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Phenyl ethynyl functional addition cure phenolic resins: Synthesis, characterisation and thermal properties

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Phenyl ethynyl functional addition curable phenolic resins were synthesised by reacting a mixture of phenol and 3-(phenylethynyl) phenol (PEP) with formaldehyde in presence of an acid catalyst. Relatively narrow molar-mass distributed polymers were obtained in good yield. The presence of PEP led to reduced molar-mass and narrow distribution of the copolymers. The resin underwent thermal curing at around 250–275°C, much lower than the cure temperature of PEP. The thermal stability and anaerobic char residue of the cured resins increased with increase in ethynyl-content and these properties were more than those of resol resin. These addition cure phenolics provided an overall increase in char of about 70% vis-à-vis resol resin when compared on the basis of uncured resins.

1. Introduction

Addition-curable phenolic resins are effective alternative to condensation phenolics for overcoming the processing problems of latter and to confer high char yielding propertiy [1, 2]. The general approach for designing such polymers is to anchor addition curable functional groups onto novolac and induce their thermal cure during processing. Thus, in an earlier work, we reported addition-curable phenolic resins, functionalised with phenylmaleimide- [3] allylphenol-phenylmaleimide- [4], propargyl- [5] and ethynylphenylazo [6] 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 [7] and could be better matrices in carbon/carbon composites [8].

In this paper, we report the synthesis of phenyl ethynyl functional, addition curable phenolic resins. Ethynyl-terminated reactive polymers have great potential for high performance composite applications [7–12]. They have many advantages over other systems, such as improved tractability, high thermal stability and good mechanical properties. High performance resins formed from acetylene-terminated monomers (ATM) are currently being developed for use under hot/wet conditions [13].

Replacement of terminal acetylene groups by phenyl ethynyl function gives scope for improving further the thermal stability of the resultant networks due to the higher aromatic-content of the crosslinks. Phenyl ethynyl groups have, of late, received a great deal of attention as a means of thermally chain extending and crosslinking polymers [10, 14, 15]. They have been used within the polymer backbone to achieve intermolecular cyclo-addition to rigidize the polymer [16]. This versatile group has also been used to obtain processable oligomers such as imide [17–21], Schiff-base [22], arylene ethers [23, 24], benozoxazole [25], and benzimidazoles [26]. Pendent phenyl ethynyl groups have been anchored onto polyphenylenes to obtain fully conjugated ladder polymers [27]. On thermal curing, they provide a three-dimensional network exhibiting an excellent combination of properties including high glass transition temperature, good thermal stability, moisture and solvent resistance, good toughness and mechanical properties. The cure mechanism is not very obvious. A radical mechanism leading to a polyene network was proposed earlier [10, 18]. It has been investigated recently for a phenyl ethynyl substituted model compound by Wood *et al.* [28]. Despite the well-known attributes of phenyl ethynyl functional resins, there has not been any attempt to develop phenolic resins bearing this group. It can, in all probability, be presumed that such a system with addition-cure characteristics would be thermally stable. This paper describes the attempts to realize phenyl ethynyl functional phenolic novolac resins. It focuses mainly on the synthesis and characterization of the resins and their cure and thermal characteristics.

2. Experimental

2.1. Materials

3-Iodo phenol, phenyl acetylene, triphenyl phosphine, bis(triphenyl phosphine) palladium (II) chloride and

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cuprous iodide were purchased from Aldrich Chemicals Inc. (WI, USA) and were used as received. Phenol (CDH, Agra, India), formalin (34 weight % aqueous solution, Sisco Research, Mumbai, India), oxalic acid (E-Merck, India) were also used without further purification.

2.2. Instruments

FTIR spectra were recorded with a Nicolet 510P instrument. The cure characteristics of the resins were studied by DSC using a Mettler DSC-20 analyser at a heating rate of 10°C/min. Thermogravimetric analysis (TGA) was performed on a Du Pont 2000 thermal analyser in conjunction with 951-thermogravimetric analyser in nitrogen atmosphere at a heating rate of 10°C/min over the temperature range from room temperature to 700°C. NMR spectra were recorded with a Brucker 400AMX spectrometer. Gel Permeation Chromatography (GPC) analysis was performed on a Waters GPC model Delt prep.3000 using THF as eluent and with DRI-R 401 refractive index and UV (at 254 nm) detectors. Polystyrene standards were used for calibration. Elemental analyses were done with a Perkin Elmer model 2400 elemental analyser. Dynamic Mechanical Analyses (DMA) were carried out on a DuPont DMA 983 with a DuPont 9900 thermal analyser in Nitrogen atmosphere.

