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Addition curable phenolic resins based on ethynyl phenyl azo functional novolac

C.P. Reghunadhan Nair*, R.L. Bindu, K.N. Ninan

Propellant and Special Chemicals Group, Vikram Sarabhai Space Center, Trivandrum 695 022, India

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Abstract

Novel addition curable phenolic resins bearing terminal ethynyl groups anchored to benzene ring through a phenyl azo linkage were realized by the coupling reaction between novolac and 3-ethynyl phenyl diazonium salt. The diazo-coupling occurred to a maximum of 50 mol%. The apparent molecular weight, determined from gel permeation chromatography showed a downward drift with increase in degree of acetylene substitution. The resin underwent curing in a broad temperature range 140–240 °C. Analyses using a model compound indicate that the curing occurs via various addition polymerization of acetylene groups. The thermal stability and anaerobic char yield of the polymers increased proportional to the crosslinking and were considerably superior to those of a conventional resole. Isothermal pyrolysis studies implied the possibility for the decomposition occurring mainly by loss of nitrogen gas, and hydrocarbon to form mostly an amorphous char. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Phenolic resin; Addition cure resins; Acetylene terminated polymer

1. Introduction

Despite the emergence of new high performance polymers with excellent properties, phenolic resins still retain a major commercial and industrial interest because of their overall performance and low cost. Their acceptance in many engineering areas is, however, impeded by some of their inherent qualities such as brittleness, poor thermo-oxidative stability and the condensation cure reaction. Cure at high temperature by condensation mechanism with evolution of volatiles necessitates application of pressure during moulding to get void-free components. Need for use of catalyst for curing and limited shelf life of the resin at ambient conditions are also major short-comings of these systems. In view of this, the need has been felt for introduction of new cure chemistry, proceeding without evolution of volatiles and allowing for extended shelf stability at ambient conditions without impairing the thermal and thermo-mechanical characteristics. The concept of addition curable phenolic resins gains significance in this context [1–3]. Addition curable phenolics based on allyl and alkenyl functional resins which are thermally less stable have been reported [4,5]. Recently, we reported a few addition curable phenolic resins with improved thermal characteristics and good mechanical performances [6–11]. Addition curable resins with improved thermal and pyrolysis characteristics will be the attractive matrices in composites for thermo-structural applications [12]. This is because, the condensation cure in conventional phenolics leaves diffusion paths that allow for rapid absorption of moisture. The absorbed moisture, in addition to weakening the interfaces of the composite, paves way for vaporization of moisture during ablative heating causing pressure build-up that leads to interface weakening. Higher char yield also leads to better heat shielding. Such matrices are good candidates for carbon–carbon composites [13].

Acetylene terminated monomers and prepolymers (ATM) have advantages over other systems such as improved tractability, processability, high thermal stability and good mechanical properties [13–19]. High char yielding nature and thermal stability qualify them as excellent matrices in carbon–carbon composites [20,21]. Good ablative characteristics of aryl acetylene-based composites have been exploited to derive rocket motor components [22]. Acetylene terminated imides have many desirable properties [23]. Further improvements in processing characteristics are achievable through reactive blending of ATM with other resin systems [24].

Although many acetylene-functional reactive prepolymers are known, such phenolic resins have so far not been

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* Corresponding author. Tel.: +91-471-564-777; fax: +91-471-415-234/36.

E-mail address: cprnair@eth.net (C.P. Reghunadhan Nair).

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reported. In this paper, we report the synthesis of an acetylene-functional, addition curable phenolic resin by a new technique. This paper discusses mainly their synthesis, characterization, cure and thermal properties.

2. Experimental

2.1. Materials

3-Amino phenyl acetylene (Kodak chemicals, UK), phenol (CDH, Agra, India), formalin (34 wt% aqueous solution, Sisco Research, Mumbai, India), oxalic acid (E-Merck, India), sodium nitrite, sodium hydroxide (SD Fine Chemicals, India) and H_2SO_4 (NICE, India) were used as received.

2.2. Techniques

FTIR spectra were recorded with a Nicolet 510P instrument. The cure characteristics of the resins were studied by DSC using a Mettler DSC-20 analyzer at a heating rate of 10 K min^{-1} over the temperature range from 30 to 350 °C in nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed on a Du Pont 2000 thermal analyzer in conjunction with 951-thermogravimetric analyzer in nitrogen atmosphere at a heating rate of 10 K min^{-1}. NMR spectra were recorded with a Bruker 400AMX spectrometer. Gel permeation chromatography (GPC) analysis was performed on a Waters GPC, model Delt prep. 3000 using THF and dimethyl formamide as eluents and with DRI-R 401 refractive index and UV (at 280 nm) detectors. Polystyrene standards were used for calibration. Elemental analyses were performed on a Perkin Elmer model 2400 elemental analyzer. XRD analysis was carried out on a Philips X-ray diffraction unit with PW 1729 X-ray generator having vertical goniometer with PW 1710 computer unit. Cu Kα radiation was used with accelerating voltage of 30 kV and tube current of 20 mA. Powder sample was used.

