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## Systematic study on highly efficient Thermal Synergistic Polymerization effect between alicyclic imide moiety and phthalonitrile: Scope, Properties and Mechanism

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### ABSTRACT

Blends of phthalonitrile (**CN**) and alicyclic imide compounds synthesized from tetrahydrophthalic anhydride (**CC**), methyl tetrahydrophthalic anhydride (**MCC**) and hexahydrophthalic anhydride (**HCC**), respectively, were prepared and characterized. Results from rheological studies demonstrated the scope of a novel Thermal Synergistic Polymerization (TSP) effect between phthalonitrile and the alicyclic imide compounds. FTIR data showed a unique phenomenon, which is, the -C=N of the phthalonitrile compound could be completely and rapidly consumed without generating any triazine ring. Further works on cured products of **CC/CN** system showed comparable or even higher thermal oxidation stability, low boiling water absorbance and moderate dielectric constant ( $\varepsilon'$  in the range of 4.8~4.5) with almost no voids compared with that of the phthalonitrile resins promoted by traditional curing system of active hydrogen. Model system was designed to study the mechanism of TSP effect of alicyclic imide moiety/phthalonitrile. The systematic characterizations by FTIR, UV-Vis, MALDI-TOF MS, free radical scavenger (DPPH), EPR, etc. showed that the TSP reaction undergoes both copolymerization and homopolymerization with no triazine formation, involving a free radical process. Structural analysis of the oligomers suggested that phthalocyanine rings were a minor component of the thermoset networks, while polyisoindolines were the primary structural motif.

### KeyWords

Phthalonitriles; Alicyclic Imide Moiety; Thermal Synergistic Polymerization; Curing Mechanism; Electron Paramagnetic Resonance; Thermosetting Resins; High Performance Polymers

### 1. Introduction

The phthalonitrile polymers constitute a class of high-temperature polymers that have a number of outstanding properties such as high glass transition temperatures ( $T_g$ ), outstanding thermal and thermo-oxidative stability, excellent mechanical properties, good moisture resistance and superior fire resistance [1-7]. In addition, phthalonitrile monomers and oligomers possess a low complex melt viscosity (0.01~1 Pa.s) which enables facile processing by cost effective, non-autoclavable processing techniques [8-10]. The combination of good processability and excellent high-temperature properties makes the phthalonitirles attractive for many military and civilian advanced technological applications [1-11].

However, the polymerization of the neat resin is extremely sluggish, which limits their wide application [4-5, 8]. To address this problem, considerable research efforts have been expended on the development for effective additions to accelerate the curing rate, for instance, Lewis acids such as phenols [7], strong organic acid [12], benzimidazole [8] and hydrogen imide [9], or Lewis bases such as organic amine [4]. However, these curing agents show many defects, such as low curing efficiency, high curing temperatures and brittle nature of the cured polymers [4, 8-9]. Thus, the study on the new curing methods becomes an important factor which determines the further application of the phthalonitrile polymers.

As we know, high performance resins based on these reactive groups of cyanate ester [13], maleimide [14], phenylethynyl [15-16] and benzocyclobutene [17] have received much attention in the past decades, in the view of scientific or industrial value. This is due to a fact that these resins cure via an addition reaction with no volatile by-products evolved during the processing stage. To further expand their application, functional combination of the different types of the resins into a new system is a common approach to obtain polymeric materials with attractive combination of properties. As is known, hetero-atoms such as nitrogen atom play an important role in tailoring the functionality of the material. In this situation, introducing heteroatom by in-situ chemical interaction, a "chemical synergistic effect" between the reactive groups including but not limited to copolymerization and reciprocal catalyzation, might provide crucial advantages, for example, producing polymers with versatile structures, good compatibility, adjustable processabilities and unique functionality. However, few efforts and breakthroughs were made on combining resins with hetero-atom reactive groups and carbon unsaturated groups. This is partly due to the difference in the reactivity of the groups by radical and ionic paths. An example very close to this concept is cyanate-bismaleimide known as B-T resins possessing attractive thermal, mechanical and dielectric properties, which have been fully studied and developed, though the underlying reaction mechanism remains unclear [18-19]. This study offers a significant promise of this new concept by achieving in-situ chemical interaction between an alicyclic imide moiety and a hetero-atom reactive group, nitrile -C≡N. As is known, alicyclic moiety widely exists in natural resources, such as turpentine [20]. Therefore,

the concept of "chemical synergistic effect" reported in our group has opened an exciting opportunity for designing new high performance thermosetting polymers.

Along with this new concept, the precious communication in our group reported that methyl tetrahydrophthalic anhydride end-capped imide compound (MCC) and phthalonitrile (CN) showed Thermal Synergistic Polymerization (TSP) effect [21]. However, the scope and mechanism of the TSP effect is not well studied and understood.

On the other hand, Electron Paramagnetic Resonance (EPR) spectroscopy is a very useful tool for the investigation of paramagnetic species [22-23]. Furthermore, EPR spectroscopy provides a unique method for determining the sites of attack of reactive free radicals on organic substrates and biomolecules. Under certain circumstances, it is possible to estimate absolute free radical concentrations and, from hyperfine splitting, to characterize individual free radicals. Therefore, structures, concentrations, and dynamics of paramagnetic compounds may be obtained from EPR measurements in the study of free radical polymerization. However, there have been no literatures reported a clearer insight into many of the fundamental mechanism of phthalonitriles, especially free radical mechanisms at high temperatures. To the best of our knowledge, this is the first time that paramagnetic signals are observed at high temperatures (>200 °C) especially for the thermosetting resins, such as phthalonitriles.

In this study, a series of alicyclic imide moiety-containing compounds (tetrahydrophthalic anhydride, methyl tetrahydrophthalic anhydride and hexahydrophthalic anhydride end-capped imide compound, namely CC, MCC and HCC) were introduced to study the scope of the TSP effect. Unexpectedly, the results indicated even the carbon saturated HCC also display TSP effect with CN, which broaden the scope of the TSP effect. The CC/CN system was chosen to fully characterize the cure behavior and properties of the derived polymers. The cured polymers showed comparable or even higher thermal oxidation stability with almost no voids compared with that of the phthalonitrile resins promoted by traditional curing system of active hydrogen [2, 4, 24-26]. Additionally, water absorbance at boiling condition and dielectric constant were characterized. Two model compounds (CC1 and CN1) were designed and synthesized to explore the TSP mechanism. Structural analysis were then investigated by systematic characterizations by FTIR, UV-Vis, MALDI-TOF MS, free radical scavenger (DPPH: 2,2diphenyl-1-picrylhydrazyl) and EPR. The results showed that the TSP reaction undergoes both copolymerization and homopolymerization, with minor phthalocyanine ring, major aromatic conjugated rings likely isoindoline and no triazine formation. The TSP reaction between alicyclic imide moiety and phthalonitrile suggests a free radical process.

