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A Novel Addition Curable Novolac Bearing Phthalonitrile Groups: Synthesis, Characterization and Thermal Properties

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Summary

Novel phenolic novolac resins, bearing phthalonitrile groups anchored to benzene ring through phenyl azo linkage were realized by the coupling reaction between novolac and phthalonitrile diazonium salt. The diazo-coupling occurred to a maximun of about 61%. The apparent molecular weight, determined form GPC showed a downward drift with increase in degree of phthalonitrile substitution. Analysis using DSC technique indicated that the resin underwent curing in a temperature range form 290 to 320°C. The curing occurred via addition polymerization of phthalonitrile groups. The thermal stability and anaerobic char yield of the polymers increased proportion to the crosslinking. The probable cure mechanics were discussed.

Introduction

Phenolic resins have been extensively studied for nearly one hundred years and are still among the best commercially available heat-resistant resins because of their high performance and low cost [1]. With the development of aerospace industry, phenolic resins, as a kind of ablative material, have been specially studied for their excellent properties [2, 3]. In carbon and silica composites, the resin characteristics play a dominant role in deciding the ablative characteristics [4]. Phenolic resole resins combined with silica and carbon reinforcements are extensively used in thermo-structural applications in aerospace field [5]. Phenolic resins also enjoy an undisputed place among the matrices for the conventional method of making carbon-carbon composites [6, 7].

Although conventional phenolics are already considered as heat resistant polymers and are currently used for the above-mentioned applications, some of the properties of phenolics need further improvement for meeting the ever-increasing performance requirements. Addition-curable phenolic resins are effective alternative to condensation phenolics for overcoming the processing problem of latter and to confer high char-yielding property [4, 8]. The general approach for designing such polymers is to anchor addition curable functional groups onto novolac and induce the thermal curing during processing. It has been reported addition-curable phenolic resins functionalised with phenylmaleimide- [9], allylpphenol-phenylmaleimide- [10], propargyl- [11], and ethylphenyl azo [12] groups. Most of these systems imparted improved thermal characteristics and good mechanical performance to composites. Addition curable phenolic resins with improved thermal and pyrolysis characteristics are desirable for application in composites for thermo-structural applications. However, the thermally fragile crosslinking resulting in some cases of addition curable phenolic resins adversely affect the thermal stability of the resultant phenolic resins. This problem can be overcame through the choice of crosslinking functions, giving rise to thermally stable networks. Phthalonitrile-based resins exhibit good thermal and oxidative properties as a result of polymerization takes place through the cyano groups by an addition mechanism yielding heterocyclic crosslinked products. With this view toward designing addition curable phenolic resins without compromising their thermal characteristics, we engaged in designing phenolic resins bearing phthalonitrile groups. In this paper, we report the synthesis of novolac resins based on phthalonitrile groups with azo bone linkage. This paper discusses mainly their synthesis, characterization, cure and thermal properties.

Experimental

Materials

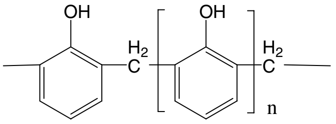
4-nitrophthalonitrile (merchandise products), phenol (Chengdu Kelong Chem. Co. PR China), formalin (37% solution Chengdu Kelong Chem. Co. PR China), zinc acetate (Chongqi Beibei Chem. Co. PR China), sulfuric acid (Chengdu Kelong Chem. Co. PR China), sodium nitrite (Tianjin Bodi Chem. Co. PR China), sodium hydroxide (Chengdu Changlian Chem. Co. PR China), pyridine (Tianjin Diyi Chem. Co. PR China) and sodium dithionate (Chengdu Kelong Chem. Co. PR China) were used without further purification.

Instruments

The chemical structure of the resins was identified by FTIR with a Nicolet 560 instrument. ^{1}H NMR spectra were recorded with Bruker AVANCE 300 MHz spectrometer. Gel permeation chromatography (GPC) analysis was performed on an Agiulent Hoolc GPC, using THF as eluent and the velocity of flow is 1.0 ml/min. Cure characteristics were studied by DSC with a Du Pont TA 2910 analyzer at a heating rate of 10°C/min over temperature rang from 30 to 400°C in nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed on a Shanghai scale instrument factory WRT-2 analyzer at a heating rate of 10°C/min in nitrogen atmosphere.

