

Novel Thermal Polymerization Synergistic Behavior of Phthalonitrile-Phenylethynyl Resins

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ABSTRACT

The phthalonitrile and phenylethynyl end-capped imide compounds and their blends are prepared and characterized. Rheological studies show that the processability of the blends can be adjusted by changing the molar concentration of the phenylethynyl component. Isothermal DSC and IR characterization spectra suggest that the adjustable processability of the blends can be interpreted by a kind of chemical interaction, “thermal polymerization synergistic effect”. Furthermore, the cured polymers exhibit excellent thermal stability and good compatibility.

KEYWORDS: phthalonitrile, phenylethynyl, thermal polymerization synergistic effect, imide, curing

INTRODUCTION

Phthalonitrile resins, as a type of high performance thermosetting materials, have been widely studied in the past decades, due to the outstanding combination of properties such as thermal and oxidative-thermal stability, low water uptake and flame-retardance.¹⁻⁴ However, the polymerization of the neat resin is extremely sluggish, thus limiting their application.⁵ Since 1970s, systematic studies have been conducted at U.S Naval Research Laboratory (NRL) to improve the resin processability by using curing additives such as amine, phenols and strong organic acid, which can promote the resin curing reaction *via* an addition reaction mechanism.^{3,6-9,10,11} This improvement expanded the potential applications of the resins for composite matrices, adhesives, electrical conductors, and carbon precursors. In the past years, considerable research efforts have been expended on phthalonitrile polymer in our laboratory, with concentration on exploring new processing approaches such as developing novel curing additive and self-promotion curing system.¹²⁻¹⁸

Phenylethynyl end-capped thermosetting resins have also received much attention.¹⁹⁻²¹ It was reported that the phenylethynyl-based imide oligomers exhibits a large processing window. The thermal cure undergoes a complex radical reaction process, involving the broken of triple bond to form radicals, subsequently chain extension, branching, crosslinking and cyclization to afford a conjugated polyene or a cyclic structure.²²⁻²³ The derived polymers exhibit unique thermal and dimensional stability, excellent chemical resistance and mechanical properties, which offer promise for advanced composites application. However, the intensively curing exothermic effect of the phenylethynyl-based resins was an unbeneficial characteristic for fabrication of thick composite sections.

In this study, phthalonitrile and phenylethynyl end-capped imide model compounds (**3PNODPA** and **3PEODPA**) and their blends (**PNPE**) were prepared, with an aim to combine their own curing characteristics, which may offer a new type of resin systems with adjustable processability and tailored properties. The results showed that the curing rate of phenylethynyl group in the blends **PNPE** slows down, while that of phthalonitrile group was significantly promoted, compared to the neat compounds. This type of chemical interaction between the groups is defined as “thermal polymerization synergistic effect”. As is mentioned above, promotion of the phthalonitrile curing reaction was usually achieved by using basic or

acidic curing agents. Unexpectedly, a free-radical producible group, phenylethynyl, can also accelerate the cure reaction of the phthalonitrile. Furthermore, the fully cured product shows comparable or even higher thermal stability relative to that of the cured neat phenylethynyl resins. These results offer promise for seeking new approach to design high performance thermosetting materials.

EXPERIMENTAL

Materials

3-phenoxyaniline was obtained from Alfa Aesar Chemical Co. Ltd, 3-phenylethynyl aniline was obtained from Shanghai Apichemical Co. Ltd, and both were used without further purification. 4-nitrophthalonitrile was obtained from Ji'nan Weido Chemical Co. Ltd, and recrystallized from ethanol. 4-(3-aminophenoxy) phthalonitrile was synthesized by the nucleophilic nitro displacement reaction according to a published literature.^{8(b)} 4, 4'-oxydiphthalic dianhydride (ODPA) was obtained from Shanghai Research Institute of Synthetic Resins. Dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP) and pyridine was purified by distillation under reduced pressure over calcium hydride. Other chemicals were used as received unless otherwise stated.