### 2. Experimental

2.1. Materials

4, 4'-oxydianiline (ODA) was obtained from Shandong Wanda Chemical Industries Co., Ltd. Cis-1, 2, 3, 6-tetrahydrophthalic anhydride (97 wt%), cis-1, 2-cyclohexanedicarboxylic anhydride (99 wt%), 2,2-diphenyl-1-picrylhydrazyl (DPPH, 96 wt%) were obtained from Aladdin Industrial Corporation (Shanghai). 4-methyl-4-cyclohexene-1, 2-dicarboxylic anhydride (95 wt%) was obtained from Puyang Huicheng electronic material Co., Ltd. Phthalic anhydride (99.7 wt%) was obtained from Tianjin Bodi Chemical Co., Ltd. 4-nitrophthalonitrile was obtained from Taixing Shengming Fine Chemical Co., Ltd. 4-phenylphenol (97 wt%) was obtained from Adamas Reagent, Co., Ltd. (Shanghai) and all of above were used without further purification. Resorcinol (99.5 wt%), dimethyl acetamide (DMAc), dimethyl sulfoxide (DMSO), Et<sub>3</sub>N, acetic acid, H<sub>2</sub>SO<sub>4</sub>, NaCl, NaHCO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, THF, CH<sub>3</sub>CN, toluene, acetone and ethanol were obtained from Chengdu Kelong Chemical Co., Ltd. Other chemicals were used as received unless otherwise stated.

### 2.2. Synthesis of alicyclic imide compounds (CC, MCC and HCC)

The tetrahydrophthalic anhydride end-capped imide compound CC (Scheme 1) was prepared from cis-1, 2, 3, 6-tetrahydrophthalic anhydride (THPA) and ODA in DMAc solvent. To a 250-mL three-neck round-bottom flask with a Dean-Stark trap was added ODA (9.63 g, 0.048 mol) and 100 mL DMAc. The dissolved solution was stirred and heated to 30 °C, then added THPA (97 wt%, 15 g, 0.096 mol) and the system was quickly dissolved completely. The resultant mixture was purged with nitrogen and maintained at 35 °C for 5 h. To the solution was added 50 mL toluene, then heated to reflux at about 133 °C and the water was removed azeotropically over a period of 5.5 h. After removing the toluene under reduced pressure and cooling to room temperature (RT), the solution was poured into water, stirred, filtered, thoroughly washed with methanol and dried. The crude product was purified by rinsing with CH<sub>2</sub>Cl<sub>2</sub> in Buchner funnel and suction flask, and the filtrate was then dried by evaporation under a vacuum at 80 °C for 6 h to remove  $CH_2Cl_2$ . The white powder was obtained in 45.9 wt% yield (10.3 g), m. p. peak at 240 °C (sharp) (DSC) at a heat rate of 10 °C/min. FTIR (KBr), 2950, 2925, 2896, 2874 and 2844 (alicyclic C-H), 1782 and 1705 (imide C=O), 1238 (Ar-O-Ar), 694 (alicyclic –CH=CH–). <sup>1</sup>H NMR (400MHz, DMSO-d<sub>6</sub>): 7.21-7.10 (dd, 8H; Ar H), 5.91 (s, 4H; alicyclic –CH=CH–), 3.26-3.25 (m, 4H; alicyclic–CH–), 2.46-2.21 (dd, 8H; alicyclic –CH<sub>2</sub>–).

The methyl tetrahydrophthalic anhydride end-capped imide compound **MCC** (Scheme 1) was prepared by 4-methyl-4-cyclohexene-1, 2-dicarboxylic anhydride (MTHPA) and ODA in acetic acid solvent. To a 250 mL round-bottom flask was added ODA (8.06 g, 0.04 mol) and 143 mL acetic acid, stirred, then added MTHPA (13.39 g, 0.08 mol) and stirred for 30 min at room temperature in argon. The suspension was then refluxed at about 130 °C for 2 h, cooled and poured into water, then filtered and thoroughly washed with water and dried. The crude product was purified by rinsing with  $CH_2Cl_2$  in Buchner funnel and suction flask, and the filtrate

was then dried by evaporation under a vacuum at 80 °C for 5 h to remove  $CH_2Cl_2$ . The light yellow powder was obtained in 26.8 wt% yield (5.3 g), m. p. peak at 166 °C (sharp) (DSC) at a heat rate of 10 °C/min. FTIR (KBr), 2963, 2946, 2921, 2900, 2848 (alicyclic C-H), 1780 and 1709 (imide C=O), 1233 (Ar-O-Ar). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.26-7.07 (m, 8H; Ar H), 5.62 (s, 2H; alicyclic –CH=CH–), 3.26-3.20 (m, 4H; alicyclic –CH–), 2.69-2.56 (m, 4H; alicyclic –CH<sub>2</sub>–), 2.34-2.25 (m, 4H; alicyclic –CH<sub>2</sub>–), 1.77 (s, 6H; –CH<sub>3</sub>).

The hexahydrophthalic anhydride end-capped imide compound HCC (Scheme 1) was prepared by cis-1, 2-cyclohexanedicarboxylic anhydride (HHPA) and ODA in acetic acid solvent. To a 100 mL round-bottom flask was added ODA (5.01 g, 0.025 mol) and 51 mL acetic acid, stirred, then added HHPA (7.79 g, 0.05 mol) and stirred for 30 min at room temperature in argon. The suspension was then refluxed at about 135 °C for 2 h, cooled and crystallized, then filtered and thoroughly washed with 1.0 wt% NaHCO<sub>3</sub> solution and water. The filtrate was then dried by evaporation under a vacuum at 80 °C for 6 h. The white powder was obtained in 83.9 wt% yield (9.9 g), m. p. peak at 250 °C (sharp) (DSC) at a heat rate of 10 °C/min. FTIR (KBr), 2941, 2857 (alicyclic C-H), 1778 and 1709 (imide C=O), 1240 (Ar-O-Ar). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.30-7.25 (m, 4H; Ar H), 7.13-7.09 (m, 4H; Ar H), 3.08-3.00 (m, 4H; alicyclic -CH-), 1.93-1.85 (m, 8H; alicyclic  $-CH_2-$ ), 1.54-1.52 (m, 8H; alicyclic  $-CH_2-$ ).

#### 2.3. Synthesis of phthalonitrile compound (CN)

To a 500 mL three-neck round-bottom flask was added resorcinol (16.52 g, 0.15 mol), 4nitrophthalonitrile (51.94 g, 0.30 mol) and 180 mL DMSO. During the course of the reaction, the  $K_2CO_3$  (62.19 g, 0.45 mol) was added in three portions at an interval of 20 min. Then the resulting mixture was heated at 40 °C for 12 h under nitrogen. After cooling, the product mixture was poured into water. The light yellow filtrate was collected by suction filtration and washed with large amount of water until the filtrate was neutral. The crude product (42.0 g) was purified by rinsing with  $CH_2CI_2$  in Buchner funnel and suction flask, and the filtrate was then dried by evaporation under a vacuum at 80 °C for 5 h to remove  $CH_2CI_2$ . The yellow-white powder was obtained in 68.7 wt% yield (28.9 g), m. p. peak at 183°C (sharp) (DSC) at a heat rate of 10 °C/min. FTIR (KBr), 2232 (C=N), 1284 (Ar-O-Ar), 1248(Ar-O-Ar). <sup>1</sup>H NMR (400MHz, DMSOd<sub>6</sub>): 8.14-8.11 (d, 2H; Ar H), 7.92 (s, 2H; Ar H), 7.63 -7.53(m, 3H; Ar H), 7.15-7.12 (m, 3H; Ar H).

