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Polymer

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

Promoting effect of methyne/methylene moiety of bisphenol E/F on phthalonitrile resin curing: Expanding the structural design route of phthalonitrile resin

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ARTICLE INFO

Keywords: Phthalonitrile Methylene Methyne Promoting effect Curing mechanism

ABSTRACT

In this paper, three phthalonitrile (PN) model compounds containing benzene ring-linked alkyl units, bisphenol A (methyl) phthalonitrile monomer (BPAh), bisphenol E (methyne) phthalonitrile monomer (BPEh) and bisphenol F (methylene) phthalonitrile monomer (BPFh), were synthesized. It was confirmed that methylene/methyne could effectively promote the curing reaction of phthalonitrile. Rheology analysis showed that the promotion effect of methylene is stronger than that of methyne, but methyl has no obvious promotion effect. The effect of DPPH on the reaction rate, added considerable evidences that the curing reaction of BPEh and BPFh involved a free radical process. Qualified thermal properties were investigated by Dynamic mechanical analysis (DMA) and thermal gravimetric analysis (TGA). For post-cured resin of BPEh and BPFh, the Tg is more than 500 $^\circ$ C, the T_{5%} were observed at 495 °C and 491 °C, and the char yield in 800 °C reached 73.1% and 71.9% respectively.

1. Introduction

Phthalonitrile resin (PN), as a high-performance polymer with plenty of excellent properties, has properties like heat-resistance, chemical resistance, low water absorption, flame retardancy, etc. [1-7]. These excellent properties endow phthalonitrile resin application potential in the fields of aerospace industry, composite materials and carbon precursors, which receive wide attention from researchers [8,9].

However, related studies have shown that [5-7], the intrinsic curing rate of phthalonitrile resin is slow, and it takes a long time to gelate above 300 °C. Adding curing agent is a prevailing route to solve the problem. Traditional curing agents include Lewis acid/base compounds, such as metal salts, strong organic acid/amine salts, amines, phenols, and some heterocyclic structures containing active hydrogen [10-13]. These curing agents could significantly reduce the initial curing temperature of the nitrile group, and the cured resin has excellent thermal, thermo-oxidative stability and outstanding thermomechanical properties.

Meanwhile, previous studies have also shown that it is expected to introduce the excellent properties of PN resins into other materials system and broaden the application by cyano-based reactive chemistry and the design of the curing system. For instance, based on the design of hydroxy-PN curing system of benzoxazine-PN [16], phenolic-PN [18], allyl-PN [19], alkynyl-PN [20] have been developed. From a scientific point of view, the reaction path of the current active hydrogen curing system is generally considered to involve ionic intermediates, such as ammonium salts [10]. However, the knowledge of the cyano reaction chemistry and curing mechanism of phthalonitrile resin is very limited. This restricts the scope of molecular design and material modification to a certain extent. In fact, in the field of foundation chemistry, the free radical reactivity of cyano groups has received extensive attention [21]. At the same time, early research has shown another path of thermal polymerization of phthalonitrile-free radical course [21]. The study found that free radical initiator tert-butanol peroxide could promote the polymerization of cyano groups, and the product contains phthalocyanine ring structure.

As we all know, the methyl/methylene/methyne groups in the alkyl group are the building blocks of aliphatic structures that make up a basic organic material system, such as synthetic polymer materials and natural polymers [24]. On the one hand, from the perspective of polymer

https://doi.org/10.1016/j.polymer.2020.123001

Received 4 June 2020; Received in revised form 26 August 2020; Accepted 31 August 2020







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Scheme 1. Synthesis of BPAh, BPFh, BPEh monomer.

