

Evaluation of Isomeric Composition of Resol-Type Phenol Formaldehyde Matrix Resins for Silica–Phenolic Composites and Its Effect on Cure Characteristics of the Resin

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ABSTRACT: The isomeric composition of several samples of resol-type phenol formaldehyde resins used for silica-phenolic composites was evaluated by ^1H - and ^{13}C -NMR spectroscopy and reverse-phase HPLC techniques. The variations in the isomeric compositions were attributed to inadvertent variations in the process parameters. A mathematical relation was determined for calculation of free phenol from ^1H -NMR measurements. The samples were cured at 160°C for 8 h in an inert atmosphere of N_2 . The extent of cure in the hardened samples was measured by FTIR analysis. The effect of isomeric composition on the extent of cure was

studied. Free phenol and *p*-hydroxymethyl phenol, exhibiting a linear correlation, were found to have a pronounced effect on the extent of cure. The cure kinetics were derived by dynamic DSC measurements. Activation energy (E) for curing exhibited a near linear correlation independently with free phenol content and the extent of cure. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2517–2524, 2003

Key words: thermosets; NMR; high-performance liquid chromatography (HPLC); differential scanning calorimetry (DSC); resins

INTRODUCTION

The technical development of the first fully synthetic resins, phenol–formaldehyde (PF) resins formed from the reaction of phenol with formaldehyde, proceeded very rapidly after the discoveries of Bakeland.^{1,2} However, the understanding of the basic chemistry of the resins lagged far behind. The structural peculiarities of these resins are attributed to the polyfunctional nature of phenol (i.e., more than one site for aromatic substitution reactions). Under different sets of conditions such as temperature, pH, and catalyst, for example, the resins will exhibit differences in their isomeric compositions, chain length, and so forth. The specific details of the structure of a phenol–formaldehyde resin have a substantial effect on the nature, extent, and rate of curing (hardening).^{1–9} Because of the excellent fire-resistance and thermal-insulation properties attributed to its ablative nature, resol-type PF resins have found extensive applications as nozzle insulation materials as carbon– or silica–phenolic composites in rocketry in recent years. These resins are generally characterized by measuring a number of average properties like bulk viscosity, free phenol con-

tent, point of trouble, and total solid content by standard physicochemical methods. Because the resin is a complex mixture of 7–8 isomeric constituents, it seemed appropriate to evaluate the isomeric composition for a deeper understanding and better tailoring of the end properties of composites derived therefrom. Guided by this premise, in this study we report on the evaluation of isomeric composition and its effect on the curing characteristics of several samples of resol-type PF resins used for the production of silica–phenolic composites as ablative nozzle throat for liquid engines.

EXPERIMENTAL

Synthesis of resols

Phenol–formaldehyde resins were prepared with a formaldehyde to phenol ratio (F/P) of 1.0 using sodium hydroxide catalyst at a pH of 8.5–8.6 according to previously published procedures.¹⁰ The polymerization reactions were carried out at $95 \pm 1^\circ\text{C}$ for 90 min, allowed to attain room temperature, neutralized with glacial acetic acid, and allowed to stand overnight for phase separation of resin and water layers. The resin layer separated and dried under vacuum. Research samples used in this study were supplied by the PFC division of Vikram Sarabhai Space Centre.

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Characterization of resins

Physicochemical methods

Free phenol was isolated by steam distillation, reacted with a measured excess of bromine, and excess back titrated with standard sodium thiosulfate solution according to ASTM D 1312-93. Free formalin was estimated using a 50-mL aliquot from the same steam distillate, reacted with hydroxylamine hydrochloride reagent, and the liberated acid was titrated with standard sodium hydroxide solution. Point of trouble (water tolerance) was measured by titrating 10 mL of resin solution in ethanol (sp. gr. 0.863) with distilled water. Bulk viscosity was measured by a Brookfield (Middleboro, MA) viscometer with sample in a 600-mL long-form beaker kept in a large volume water bath maintained at $30 \pm 1^\circ\text{C}$. The refractive index (RI) was measured with an Abbe refractometer (Bausch and Lomb, Rochester, NY). Total solid content was determined by evaporating an accurately weighed about 0.5 g sample to dryness at 170°C for 30 min.

