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ORIGINAL PAPER

Synthesis, characterization and self-promoted cure behaviors of a new phthalonitrile derivative 4-(4-(3, 5-diaminobenzoyl) phenoxy) phthalonitrile

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Abstract A new amino-containing phthalonitrile derivative 4-(4-(3, 5-diaminobenzoyl) phenoxy) phthalonitrile (DAPN) was successfully synthesized. Its structure was identified by FT-IR and ^{1}H-NMR. DAPN can be thermally polymerized by duration at 230 °C for various times under a nitrogen atmosphere, even in the absence of curing additives. The thermal properties of the cured products were characterized by TGA and DSC. The 5 and 10% weight loss temperatures ranged from 442 to 446 and 504 to 505 °C, respectively. Char yields (800 °C) were in the range of 72.7–72.9%. DSC data showed that the melting peak of the cured products disappeared due to their thermal polymerization. The insolubility in concentrated sulfuric acid and FT-IR of the cured products indicated the formation of cross-linked networks.

Keywords Amino-containing phthalonitrile derivate ·
Self-promoted curebehavior · Thermal properties · Cross-linking network

Introduction

Phthalonitrile resins were first synthesized by Keller and co-workers as a family of high-temperature resins. These resins were derived from heating the phthalonitrile monomers in the presence of a small amount of curing additives for extended periods of time at elevated temperatures. Phthalonitrile resins demonstrate potential as high-temperature polymers for use in a wide variety of applications such as

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composite matrices [1], adhesives [2], and electronic conductors [3]. A variety of bisphthalonitrile monomers containing aromatic ether [3–5], thioether [4], imide [6, 7], and sulfone linkages [8, 9] between the terminal phthalonitrile units have been synthesized at Naval Research Laboratory. Polymerization of the neat phthalonitrile monomer is extremely sluggish, requiring extended heat treatment at elevated temperature before gelation occurs [10]. Additives used to promote the cure of the phthalonitrile resins include organic amines [10], phenols [11], strong organic acids [12], strong organic acid/amine salts [13], metallic salts, and metals [14]. Currently, study of the curing agents was mainly focused on aromatic diamines by adding aromatic diamines into the melting biphthalonitrile monomer to initialize a fast cuing reaction [15, 16]. The phthalonitrile prepolymer melt viscosity is a function of both the diamine concentration and the melt temperature [1]. For a given amine concentration, higher melt temperatures result in an initial lower melt viscosity and facilitate the composite processing by resin transfer molding. However, volatilization of the diamine has been observed at an elevated temperature when curing in an open mold, resulting in the slowdown of the cure reactions.

In our laboratory, the current research was focused on design and synthesis of new phthalonitrile derivatives containing amino or hydroxy. The previous research revealed that those phthalonitrile derivatives showed self-promoted cure behaviors even in the absence of any curing additive which was necessary for the conventional biphthalonitrile/curing additive systems [17]. In this paper, a new phthalonitrile derivative containing amino groups (DAPN) was successfully synthesized. The chemical structure of this derivative was characterized by Fourier transform infrared spectrometer (FT-IR) and ^{1}H nuclear magnetic resonance (^{1}H-NMR). Its self-promoted cure behaviors were studied by heat treatment at a specified temperature for various times, and the cure reactions were monitored by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and FT-IR techniques in order to better understand its cure behaviors.

Experimental

Materials

4-Nitrophthalonitrile (Aldrich Chemical Co.); 3,5-dinitrobenzoyl chloride (Shanghai Shunqiang, Chemical Co. People's Republic of China); Anhydrous aluminum chloride (Meixing Chemical Co. People's Republic of China); Ethoxybenzene (Shanghai Pharma Co. People's Republic of China); *N*,*N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), *N*-methylpyrrolidone (NMP), tetrahydrofuran (THF), 1,2-dichloroethane (Bodi, Chemical Co. Tianjin, People's Republic of China). DMF was purified under reduced pressure over CaH_2. Other chemicals were used as received unless otherwise stated.

