European Polymer Journal 157 (2021) 110645

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

A highly heat-resistant phthalocyanine resin based on a bio-based anethole

Heng Zhang [a,b], Minghui Li [b], Caiyun Wang [a,b], Gang Huang [b], Meina Liu [a,*], Jing Sun [b,*], Qiang Fang [b,*]

[a] School of Chemical and Environmental Engineering, Shanghai Institute of Technology, 100 Haiquan Road, Shanghai 201418, PR China
[b] Key Laboratory of Synthetic and Self-Assembly Chemistry for Organic Functional Molecules, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, PR China

ARTICLE INFO

Keywords:
Anethole
Phthalocyanine resin
Thermostability
Char yield

ABSTRACT

A phthalonitrile-containing monomer derived from a plant oil (anethole) has been successfully synthesized by a facile two-step reaction in an overall yield of 84%. Upon high temperature, this monomer is converted to a cured phthalocyanine resin in the presence of a catalyst, 4,4′-bis(3-aminophenoxy)diphenyl sulfone (***m*-BAPS**). Such a cured resin displays good thermostability including high glass transition temperature ($T_g > 450$ °C), low thermal expansion coefficient (CTE, near 62.99 ppm $^\circ C^{-1}$ from 25 to 400 °C) and high char yield (>72% at 1000 °C). These data are comparable to those of the most of the common phthalocyanine resins derived from the fossil resource, suggesting that the phthalonitrile-containing monomer is a suitable precursor for the preparation of the ablation-resistant materials used on the surface of the spacecrafts.

1. Introduction

Phthalocyanine resins are a class of high-performance thermosetting materials [1,2]. Because of their outstanding properties including high thermostability, low water uptake and high char yield, phthalocyanine resins have been widely applied in the fields of aerospace, marine, adhesives and microelectronics [3–7]. The high thermostability of cured phthalocyanine resins can be attributed to the addition polymerization of monomers containing the aromatic skeletons [8], most of which derived from non-renewable fossil resources, e.g. bisphenol A [9], resorcin [10]. These petroleum-based phthalocyanine resins possess attractive heat-resistance properties [6], however, the backbone rigidity and strong intermolecular interaction often results in poor solubility or a high melting point [11,12], which leads to the difficulty in processability for fabricating composites [13]. On the other hand, with the rapidly depleting of fossil resources and rising of environment concerns, it becomes increasingly important to use the renewable feedstocks to prepare polymer materials instead of petroleum-based chemicals [14,15]. Therefore, developing phthalocyanine resins from biomass has attracted great attention. Recently, several bio-based phthalocyanine resins have been synthesized from renewable phenols, such as resveratrol [13], vanillin [16], eugenol [17], and guaiacol [18]. Although some of them show desirable heat-resistant property, the examples of phthalocyanine resin monomers with good processability that can be easily prepared are still limited [19]. Hence, it is significant to explore simple methods to convert biomass feedstocks to phthalocyanine resins.

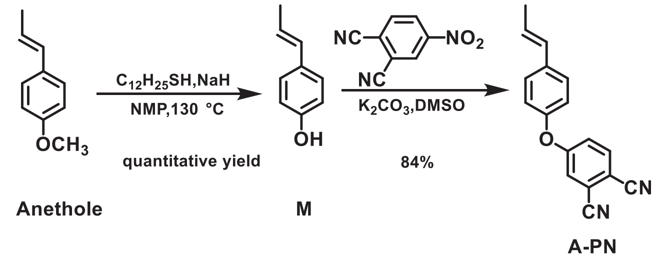
Anethole is an aromatic vegetable oil that can be easily extracted from fennel and star anise plants growing in southwest China with the yearly output of about 3000 tons [20]. Because of its abundant and renewable characteristics, anethole is an ideal feedstock to develop bio-based materials. Moreover, its bifunctional chemical structure with aromatic skeletons enables it to prepare polymer materials via few chemical modifications [21,22]. The propenyl group of anethole is taken as a naturally cross-linkable group, which can be used to develop high-performance thermosetting resins.

In this work, a bio-based phthalocyanine resin was developed with anethole as starting material. Firstly, the monomer (called as **A-PN**) is synthesized through a two-step reaction procedure (see Scheme 1) with a high overall yield. The monomer shows a low melting point of 97 °C and the good solubility in common organic solvents, indicating its good processability. In the presence of a catalysis, 4,4′-bis(3-aminophenoxy) diphenyl sulfone (***m*-BAPS**), **A-PN** is transformed at high temperature into an insoluble and infusible phthalocyanine-like resin (called as **PA-PN**, see Scheme 2). **PA-PN** displays high thermostability with a 5% weight loss temperature (T_{5d}) of 483 °C and a char yield of up to 72% at 1000 °C. Especially, the glass transition temperature (T_g) of **PA-PN** is over 450 °C. These results demonstrate that the new anethole-based phthalocyanine resin is comparable to the petroleum-based

---

* Corresponding authors.
E-mail addresses: meina.liu@sit.edu.cn (M. Liu), sunjing@sioc.ac.cn (J. Sun), qiangfang@sioc.ac.cn (Q. Fang).