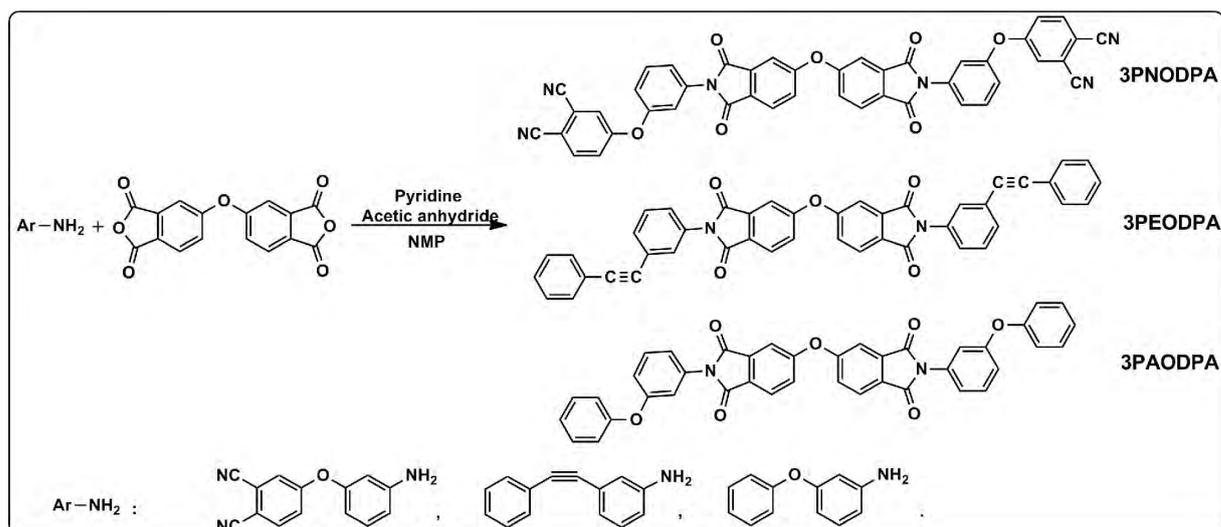
Synthesis of Compound 3PNODPA, 3PEODPA, 3PAODPA

The **3PNODPA** was prepared as follows. As shown in SCHEME 1, 4-(3-aminophenoxy) phthalonitrile (4.75 g, 20.2 mmol) was dissolved in 40 mL dry NMP in a 100 mL, three-neck round-bottom flask equipped with a teflon stirring bar, under a nitrogen atmosphere in ambient conditions. After all of the amine was dissolved, ODPA (3.10 g, 10 mmol) was then added under a nitrogen atmosphere protection, stirring continued for 6 h at room temperature. To this solution was added mixture solution of acetic anhydride (98.5%, 11.5 mL, 12.44 g; 120 mmol) and pyridine (99.5%, 8.5 mL, 8.35 g; 105 mmol) with stirring under nitrogen. Then the temperature of the reaction mixture was increased to 100 °C and held at this temperature for 3 h, and the resulting mixture was then imidized *via* chemical dehydration. After cooling to room temperature, the phthalonitrile end-capped imide compound **3PNODPA** was finally precipitated by adding the solution into distilled water, filtered, washed in methanol to remove the NMP. This light brown colored precipitates were dried under vacuum for 12 h at 50 °C. Yield: 7.15 g (96%). Compound **3PEODPA** and **3PAODPA** were prepared using appropriate reagents adopting similar procedure. The crude product was further purified *via* reflux with hot methanol for 2 h and dried before characterization by means of ¹H NMR, IR and elemental analysis.

3PNODPA: yield: 96%; mp 245 °C; ¹H NMR (400 MHz, DMSO-*d*₆, δ): 8.17-8.14 (d, 2H; Ar H), 8.10-8.07 (d, 2H; Ar H), 7.91 (s, 2H, Ar H), 7.68-7.63 (t, 6H; Ar H), 7.51-7.47 (dd, 2H; Ar H), 7.43-7.40 (d, 2H, Ar H), 7.33-7.28 (m, 4H; Ar H); IR (KBr): ν = 2234 (w, C≡N), 1778 (s, C=O), 1721 (vs, C=O), 1372 (ms, C-N), 745 cm⁻¹ (m, C=O); Anal. calcd for C₄₄H₂₀N₆O₇: C 70.97, H 2.71, N 11.29; found: C 70.77, H 2.38, N 11.26.