Measurement

^{1}H-NMR spectra were measured on a Bruker Advance-400 NMR spectrometer with DMSO-d_6 as the solvent and tetramethylsilane as the internal standard. IR spectra were recorded with a Nicolet FTIR-380 Fourier transform infrared spectrometer by the KBr salt slice method. TGA was carried out with a TA instrument Q500 at a heating rate of 10 °C min^{-1} under nitrogen. DSC was carried out with a TA instrument Q200 at different heating rates under nitrogen. Melting points of compounds at different synthesis stages were determined on a X4 melting point measurement microscope (The Third Optical Instrument Factory, Beijing, People's Republic of China).

(3, 5-Dinitrophenyl)(4-ethoxyphenyl)methanone (compound 1)

To a 250 ml three-neck flask were added 3, 5-dinitrobenzoyl chloride (30 g, 0.13 mol), ethoxybenzene (40 ml), and anhydrous aluminum chloride (25.8 g, 0.19 mol). The mixture was stirred at room temperature for 10 h. After the mixture was poured into an ice water solution of hydrochloric acid (20%), the organic layer was collected and the aqueous layer was extracted thrice with 200 ml chloroform. After washed with 1% NaOH and water, the combine extract was dried over by anhydrous sodium sulfate. A solid precipitated from the residual ethoxybenzene after the chloroform of the extract was evaporated. The solid was collected by filtrating and washed with methanol to give 7.8 g of a golden power. Yield: 19%. Mp = 136–138 °C. ^{1}H-NMR (DMSO-d_6, ppm, δ): 9.01–9.02 (m, 1H, Ar–H), 8.74–8.75 (d, 2H, Ar–H), 7.84–7.86 (d, 2H, Ar–H), 7.11–7.13 (d, 2H, Ar–H), 4.15–4.20 (dd, 3H, CH_3), 1.35–1.39 (m, 2H, CH_2). FT-IR (KBr, cm^{-1}): 3,107 (CH_3), 2,942 (CH_2), 1,660 (C=O), 1,547, 1,340 (NO_2), 1,310, 1,036 (C–O–C).

(3, 5-Dinitrophenyl) (4-hydroxyphenyl) methanone (compound 2)

To a 250 ml three-neck flask were added compound 1 (9.82 g, 0.031 mol), 1, 2-dichloroethane (140 ml), and anhydrous aluminum chloride (33.1 g, 0.25 mol). The mixture was stirred at room temperature for 3 h. The reaction was monitored by thin layer chromatography (TLC). The resulting mixture was poured into ice water solution of hydrochloric acid (20%) to give a white suspension. After the organic solvent of the suspension was evaporated at 40 °C by rotary evaporator, a white solid precipitated from the water phase. The solid was collected by filtration, washed with a large amount of water and dried at 60 °C under reduced pressure for 24 h to give 7.15 g of compound 2. Yield: 80%. Mp: 208–210 °C. ^{1}H-NMR (DMSO-d_6, ppm, δ): 10.70 (s, 1H, OH), 9.00–9.01 (m, 1H, Ar–H), 7.76–7.78 (dd, 2H, Ar–H), 6.93–6.95 (dd, 2H, Ar–H), 6.93–6.95 (dd, 2H, Ar–H). FT-IR (KBr, cm^{-1}): 3,376 (OH), 3,097(C=C–O), 1,640 (C=O), 1,537, 1,344 (NO_2), 1,290 (C–O).

4-(4-(3, 5-Dinitrobenzoyl)phenoxy) phthalonitrile (compound 3)