https://doi.org/10.1016/j.eurpolymj.2021.110645
Received 25 May 2021; Received in revised form 25 June 2021; Accepted 11 July 2021



Scheme 1. The synthesis of the monomer.

phthalocyanine resins, implying that this resin has potential application as the ablation-resistant coating on the spacecrafts. Among the bio-based phthalocyanine resins, vanillin-based phthalocyanine resins developed recently showed the most desirable heat-resistant properties [16,23]. Relative to them, **PA-PN** also displayed comparable thermostability. Considering of the abundant and easy-access of anethole, developing anethole-based phthalocyanine resins can provide a promising approach to obtain the high heat-resistant material. Here, we report the details.

2. Experimental section

2.1. Reagents and instruments

Anethole was acquired from Nanjing Chemlin Chemical Industry Co., China. 4-nitrophthalonitrile was purchased from Zhengyuan Pharmaceutical Technology Co., Ltd., Pinghu City, Zhejiang Province, China. 4,4′-Bis(3-aminophenoxy)diphenyl sulfone (***m*-BAPS**) was purchased from Ark Pharm. All solvents were used as received without further purification.

^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker 400 spectrometer. High resolution mass spectra (HRMS) were measured by a Waters Premier GC-TOF mass spectrometer. Elemental analysis was determined by an elementar vario EL III analyzer. Fourier transform infrared spectra (FT-IR) spectra were detected on a Nicolet spectrometer with KBr pellets. Differential scanning calorimetry (DSC) curves were collected by a TA Instrument of DSC Q200 at a heating rate of 10 °C min^{-1} under a nitrogen flow. Dynamic mechanical analysis (DMA) was tested with a heating rate of 5 °C min^{-1} in a nitrogen atmosphere on the DMA 800 instruments. Coefficient of thermal expansion (CTE) was detected on a NETZSCH DIL 402 expedis instrument in a nitrogen atmosphere with a heating rate of 5 °C min^{-1}. Thermo-gravimetric analysis (TGA) was measured by a NETZSCH TG 209 apparatus in a nitrogen atmosphere at a heating rate of 10 °C min^{-1} from room temperature to 1000 °C.

2.2. Synthesis of (*E*)-4-propenyl phenol (**M**)

The (*E*)-4-propenyl phenol (**M**) was synthesized by a route previously reported in a quantitative yield.[24]

^{1}H NMR (400 MHz, DMSO-d_6, ppm): 9.36 (s, 1H), 7.17 (d, $J = 8.5$ Hz, 2H), 6.69 (d, $J = 8.5$ Hz, 2H), 6.28 (dd, $J = 15.8$, 2.0 Hz, 1H), 6.09 – 5.97 (m, 1H), 1.79 (dd, $J = 6.7$, 1.8 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6, ppm): 161.64, 135.79, 133.71, 132.02(2C), 126.87, 120.47 (2C), 23.34. HRMS-EI (m/z): Calcd $C_9H_{10}O$ $[M]^+$ 134.0732; Found 134.0723.

2.3. Synthesis of monomer **A-PN**

The (*E*)-4-propenyl phenol (4.02 g, 30 mmol) was added into the mixture of 4-nitrophthalonitrile (5.19 g, 30 mmol), anhydrous K_2CO_3 (12.44 g, 90 mmol) and DMSO (50 mL) in a 100 mL round-bottom flask with magnetic stirring. The resulting solution was stirred at room temperature for 72 h. Then the reaction mixture was poured into water to precipitate. The off-white residue was filtered, washed with deionized water to neutrality and dried. The crude product was dissolved with ethyl acetate and purified by column chromatography using a mixture of petroleum ether and ethyl acetate (30:1, v/v) as the eluent. **A-PN** was obtained as a white solid in a yield of 84%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.72 (d, $J = 8.6$ Hz, 1H), 7.42 (d, $J = 8.5$ Hz, 2H), 7.29 – 7.21 (m, 2H), 7.01 (d, $J = 8.5$ Hz, 2H), 6.40 (dd, $J = 15.9$, 1.8 Hz ,1H), 6.30 – 6.20 (m, 1H), 1.92 (dd, $J = 6.5$, 1.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): 161.89, 152.10, 136.31, 135.36, 129.57, 127.81 (2C), 126.89, 121.37, 121.30, 120.66, 117.60, 115.39 (2C), 114.93, 108.68, 18.48. HRMS-EI (m/z): Calcd $C_{17}H_{17}N_2O$ $[M]^+$ 260. 0950; Found 260.0949. Anal. Calcd $C_{17}H_{17}N_2O$: C, 78.44; H, 4.65; N, 10.76; Found: C, 78.14; H, 4.93; N, 10.67.

