

Phthalonitrile Resins Derived from Vanillin: Synthesis, Curing Behavior, and Thermal Properties

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Electronic Supplementary Information

Abstract Vanillin was used as sustainable source for phthalonitrile monomer synthesis, and allyl/propargyl ether moieties were introduced to improve the processability at the minimal cost of thermal properties. The synthesis route was optimized to minimize side-reactions and simplify post-processing, and the monomers were obtained in high purity and good yields. The curing behavior, mechanism, and processability of the monomers were studied, and the thermal properties of cured polymers were evaluated. Of the two monomers, the allyl ether-containing one exhibited a wide processing window of 185 °C, and was mainly cured into phthalocyanine and linear aliphatic structures through self-catalytic curing process. Also, the glass transition temperature was higher than 500 °C. In contrast, the propargyl ether-containing monomer could only be partially cured, and heat resistance was found to be compromised. Compared with traditional petroleum-based phthalonitrile resins, the bio-based monomers could be cured without the addition of catalysts, and improvement in processability was achieved at no cost of thermal performances.

Keywords Allyl ether; Curing mechanism; Phthalonitrile; Thermal properties; Vanillin

Citation: Han, Y.; Tang, D. H.; Wang, G. X.; Sun, Y. N.; Guo, Y.; Zhou, H.; Qiu, W. F.; Zhao, T. Phthalonitrile resins derived from vanillin: synthesis, curing behavior, and thermal properties. *Chinese J. Polym. Sci.* 2020, 38, 72–83.

INTRODUCTION

Phthalonitrile resins are a family of highly thermal-stable thermosets.^[1,2] It can be applied to a wide range of fields, such as high temperature microelectronic encapsulations^[3] and advanced polymer matrices in aerospace and marine sectors.^[4,5] Generally, synthesis of their monomers mainly relies on nucleophilic substitutions between phenols and 4-nitrophthalonitrile.^[6] Besides, petroleum-based bisphenols, such as bisphenol A,^[7] biphenol,^[8,9] and resorcinol,^[3] have been most widely studied. However, severe environmental concerns were raised from using these chemicals based on fossil fuels. Furthermore, the high melting points (T_m) of these petroleum-derived phthalonitrile monomers required harsh processing conditions,^[10] and limited their scalable application as well.

On the other hand, bio-based resources are also considered to be solutions for environmental protection and oil resource saving.^[11] During these years, big progress in produ-

cing thermosets, especially epoxies and cyanate esters, from bio-based sources has been made. They exhibited comparable performances to the petroleum-based counterparts and showed great potential in application.^[12,13] However, in the case of phthalonitrile resins, the presence of flexible aliphatic chains in most bio-based reagents may bring disaster to high temperature performances, and only limited phenolic chemicals could be adopted.^[14,15] Renewable bisphenols, such as resveratrol and dihydroresveratrol, were used for the synthesis of phthalonitrile monomers, and improvement of processability and comparable thermal performances were realized.^[15] Furthermore, resveratrol-derived phthalonitrile monomer was blended into resin and could be used for composite fabrication.^[16] Catechin, which contains multiple phenolic hydroxyl units, could also be adopted for phthalonitrile resin synthesis. Qi and coworkers^[14] adjusted the stoichiometric ratio between catechin and 4-nitrophthalonitrile, and a mixture of compounds containing different degrees of phthalonitrile substitutions was obtained. The resin exhibited autocatalytic curing behavior, and the thermal stability was comparable to that of bisphenol A-derived counterparts.

Vanillin, a representative nonhazardous aromatic com-

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Received March 20, 2019; Accepted June 3, 2019; Published online September 3, 2019

pound industrially available from biomass, shows great potential in polymer synthesis.^[17] Typically, it is derived from lignin through various methods, and approaches based on oxidation could result in high yields. The presence of phenolic hydroxyl and benzaldehyde units provides various possibilities for further functionalization, and it has been adopted for both thermoset^[18,19] and thermoplastic^[20] synthesis.

In this work, vanillin was used as the source for phthalonitrile monomer synthesis. In order to ease the processing difficulty of phthalonitrile resins, flexible but crosslinkable units, such as allyl and propargyl, were introduced to lower the rigidity and intermolecular interactions. The synthesis route was designed to minimize the side-reactions and simplify the post-processing. Finally, the curing behaviors and thermal properties of these dual-functional phthalonitrile monomers were studied and compared with those of the petroleum-derived counterparts.

EXPERIMENTAL

Materials and Instruments

Vanillin, allyl bromide, and propargyl bromide were purchased from Aladdin Reagent Company (China). 4-Nitrophthalonitrile was obtained from Shijiazhuang Alpha Chemical Co., Ltd. Potassium carbonate, hydrogen peroxide (30% aqueous solution), potassium bicarbonate, boric acid, sulphuric acid (conc.), and all solvents were purchased from Beijing Chemical Works (China) and used as received. Activated carbon supported calcium oxide (CaO@AC) was prepared according to our previous publication,^[6] and stored in degassed desiccator to prevent moisture absorption. Based on the stoichiometric ratio between AC and CaO, the equivalent molecular weight for CaO@AC was 228.90 g·mol⁻¹.

¹H- and ¹³C-nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III 400 HD nuclear magnetic resonance spectrometer by using DMSO-d₆ as the solvent. The chemical shifts were reported in ppm downfield from DMSO-d₆ (2.50 ppm for ¹H-NMR and 39.52 ppm for ¹³C-NMR) as an internal standard. Coupling constants (*J*) for ¹H spectra were reported in hertz and refer to apparent peak multiplications. The abbreviations s, d, t, q, and m stand for singlet,

doublet, triplet, quartet, and multiplet in that order. High resolution mass spectrometer analysis (HRMS) was performed on a Bruker Solarix 9.4T mass spectrometer (ESI). Fourier transform infrared (FTIR) spectra were recorded in the range of 4000–400 cm⁻¹ on a Bruker Tensor-27 spectrometer using KBr pellets. Differential scanning calorimetry (DSC) measurements were carried out on a Mettler Toledo DSC822e device in the temperature range from 30 °C to 400 °C at a heating rate of 10 °C·min⁻¹ under nitrogen atmosphere. Rheological tests were conducted by using a TA AR-2000 rheometer from 50 °C to 380 °C at a heating rate of 4 °C·min⁻¹. Thermogravimetric analysis (TGA) tests were performed on a Netzsch STA 409PC instrument. Samples weighing ~10 mg were heated from 25 °C to 1000 °C at a rate of 10 °C·min⁻¹, in either nitrogen or air flowing at 50 mL·min⁻¹. Dynamic mechanical analysis (DMA) tests were performed on a DMA 242c (Netzsch, Germany) device at a fixed frequency of 1 Hz with single cantilever mode, and the oven was heated from 30 °C to 500 °C at a heating rate of 5 °C·min⁻¹ in nitrogen atmosphere. The size of the specimens for DMA measurement was 25 mm × 9 mm × 2 mm.

Synthesis

As shown in Fig. 1, the synthesis for vanillin-derived phthalonitrile monomers included three steps: allyl/propargyl functionalization, oxidation of benzaldehyde unit into phenol, and phthalonitrile functionalization.

Procedure for allyl/propargyl functionalization of vanillin

Vanillin (0.3 mol, 45.65 g), K₂CO₃ (0.33 mol, 45.61 g), and ethanol (200 mL) were added into a four-necked flask equipped with a magnetic stir bar, a thermometer, and a dropping funnel. Upon cooling to 0 °C, allyl/propargyl bromide (Br-R, 0.33 mol) was slowly added into the solution *via* dropping funnel. Then, the reaction was refluxed for 6 h, cooled to room temperature, filtered, and evaporated under vacuum. The crude product was dissolved by ethyl acetate, washed by dilute hydrochloric acid first, then by water until neutral. After evaporation and dried at 50 °C, functionalized vanillin was obtained.