To a 150 ml three-neck flask were added compound 2 (5 g, 0.017 mol), anhydrous potassium carbonate (2.63 g, 0.0019 mol), 4-nitrophthalonitrile (2.94 g, 0.017 mol) and dry DMF (42 ml). The mixture was stirred at 50 °C under nitrogen for 3 h. The reaction was monitored by TLC. The mixture was allowed to cool to room temperature and poured into 1,000 ml 1% solution of sodium hydroxide. The resulting solid was collected by filtration, washed with a large amount of water until the filtrate was neutral, and dried at 60 °C under reduced pressure for 24 h to give 5.6 g of compound 3. Yield: 78%. Mp: 180–181 °C. ^{1}H-NMR (DMSO-d_6, ppm, δ): 9.04–9.05 (m, 1H, Ar–H), 8.80–8.81 (d, 2H, Ar–H), 8.19–8.21 (d, 1H, Ar–H), 8.01–8.02 (d, 1H, Ar–H), 7.97–7.99 (dd, 2H, Ar–H), 7.62–7.65 (m, 1H, Ar–H), 7.36–7.39 (dd, 2H, Ar–H), FT-IR (KBr, cm^{-1}): 3,080 (C=C–O), 2,236 (CN), 1,662 (C=O), 1,545, 1,343 (NO_2), 1,281, 1,217 (C–O–C).

4-(4-(3, 5-Diaminobenzoyl) phenoxy) phthalonitrile (DAPN)

To a 250 ml three-neck flask were added compound 3(2 g, 0.0048 mol), stannous chloride (10.9 g, 0.048 mol), and anhydrous ethanol (100 ml). The mixture was stirred at 50 °C under nitrogen for 24 h. After the ethanol in mixture was evaporated at 30 °C, ethyl acetate (200 ml) was added, and the mixture was slowly dropped 5% water solution of potassium carbonate about 100 ml to cause a yellow precipitate. The precipitate was separated by filtration and washed twice with ethyl acetate. The combined ethyl acetate solution was washed twice with 100 ml saturated sodium chloride solution. After evaporation of solvent, 1.1 g crude product was obtained as a yellow powder in 85% yield. DAPN was further purified by column chromatography over silica gel with dichloride *n*-hexane/ethyl acetate (1:2) as the mobile phase. Mp: 215–216 °C. ^{1}H-NMR (DMSO-d_6, ppm, δ): 7.94–7.95 (d, 1H, Ar–H), 7.79–7.81 (m, 1H, Ar–H), 7.68–7.72 (d, 2H, Ar–H), 7.54–7.56 (m, 1H, Ar–H), 7.28–7.30 (m, 2H, Ar–H), 6.15 (d, 2H, Ar–H), 6.06–6.07 (m, 1H, Ar–H), 5.04 (s, 4H, NH_2). FT-IR (KBr, cm^{-1}): 3,458, 3,372, 3,229 (NH_2), 3,069 (C=C–C), 2,235 (CN), 1,643 (C=O), 1,247, 1,208 (C–O–C), 1,281 (C–N).

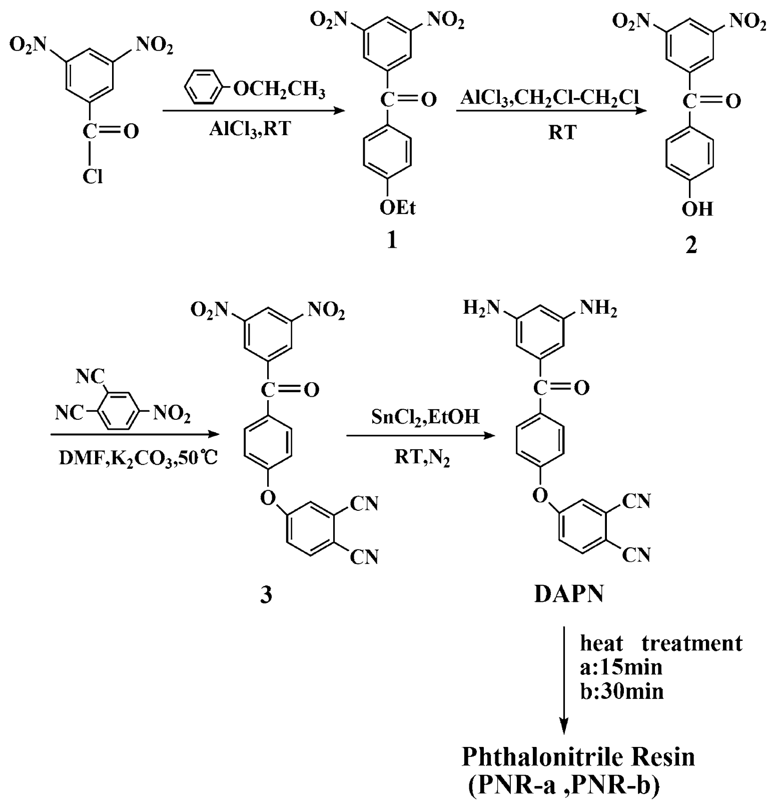
Preparation of phthalonitrile resins (PNR-a and PNR-b)