NMR measurements

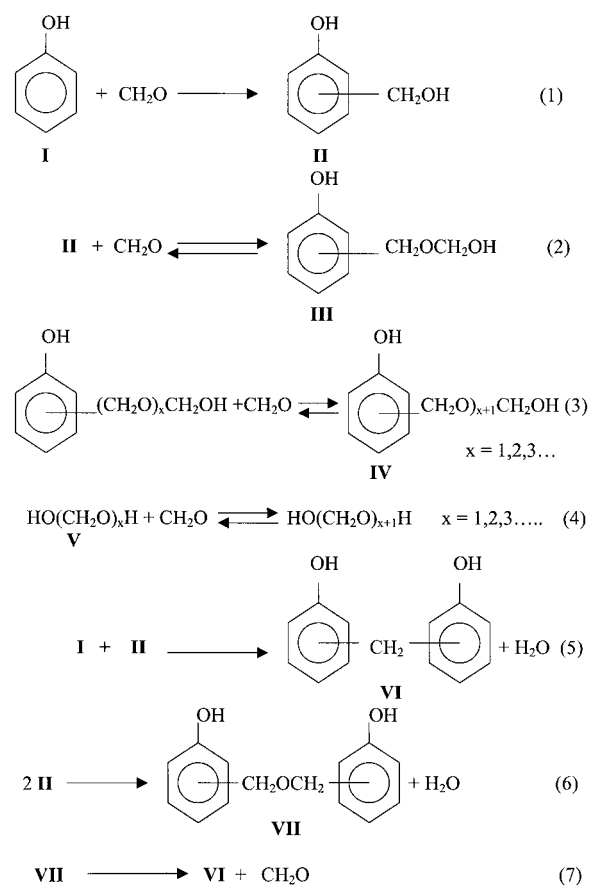
NMR spectra of the samples were recorded on a Bruker Avance 300 NMR spectrometer (Bruker Instruments, Billerica, MA) operating at 300 MHz for ^1H -NMR and 75.4 MHz for ^{13}C -NMR. All ^1H - and ^{13}C -NMR measurements were taken on an $\approx 5\%$ (w/v) solution in acetone- d_6 and CDCl_3 , respectively, using TMS as internal standard. The operating parameters for ^1H -NMR were as follows: sweep width: 3306.88 Hz; acquisition time: 4.95 s; pulse width: 9.7 μs ; pulse delay: 2 s; number of scans: 4. A proton noise decoupling technique was used for ^{13}C -NMR and other operating parameters were as follows: sweep width: 16,556.29 Hz; acquisition time: 0.99 s.; pulse width: 8 μs (corresponding to a nuclear tip angle of 90°); data points: 32; pulse delay: 2 s; number of scans: 5000.

HPLC analyses

Chromatographic measurements were done on a Waters 515 HPLC system (Waters Chromatography Division/Millipore, Milford, MA) coupled with a 410 RI detector using tetrahydrofuran (THF, HPLC grade) as eluant with a flow rate of 1.0 mL/min. A Hewlett-Packard reverse-phase (RP) NH_2 analytical column (Hewlett-Packard, Palo Alto, CA) was used for the separation of various chemical species. The sample size chosen was 200 μL [0.1% solution (w/v) in THF]. Millennium³² Chromatography Manager (Waters) was used for data reduction and computation of peak areas.

Extent of cure measurement

The samples were cured (hardened) at 160°C in an inert atmosphere of N_2 for 8 h. The extent of cure in



Scheme 1 General polymerization reaction products of phenol and formaldehyde in alkaline medium.¹¹

the hardened samples was measured using a Nicolet 510-P model FTIR spectrometer (Nicolet Analytical Instruments, Madison, WI). The spectra of powdered cured samples were scanned by KBr pellet technique with a spectral resolution of 2 cm^{-1} .

DSC

DSC thermograms were recorded on a Mettler (Nanikon, Switzerland) DSC 20 instrument using low pressure-proof aluminum pans at a heating rate of $5^\circ\text{C}/\text{min}$ under helium atmosphere purged at a rate of 50 mL/min. A sample size of $10 \pm 0.5 \text{ mg}$ was used in all cases. Cure reaction parameters and area integration of DSC curves were computed using the TA Universal Analysis software (TA Instruments, New Castle, DE).