Synthesis of novolac resin

Phenolic novolac precursor resin was prepared by reaction of phenol with formaldehyde in presence of zinc acetate. Phenol (105.3 g, 1.12mol), formaldehyde (60 ml of 37%) and zinc acetate (1.3 g) were added into a three necked flask equipped with a condensator and a mechanical stirrer and stirred at 100-102°C in an oil bath for 4 hours. The reaction was continued for 90 min under vacuum to remove the excess phenol at 140°C. The product obtained, which was yellow dope, was cooled to room temperature. The obtained solid product was grinded into powder. The powder for study was characterized by FTIR spectroscopy and ^{1}H NMR spectroscopy techniques. Yield =87%. IR (KBr) cm^{-1} 3240 (-OH), the characteristic absorption at 808 (aromatic para substitution) is very weak indicating the resin is high ortho novolac. 2935, 2871 (-φ-CH2-φ-), 3039 (aromatic C-H), 752 (aromatic ortho substituted); ^{1}H NMR (DMSO) δ 3.70-3.81 ppm (-φ-CH2-φ-), 6.60-7.30 ppm (aromatic hydrogen). According to the ^{1}H NMR spectrum, the ratio of methylene H to aromatic H is 11/21. On the assumption that the polymerization degree of novolac is n, equation (1) can be deduced [13].



$$\frac{\text{methylene H}}{\text{aromatic H}} = \frac{2n+2}{3n+8} \qquad (1)$$

Calculated based on equation (1), the polymerization degree (n) is 4.33 and the number average molecular weight (M_n) is about 447 g/mol.

Synthesis of 4-aminophthalonitrile

Sodium dithionate (47.5 g) and 270 ml water were added into a three-necked flask equipped with a condensator and a mechanical stirrer at room temperature. Prepare a solution of 10 g 4-nitrophthalonitrile mixed with 40 ml pyridine. Added the solution drop-wise to the three-necked flask within 1 hour. The reaction mixture was stirred for 1 hour and added into 90 ml H_2O. Cooled the mixture to 4°C, collected the white precipitate. Recrystallized the precipitate in hot water. 2.6 g white crystal was collected. Yield=31.4%. The product was characterized by FTIR spectroscopy. IR (KBr) cm^{-1} 2252 (-CN), 3450 and 3419 (-NH_2), 3048 (aromatic C-H).

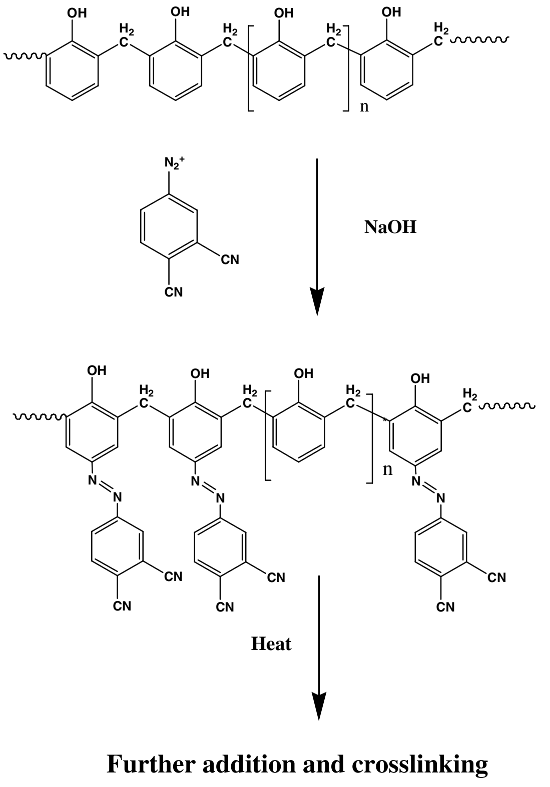
Synthesis of phthalonitrile azo novolac resin