2.3. Synthesis of 3-phenyl ethynyl phenol (PEP)

3-phenyl ethynyl phenol was synthesized by slight modification of a reported procedure [29]. Thus, 3-iodophenyl acetate was prepared from 3-iodophenol using acetic anhydride-sodium acetate reagent following the usual acetylation procedure [30]. The reactants 3-iodophenylacetate (6.6 g, 49 mmol), phenyl acetylene (7.49 g, 74 mmol) and 25 mL of triethylamine were placed under nitrogen in a three-necked flask provided with a magnetic stirrer and condenser. Triphenylphosphine (9.3 mg, 3.54 mmol), bis(triphenylphosphine) palladium (II) chloride (46.5 mg, 0.06 mmol) and Cul (18.5 mg, 0.097 mmol) were added to it and washed down with another 25 mL of triethylamine. The reaction mixture was heated to 80°C and allowed to proceed for 10 h. After the reaction, the mixture was cooled to room temperature and the precipitate (triethylammonium iodide) was filtered off. The filtrate was flash evaporated to obtain a yellow oily mass, to which 50 ml of hexane was added and stirred vigorously. A dark red solution separated out of solution, which was decanted. The remaining solution was treated with charcoal. The filtrate was concentrated and cooled to get 3-phenylethynylphenyl acetate. Yield = 50%.

3-phenylethynylphenol was obtained by trans-esterification of 3-phenylethynylphenyl acetate (7.1 g, 30.1 mmol) dissolved in 75 ml methanol along with K_2CO_3 (4.16 g, 0.0301 mol) and warming at 50°C in a round bottomed flask fitted with condenser. The reaction mixture was stirred for 5 h after which, it was added to 100 ml of water and acidified with dil. HCl to a pH of 6. The light yellow solid, which precipitated out of solution, was filtered and dissolved in ether. The ether solution was treated with charcoal, dried over sodium sulfate and filtered. The filtrate was concentrated to get the crude 3-phenylethynylphenol, which was recrystallised from hexane to afford white needles in quantitative yield. The monomer was characterized by melting point and elemental analysis.

Melting point: 87°C; (reported 86°C)[29]

Elemental analysis

Calculated for $C_{14}H_{10}O$(%):	C-86.59	H-5.15
Observed (%):	C-86.14	H-5.30

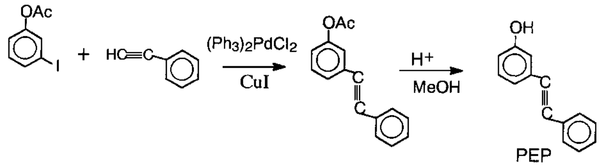
2.4. Synthesis of phenyl ethynyl functional phenol-formaldehyde resin (PEPF)

Phenyl ethynyl functional phenolic resins were prepared by polymerizing a mixture of phenol and PEP (in varying proportion) with formaldehyde under acidic conditions. In a typical case, phenol (1 g, 10.63 mmol), PEP (1 g, 5.15 mmol) and formaldehyde (1 ml of 34% formalin, 0.8 mol/mol phenol) were heated at 75°C for 10 h, in presence of oxalic acid (5 wt.%, 0.1 g) catalyst. The polymer was purified by precipitation of a solution of the polymer in acetone to water, redissolving it in acetone and reprecipitating in hexane to remove unreacted phenol and phenyl ethynyl phenol respectively. The purified polymer was dried under vacuum at 50°C for 12 h. It was characterized by spectral, elemental and GPC analyses. The same procedure was followed for various combinations of phenol and PEP and the homopolymer of PEP.