3PEODPA: yield: 96%; mp 154 °C; ¹H NMR (400 MHz, DMSO-*d*₆, δ): 8.12-8.09 (d, 2H; Ar H), 7.68-7.66 (m, 6H; Ar H), 7.63 (d, 2H, Ar H), 7.61-7.58 (m, 6H; Ar H), 7.54-7.50 (m, 2H; Ar H), 7.46-7.44 (t, 6H; Ar H); IR (KBr): ν = 2210 (w, C≡C), 1779 (s, C=O), 1721 (vs, C=O), 1371 (ms, C-N), 744 cm⁻¹ (m, C=O); Anal. calcd for C₄₄H₂₄N₂O₅: C 79.99, H 3.66, N 4.24; found: C 79.76, H 3.08, N 4.09.

3PAODPA: yield: 95%; mp 197 °C; ¹H NMR (400 MHz, DMSO-*d*₆, δ): 8.06-8.03 (d, 2H; Ar H), 7.63-7.59 (dd, 4H; Ar H), 7.56-7.50 (t, 2H; Ar H), 7.46-7.40 (t, 4H; Ar H), 7.23-7.16 (q, 4H, Ar H), 7.13-7.06 (m, 8H; Ar H); IR (KBr): ν = 1780 (s, C=O), 1722 (vs, C=O), 1374 (ms, C-N), 744 cm⁻¹ (m, C=O); Anal. calcd for C₄₀H₂₄N₂O₇: C 74.53, H 3.75, N 4.35; found: C 74.65, H 3.64, N 4.21.



SCHEME 1 Synthesis of functionalized end-capped imide compound: **3PNODPA**, **3PEODPA**, **3PAODPA**.

Preparation of Blends

All blends (**3PNODPA/3PEODPA PNPE** or **3PAODPA/3PEODPA PAPE**) were prepared by dissolving or dispersing the compounds in ethyl acetate, vacuum-distilled to remove the residual solvent, and subsequently grounded into fine powder. The molar concentrations of **3PEODPA** in the blends were adjusted to 30% and 50%, which are for the convenience marked with the symbol **PNPE-37**, **PNPE-55**, **PAPE-37**, **PAPE-55**, respectively.

Characterization

¹H NMR (400 MHz) spectra were measured on a Bruker Avance-400 NMR spectrometer with DMSO-*d*₆ as the solvent and tetramethylsilane as the internal standard. Elemental analysis was performed on an Italy CARLO ERBA 1106 elemental analyzer. Thermogravimetric analysis (TGA) was carried out with a TA instrument Q500 Thermogravimetric analyzer in flowing nitrogen of 60 mL min⁻¹ at a heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) was performed on a TA instrument Q200 Differential Scanning Calorimeter using about 3 mg of the sample at a heating rate of 10 °C min⁻¹ and a flow nitrogen rate of 50 mL min⁻¹.

Rheological measurement

The rheological behavior of the imide compound was studied by dynamic oscillation employing a TA Instruments AR-2000ex rheometer in conjunction with an environmental testing chamber for temperature control. Different dynamic curing experiments between 30 °C and the specified temperature, with a heating rate of 5 °C min⁻¹ and at the frequency of 1 Hz were performed as well. For the time sweep test, the heating rate for oscillatory temperature ramp was 50 °C min⁻¹, and the measurements were carried out during isothermal cure in the temperature of 350, 340, 330 °C, with an angular frequency of 1 Hz and an initial strain of 2.5 × 10⁻⁴. The dynamic storage modulus (*G'*) of imide compound and blends was determined in air after melting powdered samples between parallel plates in the test chamber of the rheometer. The variation of the viscoelastic properties during cure, such as loss modulus (*G''*) and dynamic viscosity ($|\eta^*|$) were also recorded as a function of the reaction time. All rheological measurements were made at low strain values (2.5 × 10⁻⁴) using 25mm-diameter parallel plates. Normal force control (1.0 × 10⁻⁴ N) was utilized throughout the tests to keep the samples taut. The dynamic storage modulus (*G'*) of phthalonitrile blends was monitored in air under isothermal conditions as a function of phenylethynyl molar concentration and time at several different specified temperatures.