The heat treatment of DAPN was performed in a TGA chamber by heating powdered samples at 225 °C for 15 and 30 min under a flow of nitrogen, respectively, and the dark stiff resins (PNR-a and PNR-b) were obtained. Resins were characterized by FT-IR spectroscopy. Thermal properties of the resins were assessed by DSC and TGA.

Results and discussion

Synthesis of phthalonitrile

The synthesis of the new amino-containing phthalonitrile derivative DAPN has been performed by the procedure described in Scheme 1. Compound 1 was synthesized by a fridel-craft reaction from 3, 5-dinitrobenzoyl chloride and ethoxybenzene in the presence of anhydrous aluminum chloride and subsequently giving compound 2 by a dealkylation reaction. After a simple nucleophilic displacement, compound 3 was obtained. Compound 3 was treated by a selective moderate reductant $SnCl_2$, resulting in the final product DAPN. Column chromatography was used for further



Scheme 1 Synthesis of DAPN and the corresponding resins (PNR-a, PNR-b)

purification. FT-IR and ^{1}H-NMR techniques were used to identify the structure of DAPN. In the FT-IR spectrum of DAPN (Fig. 1) characteristic absorption bands for amino groups presented at 3,458, 3,372, and 3,229 cm^{-1}. The absorption bands at 2,235 and 1,643 cm^{-1} are typical for cyano (CN) stretching vibration and aromatic carbonyl (C=O) stretching vibration, respectively. In the ^{1}H-NMR of DAPN (Fig. 2), the singlet peak at 5.04 ppm was corresponding to primary amine (NH_2) protons, and other peaks at 6.06–7.95 ppm were assigned to aromatic protons. All the analytical data confirmed the expected chemical structure of DAPN.

Thermal behaviors

Self-promoted cure behaviors of DAPN were investigated by TGA. Figure 3 shows the TGA curves of DAPN and the cured products. The thermogram data were compiled in Table 1. After 15 min of heat treatment of DAPN, the cured product (PAN-a) displayed a remarkable improvement in thermal properties compared to DAPN. The 5, 10% weight loss temperature and char yield (800 °C) of PNR-a increased from 263 to 442, 457 to 504 °C, and 69 to 72.7% respectively, compared to that of DAPN. Further heating of DAPN for 30 min showed a less pronounced

