

Structural Analysis of Phenolic Resole Resins

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Synopsis

The chemical structure and cure characteristics of a group of phenolic resole resins were studied by means of three major analytical techniques. In particular, the effects on structure and reactivity of formaldehyde/phenol ratio and the type of reaction catalyst used were studied. Gel permeation chromatography was used to determine resin molecular weight distributions, and NMR, to determine chemical structural features. In this connection a selective oxidation procedure, converting free methylol groups to aldehydes, has allowed unambiguous determination of methylene ether bridge structures to be made from the NMR data. The F/P ratio in a resole largely determines the type of molecular structures which are formed. However, triethylamine as a catalyst tends to favor methylene ether bridge formation, whereas sodium hydroxide favors methylene bridges. The rate and direction of subsequent thermal cure of the resoles prepared is shown by differential scanning calorimetry to depend markedly on the type of catalyst present during the curing stage. The DSC curing curves are interpreted in the light of the structural information provided by NMR.

INTRODUCTION

The nature and distribution of molecular species formed during the preparation and subsequent thermal cure of a phenol formaldehyde resole depend on reaction conditions such as formaldehyde/phenol ratio (F/P), the nature and amount of catalyst present, and the reaction time and temperature. Full characterization at the resole stage is difficult because of the complex distribution of molecular products formed and their thermal reactivity, while after the thermal cure stage the high molecular weight products formed are essentially insoluble, intractable materials. Thus, although they are one of the oldest commercially exploited polymers, it is only comparatively recently that techniques have been available which have enabled anything approaching comprehensive analyses to be carried out.

During resin preparation, there are several well-characterized types of reaction which may take place: (i) the addition of formaldehyde to phenol to form mono-, di-, and possibly trimethylol phenols; (ii) the condensation of methylol phenols with a phenolic ring hydrogen to form diaryl methanes (i.e., methylene bridges); (iii) the condensation of methylol phenols with themselves to form dibenzyl ether links (i.e., methylene ether bridges); and

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(iv) the elimination of formaldehyde from a methylene ether bridge to give a diaryl methane.

In this study, which was part of a larger program of work on the structure and properties of phenolic resoles, a set of four closely related resole resins has been prepared and characterized to investigate the effect of F/P ratio and reaction catalyst on resin structure and its subsequent reactivity.

Nuclear magnetic resonance (NMR) has been the principal analytical tool in examining the resins immediately after preparation. The difficulty which is normally experienced in distinguishing between methylol groups and methylene ether bridges has been overcome by a novel oxidation procedure utilizing manganese dioxide.

The resins have also been analyzed at the same stage of cure by gel permeation chromatography (GPC). While the technique has been put to only limited use here, its value in presenting a clear picture of molecular weight distribution has been demonstrated.

Finally, differential scanning calorimetry (DSC) has been applied to resin-impregnated paper samples in an attempt to understand how the resins react during thermal cure.

EXPERIMENTAL

Preparation of Resins

All resins were prepared from 90% phenol and 36% formaldehyde solutions with either triethylamine (TEA) or sodium hydroxide as the catalyst. A group of four resins was examined in detail. Formulations were based on two F/P ratios and the two catalysts, Table I showing the reactants used in terms of their mole ratios.

TABLE I
Mole Ratios of Reactants

Resin no.	F/P	TEA catalyst	NaOH
1	1.7/1	0.0186	—
2	1.7/1	—	0.0186
3	1.3/1	0.0262	—
4	1.3/1	—	0.0262

Resins 1 and 2 were prepared by refluxing the reactants at 75°C for 2 hr, cooling, and then vacuum distilling off the bulk of the water below 50°C. Resins 3 and 4 were refluxed at normal boiling point (98°C) for different lengths of time: resin 3 for 40 min and resin 4 for 30 min. Water was vacuum distilled from both resins at temperatures up to 50°C.

Bulk Resin Properties

Table II gives details of the results of some standard laboratory tests of the type applied to commercial phenolics in order to assess their handleability and performance characteristics.