### 2.4. Synthesis of alicyclic imide model compound (CC1)

The tetrahydrophthalic anhydride end-capped imide model compound **CC1** (**Scheme 2**) was prepared in two steps with intermediate PA-ODA-NH<sub>2</sub>. Firstly, PA-ODA-NH<sub>2</sub> was prepared in phthalic anhydride (PA) and ODA in DMAc solvent. To a 250-mL three-neck round-bottom flask was added ODA (20.02g, 0.1 mol) and 70 mL DMAc, the reaction mixture was soon dissolved,

then to the flask with a dropping funnel was added DMAc (70mL) solution of PA (14.81g, 0.1 mol) dropwise (about a drop/8~10 s) at room temperature, and then the reaction mixture was maintained for 2 h in nitrogen. To the flask was added Et<sub>3</sub>N (2.04 g, 0.02 mol), and then heated to reflux at about 160 °C for 2 h. After cooling, the resulting reaction mixture was poured into 1000 mL methanol and stirred for 4 h, filtered to remove most of phthalic imide on both sides, then the resulting filtrate was evaporated under vacuum at 65 °C for 1.5 h to remove the methanol. The concentrated solution was poured into 2000 mL water with stirring and continuously stirred for 1 h, filtered and washed thoroughly with water, giving 26.5 g crude amine intermediate after drying for 2 h at 80 °C under rotary evaporation. The crude amine intermediate was dissolved in THF solvent and filtered to remove little insoluble impurities. The filtrate was then purified by purging dry HCl gas, prepared by dropping H<sub>2</sub>SO<sub>4</sub> into NaCl and then flowing by passage through a  $CaCl_2$  drying tube, to give a lot of gray precipitate (phthalic imide on one side). After filtered, the precipitate was then dissolved in 1500 mL water and stirred for 2 h and titrated to neutral by NaHCO<sub>3</sub> solution, then filtered and washed thoroughly with water, giving 18.3 g (54.7 wt% yield) mono-capped amine intermediate PA-ODA-NH<sub>2</sub> after drying for 2 h at 80 °C under rotary evaporation. <sup>1</sup>H NMR (400MHz, DMSO-d<sub>6</sub>): 7.97-7.88 (m, 4H; Ar H), 7.37-7.34 (d, 2H; Ar H), 6.99 -6.95 (d, 2H; Ar H), 6.85-6.82 (d, 2H; Ar H), 6.64-6.61 (d, 2H; Ar H), 5.05 (s, 2H; NH<sub>2</sub>).

The model compound **CC1** was then prepared by THPA and PA-ODA-NH<sub>2</sub> in acetic acid solvent. To the 250 mL round-bottom flask was added PA-ODA-NH<sub>2</sub> (19.82 g, 0.06 mol) and 196 mL acetic acid, stirred, then added THPA (97 wt%, 9.42 g, 0.06 mol) and stirred for 2 h at room temperature in argon. The suspension was then refluxed at about 125 °C for 2 h, cooled and crystallized, then filtered and thoroughly rinsed with water and dried. The crude product was purified by rinsing with CH<sub>2</sub>Cl<sub>2</sub> in Buchner funnel and suction flask, and the filtrate was then dried by evaporation under a vacuum at 60 °C for 5 h to remove CH<sub>2</sub>Cl<sub>2</sub> to give 14.6 g light white product (52.3 wt%). The product (14.0 g) was further recrystallized from C<sub>2</sub>H<sub>5</sub>OH and CH<sub>2</sub>Cl<sub>2</sub> and dried under rotary evaporation at 60 °C for 5 h to give 9.9 g, m. p. peak at 188 °C (sharp) (DSC) at a heat rate of 10 °C /min. FTIR (KBr), 2947, 2903 and 2850 (alicyclic C-H), 1785 and 1709 (imide C=O), 1243 (Ar-O-Ar), 697 (alicyclic –CH=CH–).<sup>1</sup>H NMR (400MHz, DMSO-d<sub>6</sub>): 7.98-7.88 (m, 4H; Ar H), 7.49-7.46 (d, 2H; Ar H), 7.25 -7.15(m, 6H; Ar H), 5.94 (s, 2H; alicyclic –CH=CH–), 3.31-3.28 (m, 2H; alicyclic –CH–), 2.48-2.24 (dd, 4H; alicyclic –CH<sub>2</sub>–).<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): 7.97-7.78 (m, 4H; Ar H), 7.43-7.40 (d, 2H; Ar H), 7.26 -7.23 (m, 2H; Ar H), 7.16-7.11 (m, 4H; Ar H), 5.98 (m, 2H; alicyclic –CH=CH–), 3.27-3.25 (m, 2H; alicyclic –CH–), 2.75-2.28 (dd, 4H; alicyclic -CH<sub>2</sub>-). Anal. calcd for C<sub>28</sub>H<sub>20</sub>N<sub>2</sub>O<sub>5</sub>: C 72.41, H 4.34, N 6.03; found: C 72.45, H 4.26, N 6.05.

2.5. Synthesis of phthalonitrile model compound (CN1)

To a 250 mL three-neck round-bottom flask was added 4-nitrophthalonitrile (6.92 g, 0.04 mol), ground K<sub>2</sub>CO<sub>3</sub> (5.89 g, 0.043 mol), 4-phenylphenol (6.8 g, 0.04 mol) and 100 mL DMSO. The resulting mixture was maintained at 30 °C with stirring for 24 h in nitrogen. After cooling, the solution was poured into 2000 mL water, stirred and filtered. The precipitated product was then dried at 80 °C for 4 h under rotary evaporation. The crude product (11.5 g) was recrystallized from C<sub>2</sub>H<sub>5</sub>OH and CH<sub>3</sub>CN and dried under rotary evaporation at 80 °C for 5 h. The light green crystals were obtained in 80.5 wt% yield (9.5 g), m. p. peak at 174 °C (sharp) (DSC) at a heat rate of 10 °C/min. FTIR (KBr), 2231(C=N), 1246 (Ar-O-Ar). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): 8.13-8.10 (d, 1H; Ar H), 7.86 (s, 1H; Ar H), 7.80-7.78 (d, 2H; Ar H), 7.70-7.68 (d, 2H; Ar H), 7.50-7.43 (q, 3H; Ar H), 7.39-7.36 (m, 1H; Ar H), 7.30-7.28 (d, 2H; Ar H). Anal. calcd for C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>O: C 81.07, H 4.08, N 9.45; found: C 81.33, H 4.07, N 9.54.

### 2.6. Preparation of Blends, model blends reaction products and fabrication of cured polymers

Blends (CC/CN, MCC/CN, HCC/CN or CC1/CN1) by different molar ratios (3:7, 5:5) were prepared by dissolving or dispersing the compounds in acetone. After removing the residual solvent by vacuum evaporation, the mixture was ground into fine powder to insure homogeneity. Blends of CC1/CN1 with 20 wt% DPPH were ground by mortar and pestle, and then subjected to isothermal treatment at 300 °C for 15, 30 and 60 min.

