Polymer 224 (2021) 123723

Contents lists available at ScienceDirect

Polymer

journal homepage: http://www.elsevier.com/locate/polymer

The bio-based phthalocyanine resins with high T_g and high char yield derived from vanillin

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ARTICLE INFO

Keywords:
Heat resistant polymers
Phthalocyanine resins
Bio-based materials
Thermostability

ABSTRACT

The conversion of bio-based vanillin into the heat-resistant polymers is investigated. Firstly, converting the aldehyde group of vanillin into a vinyl group obtained 2-methoxy-4-vinylphenol (**S1**), which was then treated with nitro-phthalonitrile to give 4-(2-methoxy-4-vinylphenoxy)phthalonitrile (**S2**). Secondly, thermal polymerization between **S1** and **S2** in a different molar ratio gave a series of vanillin–based phthalocyanine (**V-PN**) resins that display high char yield and high T_g. The best result was obtained when the molar ratio between **S1** and **S2** was 1–50 and the obtained **V-PN** resin displayed a char yield of up to 76%, a T_g over 400 °C. These data are much better than those of the widely used petroleum-based phthalocyanine resins, suggesting that these bio-based functional monomers derived from vanillin are suitable as the precursors for the fabrication of the ablation-resistant materials in the application of the aerospace industry.

1. Introduction

Heat resistant polymers have been widely used in many industry fields such as electrical and electronic industry as well as aerospace and aviation industry because of their good thermostability and good mechanical properties. Among the heat resistant polymers, phthalocyanine (**PN**) resins have attracted attention for long time [1–4]. These resins are mainly prepared by an addition polymerization of phthalonitrile-containing polymers in the presence of the catalysts (aryl amines or phenols) at high temperature [5–7]. Because the formed phthalocyanine structure shows highly thermal and chemical stability and low flammability, **PN** resins have been recognized as the satisfactory ablation-resistant materials for the application in aerospace industry [8–10].

However, most of the commercialized **PN** resins are derived from petroleum-based chemicals [11–14] and the new renewable feedstock need to be explored and developed. It is noted that recently there are reports regarding to the bio-based **PN** resins. For example, Laskoski [15] and his coworkers investigated resveratrol-based **PN** resins that exhibited good processability. Zhao's group [16] reported a bio-based **PN** resin that exhibited high char yield, whereas such a resin was prepared by using a complicated route. Thus, the development of the easily synthesized bio-based **PN** resins with high performance is still necessary.

It is noted that vanillin from lignin has recently been widely used as a precursor for the preparation of the organic materials [17–22]. Although there are many investigations on the conversion of vanillin into polymers (such as epoxy resins [23–25], benzoxazines [26,27], polycarbonates [28], polyesters [29], polyacetal [30] and polyvanillin [31], most of the obtained polymers display poor thermostability. Therefore, it is desirable to investigate the conversion of vanillin into the materials with high thermostability. Hence, we designed and synthesized two precursors that were used for the preparation of the **PN** resins. The first precursor (**S1**) was prepared by converting the aldehyde group into vinyl via the witting reaction. Treating **S1** with 4-nitrophthalonitrile gave the second precursor (**S2**). The thermal polymerization between **S1** and **S2** in a different molar ratio gave a series of **V-PN** resins (Scheme 1). The best result was obtained when the molar ratio between **S1** and **S2** was 1–50. In that case, the obtained **PN** resin displayed a char yield of up to 76% and a T_g over of 400 °C. The biomass content of the new PN resins is high up to 54.5%. This result indicates that the new **V-PN** resins

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https://doi.org/10.1016/j.polymer.2021.123723
Received 24 January 2021; Received in revised form 27 March 2021; Accepted 29 March 2021
Available online 3 April 2021