The free phenol content was determined by steam distillation of a resin sample followed by measurement of the UV absorption of the aqueous distil-

TABLE II
Bulk Resin Properties

Test	Resin	1	2	3	4
S.G. at 20°C		1.195	1.242	1.191	1.200
Gel time at 120°C, min		28	18	33	15
B.S.S. solids content, %		57	75	68	61
pH		7.5	8.3	7.9	8.4
Free phenol content, %		10.1	12.0	10.7	7.4
Free formaldehyde content, %		4.8	3.6	1.2	0.2

late, on a Perkin Elmer 137 spectrometer. The primary band for UV absorption of phenol occurs at $\lambda_{\text{max}} = 212 \text{ m}\mu$. Each determination was performed in duplicate. The procedure used for free formaldehyde determination was as follows. The pH of a resin sample dissolved in methylated spirits was adjusted to 3.50. To this was added hydroxylamine hydrochloride solution, also pH adjusted to 3.50. The solutions were mixed and allowed to stand for at least 30 min. The liberated acid was then titrated back to pH 3.50 with 1*N* sodium hydroxide solution. Blank titrations were carried out and each determination was duplicated.

Instrumental Procedures

The NMR and GPC analyses were carried out directly on the liquid resins immediately after preparation. The resins were also impregnated into natural Kraft paper which was subsequently oven dried at 160°C for 4 min. The treated papers contained approximately 29% resin at a total volatile content of 8% based on total sample weight. These impregnated papers provided convenient samples for the DSC analysis.

Samples of oxidized resins were prepared for NMR as follows. Each resin sample was dissolved in acetone and shaken overnight (approximately 17 hr) at room temperature with approximately seven times its own weight of freshly prepared MnO₂.¹ The MnO₂ was then filtered off, washed thoroughly with acetone, and the filtrate containing the oxidized resin placed in a vacuum oven at room temperature for approximately 20 hr until all the acetone was removed.

The NMR spectra were obtained using a Varian T60 spectrometer operating at an applied radio frequency of 60 MHz. Samples were prepared by dissolving approximately 100 mg resin in 0.5 ml acetone-*d*₆.

For the GPC analysis, a Waters 200 chromatograph was employed. A solvent flow rate of 1 ml/min and an operating temperature of 30°C were used. Samples were approximately 3% solutions in tetrahydrofuran. A calibration plot was prepared using polypropylene glycol standards, pure phenol, etc., and is presented as Figure 3.

The DSC data were obtained using a Perkin-Elmer DSC-1B. The temperature range scanned was approximately 50°C to 220°C at 8°C/min with a range of 4 m cal/sec full-scale deflection. Samples were prepared by punching out three or four discs of resin impregnated paper which were then sealed in a small aluminum screw top pressure cell.² A similar cell was used

as a reference. The resin content of the treated papers having been determined, the weight of the resin sample was thus known.

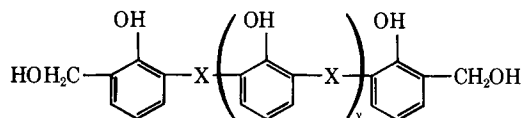
RESULTS AND DISCUSSION

NMR Analysis

Spectra of all four resins immediately after preparation are all basically similar with slightly differing functional group ratios. A typical example is presented in Figure 1, which is actually that for resin 1. Those resins incorporating TEA produce spectra with corresponding absorptions. Spectral assignments for phenolic resins are well documented.³⁻⁶ The two singlets at δ 4.75 and 4.55 are due to ortho- ArCH_2O — and para- ArCH_2O —, respectively. These could represent free methylol groups ArCH_2OH or methylene ether bridges $\text{ArCH}_2\text{OCH}_2\text{Ar}$: unfortunately it is impossible to distinguish between them from these spectra. However, if the methylol groups can be further reacted, for example, by selective oxidation to aldehydes, then the two groups may be identified. This has been achieved in the present work by a room-temperature oxidation with active manganese dioxide, as described in the experimental section.