Mechanism data were collected on samples stirred for different time at 300 °C in a 100 mL three-neck round-bottom flask with N<sub>2</sub> flow rate of 50 mL/min. Samples were ultrasonicated in acetone followed by sedimentation and filtration to remove as much as possible the soluble. The washing process was monitored by Thin Layer Chromatography (TLC) and dried by vacuum evaporation at 80 °C for 5 h prior to characterization. The panels are for the convenience marked with the symbol, RT for room temperature, m for mechanism, respectively. The model compounds (**CC1**, **CN1**) and/or blend in equimolar ratio of **CC1/CN1** (m55) are investigated by <sup>1</sup>HNMR, elemental analysis, FTIR, UV-Vis, MALDI-TOF MS and EPR characterization.

Properties data were collected on samples with two steps, prepolymers and cured polymers. The specific methods are as follows. Blend prepolymers were fabricated by the following procedure: on a 12~15-g scale in a 250 mL reaction kettle equipped with a magnetic stirrer, melting the blends at 200 °C for 4~10 min, stirring the mixture with degassing under 0.06 MPa for 20 min, quickly taking out the preheated mould from the preheated oven chamber and pouring the melt into the mould, quickly placing back into the chamber, and heated at 200 °C for 6 h, followed by 230 °C for 3 h with N<sub>2</sub> flow rate of 500 mL/min. After cooling to room temperature (RT), the prepolymers were removed out from the mould, and then placed in the muffle furnace to cure with argon flow rate of 500 mL/min. A thermal cure cycle was employed for cured polymers panel fabrication. The cycle included dwells at 270 °C, 310 °C, 330 °C, 350 °C

and 375 °C. The panels are for the convenience marked with the symbol, pc for pre-cure, ppc for pre- and post-cure, respectively. The cured polymers (**55-pc**, **55-ppc**, **37-pc**, **37-ppc** for **CC/CN** system; **M37-ppc** for **MCC/CN** system), prepared from **CC/CN** and **MCC/CN** by different molar ratios (3:7, 5:5), were characterized by FTIR, TGA, DMA, SEM, solubility, boiling water absorbance and dielectric property.

Procedure (a) for pre-cure: 200 °C for 6 h, 230 °C for 3 h, 270 °C for 6 h and 310 °C for 6 h;

Procedure (b) for pre- and post-cure: pre-cure; and post-cure (330 °C for 3 h, 350 °C for 3 h and 375 °C for 6 h).

### 2.7. Solution NMR and Elemental Analysis

High-resolution solution nuclear magnetic resonance (NMR) spectra were acquired at room temperature. <sup>1</sup>H NMR (400 MHz) spectra was measured on a Bruker Avance-400 NMR spectrometer, with CDCl<sub>3</sub> or DMSO-d<sub>6</sub> as the solvents with tetramethylsilane (TMS) as the internal standard. Elemental analysis was performed on a vario MICRO select elemental analyzer (Elementar, Germany).

### 2.8. Fourier Transform Infrared Spectroscopy (FTIR) and UV-Vis

FTIR spectra of the compounds and cured samples were recorded with a Nicolet FTIR-460 Fourier transform infrared spectrometer by KBr pellet containing KBr (about 150 mg, specpure grade for FTIR absorption spectroscopy from Tianjin Kemiou Chemical Reagent Co., Ltd.) and the sample powder (about 1.00 mg) from 4000 to 400 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> by 32 scans. UV-Vis spectra were recorded on a Shimadzu UV Pectrophotometer UV2100 at room temperature with  $CH_2Cl_2$  as the solvents.

### 2.9. TGA, DSC and Dynamic Mechanical Analysis (DMA)

TGA was carried out with a TA instrument Q500 thermogravimetric analyzer using about 7 mg of sample in flowing air or nitrogen atmosphere of 60 mL/min at a heating rate of 10 °C/min. 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 and a flow nitrogen rate of 50 mL/min.

Dynamic Mechanical Analysis (DMA) were performed using a TA-Q800 under three-point bending mode. For this, the cured samples were sanded to rectangular specimens of dimensions (30 mm × 12.5 mm × 3.2 mm). The DMA characterizations were performed for the temperature range 50~500 °C at a heating rate of 5 °C/min, a frequency of 1 Hz and a low strain value of  $2.5 \times 10^{-4}$ .

#### 2.10. Rheological Measurement

The rheological behavior of the imide compounds, phthalonitrile compounds and their blends 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 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, and the measurements were carried out during isothermal cure at temperatures of 230 °C, 250°C and 270 °C, with an angular frequency of 1 Hz and an initial strain of  $2.5 \times 10^{-4}$ . The variation of the viscoelastic properties during reaction, such as complex viscosity ( $|\eta^*|$ ) of imide compounds, phthalonitrile compounds and their blends was determined in air atmosphere after melting powder samples between parallel plates in the test chamber of the rheometer as a function of the reaction time. All rheological measurements were taken at low strain values ( $2.5 \times 10^{-4}$ ) using 25 mm-diameter parallel plates. Normal force control ( $1.0 \times 10^{-4}$  N) was utilized throughout the tests to keep the samples taut.

### 2.11. Scanning Electron Microscope (SEM)

The cured samples were hammered, and coated with Au using an auto sputter coater (SC7620). The morphology of the aggregate was confirmed by means of a field emission scanning electron microscopy (FE-SEM) microscope (Quanta 250, FEI Corporation) operating at 20 kV.

### 2.12. Boiling Water Absorption

The cured polymers for boiling water absorption test were immersed in boiling distilled water at around 98~100 °C for 60 h. The sample was removed from the boiling water, dried with filter paper, and weighed periodically to determine the amount of boiling water absorption. The water absorbance was calculated using the following equation:

### Boiling Water Absorbance (%) = $(m-m_0)/m_0 \times 100$

Where,  $m_0$  and m are the weight of the cured polymer at dry state and after immersion in boiling distilled water, respectively.

### 2.13. Dielectric Measurement

Dielectric characteristics were evaluated with a Broadband Dielectric-Impedance Spectrometer (Concept 50, Novo-control Technologies, Germany) in a broad range of frequency

 $(0.01 \sim 4 \times 10^7 \text{ Hz})$ . Dried samples were fabricated and sanded to wafer specimens of dimensions ( $\Phi 20 \text{ mm} \times 2 \text{ mm}$ ). Sliver paste was adopted as the electrodes before measurements. The measured complex impedance data were used to calculate the real ( $\epsilon'$ ), and imaginary ( $\epsilon''$ ) parts of the complex dielectric function  $\epsilon$  ( $\epsilon = \epsilon' + i \epsilon''$ ).

### 2.14. Matrix-Assisted Laser Desorption Ionization Time-Of-Flight Mass Spectrometry (MALDI-TOF MS)

MALDI-TOF MS was performed on a Shimadzu Biotech Axima Performance equipped with an  $N_2$  laser (337 nm), with alpha-cyano-4-hydroxycinnamic acid (CCA) as matrix. Samples were partially dissolved in CH<sub>3</sub>CN, and then mixed with the matrix. The mixture was spotted onto the centre of the probe tip and dried under ambient conditions. Spectra were obtained in the linear positive mode.

