomer With Unique Polymerization Behavior

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ABSTRACT: A novel benzimidazole-containing phthalonitrile monomer (BIPN) was synthesized. The chemical structure of BIPN was confirmed by various spectroscopic techniques. Differential scanning calorimetry measurement revealed that the self-promoted polymerization reaction of the BIPN proceeds extremely sluggish and showed low polymerization exothermic effect. Subsequent rheological measurement displayed that the BIPN was able to keep a stable and low melt viscosity for 4 h at 300 °C, 2 h at 310 °C, and 50 min at 330 °C. The derived BIPN polymers showed excellent thermal properties revealed by thermogravimetric analysis, which were better than those of the corresponding polymer derived from phthalonitrile monomer without benzimidazole moiety. IR analysis confirmed the occurrence of the triazine ring within the polymer crosslinking sites. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

KEYWORDS: curing of polymers; high performance polymers; high temperature materials; phthalonitrile resin

INTRODUCTION Studies on high temperature/performance resins with terminal reactive groups cured via an addition reaction have received much attention in the past decades. These resins cure via an addition reaction with no volatile byproducts evolved during the processing stage. In addition, the cured resins showed excellent thermal properties. Typical addition-type reactive groups such as cyanate, maleimide, ethynyl, and benzocyclobutene have been fully characterized.[1] Although, resins end-capped with these reactive groups have witnessed application in hi-tech fields such as optical material and microelectric industry,[2] much effort was concentrated on resins terminated with phenylethynyl (PE) group. This is due to their wide processing window and excellent combination of properties. Various spacers containing imide, phenylquinoxaline, and arylene ether moiety were introduced between PE end-caps.[3]

As is well-known, low and stable melt viscosity is of utmost importance for fabrication of thick composite components by resin transfer molding (RTM) or resin infusion methods (RIM). Hergenrother and coworkers have tried to design low molecular weight oligomeric imide resins with terminal PE groups (PEPI), enabling its processing by RTM (melt stability >2 h at 280 °C).[3(a)] Simone and Scola reported that even the lowest reactive PEPI was unlikely to keep a stable and low melt viscosity at 310 °C over 1 h.[4] Therefore, additional improvements such as introduction of flexible or asymmetric linkage are required to further reduce the viscosity of the PEPI with the processing temperature kept below 300 °C.[5] This is required since strong chain–chain interactions and the stiffness of the aromatic backbone are inherent to the nature of aromatic heterocyclic polymers (polyimide, polyphenylquinoxaline, polybenzoxazole, etc.) and result in their high melt viscosity.

On the other hand, phthalonitrile (PN) resins have been studied over the past 30 years as a class of high temperature/performance polymers,[6] having a variety of potential applications for composite matrices,[6,7] adhesives,[8] electrical conductors,[9] and carbon precursors.[10] The polymerization of the neat resins is extremely sluggish and can be promoted by various curing agents such as phenols,[11] organic amines,[12] strong organic acids,[13] strong organic acid/amine salts,[14] metals, and their salts.[15] The PN resins exhibit an attractive combination of properties, that is, outstanding thermal-oxidative stability, high glass transition temperatures (T_g), and superior flame resistance.[6] In addition, a low melt complex viscosity (0.01–1.0 Pa s) of the PN monomers or oligomers enables facile processing by the cost-effective, non-autoclavable processing techniques such as RTM, resin infusion molding, and filament winding. During the past decades, systematic studies have been conducted at Naval Research Laboratory (NRL) on PN resins in terms of cure behavior, processabilities, and properties of the PN resins.[10,16–20]

Additional Supporting Information may be found in the online version of this article.

Oligomeric imide resins with terminal PN units were also prepared and characterized at NRL.[21] Unfortunately, the same problem as that for PE end-capped imide-containing resins cannot be avoided. Low molecular weight imide spacers or chemical structure modifications were also required when processing imide-containing PN resins by RTM or RIM.

The previous investigation, in our laboratory, on amino or hydroxy-containing PN model compounds (APN or HPN) demonstrated that APN or HPN showed a self-promoted thermal polymerization even in the absence of curing additives.[22–24] The systematic investigation on the thermal polymerization behaviors of the HPN indicated that the polymerization proceeds more readily with stronger acidity of the hydroxy group.[24] Therefore, curing of the PN derivatives containing amino or hydroxy groups offers a new and alternative processing mode for PN resins, having the potential of expanding their application range. However, the introduction of amino or phenol groups to PN resulted in undesirable thermal properties.