2.3. Synthesis of novolac resin

Phenolic novolac precursor resin was prepared by reacting phenol with formaldehyde in presence of an acid catalyst. Phenol (500 g, 5.31 mol) and oxalic acid (25 g) were taken in a three necked flask and stirred at 90 °C in an oil bath. Formaldehyde (348 ml of 34% formalin; 4.25 mol; 0.8 mol per mol phenol) was added drop-wise to it. The reaction was continued for 8 h under stirring at 90 °C. The reaction mixture was extracted several times with hot water to remove unreacted phenol and the catalyst. The polymer was fractionated to narrow down the dispersity using a water–methanol mixture and dried under vacuum at 50–60 °C for 10 h. The fraction selected for the study was characterized by GPC and by ^{1}H NMR spectroscopy techniques.

2.4. Synthesis of ethynyl phenyl azo novolac resin

Ethynyl phenyl azo novolac (EPAN) resins were prepared by coupling reaction between 3-ethynyl phenyl diazonium sulfate and phenolic novolac resin in presence of a base catalyst. 3-Amino phenyl acetylene (10 g, 0.085 mol) was added drop-wise to 50 ml 50% H_2SO_4 solution. The solution was stirred well and cooled to −5 °C. To this solution, cold sodium nitrite solution (10 g in 40 ml distilled water) was added drop-wise at 0 °C and stirred well. After diazotization, the solution was filtered and the filtrate was added drop-wise (first slowly) to a solution of sodium salt of novolac (8 g dissolved in 80 ml 1N NaOH) at 0 °C and stirred well. After the addition, the solution was kept at the same temperature for 4 h by occasional stirring. The reaction mixture was then added drop-wise to distilled water and the pH adjusted to 7 by adding dilute H_2SO_4. The precipitated polymer was filtered. It was dissolved in acetone and precipitated in water. The isolated product was dried in vacuum at 40 °C for 10 h. Yield = 75–80%. It was characterized by elemental analysis, FTIR spectroscopy, ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy and GPC.

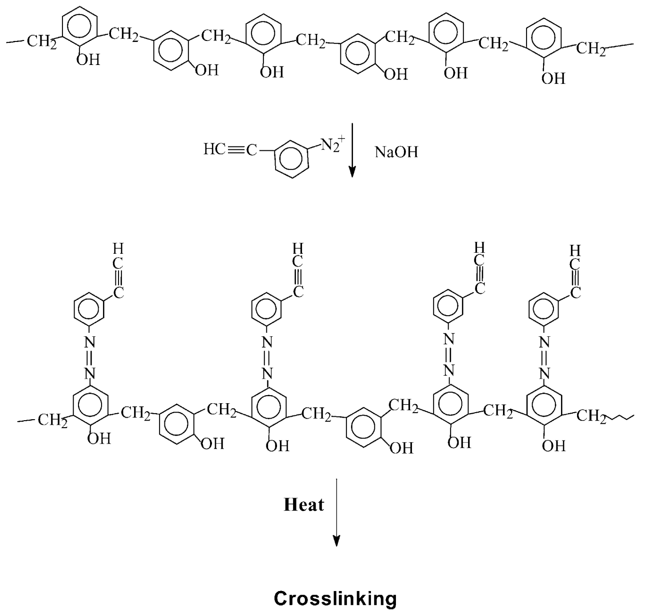
2.5. Synthesis of 4-(3-ethynyl phenyl azo) phenol

4-(3-Ethynyl phenyl azo) phenol (EPAP) was synthesized in a similar way as EPAN by the coupling reaction between ethynyl phenyl diazonium sulfate and phenol. 3-Amino phenyl diazonium sulfate prepared as above was added drop-wise to a solution of sodium salt of phenol (8 g, 0.085 mol) in distilled water at 0 °C and stirred well. The reaction was continued for 4 h by occasional stirring at the same temperature. The product obtained was purified by recrystallised from methanol–water mixture and was dried under vacuum at 40 °C for 10 h. Yield = 87%. It was characterized by elemental analysis, NMR spectroscopy and FTIR spectroscopy.

Melting point 99 °C. *Elemental analysis.* Calculated for $C_{14}H_{10}N_2O$ (%): C, 75.68; H, 4.50; N, 12.60. Experimental: C, 75.48; H, 4.82; N, 12.70.

3. Results and discussion

Phenolic resins substituted with varying percentage of ethynyl functions linked via an azo group (EPAN resins) were synthesized by reaction of 3-ethynyl phenyl diazonium sulfate with novolac resin as per Scheme 1. The precursor novolac was prepared by conventional method. Novolac polymer with a relatively narrow molecular weight distribution was obtained by fractionation using methanol–water system. The fraction used in this work possessed M_n = 700 g mol^{-1} and a polydispersity index of 2.8 as estimated by GPC. The *ortho–para* substitution of the phenyl rings could be estimated from the relative intensities of the various methylene protons (*ortho–ortho*, *ortho–para*, *para–para*) in the proton NMR spectrum. From this, the



Scheme 1.

free *para* position was estimated to be 55 mol%, the error in the estimation being roughly 5%. The degree of ethynyl substitution was varied by regulating the quantity of 3-ethynyl phenyl diazonium salt in the reaction mixture. The resins were purified by dissolving in acetone and precipitating in water and water–methanol mixture. They were characterized by elemental analysis, FTIR spectroscopy, NMR spectroscopy and GPC.