4-(Allyloxy)-3-methoxybenzaldehyde (1a) was prepared from vanillin and allyl bromide as brown viscous liquid. Yield: 94% (54.21 g). ¹H-NMR (400 MHz, DMSO, δ, ppm): 9.84 (s), 7.53 (dd, *J* = 8.2, 1.7 Hz), 7.40 (d, *J* = 1.6 Hz), 7.17 (d, *J* = 8.3 Hz), 6.05

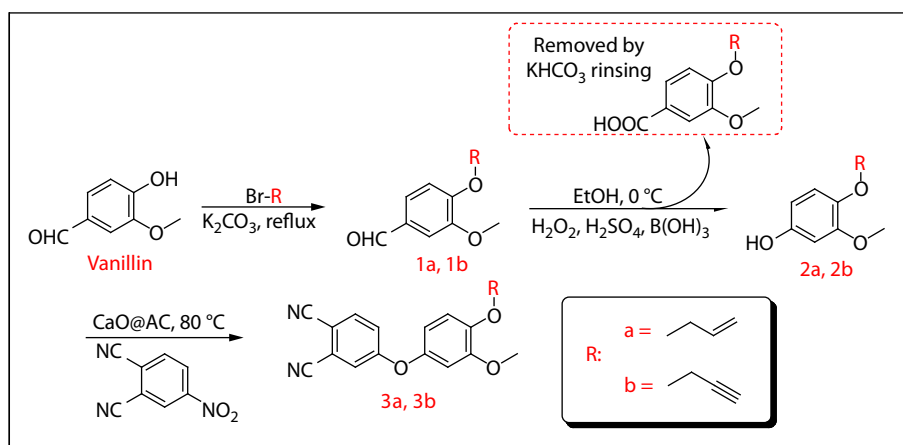


Fig. 1 Synthesis routes to dual-functional monomers.

(ddd, $J = 15.9, 10.6, 5.3$ Hz), 5.42 (dd, $J = 17.3, 1.5$ Hz), 5.29 (dd, $J = 10.5, 1.2$ Hz), 4.68 (d, $J = 5.3$ Hz), 3.84 (s). ^{13}C -NMR (101 MHz, DMSO, δ , ppm): 191.26, 153.01, 149.32, 133.01, 129.74, 125.81, 118.12, 112.41, 109.72, 68.98, 55.51. HRMS (ESI, m/z): $[\text{M} + \text{Na}]^+$ Calcd. for $\text{C}_{11}\text{H}_{12}\text{O}_3\text{Na}^+$ 215.067865; Found 215.068043; Error 0.8 ppm. FTIR (ν , cm^{-1}): 3082 ($=\text{C}-\text{H}$ stretching), 1649 ($\text{C}=\text{C}$ stretching), 1683 ($\text{C}=\text{O}$ stretching), 1587 and 1509 (aromatic $\text{C}=\text{C}$ stretching).

4-(Prop-2-yn-1-yloxy)-3-methoxybenzaldehyde (1b) was prepared from vanillin and propargyl bromide as pale yellow powder. Yield: 96% (54.78 g). ^1H -NMR (400 MHz, DMSO, δ , ppm): 9.85 (s), 7.55 (dd, $J = 8.2, 1.7$ Hz), 7.41 (d, $J = 1.6$ Hz), 7.22 (d, $J = 8.3$ Hz), 4.94 (d, $J = 2.3$ Hz), 3.84 (s), 3.62 (t, $J = 2.3$ Hz). ^{13}C -NMR (101 MHz, DMSO, δ , ppm): 191.33, 151.80, 149.42, 130.31, 125.40, 112.89, 109.94, 78.78, 78.53, 56.13, 55.54. HRMS (ESI, m/z): $[\text{M} + \text{Na}]^+$ Calcd. for $\text{C}_{11}\text{H}_{10}\text{O}_3\text{Na}^+$ 213.052215; Found 213.052250; Error 0.2 ppm. FTIR (ν , cm^{-1}): 3250 ($=\text{C}-\text{H}$ stretching), 2114 ($\text{C}\equiv\text{C}$ stretching), 1692 ($\text{C}=\text{O}$ stretching), 1593 and 1513 (aromatic $\text{C}=\text{C}$ stretching).

Procedure for oxidation of allyl/propargyl-functionalized vanillin to phenols

Functionalized vanillin (0.2 mol), boric acid (0.8 mol, 49.46 g), and tetrahydrofuran (200 mL) were added into a four-necked flask equipped with a magnetic stir bar, a nitrogen inlet/outlet, a thermometer, and a dropping funnel. Upon cooling to -10°C under ethanol/liquid nitrogen bath, 30 mL of conc. H_2SO_4 was carefully added into the flask. Then, 65 mL of H_2O_2 (30% aq.) was added into the flask via the dropping funnel. The temperature of the reaction was kept around 0°C by adding liquid nitrogen into the ethanol bath. Monitored by thin layer chromatography (TLC), once all allyl/propargyl functionalized vanillin was consumed, the mixture was poured out, neutralized by dilute KHCO_3 aq., and evaporated under vacuum. The remaining mixture was dissolved into ethyl acetate, washed twice by dilute KHCO_3 (aq.), then by water until neutral. After evaporation and dried at 50°C , the phenol was obtained.

4-(Allyloxy)-3-methoxyphenol (2a) was prepared from 1a as brown viscous liquid. Yield: 78% (28.11 g). ^1H -NMR (400 MHz, DMSO, δ , ppm): 8.99 (s), 6.74 (d, $J = 8.6$ Hz), 6.40 (d, $J = 2.7$ Hz), 6.22 (dd, $J = 8.6, 2.7$ Hz), 5.99 (ddd, $J = 22.5, 10.6, 5.4$ Hz), 5.33 (dd, $J = 17.3, 1.7$ Hz), 5.19 (dd, $J = 10.5, 1.3$ Hz), 4.39 (d, $J = 5.3$ Hz), 3.70 (s). ^{13}C -NMR (101 MHz, DMSO, δ , ppm): 152.40, 150.41, 140.47, 134.55, 116.95, 116.17, 105.82, 100.95, 70.35, 55.36. HRMS (ESI, m/z): $[\text{M} + \text{Na}]^+$ Calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_3\text{Na}^+$ 203.067865; Found 203.067977; Error 0.6 ppm. FTIR (ν , cm^{-1}): 3429 (associated $\text{O}-\text{H}$ stretching), 3082 ($=\text{C}-\text{H}$ stretching), 1647 ($\text{C}=\text{C}$ stretching), 1605 and 1511 (aromatic $\text{C}=\text{C}$ stretching).

4-(Prop-2-yn-1-yloxy)-3-methoxyphenol (2b) was prepared from 1b as brown viscous liquid. Yield: 76% (27.08 g). ^1H -NMR (400 MHz, DMSO, δ , ppm): 9.09 (s), 6.81 (d, $J = 8.6$ Hz), 6.42 (d, $J = 2.6$ Hz), 6.24 (dd, $J = 8.6, 2.7$ Hz), 4.59 (d, $J = 2.3$ Hz), 3.70 (s), 3.47 (t, $J = 2.3$ Hz). ^{13}C -NMR (101 MHz, DMSO, δ , ppm): 153.15, 150.73, 139.26, 117.36, 105.77, 100.86, 79.96, 77.72, 57.40, 55.38. HRMS (ESI, m/z): $[\text{M} + \text{Na}]^+$ Calcd. for $\text{C}_{10}\text{H}_{10}\text{O}_3\text{Na}^+$ 201.052215; Found 201.052282; Error -0.3 ppm. FTIR (ν , cm^{-1}): 3421 (associated $\text{O}-\text{H}$ stretching), 3287 ($=\text{C}-\text{H}$ stretching), 2122 ($\text{C}\equiv\text{C}$ stretching), 1608 and 1511 (aromatic $\text{C}=\text{C}$ stretching).