chemistry, the free radical activity derived from such classic carbon chain units has been established [25,26]. On the other hand, compared to traditional active hydrogen curing systems (amino groups/phenols/acids, etc.), the carbon chain unit is relatively inert, and its structure has better chemical resistance and stability during the functionalization process [22]. Therefore, we assume whether the alkyl chain can effectively initiate the thermal polymerization of phthalonitrile. The study on this scientific issue is expected to provide a new route for the design of PN resin system and a new opportunity for its modification, such as the high-performance of biomass [17]. However, as far as we know, there are few systematic and in-depth studies on this issue. Recently, our laboratory has developed a new curing system that promotes the polymerization of phthalonitrile resins with imide cycloaliphatic moiety. The research provides essential cases for curing PN resins with alkyl units. The study found that a unique synergistic curing behavior existed between imide cycloaliphatic moiety and phthalonitrile unit [23], and the cured resins showed excellent thermo-oxidative stability and thermomechanical properties. It is believed that the mechanism of thermal polymerization is related to the free radical intermediate stabilized by the conjugation effect at high temperature [23]. However, from the perspective of basic research, relatively complex alkyl radicals (including methyl-methylene-methyne radicals) limit the understanding of reaction sites and mechanisms. From the perspective of applied research, it restricted the design flexibility of the PN resin system [22].

According to previous reports, free radicals derived from benzene ring methylene/methyne groups have relative stability [27a-c], and the modifiability of benzene ring units can also provide opportunities for material design [17] [28]. In this work, the simple structural units were introduced into monomer to verify whether it could effectively accelerate the polymerization of PN. The curing system is expected to provide a basic model system for the research on the free radical polymerization mechanism of phthalonitrile resin and a flexible and rich design approach for PN resin. Based on this assumption, three PN model compounds containing benzene ring-linked alkyl units, bisphenol A (methyl) phthalonitrile monomer (BPAh), bisphenol E (methyne) phthalonitrile monomer (BPEh) and bisphenol F (methylene) phthalonitrile monomer (BPFh) were designed and synthesized. By comparing the curing behavior, it is proved that methylene/methyne could effectively promote the reaction of phthalonitrile, in which the promotion effect of methylene is stronger than that of methyne, and the cured product has qualified thermal properties. This research greatly expanded the design scope of PN resin and its curing system, and laid the foundation for the subsequent mechanism research and application research.

2. Experimental

2.1. Materials

4-Nitrophthalonitrile was purchased from Jiangsu Taixing Shengming Fine Chemical Co. Ltd. 4,4-ethylenebisphenol was purchased from Shanghai Titan Technology Co. Ltd. Dimethyl sulfoxide (DMSO), N, *N*dimethylformamide (DMF), potassium carbonate, bisphenol A, bisphenol F, acetonitrile and methanol were purchased from Chengdu Kelong Chemical Reagent Co. Ltd. For direct use after purchase. All the materials were used without further purification.

2.2. Synthesis of monomer (BPAh, BPFh, BPEh)

The synthesis of bisphenol A phthalonitrile monomer (BPAh) is shown in Scheme 1. Firstly, 4-nitrophthalonitrile (9.12 g, 0.053 mol), bisphenol A (5.01 g, 0.022 mol) and 35 mL of dimethyl sulfoxide were added to a 50 mL three-necked bottle in sequence under nitrogen condition. Then, stirred 4-nitrophthalonitrile and bisphenol A at room temperature until completely dissolved. Subsequently, the grounded potassium carbonate powder (4.32 g, 0.032 mol) was added to the solution. Reaction carried out at 30 °C for 12 h. At the end of reaction, deionized water was empolyed to wash solution until the PH of the filtrate became netural. Finally, the crude product was stirred with 80 mL of methanol, washed and filtered, and the filter cake was dried in a rotary evaporator at 70 °C for 4 h to obtain a yellow product BPAh (9.43 g, yield 89.2 wt%).

¹H NMR (400 MHz, DMSO- d_6): 8.14–8.07 (d, 2H, Ar–H), 7.82–7.78 (d, 2H, Ar–H), 7.42–7.30 (dd, 6H, Ar–H), 7.17–7.09 (d, 4H, Ar–H), 1.76–1.62 (s, 6H, aliphatic-CH). FTIR (KBr, cm⁻¹), 2970 (-CH₃), 2231 (-C=N), 1502 (benzene), 1281 (Ar-O-Ar).

The synthesis of bisphenol F phthalonitrile monomer (BPFh) is shown in Scheme 1. Firstly, 4-nitrophthalonitrile (6.92 g, 0.040 mol), bisphenol F (3.01 g, 0.015 mol) and 20 mL of dimethyl sulfoxide were added to a 50 mL three-necked flask under nitrogen condition. Then, stirred 4-nitrophthalonitrile and bisphenol F at room temperature until completely dissolved. Subsequently, the grounded potassium carbonate powder (2.59 g, 0.019 mol) was added to the solution. Reaction carried out at 30 °C for 12 h. At the end of reaction, deionized water was empolyed to wash solution until the PH of the filtrate became netural. Finally, the crude product was purified by recrystallization from acetonitrile, filtered, and the filter cake was dried in a rotary evaporator at 70 °C for 4 h to obtain a brownish yellow product BPFh (5.23 g, yield 77.1 wt%).