3.1. Characterization

The purified polymer (EPAN) was characterized for its degree of ethynyl phenyl azo substitution from the nitrogen-content obtained by microelemental analysis. The polymer composition calculated from nitrogen-content is given in Table 1. The degree of substitution was varied from 24 to 50 mol%. A maximum substitution of 50 mol% could only be achieved, despite using excess of the diazonium salt. The FTIR spectrum of the polymer showed characteristic absorption due to the C–H group of acetylene (≡C–H) at 3289 cm^{-1}. The hydroxyl group absorptions appeared at 3300–3600 cm^{-1}, aromatic groups at 1550–1600 cm^{-1}, and the azo group absorption at 1593 cm^{-1}. Proton NMR spectrum of the EPAN resin showed signals at 2.5 ppm due to acetylene protons and at 6.6–7.2 ppm due to aromatic protons. The methylene bridges appeared as broad signals at 3.4–3.9 ppm and OH at 7.6 ppm.

The coupling of diazonium salt is known to occur preferably at *para* position of the phenol. Coupling at *ortho* position practically does not take place if the *para* position is free [25,26]. The preference for *para* position arises especially when the diazonium ion is not so reactive as in the present case. In the present case too, the coupling of the diazonium 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 (structure discussed later). Despite using excess diazonium salt for the novolac, the extent of substitution did not exceed 50%, which tallies quite well with the availability of free *para* position (55%). All these lead 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. ^{13}C NMR spectrum showed signals due to $-C{\equiv}CH$ at 82 and 81.5 ppm. A multitude of signals due to various C–N and C–O groups were found at 150–161 ppm, in addition to other signals due to aromatic carbons (115–135 ppm) and methylene bridge carbons (29–34 ppm). A typical ^{13}C NMR spectrum with the assignments is shown in Fig. 1.

Molecular weight characteristics of the polymers were determined by GPC and are 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 the polymer computed from GPC data decreased from 700 to 330 g mol^{-1} and the M_w correspondingly from 1970 to 1200 g mol^{-1}, on enhancing the diazo-coupling from 0 to 50%. The isolated polymers showed a reasonably good distribution in all cases. Polymodal distribution indicating any polymer degradation or selective substitution was not observed. The polymer was isolated in good yield, ruling out the possibility for the decrease in molecular weight caused by selective isolation of the low molar mass components. Hence, the apparent

Table 1
Molecular characteristics of EPAN systems

Polymer ref.	N-content (wt%)	Extent of azo coupling (mol%)	$[\eta]$ in THF, 30 °C (dl g^{-1})	Molecular weight by GPC (g mol^{-1})			$[\eta]M_n$ (dl mol^{-1})
				M_n	M_w	M_p	
Novolac	0	0	0.155	700	1970	1840	108.5
EPAN-1	4.9	24	0.134	520	1570	2030	69.68
EPAN-2	6.6	35.8	0.085	430	1460	1950	36.55
EPAN-3	7.5	43	0.107	350	1240	1330	37.45
EPAN-4	8.2	49.7	0.074	330	1180	1110	24.42

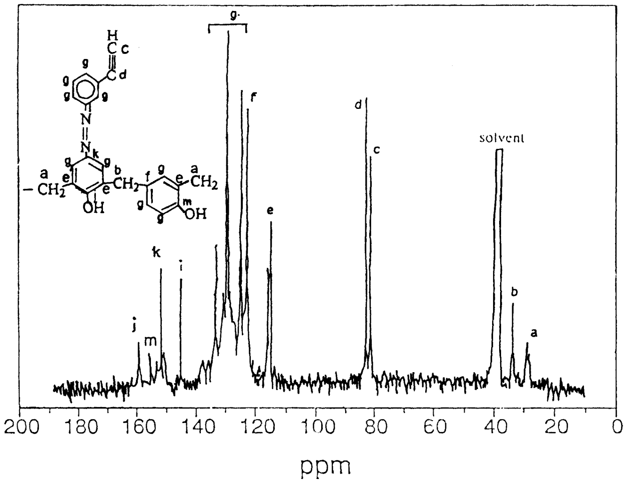


Fig. 1. ^{13}C NMR spectrum of EPAN resin in d_6 acetone.

decrease in molecular weight could, in all probability, be a consequence of reduced hydrodynamic volume of the macromolecules with increase in the extent of diazo-coupling. The ethynyl phenyl diazo group is rigid and is coplanar to the phenol group. Incorporation of this group in a regular and comb-like pattern to the novolac backbone must be conducive for decreasing the hydrodynamic volume of the polymer as a whole. Such phenomena of reduced hydrodynamic volume are common in hyperbranched polymers [27]. Since GPC senses the hydrodynamic volume in terms of the molecular weight, the computed apparent molecular weight decreases as the degree of diazo-branching increases. The product of molar mass (M_n) and $[\eta]$ is given in Table 1. This factor is proportional to the hydrodynamic volume and shows a systematic decrease with increase in degree of substitution. This confirms that the decreasing molecular weight is a consequence of the reduced apparent hydrodynamic volume. The GPC pattern of the EPAN resins, showing a systematic drift towards high elution volume with increased extent of diazo-coupling is shown in Fig. 2.

Table 2
DSC cure characteristics of EPAN systems (heating rate: 10 °C min^{-1} in N_2; T_i, onset cure temperature; T_{max}, peak temperature; T_e, cure end temperature in DSC)

Polymer ref.	T_i (°C)	T_{max} (°C)	T_e (°C)	(H (J g^{-1})	ΔH^a (J mol^{-1})
EPAN-1	150	204	235	16.2	9050
EPAN-2	140	207	225	21.8	9090
EPAN-3	172	195	220	25.3	9320
EPAN-4	150	204	230	35.6	11 960
EPAP	175	225	270	70.5	15 650

[a] Heat of polymerization per mole of acetylene group.