As an extension of this work, a benzimidazole ring with acidic hydrogen proton was introduced into PN resin (benzimidazole-containing phthalonitrile, BIPN). This is because benzimidazole ring having excellent thermal properties would be more compatible with thermally stable polymers relative to amino or hydroxy groups. We believe that the BIPN may exhibit a similarly or more intensely self-promoted polymerization reaction relative to the HPN, due to the strong acidity of N—H proton on benzimidazole ring. Unexpectedly, an extremely mild self-promoted polymerization was observed for BIPN. Inspired by this result, it would be possible to employ higher initial processing temperatures (in excess of 300 °C) resulting in an initial lower melt viscosity, and then the molecular weight range of the aromatic heterocyclic spacers can be broadened and more flexible chemical structures can be introduced into the spacers. In this work, a type of novel high performance thermosetting resin with unprecedented polymerization behavior (outstanding melt stability (>300 °C) and low polymerization exothermic effect) was found.

EXPERIMENTAL

Materials

4-Nitrophthalonitrile was purchased from Aldrich Chemical Co. (Aldrich). Dimethyl sulfoxide (DMSO), dicyclohexylcarbodiimide (DCC), potassium carbonate, and tetrahydrofuran (THF) were purchased from Tianjin BoDi. 3,5-Dihydroxybenzoic acid, 4-hydroxybenzoic acid, and other chemicals were purchased from Chengdu Kelong chemical reagent and used as received.

Synthesis of Benzimidazole-Containing Phthalonitrile Monomer

Synthesis of Compound 1

To a solution of *o*-phenylenediamine (10.2 g, 0.094 mol) and 3,5-dihydroxybenzoic acid (13.86 g, 0.09 mol) in THF (132 mL) were added dicyclohexylcarbodiimide (19.47 g, 0.094 mol) under nitrogen atmosphere. The mixture was stirred in ice water bath for 24 h. The reaction mixture was filtered and the filtrate was collected. The product, *N*-(2-aminophenyl)-3,5-dihydroxybenzamide, was obtained by bubbling with dry hydrogen chloride into the reaction system, collecting the white precipitate by filtration, subsequently neutralizing the mixture of the white precipitate/THF with NaHCO$_3$, and evaporation of THF after filtration under reduced pressure. The yield was 35% and the product was used in the next synthetic step without further purification.

A solution of *N*-(2-aminophenyl)-3,5-dihydroxybenzamide (4.00 g, 0.011 mmol) in acetic acid (51 mL) was refluxed at 120–130 °C under nitrogen atmosphere for 16 h. After cooling, the solution was maintained at room temperature over night for crystallization. The resulting precipitate (compound **1**) was collected by filtration and dried at 70 °C under reduced pressure for 24 h. The yield was 75%. IR (KBr, cm^{-1}): 3195 (O—H stretching), 1608 (C=N stretching). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.80 (s, 1 H, imidazole NH), 9.54 (s, 2 H, OH), 7.57 (s, 2 H, Ar—H), 7.2 (d, 2 H, Ar—H), 7.01 (s, 2 H, Ar—H), 6.37 (s, 1 H, Ar—H).

Synthesis of BIPN Monomer

To a 100-mL three-neck flask were added 4-nitrophthalonitrile (1.73 g, 10 mmol), compound **1** (1.13 g, 5 mmol), anhydrous potassium carbonate (2.41 g, 0.017 mol) and 30 mL of DMSO. The mixture was stirred at 30 °C under nitrogen for 24 h and then poured into a large amount of water. Then the solution was acidified to pH = 2 by adding concentrated hydrochloric acid. The resulting precipitate was collected by filtration, washed with water until the filtrate was neutral, dried at 70 °C under reduced pressure for 24 h. The yield was 90%. IR (KBr, cm^{-1}): 3587 (N—H stretching), 2233 (C—N stretching), 1597 (C—N stretching). ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.00 (s, 1 H, imidazole NH), 8.19–8.21 (d, 2 H, Ar—H), 8.01 (d, 2 H, Ar—H), 7.87 (d, 2 H, Ar—H), 7.66–7.73 (dd, 2 H, Ar—H), 7.54–7.56 (d, 2 H, Ar—H), 7.32 (d, 1 H, Ar—H), 7.21–7.28 (m, 2 H, Ar—H). Elem. Anal.: calcd for $C_{29}H_{14}N_6O_2$ (H_2O): C, 70.16; H, 3.25; N, 16.93. Found: C, 69.99; H, 3.31; N, 16.84.