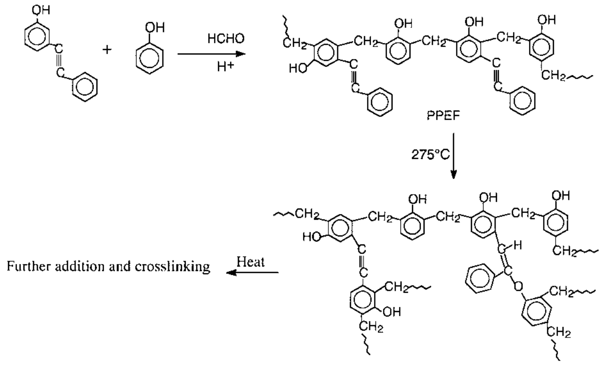
3. Results and discussion

Phenyl ethynyl phenol was synthesized as per the Scheme 1. The purity of the monomer was confirmed from melting point and elemental analysis.

Phenyl ethynyl functional novolac phenolic resins (PEPF) were prepared by copolymerising phenol, phenyl ethynyl phenol and formaldehyde under acid medium (Scheme 2). The molar ratio of phenols to



Scheme 1 Synthesis of PEP.



Scheme 2 Synthesis of PEPF and mechanism of crosslinking.

formaldehyde was maintained as 1:0.8. The percentage of functionalisation was varied by regulating the quantity of phenyl ethynyl phenol in the reaction mixture from 25–100%.

3.1. Optimization of reaction time

The polymerization reaction was performed at 75°C, since at this temperature the loss of formaldehyde by evaporation will be minimum and the reaction proceeds at a reasonably good rate. The reaction time was optimized by monitoring the reaction mixture by GPC at different time intervals. It was observed that the molecular weight increased and the distribution became broader as the reaction progressed. The relative concentrations of the polymer and the starting phenol reactants were determined by measuring the area under the GPC curves corresponding to each component. The product evolution with time is shown in Fig. 1. The polymer was formed in about 74% yield after 10 h for PEPF 100 (Table I). Polymer with reasonably good molecular weight distribution was obtained during this time. The polymer was purified by repeated precipitation in hot hexane after washing with warm water. The absence of the monomer in the purified polymer was confirmed from GPC, where the peaks due to the monomers were absent.

3.2. Characterisation of polymers

The copolymers obtained were characterised by FTIR, NMR, elemental analysis and GPC. The IR spectrum of the polymer showed a weak absorption at 2210 cm^{-1} due to the acetylene (C≡C) groups. The hydroxyl group absorptions are located at 3300–3600 cm^{-1}. The spectrum shows other characteristic absorptions due to aromatic groups at 1550 and 1600 cm^{-1}. A typical IR spectrum is shown in Fig. 2. ^{1}H NMR showed broad signals due to methylene bridges at 3.8–4.7 ppm and aromatic carbons at 6.7–7.4 ppm. The signals due to the methylene bridges formed between PEP moieties appeared at a lower field in comparison to the other methylene groups, due to the electron-withdrawing effect of the pendant phenyl group conjugated through the acetylene groups. Typical copolymer NMR is shown in Fig. 3. ^{13}C NMR spectrum of the polymers showed signals due to acetylene carbons at 89.4 ppm and 94–98 ppm, which confirms the incorporation of PEP in the polymer backbone. The acetylene carbons attached to the phenolic ring appeared broad at a higher ppm (94–98 ppm). The splitting in these signals is due to the effect of *ortho*- or *para*-methylene substitution in the phenolic ring. The acetylene carbon adjacent to the pendant phenyl ring also was split, although to a minor extent. Methylene carbon appeared at comparatively lower field than in conventional novolac. ^{13}C NMR of the homopolymer of PEP with possible assignments is shown in Fig. 4. The copolymer spectra were more complex. There was no spectral evidence for the presence of any —CH_2—O— linkage in the polymer.