From the spectra of the oxidized samples, the peaks due to ortho- and para- ArCH_2O — can be seen to be diminished due to removal of methylol groups, and a new peak appears at around δ 10 which indicates the new aldehyde groups formed. The NMR spectrum of resin 1 following oxidation is shown in Figure 2. That all the methylol groups were oxidized is demonstrated by the fact that no —OH peak appears at around δ 5.6 since phenolic —OH groups adjacent to carbonyl groups absorb at δ 11–12.⁷ Thus, the $\text{ArCH}_2\text{OCH}_2\text{Ar}$ groups remain unincumbered. It may be the case that some methylol groups were oxidized beyond the aldehyde stage to acids or that aldehydes were converted to acetals, but this is unimportant for our analysis. The significant point is that knowing from the first spectra the total numbers of ArCH_2O — groups, the ArCH_2OH proportion can be calculated when $\text{ArCH}_2\text{OCH}_2\text{Ar}$ is known independently. Thus, integration of peak areas (the final figures being an average of instrument integrations and results obtained by cutting out peaks followed by accurate weighing) for the four initial resins plus the four oxidized resins enabled the following groups to be quantitatively determined: ArH , OH, *o*- ArCH_2O —, *p*- ArCH_2O —, ArCH_2Ar , and $\text{ArCH}_2\text{OCH}_2\text{Ar}$.

In order that direct structural comparisons could be made between the types of resins, the following model was proposed for the bulk structure of the unoxidized resins:



where $\text{X} = -\text{CH}_2\text{OCH}_2-$ or $-\text{CH}_2-$ and $y =$ probably 1 or 2.