¹H NMR (400 MHz, CDCl3, 8): 7.75–7.70 (d, 1H, -C6H3), 7.32–7.30 (s, 2H, -C6H3), 7.32–7.25 (t, 2H, Ar–H), 7.02–7.06 (d, 2H, -C6H4), 4.06 (s, 1H, –CH2-).

FTIR (KBr, cm⁻¹) of BPFh: 3080 and 3040 (aromatic-CH), 2930 (aliphatic-CH), 2232 (C \equiv N), 1089 and 1018 (Ar-O-Ar).



Fig. 1. TGA curves of BPAh, BPEh and BPFh monomers.

| Table 1 | |
|--|--|
| Thermal properties of compounds BPFh, BPEh and BPAh. | |

| Sample T _{2%} | (°C) T _{5%} (° | C) Char yie | eld (%) at 800 °C T_m (°C) |
|------------------------|-------------------------|-------------|------------------------------|
| BPAh 353 | .2 377.3 | 3.8 | 197.7 |
| BPEh 355 | .2 384.8 | 35.3 | 203 |
| BPFh 339 | .0 362.8 | 44.3 | 197.5 |

The synthesis of bisphenol E phthalonitrile monomer (BPEh) is shown in Scheme 1. Firstly, 4,4-ethylenebisphenol (7.006 g, 0.033 mol) and 60 mL of DMF were added to a 250 mL three-necked bottle. The grounded potassium carbonate powder (9.12 g, 0.066 mol) was added and stirred at room temperature under nitrogen condition, then, added toluene and stirred. When the temperature was raised to 145 °C, toluene begins to reflux obviously. After the water in the system is removed, continue to reflux for 2 h and then evaporate the toluene to cool to 70 °C, the 4-nitrophthalonitrile (14.10 g, 0.082 mol) was added to the solution. Reaction carried out at 70 °C for 12 h. At the end of reaction, deionized



Fig. 2. DSC curves of BPAh, BPEh and BPFh monomers.



Fig. 3. (a) 310 °C isothermal rheological curve of BPAh, BPEh and BPFh monomers; (b) 270 °C isothermal rheological curve of BPEh, BPEh monomers.



Fig. 4. (I) TGA curves of BPEh monomer in nitrogen; (II) DSC secondary scan curves of BPEh; (III) TGA curves of BPFh monomer in nitrogen; (IV) DSC secondary scan curves of BPFh; a:270 °C/7 h,310 °C/5 h; b:270 °C/7 h,310 °C/5 h; a:270 °C/7 h,310 °C/5 h; b:270 °C/7 h,310 °C/5 h; b:270 °C/7 h; b:

water was empolyed to wash solution until the PH of the filtrate became netural. The product obtained twice was dried in a vacuum oven at 100 $^{\circ}$ C for 5 h to obtain 11.33 g of the product BPEh (yield 74.28 wt%).

¹H NMR (400 MHz, DMSO-*d*₆): 8.15–8.08 (d, 2H, Ar–H), 7.81–7.76 (d, 2H, Ar–H), 7.46–7.39 (d, 4H, Ar–H), 7.38–7.32 (dd, 2H, Ar–H), 7.18–7.10 (d, 4H, Ar–H), 4.32–4.24 (q, H, aliphatic-CH), 1.67–1.58 (d, 3H, aliphatic-CH3).

FTIR (KBr, cm^{-1}): 3080 and 3040 (aromatic-CH), 2885 (aliphatic-CH), 2940 (-CH3), 2230 (C \equiv N), 1089 and 1014 (Ar-O-Ar).