RESULTS AND DISCUSSION

Different reaction mechanisms were proposed by different investigators¹¹⁻¹³ for the synthesis of phenol-formaldehyde resins and the general type reaction products formed are given in **Scheme 1**. The first step

TABLE I
Physicochemical Properties of PF Resins

Polymer no.	Viscosity (30°C) cps	Free phenol (%)	Free formalin (%)	Point of trouble (mL H ₂ O)	Total solids (%)	Sp. gr.	RI
I	554	17.1	0.10	14.7	73.3	1.198	1.571
II	480	18.0	0.15	15.1	72.9	1.200	1.570
III	410	17.8	0.15	15.0	72.9	1.197	1.570
IV	470	18.9	0.10	15.1	72.9	1.198	1.570
V	410	18.3	0.10	13.9	74.8	1.191	1.572
VI	400	18.9	0.10	14.2	75.0	1.192	1.571
VII	560	20.5	0.15	15.4	75.0	1.196	1.574

is the formaldehyde substitution on the free *ortho*- and *para*-positions of the phenol ring leading to *ortho*- and *para*-hydroxymethyl phenols (II), which may further react with formaldehyde producing di- and trihydroxymethyl phenols and may also participate in equilibrium reactions with formalin-forming hemiformals and polyformals (III and IV). These reactions are also accompanied by cocondensation-type reactions between two molecules (substituted or not) leading to

diphenylmethane-type methylene bridges (VI) and dibenzyl ether-type bridges (VII).

Physicochemical properties

The PF resins were characterized by standard physicochemical methods and the results are given in Table I. All polymers were produced with a F/P ratio = 1.0

