



Inspiration from a new lignin-derived phthalonitrile resin: Unique curing behavior, and thermal properties

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ABSTRACT

In this paper, a novel lignin-based phthalonitrile monomer (BPN) was synthesized with a biomass content of 54%. Its structure was confirmed by infrared spectroscopy (IR), ^1H NMR spectroscopy and elemental analysis. The curing behavior of BPN was studied by rheological analysis. The thermal polymerization mechanism was discussed by bisphenol A based phthalonitrile (BAPh) control experiment, *in situ* IR and solid-state ^{13}C NMR. We proposed the curing mechanism of "methyne-activated phthalonitrile thermal polymerization". The thermo-mechanical and thermal properties of the cured product were characterized by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA), respectively. The results show that the cured BPN has a comparable glass transition temperature ($T_g = 400\text{ }^\circ\text{C}$) and better thermal stability than petroleum-based BAPh. On the other hand, compared with previous bio-based phthalonitrile resins, the cured BPN exhibits comparable or superior thermal properties and a higher biomass content.

1. Introduction

Recent concerns about the decreasing fossil feedstock and the increasing environmental pollution have resulted in a worldwide initiative toward the development of polymers derived from renewable resources [1–5]. The development and utilization of biomass resources is considered as an effective way to save fossil fuels and protect our living environment. Up to now, a large number of bio-based high-performance polymers have been synthesized based on renewable biomass, such as bio-based polyesters derived from furan [6], bio-based epoxy resins synthesized from plant oils [7], bio-based polyurethanes [8] and bio-based cyanate esters [9,10] prepared from lignin, etc. The raw materials of these bio-based polymers are green and sustainable, and even show better performance than petroleum-based polymers in some aspects [11,12]. Thus, it is very promising to develop bio-based polymers as alternatives to petroleum-based polymers.

Among the numerous biomass resources, lignin, as the second abundant biopolymers on earth extracted from wood or annual plant, is a low-cost sustainable resource with an annual production of about 40–50 million tons and has attracted increasing attentions of researchers [13–15]. Nowadays, lignin and its derivatives have been investigated as agricultural additives, petroleum extraction active agents, building materials additives, water pollution treatment agents, and so on [9,14]. In these applications, the preparation of sustainable polymer

resins or composites has always been an important approach in the development and utilization of lignin. Although there are high thermal stability aromatic rings and phenolic hydroxyl groups that can offer various chemical modification in lignin, the complexity of their structures and low functional ratio (hydroxyl to aromatic ring) have long restricted the high value-added and efficient utilization of lignin [9,16–18]. Currently, more than 90% of lignin is merely used as a relatively low value-added fuel [14,19,20]. One significant way to circumvent these problems is to use well-defined phenolic compounds derived from lignin [17]. Among the candidate phenols, the most representative phenols are creosol and vanillin [9,17,21]. In recent years, vanillin-based epoxy resins [16,18], unsaturated polyesters, benzoxazine resins [21–23] and creosol-based cyanate esters [9] have been reported successively.

Phthalonitrile resin is a classical thermosetting resin with high performance. During thermal polymerization process, phthalonitrile monomers can form densely cross-linked polymers through the addition reaction mechanism of nitrile groups, thus exhibiting excellent thermal and thermo-oxidative stability, high glass transition temperature and outstanding flame resistance [24–29]. These excellent properties provide a variety of applications for phthalonitrile resins, such as aerospace, submarine and microelectronics [26,30–33]. Recently, the synthesis and preparation of bio-based phthalonitrile resins have received much attention. In 2016, Keller *et al.* first reported the bio-based

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phthalonitrile resins prepared from resveratrol and its derivatives [34]; subsequently, the catechin-based phthalonitrile resins have been investigated by Jian and coworkers [35], and the result suggest that this bio-based resin has higher thermal performance than bisphenol A based phthalonitrile (BAPh); Liu *et al.* reported the bio-based phthalonitrile prepared from biomass cloves [12], and the experimental data again illustrated the bio-based phthalonitrile resins have comparable performance to traditional petroleum-based phthalonitrile resin.

However, the polymerization of neat phthalonitrile resin is extremely slow, and curing agent containing active hydrogen is often needed to accelerate the curing rate of nitrile groups by ionic addition [29,36–38]. Therefore, the majority of phthalonitrile resins, including the bio-based equivalents, are required to add curing agents or curing components containing active hydrogen, such as organic amines, organic acids, phenols, etc. [26–27]. Lately, our group found that alicyclic imide compounds without active hydrogen moiety could also effectively accelerate the polymerization of phthalonitrile and provided phthalonitrile thermosets with excellent comprehensive properties. The reaction process is likely to involve free radicals reactive sites [39–41].

Recently, our group is devoted to the research on green and sustainable development of high performance polymers, through introducing bio-based building block such as adenine and L-tyrosine [42–46]. As a continuous work of this motivation, as well as an effective utilization of biomass resources, we aim to prepare a new bio-based phthalonitrile monomer (BPN) derived from creosol that is one of the representative derivative phenols in lignin, and try to investigate whether alkyl unit can directly promote the thermal polymerization of nitrile groups. The thermal polymerization behavior and curing mechanism of BPN monomer, and the thermomechanical properties of the cured product were investigated. The results suggest that the cured resin has a high glass transition temperature, good thermal properties, and exhibits excellent thermal stability comparable to that of typical petroleum-based phthalonitrile resins; BPN also has a higher biomass content relative to previously reported bio-based phthalonitrile resins. More importantly, this study indicates that aliphatic alkyl groups can significantly accelerate the thermal polymerization of phthalonitrile resin under certain conditions, showing a chemical behavior of “alkyl-activated phthalonitrile thermal polymerization”. Considering the widespread presence of alkyl units in biomass resources [14], a significant inspiration is that this chemistry will provide an alternative modification method for high value-added utilization of biomass. In the future, we will further explore the mechanism of “alkyl-activation phthalonitrile thermal polymerization” and the relationship between alkyl structure and polymerization behavior; using commercial macromolecular lignin (e.g. kraft lignin) as a case, by this unique chemical behavior, we will continue to seek straightforward approach on the high value-added utilization of biofeedstocks.

2. Experimental

2.1. Materials

2-methoxy-4-methylphenol (98 wt%) and acetaldehyde were obtained from Chengdu Best Reagent Co., Ltd. 4-nitrophthalonitrile was obtained from Taixing Shengming Fine Chemical Co., Ltd. Concentrated HCl, potassium carbonate, Dimethyl sulfoxide (DMSO), bisphenol A, ether, n-hexane were purchased from Chengdu Kelong Chemical Co., Ltd. All above materials were of reagent grade and used without further purification.