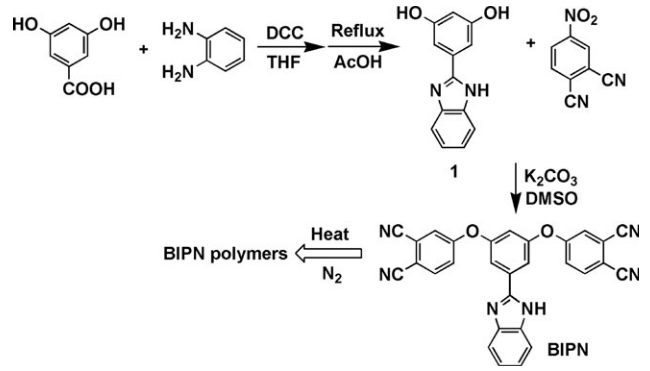
Synthesis of BIPN Polymers

The BIPN polymers were produced by heat treatment in thermogravimetric analysis (TGA) chamber under nitrogen with a flow rate of 50 mL/min with conditions: 310 °C for 4 h or 310 °C for 8 h or 310 °C for 8 h, 330 °C for 2 h, 350 °C for 8 h or 310 °C for 8 h, 330 °C for 2 h, 350 °C for 8 h, 375 °C for 8 h (post-cured polymer).

Synthesis of Model Benzimidazole-Containing Phthalonitrile Compound (MBIPN)

Synthesis of Compound 1′

To a 100-mL three-neck flask were added 4-nitrophthalonitrile (1.74 g, 0.01 mol), 4-hydroxybenzoic acid (1.38 g, 0.01 mol), anhydrous potassium carbonate (3.00 g, 0.021 mol), and 20 mL of DMSO. The mixture was stirred at 30 °C under nitrogen for 24 h and then poured into a large amount of water. Then the solution was acidified to pH = 2 by adding concentrated hydrochloric acid. The resulting white



SCHEME 1 Synthesis and polymerization of BIPN monomer and polymers.

precipitate was collected by suction filtration, and washed with water until the filtrate was neutral, dried at 70 °C under reduced pressure for 12 h. Yield: 2.17 g, 82%. The crude product was used in the next reaction without purification. IR (KBr, cm^{-1}): 2230 (C—N stretching), 1675 (C=O stretching). ^1H NMR (400 MHz, DMSO-d_6): δ 13.01 (s, 1 H, COOH), 8.14–8.16 (d, 1 H, Ar—H), 8.02–8.04 (d, 2 H, Ar—H), 7.92–7.93 (d, 1 H, Ar—H), 7.52–7.55 (dd, 1 H, Ar—H), 7.25–7.27 (s, 2 H, Ar—H).

Synthesis of Compound 2′

To a solution of *o*-phenylenediamine (1.14 g, 10.1 mmol) and compound **1′** (4.06 g, 0.01 mol) in THF (50 mL) were added dicyclohexylcarbodiimide (2.16 g, 10.4 mmol) under nitrogen atmosphere. The mixture was stirred in ice/water bath for 24 h and then filtered. The filtrate was poured into a large amount of water. The resulting precipitate was collected by filtration and dried at 55 °C under reduced pressure for 12 h. The crude product was purified by purging dry HCl gas into its THF solution, producing hydrochloric acid salt precipitate, which was collected by filtration and then neutralized using 5 wt % aqueous solution of Na_2CO_3. Yield: 1.24 g, 35%. IR (KBr, cm^{-1}): 3458, 3371 (N—H symmetrical and asymmetrical stretching), 2230 (C—N stretching), 1645 (C=O stretching). ^1H NMR (400 MHz, DMSO-d_6): δ 9.87 (s, 1 H, amide NH), 8.11–8.17 (m, 3 H, Ar—H), 7.89–7.90 (d, 1 H, Ar—H), 7.48–7.51 (dd, 1 H, Ar—H), 7.31–7.33 (d, 2 H, Ar—H), 7.20–7.22 (d, 1 H, Ar—H), 7.03–7.07 (t, 1 H, Ar—H), 6.90 (d, 1 H, Ar—H), 6.75 (s, 1 H, NH_2).