3.2. Thermal curing of EPAN resins

DSC analysis of the systems showed a broad cure exotherm ranging from 140 to 240 °C due to curing of acetylene groups. A typical DSC thermogram of the resin along with that of a model compound, i.e. EPAP is given in Fig. 3 and DSC data are compiled in Table 2. All polymer samples cure at a temperature window lower than that of the model compound. EPAP cures at a higher temperature (175–270 °C). In fact, the DSC exotherm is apparently incomplete due probably to the further curing of unsaturated groups generated in the first cure step.

It has earlier been reported that the cure kinetics of acetylene groups is dependent also on their concentration and distribution in the backbone [28], higher concentration in a chain facilitating the curing. In the present case too, cure temperature is lowered for the polymer. However, the heat of curing was found to increase 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 acetylene groups. The variation of heat of polymerization on extent of functionalization is demonstrated in Fig. 4.

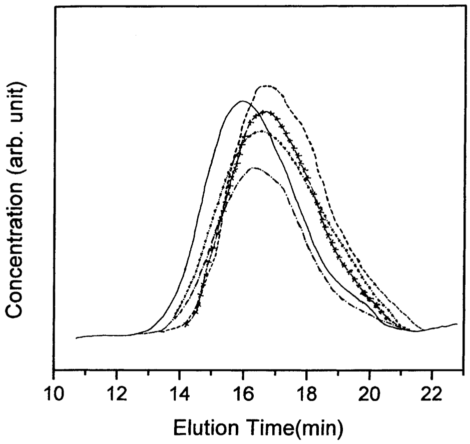


Fig. 2. GPC profile of various EPAN resins in THF. (—): Novolac; (–·–·–): EPAN 1; (···): EPAN 2; (– × – × –): EPAN 3; (- - -): EPAN 4.

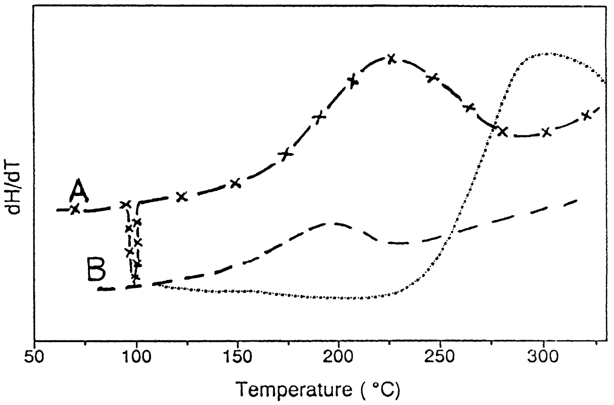


Fig. 3. DSC thermogram in N_2. (- - -): EPAP; (– × – × –): EPAN; (···): methanol insoluble part from cured EPAN; heating rate: 10 °C min^{-1}. Y axis for each is in arbitrary scale.

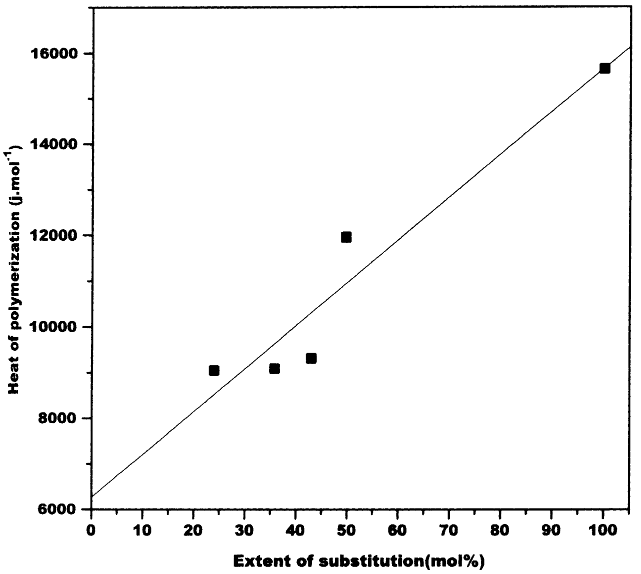
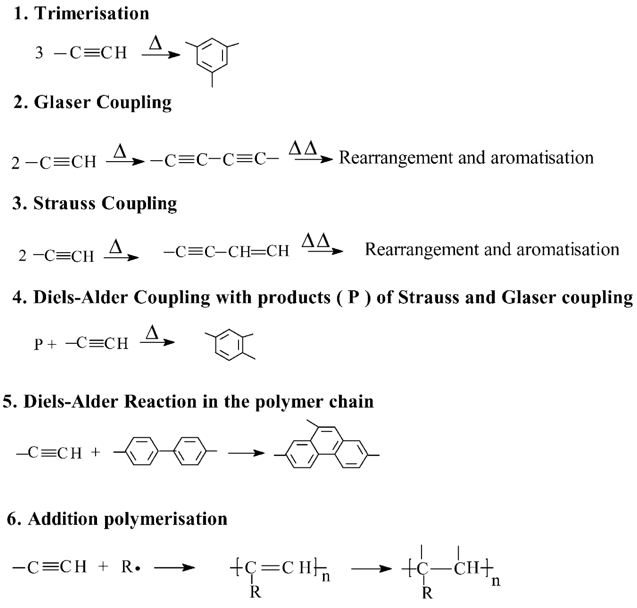


Fig. 4. Variation of heat of curing with extent of acetylene substitution.