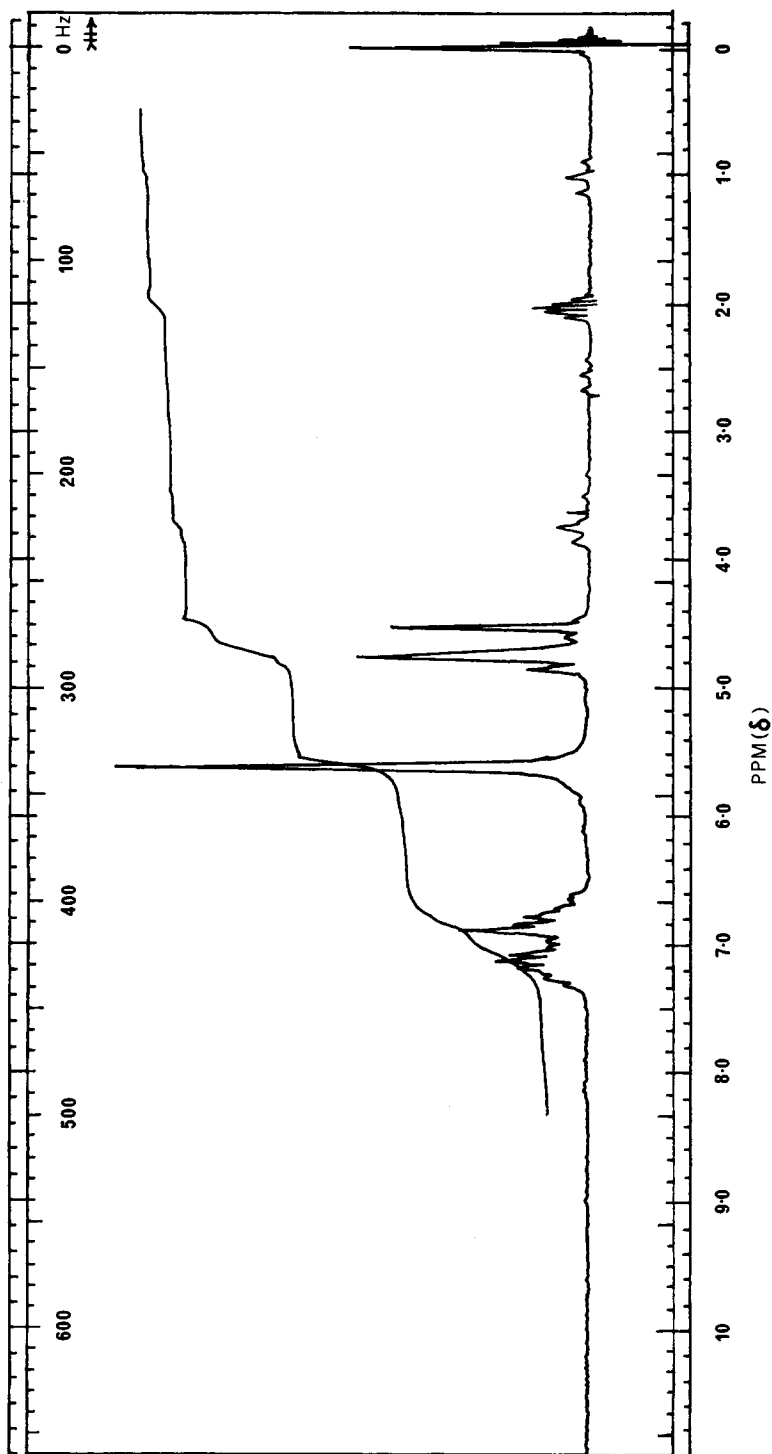


Fig. 1. NMR spectrum of resin 1.