### 2.15. Electron Paramagnetic Resonance (EPR)

EPR spectra were recorded on a Bruker A300-10/12 EPR spectrometer (Bruker BioSpin GmbH) equipped with an X-band microwave bridge. Temperature control was achieved using a Bruker A4131VT variable-temperature controller, calibrated using an independently calibrated thermocouple. Model compounds or their blends were respectively placed in a quartz tube (o. d. 5 mm × 180 mm), vacuumed (>10<sup>-3</sup> Pa), purged with Argon (120 Torr), and then sealed. The sample tube was put into the cavity of the EPR spectrometer at room temperature. The EPR cavity was then heated to the required high temperatures from around melting point to 573 K, with temperatures controlled by purging with high purity dry nitrogen and circulating water cooling series disc system. A number of spectra of the derived signals were then recorded at required temperatures after melting via repeated rapid scans typically with a scan time of ca. 41.943 s. The amplitude and frequency of the modulation were respectively 1.00 G and 100.00 kHz, operating at a microwave power of about 20.05 mW and a microwave frequency of about 9.44 GHz. The instrumental conditions were set at a centre field of 3369.450 G and a sweep width of 100.000 G.

### 3. Results and discussion

### 3.1. Rheological Processing Evaluation



Scheme 1. Synthesis and preparation of CC, MCC, HCC, CN and their polymers



Fig. 1. Complex viscosity ( $|\eta^*|$ ) as a function of temperature for compounds CC, MCC, HCC, CN and their blends



**Fig. 2.**Complex viscosity (|n\*|) as a function of time for compounds **CC**, **CN** and their blends with molar ratio 5:5 or 3:7 at 230°C, 250 °C and 270 °C

As shown in **Scheme 1** and **Fig. 1**, rheological characterizations on phthalonitrile (**CN**) and a series of alicyclic imide moiety-containing compounds (tetrahydrophthalic anhydride, methyl tetrahydrophthalic anhydride and hexahydrophthalic anhydride end-capped imide compound, namely **CC**, **MCC** and **HCC**) were conducted to study the scope of the TSP effect. The results indicated even the carbon saturated **HCC** also display TSP effect with **CN**, broadening the scope of the TSP effect. Obviously, the activity of the TSP effect depends on the alicyclic imide structure, with the carbon unsaturated **CC/CN** system having higher reactivity (**Fig. S1**). Among them, the **MCC/CN** system showed a 130 °C processing window, which is larger than most of the reported phthalonitrile system.

To systematically study the cure character and properties of the TSP effect and derived polymers, **CC/CN** system was chosen to further investigation. Viscosity measurements on phthalonitrile **CN** blends were conducted at several temperatures to determine the optimum **CC** molar concentration and temperature for composite processing. The thermal polymerization behaviors of the **CC/CN** blends (molar ratio 3:7, 5:5) and their respective compounds were studied by rheological measurements. The complex viscosities change as a function of reaction time for the blends and their respective compounds at 230 °C, 250 °C and 270 °C are shown in **Fig. 2**. As shown in the **Fig. 2**, all the samples exhibit an initial dynamic viscosity around 0.1 Pa.s after melting. As we all know, the polymerization of the neat phthalonitrile resins is extremely sluggish (**Fig. 2**, **CN-270 °C**)[8-9], we put the plot of the neat alicyclic imide compound **CC** in the **Fig. 2**, and the data shows that there is no obvious complex viscosity increasing tendency with

still below 10 Pa.s after 3 h at 270 °C (Fig. S2, TGA and DSC of CC1, FTIR and <sup>1</sup>H NMR of CC1 with TGA 300 °C & 1 h in N<sub>2</sub>). Unexpectedly, as shown in the Fig. 2, when these two inertly compounds were mixed together (CC-CN-37, CC-CN-55), they showed exciting polymerization behaviors at elevated temperatures. And we named this unique curing behavior as Thermal Synergistic Polymerization (TSP). The comparison between CC-CN-37 and CC-CN-55 of Fig. 2 reveals that the polymerization rate of CC/CN blends could be related to the homopolymerization rates of CC and CN and their copolymerization rate. Further, it can be easily controlled by varying the concentration of the alicyclic imide compound, which is, at a higher CC molar ratio concentration, the dynamic viscosity of the blend increases at a faster rate. Additionally, with increasing temperature above 250 °C, the complex viscosity increase sharply, indicating that the curing temperature of the phthalonitrile blend, which is usually a high temperature (above 300 °C) process with a long time, is greatly decreased. Also, there is a large and adjustable process window at relatively low temperatures such as 230 °C with low alicyclic imide compound concentration, helpful in the fabrication of large size composite sections [4, 8-9]. This unique TSP effect inspires us to find out its intrinsic mechanism. Their three possibilities arising from these reactions are (1) homopolymerization of alicyclic imide and phthalonitrile groups independently, (2) copolymerization of alicyclic imide with the phthalonitrile groups, (3) alicyclic imide accelerated the polymerization of phthalonitrile groups like traditional curing system of active hydrogen. The mechanisms of thermosetting resin are still hard to be figured out, and we will try to make some explanations for this unique polymerization behavior by the studies of model compounds in the final section of this article.

### 3.2. Cured Polymers Physical Properties Evaluation

To evaluate physical properties of the cured phthalonitrile blend polymers, a series of the cured samples were fabricated in the mould (cavity dimensions of 32 mm × 14 mm × 8 mm or  $\Phi$ 20 mm × 2 mm), hammered to pieces or sanded to rectangular specimens of dimensions (30 mm × 12.5 mm × 3.2 mm) for characterizations of morphology of the cross section, solubility, DMA, boiling water absorbance, dielectric, thermal and thermal-oxidative properties.



Fig. 3. FTIR-DMA-TGA plots of 5:5 and 3:7 molar ratio CC/CN cured polymers at different duration time and temperatures

3.3. FTIR, DMA, Thermal and Thermal-Oxidative Properties

As shown in **Fig. 3**(a), FTIR data shows that there is no obvious -C=N absorption (2230 cm<sup>-1</sup>) of the cured polymers (55-pc, 55-ppc, 37-pc, and 37-ppc). New absorption peaks at 3285 cm<sup>-1</sup> attributed to an N-H stretching and 1011 cm<sup>-1</sup> attributed to metal-free phthalocyanine ring vibration indicated the formation of phthalocyanine polymers [10, 27-29], and the low intensity peaks assigned to phthalocyanine polymers suggest that they are a minor component of the thermoset material. Additionally, another new absorption peak at 1092 cm<sup>-1</sup> of 55-pc, 55-ppc and 37-pc, 37-ppc was observed, which is frequently assigned to isoindoline in the reported literatures [30]. The results are consistent with the UV data from model compounds study. Significantly, no triazine absorptions are observed. This result is consistent with our previous report [21]. It has been reported that due to the steric hindrance of the un-reacted -C=N groups at the ortho-position of triazine ring, there would be some -C≡N groups left (about 1/3) during the formation of triazine with strong absorption in FTIR spectra at around 1520 and 1360 cm<sup>-1</sup> of conventional phthalonitrile resins [10, 27, 34]. These spectroscopic features imply that the curing system is very unique and characteristic, which is useful for detection of the curing mechanism as described later to explain the phenomenon of no occurrence of triazine and -C=N absorption.