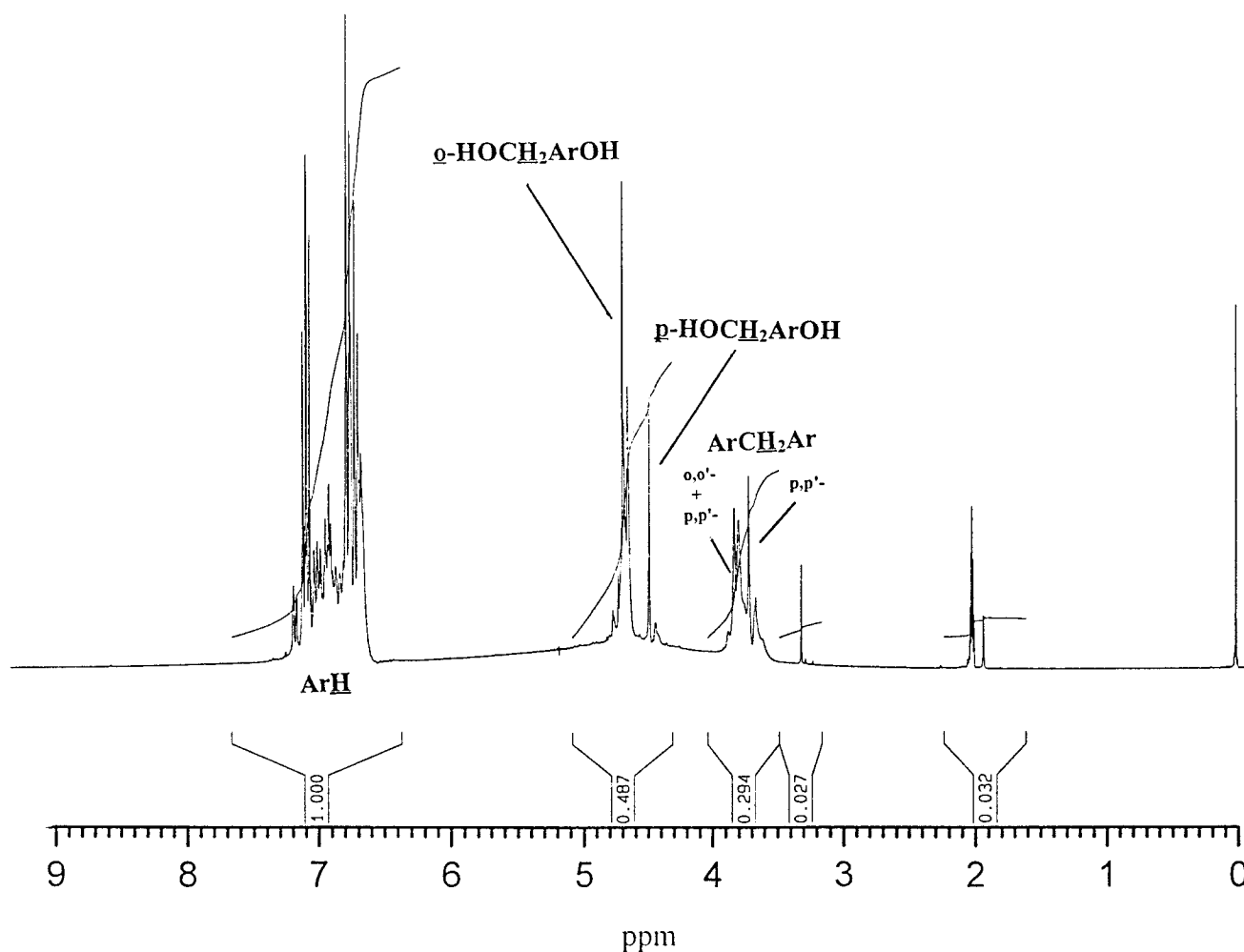


Figure 1 ¹H-NMR spectrum of polymer VI.

TABLE II
Number-Average Structures of PF Resins Calculated from $^1\text{H-NMR}^a$

Polymer no.	R_A	R_{HM}	R_{MB}	r_{HM}	r_{MB}	\bar{n}	$\bar{M}_n(\text{OH})$	F/P	Free phenol ^b (%)
I	3.78	0.44	0.37	2.75	0.93	1.59	180	1.22	15.2
II	3.85	0.46	0.32	2.11	0.94	1.47	165	1.16	17.5
III	3.93	0.46	0.31	2.38	0.73	1.45	160	1.06	18.3
IV	3.93	0.48	0.27	2.25	0.72	1.37	155	1.06	19.7
V	3.94	0.47	0.29	2.22	0.90	1.41	160	1.05	19.0
VI	3.97	0.48	0.28	2.76	0.82	1.39	155	1.02	19.0
VII	4.02	0.49	0.25	3.12	0.86	1.33	150	1.01	20.5

^a R_A , average number of aromatic ring protons per aromatic ring ($=A_2/A_1$); R_{HF} , average number of benzyl-type hemiformal groups per aromatic ring ($=A_3/4A_1$); R_{HM} , average number of hydroxymethyl groups per aromatic ring [$=(A_4 + A_5)/2A_1$]; R_{MB} , average number of diphenylmethane-type methylene bridges per aromatic ring [$=(A_6 + A_7)/2A_1$]; r_{HM} , ratio of the number of *o*-hydroxymethyl groups to the number of *p*-hydroxymethyl groups ($=A_4/A_5$); r_{MB} , ratio of the number of *p,p'*-methylene bridges to the number of *o,o'*- plus *o,p'*-methylene bridges ($=A_7/A_6$); \bar{n} , average number of aromatic rings per molecule [$=(1 - (R_{MB})^{-1})$]; $\bar{M}_n(\text{OH})$, number-average molecular weight [$=\bar{n}(89 + R_A + 61R_{HF} + 31R_{HM} + 14R_{MB})$].

^b Free phenol = $[1 - (R_{HM} + R_{MB})] \times 94 \times 100 / (124 - 18R_{MB})$.

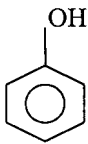
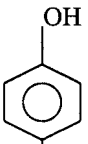
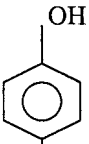
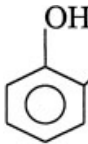
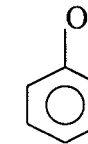
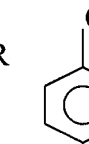
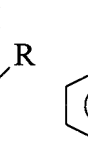
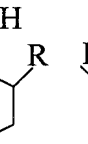
under identical conditions and inadvertent variations in process parameters resulted in polymers I–VII.

Number-average structures by $^1\text{H-NMR}$

A typical $^1\text{H-NMR}$ spectrum of polymer VI taken in acetone- d_6 is shown in Figure 1. The spectral peak assignments and the computation of number-average structures were done according to the method of Woodbrey et al.¹¹ It is observed that under the present experimental conditions, benzyl-type hemiformals [$\text{Ar}(\text{CH}_2\text{O})_2\text{H}$; 4.95–4.76 ppm] and dibenzyl ether-type methylene linkages [$\text{Ar}(\text{CH}_2)_2\text{O}$; ~ 4.45 ppm] were not formed in measurable quantities. The number-average structures of resol resins without ether