TABLE I Composition and molecular weight characteristics of the PEPF resins (conversion: 74–80%)

Polymer Ref.	PEP in Feed (wt.%)	PEP in* Copolymer (wt.%)	Molecular Weight by GPC				
			M_n	M_w	M_p	M_w/M_n	Dpn
PEPF 25	25	24.0	780	3220	1600	4.1	6.5
PEPF 50	50	49.0	820	2720	1400	3.3	5.9
PEPF 75	75	73.8	620	1510	860	2.5	4.4
PEPF 100	100	100	650	1270	960	1.9	3.2

*After Accounting for CH_2-groups

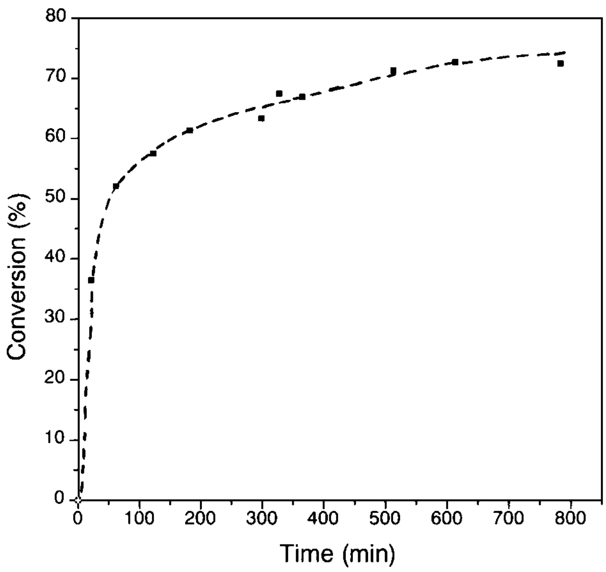


Figure 1 Monomer conversion with time for the polymerisation of PEP with formaldehyde.

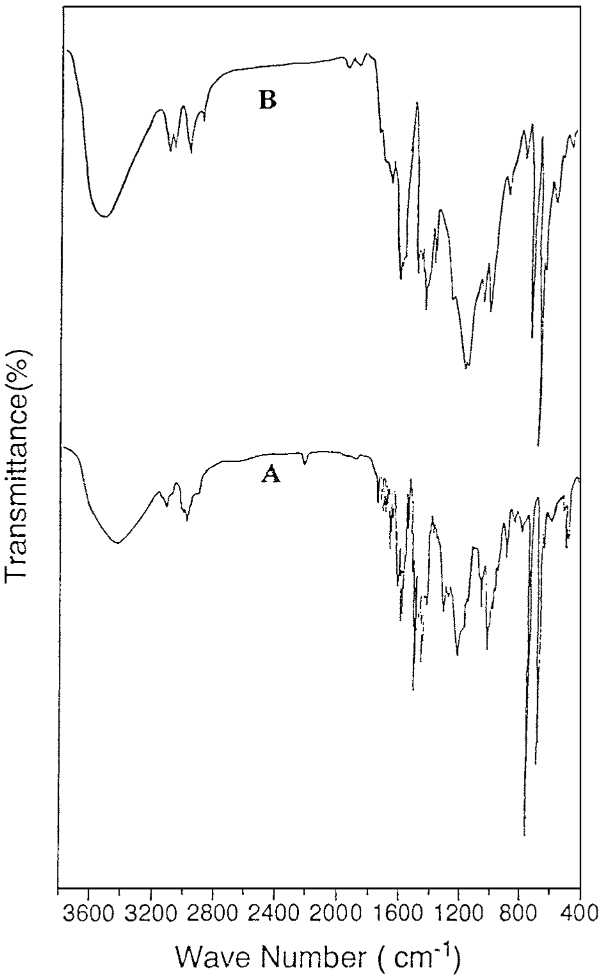


Figure 2 FTIR spectra of (A) PEPF-100 and (B) cured PEPF-100.

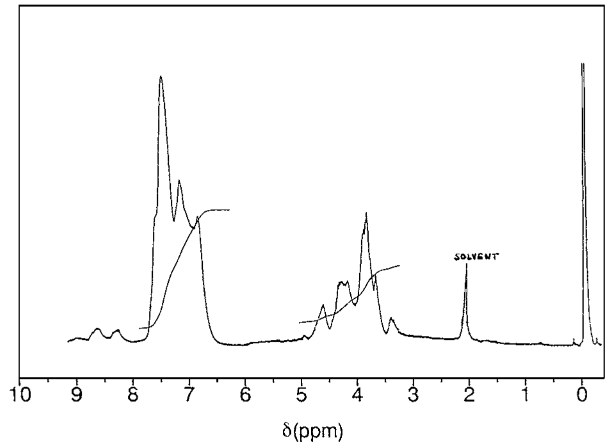


Figure 3 Proton NMR of PEPF-75 in d_6 acetone.