Phthalonitrile azo novolac resins (PAN) were prepared by the coupling reaction between phthalonitrile diazonium sulfate and phenolic novolac resin in presence of a base catalyst. 4-aminophthalonitrile (2.5 g) was dissolved in 20 ml 70% H_2SO_4 solution. The obtained solution was cooled to 0-5°C. Added sodium nitrite solution (2.7 g in 20 ml distilled water) drop-wise into the aminophthalonitrile solution and stirred well at 0-5°C to form the diazonium sulfate solution. The resultant solution was filtered and the filtrate was added drop-wise to a solution of sodium salt of novolac (1.5 g in 15 ml 1mol/L NaOH) at 5°C in 1 hour, stirred well. The pH of the reaction mixture was kept at 8 by adding the solution of NaOH during the reaction process, the solution was kept at the same temperature for 4 hours by occasional stirring. Adjusted the pH value of the reaction mixture to 7 using dilute solution of H_2SO_4. The precipitated polymer was washed with hot water and filtered. The isolated product was dried under vacuum at 50°C for 10 hour. PAN resins were characterized by FTIR spectroscopy, ^{1}H NMR and GPC. Thermal characters of the resins were assessed by DSC and TGA.

PAN resins with varying phthalonitrile contents were synthesized utilizing the same procedure as mentioned above.

Results and discussion

Phenolic resins substituted with varying percentage of phthalonitrile functions linked via azo linkage (PAN resins) were synthesized by reaction of phthalonitrile diazonium sulfate with novolac resin as per scheme 1. The precursor novolac was prepared in presence of zinc acetate. In the FTIR spectrum of novolac, the badly weak characteristic absorption at 880 cm^{-1} (due to the aromatic para substitution) verified the resultant resin is high ortho novolac. The number average molecular weight (M_n) of novolac was calculated from the ratio of methylene protons to aromatic protons according to the ^1H NMR spectrum. 4-aminophthalodinitrile was prepared by the reducing reaction of 4-nitrophthalonitrile. For PAN resins, the para substitution of phenyl ring could be estimated from the ratio of relative intensities of the various methylene protons (3.81-3.95 ppm) to para-protons of phenol (6.70-6.99 ppm) in the ^1H NMR spectra. The error in the estimation is roughly 5%. By regulating the quantity of phthalonitrile diazonium salt added in the reaction mixture, degree of phthalonitrile substitution was varied. After washed with hot water and filtration, the resins were purified and were dried under vacuum at 50°C for 10 hours.



Scheme 1. Synthesis of the PAN resins and crosslinking.

Characterization of polymer

The purified polymer (PAN) was characterized for its molecular structure and the degree of phthalonitrile azo substitution by FTIR spectroscopy and ^1H NMR spectroscopy. The FTIR spectrum of PAN showed characteristic absorption due to the -CN groups of phthalonitrile at 2217 cm^{-1}, the hydroxyl group absorptions appeared at 3300-3600 cm^{-1}, aromatic groups at 1491-1632 cm^{-1}, the azo group absorption at 1530 cm^{-1}. ^1H NMR spectrum of the PAN resin showed signals at 3.81-3.95 ppm due to $-CH_2-$ and at 6.70-6.99 ppm due to the para-protons of phenol. Protons of phthalonitrile appeared as broad signals at 7.89-8.39 ppm. The degree of substitution can be calculated from the ratio of various methylene protons to para-protons of phenol in the ^1H NMR spectra. The polymer composition calculated in this way is given in Table 1. The degree of the substitution was varied from 23 to 61 mol%. A maximum substitution of about 61 mol% could only be achieved, despite using excess of the diazoumiun salt. The molecular weights of PAN resins were determinated by GPC analysis, using THF as eluent, and the velocity of flow is 1.0 ml/min.