Procedure for phthalonitrile functionalization

4-Nitrophthalonitrile (0.1 mol, 17.31 g), vanillin-derived phenol (0.1 mol), CaO@AC (0.1 mol, 22.89 g), and 100 mL of acetonitrile were added into a three-necked flask equipped with a magnetic stir bar, a nitrogen inlet/outlet, and a thermometer. After nitrogen purging for 0.5 h, the reaction mixture was gently heated to 80°C and monitored by TLC. Once all 4-nitrophthalonitrile was consumed (typically 6 h), the mixture was allowed to cool down to room temperature, filtered, and precipitated into water. The precipitant was collected, washed first by dilute HCl solution, then by water until neutral. Finally, the products were dried under vacuum at 50°C .

4-(4-(Allyloxy)-3-methoxyphenoxy)phthalonitrile (3a) was prepared from 2a and 4-nitrophthalonitrile as brown powder. Yield: 92% (28.18 g). ^1H -NMR (400 MHz, DMSO, δ , ppm): 8.07 (d, $J = 8.8$ Hz), 7.71 (d, $J = 2.5$ Hz), 7.33 (dd, $J = 8.8, 2.5$ Hz), 7.04 (d, $J = 8.8$ Hz), 6.88 (d, $J = 2.6$ Hz), 6.69 (dd, $J = 8.7, 2.7$ Hz), 6.05 (ddd, $J = 22.4, 10.6, 5.3$ Hz), 5.40 (dd, $J = 17.3, 1.5$ Hz), 5.26 (d, $J = 10.5$ Hz), 4.56 (d, $J = 5.3$ Hz), 3.75 (s). ^{13}C -NMR (101 MHz, DMSO, δ , ppm): 161.89, 150.42, 147.05, 145.55, 136.14, 133.71, 121.78, 121.21, 117.62, 116.53, 115.92, 115.41, 114.21, 111.77, 107.52, 105.60, 69.32, 55.77. HRMS (ESI, m/z): $[\text{M} + \text{Na}]^+$ Calcd. for $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_3\text{Na}^+$ 329.089663; Found 329.089905; Error -0.7 ppm. FTIR (ν , cm^{-1}): 3084 ($=\text{C}-\text{H}$ stretching), 2228 ($\text{C}\equiv\text{N}$ stretching), 1639 ($\text{C}=\text{C}$ stretching), 1604 and 1509 (aromatic $\text{C}=\text{C}$ stretching).

4-(3-Methoxy-4-(prop-2-yn-1-yloxy)phenoxy)phthalonitrile (3b) was prepared from 2b and 4-nitrophthalonitrile as red-dish brown powder. Yield: 94% (28.60 g). ^1H -NMR (400 MHz, DMSO, δ , ppm): 8.08 (d, $J = 8.8$ Hz), 7.73 (d, $J = 2.5$ Hz), 7.35 (dd, $J = 8.8, 2.5$ Hz), 7.10 (d, $J = 8.7$ Hz), 6.91 (d, $J = 2.6$ Hz), 6.73 (dd, $J = 8.7, 2.6$ Hz), 4.80 (d, $J = 2.1$ Hz), 3.76 (s), 3.59 (d, $J = 2.1$ Hz). ^{13}C -NMR (101 MHz, DMSO, δ , ppm): 161.76, 150.61, 147.76, 144.38, 136.18, 121.93, 121.33, 116.57, 115.95, 115.44, 115.00, 111.67, 107.64, 105.71, 79.18, 78.39, 56.42, 55.82. HRMS (ESI, m/z): $[\text{M} + \text{Na}]^+$ Calcd. for $\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_3\text{Na}^+$ 327.074013; Found 327.074150; Error -0.4 ppm. FTIR (ν , cm^{-1}): 3270 ($=\text{C}-\text{H}$ stretching), 2228 ($\text{C}\equiv\text{N}$ stretching), 2131 ($\text{C}\equiv\text{C}$ stretching), 1608 and 1507 (aromatic $\text{C}=\text{C}$ stretching).

Procedure for Thermal Curing

Thermal curing was conducted in nitrogen purged oven. The monomers were cured according to the following conditions: 170°C for 1 h, 200°C for 1 h, 250°C for 4 h, 280°C for 3 h, 315°C for 5 h, and 375°C for 5 h. Upon cooling, the cured polymers were taken out, and the polymers derived from 3a and 3b were designated as cured-3a and cured-3b, respectively.

RESULTS AND DISCUSSION

Design and Synthesis of Dual-functional Phthalonitrile Monomers

The presence of phenolic hydroxyl and benzaldehyde units on vanillin offers wide options for dual-functional phthalonitrile monomer synthesis. Specifically, phenolic hydroxyl could be used for nucleophilic substitutions, while benzaldehyde unit could be either reduced to alcoholic hydroxyl or oxidized to phenolic hydroxyl.^[17] Allyl/propargyl ether units would be introduced to ease the processing difficulty at a minimal cost of

thermal-mechanical performances.^[21] And allyl/propargyl functionalizations could be achieved *via* nucleophilic substitutions of bromides by alcoholic/phenolic hydroxyl groups. Further, phthalonitrile functionalization relied on the aromatic nucleophilic substitution between phenolic hydroxyl and 4-nitrophthalonitrile. Consequently, potential routes to dual-functional monomers containing both phthalonitrile and allyl/propargyl ether units were proposed as shown in Scheme S1 (in the electronic supplementary information, ESI). In routes S1(a) and S1(b), phthalonitrile moiety was first introduced, and the reaction could be finished in high purity and yields. However, the nitrile groups were not stable under strong basic or acidic environments, and complicated purification (typically column chromatography) should be performed to remove the hydrolyzed by-products from 4-(4-formyl-2-methoxyphenoxy)phthalonitrile. Such process would bring disaster to scalable synthesis, and was thereby abandoned. In contrast, route S3 would be the more suitable. The first step was a mature and reliable reaction for grafting allyl or propargyl moieties, which could be accomplished in high purity and yields.^[21] The only side-reaction involved in the second step was the oxidation of benzaldehyde into carboxyl unit. Luckily, the acidity of the by-product differed a lot from that of the desired product, so it could be washed away easily by weak bases such as KHCO_3 . Thus, excellent purity and acceptable yields would be guaranteed. The third step was finished *via* our recently developed protocol, where CaO@AC was used as the catalyst for the nucleophilic substitutions between phenolic hydroxyl and 4-nitrophthalonitrile.^[6] The use of supported calcium oxide greatly suppressed water-induced

side-reactions and ensured clean synthesis of desired dual-functional monomers. Finally, the optimized synthesis route is shown in Fig. 1.