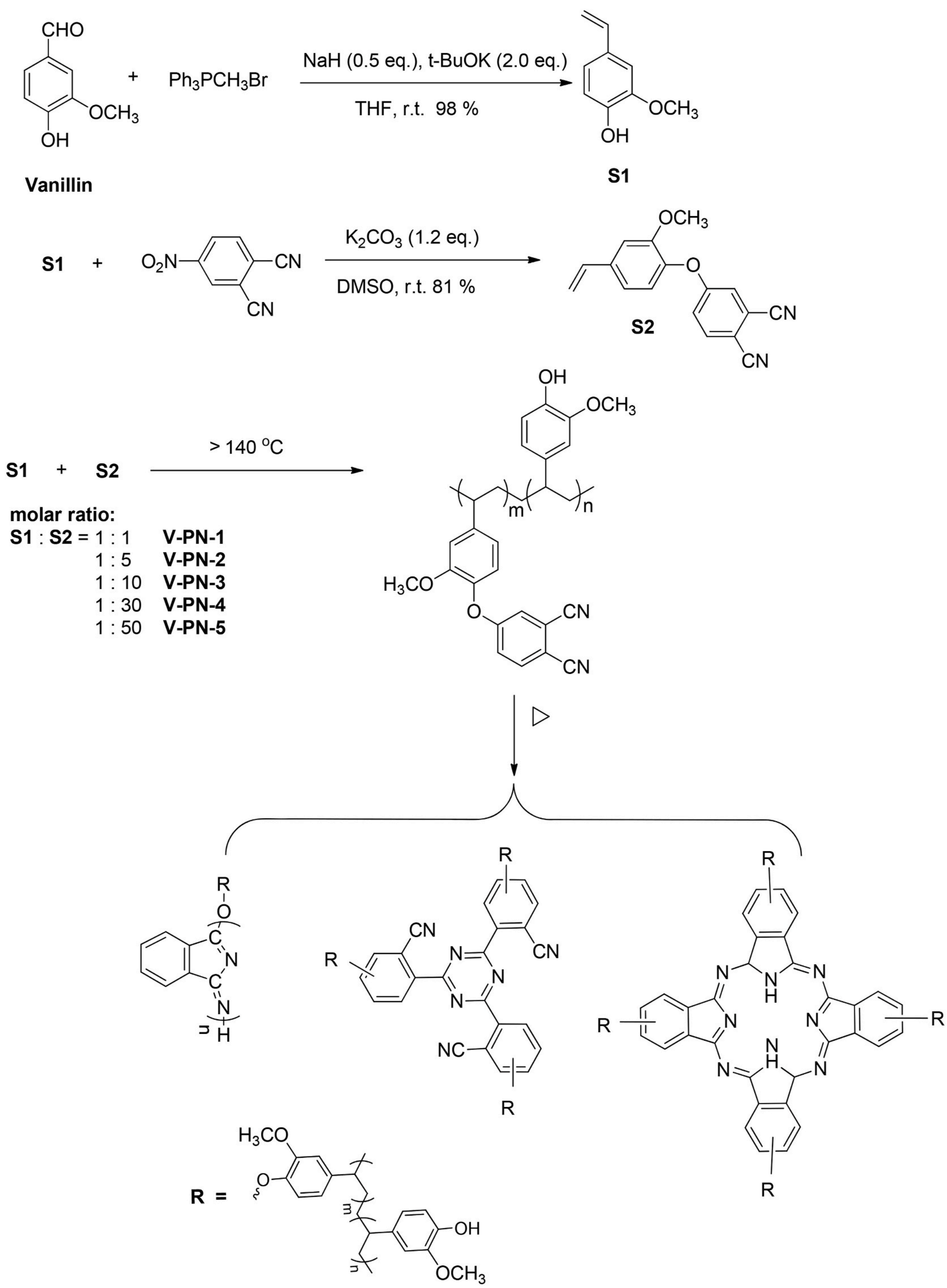
can be prepared from bio-based vanillin. Here, we report the details.

2. Experimental section

2.1. Materials and instruments

Vanillin was purchased from Shanghai Macklin Biochemical Co., Ltd. 4-Nitrophthalonitrile was purchased from Zhengyuan Pharmaceutical Technology Co., Ltd. All solvents were dried over anhydrous Na_2SO_4 before use.

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 spectrometer with tetramethylsilane (TMS) as the internal standard and DMSO-d_6 as the solvent. Fourier transform infrared spectra (FT-IR) were characterized on Thermo Scientific Nicolet spectrometer using a Smart Orbit Diamond from 400 to 4000 cm^{-1}. High-resolution mass spectra (HRMS) were characterized on an Agilent TOF/LC-MS 1260–6230B instrument. Elemental analysis (EA) was collected on an Elementar vario EL III instrument. Differential scanning calorimetry (DSC) analysis were operated with a Q200DSC (TA, US) at a heating rate of 5 °C min^{-1} between 40 and 400 °C under N_2 flow with a flowing rate of 50 mL min^{-1}. Thermogravimetric analysis (TGA) was detected on NETZSCH TG 209F1 apparatus at a heating rate of 10 °C min^{-1} from room temperature to



Scheme 1. Procedure for the synthesis of the V-PN resins.