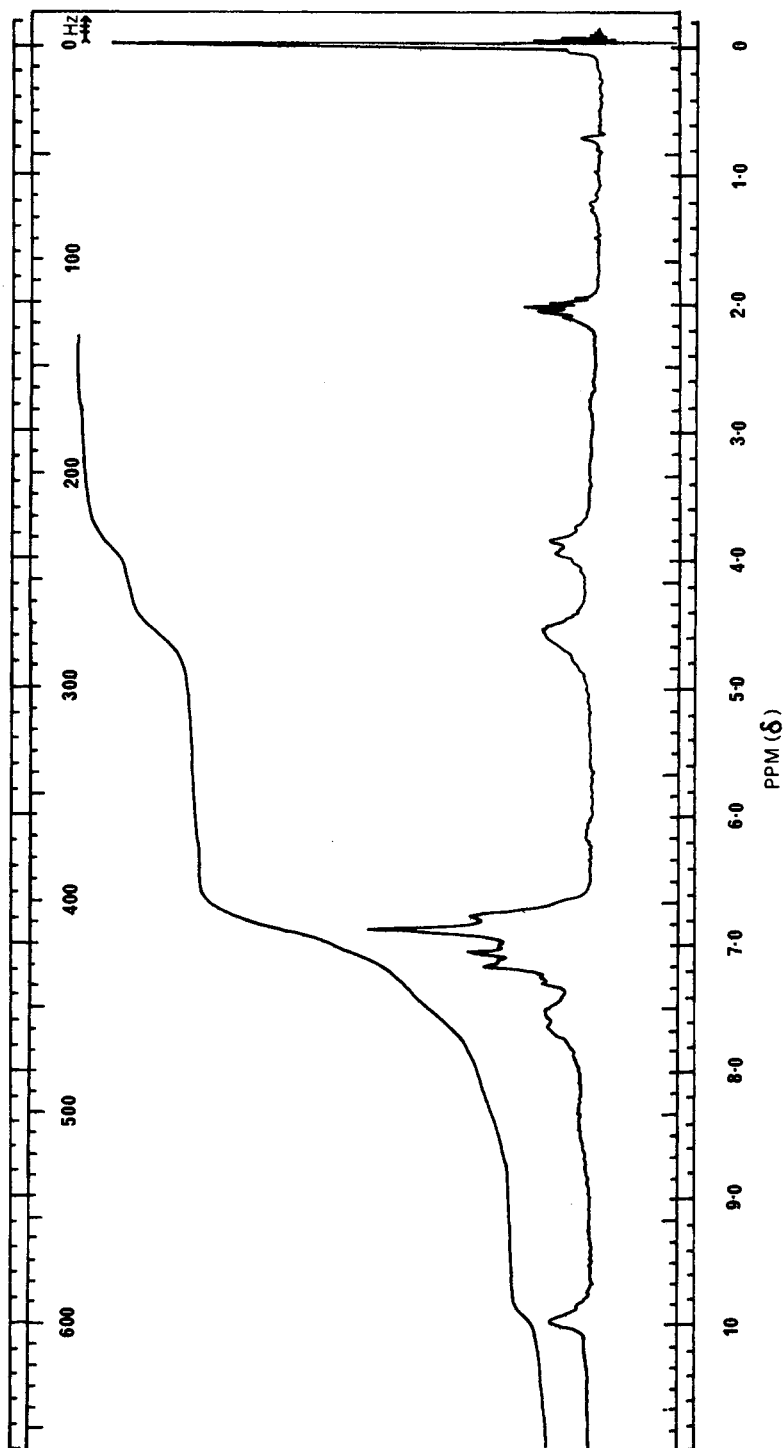


Fig. 2. NMR spectrum of resin 1 after oxidation.

TABLE III
Relative Numbers of Protons from NMR

Nonoxidized Samples						
Resin no.	ArH	OH	<i>o</i> -ArCH ₂ O	<i>p</i> -ArCH ₂ O	Ortho + para (= B)	ArCH ₂ Ar (= D/2)
1	3.00	2.35	1.66	0.73	2.40	0.30
2	3.00	2.64	1.67	0.80	2.47	0.34
3	3.00	2.10	1.40	0.45	1.85	0.55
4	3.00	2.65	1.36	0.41	1.77	0.90

Oxidized Samples		
Resin	-CHO	ArCH ₂ OCH ₂ Ar (= C)
1	0.28	1.21
2	0.28	1.21
3	0.27	0.74
4	0.29	0.61

TABLE IV
Group Ratios from NMR

Resin no.	Ortho/para (= A)	ArCH ₂ OH (= E, = B-C)	C/D	E/C	E/D	E/(C + D)
1	2.28	1.19	2.02	0.98	1.98	0.66
2	2.09	1.26	1.81	1.04	1.88	0.67
3	3.12	1.11	0.68	1.50	1.02	0.61
4	3.32	1.16	0.34	1.90	0.64	0.48

Thus, the value for the number of protons per aryl ring was arbitrarily set at three, i.e., ArH = 3, implying that there are no trisubstituted aryl rings present at this stage.

From the values for the relative numbers of protons in Table III, the group ratios in Table IV were calculated.

The following conclusions may be derived from the group ratios in Table IV. From column A it is clear that there is a much higher proportion of ortho substitution on the phenolic nucleus than para substitution, for all four resins, as expected. Note that this ratio excludes substituted methylol groups which have further reacted to diaryl methanes, which could be ortho or para substituted. In fact, careful examination of the spectra shows them to be mainly ortho substituted.⁴ The ortho/para ratio is higher for the two resins with $F/P = 1.3$ (3 and 4) than for those with $F/P = 1.7$ (1 and 2) and appears to be independent of catalyst.

The ratio C/D indicates that the resins with most formaldehyde present (i.e., 1 and 2, $F/P = 1.7$) favor production of a resole in which ether bridges outnumber diaryl methanes, whereas those with less formaldehyde (i.e., 3 and 4, $F/P = 1.3$) produced fewer ethers and more diarylmethanes.

The same conclusions can be drawn from ratios E/C and E/D, which relate the number of methylol groups to ethers and diarylmethanes, respectively. It is also of note that the number of free methylol groupings is more or less the same for all four resins (column E). For the same F/P ratio, the column C/D also indicates that NaOH as catalyst (resins 2 and 4) produces more diarylmethanes than does TEA (resins 1 and 3).