The chemical structures of all compounds were confirmed by ^1H -NMR (Fig. 2, enlarged spectra shown in Figs. S1–S6 in ESI), ^{13}C -NMR (Fig. 3, enlarged spectra shown in Figs. S7–S12 in ESI), FTIR (Fig. 4), and HRMS, and no visible impurities could be found in the NMR spectra. In the ^1H -NMR spectra, all protons were assigned to the corresponding structures, and the integrations, multiplications, and coupling constants for proton signals matched well with corresponding chemical environments. Taking allyl-containing compounds (1a–3a) as examples, after the first step, the signal for phenolic hydroxyl vanished due to allyl grafting, and the characteristic signals arising from allyl (H2–H5) could be detected. After the second step, the signal for benzaldehyde proton disappeared; in the meantime, the signal for newly generated phenolic hydroxyl was found. After the third step, the appearance of proton signals from phthalonitrile moiety was accompanied by the disappearance of hydroxyl signal. Similar transformations could be found in ^1H -NMR spectra for compounds 1b–3b, except for the characteristic signals from propargyl moiety. ^{13}C -NMR was used to further confirm the chemical transformations, and all carbon atoms were assigned to the corresponding structures. The appearance of allyl/propargyl related signals, disappearance of benzaldehyde signals, and emerging of phthalonitrile-related signals were respective characteristic changes during the three-step synthesis. It should be noted that for monomer 3a, C2 signal (69.32 ppm) was the only

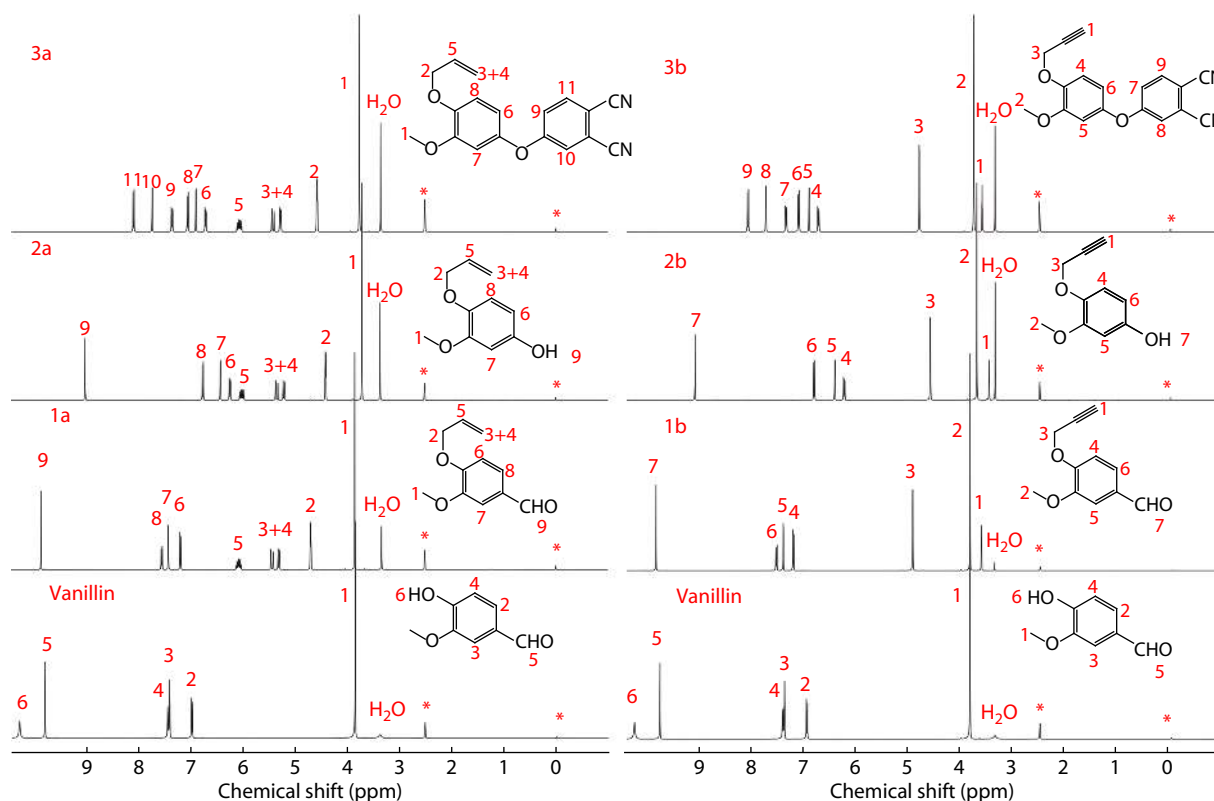


Fig. 2 ^1H -NMR spectra for vanillin, compounds 1a–3a, and compounds 1b–3b.

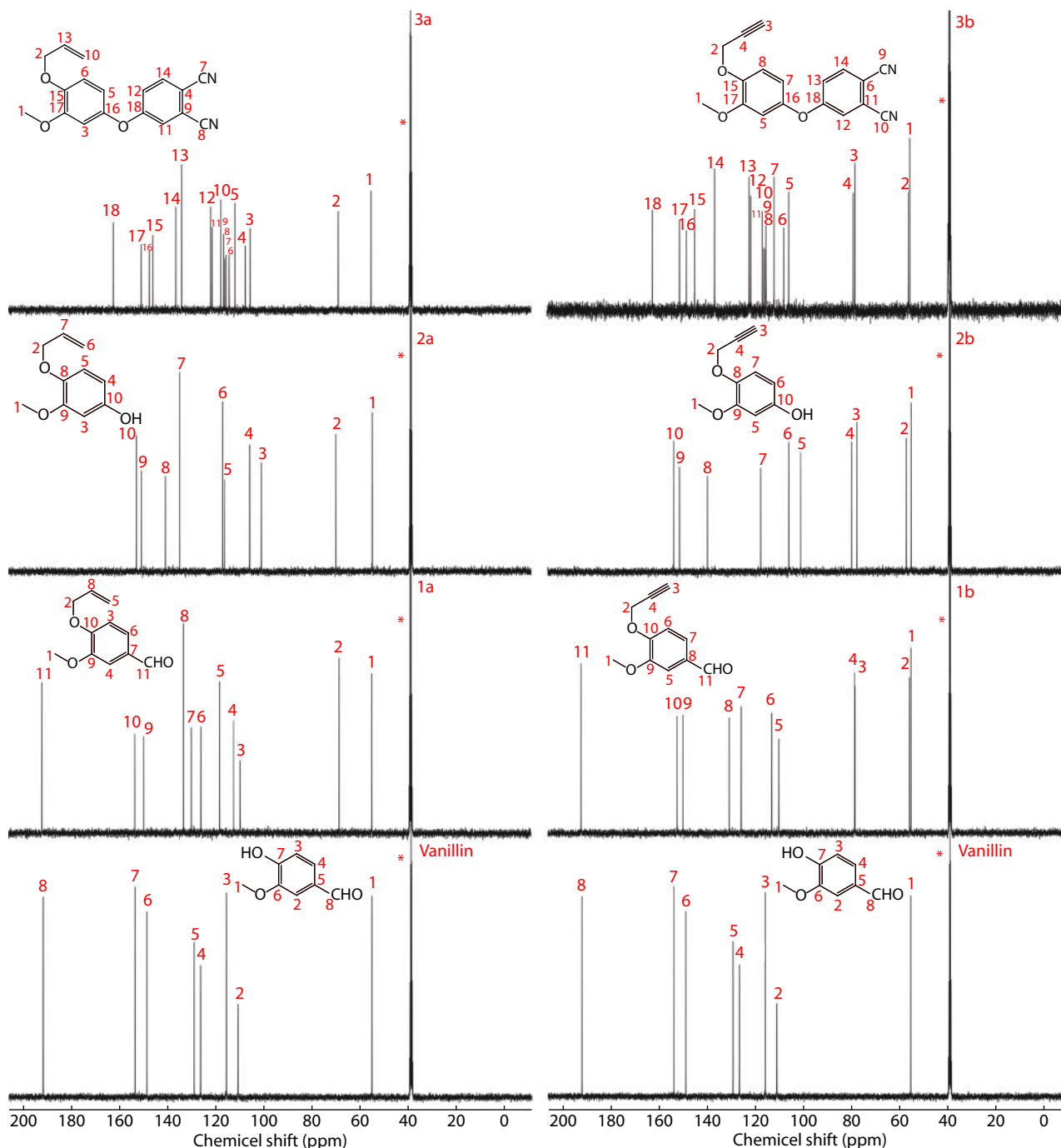


Fig. 3 ^{13}C -NMR spectra for vanillin, compounds 1a–3a, and compounds 1b–3b.