2.3. Preparation of resin

According to the TGA and rheological curves of BPEh and BPFh monomers and related literature [17,23], the curing procedures of BPEh

Table 2

TGA of BPEh, BPFh resin compared with conventional PN resin.

| Sample | T ₅ (°C) | Char yield (%) at 800 $^\circ\text{C}$ | Reference |
|----------|---------------------|--|-----------|
| BPEh(a) | 446 | 73.3 | this work |
| BPEh(b) | 474 | 71.9 | this work |
| BPEh(c) | 495 | 73.1 | this work |
| BPFh(a) | 475 | 73.8 | this work |
| BPFh(b) | 485 | 72.5 | this work |
| BPFh(c) | 491 | 71.9 | this work |
| 3BOCN/MI | 400 | 63 | [43] |
| DPBA-Ph | 466.8 | 73.4 | [45] |
| BPH/APN | 537 | 70 | [44] |

and BPFh are determined as:

| a: | 270 | °C/7 | h, | 310 | °C/5 | h; | | | | | | |
|----|-----|------|----|-----|------|----|-----|------|----|-----|------|----|
| b: | 270 | °C/7 | h, | 310 | °C/5 | h, | 330 | °C/3 | h; | | | |
| c: | 270 | °C/7 | h, | 310 | °C/5 | h, | 330 | °C/3 | h, | 350 | °C/3 | h; |

Put a certain amount of prepared BPEh and BPFh powder monomers into an aluminum grinding tool, and perform reaction curing in a nitrogen atmosphere in a muffle furnace in three procedures of a, b and c respectively.

2.4. Characterization

 $^{1}\mathrm{H}$ NMR (400 MHz) was measured by a Bruker Avance-400 nuclear magnetic spectrometer, with DMSO- d_{6} or CDCl3 solvent and tetramethylsilane (TMS) as internal standard.

Thermal gravimetric analysis (TGA) was tested by a TA Q500 thermogravimetric analyzer at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere (60 mL min⁻¹). and the experimental temperature range from 40 to 800 °C. The quality for monomer testing is around 5.0 mg, and the quality for resin testing is around 6.0 mg. All the testing samples were grinded to powder before loaded in the TGA chamber.

Differential scanning calorimetry (DSC) is performed on TA Q200at a heating rate of 10 $^{\circ}$ C min⁻¹ under nitrogen atmosphere (60 mL min⁻¹).

Rheological experiments were conducted on a TA instruments AR-2000ex rheometer in conjunction with an environmental testing chamber for temperature control. The measurements were made using 25 mm diameter parallel plates at a constant strain value of 2.5×10^{-4} and a frequency of 1 Hz. The temperature of isothermal time scan is 270 °C and 310 °C respectively, and the experimental atmosphere is air atmosphere.

Fourier transform infrared (FT-IR) was recorded on a Nicolet FT-IR-380 Fourier transform infrared spectrometer using KBr pellets from 4000 to 400 cm⁻¹ at a resolution of 4 cm⁻¹ with 16 scans. *In situ IR* was measured with the identical method on the same spectrometer with a



Fig. 5. (a) DMA curves of cured BPEh; (b) DMA curves of cured BPFh.



Fig. 6. (a) FTIR spectra of BPEh monomer and BPEh polymer; (b) FTIR spectra of BPFh monomer and BPFh polymer.



Fig. 7. The UV–Vis spectra of BPEh and BPFh polymer.

microheater. We use the area of the chemical stable benzene ring structure (1530 $\rm cm^{-1}$ to 1450 $\rm cm^{-1}$) as a benchmark to calculate the conversion of cyano groups.

Solid-state UV–Vis reflectance spectra was analyzed with a UV–Vis spectrophotometer (UV-3600, Shimadzu, Japan) from 1000 to 200 nm.

Dynamic mechanical analysis (DMA) was recorded on a TA instrument DMA Q800 at a heating rate of 5 °C min⁻¹ from 50 to 500 °C with a load frequency of 1 Hz in nitrogen atmosphere. The curing procedures of blend sample is: a: 270 °C/7 h, 310 °C/5 h; b: 270 °C/7 h, 310 °C/5 h, 330 °C/3 h; c: 270 °C/7 h, 310 °C/5 h, 330 °C/3 h; 350 °C/3 h; The size of the blends is polished to: 33.0 mm \times 14.0 mm \times 3.5 mm.