2.2. Synthesis of lignin-derived phthalonitrile monomer (BPN) and bisphenol a based phthalonitrile monomer (BAPh)

2.2.1. Lignin-derived phthalonitrile monomer (BPN)

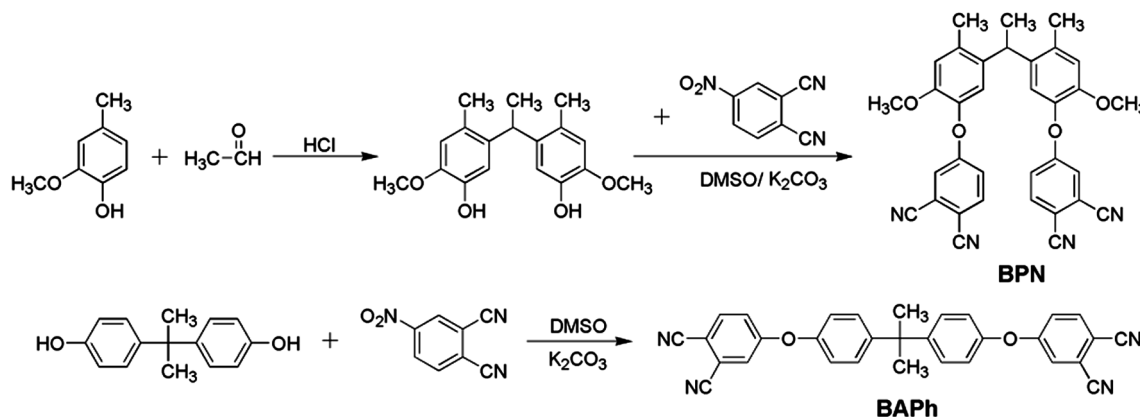
The intermediate product bisphenol was prepared according to the previous report [9]. Then bisphenols (0.01 mol), 4-nitrophthalonitrile (0.02 mol) and 60 mL DMSO were added to a 100 mL three-neck round-bottom flask. And ground K_2CO_3 (0.03 mol) was added in three portions at an interval of 20 min during the course of the reaction. The mixture was heated at 40 °C for 12 h under nitrogen. Then the product was washed with a large amount of water and the light white filtrate was collected by suction filtration, dried under vacuum. The white powder was obtained in 90 wt% yield; m. p. 200 °C; FTIR (KBr, cm^{-1}): 2968 ($-CH_3$), 2850 ($-O-CH_3$), 2228 ($-CN$), 1502 (aromatic), 1246 ($C-O-C$); 1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.68 (m, 2H; Ar H), 7.17 (dd, 2H; Ar H), 7.02 (t, 2H; Ar H), 6.85 (s, 2H; Ar H), 6.76 (s, 2H; Ar H), 4.29 (q, 1H; alicyclic $-CH-$), 3.74 (s, 6H; $-OCH_3$), 2.29 (d, 6H; Ar- CH_3), 1.46 (t, 3H; alicyclic $-CH_3$). Anal. calcd for $C_{34}H_{26}N_4O_4$: C 73.63, H 4.73, N 10.10; found: C 73.34, H 4.46, N 10.26.

2.2.2. Bisphenol A based phthalonitrile monomer (BAPh)

The phthalonitrile monomer BAPh was synthesized according to our previous report [47]. M. p. 195 °C; FTIR (KBr, cm^{-1}): 2970 ($-CH_3$), 2231 ($-C\equiv N$), 1502 (aromatic), 1281 (Ar-O-Ar); 1H NMR (400 MHz, DMSO- d_6): 8.14–8.07 (d, 2H; Ar H), 7.80 (d, 2H; Ar H), 7.36 (dd, 6H; Ar H), 7.13 (d, 4H; Ar H), 1.69 (s, 6H; $-CH_3$) (see Scheme 1).

2.3. The preparation of phthalonitrile polymer

The cured resin was fabricated by degassing in a flask (-0.04 MPa) at 220 °C about 15 min with vigorous stirring, and then the melted BPN was quickly poured into the preheated mould, subsequently placed in an oven and heated with N_2 flow rate of 500 mL/min at 290 °C for 6 h, 310 °C for 6 h.



Scheme 1. The synthesis of BPN and BAPh.

2.4. Characterization

The rheological behaviors of lignin-derived phthalonitrile monomer (BPN) and bisphenol A based phthalonitrile (BAPh) were 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 with a heating rate of 5 °C/min between 30 °C and the specified temperature were performed as well. For the time sweep test, and the measurements were carried out during isothermal cure at temperatures of 290 °C and 310 °C. All rheological measurements were carried out at low strain values (2.5×10^{-4}) and at the frequency of 1 Hz using 25 mm-diameter parallel plates. Normal force control (1.0×10^{-4} N) was utilized throughout the tests to keep the samples taut. ^1H NMR was obtained with a Bruker Avance III HD 400 MHz NMR spectrometer with CDCl_3 as the solvent and tetramethylsilane (TMS) as the internal standard. Solid-state cross polarization-magic angle spinning (CP-MAS) ^{13}C nuclear magnetic resonance (NMR) spectra were obtained with a Bruker AVANCE III 500 MHz NMR spectrometer operating at a frequency of 125.75 MHz equipped with a chemmagetics solid probe. BPN and the cured resin were packed into a 2.5 mm zirconia rotor. The spectra were carried out with the acquisition time of 0.041 s and relaxation delay of 2.0 s, and the number of scan was 2046. Elemental analyses (EA) were performed on a Flash EA 1112 Organic Element Analyzer. Fourier-Transform Infrared Spectroscopy spectra of monomer and the cured samples were recorded with a Nicolet FTIR-380 Fourier transform infrared spectrometer by a KBr pellet from 4000 to 600 cm^{-1} at a resolution of 4 cm^{-1} by 32 scans. *In situ* IR spectra were measured by a KBr pellet using a Nicolet FTIR-380 Fourier transform infrared spectrometer by KBr pellet from 4000 to 600 cm^{-1} at a resolution of 4 cm^{-1} by 16 scans in air atmosphere. Measurement was conducted using a home-made sample disk holder equipped with a microheater, at PT100 thermal resistance. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer instruments TGA Model 4000 at a heating rate of 10 °C min^{-1} from 40 °C to 800 °C under a air or nitrogen purge of 60 mL/min. Dynamic Mechanical Analysis (DMA) were performed on a TA instruments Q800 under three-point bending mode at a frequency of 1 Hz and a low strain value of 2.5×10^{-4} with a heating rate of 5 °C/min from 40 to 430 °C, and the cured sample was sanded to rectangular specimens of dimensions (29 mm \times 12 mm \times 2.5 mm) before the test.