Column E/(C + D) indicates that the overall degree of condensation of benzyl alcohols is similar for both resins with $F/P = 1.7$ and is less than for the other pair with $F/P = 1.3$, especially for resin 4 in combination with NaOH. Thus, resins 1 and 2 are similar in nature and consist predominantly of methylol groups and ether links and are generally less condensed than resins 3 and 4. Resin 4 is in the most advanced state of condensation, consisting of benzyl alcohols and largely diaryl methanes.

Gel Permeation Chromatography

The results of GPC analysis of the four resins are shown in Figure 4. The resins with the higher F/P ratio (1 and 2) clearly have a much narrower molecular weight distribution than the lower F/P ratio resins. For either pair of resins with the same F/P ratio, sodium hydroxide tends to lead to more high molecular weight material relative to TEA. This is indicated by comparing peaks at 29 counts for resins 3 and 4.

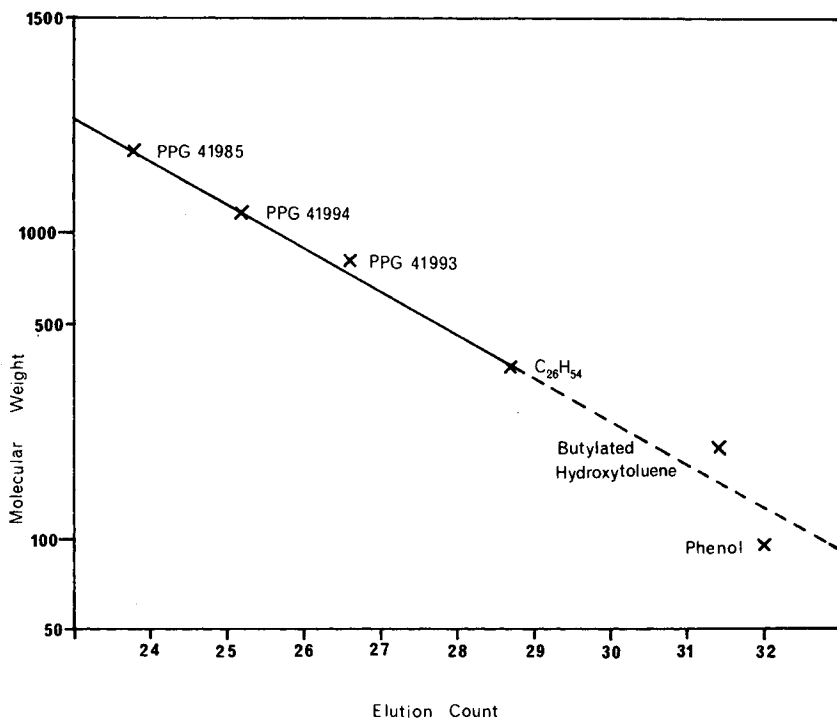


Fig. 3. GPC calibration graph.