Fourier-Transform infrared spectroscopy (IR)

The samples for IR test are prepared by heat treatment in TGA chamber under isothermal condition in N₂. The detailed isothermal TGA program was shown as follow: in flowing nitrogen of 60 mL min⁻¹, at a heating rate of 50 °C min⁻¹ from room temperature (RT) to specified temperature and kept isothermal at that temperature for several different times, then quenched to RT. IR spectra of the cured samples were recorded with a Nicolet FTIR-460 Fourier transform infrared spectrometer by KBr pellet from 4000 to 400 cm⁻¹ at a resolution of 4 cm⁻¹ by 32 scans.

Isothermal Differential Scanning Calorimetry (DSC)

3.5–4.0 mg samples were loaded into the aluminum sample pan. To measure the total cure heat, Q_T , evolved during the complete cure, dynamic DSC analysis was carried out from RT to specified temperature at the heating rate of 50 °C min⁻¹ and the samples was kept at that temperature for several different times, and then quenched to RT, followed by performing second scan to 450 °C to record the remained heat. All tests were performed under nitrogen atmosphere at a flow rate of 50 mL min⁻¹.

RESULTS AND DISCUSSION

Rheometric studies

Rheometric measurements were performed on the compound and blends of different molar ratios. FIGURE 1(a) compares the storage modulus, G' , of the equi-molar ratio blends **PNPE** (**PNPE-55**) as a function of time at 350, 340 and 330 °C. The data revealed that the higher the temperature, the faster the modulus increased. The initial melt viscosity is very low, and maintained at about 0.09~0.2 Pa.s for a relatively long time. The rheological behavior of the blends indicated that there is a very large process window advantage for these materials. Then, we change the molar ratio of blends **PNPE** to further confirm their adjustable thermal processing features.

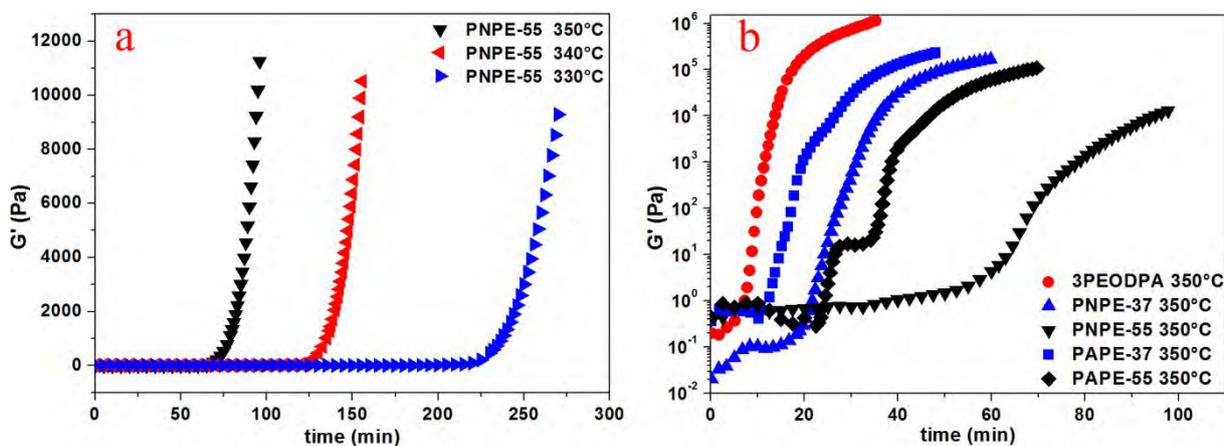


FIGURE 1 Storage modulus (G') as a function of time for (a) blends (**PNPE-55**) at various temperatures: 350, 340 and 330 °C, (b) compound **3PEODPA** and blends **PNPE** or **PAPE** with different molar ratio.

In FIGURE 1(b), storage modulus is shown as a function of time at 350 °C for the phenylethynyl-based compound **3PEODPA** and the phthalonitrile-containing blends **PNPE** or phenoxy-containing blends **PAPE** therefrom. All of the samples exhibited a storage modulus of less than 1 Pa at 350 °C. When held at 350 °C for a period of time, the storage modulus of the blending compositions with higher phenylethynyl concentrations increased at a faster rate. The studies revealed that the polymerization rate of blends **PNPE** can be easily controlled by varying the concentration of compound **3PEODPA**, which is, the higher the phenylethynyl concentration, the faster the curing rate, or vice versa. The results also revealed that there is

a large and adjustable process window, which is helpful in the fabrication of large size composite sections. Interestingly, through a comparative study of the thermal behavior of **PNPE** and **PAPE**, we could find that the trend of thermal polymerization rate of **PNPE** slowed down significantly compared with the neat compound **3PEODPA**, which cannot be mainly attributed to the physical dilution effect of the blends. Therefore, we hypothesized that there occurred unknown synergistic effects or chemical interaction between phenylethynyl and phthalonitrile groups. To verify it, we conducted isothermal IR and DSC studies.