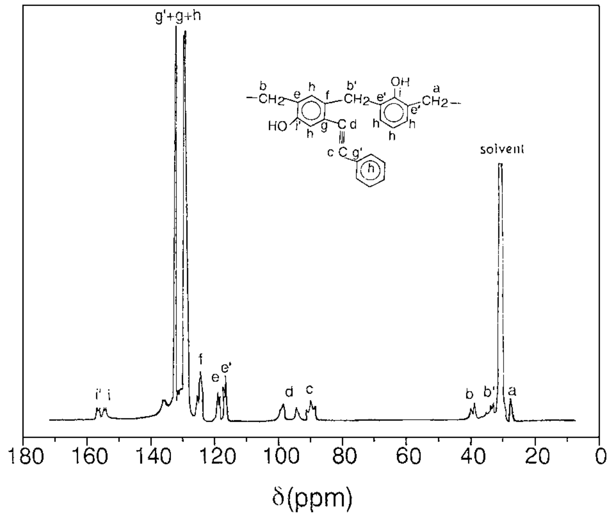


Figure 4 ^{13}CNMR of PEPF-100 in d_6 acetone.

Composition of the copolymer was determined from elemental analysis (carbon-content) and is given in Table I. The copolymer composition was only marginally different from the feed composition. The distribution of phenols in the copolymers can be considered as statistical, since the feed and copolymer compositions are practically the same.

The molecular weight characteristics of the polymers were determined by GPC, done in tetrahydrofuran (THF) and are in the range of peak molecular weight (Mp) 1600–850 g/mol, number average molecular weight (Mn), 620–780 g/mol, and weight average molecular weight 1270–3220 g/mol. The molecular weight characteristics of the polymers are compiled in Table I. It was found that as the percentage of phenyl ethynyl function in the reaction mixture increased, polymer possessed decreased molecular weight and degree of polymerization despite a constant P/F ratio of 1:0.8. This may be due to the less reactivity of the PEP towards formaldehyde in comparison to phenol. The molecular weight distribution became narrower as the PEP-content increased in the polymer for more or less the same conversion. The GPC traces of purified polymer are shown in Fig. 5.

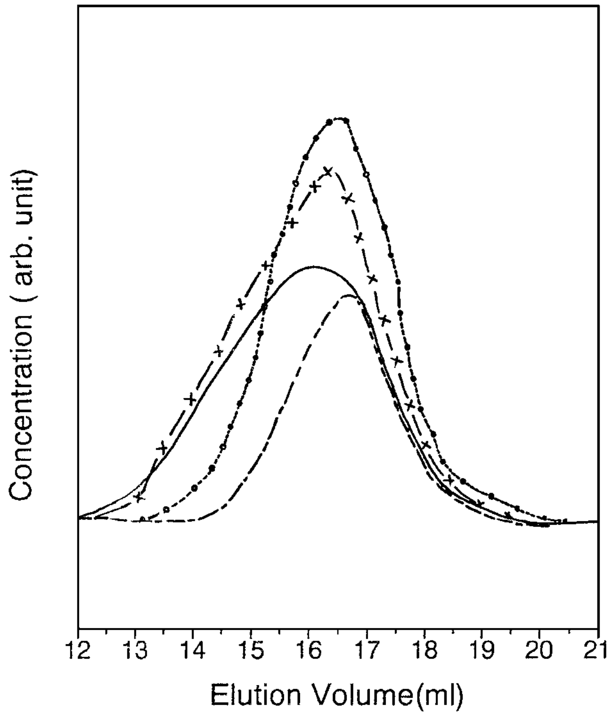


Figure 5 GPC profiles of purified polymers, x-x-x-: PEPF-25; —: PEPF 50; - - ●- - -●- - -: PEPF-75; - - - -: PEPF-100.