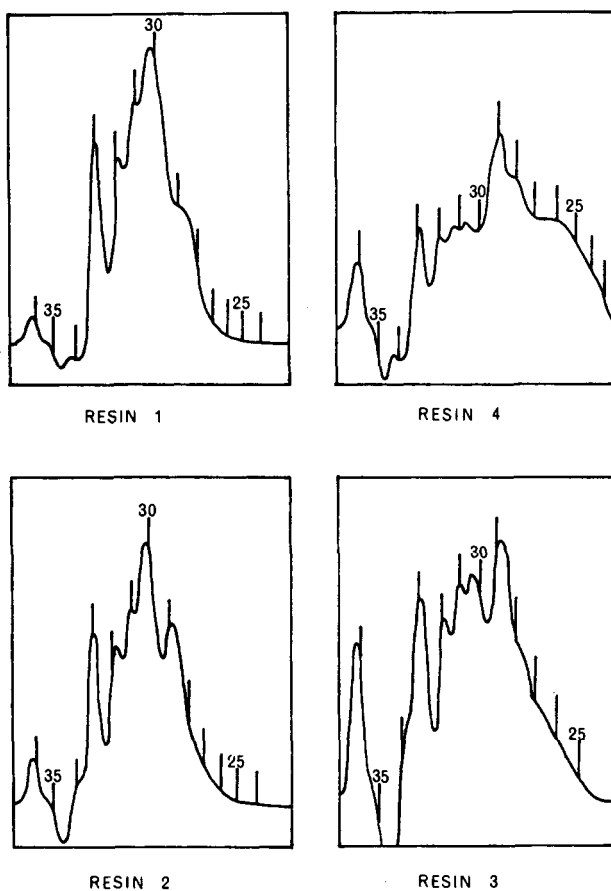


Fig. 4. GPC chromatograms of resins.

Precise identification of the various peaks has not been made in the present work although Figure 3 shows the GPC calibration curve which enables molecular weights to be assigned to each peak. Figure 5 also shows how the cumulative percentage of material by weight increases with increasing molecular weight for two resins (2 and 4) with the same catalyst but different amounts of formaldehyde.

Recent work by Wagner and Greff³ and by Duval, Bloch, and Kohn⁸ has in fact attempted to identify peaks in gel permeation chromatograms of various phenolic resoles by making use of model compounds. A brief qualitative description of the chromatograms in Figure 4 can be made as follows. Starting at the low molecular weight end the first peak corresponds to air, and the second peak (negative), to water. Any free formaldehyde in the resin co-elutes with the water. The next peak, at 33 counts, corresponds to phenol, and for all the resins there occur four further distinct peaks, at approximately 32, 31, 30, and 29 counts. The peaks at 32 and 31 probably correspond to mono- and dimethylol phenols, respectively.

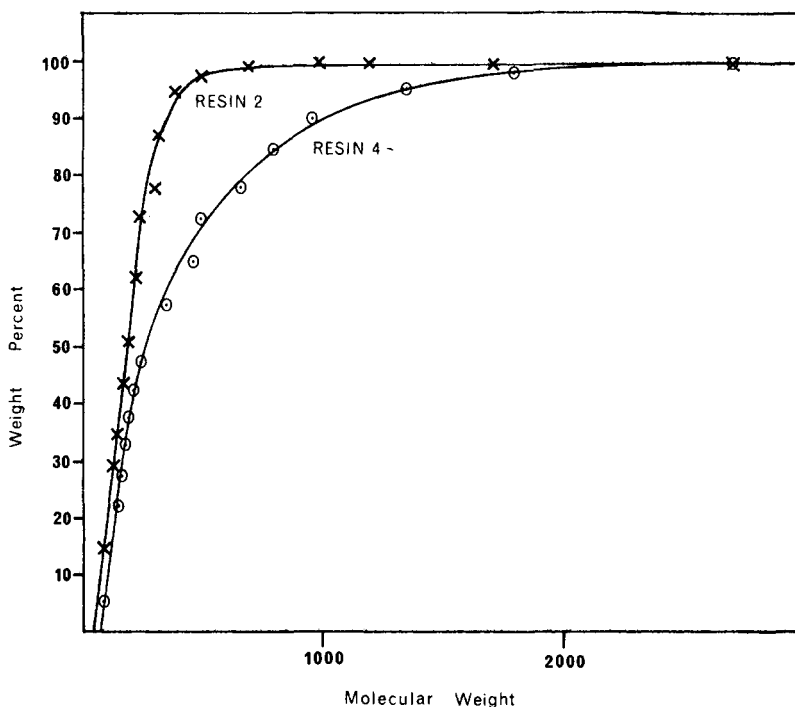


Fig. 5. Cumulative weight per cent of species of given molecular weight.