MALDI-TOF MS was performed on a Germany Bruker autoflex III equipped with an N₂ laser (337 nm). BPEh and BPFh samples were made under the conditions of 270 °C/2 h and 270 °C/0.5 h respectively, samples were partially dissolved in THF, and then mixed with the matrix. Spectra were obtained in the linear positive mode. Except for a few cases, methyl-cyano-4-hydroxycinnamic acid (CHCA) was used as the matrix, there are no additives in most cases.

Molecular Electrostatic Potential (MEP) is simulated by molecular simulation technology for free radicals derived from BPEh and BPFh monomer (R-BPEh and R-BPFh). All simulations were performed by Materials Studio 8.0 software. All the Geometry Optimization of monomer by Dmol³ (Quality: fine, Functional: GGA-PBE, basis set: DNP, Basis file: 4.4, Properties: Electron density, Electrostatics).

3. Results and discussion

3.1. Study on thermal performance and curing behavior of monomer

As shown in Fig. 1, TGA was carried out to study the thermal properties of three monomers introduced in this paper. The temperature at 2% weight loss ($T_{2\%}$), the temperature at 5% weight loss ($T_{5\%}$) and the char yield at 800 °C are listed in Table 1. It can be seen from Fig. 1 that the thermal stability of the compounds BPFh, BPEh and BPAh in a nitrogen atmosphere showed a clear difference. The temperature of 2% and 5% of BPFh weight loss is 339 °C and 362.8 °C, while the 2% and 5% weight loss Temperature of BPAh is 353.2 °C and 377.3 °C, BPEh 2% and

5%weight loss temperature 355.2 °C and 384.8 °C, which is significantly higher than that of compound BPFh. The reason may be that earlier decomposition of BPFh than BPAh and BPEh. However, as the temperature continues to rise, when the experimental temperature goes up to 800 °C, the char yield of the BPFh and BPEh compounds at 800 °C reaches 44.3% and 35.3%, respectively, and the control group BPAh almost completely decomposes. And only less than 4% of the quality remains. This indicates that the BPFh and BPEh samples may have undergone curing reaction during the temperature increase. According to previous reports [17], BPAh does not have a self-promoting effect and mainly used for control group in this study.

DSC was used to study the thermal behavior of the BPFh, BPEh and BPAh samples during heating process, as shown in Fig. 2. It can be seen that the BPFh, BPEh and BPAh samples all have obvious endothermic peaks around 200 °C, which may be caused by the melt flow of the sample around this temperature, and their melting points are 197.5 °C, 203.0 °C and 197.7 °C respectively, which indicated BPAh compounds have obvious advantages for the comparative study of BPFh and BPEh compounds. However, it's easy to noticed that the BPFh, BPEh and BPAh samples showed only one endothermic peak in the measured temperature range, but no obvious exothermic peak. Combined with the results of TGA and the rheological results below, it is speculated that for the phthalonitrile compound derived from bisphenol A, this may be due to the fact that the sample cannot accelerate the polymerization of the monomer by self-curing during the heating process, so the location of its exothermic peak cannot be detected. For phthalonitrile compounds derived from bisphenol F and E, this may be due to the slow curing rate of the sample and the mild reaction in the temperature range tested, The curing exothermic peak of the BPFh and BPEh samples is higher than the temperature range that can be tested by DSC, so the location of its exothermic peak is not detected.

The molecular structure of BPEh and BPFh does not contain the traditional active hydrogen structure that can accelerate PN curing. Meanwhile, combined with the previous research of our research group on alicyclic imide compounds/phthalic acid resin [23] and the related Lignin-based PN research [17], we speculated that the reactive "active hydrogen" generated by the alkyl group in the BPEh and BPFh molecules



Fig. 8. In situ FTIR of BPEh monomer heated from 200 to 310 °C. (a): the stretching vibration of nitrile (-CN) (b): the stretching vibration of -C=N in polytriazine.; (c): the stretching vibration of N-H isoindoline; (d): the stretching vibration of -CH-.

at high temperature accelerates the polymerization of the nitrile group. In order to further analyze the possible alkyl (methyne or methylene) reaction sites, we studied the isothermal rheological behavior of BPEh and BPFh monomers. As shown in Fig. 3 (a), under the isothermal conditions of BPEh and BPFh at 310 °C, the viscosity of BPFh increases rapidly at 30 min, and the viscosity of BPEh increases rapidly at 85 min. Combined with the char yield of BPAh in TGA, BPEh and BPFh are further verified a rapid curing reaction occurred at 310 °C. In addition, the isothermal time scan at 310 °C that BPFh has a faster curing effect than BPEh. At the same time, in order to further understand the difference between the curing effects of BPEh and BPFh, We performed a 270 °C isothermal time scan of BPEh and BPFh, as shown in Fig. 3 (b). the viscosity of BPFh increased rapidly at about 3 h, and the viscosity of BPFh increases significantly at 7 h. Two sets of isothermal rheological data indicate that the curing efficiency of BPFh is higher than that of BPEh.