Isothermal IR and DSC

Isothermal cure conversion curves derived from IR and DSC measurements for the samples at three different temperatures are shown in FIGURE 2.

For IR measurement, the absorption peak data of the functional groups were normalized to obtain the correlation between conversion and time. The reaction conversion of the samples during the curing process can be given by the consumption of C≡C triple bonds and C≡N triple bonds through the calculation of the decreased intensities of the bands at 2208 cm⁻¹ (ν_{C=C}) and 2234 cm⁻¹ (ν_{C=N}), respectively. The absorption of imide C=O stretching around 1720 cm⁻¹ and 1780 cm⁻¹, inert from the reactions, can be used as internal standard.²⁴ Therefore, the reaction conversion α was calculated by eq. (1) and (2)

$$\alpha_{CC} = 1 - \left(\frac{I^{2208}}{I^{1720+1780}} \right)_t / \left(\frac{I^{2208}}{I^{1720+1780}} \right)_{t=0} \quad (1),$$

$$\alpha_{CN} = 1 - \left(\frac{I^{2234}}{I^{1720+1780}} \right)_t / \left(\frac{I^{2234}}{I^{1720+1780}} \right)_{t=0} \quad (2).$$

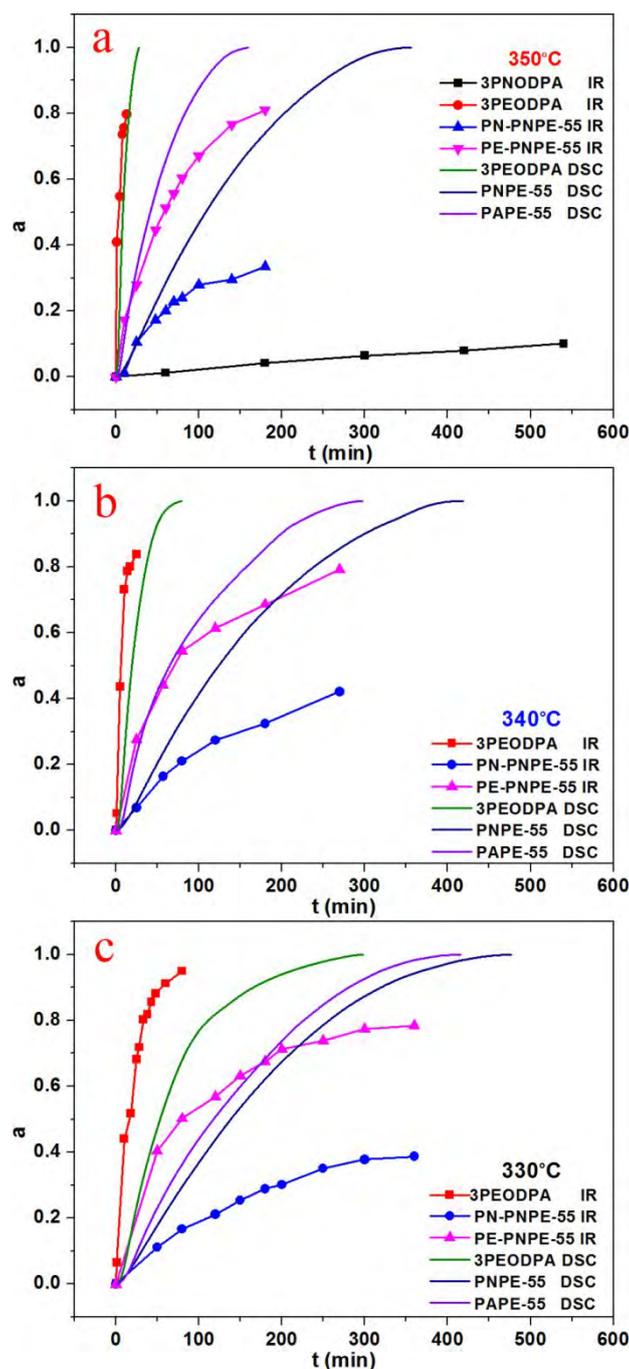


FIGURE 2 Conversion vs. time by isothermal IR and DSC at 350, 340 and 330 °C for compound **3PEODPA** or **3PNODPA** and blends **PNPE-55** or **PAPE-55**.