characteristic signal which was far away from neighboring signals, and might be potentially used for curing mechanism analysis, while for monomer 3b, the propargyl-related carbons (C3 at 78.39 ppm and C4 at 79.18 ppm) could be adopted for monitoring the curing process. Unfortunately, all nitrile-related signals were embedded in the forest of signals, and little information on curing could be derived from them. After that, HRMS was used to confirm the formula of the compounds. All the molecular ions were detected in $[\text{M} + \text{Na}]^+$ form, and the errors were all below 1.0 ppm.

In addition, FTIR spectroscopy (Fig. 4) was further used to monitor the transformations of functional groups, and characteristic vibrations were labeled on the images. After the first step, the broad signals for associated hydroxyl O—H vibration (around 3300 cm^{-1}) disappeared, accompanied by the occurrence of alkene-/alkyne-related signals. After the second step, the benzaldehyde-related C=O vibration vanished, and associated O—H vibrations for newly formed phenolic hydroxyl units were found around 3400 cm^{-1} . After the third step, nitrile C≡N stretching signals could be detected at

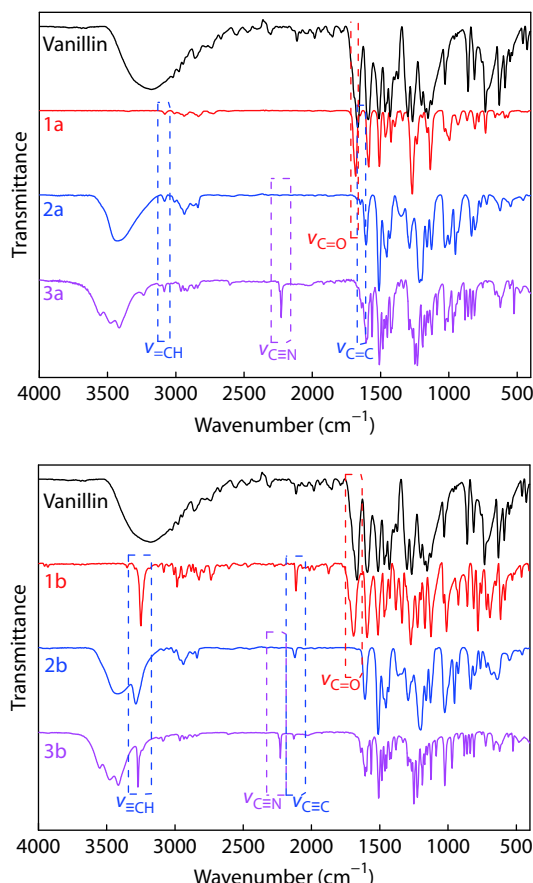


Fig. 4 FTIR spectra for vanillin, compounds 1a–3a, and compounds 1b–3b.

2228 cm^{-1} . Moreover, the signals for allyl-related structures (3084 and 1639 cm^{-1}), propargyl-related structures (3270 and 2131 cm^{-1}), and nitrile-related structures (2228 cm^{-1}) did not overlap with neighboring ones and could be used for curing mechanism analysis.

Curing Behavior, Mechanism, and Processability

Initially, the DSC measurements (Fig. 5) were performed on monomers 3a and 3b to evaluate their melting and curing behaviors, and relevant parameters are summarized in Table 1. T_m for monomer 3a was 94.5 $^{\circ}\text{C}$, while that for 3b was 130.4 $^{\circ}\text{C}$. Typically, T_m s of petroleum-based phthalonitrile monomers were around 200 $^{\circ}\text{C}$.^[8,22] Obviously, the existence of flexible allyl/propargyl ether and methoxyl moieties in monomers 3a and 3b lowered T_m s by reducing molecular rigidity and intermolecular interactions. Furthermore, T_m for 3a was much lower than that of 3b as allyl was more flexible than propargyl. Attributed to much lower T_m , the composite processing temperature could be greatly lowered, and low cost composite fabrication

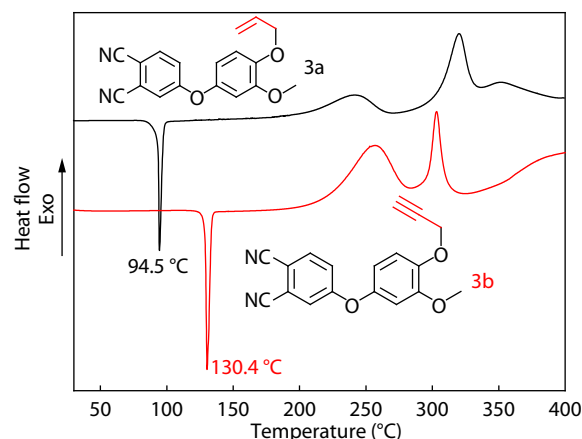


Fig. 5 DSC curves for monomers 3a and 3b.

technology, such as RTM, could be considered.

After the sharp melting endothermic signal, three broad exothermic signals could be detected for both monomers, but in different temperature ranges. The initial (T_i) and peak (T_p) temperatures and enthalpy (ΔH) values were derived from the corresponding curves and are listed in Table 1. According to the monomers' chemical structures, the first exothermic signals could be associated with the rearrangement of allyl/propargyl ether.^[23,24] Since the *para*-positions were already occupied, Claisen rearrangement was the only possibility.^[24] The rearrangement occurred at much lower temperatures when compared with other similar allyl/propargyl ether-containing compounds.^[1,25] This phenomenon might be related to the chemical environments—one *ortho*- and the *para*-positions were substituted by other ethers. These electron-donating groups would promote the rearrangement remarkably.^[24] Furthermore, the enthalpy values for monomers 3a and 3b differed a lot. Altered chemical transformations should have occurred, and would be analyzed and discussed by FTIR and rheological measurements. The second exothermic signals corresponded to the catalyzed curing of phthalonitrile moiety, and rearrangement-generated phenolic hydroxyl might be the catalyst. However, obvious differences in both T_{p2} and ΔH_2 values for these two monomers were found. It could be ascribed to different curing pathways or degrees of curing, and would be discussed later by FTIR. The third exothermic signals should be associated with the self-polymerizations of allyl or propargyl units. For monomer 3a, the third exothermic signal arose immediately after the second one, and completed at around 380 $^{\circ}\text{C}$, while for 3b, the self-polymerization did not occur until 350 $^{\circ}\text{C}$, and had not finished before 400 $^{\circ}\text{C}$. Once again, these variations should be relevant to the differences in either reactivities or pathways, and would be discussed by FTIR and solid ^{13}C -NMR.

Table 1 Parameters calculated from DSC measurements of different monomers.