3.2. Thermal properties of resin

As shown in Fig. 4, TGA shows that the char yield of the two monomers after curing BPEh and BPFh is significantly higher than that of the monomer. The carbon residue under different curing procedures is greater than 70%. Compared with monomers, as curing time increases, the $T_{5\%}$ of the two resins also increases. Under the curing conditions of procedure c, the $T_{5\%}$ of the two resins is close to 500 °C, indicating that as the temperature increases, the cyanide conversion rate of the base is increased, and the degree of crosslinking of the resin is enhanced, so that the resin shows good base heat and thermal stability. In the DSC secondary scanning curves of BPEh and BPFh resins, there is no obvious exothermic and endothermic peaks, it is speculated that the monomers may basically react completely at this time. It is worth noting that there is no obvious turning point in the DSC curve, which implies that no obvious Tg is observed in the range of 350 °C, which proved that the resin has good basic thermal properties. Table 2 lists the basic thermal performance data of BPEh and BPFh resins under different curing procedures and PN resins promoted by traditional curing agents. It can be seen that compared with 3BOCN/MI system, BPEh and BPFh resins have different curing procedures the thermal performance below shows certain advantages. Compared with DPBA-Ph and APN/BPH systems, BPEh and BPFh resins also have comparable thermal properties. This shows indirectly that BPEh and BPFh have undergone polymerization.

Dynamic mechanical analysis (DMA) was employed to analyze thermo-mechanical properties of BPEh and BPFh resins. As shown in Fig. 5, It can be observed from tan δ that both resins have two secondary transitions with a temperature range from 100 °C to 300 °C. The maximum testing temperature of DMA was set to 500 °C because of the $T_{5\%}$ of the resin. Meanwhile, the tan δ of the two resins does not form a complete peak at around 500 °C. Thus, according to the peak of tan δ , it can be rationally estimated that the Tg of the two resins is more than 500 °C. In addition, the storage modulus of the resin did not decrease in the order of magnitude, suggesting again that the resin has qualified thermo-mechanical properties.



Fig. 9. In situ FTIR of BPFh monomer heated from 200 to 310 °C. (a): the stretching vibration of nitrile (-CN) (b): the stretching vibration of -C=N in polytriazine.; (c): the stretching vibration of N-H isoindoline; (d): the stretching vibration of $-CH_2$ -.

3.3. Discussion of curing mechanism

Compared with calorimetry and rheology, infrared could show the reaction of functional groups. We analyzed the structural evolution of BPEh and BPFh before and after curing by off-situ FTIR. As shown in Fig. 6, there is a strong nitrile peak (2232 cm^{-1} ,2230 cm^{-1}) for both monomers; compared to the monomer, the nitrile peak in the cured product has a significant decrease. Relative reports pointed out that [29-31], isoindoline also has characteristic diffraction peaks at 1720 cm^{-1} , 1660 cm^{-1} , and from the results in Fig. 6, it can be seen that BPEh and BPFh resins are at 1720 cm^{-1} The 1660 cm^{-1} have the diffraction peak attributed to isoindoline, which further indicates that the BPEh and BPFh samples may generate isoindoline structure during the curing reaction. At the same time, it is generally believed that if the phthalonitrile group reacts to form a triazine ring during the curing reaction, there will be more obvious peaks at 1520 cm^{-1} and 1360 cm^{-1} in the infrared spectrum [10,32], and it can be seen from Fig. 6 that under the experimental conditions, a clear sharp peak is indeed observed at the position assigned to the characteristic peak of the triazine ring, so it is speculated that BPEh and BPFh samples may generate three during the curing reaction. Azine ring structure. Interestingly, this is different from our previous studies on the acceleration of the polymerization of phthalonitrile resins with imide cycloaliphatic structural elements [23] and the PN resin (BPN) derived from creosol [17]. The characteristic peak of the phthalocyanine ring (1010 cm⁻¹) and the characteristic peak position of the ether bond in BPEh and BPFh (1017 cm^{-1} [33]) have a certain overlap, it is difficult to determine the formation of phthalocyanine by