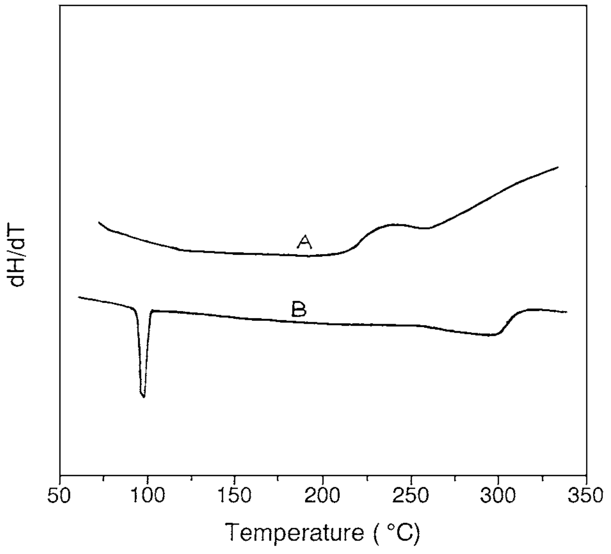


Figure 6 DSC thermograms of (A) PEPF-100 and (B) PEP, heating rate 10°C/min.

3.3. Cure characterization and thermal curing

Differential Scanning Calorimetry of the monomer (phenyl ethynyl phenol) showed that the curing of phenyl ethynyl group takes place at 320–350°C. However, in the case of polymer, the cure onset was observed at a significantly lower temperature of 235°C. The cure exotherm appeared in a broad range from 235°C to 280°C. Typical DSC thermograms are shown in Fig. 6. It is generally observed that as the number of functional groups increases, the cure becomes facilitated in case of acetylene functional polymers. This phenomenon has been observed in previous studies on propargyl ether novolac [5] and ethynylphenylazo novolac [6]. This arises from a kind of pseudo catalysis

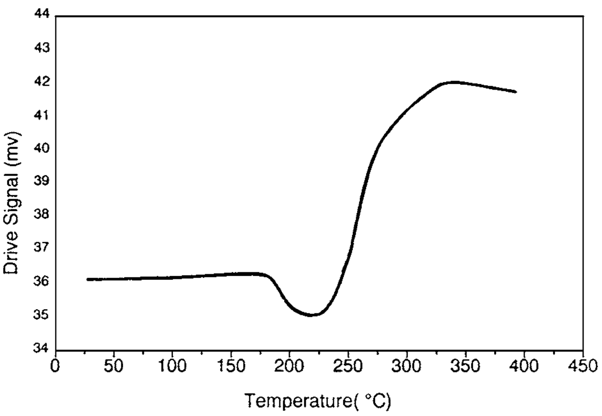


Figure 7 Non-isothermal DMA of PEPF resin at 1 Hz in N_2. Heating rate 5°C/min.

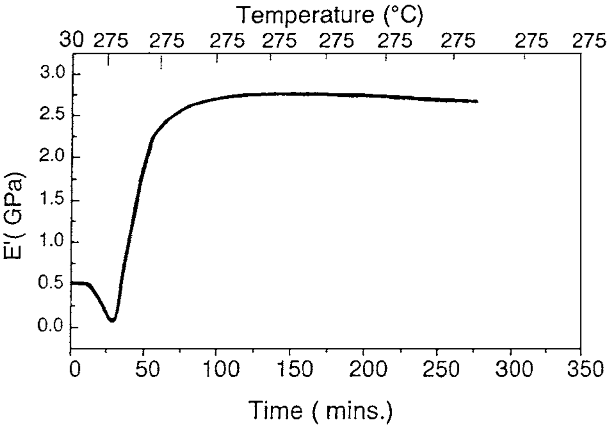


Figure 8 Isothermal DMA of PEPF resin at 275°C at 1 Hz in N_2. Heating rate for dynamic part 10°C/min.