3. Result and discussion

3.1. Preparation and characterization of lignin-based phthalonitrile monomer (BPN)

BPN was prepared from the reaction of 2-methoxy-4-methylphenol with acetaldehyde in HCl solvent, followed by a simple nucleophilic displacement reaction between 4-nitrophthalonitrile and intermediate product bisphenol under basic conditions in DMSO. The BPN monomer can be purified by recrystallization in acetonitrile and is soluble in common organic solvents such as acetone, methylene chloride, and chloroform. Its structure was confirmed by FTIR and ^1H NMR, and element analysis. As seen in Fig. 1, we can easily distinguish the final product BPN. The most obvious feature is the absence of the phenol –OH protons in bisphenol appearing about 8.5–8.6 ppm [9,34]. Meanwhile, the appearance of the terminal phthalonitrile protons in BPN could be observed at 7.0 and 7.2, 7.7 ppm, respectively. In addition, the protons of the alkyl moiety in BPN appeared in the high field 4.29 (–CH), 3.74 (–OCH₃), 2.29 (aromatic –CH₃), 1.46 ppm (aliphatic –CH₃). In general, the obtained spectra agree well with the proposed molecular structure.

3.2. Curing behavior evaluation

Rheological analysis was performed to evaluate the thermal

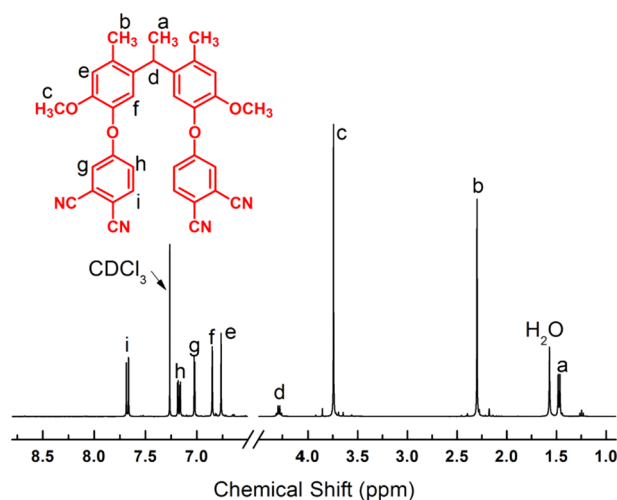


Fig. 1. ^1H NMR spectra of the BPN monomer.

polymerization behavior of the BPN monomer. As shown in Fig. 2, in the temperature ramping mode of rheological test, the monomer first melted at about 200 °C; then the complex viscosity (0.01–0.1 Pa·s) remained stable without any obvious increase within 330 °C, showing a wide processing window. While in the isothermal rheological test, the BPN exhibited significant viscosity growing behavior during the isothermal process at 290 °C and 310 °C, exhibiting a significant thermal polymerization behavior. The required time for BPN curing obviously decreased with the increase of isothermal temperature. Interestingly, there is no traditional active hydrogen moiety (such as amino, phenolic hydroxyl groups) in BPN molecule. Therefore, our attention turned to other potential activation sites. Zhou et al.'s research shows that phthalonitrile containing-methoxy does not exhibit noticeable curing behavior [48]. Based on previous researches on alicyclic imide compounds/phthalonitrile system [40], we speculate that the reactive radicals generated from the alkyl (methyne or methyl) in BPN monomer at high temperature may accelerate the polymerization of nitrile groups. In order to analyze the possible reaction sites, bisphenol A based phthalonitrile (BAPh) containing methyl unit was selected as a comparison, and the isothermal rheological behavior of BAPh was investigated (in Fig. 2). The results show that there is no apparent viscosity growth at 310 °C under even longer isothermal time condition.

Based on above experimental data, we preliminarily proposed that the free radicals generated by the methyne units in BPN monomer under elevated temperature accelerated the polymerization of nitrile groups, showing the mechanism of “methyne-activated phthalonitrile thermal polymerization”. It is rational that the homolysis of covalent bonds of methyne unit can occur at high temperature conditions, a relatively stable tertiary carbon radical and a relatively high reactive hydrogen radical are formed [49]. On the basis of this assumption, hydrogen radicals or tertiary carbon radicals may promote the thermal polymerization of BPN. The phenomenon of free radicals generated from covalent bond homocleavage has been reported for lignin and polymers containing tertiary carbon units, such as polystyrene, polyacrylonitrile, polyvinyl chloride [50–52]. Although the speculation mentioned here is somewhat intuitive, at least it shows that the idea of using alkyl moiety to accelerate the curing of phthalonitrile is feasible.

3.3. Curing mechanism discussion

3.3.1. Infrared analysis

For understanding the curing reaction mechanism of this system, FTIR was conducted to qualitatively analyze the structural evolution of BPN monomer and the cured product. As shown in Fig. 3, there is a strong absorption peak of nitrile group (2229 cm^{-1}) in BPN monomer,