Table 1. Molecular characteristic of PAN systems

Polymer ref.	Azo coupling (mol%)	[η] in THF, 30°C (dl g^{-1})	Molecular weight by GPC (g mol^{-1})			[η] M_n (dl mol^{-1})
			M_n	M_w	M_p	
Novolac	0	0.096	1014	3021	7262	97.34
PAN-1	23	0.100	786	1140	1542	78.60
PAN-2	46	0.099	703	872	1154	69.60
PAN-3	56	0.079	608	768	891	48.03
PAN-4	61	0.066	621	747	873	40.99

The coupling of diazomium salt occurs preferably at para position of the phenol. Coupling usually doesn't take place at ortho position if the para position is free [14,15]. In this present case, the coupling of the diazomium salt is expected to occur preferably at the free para position of the novolac. When phenol was used, the para substituted azo compound was formed in near quantitative yield. Despite using excess diazomium salt in diazo-coupling reaction, the extent of substitution did not exceed 61%. This leads to the hypothesis that the diazo-coupling in novolac is limited to the para position. The absence of coupling at the ortho position is attributable to the possible steric hindrance. The reduced reactivity of the diazonium ion can be an additional factor. Molecular weight characteristics of the polymers were determined by GPC and were given in Table 1. Interestingly, and contrary to expectation, the apparent molecular weight of the polymers determined by GPC showed a downward drift with increasing extent of diazo-coupling of the phenolic resins. The M_n of polymer computed from GPC data decreased from 1014 to 621g/mol and the M_w correspondingly from 3021 to 847 g/mol, on enhancing the diazo-coupling from 0 to 61%. The polymers were shown a reasonably good distribution in all cases. The apparent decrease in molecular weight could be a consequence of reduced hydrodynamic volume of the macromolecules with increase of the extent of diazo-coupling. The phthalodinitrile azo group is rigid and non-coplanar to the phenol group. Incorporation of this group on a regular and comb-like pattern to the novolac backbone must be conductive for decreasing the hydrodynamic volume of the polymer as a whole. Such phenomena of reduced hydrodynamic volume are common in hyperbranched polymers [16]. Since GPC senses the hydrodynamic volume in terms of the molecular weight, the computed apparent molecular weight decreases as the degree of azo-branching increased.

Solubility rheologic properties are crucial processing parameters of a matrix-resin for the preparation of composite materials. The PAN resins were soluble in common organic solvents such as acetone, methylethylketone and tetrahydrofuran, etc.

Thermal curing of PAN resins

Cure characteristics were determined with DSC analysis technique. The DSC curve of typical PAN resin in Figure 1 showed two exotherms confirming a two-step curing process. The first broad exotherm was at 200-270°C, and the second exotherm ranged from 310 to 340°C. The curing exotherms data of novolac resin and the PAN systems was compiled in Table 2.

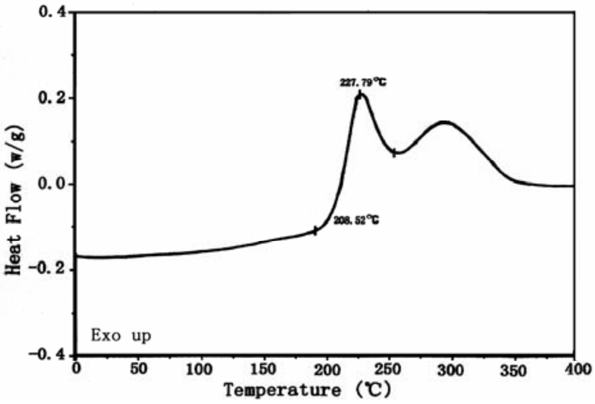


Figure 1. DSC thermogram of PAN-3 in N_2. Heating rate: 10°C/min; Size: 7.8330 mg.

Table 2. DSC cure charactristics of PAN systems (heating rate: 10°C/min in N_2; T_i, onset cure temperature; T_{max}, peak temperature; T_e, cure end temperature in DSC)

Polymer ref.	T^a_i(°C)	T^a_{max}(°C)	T^a_e (°C)	ΔH^a (J/g)	T^b_{max} (°C)
Novolac	157	162	254	30.3	–
PAN-1	198	224	267	67.8	337
PAN-2	206	221	270	69.0	321
PAN-3	208	227	274	85.9	313
PAN-4	225	249	275	104.1	310

[a]The first exotherm of the samples; [b]The second exotherm of the samples.