the FTIR. UV–Vis is a classic method to confirm the phthalocyanine ring, as shown in Fig. 7, the peak of phthalocyanine rings at around 603 nm [23,47,48] were observed for the cured resins. It is worth noting that the methyne group (2878 cm⁻¹) in the BPEh monomer structure [27] and the methylene group (2915 cm⁻¹) in the BPFh monomer [37] could be observed in Fig. 6. There is a significant decrease before and after curing reaction, which suggests that methine and methylene may participate in the curing reaction of the nitrile group, and even be the key factor to initiate the polymerization of the nitrile group.

Because the off-situ infrared sample preparation and other processes have a great influence on the test results, and in-situ infrared can eliminate the interference of these aspects on the test results [35,36], so further observation of BPEh and BPFh samples through in-situ infrared changes in groups during the heating process. Fig. 8 (a) and 9 (a) are the in-situ infrared spectra of the BPEh and BPFh samples at 2250-2200 cm⁻¹, it's easy to find that as the temperature increases, the characteristic diffraction peak (2228 cm⁻¹) belongs to the nitrile is obviously weakened, indicating that the nitrile group participated in the curing process of the BPEh and BPFh. In order to further verify whether the triazine ring was formed during the reaction, Fig. 8 (b) and 9 (b) gave the in-situ infrared spectra of the BPEh and BPFh samples at 1550-1300 cm⁻¹ respectively. As the temperature rises, new absorption peaks gradually appear at the positions of the characteristic diffraction peaks of the triazine ring $(1520 \text{ cm}^{-1} \text{ and } 1360 \text{ cm}^{-1})$, which is consistent with the results of off-situ infrared, further verifying the triazine Ring formation. It has been documented that [29-31], the formation of isoindoline also shows significant absorption peaks near 1720 cm⁻¹ and



Scheme 2. The proposed reaction mechanism of BPEh and BPFh.

1660 cm⁻¹. Fig. 8 (c) and 9 (c) are the in-situ infrared spectra of the BPEh and BPFh samples at 2000-1300 cm⁻¹ respectively. Obviously, as the temperature increases, a new absorption peaks of BPEh samples appeared at 1740 cm⁻¹ and at 1660 cm⁻¹, new absorption peaks of BPFh samples appeared at 1720 cm⁻¹ and 1660 cm⁻¹, indicating that the BPEh and BPFh samples formed an isoindolin structure during the curing process.

In order to further study the structure of the polymerization product, BPEh and BPFh samples were performed on MALDI-TOF MS. The test results of BPEh are shown in Figure S1 and Table S1, and that of BPFh are shown in Figure S2 and Table S2. It could be observed that two precured resins show typical oligomer characteristics, the m/z at 1887.12 and 1810.95 correspond to the tetramers of BPEh and BPFh respectively

(calculated values are: 1887.56 and 1809.52), this tetramer is probably related to the formation of phthalocyanine ring. In addition, the dimer could be attributed to the copolymer/homopolymer isoindoline structure, and the trimer may be related to the triazine ring or the polyisoindoline.

In order to further investigate the basis for the two cured model compounds to be cured, we analyzed the possible structures BPEh (–CH–, 2878 cm⁻¹) and BPFh (-CH2-, 2915 cm⁻¹) in situ infrared. As shown in Fig. 8 (d) and Fig. 9 (d), the methyne absorption peak of the BPEh sample and the methylene absorption peak of the BPFh sample, respectively, it can be seen that as the temperature increases, the methyne absorption peak The absorption peak of (2878 cm⁻¹) methylene group (2915 cm⁻¹) was significantly weakened, suggesting that



Fig. 10. Cyano conversion as a function of times at 250 °C and 270 °C.

methyne group and methylene group are likely to participate in the curing process of nitrile group. This is also consistent with offline infrared.