Scheme 2.

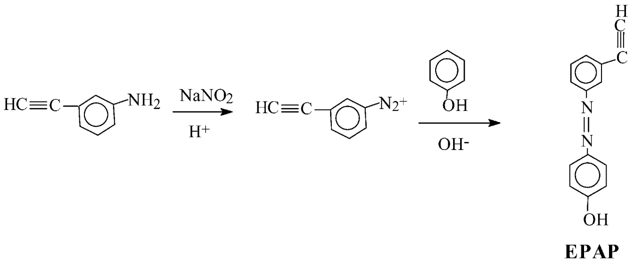
3.3. Thermal cure

The resins could be thermally cured in the temperature window indicated by DSC. Since the network structure depends on the ultimate cure temperature [16], all resins were uniformly cured at 225 °C for 2 h in vacuum.

3.3.1. Cure mechanism

The major objective of the present work was not to establish the cure mechanism, but to derive information on the material property for desired applications. However, some insight was obtained into the overall cure mechanism. The cure mechanism of acetylene resins is not sufficiently clearly known [14–16]. However, many previous studies have shown that the curing occurs by a combination of different mechanisms [29,30]. Polymers bearing acetylene groups are believed to be hardened by trimerization [31], Glaser coupling [32], Strauss coupling [33], Diels–Alder reaction with participation of products of Glaser and Strauss coupling, Diels–Alder coupling with the aromatic backbone, free radical polymerization with the formation of linear and branched products [34], etc. The extent of trimerization is reported to be less at reduced cure temperature [29]. In majority of the cases, the cyclotrimerization to aromatics is known to occur to less than 30%. Crosslinking predominates at higher cure temperatures. Many studies, based on the analyses of compounds formed during thermal polymerization of monofunctional model compounds confirmed that low molar mass are formed initially by way of Strauss coupling, Sabourin [35] and Glaser dimers and diene–diene dimers. In the second stage, species with higher molar mass are formed by chained conjugated dienes [36–38]. Several other similar studies also substantiate these mechanisms [39–42]. The various mechanisms are depicted in Scheme 2. Since the resin in the present study is basically acetylene-functional, a similar cure mechanism is expected.

Since it was difficult to derive evidences for reaction mechanism directly by analyses of the insoluble cured resins, some attempt was made to understand it from the thermal polymerization of the model compound, EPAP. It was synthesized as per Scheme 3 and characterized by elemental analysis, ^{13}C and ^{1}H NMR spectroscopy. The ^{13}C NMR spectrum is given in Fig. 5 and proton NMR spectrum in Fig. 6, both conforming to the *para* azo substituted structure. This product was formed in excellent yield, ruling out the possibility for *ortho* coupling of diazonium salt. On heating at 170 °C for 2 h, EPAP polymerized with the formation of about 60% of methanol insoluble fraction. This fraction was very slightly soluble (less than 2%) in DMSO/DMF posing difficulty for NMR spectral analysis in solution. However, the solubility was enough for a GPC analysis in DMF. The methanol soluble part contained unreacted monomer (evident also from its FTIR spectrum), and possibly low molar mass addition products which were not separated. The mixture was analyzed by spectral and GPC analyses. The GPC spectra of EPAP, the methanol



Scheme 3.

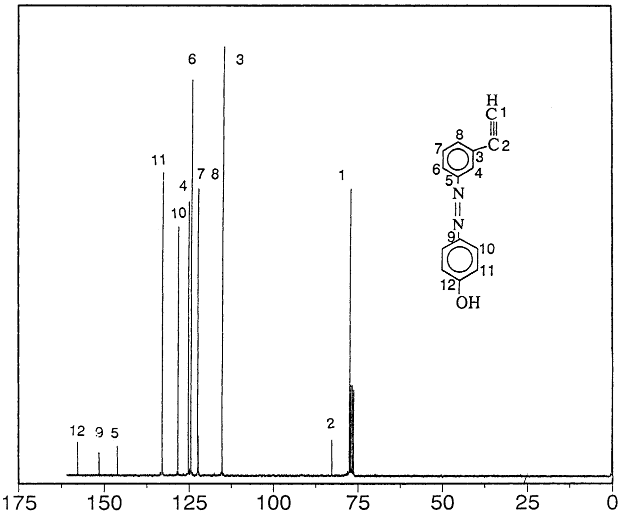


Fig. 5. ^{13}C NMR spectrum (in $CDCl_3$) of EPAP.