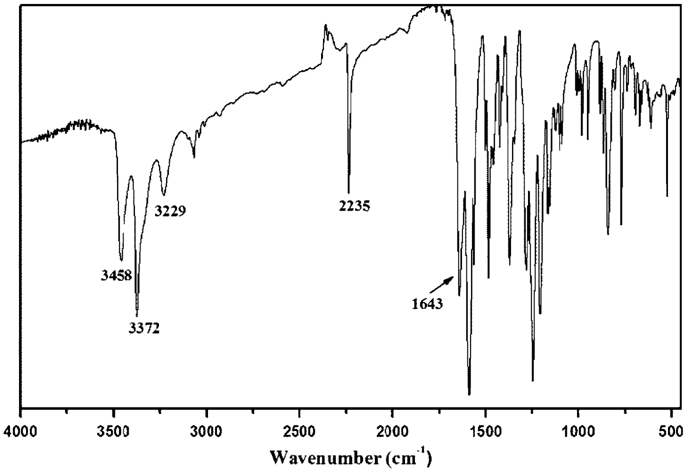


Fig. 1 FT-IR spectrum of DAPN

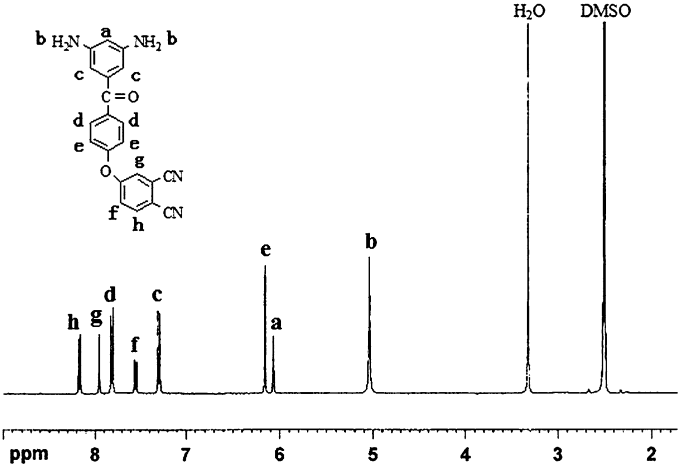


Fig. 2 ^{1}H-NMR spectrum of DAPN measured in DMSO-d_6

progression in the thermal properties. The TGA curve of PNR-b was almost identical with that of PNR-a. The rapid weight loss at around 500 °C for all samples is probably attributed to the thermal decomposition.

Cure reactions of DAPN were characterized by DSC at different heating rates by integration of the exothermic peak due to the amine–cyano or cyano–cyano reaction (Fig. 4). An exothermic peak was observed on the DSC curve using heating rate of 0.5 °C min^{-1}, corresponding to the amine–cyano or cyano–cyano reaction. However, only single endothermic peak was observed when the DSC analysis was performed at a heating rate of 3 or 10 °C min^{-1}. This is probably due to the

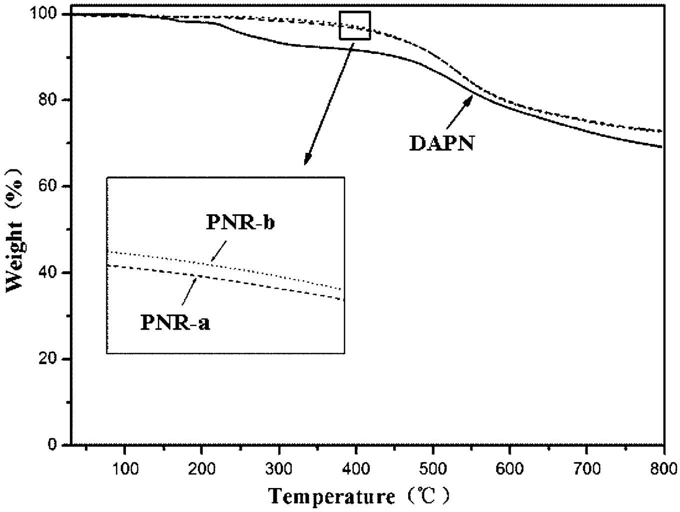


Fig. 3 TGA curves of DAPN and PNR-a, PNR-b

Table 1 The thermogram data of DAPN, PNR-a, PNR-b

Samples	T_{d5} (°C)	T_{d10} (°C)	Char yield (%)
DAPN	263	457	69.3
PNR-a	442	504	72.7
PNR-b	446	505	72.9

T_{d5}, Weight loss was 5%; T_{d10}, weight loss was 10%

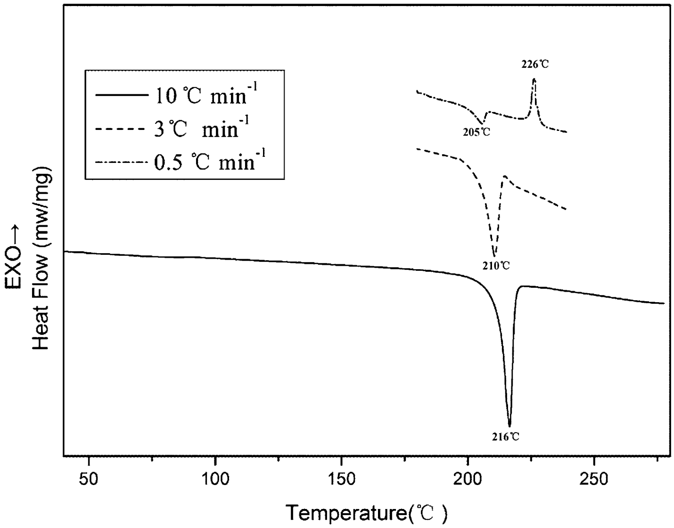


Fig. 4 DSC curves of DAPN at various heating rates

reaction rate being so rapid that the exotherm peak is overlapped by the melting endotherm transition.