Synthesis of MBIPN

A solution of compound **2′** (4.00 g, 0.011 mmol) in acetic acid (51 mL) was refluxed for 6 h. After cooling to room temperature, the reaction solution was poured into ice water. The resulting precipitate was collected by filtration and purified by recrystallization from methanol/acetonitrile mixed solvents. Yield: 1.84 g, 50%. IR (KBr, cm^{-1}): 3579 (N—H stretching), 2230 (C—N stretching), 1595 (C=N stretching). ^1H NMR (400 MHz, DMSO-d_6): δ 12.99 (s, 1 H, imidazole NH), 8.27–8.29 (d, 2 H, Ar—H), 8.14–8.16 (d, 1 H, Ar—H), 7.93–7.94 (d, 1 H, Ar—H), 7.60 (s, 2 H, Ar—H), 7.52–7.54 (dd, 1 H, Ar—H), 7.36–7.38 (d, 2 H, Ar—H), 7.20–7.22 (m, 2 H, Ar—H). Elem. Anal.: Calcd for $C_{21}H_{12}N_4O(H_2O)$: C, 71.18; H, 3.98; N, 15.81. Found: C, 71.90; H, 4.21; N, 15.48.

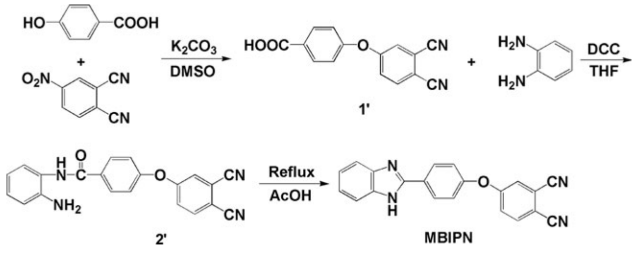
Characterization

^1H NMR (400 MHz) was measured on a Bruker Avance-400 NMR spectrometer with DMSO-d_6 as the solvent and tetramethylsilane as the internal standard. IR spectra were recorded with a Nicolet FTIR-380 Fourier transform infrared spectrometer by KBr pellet. Elemental analyses (EA) were performed on a Italy CARLO ERBA 1106 elemental analyzer. TGA was carried out with a TA instrument Q500 thermogravimetric analyzer at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was performed on a TA instrument Q200 differential scanning calorimeter under nitrogen atmosphere at a heating rate of 10 °C/min. Rheological experiments were conducted on a TA instruments AR-2000 rheometer in conjunction with an environmental testing chamber for temperature control. The measurements were made using a 25 mm diameter parallel plates at low strain values (2.5×10^{-4}) and a frequency of 1 Hz. The sample specimen disks, 25 mm in diameter, and 1.0–1.1 mm thick, were prepared by press-molding the BIPN powder (around 0.5 g) at room temperature. The compacted sample disk was subsequently loaded in the rheometer fixture. The dynamic storage modulus as a function of temperature was measured from 50 to 400 °C at a heating rate of 5 °C/min in air. The dynamic storage modulus of BIPN was also monitored at 300, 310, and 330 °C in air as a function of time, where the temperatures were rapidly ramped to required values at a heating rate of 50 °C/min and equilibrated for 1 min, respectively.

RESULTS AND DISCUSSION

Monomer Synthesis

The BIPN monomer was synthesized in three steps (Scheme 1). Direct condensation between 3,5-dihydroxybenzoic acid and 1,2-phenylenediamine using dicyclohexylcarbodiimide (DCC) as the dehydration catalysis and subsequent cyclodehydration in acetic acid afforded compound **1**. The BIPN was readily synthesized by simple nucleophilic displacement between compound **1** and 4-nitrophthalonitrile in the yield of 90%. The chemical structure of the BIPN was unambiguously confirmed by IR, ^1H NMR, and EA. The model benzimidazole-containing PN (MBIPN) compound was synthesized according to Scheme 2. Its chemical structure was also verified by IR, ^1H NMR, and EA.



SCHEME 2 Synthesis of MBIPN compound.