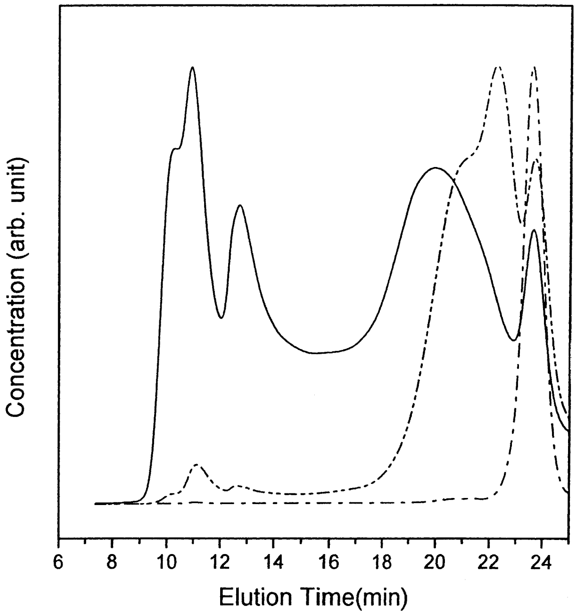


Fig. 7. GPC traces of (– – –): EPAN; (– - – -): methanol soluble fraction; (—): methanol insoluble fraction in DMF, UV (280 nm) detection.

and DMF soluble fractions (all in DMF with UV detection) are shown in Fig. 7. EPAP appeared at an elution time of 23.5 min. The methanol soluble fraction contained EPAP and two other components. The component at 22 min is expected to be the dimer formed by Glaser and Strauss coupling. The one at 20.1 min with approximately thrice the molar mass of the monomer can be attributed to the cyclic trimer. GPC also showed presence of minor amount of higher molar mass species in this fraction. The methanol insoluble part showed a multimode distribution and indicated presence of EPAP. The broad peak centered at 20 min encompasses the low molar mass oligomers formed by the various mechanisms. The high molar mass products appeared as well separated peaks at 13, 11 and 10.5 min. This part, in all probability, contained the linearly polymerized polyenes and branched polymers (prior to crosslinking). Since the polymerization temperature is lower (170 °C) than the one required for complete insolubilization (220 °C), crosslinking is avoided. The methanol insoluble fraction possessed further curing sites, possibly unsaturation groups formed through addition reaction of acetylene as evident in its DSC (included in Fig. 3) which showed a cure exotherm starting at 230 °C. It was transformed to a completely insoluble product on heating at 220 °C.

The ^{1}H NMR spectrum of the methanol soluble part showed presence of very minor signals at 5.55 and 5.95 ppm due to =C–H groups formed by the addition reaction among acetylene groups (Fig. 8). Minor signals at 6.7 could be assignable to the =CH–O– groups formed possibly by the addition of phenolic OH to acetylene and the signals at 3.8 ppm could be due to –CH–O– groups

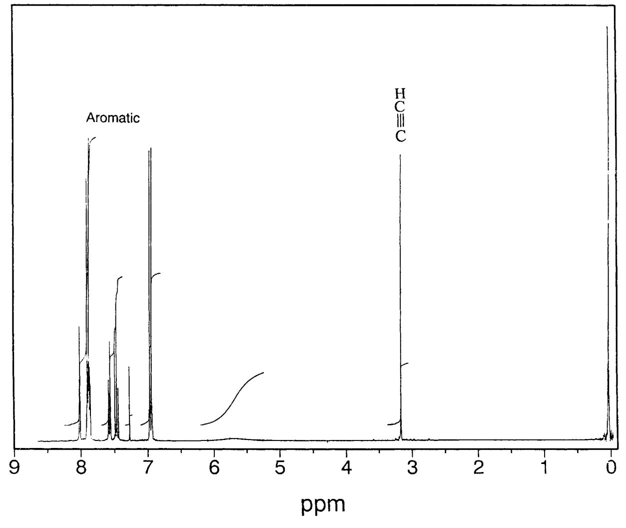


Fig. 6. ^{1}H NMR spectrum (in $CDCl_3$) of EPAP.

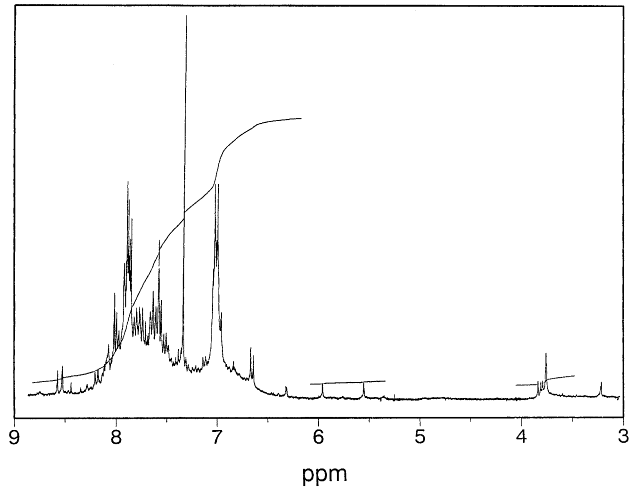


Fig. 8. ^{1}H NMR spectrum (in $CDCl_3$) of methanol soluble part of polymerized EPAP.