1000 °C under N_2 atmosphere. Dynamic mechanical analysis (DMA) was recorded on a DMA Q800 instrument with a heating rate of 5 °C min^{-1} in air.

2.2. Synthesis of S1

This monomer was synthesized according to the procedure previously reported [32]. To a stirring solution of methyltriphenylphosphonium bromide (50.10 g, 1.0 mol) in THF (200 mL) was added NaH (1.92 g, 0.5 mol) and potassium tert-butoxide (35.90 g, 2.0 mol) at room temperature. After addition, the mixture was stirred for an additional 10 min. Then a solution of vanillin (20.00 g, 1.0 mol) in THF (80 mL) was added dropwise to the mixture. After stirred at room temperature for 2 h, the reaction mixture was neutralized with dilute HCl and extracted with ethyl acetate. The organic layer was combined, washed with saturated brine, dried over anhydrous Na_2SO_4, and filtered. After removal of the solvent under reduced pressure, the obtained residue was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (9:1, v/v) as the eluent to give **S1** as a colorless liquid in a yield of 97%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.93 (s, 1 H), 6.91 (s, 1 H), 6.87 (d, 1H), 6.64 (d, 1 H), 5.67 (s, 1 H), 5.58 (d, 1 H), 5.12 (d, 1 H), 3.90 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$, δ): 146.55, 145.54, 136.51, 130.16, 120.03, 114.32, 111.42, 107.99.

2.3. Synthesis of S2

To a stirring solution of **S1** (5.00 g, 1.0 mol) and 4-nitrophthalonitrile (5.77 g, 1.0 mol) in DMSO (100 mL) was added anhydrous K_2CO_3 (5.53 g, 1.2 mol) at room temperature. After stirred for an additional 5 h under nitrogen, the reaction mixture was poured into water (near 500 mL). The formed solid was filtered, washed with water and dried at air. Pure **S2** was obtained by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (9:1, v/v) as the eluent in a yield of 81%. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 7.99 (d, 1 H), 7.63 (d, 1 H), 7.31 (s, 1 H), 7.21 (q, 1 H), 7.15 (d, 1 H), 7.10 (d, 1 H), 6.73 (d, 1 H), 5.87 (d, 1 H), 5.27 (d, 1 H), 3.73 (s, 3 H). ^{13}C NMR (126 MHz, DMSO-d_6, δ): 161.75, 151.54, 141.04, 137.11, 136.57, 136.40, 122.92, 121.57, 120.80, 119.94, 116.94, 116.43, 115.90, 115.57, 111.52, 108.00, 56.27. HRMS-ESI (*m/z*): calcd $[M + Na]^+$, 299.0789; found, 299.0791. Anal. Calcd: C, 73.90; H, 4.38; N, 10.14. Found: C, 73.925; H, 4.60; N, 10.11.

2.4. Preparation of V-PN resins

To a mixture of **S1** and **S2** in a different molar ratio added dichloromethane under stirring. After addition, the formed solution was further treated with ultrasound for 5 min. After removal of the solvent under reduced pressure at room temperature, the obtained residue was cured according to the DSC curve. Taking **V-PN-5** as an example, put 1 equivalent of **S1** and 50 equivalents of **S2** into a glass tube with a horizontal bottom surface, slowly raised the temperature to 130 °C and kept it for 2 h under vacuum conditions, then heated up to 150 °C in a nitrogen atmosphere and kept at 150 °C for 1 h, 200 °C for 2 h, 250 °C for 2 h, 340 °C for 3 h, 370 °C for 4 h, and decreased to room temperature at a rate of 10 °C min^{-1}. The above processes were all carried out in a quartz tube furnace.

2.5. Water uptake test

The water uptake test of **V-PN-5** was carried out by immersing the samples in boiling water. Two samples were tested parallelly with the rectangle shapes having the mass of 1.6631 g and 0.1015 g, respectively. The water uptake values were calculated by weighing the samples three times and averaging.