One of the most fundamental measurements made on high performance polymers (hightemperature polymers) is the measurement of glass transition,  $T_g$ . DMA were performed on the cured polymers to estimate the  $T_g$ . A comparison of storage modulus (G') vs. temperature and tan  $\delta$  vs. temperature plots for the cured polymers at different cure extents with different molar ratios made from **CC/CN** blends are shown in **Fig. 3**(b) and **Fig. 3**(c), respectively. The DMA data are shown in **Table 1**.

Fig. 3(b) shows plots of the storage modulus up to 450 °C or 500 °C for the cured polymers. The plots present impressive initial storage modulus at about 2515, 3261, 4304, and 3610 MPa for **55-pc**, **55-ppc**, **37-pc**, and **37-ppc**, respectively. When heated from 50 °C to 500 °C, the storage modulus for **37-ppc** changed from 3610 to 1021 MPa. The measurements revealed the samples that were cured to procedure (a) (310 °C for 6 h) and additional high temperature treatment, procedure (b) (375 °C for 6 h), exhibited a significant  $T_g$  increase from the maximum of tan  $\delta$ . Moreover, all of data showed far higher storage modulus than that of resorcinol-based phthalonitrile polymers (about 1000 MPa before and after DMA characterization) [6].

The multiple transitions as estimated on the basis of tan  $\delta$  peak for procedure (a) are at approximately 175 °C, 208 °C, 260 °C for the 5:5 molar ratio samples, this is probably due to the presence of several different types of oligomeric structures with different molecular weight with the increased concentration of **CC** relative to **37-pc**. For procedure (b), no obvious  $T_g$  are observed in the range of 500 °C for both molar ratio samples. With longer exposure at 375 °C, the samples have progressed to afford a resin with a high crosslink density (**Table S1**) and mechanical properties reflecting its glassy state over the entire temperature range of the measurements, which shows that the cured polymers have excellent thermal properties, compared with other phthalonitrile polymers [2, 4, 6, 24-26].

Camples	55 mg	FE ppc	27 mc	27 mmc
Samples	55-hr	22-hhc	57-bc	21-hhc
G' at 50 °C	2515 MPa	3261 MPa	4304 MPa	3610 MPa
G' at 500 °C	314 MPa	1059 MPa	*488 MPa	1021 MPa
Retention of G'	12.5%	32.5%	*11.3%	28.3%
T <sub>5%</sub> (N <sub>2</sub> )	363 °C	486 °C	371 °C	508 °C
T <sub>10%</sub> (N <sub>2</sub> )	397 °C	524 °C	405 °C	536 °C
char yield at 800 °C(N <sub>2</sub> )	50.2%	70.5%	41.9%	72.2%
T <sub>5%</sub> (Air)	379 °C	496 °C	366 °C	507 °C
T <sub>10%</sub> (Air)	421 °C	529 °C	413 °C	538 °C
char yield at 800 °C(Air)	0.0%	0.5%	0.4%	0.8%

Table 1 The DMA and TGA data of cured polymers

\*: data at 400 °C.

The thermal and thermal-oxidative properties of the cured **CC/CN** blends at different cured extents with different molar ratios were evaluated up to 800 °C in TGA chamber at a heating rate of 10 °C/min under nitrogen and air atmosphere. The data (**Table 1**) showed comparable thermal and thermal-oxidative stability compared with resorcinol-based phthalonitrile polymers cured by BAPS or m-APB in N<sub>2</sub> or in air atmosphere [6].

**Fig. 3**(d) shows the thermal stability of the cured polymer samples in N<sub>2</sub> atmosphere. Both of the cured polymers **37-ppc** and **55-ppc** show good thermal stabilities up to 450 °C and begin to lose weight at higher temperatures in N<sub>2</sub> atmosphere. The significant enhancement trend of thermal stability from procedure (a) to procedure (b), indicating the stabilities of the cured polymer samples were depended on the cure cycle and cure temperatures [1-8, 13-17, 24-26].

**Fig. 3**(e) shows the thermal-oxidative stability of the cured polymer samples in air atmosphere. The char yields of all samples were found to be  $0.0^{-0.8}$  % after heated to 800 °C. On the other hand, both of the cured polymers **55-ppc** and **37-ppc** did not exhibit obvious weight loss before the scanning temperature reached 450 °C in air atmosphere, similarly in N<sub>2</sub> atmosphere, while undergoing catastrophic weight loss between 600 °C and 750 °C in air atmosphere, implying superior performance in thermal-oxidative stability [9, 24-26].

#### 3.4. Morphological studies



Fig. 4. SEM images of the cured polymers 55-ppc (a, b) and 37-ppc (c, d)

The fractured cross section morphologies of **55-ppc** and **37-ppc** were studied by FE-SEM. The fractured cross section morphologies of the cured polymer samples **55-ppc** and **37-ppc** are shown in **Fig. 4**(a, b) and **Fig. 4**(c, d), respectively. As seen from the comparison of **Fig. 4** in the same magnifications by 500 and 20,000, voids appear in the cured sample **55-ppc**. The most likely reason is oligomers or unreacted reactants such as **CC** volatilizing during high temperature treatment in fabrication process. Moreover, no voids or air gaps of the sample **37-ppc** were detected, indicating homogeneity, densification characteristic of this kind of thermosets. These results could be attributed to the good characteristics of the alicyclic imide and phthalonitrile blend resins, which can be polymerized into voids-free thermosets.

### 3.5. Boiling Water Absorption Capability



Fig. 5. Boiling water absorption and dielectric property of the cured polymers 55-ppc, 37-ppc and M37-ppc

Low water absorption capability [31], a key aspect of polymer networks, was determined by absorption experiments in boiling distilled water over a course of 60 h on several bulk samples of polymers **55-ppc**, **37-ppc** and methyl tetrahydrophthalic imide/phthalonitrile polymers, **M37-ppc**. **Fig. 5**(a) shows the water absorption properties of the cured polymers in boiling distilled water. As shown in **Fig. 5**(a), the cured polymers **55-ppc**, **37-ppc**, and **M37-ppc** showed a maximum boiling water amount of approximately 2.4%, 1.9% and 2.7%, respectively, after 60 h immersion, which is lower than that of other phthalonitrile-based polymers (about 3.0%) [32]. The sample **55-ppc** was more susceptible than **37-ppc** to water penetration under the same conditions due to voids or air gaps observed in SEM which is probably caused by the volatilization of unreacted **CC**. For **M37-ppc**, the boiling water absorbance increases gradually with time increase with a maximum boiling water absorptivity can be controlled by the proper selection of alicyclic imide moiety.