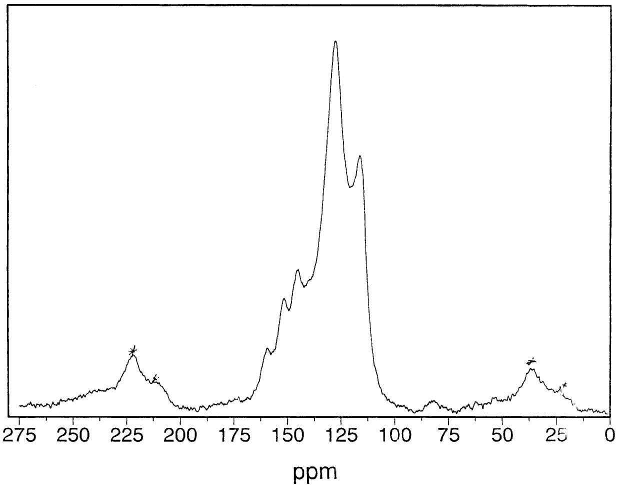


Fig. 9. CP MAS NMR spectrum of methanol insoluble part of polymerized EPAP.

formed by addition reactions of =CH–O– groups. The aromatic region looked more complex due to a multitude of signals arising from various products. The solid state (CP MAS) ^{13}C NMR spectrum of the methanol insoluble part (Fig. 9) gave very broad spectrum in the 100–170 ppm range (the peaks at around 35 and 225 ppm are side bands). However, an isolated broad peak 70–90 ppm could be assigned to the acetylene groups (≡C–) formed by Glaser and Strauss coupling. No clear evidence for –CH–O– group was obtained in this product. The FTIR spectrum of the insoluble part (given in Fig. 10 along with that of EPAP) indicated complete disappearance of the peak at 3289 cm^{-1} due to the C–H group of terminal acetylene. On raising the cure temperature of EPAP to 200 °C, the insoluble proportion increased further to about 80%, and a temperature of 220 °C provided a completely insoluble material. The formation of high molar mass intermediate species, which are transformed to insoluble crosslinked polymers, implies that the major part of acetylene curing occurs by linear addition and crosslinking in league with the reported mechanism. The present study does not focus on the estimation of the relative weightage of each cure mechanism in the overall cure process.

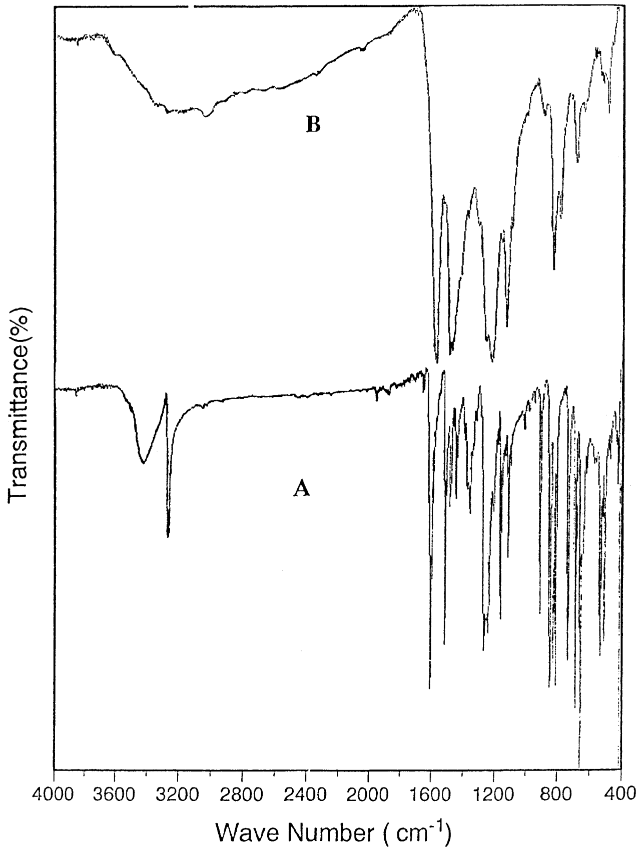


Fig. 10. FTIR spectra of (A) EPAP and (B) its polymer (cured at 170 °C).

3.4. *Cure monitor by FTIR spectroscopy*

The isothermal cure of the EPAN systems was monitored by FTIR spectra from the disappearance of the absorption at 3289 cm^{-1}. The peak at 2922 cm^{-1} (due to CH_2 group) was used as the internal reference. The curing of the resin proceeded to only 82% after 2.5 h of heating at 200 °C, whereas increasing the temperature to 225 °C resulted in complete cure in 2 h. Hence, the latter schedule was followed for curing all polymers.

3.5. *Thermal characterization of cured polymer*

The thermal stability of the cured polymers was assessed by TGA. Despite possessing thermally fragile crosslinks resulting from the addition polymerization of the acetylene groups, the systems showed very good thermal stability. The thermograms of the cured polymers are shown in Fig. 11 along with that of cured resole (phenol–formaldehyde ratio, 1:1) for a comparison. The decomposition occurs apparently in a single step. The initial decomposition temperature (T_i) is higher for EPAN systems and is at around 370–390 °C as against resole starting to decompose significantly at around 300 °C. The T_i values increase with increase in crosslink density.