The quantitative results are shown in FIGURE 2. The **PN-PNPE-55** and **PE-PNPE-55** represents the functional group $C\equiv N$ and $C\equiv C$ in the blends **PNPE-55**, respectively. The reaction conversion of the samples increased with the increase of cure time, when heated at 350, 340, 330 °C in nitrogen atmosphere, respectively. It was easily found that the higher the heat treatment temperature, the faster the reaction rate of the **3PEODPA**, **PN-PNPE-55** or **PE-PNPE-55**. A very valuable result is that the reaction rate of functional group $C\equiv C$ in blends **PNPE-55** is lower than that of the neat compound **3PEODPA**, while the reaction rate of functional group $C\equiv N$ is higher than that of the neat compound **3PNODPA**. It unambiguously showed the introduction of phenylethynyl into the phthalonitrile system accelerates the $C\equiv N$ curing process, and the curing rate of phenylethynyl was inhibited by phthalonitrile groups. The

phenomenon, which is defined as “thermal synergistic polymerization effect” between C≡C and C≡N groups, could be responsible for the adjustable curing behavior of the blends **PNPE**. In addition, considering the another important fact that the temperature (330-350 °C) independency of the C≡N curing reaction in the blends **PNPE-55** (FIGURE 2), the thermal polymerization behavior of the C≡N groups was mainly associated with thermal polymerization activity of C≡C groups.