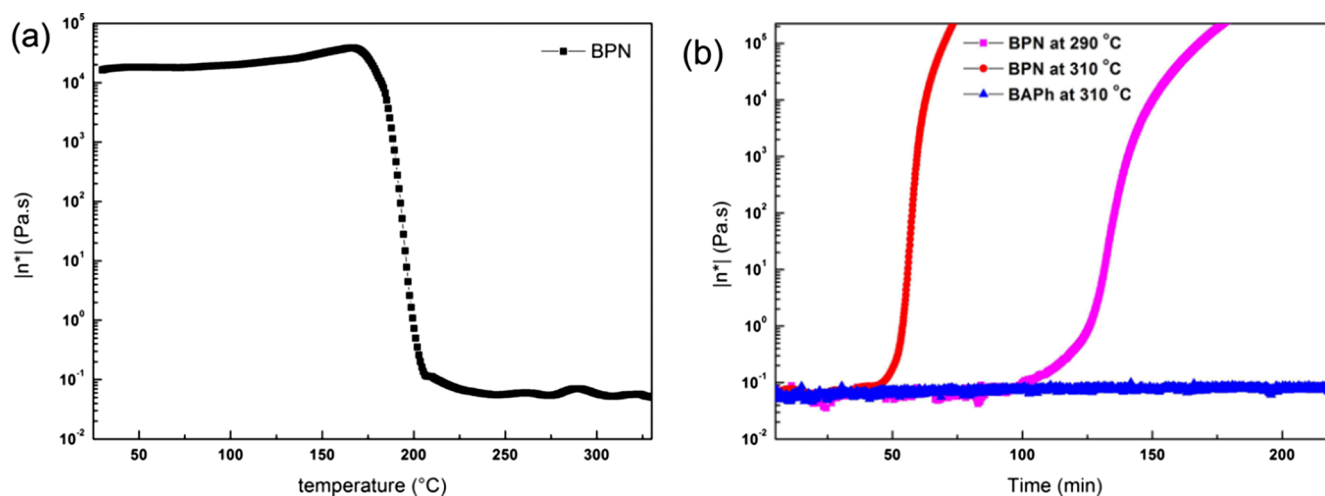


Fig. 2. Complex viscosity as a function of temperature (a) and time (b) of BPN and BAPh at 290 and 310 °C.

and no obvious hydroxyl absorption peaks are observed in the wavenumber range of 3500 to 3100 cm^{-1} . The IR result shows once again that there is no residual phenolic hydroxyl group in BPN, which is consistent with the result of the monomer's ^1H NMR spectra. Normally, the curing mechanism of traditional phthalonitrile resins involves phthalocyanine, isoindoline and triazine formation (shown in [Supplementary material](#)). While for BPN polymer, the nitrile peak was significantly decreased. Meanwhile, new peaks at 1010 and 1090 cm^{-1} appeared, which were attributed to phthalocyanine ring and isoindoline absorptions, respectively. However, the characteristic peaks of triazine at 1360 and 1520 cm^{-1} cannot be observed. This result is in complete agreement with the structure of the cured products in our previous studies on alicyclic imide compounds/phthalonitrile curing systems [39,40], suggesting that the curing mechanisms of these two systems may have common characteristics.

In order to further understand the polymerization process, the curing mechanism of BPN was discussed quantitatively by *in situ* infrared measurement. A two-steps *in situ* infrared test was used. The first stage is a temperature ramping, in which the temperature rises from room temperature to 310 °C. The second stage is an isothermal test, and the duration time is 70 min. For avoiding the influence of physical factors, such as phase transformation, on the infrared data in the

system, we mainly focus on the structural changes after monomer melting.

As shown in [Fig. 4](#), there are five alkyl absorption peaks between 3000 cm^{-1} and 2800 cm^{-1} , which are assigned to the asymmetric stretching vibration peak of the methyl group at 2965 cm^{-1} and the symmetric stretching vibration peak at 2872 cm^{-1} , the asymmetric stretching vibration peak of the methoxy group at 2934 cm^{-1} and the symmetric stretching vibration peak at 2850 cm^{-1} , as well as the methyne stretching vibration peak at 2907 cm^{-1} , respectively. With the increase of temperature, the absorption peak of nitrile group at 2228 cm^{-1} gradually decreased, and new peaks at 1090 and 1010 cm^{-1} attributed to isoindoline and phthalocyanine absorptions could be observed, which indicated that the curing reaction has occurred [40]. On the other hand, we also noticed that the methyne absorption peak at 2907 cm^{-1} gradually weakened. During the isothermal process (in [Fig. 5](#)), it could be observed clearly that the phthalocyanine absorption peak gradually increased and the nitrile absorption peak continued to weaken, indicating that the curing reaction was in progress. We also failed to observe the characteristic peak of triazine ring at 1520 and 1360 cm^{-1} throughout the whole process [34], which is consistent with the infrared result mentioned-above.

To directly discuss the relationship between alkyl and nitrile

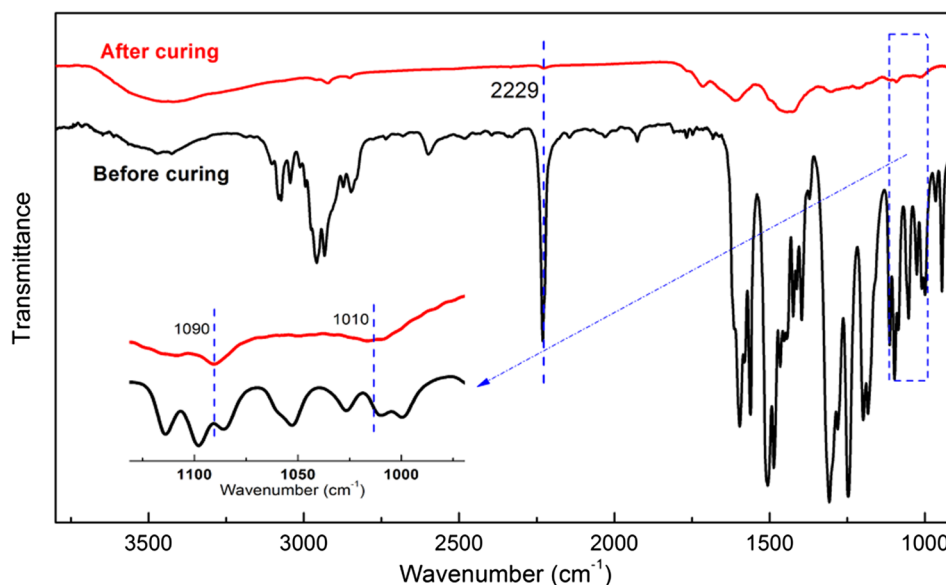


Fig. 3. FTIR spectra of BPN monomer and BPN polymer.