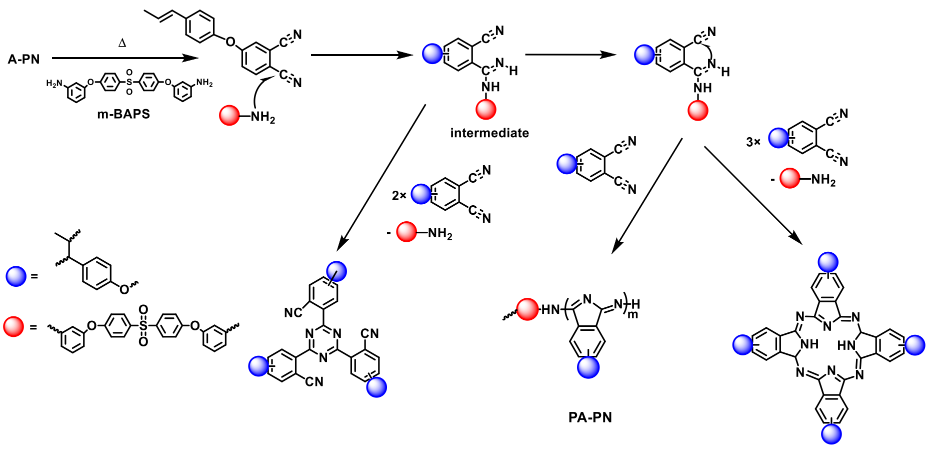
2.4. Preparation of cured sample

A-PN monomer (2 g) and 4 wt% ***m*-BAPS** was placed in a flat-bottom glass tube, which was maintained at 100 °C in a vacuum for 2 h to remove residual solvent. Then the tube was sealed and the temperature was then increased and kept at 260 °C for 1 h, 270 °C for 2 h, 300 °C for 0.5 h, and 323 °C for 1 h, 380 °C for 4 h, respectively. Therefore, a fully cured sample was obtained.

3. Results and discussion

3.1. Synthesis and characterization of **A-PN**

The new monomer **A-PN** was converted from anethole by a two-step route as shown in Scheme 1. The intermediate product (*E*)-4-



Scheme 2. The produce for the synthesis of **PA-PN**.

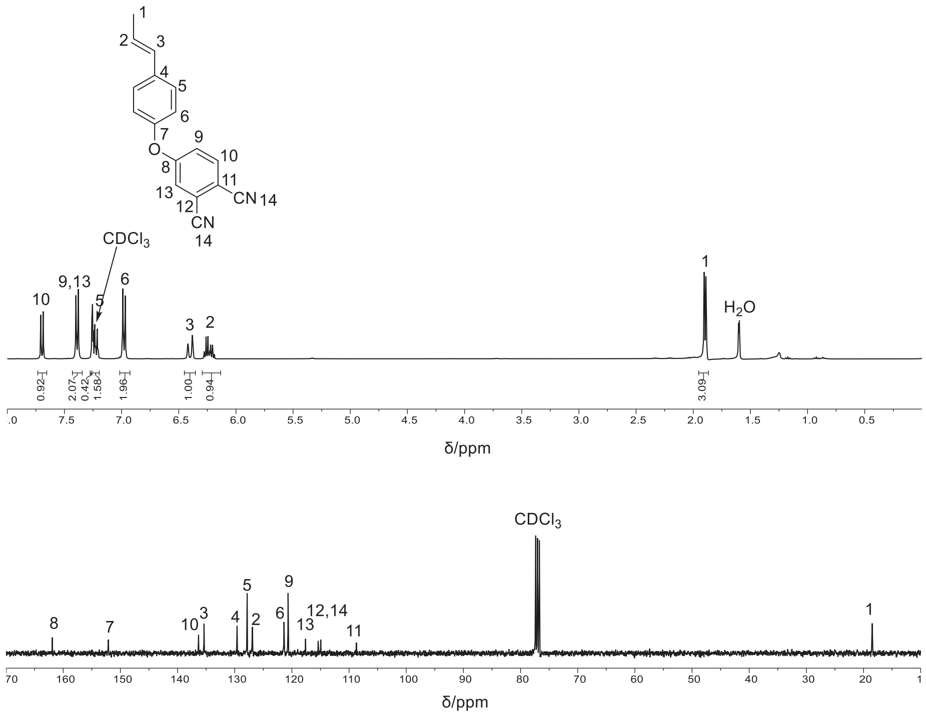


Fig. 1. The ^{1}H NMR and ^{13}C NMR spectra of monomer **A-PN**.

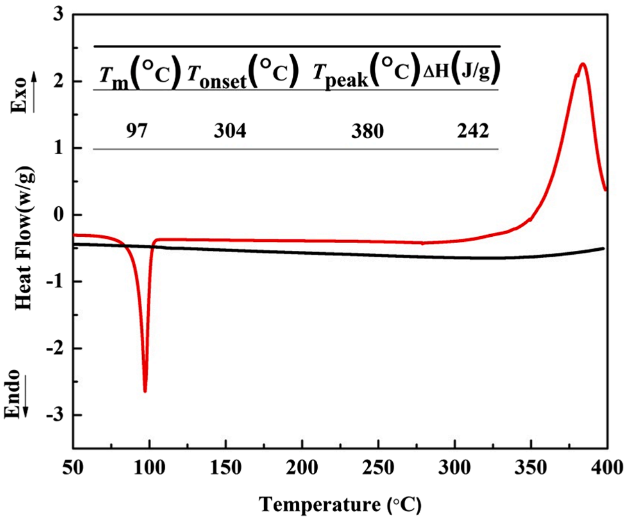


Fig. 2. DSC traces of **A-PN** with 4 wt% ***m*-BAPS** under N_2 with a heating rate of 10 °C min^{-1}.