3. Results and discussion

3.1. Synthesis and characterization

The monomer **S1** was synthesized from vanillin via traditional Witting reaction to convert the aldehyde group into vinyl. By treating **S1** with 4-nitrophthalonitrile, phthalonitrile monomer **S2** was prepared by a facile one-step reaction. The chemical structure of **S2** was characterized by ^{1}H NMR, ^{13}C NMR, HRMS, FT-IR spectra and elemental analysis. As can be seen from ^{1}H NMR spectrum of **S2** (Fig. 1), the peaks in the region of 7.0–8.0 can be ascribed to the aromatic hydrogens, and the characteristic peaks of vinyl group appear at 6.73 ppm, 5.87 ppm and 2.28 ppm. All characteristic carbon signal peaks are consistent with the proposed structures (Fig. 1).

A series of **PN** resins (**V-PN**) were prepared by thermal-polymerization of the monomer **S1** and **S2** in different molar ratios (from 1:1–1:50). At high temperature, the **V-PN** resins can form cross-linked networks due to the addition polymerization of phthalonitrile groups in the presence of the phenol groups as catalysts.

3.2. Curing behaviors of V-PN resins

The curing behaviors of the series of **V-PN** resins were monitored by DSC and FT-IR. As shown from the results of DSC (Fig. 2 and Table 1), during the first scan, the melting points of **V-PN** resins are measured in the range of 114–129 °C, and there are two exothermic peaks can be observed for each sample. The first peak is attributed to the polymerization of the C═C bond. The second peak can be ascribed to the polymerization of phthalonitrile groups. Due to the different reactivity of monomer **S1** and **S2**, with the molar ratio of **S2** increasing, the peak temperature of polymerization of C═C bond for each **V-PN** decreases, whereas the peak temperature of polymerization of phthalonitrile groups increases. For **V-PN-5** (the molar ratio of **S1**:**S2** = 1:50), the first peak temperature is closer to the homopolymerization temperature of **S2** (shown in Fig. S2, Supporting Information), and the temperature of the second exothermic peak reaches to 372 °C. At the second scans in the DSC curves of **V-PN** resins, no obvious exothermic peaks can be observed, suggesting that the monomers were completely cured.

The curing behavior of **V-PN** resins can also be confirmed by the FT-IR spectrum (Fig. 3 and Fig. S3). Taking **V-PN-5** resin as an example, when heating the mixture of **S1** and **S2** to 300 °C, the characteristic absorption peak attributed to the stretching vibration of vinyl group at 986 cm^{-1} and 3074 cm^{-1}disappears, whereas the characteristic absorption peak of C≡N at 2221 cm^{-1} still exists. It demonstrates that the polymerization of C═C bond in monomers can proceed at the lower temperature, which is consistent with the results of DSC. After heating to 370 °C, the characteristic absorption peak belonging to cyano group at 2221 cm^{-1} disappeared, and the absorption peaks at 1025 cm^{-1} attributed to phthalocyanine groups and the absorption peaks at 1360 cm^{-1} ascribed to triazine groups appear, indicating the **V-PN** resins was further cured by the additional polymerization of phthalonitrile groups in the catalysis of hydroxyl groups.

3.3. Thermostability and mechanical properties of cured V-PN resins

The thermostability of **V-PN** resins were studied by TGA. As shown in the results of TGA (Fig. 4, Fig. S4 and Table 2), the cured **V-PN** resins exhibit the high 5% weight loss temperatures (T_{5d}) of 419–486 °C. Especially, they also give high char yield up to 76% at 1000 °C under N_2 atmosphere. With the molar ratio of **S2** increased, the T_{5d} and char yield of **V-PN** resins elevate. The **V-PN-5** resin display the best heat-resistant properties with the T_{5d} of 486 °C and the high char yield of 76%. The weight loss temperatures and char yields of other reported **PN** resins are summarized in Table 2. As shown from Table 2, the thermostabilities of bio-based V-PNs are comparable to those of the PN resins derived from petroleum-based materials. The excellent properties can meet the