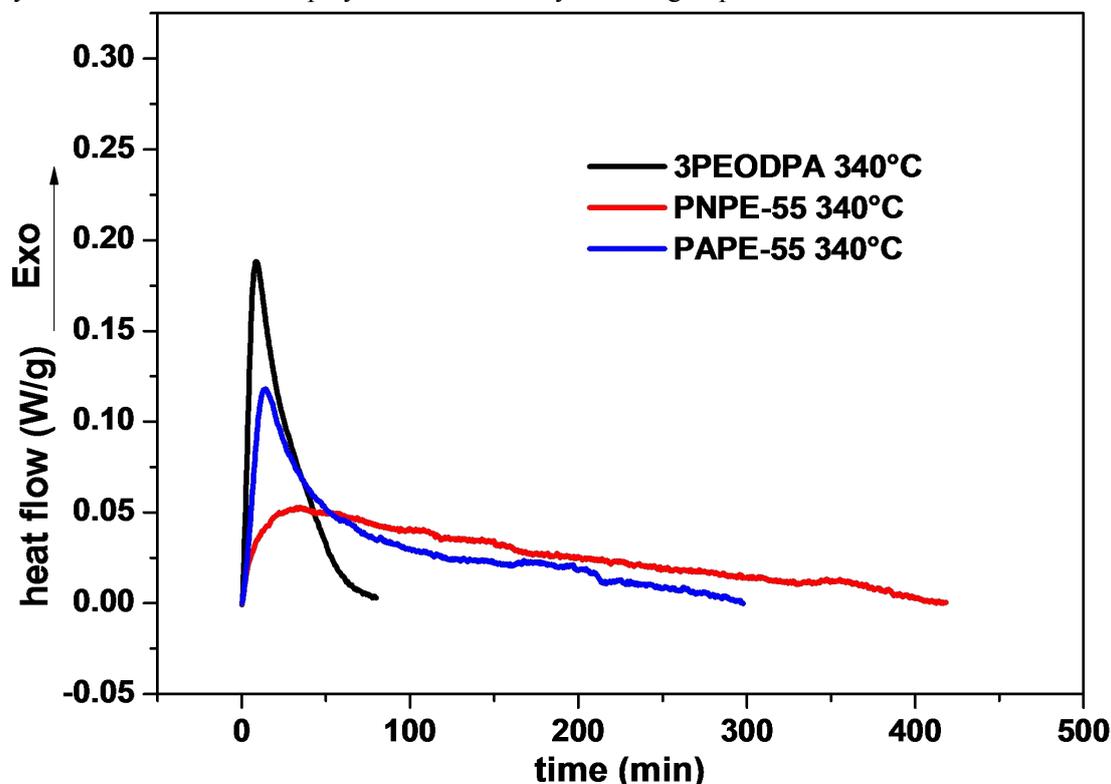


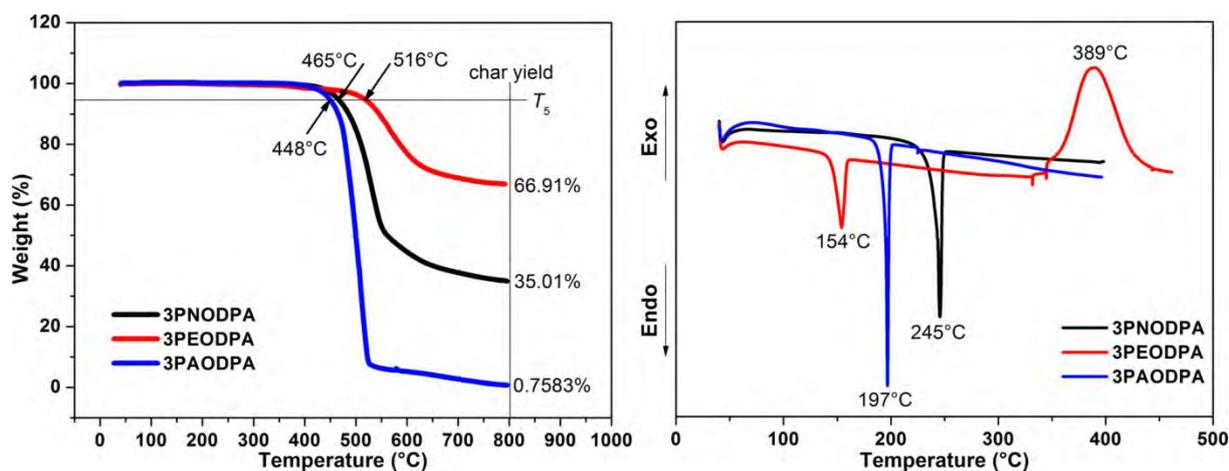
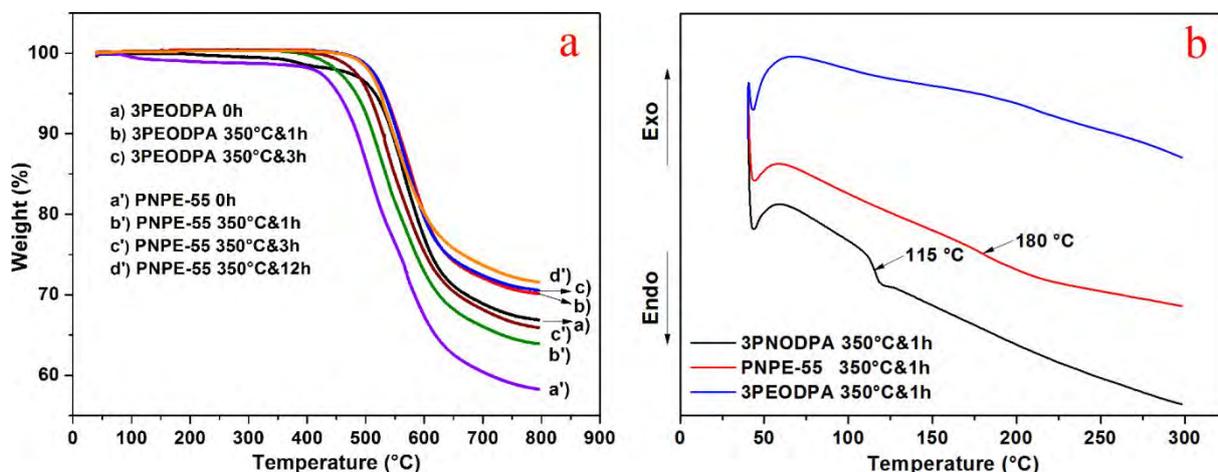
FIGURE 3 isothermal DSC curves of samples at 340 °C