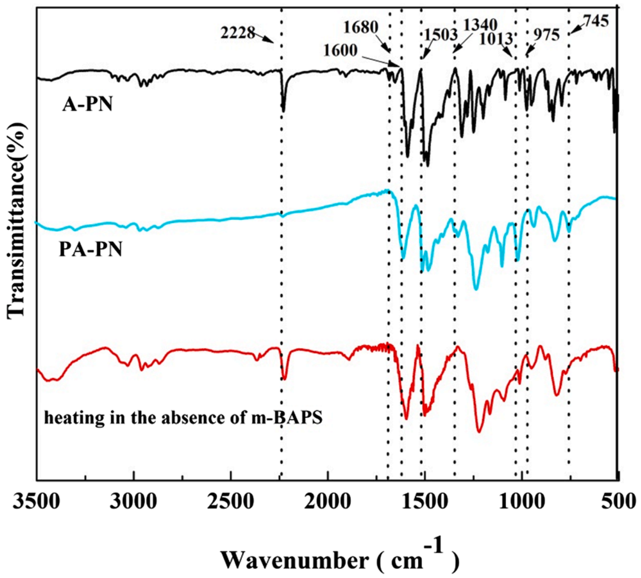


Fig. 3. FT-IR spectra of **A-PN** before and after curing.

propenylphenol (**M**) was obtained from demethylation of anethole, and then **M** reacts with 4-nitrophthalonitrile to obtain the target monomer. **A-PN** was prepared in a high overall yield of 84%. The chemical structure of **A-PN** was characterized by the ^{1}H NMR, ^{13}C NMR spectroscopy (see Fig. 1), HR-MS and elemental analysis. The obtained **A-PN** monomer is a white solid and soluble in most common organic solvents, such as acetone, ethyl acetate, chloroform and toluene. As shown in ^{1}H NMR spectrum of **A-PN** (Fig. 1), the characteristic peaks at the range from 7.01 to 7.72 ppm are assigned to the hydrogen in benzene ring. The peaks appear at the range from 6.20 to 6.40 ppm are ascribed to the hydrogen at the vinyl group. The peak at 1.92 ppm is attributed to hydrogen in methyl group. ^{13}C NMR spectrum also indicates that the carbon signal peaks are in accordance with the proposed structure.

3.2. *Curing behavior of* ***A-PN***

The monomer **A-PN** can be cross-linked in the presence of a catalysis (***m*-BAPS**) under high temperature. Thermal cross-linking behavior of **A-PN** was monitored by DSC. As shown in Fig. 2, at the first scan from 40 to 400 °C, **A-PN** displays a melting point of 97 °C, an onset curing temperature of 304 °C and a maximum peak temperature at 380 °C. No obvious exothermic peak is observed at the second scan, indicating the curing reaction of **A-PN** has completed.

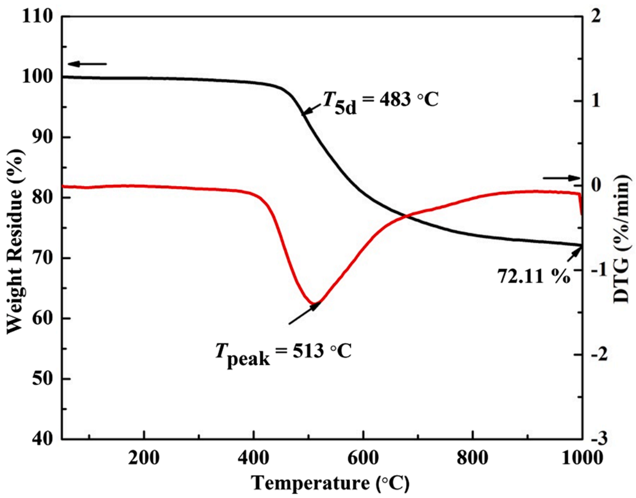


Fig. 4. TGA curves of **PA-PN** in N_2 with a heating rate of 10 °C min^{-1}.