bridges were determined using the following ratios. A_1 = relative number of phenolic hydroxyl protons, ArOH , the value of which cannot be measured for resols because of exchange among the phenolic and other types of hydroxyl protons present; A_2 = relative number of aromatic ring protons, ArH , 7.74–6.62 ppm; A_3 = relative number of methylene protons in benzyl-type hemiformal groups, $\text{Ar}(\text{CH}_2\text{O})_2\text{H}$, 4.95–4.76 ppm (not observed); A_4 = relative number of methylene protons in *o*-hydroxymethyl groups, *o*- HOArCH_2OH , 4.76–4.60 ppm; A_5 = relative number of methylene protons in *p*-hydroxymethyl groups, *p*- HOArCH_2OH , 4.50–4.43 ppm; A_6 = relative number of methylene protons in *o,o'*- and *o,p'*-diphenylmethane-type methylene bridges, *o,o'*- plus *o,p'*-

TABLE III
Quantification of Isomeric Composition by $^{13}\text{C-NMR}^a$

Polymer no.	Chemical species/chemical shift ^b (ppm)								M_n
									
	(158.1)	(157.3)	(156.1)	(155.9)	(154.0)	(153.7)	(152.6)	(151.1)	
I	15.7	5.4	19.1	16.0	15.9	4.1	19.0	4.8	163
II	18.1	6.1	20.2	17.7	13.9	3.6	20.3	0.0	159
III	18.7	6.3	20.4	18.2	13.6	2.9	19.9	0.0	158
IV	18.2	6.8	16.9	18.9	14.2	3.5	21.5	0.0	158
V	19.6	6.5	20.3	19.2	12.4	3.2	18.6	0.0	157
VI	20.4	6.9	19.7	18.6	12.7	2.8	18.8	0.0	156
VII	19.1	7.1	19.2	18.3	13.9	2.8	19.6	0.0	157

^a Isomeric composition = $(P_i M_i / \sum P_i M_i) \times 100\%$; $M_n = \sum P_i M_i / \sum P_i$, where P_i is the spectral peak intensity of species i , and M_i is the molecular weight of species i .

^b R = $-\text{CH}_2\text{OH}$; R' = $-\text{CH}_2-\text{Ar}$.

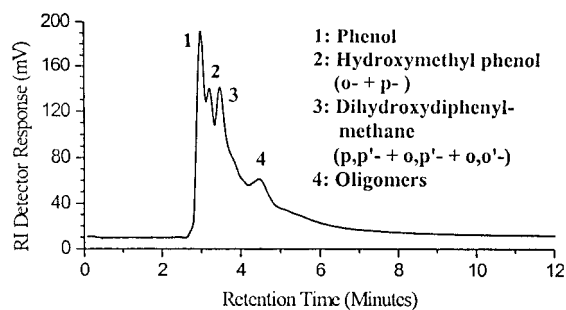


Figure 2 HPLC of polymer IV.

TABLE V
IR Absorption Characteristics of Cured Phenolic Resins

Polymer no.	Relative optical density		
	$\frac{[I]_{818}}{[I]_{754}}$ (R)	$\frac{[I]_{1595}}{[I]_{818}}$ (R ₁)	$\frac{[I]_{1595}}{[I]_{754}}$ (R ₂)
I	0.7362	1.7333	1.2822
II	0.8682	1.5071	1.2499
III	0.9134	1.3480	1.2831
IV	0.9620	1.3750	1.2983
V	0.9316	1.8064	1.6970
VI	0.9714	2.4840	2.2143
VII	0.9926	1.7778	1.4545

TABLE IV
Isomeric Composition by HPLC Analysis^a

Polymer no.	Free phenol	Hydroxymethyl phenol (<i>o</i> - + <i>p</i> -)	Dimer <i>p,p'</i> - + <i>o,o'</i> - + <i>o,p'</i>	Oligomer
I	17.5	17.6	36.6	28.3
II	18.0	19.2	36.6	26.2
III	17.8	14.1	36.8	31.3
IV	19.5	14.0	36.5	30.0
V	18.2	17.3	38.5	26.0
VI	19.2	16.8	39.1	24.9
VII	19.8	16.7	39.7	23.8

^a Isomeric composition is given as weight percentage.

HOArCH₂ArOH, 3.90–3.71 ppm; A₇ = relative number of methylene protons in *p,p'*-diphenylmethane-type methylene bridges, *p,p'*-HOArCH₂ArOH, 3.67–3.48 ppm. The values of A₁ were obtained by calculation from other experimental integrals, that is, A₁ = (1/5)[A₂ + (A₃/4) + (1/2)(A₄ + A₅) + A₆ + A₇]. The various number-average structures were calculated from the above integrals (A₁–A₇); the details of calculation¹¹ and the values obtained are given in Table II.