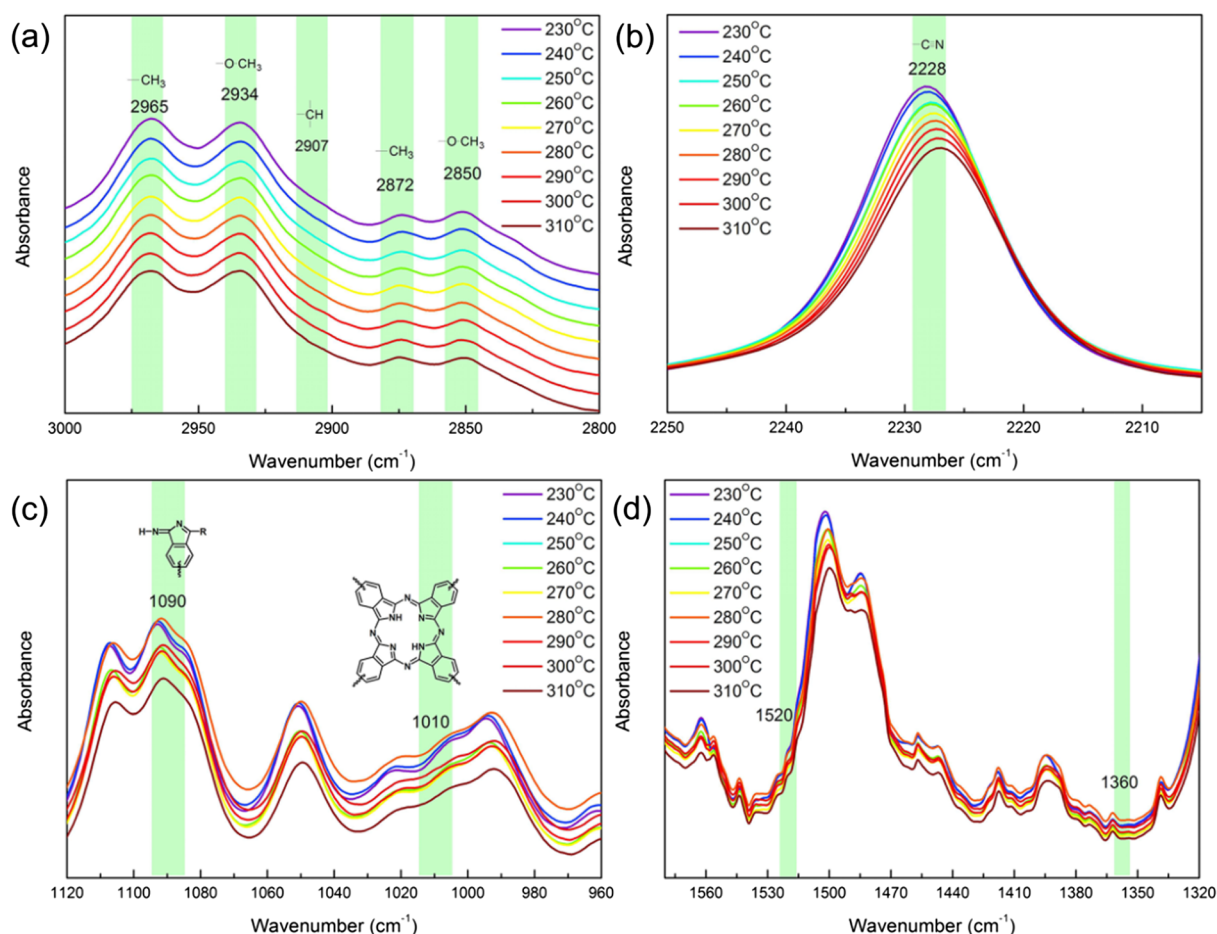


Fig. 4. *In situ* FTIR of BPN monomer heated from 230 to 310 °C, a: the stretching vibration of C–H in methyl (–CH₃) and methyne (–CH); b: the stretching vibration of nitrile (–CN); c: the stretching vibration of N–H in phthalocyanine and isoindoline; d: the typical stretching vibration –C=N in polytriazine.

reactions, the *in situ* IR data of two stages were normalized (shown in [Supplementary material](#)) by using the characteristic peak of benzene ring (around 1500 cm⁻¹) as the internal standard, and peak-fitting method was adopted (in [Fig. 6](#)). As shown in [Fig. 7a](#), the conversion of methyl and methoxy groups remained almost unchanged (less than 5%) during the stage of temperature ramping, indicating that these units remained relatively stable and had little contributions to the polymerization during the heating process. While nitrile groups showed a clear polymerization conversion, and methyne groups also exhibited obvious conversion behavior that enhances significantly with increasing temperature and then tends to be level-off, implying that there is a close correlation between them. During the isothermal process (in [Fig. 7b](#)), the conversion of methyne and nitrile groups continued to increase over time; and the conversions of other alkyls still remained below 5%. Again, these data indicated that methyne may be associated with the reaction of nitrile groups.

3.3.2. Solid-state ¹³C NMR analysis

Solid-state ¹³C NMR analysis of the BPN monomer and the cured product was performed to investigate the reaction sites during the curing process. For the BPN, the main ¹³C NMR signals were ascribed as follows (in [Fig. 8](#)): (1) methyl carbon (aromatic-CH₃, labeled as *i*) connecting aromatic ring signals at 23 ppm; (2) methyl carbon (aliphatic-CH₃, labeled as *j*) connecting methyne signal at 28 ppm; (3) The prominent signal appears at 40 ppm, attributed to methyne carbon (labeled as *k*) [9]; (4) methoxy carbon signal at 60 ppm (labeled as *h*); (5) nitrile carbon signals appear at 117 ppm (labeled as *g*) [9,29]; other aromatic carbon signals occur between 100 ppm and 170 ppm.

Despite limitations of the testing method itself, such as the problem

of spectral line broadening, some useful chemical information from the cured BPN solid-state ¹³C spectra can be derived [53]. Compared to BPN monomer, the signals at 40 ppm of the cured sample decreased significantly, and the conversion calculated from the change in methyne peak area was around 85%; while there were no obvious changes in methyl and methoxy signal peaks. Additionally, other new alkyl signals were not observed. Nitrile carbon signals were overlapped by aromatic ring signals of the cured BPN, and it is difficult to accurately determine whether nitrile groups are completely consumed. The results of solid-state ¹³C NMR provide more evidence for the curing mechanism of “methyne-activated phthalonitrile thermal polymerization” and are consistent with the results of *in situ* IR test.

In summary, we proposed the curing reaction mechanism of BPN as shown in [Scheme 2](#). The homolysis of covalent bonds of methyne unit in BPN monomer forms a relatively stable tertiary carbon radical and a relatively high reactive hydrogen radical at elevated temperature. The radicals attack the active sites (nitrile groups) of the monomer, thereby promoting the polymerization reaction of phthalonitrile.