The degree of the thermal cross-linking reaction of **A-PN** was characterized by FT-IR, and the results are depicted in Fig. 3. As can be seen from Fig. 3, the characteristic absorption peak of the -C≡N group at 2228 cm^{-1} disappears after thermal curing, and the absorption peaks at 1600 cm^{-1} and 745 cm^{-1} appear, indicating the formation of isoindoline units. The absorption peak at 1013 cm^{-1} can be observed in **PA-PN**, which is assigned to the vibration of phthalocyanine units.[25,26] The appearance of the absorption peaks at 1340 cm^{-1} and 1503 cm^{-1} represents the formation of triazine units.[27] In addition, the characteristic peaks attributed to alkene = C-H at 975 cm^{-1} and 1680 cm^{-1} also disappear, suggesting the alkene units involved in the polymerization.[23]

It is noted that the characteristic absorption peaks of double bond in **A-PN** completely disappear after the monomer is cured at near 350 ℃ (see Figure S1 in Supporting Information), indicating that both the double bond and the cyano groups participate the curing reaction. In order to ascertain when the polymerization of propylene double bond occurs in **A-PN,** the relevant experiments were carried out on DSC and FT-IR. Firstly, the curing behaviors of anethole with and without catalyst were investigated, and the results indicated that no exothermic peaks were observed in the DSC traces (see Figure S2 in Supporting Information), implying that anethole does not occur thermal polymerization, even in the presence of a catalyst (the endothermic peaks at about 240 °C are attributed to the evaporation of anethole). Considering that the ease of volatilization of anethole at high temperature, the measurement of the curing behavior of anethole needs to be improved. Thus, a derivative of anethole was synthesized to further study the curing behavior of anethole. As can be seen from Figure S2 in the Supporting Information, the derivative **(8F-A)** only shows an endothermic peak of melting at 112 °C and does not give an exothermic peak in its DSC trace, clearly confirming that the double bond does not polymerize at high temperature. The FT-IR spectrum of **A-PN** after curing at high temperature in the absence of a catalyst (Fig. 3) indicates that the characteristic peaks attributed to propylene group at 975 cm^{-1} and 1680 cm^{-1} disappear and the peak belonged to -C≡N group at 2228 cm^{-1} becomes weak, meaning that the double bond reacts with the -C≡N in **A-PN**. Such a result is similar to the reaction between a cyanate ester and a bismaleimide, forming a cyclic product.[28] To know the effect of the temperature on the reaction degree between the propylene group and the -C≡N group, the curing behavior of **A-PN** with 4 wt% catalyst at different temperatures was also studied, and the results are displayed in Figure S1. As can be seen from Figure S1 in Supporting Information, complete curing of **A-PN** with ***m*-BAPS** occurs at 380 °C.

Table 1
The thermostability of PN-based resins.

Resins	Feedstock	T_{5d} (℃)	T_g (℃)	Residual mass(%)	Ref
PA-PN	anethole	483	>450	72	This work
Poly (BPN)	lignin	417	400	72	[31]
Poly (EPN)	eugenol	465	394	78 (800 °C)	[18]
Poly (GPN)	guaiacol	484	392	75 (800 °C)	[18]
TBHQPh	1,3,5-benzenetricarbonyltrichloride	536	>500	74	[32]
PIPN	4,4′-oxydiphthalic anhydride	518	–	69 (800 °C)	[33]
HPPN	bisphenol A(PPO)	391	351	65 (800 °C)	[34]
TPN	L-Tyrosine	450	455	71 (800 °C)	[35]
Poly(BA-ph)	bisphenol A	439	300	66 (800 °C)	[36]
4a	resveratrol	510	>400	65	[13]
4b	resveratrol	500	>400	62	[13]
BA-ph/ BPA	bisphenol A (BPA)	443	299	65 (800 °C)	[37]
Bis-ADPN/ DDS	Bisphenol A	478	>400	62 (800 °C)	[38]
Cured-3a	Vanillin	482	>500	78	[23]
Cured-3b	Vanillin	477	>500	76	[23]
V-PN	Vanillin	486	>400	76	[16]
HBPPN	4-hydroxybenzoic acid	452	>329	66 (900 °C)	[39]
BDS	bis-(4-hydroxyphenyl) sulfone	436	322	57	[40]
Cured 5d	1,6-dihydroxynaphthalene	551	>500	66.5	[41]

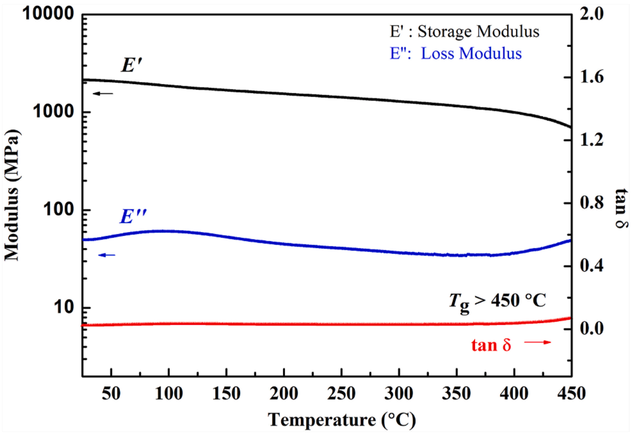


Fig. 5. DMA curves of **PA-PN** at a heating rate of 5 °C min^{-1}.