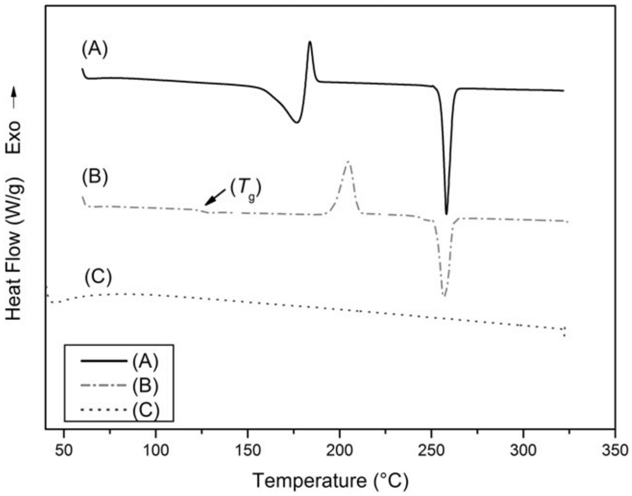


FIGURE 1 DSC curves of BIPN under nitrogen atmosphere: (A) First scan at a heating rate of 10 °C/min; (B) second scan at a heating rate of 10 °C/min immediately after first scan; (C) Second scan at a heating rate of 20 °C/min immediately after isothermal scan at 310 °C for 8 h in the DSC.

Polymerization Behavior of BIPN

The thermal behaviors of the BIPN were studied by DSC. The DSC first and second scan curves are plotted in Figure 1(A, B). Two endothermic peaks at approximately 175 °C and 250 °C are corresponding to loss of crystalline water and melting transition of BIPN, respectively. The crystalline water loss can be confirmed by its TGA result that a 3.44% weight loss between 80 and 180 °C was found, which is consistent well with the calculated value of 3.62%. The elemental analysis result of the BIPN also supported this inference. An exothermic peak at approximately 185 °C can be attributed to the recrystallization of the BIPN after loss of the crystalline water. A glass transition was observed at about 120 °C in the second scan curve, in which the crystallization and melting peaks of the BIPN were similar to those in the first scan curve. Neither curve showed any exothermic peaks at elevated temperatures due to curing, implying that the polymerization is progressing at a very slow rate. This nature is totally different compared to those of other thermosetting resins. Following the heat treatment (310 °C for 8 h) in the DSC chamber, the sample did not show a T_g, indicating that its crosslinking density had increased to a point where little molecular mobility was present within the polymeric backbone [Figure 1(C)]. After heat treatment in the DSC, the insolubility of the BIPN polymers in solvents such as NMP, DMF, and concentrated H_2SO_4 further indicated the occurrence of the crosslinking reaction (Supporting Information Table S1).

Rheological measurements were conducted to further elucidate the polymerization behavior of the BIPN. The storage modulus of the BIPN monomer was tested as a function of temperature from 50 to 400 °C (Supporting Information Fig. S1). The monomer displayed a rapid decrease in modulus on melting at 250 °C, and did not show a distinctive increase in modulus within the temperature range of 250–400 °C.

Inspired by these results, it is interesting to investigate the melt stability of the BIPN above 300 °C. Modulus versus time measurements at different temperatures of 300, 310, and 330 °C were conducted, as shown in Figure 2. The data showed that a stable and low modulus can be kept for an unexpectedly long time. The BIPN did not show a distinctive increase in modulus within 4 h dwell at 300 °C, 2 h at 310 °C, and 50 min at 330 °C. On the other hand, a rapid increase in modulus for BIPN can be observed after 5 h dwell at 300 °C, 2.5 h at 310 °C, and 1 h at 330 °C. In contrast, model PN monomer, 1,3-bis(3,4-dicyanophenoxy)benzene, did not show an increase in modulus even after 5.5 h dwell at temperature of 310 °C (Supporting Information Fig. S2). The result unambiguously indicated the role of benzimidazole ring in promoting the polymerization rate of the PN resins. This unique polymerization behavior is not only advantageous for BIPN to be processed into thick composite sections by the cost-effective, non-autoclavable processing techniques such as RTM or RIM, but also it can afford more flexibility for the design of the aromatic heterocyclic spacers between PN end-caps. To the best of our knowledge, the polymerization behavior of the BIPN monomer was unprecedented among currently studied resin systems such as PE resin, for which even the lowest reactive PEPI is unlikely to keep a stable and low melt viscosity at 310 °C over 1 h.[4]