The ratio of the number of *o*-hydroxymethyl groups (*o*-HOArCH₂OH; 4.76–4.60 ppm) to the number of *p*-hydroxymethyl groups (*p*-HOArCH₂OH; 4.50–4.43 ppm) was provided by the *r*_{HM} value. A value of *r*_{HM} = ≈ 2.0 obtained in the present study indicates that hydroxy methylation at the *o*-position is much faster than that at the *p*-position and the present value obtained is much lower than the value of 4.18 reported by Woodbrey et al.¹¹ This could probably be attributed to the fact that a higher reaction temperature (90–95°C) used in the present study would have substantially increased hydroxymethylation at the *p*-position. Further, the advancement of the condensation reaction was much less in the present case, leaving a comparatively higher proportion of *p*-hydroxymethyl phenol in the reaction mixture. The *r*_{MB} value = ≈ 1.0 [*r*_{MB} = no. of *p,p'*-methylene bridges/(no. of *o,o'*- + *o,p'*-methylene bridges)] indicates that under the present experimental conditions, *p,p'*-condensation was almost equal to the combined *o,o'*- and *o,p'*-condensations and much faster than the individual

o,o'- or *o,p'*-condensations. A value of *r*_{MB} = 1.44 was reported by Woodbrey et al.¹¹ Free phenol content in the resin was calculated from the average number of hydroxymethyl groups (R_{HM}) and diphenylmethane-type methylene bridges (R_{MB}) per aromatic ring. The free phenol content computed from ¹H-NMR measurements are presented in Table II and are quite comparable to the values obtained by standard chemical analysis. The monomer feed ratio was calculated from the relation F/P = [(A₄ + A₅)/2 + A₆ + A₇]/A₁ and was found to be higher than the charged ratio of 1.0 mainly because of loss of free phenol during synthesis and purification.¹¹

Isomeric composition

¹³C-NMR spectra

The residuals and the different species formed during the polymerization reaction were identified and quantified by ¹³C-NMR based on the method of Grenier-Loustalot et al.¹⁴ Particular attention was paid to the zone 160–150 ppm of quaternary carbons bearing hydroxyl groups. These quaternary carbons were stereosensitive to the chemical environments. In particular, the bands around 156, 153, and 151 ppm (*para*-substituted carbons of phenol rings) and 155.7, 154, and 151 (attributed to *ortho*-substituted carbons of phenol rings) were the probes used to characterize the prod-

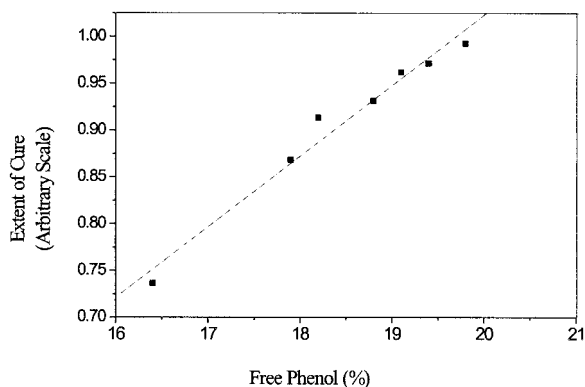


Figure 3 Plot of extent of cure versus free phenol (%).

ucts formed and the band at 158.1 ppm was used for the assay of residual phenol. The results are presented in Table III. The residual phenol contents calculated from ^{13}C -NMR are in good agreement with the values obtained by ^1H -NMR and chemical analysis. Further, the results obtained for M_n are also consistent with ^1H -NMR values. A very small quantity of the dimer formed from trimethylol phenol was found in the case of polymer I. This is quite reasonable given that the net F/P ratio was the highest for polymer I.

Methylene carbons formed between two aromatic rings during the reaction were used as a comparative index of cocondensations by probing the 45- to 30-ppm resonance bands (40 ppm: p,p' -; 35 ppm: o,p' -; 30 ppm: o,o' -linkages). The relative quantities of various methylene linkages as estimated from the 45- to 30-ppm region are in good agreement with the values calculated using the 160- to 150-ppm region. Contrary to earlier observations,¹⁴ o,o' -linkages were formed in comparable quantities, about 80% of p,p' -linkages.