3.3. *Thermostability*

Thermostability of the **PA-PN** was measured by TGA, and the results are exhibited in Fig. 4**.** It is seen that **PA-PN** displays a T_{5d} of about 483 °C and a maximum peak weight loss temperature of 513 °C in N_2, respectively. It is noted that **PA-PN** has a char yield of 72.11 % in N_2 at 1000 °C, indicating that this resin possesses high heat-resistance. For comparison, the thermostability of petroleum-based PN resins and some reported bio-mass PN resins are summarized in Table 1. These data demonstrate that **PA-PN** has higher T_{5d} and char yield than most of the bifunctional phthalocyanine resins (Table 1). Moreover, **PA-PN** also displays better thermostability than the phthalocyanine resins derived from lignin and guaiacol. Compared with vanillin-based phthalocyanine

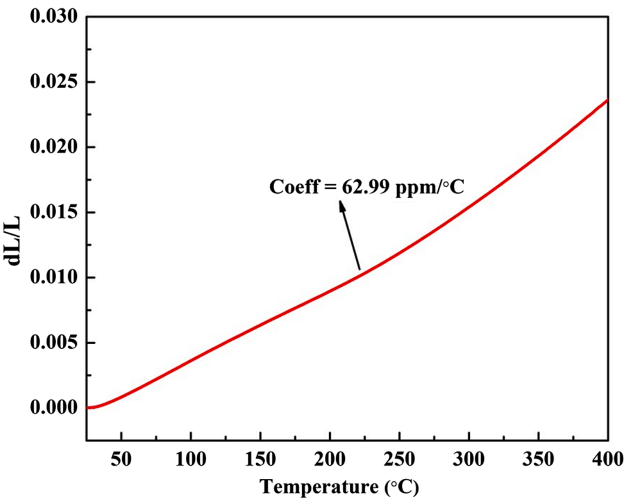


Fig. 6. CTE curves of **PA-PN** at a heating rate of 5 °C min^{-1}.

resins and other heat-resistant polymers, **PA-PN** also has excellent thermostability [16,23,29,30]. These results reveal that **PA-PN** can be used as heat-resistant materials in aerospace field.

The thermomechanical properties of **PA-PN** were evaluated by DMA. T_g can be obtained from the maximum value of tan δ in the DMA curve. As shown in Fig. 5, the tan δ value of **PA-PN** does not change significantly at around 450 °C. Thus, it can be estimated that T_g of **PA-PN** is more than 450 °C, which is higher than most phthalocyanine resins derived from biomass or petroleum feedstock. At the temperature range from 25 to 400 °C, the storage modulus (E') of **PA-PN** resin changes from 2.1 GPa to 1.0 GPa, indicating the mechanical properties are stable even in high temperature condition. The high T_g and storage modulus of the resin are attributed to the formation of phthalocyanine rings with cross-linked structures in the cured product. Furthermore, the dimensional stability is conducted by thermal dilatometer. As shown in Fig. 6, the cured polymer exhibits a CTE of 62.99 ppm $°C^{-1}$ at the range from 25 to 400 °C. The low CTE demonstrates that **PA-PN** has outstanding dimensional stability at a wide temperature range.

4. Conclusions

A bio-based phthalonitrile-containing monomer based on a plant oil (anethole) was facilely synthesized. This monomer was cured using a commercial curing agent (***m*-BAPS**) at high temperature to form a highly cross-linked network with the phthalocyanine structure (**PA-PN**), displaying good thermostability with a T_{5d} of 483 °C, a T_g of over 450 °C and a char yield of 72% at 1000 °C. Moreover, **PA-PN** also exhibits high dimensional stability with a CTE of 62.99 ppm $°C^{-1}$ at the ranges of temperatures varying from 25 to 400 °C. In comparison with the common petroleum-based phthalocyanine resins, bio-based **PA-PN** possesses comparable thermostability and dimensional stability. This work provides a new way to develop the bio-based phthalocyanine resins. The obtained resins are suitable as an alternative of the petroleum-based phthalocyanine resins.

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 material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2021.110645.

References

[1] K.e. Zeng, K.e. Zhou, S. Zhou, H. Hong, H. Zhou, Y. Wang, P. Miao, G. Yang, Studies on self-promoted cure behaviors of hydroxy-containing phthalonitrile model compounds, Eur. Polym. J. 45 (4) (2009) 1328–1335.

[2] Y. Liu, Z. Liu, W. Peng, Z. Lu, J. Hu, K. Zeng, G. Yang, Copolymerization modification: improving the processability and thermal properties of phthalonitrile resins with novel comonomers, Polym. Int. 68 (4) (2019) 724–734.

[3] S. Ji, P. Yuan, J. Hu, R. Sun, K. Zeng, G. Yang, A novel curing agent for phthalonitrile monomers: Curing behaviors and properties of the polymer network, Polymer 84 (2016) 365–370.

[4] D. Wu, Y. Zhao, K.e. Zeng, G. Yang, A novel benzimidazole-containing phthalonitrile monomer with unique polymerization behavior, J. Polym. Sci. Pol. Chem. 50 (23) (2012) 4977–4982.