Based on the experimental results above, we preliminarily speculate that the "active hydrogen" generated by the methylene units in the BPFh and BPEh under high temperature conditions promotes the polymerization reaction of the nitrile group, that is, the mechanism of "methylene/methyne activated phthalonitrile thermal polymerization". As shown in Scheme 2. Because the methyne structure can homogenize the covalent bond under high temperature conditions, forming a relatively stable tertiary carbon radical and a highly reactive hydrogen radical, while the methylene structure under high temperature conditions, relative to methyl groups are more prone to homogenous cleavage of covalent bonds, forming a relatively stable carbon radical and a highly reactive hydrogen radical [34]. Among them, hydrogen radicals or tertiary carbon radicals may promote the polymerization of phthalonitrile. This phenomenon of free radicals generated by the homolysis of covalent bonds has been reported in the research of lignin and polymers containing tertiary carbon structures (such as polystyrene, polyacrylonitrile, polyvinyl chloride, etc.) [38-40]. In summary, we speculate that this phenomenon of accelerating the polymerization of phthalonitrile groups based on the structure of diphenylmethane may achieve the curing reaction of the monomer through the free radical pathway.

2, 2-Diphenyl-1-picryl hydrazine (DPPH), a well-known high temperature free radical scavenger [23,46], was selected to further understand the role of free radicals involving in the polymerization of phthalonitrile unit in our cases. The cyano conversions of BPEh and

BPFh were determined from data of in-situ FTIR, and compared with these of resin system DPPH-containing resin system (20 wt%), as shown in Fig. 10. We use the area of the chemical stable benzene ring structure (1530 cm⁻¹ to 1450 cm⁻¹) as a benchmark to calculate the conversion of cyano groups. The conversion of cyano groups of the DPPH-containing resin system is much lower at initial stage of the duration both at 250 and 270 °C compared with these of BPEh and BPFh. The results indicated that there is a certain inhibitory effect. Unexpectedly, the conversion of cyano groups gradually increased for an extended period of time, which probably indicated that the DPPH also played an accelerated role in the later isothermal stage. It is worth noting that the cyano conversion of the BPFh-DPPH blending has two different acceleration stages for 270 °C duration, which could be related to the presence of two hydrogen protons in BPFh. The reaction mechanism of cyano polymerization accelerated by DPPH could be complicated, but the results added considerable evidences that the curing reaction of BPEh and BPFh involved a free radical process.

In addition, the Molecular Electrostatic Potential (MEP) is simulated by molecular simulation technology for free radicals derived from BPEh and BPFh monomer (R-BPEh and R-BPFh), as shown in Fig. 11. For R-BPEh and R-BPFh, the electrons are mainly distributed near the cyano group. Except for the hydrogen atom, the electron distribution near the aliphatic carbon after radicalization is relatively low. Therefore, it is reasonable to consider that the aliphatic carbon is a potential reaction site to cyano group. Although this could not be a direct evidence of its radical polymerization, it can provide more understanding of the reaction site.



Fig. 11. The electrostatic potentials mapping of free radicals derived from R-BPEh and R-BPFh.

4. Conclusion

In this paper, a bis-phthalonitrile-terminated compound bisphenol A, F, E with a symmetric molecular structure was synthesized. The rheological research results show that: BPEh and BPFh could undergo curing reaction, the promotion effect of methylene is stronger than methyne, and methyl has no obvious promotion effect. DMA shows that the Tg of the cured resins is more than 500 °C and the storage modulus of the resin did not decrease in the order of magnitude, indicating that the resin has qualified thermo-mechanical properties. According to FTIR and UV-Vis, isoindoline and triazine ring structures exist in the cured products. During the curing reaction, infrared showed that the content of methyne and methylene in BPEh and BPFh decreased, which further implied that the methyne and methylene participated in the curing reaction of the nitrile group. The effect of DPPH on the reaction rate, added considerable evidences that the curing reaction of BPEh and BPFh involved a free radical process. The research further expands the design scope of phthalonitrile resin curing system. The new resin systems based on BPEh and BPFh also lay a foundation for the subsequent mechanism research and application research. In the future, theoretical simulation and experimental science will be combined to explore the reaction mechanism from the perspective of thermodynamics and kinetics.

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.

Acknowledgments

The authors thank the Analytical & Testing Center, Sichuan University, P. R. China for supplying the Materials Studio 8.0 program.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2020.123001.

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