DSC thermograms at the heating rate of 10 °C min^{-1} were obtained from samples cured in nitrogen at 230 °C for 15 and 30 min, respectively (Fig. 5). Both DSC curves showed very small but broad cure exotherm between 100 and 250 °C, indicating that the cure reactions of samples tend to be very slow. Meanwhile, no Tg transitions were observed on DSC curves.

Solubility

Solubility of DAPN and the corresponding resins were tested in various solvents (Table 2). DAPN showed excellent solubility in organic solvent such as ethanol, THF, DMSO, NMP, and DMF. Nevertheless, the cured products were insoluble in those organic solvent. Besides, they were almost insoluble in concentrated sulfuric acid (H_2SO_4), indicating that the cross-linked networks of the resins were fully developed.

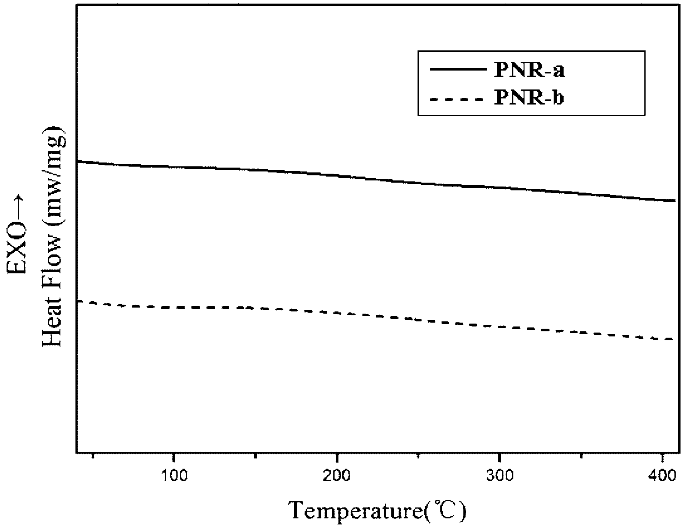


Fig. 5 DSC curves of PNR-a, PNR-b

Table 2 Solubility of DAPN and PNR-a, PNR-b

Samples	Acetone	Ethanol	THF	DMF	NMP	DMSO	H_2SO_4
DAPN	+	+	+	+	+	+	+
PNR-a	–	–	–	–	–	–	–
PNR-a	–	–	–	–	–	–	–

+, Soluble at room temperature; –, insoluble at room temperature

FT-IR analysis

FT-IR was also used to monitor the polymerization reaction (Fig. 6). Although the cured product spectra were broadened and reduced in intensity, the FT-IR spectra could provide more insight into the cure chemistry. Possible cross-linked structures of phthalonitrile resins such as triazine, isoindoline, dehydrophthalocyanine, and phthalocyanine have been reported previously [18–26], as shown in Fig. 7. The nitrile absorptions of PNR-a at around 2,230 cm^{-1} decreased in intensity. The peak assigned to nitrile absorptions of PNR-b showed less pronounced change in intensity compared to that of PNR-a; this phenomenon indicated that cure reactions tended to be very slow. A new shoulder peak at 1,620 cm^{-1} was observed and attributed to the characteristic absorptions of isoindoline [11]. Furthermore, a noticeable characteristic absorption of phthalocyanine ring at 1,010 cm^{-1} [18] was observed. These spectra observations indicate that multiple reaction mechanisms operate in the cure reactions of DAPN. In this study, no further attempts were made to cure the model compounds at elevated temperatures, but it is reasonably believed that it may contribute to the thermal properties of the cured products. This will be discussed in the future reports.