Thermal Properties of BIPN Polymers

The BIPN polymers were produced by heat treatment in TGA chamber under nitrogen with a flow rate of 50 mL/min (Scheme 1). Figure 3 shows the TGA curves of the BIPN monomer and polymers. The thermal stability was found to be a function of the curing cycle. As the cure time and temperature was increased, an improvement in the thermal stability was observed. However, further heating of the BIPN to 350 °C showed a less pronounced progression in the thermal properties. Fortunately, the char yields or weight retention (800 °C) of the BIPN post-cured polymer were still in excess

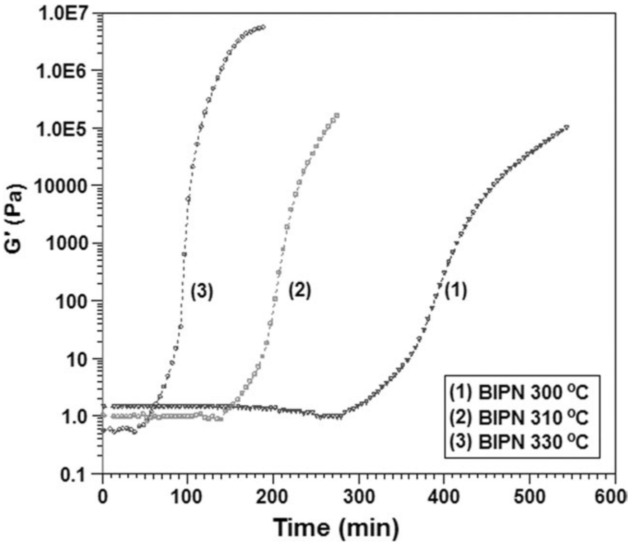


FIGURE 2 Storage modulus vs. time curves for BIPN monomer at 300, 310, and 330 °C.

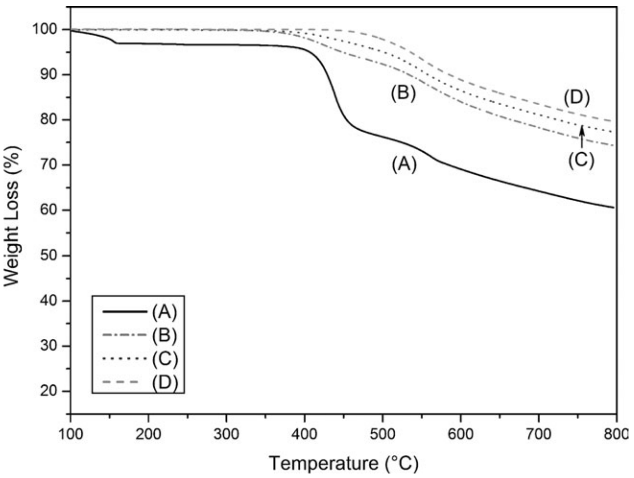


FIGURE 3 TGA curves of powdered BIPN (A) in nitrogen and BIPN polymers cured with conditions: (B) 310 °C for 4 h; (C) 310 °C for 8 h; (D) 310 °C for 8 h, 330 °C for 2 h, 350 °C for 8 h.

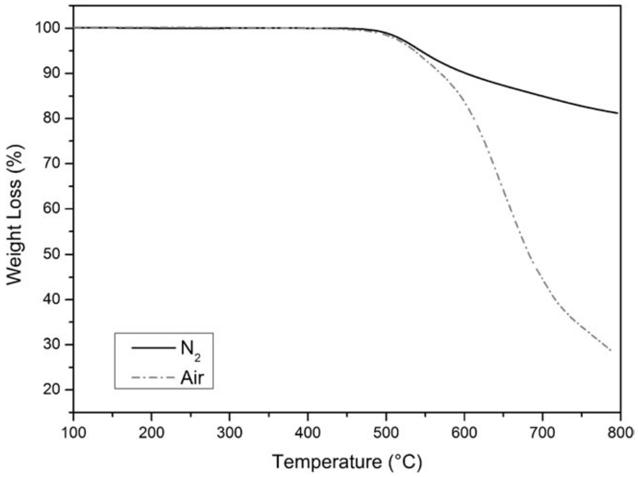


FIGURE 4 Thermal and thermo-oxidative stability of BIPN post-cured polymer (310 °C for 8 h, 330 °C for 2 h, 350 °C for 8 h, 375 °C for 8 h) under nitrogen and air atmosphere.

of 80% in N_2 and 25% in air (Figure 4). The values were higher than those of the 1,3-bis(3,4-dicyanophenoxy)benzene-based PN polymer,[25] suggesting that introduction of benzimidazole ring is effective in maintaining the outstanding thermal properties of PN resins.