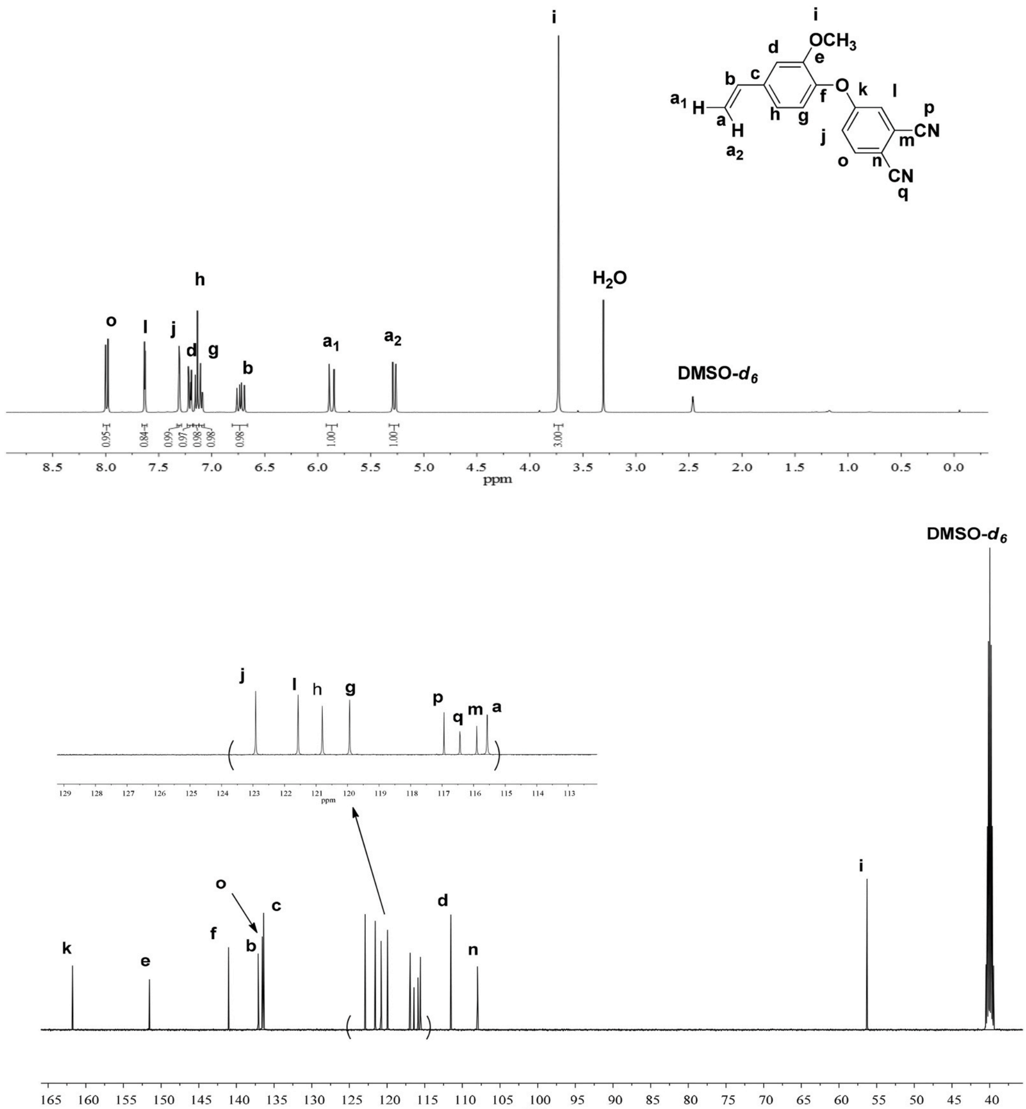


Fig. 1. [1]H NMR (top, 400 MHz, DMSO-d_6) and [13]C NMR (down, 100 MHz, DMSO-d_6) spectra of **S2**.

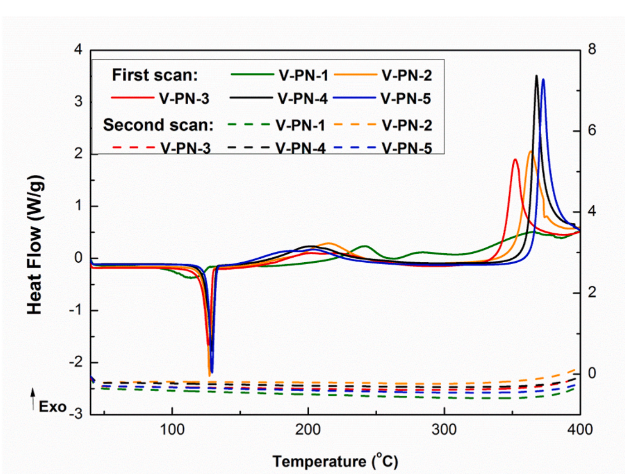


Fig. 2. DSC curves of **V-PN** resins at a heating rate of 5 °C min^{-1} under a flow of nitrogen.