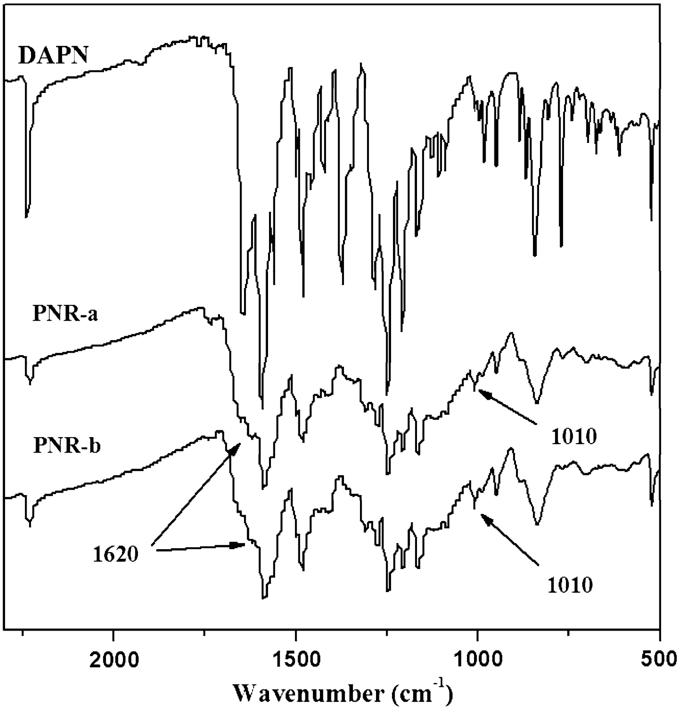
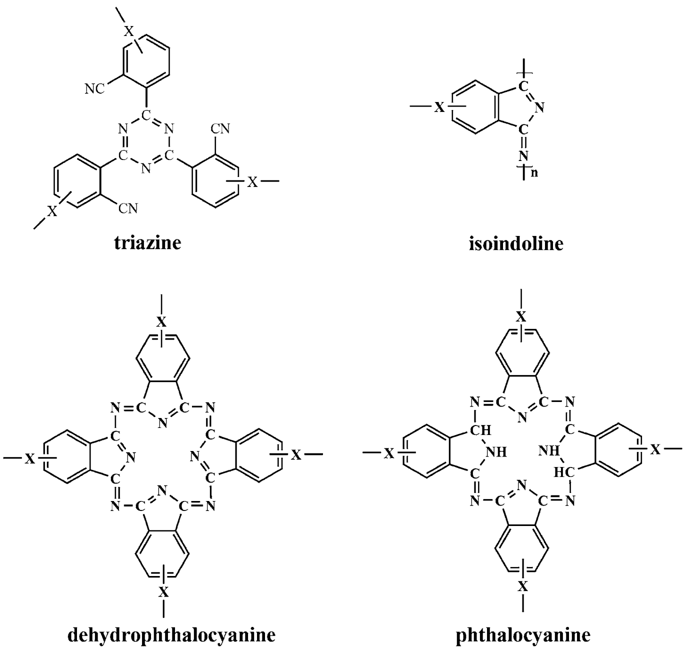


Fig. 6 FT-IR spectra of DAPN and after heat treatment at 230 °C



triazine

isoindoline

dehydrophthalocyanine

phthalocyanine

Fig. 7 Possiible cross-linked structures of phathalonitrile resins

Conclusions

The described synthetic scheme provides a method for the preparation of an amino-containing phthalonitrile derivative (DAPN) and the corresponding resins. The cured products displayed excellent thermal properties and solvent resistance. The thermal cure reactions of DAPN progressed at a slow rate after heat treatment for a period of time at 230 °C. After curing, the samples showed no Tg transition. Solubility test indicated the formation of cross-linked networks of the resins. Multiple reaction mechanisms are operational in the DAPN cure reactions, determined by FT-IR analysis. The further studies on cure mechanisms and cure kinetics of DAPN are proceeding in our laboratory.

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