Isothermal DSC measurements were conducted to provide further evidence of “thermal synergistic polymerization effect” (FIGURE 3). The cure reaction exothermic heat is assumed to be directly proportional to the extent of reactant conversion.²⁵ The degree of conversion α can be calculated by eq. (3)

$$\alpha = \frac{Q}{Q_T} \quad (3).$$

Where Q is the heat of reaction of partially cured samples and Q_T is total exothermic heat. The times to reach $\alpha = 0.8$ at 350, 340 and 330 °C were 15.9, 36.3, 111.1 min for **3PEODPA**, 203.0, 238.6, 257.1 min for **PNPE-55**, 83.3, 157.2, 226.3 min for **PAPE-55**, respectively, shown in FIGURE 2. It was expected that the conversion trend from isothermal DSC agrees well with that of IR data. The results strongly suggested that both characterization data are credible, and the DSC exothermic peak can be mainly attributed to the group C≡C cure reaction. Thus, the DSC results also indicated that the thermal polymerization of the C≡C group was inhibited by C≡N group involving a chemical interaction not completely by physical dilution effect of blending, in fact which only plays a minor role under higher curing temperature of 350 °C.

Thermal Properties


 FIGURE 4 TGA and DSC curves of the compounds **3PNODPA**, **3PEODPA** and **3PAODPA** in N_2

 FIGURE 5 Thermal properties in N_2 of the compound and the cured polymers after successively isothermal TGA measurements. Glass transition temperature (T_g) determined on the cured samples by DSC at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ in the second heating scan.

In FIGURE 4, thermal properties of the compounds were shown by TGA and DSC. And thermal properties of the cured samples were evaluated by TGA and summarized in FIGURE 5(a). All of the polymers derived from **3PEODPA** and **PNPE-55** exhibited excellent thermal stability with the temperatures at 5 wt% of weight loss in the range of $532\text{--}533\text{ }^\circ\text{C}$ and of $483\text{--}525\text{ }^\circ\text{C}$ in nitrogen, respectively. The residual weight retentions at $800\text{ }^\circ\text{C}$ for the cured polymers exceeded 63%. The slower enhancement trend in thermal stability for **PNPE-55** further implied the lower cure reaction rate relative to the neat **3PEODPA**. Fortunately, the polymer from **PNPE-55** cured at $350\text{ }^\circ\text{C}$ for 12 h, showed comparable or higher thermal stability relative to that from the neat **3PEODPA**, indicating the introduction of the **3PNODPA** into the **3PEODPA** system did not compromise the thermal stability of the material. The DSC curves of the samples cured at $350\text{ }^\circ\text{C}$ for 1 h were shown in FIGURE 5(b). After isothermal treatment, the blends **PNPE-55** showed a single T_g at $180\text{ }^\circ\text{C}$, much higher than that of the neat **3PNODPA**. This result probably indicated a good compatibility characteristic for the cured blends **PNPE-55**. With this benefit, one can imagine that the promise for introducing various material modification techniques such as Interpenetrating Polymer Network (IPN) is also possible for this new high performance polymer.

CONCLUSIONS

The phthalonitrile and phenylethynyl end-capped imide compounds (**3PNODPA** and **3PEODPA**) were

synthesized from 4, 4'-oxydiphthalic anhydride (ODPA) with 4-(3-aminophenoxy) phthalonitrile or 3-phenylethynyl aniline by imidization of chemical dehydration. The model compound **3PAODPA** with phenoxy end-capped imide compound was also synthesized for comparison. Then a series of blends composed of **3PNODPA** or **3PAODPA** and **3PEODPA** were prepared. Rheometric studies show that the processability of the blends can be adjusted by changing the molar concentration of **3PEODPA**. A significant slowdown of cure reaction of phenylethynyl system was observed by adding phthalonitrile compound, compared to the neat phenylethynyl compound, which cannot be mainly attributed to the physical dilution effect of the blends. Isothermal DSC and IR characterization results suggest that the adjustable processability of the blends can be mainly attributed to a novel "thermal polymerization synergistic effect", a kind of chemical interaction between **3PEODPA** and **3PNODPA**. The cured polymers exhibited excellent thermal stability and good compatibility. Further investigation for the curing mechanism is currently in progress, which will be reported in a separate paper.

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