All of the curing scans of PAN systems had nearly identical sharp exotherms occurring around 224 to 249°C possibly corresponding to partially decomposition of azo bonds. The second exotherm peaks were around 310 to 330°C, which should due to the addition polymerization of nirile groups.

It has been reported earlier that the cure kinetics of some addition-cure-type phenolics are dependent much on their concentration in the backbone [17], higher concentration in chain facilitating the curing. In the present case too, cure temperature is lowered for the polymer. However the cure temperature was higher than novolac resins. Such phenomenon was possibly induced by decomposition of azo bonds of the first curing step. During this step, decomposition of azo bonds needed extra energy, so that the onset cure temperature was higher than novolac. The onset cure temperature was gradually elevated with the increase of azo bonds in PAN resins.

The heat of curing exotherm for the first curing step was found to increase nearly linearly with the degree of substitution. This implied that the extent of cure and possibly the cure mechanism also could be influenced by the concentration of phthalonitrile groups. The variation of heat of polymerization on extent of fuctionalization is demonstrated in Figure 2.

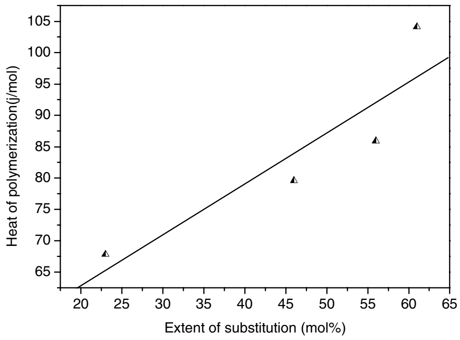


Figure 2. Varition of heat of curing with extent of phthalonitrile substitution.

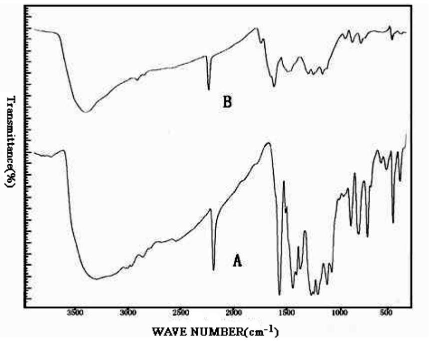


Figure 3. FTIR spectra of (A) PAN and (B) it's polymer (heated at 220°C for 2 hours).

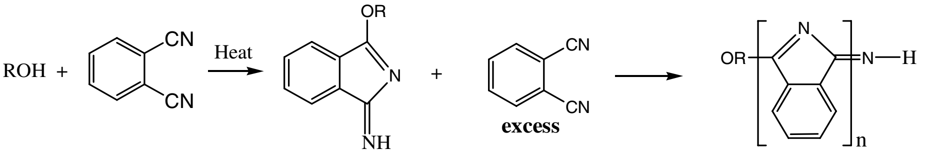
The cure of the PAN systems was monitored by FTIR spectra (Figure 3). After heated at 220°C for 2 hours ,the characteristic absorption of nitrile at 2315cm^{-1} almost didn't minish, this phenomenon indicated most of the –CN wasn't cured after heated at 220°C, the curing of nitrile group needs higher temperature. In Fig. 3, the absorption at 1530 cm^{-1} (due to the azo bonds) was appreciably weaker, it corresponded to the partly decomposition of azo bonds.

Thermal cure

The resins could be thermally cured in the temperature window indicated by DSC. Since the net work structure depends on the ultimate cure temperature[12], all resins were uniformly cured at 320°C for 2 hours during the proceeding of TGA analysis.