#### 3.6. Dielectric Property

The dielectric constant ( $\varepsilon'$ ) or relative static permittivity of a material represents the capacitance of the material relative to a vacuum and is important in many industrial applications [33]. The variation of the real part of the dielectric function,  $\varepsilon'$ , as a function of frequency for samples at room temperature is illustrated in **Fig. 5**(b). The general trend for the order of dielectric permittivity observed in the whole frequency range for **55-ppc** and **37-ppc** is  $\varepsilon'$  (**37-ppc**)> $\varepsilon'$  (**55-ppc**). The results suggest that the dielectric properties of the sample **55-ppc** possess better frequency stability, within the range of 4.8~4.5 in frequency from 1 Hz to 1 MHz. From the graph it is clear that the real part of the dielectric function shows a strong frequency

dependence below a certain frequency (1 Hz), while above this frequency the value of  $\varepsilon'$  becomes almost constant for the samples. The decrease of  $\varepsilon'$  with increase in frequency may be attributed to electrical relaxation processes.

#### 3.7. Discussion on Polymerization Mechanism



Scheme 2. Synthesis and preparation of model compound CC1, CN1 and their reaction product

This work reported that -C=N groups can be fully consumed by the addition of alicyclic imide compound, and this phenomenon has never been reported in the traditional curing system of active hydrogen which promoted phthalonitrile systems. Thus, to explore the curing mechanism of TSP effect of the alicyclic imide/phthalonitrile (CC/CN, MCC/CN, and HCC/CN) systems becomes a significant work. And due to the insoluble and infusible nature and the diversity structures of products of thermosetting resins, the research on the curing mechanism of thermosetting resins becomes a challenging work.

In order to explore the curing mechanism of TSP effect, two kinds of representative model compounds were designed and synthesized (**Scheme 2**), namely, the mono alicyclic imide end-capped model compounds (**CC1**) and mono phthalonitrile terminated model compound (**CN1**). Two model compounds were mixed in the molar ratio of 5:5 and isothermal treatment at 300 °C in N<sub>2</sub> to explore the structures and curing mechanism by NMR, FTIR, isothermal TGA-FTIR, UV-Vis, radical scavenger (DPPH), EPR and MALDI-TOF MS. Here, we should have discussed the NMR characterization. While as data of <sup>1</sup>H NMR and <sup>13</sup>C NMR were relatively arguable and need to be further studied, more NMR data such as Deuterated or 13-Carbon labelled characteristic reactive sites of **CC1** will be reported in another paper.

The reasons for choosing the 5:5 molar ratio and the temperature 300 °C are as follows: (1) -  $C \equiv N$  group reacts completely as much as possible, (2) a faster curing reaction rate at the same temperature, (3) a less vaporization content and a shorter time at the same molar concentration.





Fig. 6. FTIR spectra of the model compound blends and their 300 °C & 1 h reaction products

From FTIR spectra comparison of **CC1/CN1** blend **m55**, **m55-a** and **m55-b** (TLC in **Fig. S3**) in **Fig.6**, it is clear that the absorption of -C≡N (2231 cm<sup>-1</sup>) completely disappeared, without observing any absorption of triazine ring (1520 and 1360 cm<sup>-1</sup>), which is consistent with the result of the cured polymers **CC/CN** system. Therefore, these results indicate that the polymerization of alicyclic imide/phthalonitrile system follows some unique mechanism compared with typical phthalonitrile polymerization style. The characteristic absorptions of phthalocyanine and isoindoline structures are overlapped with model compounds **CC1** and **CN1**, which will be confirmed later by other techniques such as UV-Vis and MALDI-TOF MS.

The UV-Vis absorption of the cured products in  $CH_2Cl_2$  (partially dissolved) are shown in **Fig. 7**. **Fig. 7** shows two obvious absorption bands at 666 and 700 nm, which are attributed to the characteristic of phthalocyanine ring [27] though the intensity of characteristic absorption peaks of phthalocyanine structure was low in the FTIR spectra. Combination of these results, we can infer that phthalocyanine formation was a minor process in the polymerization. Additionally, absorption bands from 300 to 550 nm and from 570 to 660 nm indicated occurrence of reaction products with different aromatic conjugated structures formation such as isoindoline structures.



Fig. 7. UV-Vis spectra of the model compounds and their 300 °C & 1 h reaction products



3.10. MALDI-TOF MS Characterization

As discussed above, FTIR and UV-Vis spectra analysis imply formation of reaction products with phthalocyanine and isoindoline structures. However, the polymerization mechanism and the structures of the products are still unclear. MALDI-TOF MS technology has been widely used to give much insight into the structure of polymer [35-40]. Here, we tried our best effort to

thoroughly study on the structures of the derived **CC1/CN1** model system polymers by MALDI-TOF MS. The MALDI-TOF MS spectra of **m55-a** and **m55-b** (before and after ultrasonicated in acetone) are presented in **Fig. 8**.

m55-a	m55-b	structure	m/z calculated		
m/z measured	m/z measured		, _ calculated	polymerization style	
1186.77	1186.24	(0:4)H <sup>+</sup>	1185.37	CN1, homopolymerization	
1227.49	1227.08	(2:1)H <sup>+</sup>	1225.38	copolymerization	
1541.88	1541.17	$(2:2)Na^+$	1543.45	copolymerization	
1855.87	1855.57	$(4:0)H^+$	1857.57	CC1, homopolymerization	
2642.21	2641.18	(5:1)Na $^{+}$	2639.78	copolymerization	
2810.11	2810.36	(6:0)Na⁺	2807.83	CC1, homopolymerization	
3428.09	3427.48	(1:10)H⁺	3426.05	copolymerization	

Table 2 The MALDI-TOF MS	peaks and the corres	ponding structures o	of m55-a and m55-b
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x= the number of **CC1**, y= the number of **CN1**, Z= the species of cation ions.

As shown in Fig. 8, m55-a shows a characteristic molecular weight distribution of polymers. The representative peaks of m/z at 1855.87 and 1186.77 corresponding to tetramer of CC1 (calcd: 1857.57, (4:0) $H^+$ ), and tetramer of **CN1** (calcd: 1185.37, (0:4) $H^+$ ) confirming the formation of phthalocyanine (Fig. 7), were observed in the MALDI-TOF MS spectra, indicating the homopolymerization of CC1 and CN1 independently or the CC1 and CN1 can be reacted into homopolymers in the presence of each other. In addition to the main peaks of m/z at 1855.87 and 1186.77, there are a series of typical polymer peaks at the range of m/z at 1000~4500, and these peaks can provide us more details of the TSP effect between tetrahydrophthalic imide and -C=N groups (Table S2). As the intensity of phthalocyanine is too low to be observed, m55-a was ultrasonically washed to get acetone insolubilities **m55-b**, which was also characterized by MALDI-TOF MS with data presented in the Table S2. Comparison between the spectra of m55-a and m55-b authenticated that phthalocyanine formation was a minor process in the polymerization (Fig. 6, Fig. 7, and Fig. 8). As shown in enlarged spectra of Fig. 8, since there are many species of polymers and the existence of fragments, cation ions and **CC1** precursors, it is difficult to find out the actual structures of these small peaks and some peaks data are shown in **Table 2.** The molecular ion peaks are all labelled in the (x:y)Z format, where x = the number of **CC1** for the reactive product precursors, y = the number of **CN1** for the reactive product precursors, Z = the species of cation ions. And it is important to stress that the polymer fragment ions depends primarily on the extent of precursors ion "breakage" caused by collision impact with gas and the cation ions such as Na<sup>+</sup>, which widely exist in the nature world [41-45].