caused by local enhancement of functional group concentration. The cure characterization was done by dynamic mechanical analysis (DMA) too. Since the resin could not be shaped, the DMA characterization was done using a single ply glass prepreg of it. The non-isothermal DMA depicted in Fig. 7 showed a single-stage curing, starting at 225°C. A sharp increase in storage modulus (E') was observed at around 275°C. Isothermal DMA at 275°C, shown in Fig. 8 indicated that the storage modulus (E') became stagnant in about 1 h at this temperature, implying the completion of cure under this condition. Hence all the resins were cured by heating them in vacuum at 275°C for minimum one hour. The cured polymer was insoluble in all solvents. FTIR spectra indicated no major change in the absorption pattern except for the disappearance of the weak $C{\equiv}C$ absorptions at 2210 cm^{-1}. The other notable changes that occurred on curing is an increase in the relative intensities of the absorption at 3150 cm^{-1} ($=C{-}H$) and at 1630 cm^{-1} (likely $C{=}C$ stretch). This is due to an increase in concentration of these groups formed by way of polymerization of ethynyl groups during curing.

The cure mechanism of phenyl ethynyl group has not been reported unambiguously. Although earlier proposals concern polyaddition of ethynyl groups as the probable mechanism [10, 18], Wood *et al.* [28]. investigated the cure mechanism of a model compound viz; 4-phenoxy-4′ phenylethynyl benzophenone and proposed that the cure takes place principally by the following reactions, (1) dimerization of ethynyl groups by head-head addition, accompanied by phenyl group migration (2) addition of phenoxy group to the triple bond accompanied by phenyl group migration, and (3) dimerization through formation of pseudo cyclobutadiene, rearranging to an ethynyl derivative and with elimination of diphenyl acetylene. Strong evidences existed for mechanism 2 and 3 rather than for 1. Thus, the cure mechanism appears complex and specific to the structure of phenyl ethynyl substituted compound. In the present work, no attempt was made to establish the actual cure mechanism since the main objective was to demonstrate the feasibility of designing phenyl ethynyl novolac and study of its characteristics. However, similarity in structure of the present compound with the one investigated by Wood *et al.*[28] permits us to propose the major cure mechanism as shown in Scheme 2. The addition of phenolic OH across the triple bond is more feasible than that of phenoxy group as proposed in model study. The resultant network could contain unsaturated groups, part of which may undergo further thermal polymerization. The increase in absorption of $=C{-}H$ and $C{=}C$ groups in the FTIR spectrum of the cured product lends support to this hypothesis. However, since the OH absorption did not decrease substantially, the other mechanisms, (1) and (3) may also be operative to significant extents. It is also likely that the polyaddition of ethynyl groups takes place. An attempt was done to identify the possible type of polymers formed from curing of PEPF by effecting the thermal polymerization of PEP. The high resolution GPC analysis of the products formed from PEP heated at 275°C for 2 h in vacuum is shown in Fig. 9. Evidently the conversion is less than quantitative, in tune with the DSC behaviour of the monomer. From the relative

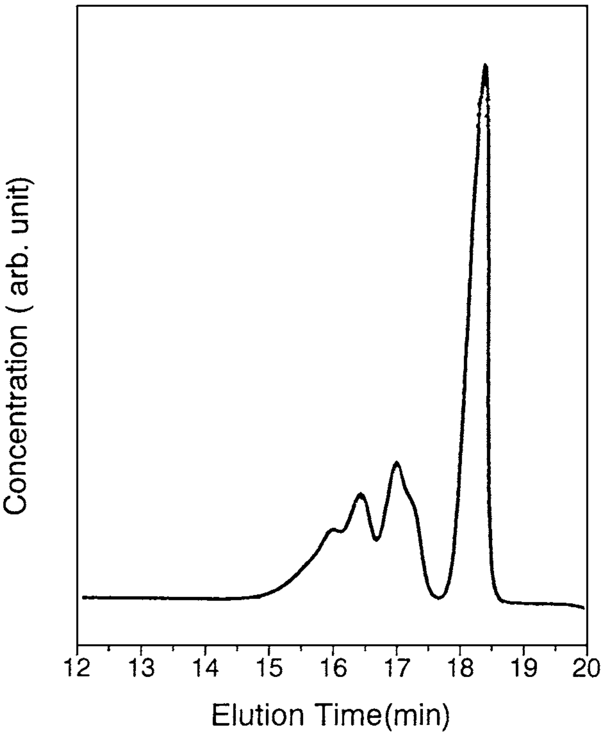


Figure 9 GPC traces of products formed from thermal polymerization of PEP.