	Melting T_{i1} ($^{\circ}\text{C}$)	1 st Exothermal			2 nd Exothermal			3 rd Exothermal		
		T_{i1} ($^{\circ}\text{C}$)	T_{p1} ($^{\circ}\text{C}$)	ΔH_1 ($\text{J}\cdot\text{g}^{-1}$)	T_{i2} ($^{\circ}\text{C}$)	T_{p2} ($^{\circ}\text{C}$)	ΔH_2 ($\text{J}\cdot\text{g}^{-1}$)	T_{i3} ($^{\circ}\text{C}$)	T_{p3} ($^{\circ}\text{C}$)	ΔH_3 ($\text{J}\cdot\text{g}^{-1}$)
3a	94.5	201.1	241.5	168.4	294.6	319.8	256.7	337.4	351.9	144.6
3b	130.4	203.9	256.7	420.2	286.2	303.0	181.6	346.8	— ^a	— ^a

T_i : initial temperature; T_p : peak temperature; ΔH : enthalpy; ^a Out of detect range.

Rheological measurements (Fig. 6) were performed to evaluate the processability of dual-functional monomers, and provide further details for the rearrangement process as well.

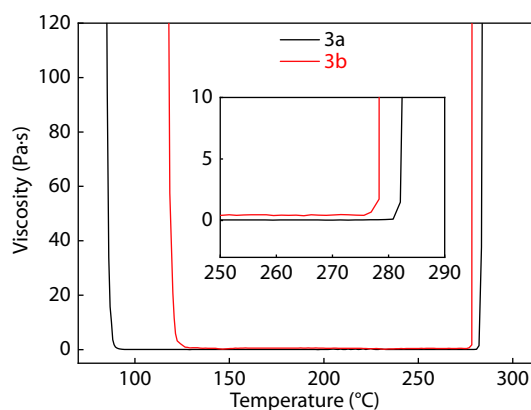


Fig. 6 Viscosity-temperature relationships for different monomers.

After T_m , sharp decreases were found immediately in viscosity for both monomers. The viscosity was almost constant before gelation. It should be noted that the viscosity of monomer 3a (~ 0.08 Pa·s) was lower than that of 3b (~ 0.45 Pa·s), which corresponded to their differences in molecular flexibility. Furthermore, the gelation temperature was a little lower than T_{i2} derived from DSC, for the reason that rheological measurements were performed at a much slower rate of $4^\circ\text{C}\cdot\text{min}^{-1}$. The temperature difference between melting and gelation could be defined as the processing window. As shown in Table 2, the processing windows of monomers 3a (185°C) and 3b (148°C) were much wider than those of petroleum-based counterparts. The combination of lower viscosity and wider processing window would ensure better resin infiltration while liquid processing technologies were adopted. Furthermore, the viscosity changes above 250°C are enlarged and shown as the inset image. This range of temperatures corresponded to the first exothermic signal in DSC curves. The almost unchanged viscosity implied that only intra-

Table 2 Comparison of bio-based and petroleum-based phthalonitrile resins.

Table 2. Comparison of bio-based and petroleum-based phthalonitrile resins.						
	Monomer		Cured polymer			Reference
	Structure	T_m (°C)	Processing window (°C)	T_g (°C)	T_{d5} (°C)	
Bio-based		94.5	185	> 500	482	This work
		130.4	148	> 500	477	This work
		100–125 (T_g)	~ 100	> 400 ^a	510	[15]
		75	~ 125	> 400 ^a	500	[15]
Petroleum-based		232	< 20	> 450 ^b	> 500	[8]
		197	~ 70	> 400 ^c	461	[22]
		185	~ 60	> 400 ^c	503	[22]

^a Cured with 4-(4-aminophenoxy)phthalonitrile; ^b Cured with bis(3-(4-aminophenoxy)phenyl)sulfone; ^c Cured with 1,3-bis(3-aminophenoxy)benzene.

molecular transformations occurred within this range. However, Nair and coworkers stated that the Claisen rearrangement of propargyl ether was accompanied with the intermolecular curing of phthalonitrile moieties, as evidenced by gelation in rheological measurements.^[1] Such big differences should be attributed to the chemical environments. The rearrangement occurred in the monomers 3a and 3b much earlier, and almost no intermolecular curing proceeded within this range.

FTIR (Fig. 7) and solid ^{13}C -NMR (Figs. S13 and S14 in ESI) measurements were performed to get further evidences for curing behaviors. Upon heated to 375 °C, cured polymers were obtained. In FTIR for cured-3a, the bands for the alkene unit (3084 and 1639 cm^{-1}) disappeared, while the broad disassociated hydroxyl vibration band (around 3600 cm^{-1}) occurred. In solid ^{13}C -NMR, C2 signal (allyl $-\text{CH}_2-$) was no longer observed, and a new bundle of strong signals was found in the range of 10–35 ppm (aliphatic $-\text{CH}_2-$). Thus, it could be predicted that allyl ether had completely rearranged and mostly cured into aliphatic chains. In addition, the nitrile $\text{C}\equiv\text{N}$ stretching band (2228 cm^{-1}) significantly diminished, accompanied by the hydroxyl-catalyzed formation of phthalocyanine (1014 cm^{-1}), triazine (1360 cm^{-1}), and isoindoline (1708 cm^{-1}) structures.^[26,27] It could be clearly seen that the crosslinking mainly ended in phthalocyanine,

and only a bit of isoindoline and triazine were found. For cured-3b, all alkyne-related FTIR bands (3270 and 2131 cm^{-1}) vanished after curing, and C3 and C4 signals (propargyl $\text{C}\equiv\text{C}$) were no longer detectable in solid ^{13}C -NMR. However, no obvious hydroxyl vibration was observed in the FTIR spectra, and the bundle of solid ^{13}C -NMR signals for aliphatic $-\text{CH}_2-$ (in the range of 10–35 ppm) was much weaker than that of cured-3a. Hence, it could be inferred that the propargyl ether had completely rearranged but partially cured. Similarly, a remarkable reduction in nitrile-related band (2228 cm^{-1}) and appearance of phthalocyanine (1008 cm^{-1}), triazine (1350 cm^{-1}), and isoindoline (1701 cm^{-1}) structures were found. But for cured-3b, a large portion of isoindoline remained.

Based on the details analyzed by DSC, rheological, FTIR spectroscopy, and solid ^{13}C -NMR measurements, the curing mechanism for 3a could be summarized as follows. In the first stage (200–280 °C), only [3,3]-sigmatropic (Claisen) rearrangement of allyl aryl ether occurred. Because of the occupation of the *para*-position, succeeding Cope rearrangement of dienone intermediate was prohibited. Later, the re-aromatization of the dienone intermediate induced the formation of *ortho*-allyl phenol due to a rapid enolization.^[24] In the second stage (above 280 °C), intermolecular catalytic polymerization of phthalonitrile moieties was triggered. Initiated via the protonation of one nitrile nitrogen, amidine intermediate was formed via nucleophilic attack by base at carbon. Later on, intermolecular trimerizations yielded triazine, while intramolecular linear polymerizations yielded isoindoline and tetramerizations yielded phthalocyanine. Judging from FTIR spectra, intramolecular polymerizations were the primary route, and the majority of isoindoline transformed into phthalocyanine at higher temperatures.^[28,29] The third stage took place at around 330 °C, where self-polymerization of allyl group was triggered, and aliphatic chains remained within the cured polymer. The corresponding pathways are shown in Fig. 8(a). However, the pathways for monomer 3b were somehow different from those for 3a. In the first stage (200–280 °C), the rearrangement of propargyl aryl ether proceeded smoothly to afford chromene structures. The mechanism included [3,3]-sigmatropic (Claisen) rearrangement to *ortho*-allenyl phenol, [1,5]-hydrogen shift, and electrocyclic ring closure.^[24] Since *ortho*-allenyl phenol intermediate was not stable, the triple-bond tended to transform into chromene, and the enthalpy (ΔH_1) would be much higher. Given that there were no disassociated phenols left after the first stage, the catalyst of the second stage (280–330 °C) was different from that of 3a. The lone pair electrons on chromene oxygen would ionize nitrile groups on neighboring molecules, yielding amidine intermediates. Then, the following polymerizations tended to be faster under ionized environments (lower T_{i2} and T_{p2}). According to FTIR analysis, a quantity of isoindoline units left after curing. Such insufficient reaction might be related to the steric hindrance induced by chromene structures. Consequently, the total heat release (ΔH_2) would be much lower than that of 3a. Referring to DSC and solid ^{13}C -NMR analysis, it was reasonable to predict that, in the third stage (above 350 °C), the self-polymerization of chromene structures had not completed at