3.4. Dynamic mechanical analysis

DMA was used to estimate the thermomechanical properties of the cured BPN. As shown in [Fig. 9](#), the storage modulus values for the cured polymer gradually varied from 2278 MPa to 1091 MPa when heated from 35 to 300 °C. Further heating of the thermoset to 430 °C resulted in an obvious decrease in the storage modulus with a subsequent peaking (about 400 °C) in the tan δ indicating an viscoelastic transition assigned to the T_g [9]. These results suggest that the bio-based polymer has excellent thermomechanical performance, which is important for

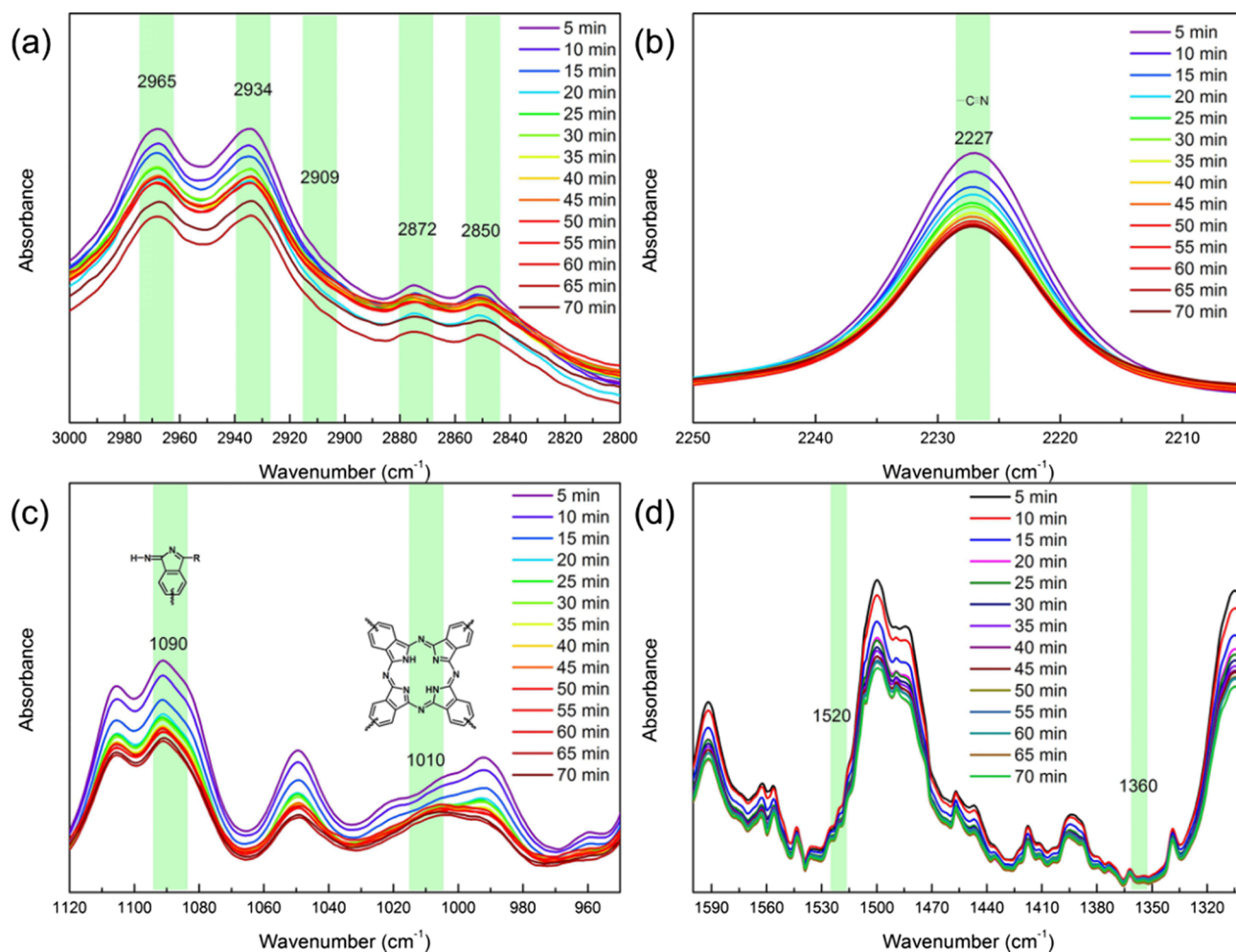


Fig. 5. *In situ* FTIR of BPN monomer isothermal temperature at 310 °C as a function of time.

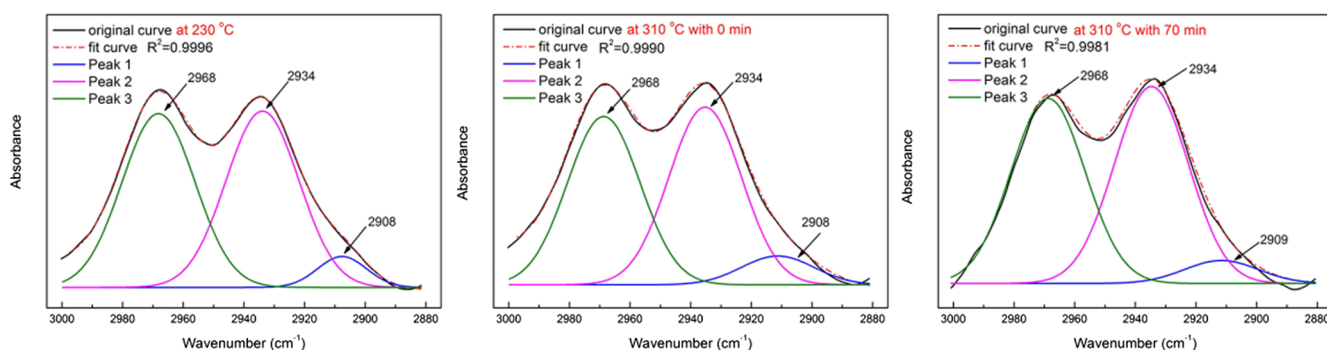


Fig. 6. *In situ* FTIR peak fits at different stages (fitting degree $R^2 \geq 0.998$).

expanding the applications scope of lignin in the field of high performance polymer [34].

3.5. Thermal and thermo-oxidative properties

The thermal and thermo-oxidative properties were evaluated by TGA analysis between 40 °C and 800 °C at a heating rate of 10 °C min⁻¹. Fig. 10 shows the thermogravimetric curve and derivative weight curve of the cured resin BPN in N₂ and air atmosphere, respectively. The temperature of 95% weight retention ($T_{5\%}$), and char yield percentage (Yc) at 800 °C for the cured BPN resin are collected in Table 1.

The cured polymer showed 95% weight retention at 417 °C and char yield of about 72.5% after heating to 800 °C in a nitrogen atmosphere.