Fig. 9. MALDI-TOF MS spectra of m55 at 300 °C for15, 30 and 60 min



Fig. 10. MALDI-TOF MS spectra of m55 with 20 wt% DPPH at 300 °C for 15, 30 and 60 min

On the other hand, reaction products of **CC1/CN1** and **CC1/CN1** with 20 wt% DPPH at 300 °C for different time (15, 30 and 60 min) were also characterized by MALDI-TOF MS. The MALDI-TOF MS spectra of **m55-15**, **30**, **60** and **m55&20wt%DPPH-15**, **30**, **60** are presented in Fig. 9 and **Fig. 10**. The polymerization process of **CC1/CN1** system are shown in **Fig. 9**. At an initial stage (before 30 min), molecular weight is not significantly increased. While in the further stage such as isothermal for 60 min, large amount of polymeric derivatives (especially copolymerization) started to emerge with molecular weight increase.

In the past two decades, many researchers have explored the radical reaction mechanism of the aliphatic or aromatic nitriles [9, 46-49]. Among these studies, H. J. P. de Lijser, et al. reported that the alicyclic radicals can initiate the reaction of benzonitrile by carbon radical reactive site [48]. It is rational for us to believe that the curing reaction of alicyclic imide moiety/phthalonitrile systems is a high temperature free radical process. And **Fig. 10** shows the polymerization process of **CC1/CN1** system with free radical scavenger DPPH. The spectra data exhibit characteristic inhibiting polymerization, implying that the TSP reaction involved a free radical process.

#### 3.11. EPR Characterization

To further clarify the nature of the reaction intermediates, EPR characterizations of **CC1**, **CN1** and **m55** were studied, and a series of EPR spectra at elevated temperatures were reported (**Fig. 11**, **Fig. 12**, and **Fig. 13**). As shown in **Fig. 11**, a promising result was observed that **m55** shows weak EPR signals at 463 K and the intensity of the signals gradually increased with elevated temperatures. The signal was obvious at 543 K with centre magnetic field at around 3367.5 G and its intensity continued to increase within the range of scanning temperature. This result suggests that some free radical intermediates formed such as polyisoindolines or other conjugated structures that can delocalize the radicals along the polymer chain, which making the intermediates stable at high temperatures and further initiate polymerization.

**Fig. 12** shows that the EPR signal intensity of **m55** increase with scanning time equilibrating at 543 K, further verifying the existence of the free radical intermediates and their stable characteristics at high temperatures. As no hyperfine splitting structures were observed in our following investigation [50-51], the type of the involving free radical intermediates still needs to be further studied.

Meanwhile, free radical scavenger DPPH characterization on the TSP effect further confirmed the reaction has some relationships with free radical mechanism (**Fig. 10**, **Fig. S4-S5**).



Fig. 11. EPR spectra of m55 at elevated temperatures



Fig. 12. EPR spectra of m55 at 543 K isothermal for a period of time



Fig. 13. EPR spectra of CC1 and CN1 at elevated temperatures

Further, EPR data were also collected *in-situ* on the model compounds and shown in **Fig. 13**. Weak EPR signals were observed in the model compound **CN1**, which suggests that any radical mechanism would begin with the phthalonitrile monomer. The sluggish curing characteristic of neat phthalonitrile resin could be attributed to the relatively lower content of free radicals than that of **m55**. No EPR signals were observed in the model compound **CC1**. These results further authenticated the mechanism of TSP effect between alicyclic imide moiety and phthalonitrile.

### 3.12. Mechanism Discussion

Based on the above discussion, a rational explanation for the mechanism of the TSP effect (**Scheme 3**) can be proposed and some significant results or evidences can be summarized as follows:



Scheme 3. Proposed radical polymerization mechanism of alicyclic imide/phthalonitrile system

1. The alicyclic double bond (–CH=CH–) of alicyclic imide based on tetrahydrophthalic anhydride may only play a minor role in the TSP effect. Carbon saturated alicyclic imide moiety based on hexahydrophthalic anhydride compound (HCC) also shows the TSP effect with the phthalonitrile compound (CN) (Fig. 1 and Fig. S6).

2. MALDI-TOF MS indicates that both copolymerization and homopolymerization existed in the TSP process. In our cases, both of phthalonitrile and alicyclic imide moiety (**CC**, **MCC** and **HCC**) hardly showed obvious homopolymerization under investigated range of temperatures. Significantly, for blends of them, both of copolymerization and homopolymerization can be activated. This characteristic is different from usual thermal copolymerization and epoxy-cure agent system.

3. As is known, hetero-atom containing unsaturated groups, such as C=N, usually polymerize by ionic paths. In this paper, EPR technique and free radical scavenger DPPH were used to *insitu* or *off-situ* discuss this issue. The data firstly demonstrated the TSP effect occurred probably involving a free radical path.

### 4. Conclusions

The alicyclic imide moiety based **CC**, **MCC** and carbon saturated **HCC** showed a unique phenomenon namely Thermal Synergistic Polymerization (TSP) effect between alicyclic imide moiety and phthalonitrile.

The fully study on the curing behaviors, the thermal and mechanical properties, boiling water absorption and dielectric properties of **CC/CN** blends and their cured products showed that the **CC/CN** synergistic polymerization system not only possessed outstanding processing performance, but also showed excellent thermal and mechanical properties, low boiling water absorbance and moderate dielectric constant ( $\varepsilon$ ' in the range of 4.8~4.5).

In order to explore the polymerization mechanism of this unique TSP effect, the model compounds **CC1**, **CN1** and their blends were designed and characterized by FTIR, UV-Vis, MALDI-TOF MS, free radical scavenger (DPPH), EPR, etc. The high-efficiency of C≡N transformation of the system undergoes both copolymerization and homopolymerization with no triazine formation, involving a free radical process. The structures of the oligomers derived from model compounds contain a minor phthalocyanine ring and major aromatic conjugated rings likely isoindoline.

This study opens an exciting opportunity for designing new high performance thermosetting polymers.

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### Appendix A. Supplementary data

Synthesis and Characterization of CC, MCC, HCC, CC1, CN and CN1. Fig. S1–S6 and Table S1-S2.

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## Highlights

- Both of alicyclic imide moiety and phthalontrile hardly show obvious homopolymerization. Significantly, for blends, both of copolymerization and homopolymerization can be activated, which can be defined as Thermal Synergistic Polymerization effect.
- -C=N of the phthalonitrile could be completely and rapidly consumed. Mechanism analysis suggested both copolymerization and homopolymerization with no triazine, minor phthalocyanine rings and primary polyisoindolines structures formation, involving a free radical process.
- The cured polymers showed excellent thermal properties, low boiling water absorbance and moderate dielectric constant.