The EPAN systems yield higher amount of char in comparison to the resole. The char residue increases with increase in the percentage of diazo-coupling (see Table 3). Against a char residue of 60% in resole, EPAP gives 72–

Table 3
Thermal decomposition characteristics of EPAN resins

Polymer ref.	T_i (°C)	T_{max} (°C)	T_e (°C)	Char at 700 °C (wt%)
Resole	300	470	700	60
EPAN 1	370	500	700	70.2
EPAN 2	380	505	700	74.2
EPAN 3	380	520	700	74.3
EPAN 4	390	525	700	75.6

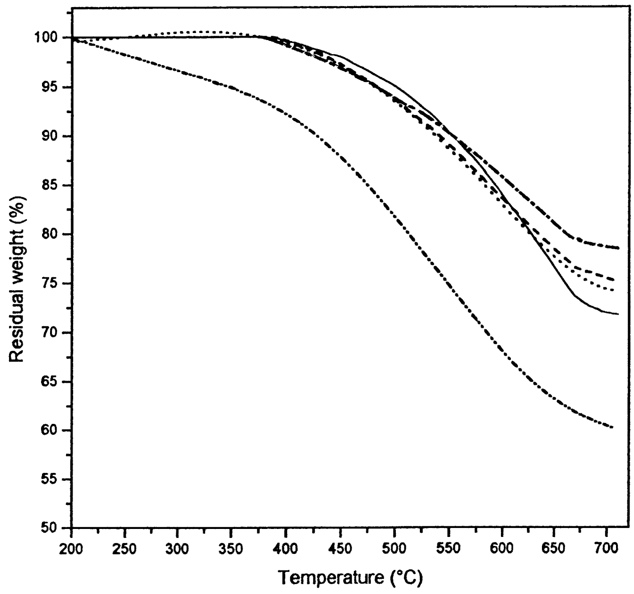


Fig. 11. TGA thermograms of cured resins in N_2. Heating rate: 10 °C min^{-1}. (—): EPAN 1; (···): EPAN 2; (- - -): EPAN 3; (–·–·–): EPAN 4; (–··–··–): resole.

75% char at 700 °C. It may be remarked that the resole already looses a mass of 22–28% during the condensation cure, whereas EPAN is practically addition curable. The mass-loss on curing is less than 1%. Thus, the gain in char yield based on virgin resin is about 65% for the present system in comparison to resole.

3.6. Isothermal pyrolysis

Study for understanding of the carbonization process was performed by isothermal pyrolysis and analysis of the derived char. The pyrolysis data are important from the point of view of its application as ablative materials and as matrices for the preparation of carbon–carbon composites [43]. The anaerobic pyrolysis was done at 700 and 900 °C and the char yield and nature of char were analyzed for one typical case of EPAN-2. The isothermal pyrolysis at temperatures of 700 and 900 °C was effected in an inert atmosphere of argon for different time intervals. The char obtained after pyrolysis was gravimetrically estimated and analyzed for composition by elemental analysis. The percentages of char remaining after pyrolysis at 700 °C for 1 and 2 h, and at 900 °C for 2 h are compiled in Table 4. During curing, these systems manifested negligible mass-loss. The pyrolysis data showed that the char is nearly stabilized for this temperature regime and duration. EPAN furnished 79–76% of char under these conditions in contrast to cured resole giving less than 60% residue. The char was analyzed by elemental analysis for their composition and also by FTIR spectroscopy and XRD. The percentages of C, H and N in the residue obtained after pyrolysis at 700 °C for 1 and 2 h are given in Table 4. The elemental composition is nearly the same for both pyrolysis time intervals and the char was found to contain about 80% carbon. Whereas the increase in carbon content is marginal, there is significant decrease in nitrogen and hydrogen concentration of the char in comparison to the virgin material. Decomposition of azo group as nitrogen may, in all probability, be occurring during this stage. The relative increase in oxygen percentage is a result of loss of other elements. On increasing the pyrolysis time at 700 °C, there is no major change in the char composition. On increasing the pyrolysis temperature to 900 °C for 2 h, the percentage of carbon in the char increased and those of oxygen and nitrogen decreased. This implied loss of nitrogen and oxygen at this stage, the latter possibly as oxides of nitrogen or carbon. The char possesses significant amount of oxygen. Complete pyrolysis for elimination of oxygen needs still higher temperature, which remains to be investigated.

Table 4
Composition of char formed after pyrolysis for EPAN-2

Pyrolysis conditions	Char (%)	C (%)	H (%)	N (%)	O (%)[a]
No pyrolysis	–	75.1	4.9	6.6	10.4
1 h at 700 °C	79	80.6	1.1	2.4	15.9
2 h at 700 °C	76	80.0	1.0	2.9	16.1
2 h at 900 °C	74	85.5	1.9	1.0	12.6

[a] Estimated by difference.

FTIR spectra of the pyrolyzed samples showed weak broad absorption at 1000–1200 cm^{-1}. This may be assigned to the residual C–O and C–N linkages present in the char. The limited pyrolysis temperature is not adequate to eliminate the oxygen atoms. The FTIR spectra are nearly the same for pyrolyzed resole and EPAN system. Very minor absorption corresponding to C–H groups and C–OH groups were observed at 2900–2980 and 3300–3600 cm^{-1}, respectively. The spectra resembled that of commercial charcoal.

The XRD analysis of the char showed to be amorphous in nature except for a weak scattering at $2\theta = 26.5$, attributable to a minor crystallinity.

4. Conclusions

Addition curable phenolic resins bearing terminal acetylene group, 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 3-ethynyl phenyl diazonium salt. A maximum of 50 mol% coupling, in league with the availability of free *para* position in the precursor novolac could be achieved. These resins showed broad cure exotherm in the range 140–240 °C. The curing occurred by known mechanisms. The polymers exhibited enhanced thermal stability and anaerobic char in comparison to resole. Isothermal pyrolysis at limited temperature regime showed that complete pyrolysis of the EPAN system is not achievable under these conditions. The higher proportion of char shows the prospects for potential application of this resin in ablative compositions and in carbon–carbon composites.

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