When heated under an air atmosphere, the thermoset exhibited 95% weight retention at 422 °C with catastrophic decomposition occurring between 500 and 800 °C. In addition, DTG curves showed a rapid weight decrease with increasing temperature and reached a maximum rate at around 422 °C in both nitrogen and air, attributable to the decomposition of alkyl groups [29] and low cross-linked parts [24] in BPN thermoset under high temperature conditions. Unlike in the inertial atmosphere, the cured products were decomposed dramatically at higher temperatures in air, indicating that the thermoset was strongly oxidized [46]. To sum up, the cured BPN exhibits excellent thermal and thermo-oxidative stabilities comparable to that of the petroleum-based BAPH [47].

What's more, according to the study of Van Krevelen [55], there is a

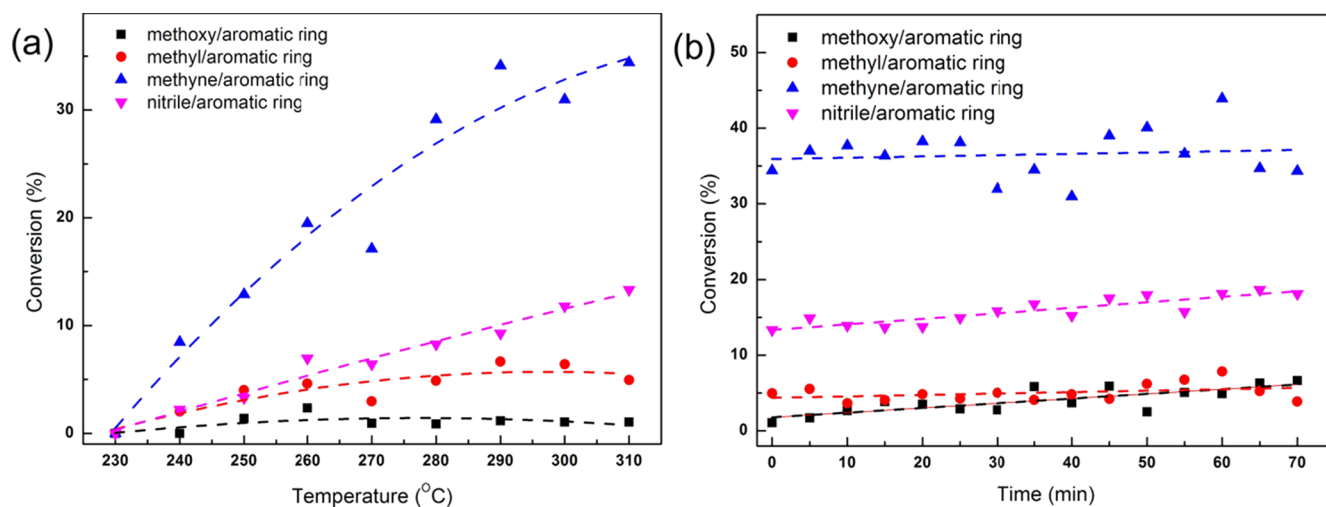


Fig. 7. The conversion of different groups as a function of (a) Temperature and (b) Time measured by *in situ* IR (black–methoxy/aromatic ring; red–methyl/aromatic ring; blue–methyne/aromatic ring; pink–nitrile/aromatic ring).

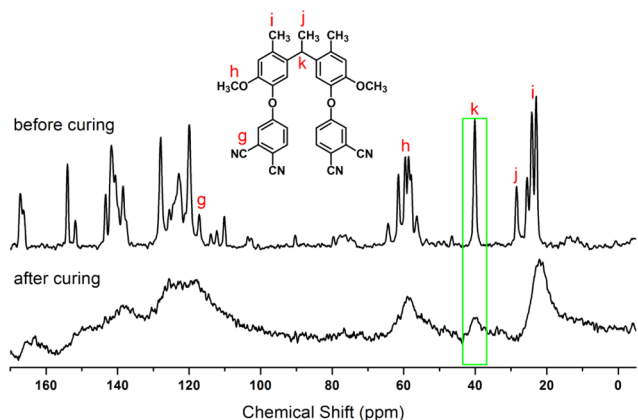


Fig. 8. Solid-state CP-MAS ^{13}C NMR spectra of BPN monomer and polymer.

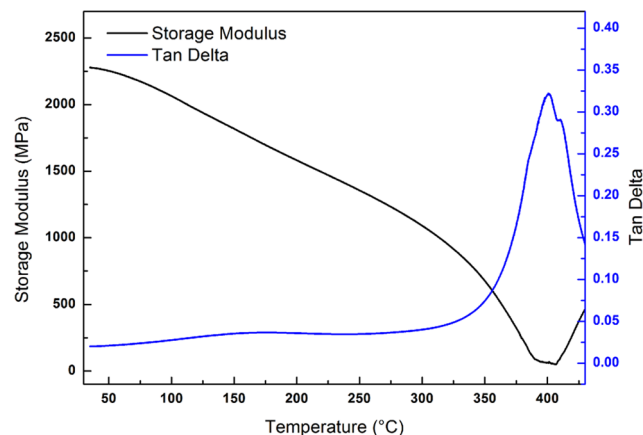


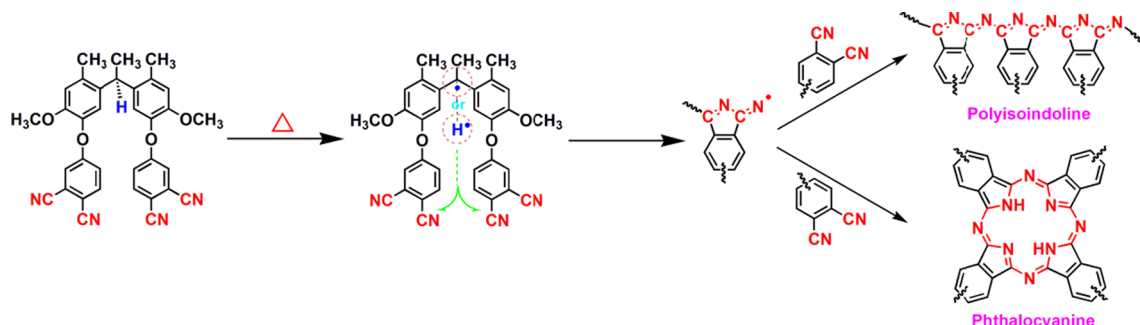
Fig. 9. Dynamic mechanical properties of BPN resin.

linear relationship between limiting oxygen index (*LOI*) and char residue for halogen-free polymers, as follows,

$$LOI = 17.5 + 0.4Y_c$$

where Y_c is the char yield in nitrogen; *LOI* is defined as the minimum fraction of oxygen in an oxygen-nitrogen mixture just sufficient to maintain combustion of the specimen after ignition [55]. On the basis of the char yield at 800 °C in nitrogen, the calculated *LOI* value of the cured BPN polymer is 46.5. It is well known that the *LOI* value of 26 or higher can be considered as a flame-retardant material [54,55]. Thus, it is obvious that the BPN polymer has excellent flame resistance and is promising for improving the flame retardancy of lignin.