HPLC

The major isomeric constituents present in the resin were fractionated by HPLC using a Hewlett-Packard NH_2 analytical column.¹⁵ A typical chromatogram is given in Figure 2. Free (residual) phenol in the chromatogram was identified and quantified using authentic samples of phenol. Other chemical species were quantified by peak area measurements and identified by comparison with the quantities determined from ^{13}C -NMR and the results obtained are given in Table IV. The free phenol content measured with the present HPLC method is in excellent agreement with the values generated by standard chemical analysis and ^1H - and ^{13}C -NMR methods, indicating that this method could be used as a quick method for estimation of free phenol in resol-type resins. Under the isocratic HPLC conditions used in the present study, o - and p -hydroxymethyl phenols could not be resolved and appeared as a single peak. Similarly, the different

binuclear moieties with p,p' -, o,p' -, and o,o' -linkages could not be separated and eluted simultaneously. However, Grenier-Loustalot et al.¹⁴ could resolve the different isomeric components present in resol-type resins using gradient elution techniques with Spherisorb ODS-2 analytical column.

Effect of isomeric composition on extent of cure

FTIR studies

The cured resins were characterized by their IR spectra and the relative intensities (I) of absorptions at 818 and 754 cm^{-1} ($R = [I]_{818}/[I]_{754}$), which can be assigned to the C—H out-of-plane deformations, were considered as a measure of the extent of ring substitution.^{16,17} In addition, the intensity of peak at 1595 cm^{-1} (aromatic C=C stretching) is expected to be nearly constant and its ratio to the intensities of peaks at 818 and 754 cm^{-1} were also considered to determine the extent of cure and the results obtained are given in Table V.

The effect of isomeric composition on the extent of cure was evaluated by studying the variation of R (Table V) with the constituent chemical species present in the resin. The excellent linearity obtained for R versus free phenol content plot as shown in Figure 3 indicates that curing is mostly controlled by the quantity of free phenol present in the resin. This could be reasoned by the fact that an aromatic ring functionality of three (two o - and one p -) in free phenol controls cocondensation, leading to a three-dimensional network (curing) through methylene linkages, and prevents formation of ether linkages by condensation through hydroxymethyl groups as revealed by ^1H - and ^{13}C -NMR. The formation of ether linkages is undesirable from the perspective of thermal stability of the hardened resin. Thus free phenol in the resin provides a double advantage, that is, increasing the extent of cure and preventing formation of ether link-

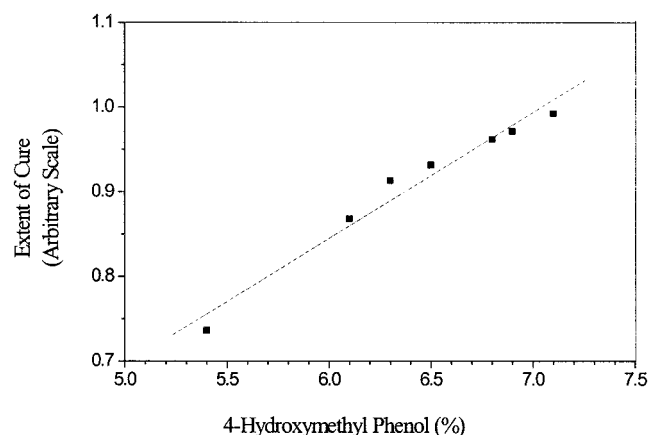


Figure 4 Plot of extent of cure versus 4-hydroxymethyl phenol (%).

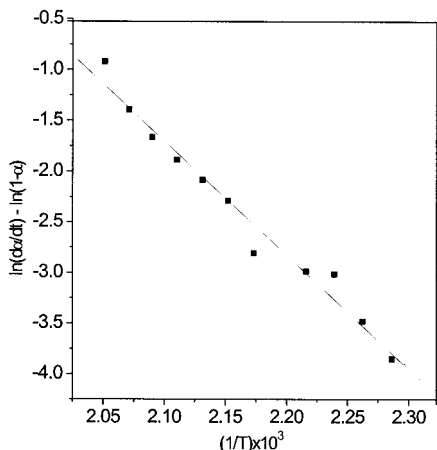


Figure 5 Chatterjee-Conrad plot for polymer VII.

ages, both contributing to enhanced thermal stability of the cured product. *p*-Hydroxymethyl phenol is known to have a higher cocondensation reactivity compared to that of its *o*-isomer and thus is expected to have a pronounced effect on the extent of cure—this was also found to be so in the present study (Fig. 4).