Table 1
The curing behavior of **S1** and **S2** with different molar ratios.

	T_m (°C)	T_{onset1} (°C)	T_{peak1} (°C)	T_{onset2} (°C)	T_{peak2} (°C)
S1	–	117	208	–	–
S2	129	138	179	–	–
V-PN-1 (**S1**: **S2** = 1: 1)	114	170	241	307	364
V-PN-2 (**S1**: **S2** = 1: 5)	127	144	215	324	363
V-PN-3 (**S1**: **S2** = 1: 10)	126	138	220	314	352
V-PN-4 (**S1**: **S2** = 1: 30)	129	143	202	334	367
V-PN-5 (**S1**: **S2** = 1: 50)	129	140	188	344	372

requirements for heat-resistant resins in the aerospace industry. The **V-PN** resins can be ideal alternative candidates for commercialized petroleum-based **PN** resins prepared from bisphenols.

The thermomechanical properties of cured **V-PN** resins were studied by DMA. Taking **V-PN-5** resin as an example, as shown from the DMA curve (Fig. 5), the storage modulus of cured **V-PN-5** at room

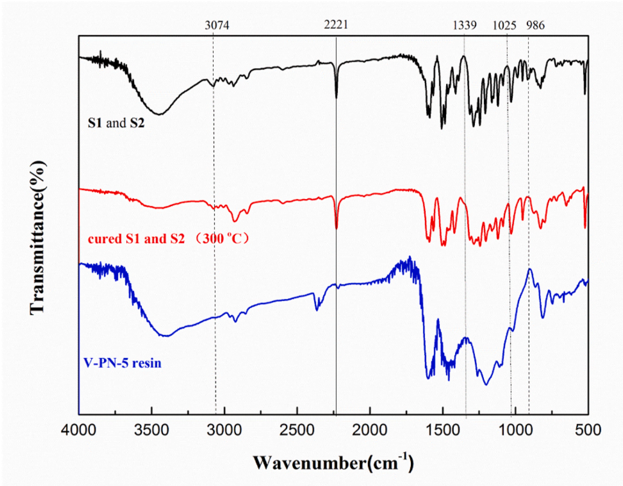


Fig. 3. FT-IR spectra of the mixture of **S1** and **S2**, cured **S1** and **S2** (300 °C) and **V-PN-5** resin.

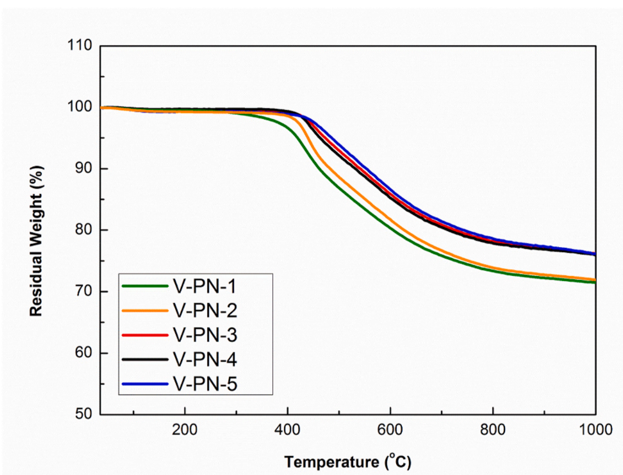


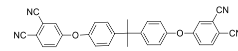
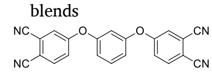
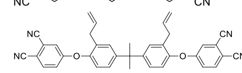
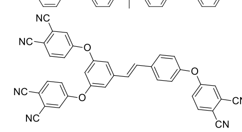
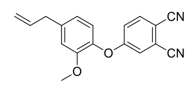
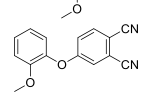
Fig. 4. TGA curves of cured **V-PN** resins at a heating rate of 10 °C min^{-1} under a flow of nitrogen.

temperature is as high as 2.9 GPa, and it still has a storage modulus of 1.6 GPa at the temperature up to 400 °C. It demonstrates that the **V-PN-5** resin has a stable mechanical property in the wide range of temperature. No obvious change was observed in the tan δ curve, indicating that the glass transition temperature (T_g) of the **V-PN-5** resin is higher than 400 °C.