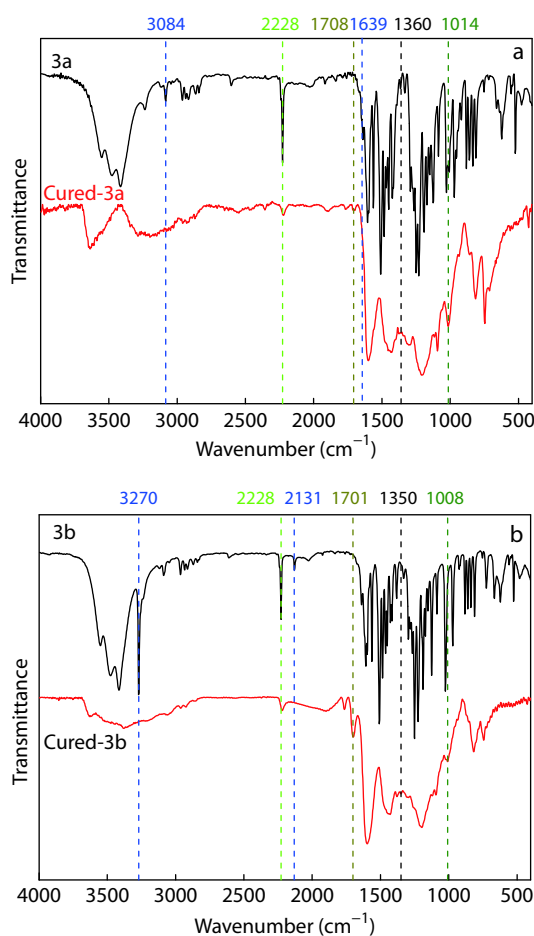


Fig. 7 FTIR spectra for (a) 3a and cured-3a, and (b) 3b and cured-3b.

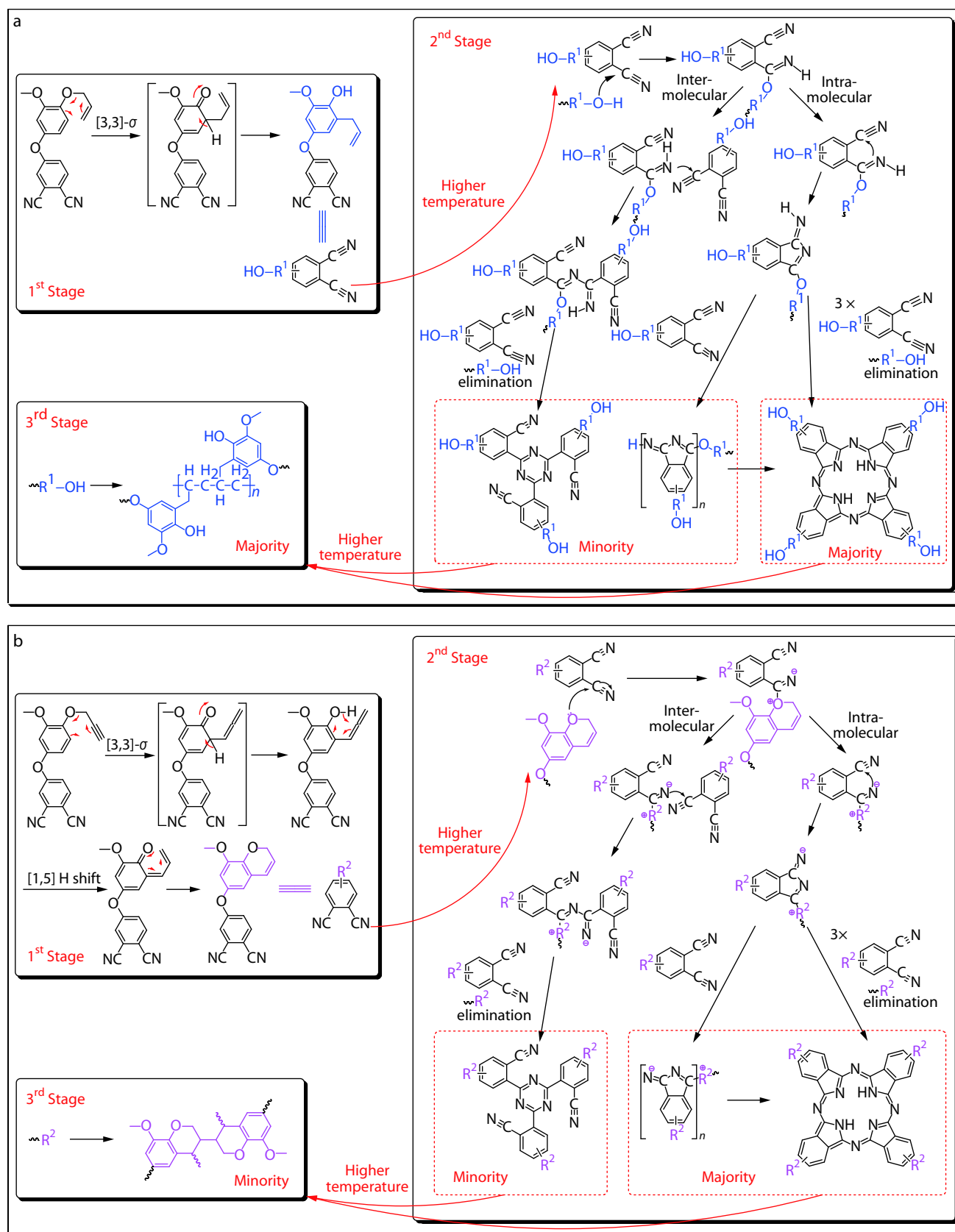


Fig. 8 Proposed curing pathways for (a) 3a and (b) 3b.

375 °C. The corresponding pathways are shown in Fig. 8(b).

Additionally, TGA measurements were performed on monomers 3a and 3b, and the curves are shown in Fig. S15 (in ESI). Taking into consideration that both monomers would start to decompose when being heated to 250 °C, and the Claisen rearrangement occurred in the range of 200–250 °C, curing steps at relatively low temperatures were essential. Consequently, the final curing program was designed as 170 °C for 1 h, 200 °C for 1 h, 250 °C for 4 h, 280 °C for 3 h, 315 °C for 5 h, and 375 °C for 5 h. Encouragingly, the total weight loss of cured-3a and cured-3b was both lower than 1 wt% after being cured as programmed procedures.

Thermal Properties

Cured phthalonitrile polymers were obtained by heating monomers with programmed procedures. TGA tests were performed under nitrogen and air atmospheres to evaluate their thermal stability and oxidation resistance, respectively. Corresponding thermal gravity and first-order derivative curves are shown in Fig. 9, and the parameters including 5% weight loss temperatures (T_{d5}) and residual weights at 1000 °C are labeled in the figure. Under nitrogen atmosphere, both cured polymers exhibited excellent thermal stability. Catastrophic weight losses were found during 500–700 °C, and the residual weights were higher than 75% at 1000 °C. In comparison, cured-3b exhibited relatively low T_{d5} and residual weight at 1000 °C, which should

result from its lower crosslinking degree as previously discussed.