Cure kinetics by DSC

The cure kinetics of the resins were studied by dynamic DSC at a heating rate of 5°C/min in an inert atmosphere of helium. The fractional conversion α , calculated from the fractional and total areas under the DSC curve, was used for computation of kinetic parameters using the Chatterjee-Conrad method.¹⁸ In this method, $[\ln(d\alpha/dt) - \ln(1 - \alpha)]$ is plotted against $1/T$ and the activation energy (E) was calculated from the slope. The complete curing reaction took place in a single stage as evidenced from the Chatterjee-Conrad plot (Fig. 5). The kinetic parameters obtained by this method are summarized in Table VI. These results show that the activation energy for curing showed a decreasing trend with increase in free phenol content (Fig. 6), indicating that free phenol enhances curing by decreasing E . Further, the E values showed a near linear inverse correlation with the extent of cure (Fig. 7). These results corroborate the earlier inferences that

TABLE VI
Cure Kinetic Parameters DSC Analysis^a

Polymer no.	T_i (°C)	T_c (°C)	T_p (°C)	ΔH (J/g)	E (kJ/mol)	r
II	137.5	200.7	169.4	179.0	115.0 ± 6.4	0.9764
V	138.0	217.0	174.4	435.5	109.5 ± 4.1	0.9903
VI	162.0	210.0	176.0	616.6	108.4 ± 5.9	0.9898
VII	160.0	219.0	175.4	608.9	102.8 ± 7.7	0.9757

^a T_i ; cure initiation temperature; T_c ; cure completion temperature; T_p ; cure peak temperature; E , activation energy; r , correlation coefficient.

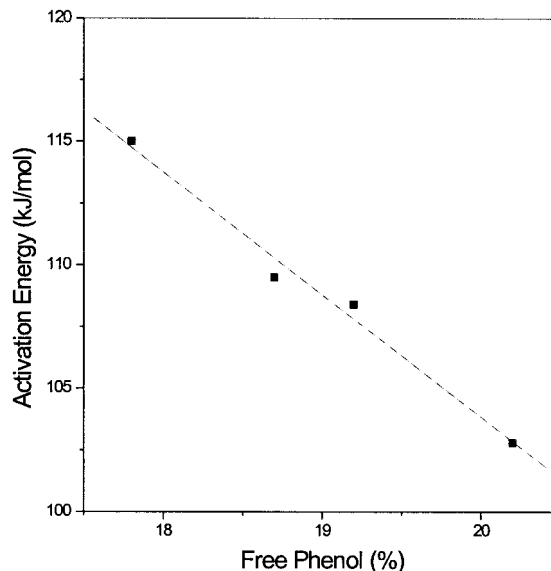


Figure 6 Plot of activation energy (E) versus free phenol (%).

free phenol increases the extent of cure in phenolics.

CONCLUSIONS

The important conclusions that can be drawn from the present study are as follows:

1. The isomeric composition of resol-type PF resins has a pronounced effect on the extent of cure obtained with these systems.
2. Residual phenol and *p*-hydroxymethyl phenol play a major role in the curing of resols and they independently exhibited linear correlation with the extent of cure.

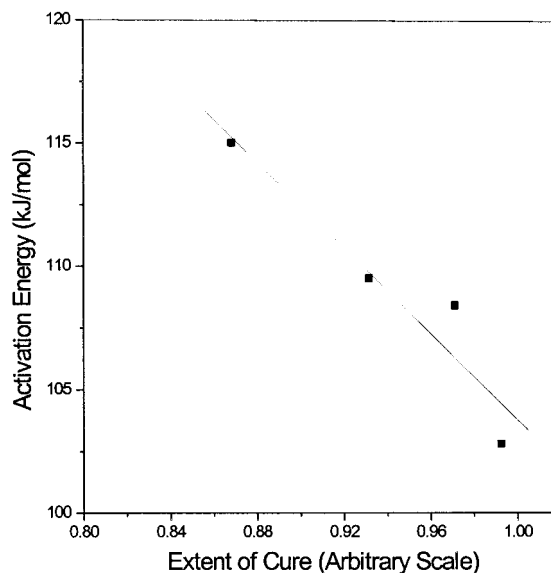


Figure 7 Plot of activation energy (E) versus extent of cure.

3. Free phenol decreases the activation energy of curing, facilitating the attainment of an even greater extent of cure.
4. Activation energy (E) of curing exhibited a near linear inverse correlation with the extent of cure.

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