[5] F. Zhao, R. Liu, C. Kang, X. Yu, K. Naito, X. Qu, Q. Zhang, A novel high-temperature naphthyl-based phthalonitrile polymer: synthesis and properties, RSC Adv. 4 (16) (2014) 8383–8390.

[6] G. Yu, C. Liu, X. Li, J. Wang, X. Jian, C. Pan, Highly thermostable rigid-rod networks constructed from an unsymmetrical bisphthalonitrile bearing phthalazinone moieties, Polym. Chem. 3 (4) (2012) 1024–1032.

[7] M. Laskoski, A. Neal, T.M. Keller, D. Dominguez, C.A. Klug, A.P. Saab, Improved synthesis of oligomeric phthalonitriles and studies designed for low temperature cure, J. Polym. Sci. Pol. Chem. 52 (12) (2014) 1662–1668.

[8] M. Laskoski, D.D. Dominguez, T.M. Keller, Synthesis and properties of a bisphenol A based phthalonitrile resin, J. Polym. Sci. Pol. Chem. 43 (18) (2005) 4136–4143.

[9] M. Xu, D. Ren, L. Chen, K. Li, X. Liu, Understanding of the polymerization mechanism of the phthalonitrile-based resins containing benzoxazine and their thermal stability, Polymer 143 (2018) 28–39.

[10] T.M. Keller, D.D. Dominguez, High temperature resorcinol-based phthalonitrile polymer, Polymer 46 (13) (2005) 4614–4618.

[11] D. Kumar, V. Choudhary, Studies on crosslinking and thermal behavior of phthalonitrile end-capped imide monomer in presence of aromatic amines, J. Appl. Polym. Sci. 135 (17) (2018) 46151, https://doi.org/10.1002/app.v135.1710.1002/app.46151.

[12] Y. Han, D. Tang, G. Wang, Y. Guo, H. Zhou, W. Qiu, T. Zhao, Low melting phthalonitrile resins containing methoxyl and/or allyl moieties: synthesis, curing behavior, thermal and mechanical properties, Eur. Polym. J. 111 (2019) 104–113.

[13] M. Laskoski, J.S. Clarke, A. Neal, B.G. Harvey, H.L. Ricks-Laskoski, W.J. Hervey, M. N. Daftary, A.R. Shepherd, T.M. Keller, Sustainable high-temperature phthalonitrile resins derived from resveratrol and dihydroresveratrol, ChemistrySelect 1 (13) (2016) 3423–3427.

[14] B.G. Harvey, A.J. Guenthner, W.W. Lai, H.A. Meylemans, M.C. Davis, L. R. Cambrea, J.T. Reams, K.R. Lamison, Effects of o-methoxy groups on the properties and thermal stability of renewable high-temperature cyanate ester resins, Macromolecules 48 (10) (2015) 3173–3179.

[15] J.M. Raquez, M. Deléglise, M.F. Lacrampe, P. Krawczak, Thermosetting (bio) materials derived from renewable resources: a critical review, Prog. Polym. Sci. 35 (4) (2010) 487–509.

[16] C. Wang, M. Shi, L. Fang, M. Dai, G. Huang, J. Sun, Q. Fang, The bio-based phthalocyanine resins with high Tg and high char yield derived from vanillin, Polymer 224 (2021), 123723.

[17] Y.i. Ning, D.-S. Li, M.-C. Wang, L. Jiang, Bio-resourced eugenol derived phthalonitrile resin for high temperature composite, J. Appl. Polym. Sci. 138 (30) (2021) 50721, https://doi.org/10.1002/app.v138.3010.1002/app.50721.

[18] A. Wang, A.Q. Dayo, L. Zu, Y. Xu, D. Lv, S. Song, T. Tang, W. Liu, J. Wang, B. Gao, Bio-based phthalonitrile compounds: synthesis, curing behavior, thermomechanical and thermal properties, React. Funct. Polym. 127 (2018) 1–9.

[19] Y. Liu, J. Hu, R. Li, C. Li, B.o. Liang, Y. Liu, W. Peng, K.e. Zeng, G. Yang, A prospective partial bio-based diamine-adenine-monomer platform for high performance polymer: a case study on phthalonitrile resin, Polym. Degrad. Stabil. 167 (2019) 114–123.

[20] C. Wang, J. Sun, Y. Tao, L. Fang, J. Zhou, M. Dai, M. Liu, Q. Fang, Biomass materials derived from anethole: conversion and application, Polym. Chem. 11 (5) (2020) 954–963.

[21] Y. Tao, F. He, K. Jin, J. Wang, Y. Wang, J. Zhou, J. Sun, Q. Fang, Facile conversion of plant oil (anethole) to a high-performance material, Polym. Chem. 8 (13) (2017) 2010–2015.

[22] F. He, Y.u. Gao, K. Jin, J. Wang, J. Sun, Q. Fang, Conversion of a biorenewable plant oil (Anethole) to a new fluoropolymer with both low dielectric constant and low water uptake, ACS Sustain. Chem. Eng. 4 (8) (2016) 4451–4456.