The trend of oxidation resistance was somehow different from that of thermal stability. In oxidative environment, the cured phthalonitrile polymers were completely burned out. It could be seen from the first-order derivative that the oxidation was divided into two stages. The first occurred in the range of 400–500 °C, possibly owing to the methoxyl cutting off, and the second occurred in the range of 500–900 °C, which involved the oxidation of cured polymer backbones. Cured-3b endured a more dramatic weight loss around 600 °C, and was completely burnt out earlier at 800 °C. Such phenomenon should come from the insufficient curing of both phthalonitrile (more isoindoline) and chromene structures.

Similarly, it could be seen from the DMA measurements (Fig. 10) that the heat resistance of cured-3b was lower, and the lower storage modulus (E') was another evidence for insufficient curing. Dramatic increase in E' was detected in the range of 300–400 °C for cured-3b, whereas limited changes were found in the same region for cured-3a. This increase should be associated with the insufficient catalytic activity of chromene oxygen moieties, and 375 °C for 5 h was not enough for the curing of both phthalonitrile and propargyl units. As observed in other studies,^[30–32] the vibration during DMA tests might facilitate the post-curing of sterically hind or thermodynamically isolated reactive moieties, and induced the increase in E' . However, higher post-curing temperatures could not be applied to the polymers, for they started to slightly decompose from 420 °C. In addition, E' for cured-3b was found to decrease gradually above 400 °C, accompanied by the increase of loss tangent. Nevertheless, introduction of additional catalyst might enhance the crosslinking, and avoid post-curing during application. For cured-3a, no obvious changes for both E' and loss tangent could be found below 500 °C. The glass transition temperature (T_g) was typically defined as the peak temperature in the loss tangent curve, and T_{g5} for both cured polymers were not observed prior to their decomposition. Anyway, the smooth loss tangent and E' curves indicated that the heat resistance of cured-3a was much higher.

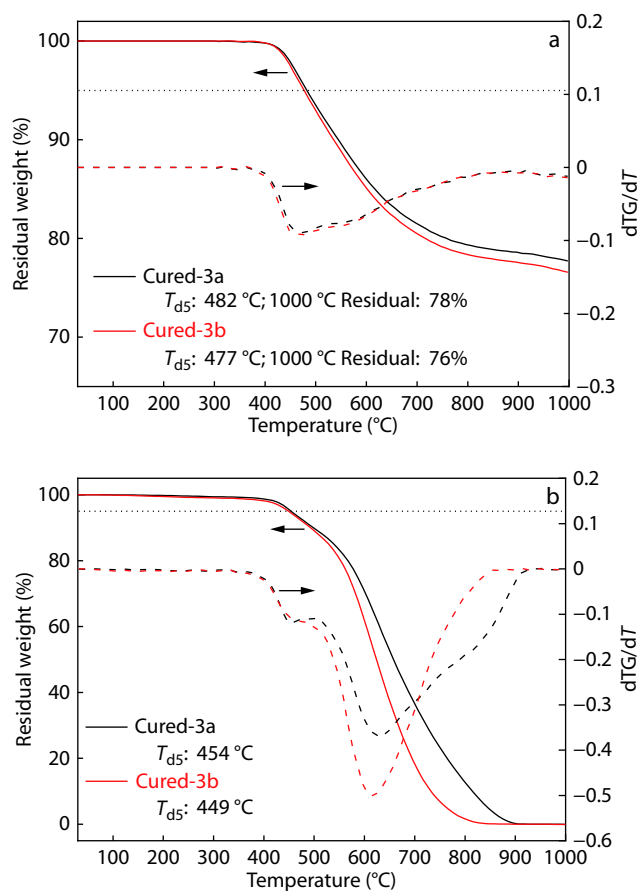


Fig. 9 TGA and DTG profiles of cured-3a and cured-3b under (a) nitrogen and (b) air atmosphere.

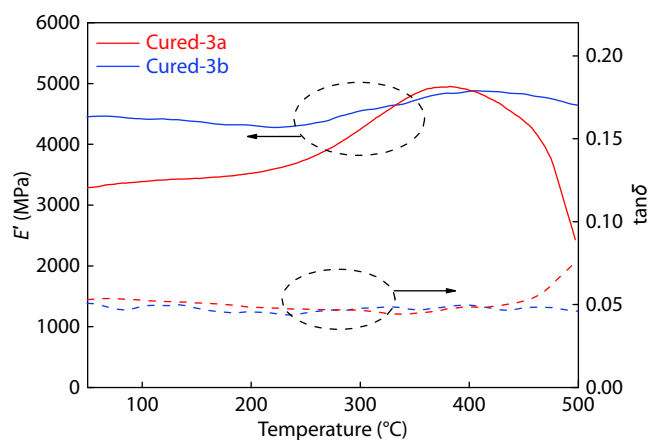


Fig. 10 DMA profiles of cured-3a and cured-3b under nitrogen atmosphere.

Comparison

As a family of high temperature thermosets, the primary consideration for phthalonitrile resins is their thermal performances. T_{d5} and T_g are commonly used to evaluate the thermal stability and heat resistance, respectively. Another concern is the processability, for which high T_m related harsh processing conditions are big challenges, especially for liquid composite manufacturing. The parameters, such as T_m , processing window, T_{d5} , and T_g , of bio-based and representative petroleum-based phthalonitrile resins are gathered in Table 2. Compared with traditional petroleum-based monomers, 3a exhibited extremely low T_m and wide processing window, as well as comparable thermal properties. Last but not least, 3a and 3b could be polymerized via self-catalytic processes, and no additional catalysts were needed.

CONCLUSIONS

In this study, dual-functional phthalonitrile monomers containing allyl/propargyl ether moieties were synthesized via a three-step process by using sustainable vanillin as the starting material. And the route was designed to minimize side-reactions and simplify post-processing. The chemical structures of obtained monomers were confirmed by ^1H - and ^{13}C -NMR, HRMS, and FTIR, spectroscopies. Their curing behavior, mechanism, and processability were studied and then discussed. Both monomers exhibited low T_m and wide processing window, and the lowest T_m was observed on 3a (allyl ether containing, 94.5 °C). The curing, which contained three stages, could be accomplished through self-catalytic processes. For 3a, the three stages included Claisen rearrangement of allyl ether to *ortho*-allyl phenol, phenolic hydroxyl catalyzed curing of phthalonitrile moiety, and self-polymerization of alkene units. And the main cured structures were phthalocyanine and aliphatic chains. As for 3b, it included rearrangement of propargyl ether to chromene structures, oxygen lone pair catalyzed curing of phthalonitrile moiety, and self-polymerization of chromene structures. And isoindoline and phthalocyanine were found to be the main cured structures. Encouragingly, T_g s of the cured polymers were higher than 500 °C, which are comparable to petroleum-based counterparts.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-019-2311-3>.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 51803059 and 51873215), Guangdong Innovative and Entrepreneurial Research Team Program (No. 2016ZT06C322), and National Defense Science and Technology Innovation Special Zone Project. The authors gratefully thank the Young Elite Scientist Sponsorship Program by CAST (YESS) and the Youth Innovation Promotion Association of CAS (No. 2017047). The measurements of solid

^{13}C -NMR were performed at the Center for Physicochemical Analysis and Measurements in ICCAS. The help from Ms. Ningning Wu was acknowledged.

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