Recent works on bio-based thermosets are compared with this work



Scheme 2. The proposed reaction mechanism of BPN.

in terms of biomass content, glass transition temperature (T_g) and char yield percentage. As shown in Fig. 11, lignin-based BPN has higher char yield and superior thermomechanical properties relative to bio-based epoxy resins and benzoxazine resins and cyanate esters; Compared to other bio-based phthalonitrile resins, it still exhibits comparable or even better thermal properties and has higher biomass content.

4. Conclusion

In this paper, a novel bio-based phthalonitrile monomer derived from lignin was synthesized, and its curing behavior, mechanism and the thermal properties of the cured resin were investigated. The

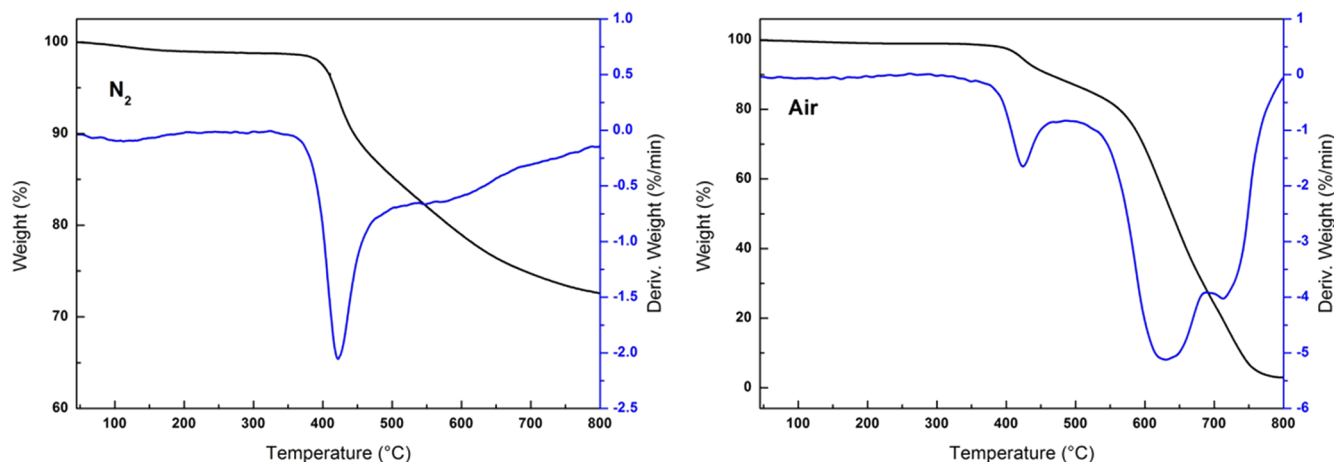


Fig. 10. The TGA and DTG curves of BPN polymer in atmospheres of N_2 (left) and air (right).

Table 1
Comparisons of thermal properties of BPN resin with BAPh resin.

Atmosphere	BPN resin			BAPh resin		
	$T_{5\%}$ ($^{\circ}C$)	Yc (800 $^{\circ}C$, %)	LOI	$T_{5\%}$ ($^{\circ}C$)	Yc (800 $^{\circ}C$, %)	LOI
N_2	417	72.5	46.5	391	65	43.5
Air	422	2.9		402	9.6	

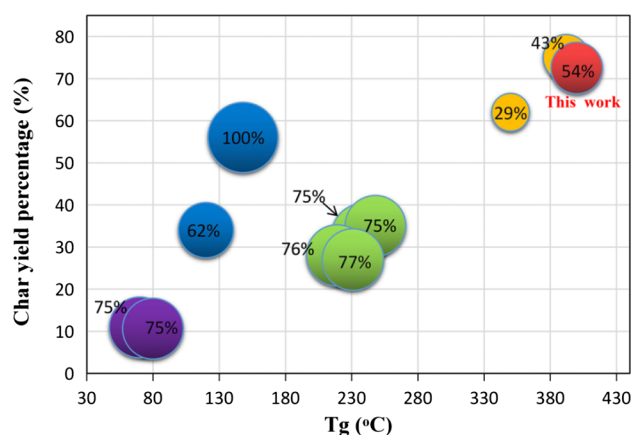


Fig. 11. A comparison of this work to recent works about bio-based thermosets in terms of biomass content, glass transition temperature (T_g), and char yield percentage (the size of the ball represents the relative biomass content; purple-epoxy resins [18], blue-benzoxazine resins [22,56], green-cyanate esters [9], yellow-other phthalonitrile resins [12,34], red-this work). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

rheological and IR results show that the resin can undergo obviously thermal polymerization without the addition of traditional curing agents. By comparing with the rheological behavior of BAPh, we proposed the mechanism of “methyne-activated phthalonitrile thermal polymerization”, and provide strong evidences for the reaction mechanism by *in situ* IR and solid-state ^{13}C NMR. The DMA and TGA data show that the cured product has a high glass transition temperature ($T_g = 400$ $^{\circ}C$), good thermal properties with weight retention of 95% at around 420 $^{\circ}C$ both in N_2 and air, exhibiting excellent performance comparable to traditional petroleum-based phthalonitrile resins; it also has a high biomass content (more than 50%).

Due to the wide existence of alkyl units in biomass, the results of this study are expected to provide an alternative approach for high value-added utilization of lignin or other renewable resources. In the

near future, we will systematically study the relationship between different alkyl structures and phthalonitrile thermal polymerization behavior, and further discuss the curing mechanism. By taking commercial lignin as an example, continuous study will be performed on the high value-added utilization of biomass with a straightforward route, through this unique chemistry of “alkyl-activated phthalonitrile thermal polymerization”.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eurpolymj.2019.109351>.

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