3.4. Water uptake

The cured **V-PN-5** resin was immersed in boiling water for 120 h to detect the water uptake. In the first 24 h, the sample was taken out and weighted every 6 h. After that, it was measured every 12 h. The water uptake of cured **V-PN-5** resin increases sharply in the first 24 h after immersing, and reaches the maximum value of 2.4% in 48 h (Fig. S5). Then the water uptake of cured **V-PN-5** resin remains relatively constant even after immersing for 120 h. The results show that the water uptake of cured **V-PN-5** resin is equivalent to those of commercialized bisphenol-A-based **PN** resins [6], indicating that the cured **V-PN-5** resin has a better water-resistant property. Furthermore, the thermostability of **V-PN-5** after water uptake has been studied, and the result shows in Fig. S6. The T_{5d} and char yield of **V-PN-5** after water uptake is 486 °C and 76%, respectively, which is almost no change relative to that before water uptake. The results indicate that the low water uptake of **V-PN-5** resin makes for its endurance in moist conditions.

Table 2
Thermostability of the **V-PN** resins and other reported **PN** resins.

Structure	T_{5d} (°C)	T_{10d} (°C)	R% (1000 °C)	Reference
V-PN-1 (**S1**: **S2** = 1: 1)	419	457	71	this work
V-PN-2 (**S1**: **S2** = 1: 5)	439	482	72	this work
V-PN-3 (**S1**: **S2** = 1: 10)	463	531	75	this work
V-PN-4 (**S1**: **S2** = 1: 30)	473	541	76	this work
V-PN-5 (**S1**: **S2** = 1: 50)	486	553	76	this work
	472	502	70	[33]
Copolymerization of bisphthalonitrile/benzoxazine blends	447	506	73	[5]
	503	–	70	[9]
	466	510	73	[34]
	510	–	65	[15]
	465	527	77 (800 °C)	[35]
	484	536	75 (800 °C)	[35]

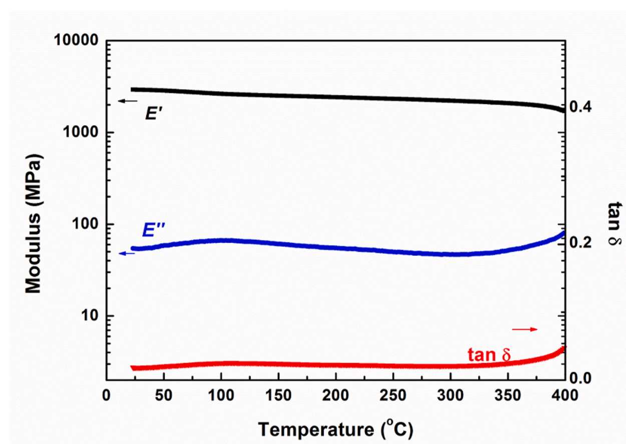


Fig. 5. DMA curves of cured **V-PN-5** resin at a heating rate of 5 °C min^{-1} in air.

4. Conclusion

In summary, we designed and synthesized new monomer **S1** and phthalocyanine monomer **S2** from vanillin. A series of **PN** resins were prepared from the thermal polymerization of the two monomers in a different molar ratio. Those bio-based **PN** resins exhibited excellent heat-resistant property. Among them, the cured **V-PN-5** resin displayed the best comprehensive properties with the T_{5d} of 486 °C, high residual mass of 76%, high T_g over 400 °C and low water uptake of 2.4%, which were better than those of commercialized bisphenol-A-based **PN** resins. Our strategy of developing **PN** resins from vanillin not only broadens the resource of raw materials for preparing **PN** resins, but also provides the ideal alternative candidates for traditional petroleum-based **PN** resins.

CRediT authorship contribution statement

Caiyun Wang: Synthesis, Investigation, Data curation, Writing – original draft. **Manling Shi:** Writing – review & editing. **Linxuan Fang:** Synthesis and, Writing – review & editing. **Menglu Dai:** Writing – review & editing. **Gang Huang:** Writing – review & editing. **Jing Sun:** Supervision, Writing – review & editing. **Qiang Fang:** Supervision, Conceptualization, Writing – review & editing.

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.

Acknowledgements

Financial support from the Ministry of Science and Technology of China (2017YFB0404701), the Natural Science Foundation of China (NSFC, No. 21975278, 21774140, 22075311 and 21774142) and the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant XDB 20020000) are gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2021.123723.

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