Cure mechanism of PAN resins

The present work was not to establish the cure mechanism. In fact, the exact cure mechanism is still obscure because of the numerous ways in which polymerization can proceed combined with the fact that few characterization techniques are available to study these complex thermosetting structures [12, 17] However, some insight was obtained into the cure mechanism. Polymers with nitrile groups are believed to been solidified by reaction between phenylic hydroxy and o-dinitrile benzene [18]. The cure mechanism is demonstrated in Scheme 2. The phenylic hydroxy probably attacks the nitrile groups of the o-dinitrile benzene to afford initially a l-aryloxyisoindolenine unit, which reacts with other nitrile groups to form polymeric materials. Since the resin in the present study is basically o-dinitrile benzene- functional, a similar reaction is expected in our present case. When heated, hydroxy of PAN resins could induce the polymerization of phthalonitrile groups as the same mechanism to form cued polymers.



Scheme 2. Addition polymerization mechanism of phthalonitrile.

Thermal characteristics of cured PAN resins

Thermal stability of the cured polymers was assessed by TGA. Heating rate was 10°C/min in nitrogen atmosphere. PAN systems were cured during the TGA analysis proceeding by keeping the resins at 320°C for 2 hours. The systems showed very good thermal stability. The thermogram data of the cured polymers are compiled in Table 3. The thermograms of cured polymers are shown in Figure 4. Degradation occurred apparently in two steps. Small weight loss peaks appeared around 230 to 260°C. After cured at 320°C for 2 hours, large mass loss peaks appeared from 540 to 700°C.

As the resins were cured at 320°C for 2 hours during TGA analysis, the resins were not cured, or not cured completely before temperature reached 320°C. Weight loss in this temperature range was probably caused by some minor degradations such as decomposition of azo bond (discussed in "Thermal curing of PAN resins"), partly degradation of incompletely cured resins. The curves of TGA between 320 to 700°C corresponded with the cured polymer.

The cured PAN systems yield higher amount of char. The char residue of cured polymers from PAN-1 to PAN-3 are about 80% at 700°C. However, when the degree of the substitution reached 61% the char residue drops to 58.21%. This phenomenon should be studied in further.

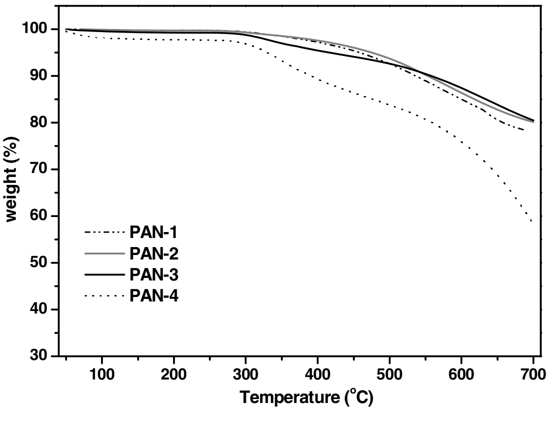


Figure 4. TGA thermograms of cured resins in N_2. Heat rate 10°C/min. Temperature rang: 30-700°C.

Table 3. Thermal decomposition characteristics of PAN resins

Polymer ref.	T_i(°C)	T_{max}(°C)	T_e (°C)	Char at 700°C (Wt%)
PAN-1	250	560	700	78.07
PAN-2	240	580	700	80.10
PAN-3	230	540	700	80.45
PAN-4	240	570	700	58.21

Conclusions

Addition curable phenolic resins bearing phthalonitrile groups, anchored to benzene ring through a phenyl azo linkage were realized by a novel and simple synthesis strategy involving the coupling reaction between novolac and phthalonitrile diazomium salt. The maximum degree of azo coupling only could reach about 61%. The resins have excellent process characteristic. According to the results of DSC analysis, PAN resins showed two broad cure exotherms in the rangs 200-270°C and 310-340°C. The curing occurred by known mechanisms. The thermal cure of the resins could be facilitated with increase in phthalonitrile content, and the content of phthalonitrile groups of 20-50% is appreciated in view of thermal properties. However, when the content of phthalonitrile groups reached about 61%, the char residue dropt down badly. The reason should be investigated in the further study. The high proportion of char of shows the prespects for potantial application of the this resin in ablative compositions and in carbon-carbon composites.

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