[23] Y. Tao, J. Zhou, J. Wang, Y. Wang, J. Sun, Q. Fang, High performance low dielectric constant polymer with good film-forming ability developed from renewable plant oil (anethole), Macromol. Chem. Phys. 219 (2018) 1800133.

[24] A.S. Singh, S.K. Shukla, A.K. Pandey, D.N. Tripathi, N.E. Prasad, Synthesis and evaluation of catalytic curing behavior of novel nitrile-functionalized benzoxazine for phthalonitrile resins, Polym. Bull. 75 (8) (2018) 3781–3800.

[25] S. Liao, H. Wu, X. He, J. Hu, R. Li, Y. Liu, J. Lv, Y. Liu, Z. Liu, K. Zeng, G. Yang, Promoting effect of methyne/methylene moiety of bisphenol E/F on phthalonitrile resin curing: expanding the structural design route of phthalonitrile resin, Polymer 210 (2020), 123001.

[26] C. Gao, H. Gu, A. Du, H. Zhou, D. Pan, N. Naik, Z. Guo, Polyaniline facilitated curing of phthalonitrile resin with enhanced processibility and mechanical property, Polymer 219 (2021), 123533.

[27] Y. Han, D. Tang, G. Wang, Y. Sun, Y. Guo, H. Zhou, W. Qiu, T. Zhao, Phthalonitrile resins derived from vanillin: synthesis, curing behavior, and thermal properties, Chinese J. Polym. Sci. 38 (1) (2019) 72–83.

[28] L. Wan, X. Zhang, G. Wu, A. Feng, Thermal conductivity and dielectric properties of bismaleimide/cyanate ester copolymer, High Volt. 2 (3) (2017) 167–171.

[29] J. Tong, S. Diao, K. Jin, C. Yuan, J. Wang, J. Sun, Q. Fang, Benzocyclobutene-functionalized poly(m-phenylene): a novel polymer with low dielectric constant and high thermostability, Polymer 55 (16) (2014) 3628–3633.

[30] J. Hou, X. Chen, J. Sun, Q. Fang, A facile conversion of a bio-based resveratrol to the high-performance polymer with high Tg and high char yield, Polymer 200 (2020), 122570.

[31] Y. Liu, Z. Liu, W. Peng, Z. Lu, J. Hu, K. Zeng, G. Yang, Inspiration from a new lignin-derived phthalonitrile resin: unique curing behavior, and thermal properties, Eur. Polym. J. 121 (2019), 109351.

[32] Y. Zu, F. Zhang, D. Chen, L. Zong, J. Wang, X. Jian, Wave-transparent composites based on phthalonitrile resins with commendable thermal properties and dielectric performance, Polymer 198 (2020), 122490.

[33] J. Hu, Y. Liu, Y. Jiao, S. Ji, R. Sun, P. Yuan, K.e. Zeng, X. Pu, G. Yang, Self-promoted phthalimide-containing phthalonitrile resins with sluggish curing process and excellent thermal stability, RSC Adv. 5 (21) (2015) 16199–16206.

[34] J. Ma, K. Cheng, J. Lv, C. Chen, J. Hu, K. Zeng, G. Yang, Phthalonitrile-PPO blends: cure behavior and properties, Chinese J. Polym. Sci. 36 (4) (2017) 497–504.

[35] W. Peng, F. Yao, J. Hu, Y. Liu, Z. Lu, Y. Liu, Z. Liu, K. Zeng, G. Yang, Renewable protein-based monomer for thermosets: a case study on phthalonitrile resin, Green Chem. 20 (22) (2018) 5158–5168.

[36] Y.-l. Xu, A.Q. Dayo, M. Derradji, J. Wang, W.-B. Liu, S. Song, T. Tang, Copolymerization of bisphthalonitrile/benzoxazine blends: curing behavior, thermomechanical and thermal properties, React. Funct. Polym. 123 (2018) 97–105.

[37] Z. Chen, X. Yang, M. Xu, X. Liu, Preparation and properties of bisphenol A-based bisphthalonitrile polymers, High Perform. Polym. 26 (1) (2014) 3–11.

[38] D. Kumar, V. Choudhary, Curing kinetics and thermal properties of imide containing phthalonitrile resin using aromatic amines, Thermochimica Acta 693 (2020), 178749.

[39] Z.-L. Wang, X.-Y. Liu, Y. Han, Y. Guo, H. Zhou, J. Wang, W.-B. Liu, T. Zhao, Preparation and characterization of phthalonitrile resin within hyperbranched structure, High Perform. Polym. 32 (8) (2020) 963–972.

[40] X. Peng, H. Sheng, H. Guo, K. Naito, X. Yu, H. Ding, X. Qu, Q. Zhang, Synthesis and properties of a novel high-temperature diphenyl sulfone-based phthalonitrile polymer, High Perform. Polym. 26 (7) (2014) 837–845.

[41] Y. Zu, L. Zong, J. Wang, X. Jian, Enhanced thermal property via tunable bisphenol moieties in branched phthalonitrile thermoset, Polymer 172 (2019) 372–381.