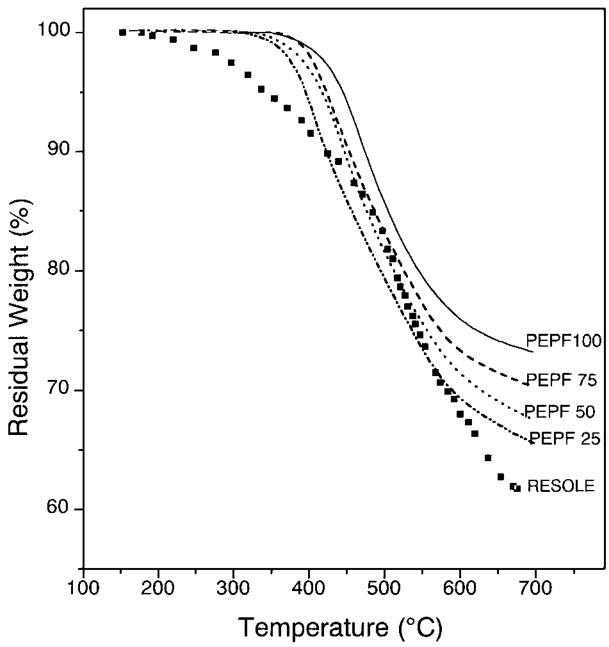


Figure 10 TGA traces of cured polymers in N_2. Heating rate 10°C/min.

retention time corresponding to each peak, the product mixture was identified to contain a significant proportion of trimer and tetramer and less amount of higher molar mass fractions, almost in conformation to the observation made by Wood *et al.* No attempt was done to isolate the fractions and identify them.

3.4. Thermal characteristics

The cured polymers were analyzed for their thermal stability by TGA which are shown in Fig. 10 for polymers with different degree of phenyl ethynyl functionalisation. For comparison, the TGA of cured resol (F/P ratio: 1.0) is also included. TGA of the cured polymers showed apparently a single step decomposition pattern starting above 335°C (see Table II). Ti, T_m and the char residue increased with increase in PEP-content and consequently the crosslink density. T_i increased from 300 for resol to 370°C for PEPF-100. The change in T_m was less significant. The resins left char in the range from 65.5 to 73.2% on enhancing the PEP content in the copolymer from 24.5–100%. This value is substantially higher than that of resol which gives char around 60% only. Thus, the phenyl ethynyl functionalization results in an increase in the overall thermal stability of the polymer. The stabilisation effect is felt particularly at initial stages and at higher temperature regime. It is also to be remarked that resol already looses about 26–28% volatiles during the condensation cure, whereas the PEPF systems are absolutely addition curable. Thus, the effective char residue in PEPF series is almost 70% more than that of resol. The increase in T_i values is a consequence of reduced concentration of methylene bridges, which is known to be the triggering point for thermal the degradation [31]. However, the decomposition at higher temperature is quite rapid probably due to the thermal decomposition occurring at the unsaturated crosslinking moieties.

TABLE II Thermal decomposition characteristics of PEPF resin (TGA in N_2, heating rate: 10°C/min)

Polymer Ref.	T_i(°C)	T_e(°C)	T_m(°C)	Char at 700°C
PEPF 25	335	620	400	65.5
PEPF 50	350	620	440	67.5
PEPF 75	360	640	450	70.3
PEPF 100	370	645	460	73.2
Resol	300	650	460	60

T_i, T_e and T_m are temperatures for onset of decomposition, end of major decomposition and maximum decomposition respectively.

4. Conclusions

Thermally stable addition curable phenolic resins were obtained on copolymerising PEP with phenol and formaldehyde. Regulating the feed composition could control the extent of ethynyl functionalisation. Narrow molecular weight distribution resulted on enhancing the PEP-content in the copolymer, but this caused a diminution in degree of polymerisation. The resin underwent a single-step cure at around 250–275°C. The cure optimisation was done by DMA studies. The cured resins exhibited enhanced thermal stability and anaerobic char residue vis-à-vis resol and these properties increased directly with the extent of ethynyl functionalisation.

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