The polymerization reaction was monitored by IR technique, as shown in Figure 5. Nitrile group absorption peak was at around 2227 cm^{-1} for BIPN monomer, which obviously diminished in intensity after heat treatment. A less pronounced change in absorption peak of nitrile group was observed for the BIPN polymers and post-cured polymer. The tendency is consistent with that of polymer thermal property improvement. New absorption peaks at 1520 cm^{-1} were observed, indicating the formation of triazine ring during the polymerization of the PN groups.[26] In addition, the nitrile absorptions of the polymers shifted to lower wavenumbers relative to that of the BIPN monomer, similar to a previous report when cyano groups are converted to triazine ring.[26]

Thermal Behavior of Model Compounds

Thermal behaviors of MBIPN compound and model hydroxy-containing PN (*m*-HPN) were comparatively studied by DSC and rheology analysis to further understand the unique polymerization behaviors of BIPN. *m*-HPN displayed an obviously exothermic peak at about 230 °C, which was not observed for MBIPN on the DSC curve (Supporting Information Fig. S3). The rheological measurement also indicated that the cure reaction for the MBIPN was much less intense relative to hydroxy-containing PN (Supporting Information Fig. S4). One should keep in mind that MBIPN has much stronger acidic hydrogen proton (N—H proton) relative to that of *m*-HPN (—OH proton), determined by their different chemical shift on the ^{1}H NMR spectra. The results seems to be contradictory to the previously obtained principle that the self-promoted polymerization reaction proceeds more intensely and rapidly under stronger acidic conditions.[24] It has been proposed that the polymerization of PN monomer was promoted through protonated nitrile groups undergoing nucleophilic attack by Lewis base.[14] Our previous results on hydroxy-containing PN model compounds can also be interpreted using this mechanism.[24] However, in this article, we believe new interpretation about the unique polymerization behavior of the BIPN may be proposed. This will be our concern in the future.

CONCLUSIONS

A novel BIPN monomer was synthesized. Benzimidazole ring is responsible for the self-promoted polymerization reaction of the BIPN. The unique polymerization behavior (outstanding melt stability (>300 °C) and low polymerization exothermic effect) of the BIPN is favorable to processing into complex composite structures by RTM or RIM, and afforded more

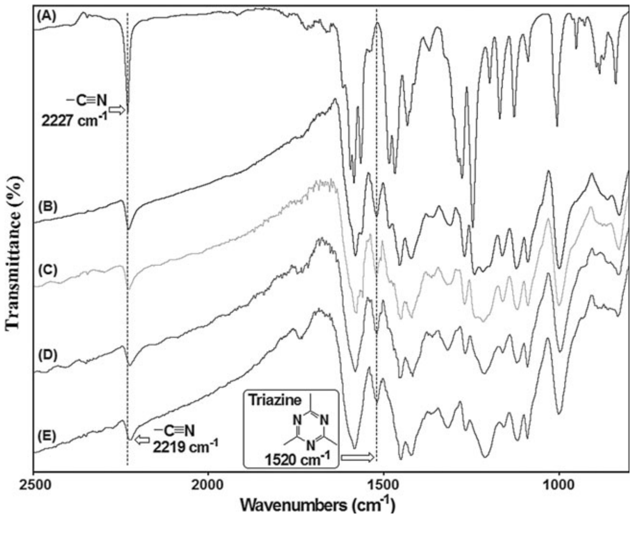


FIGURE 5 IR spectra of BIPN (A) and BIPN polymers cured under conditions: (B) 310 °C for 4 h; (C) 310 °C for 8 h; (D) 310 °C for 8 h, 330 °C for 2 h, 350 °C for 8 h; (E) BIPN post-cured polymer.

flexibility for designing aromatic heterocyclic spacers. Improvement in the thermal properties of the BIPN polymers can be attributed to addition-type polymerization reaction of PN groups and resultant triazine formation. Studies on model compounds (MBIPN and *m*-HPN) showed that the thermal polymerization of the MBIPN was significantly less intense relative to that of hydroxy-containing PN, although MBIPN has much stronger acidic hydrogen proton. These results imply a significant breakthrough and a new opportunity for designing high temperature/performance resins. To explain the origin of the BIPN unique cure behavior, more in-depth studies on polymerization mechanism will be reported in a separate paper.

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