The peak at 30, equivalent to a molecular weight of 230, could correspond with trimethylol phenols or possibly with dinuclear phenols; the 29 peak arises from tetramethylolated dinuclear phenols or possibly from trinuclear compounds. Resin 4, at least, must contain a significant proportion of polynuclear phenols. Although not a complete analysis, the work does demonstrate the valuable potential of GPC in determining the effects of F/P ratio, catalyst, reaction time, and so on, on the molecular weight distribution of the resin produced and adds to the information gained from the NMR analysis.

Differential Scanning Calorimetry

The NMR and GPC data give information about the chemical structure of the resoles at the preparation stage. The DSC traces give information about the crosslinking reactions which occur when the resin structures initially formed are subjected to a specific heating rate program. A full analysis of the complex reactions occurring during cure is not possible, but a broad general interpretation of the DSC data can be proposed in the light of the information derived from NMR and GPC.

The DSC curves consist of either a single peak or of two overlapping exothermic peaks. The peak temperatures should not be interpreted in an absolute sense since they are related to heating rate, the peak temperature

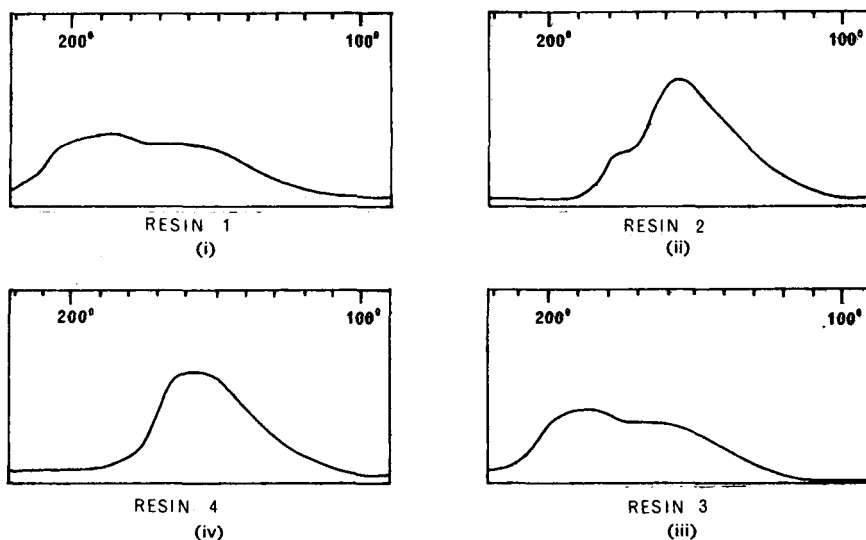


Fig. 6. DSC traces of resins.

moving to lower values with reduced scan speed. However, with a fixed set of conditions, the occurrence of peak 1 at approximately 155°C, often accompanied by peak 2 at approximately 185°C in all the samples examined, is a clear indication that two separate reactions, or closely related sets of reactions, occur in each resin.

Scans (i) to (iv) (Fig. 6) indicate that the relative occurrence of the two reactions depends largely on the catalyst used and, to a secondary extent, on the F/P ratio. This is confirmed by scans (v) to (viii) (Fig. 7), which were obtained by adding further triethylamine or sodium hydroxide to the original amine-catalyzed resins. This was done in order to determine whether the catalyst dictates the direction of the crosslinking reaction by virtue of its presence during the thermal cure, or because it was present during the initial phenol/formaldehyde reaction stage, thus producing a resin which would cure in a particular manner. In the case of amine-catalyzed reactions, it was initially thought possible that after preparation no amine would remain in the resin for the subsequent cure stage. Therefore, extra amine was added, prior to the DSC run, and to a separate pair of samples extra sodium hydroxide was added. NMR spectra later disproved this idea, but comparison of scans (vii) and (viii) (Fig. 7) with scan (iii) (Fig. 6) reinforces the conclusion that the presence of one or other catalyst largely determines the nature of the subsequent curing reactions. Further, it seems to be the case that sodium hydroxide preferentially catalyzes the reaction or reactions which give rise to peak 1 and that triethylamine has the same effect with respect to peak 2. In each case, addition of further amine causes increase in peak 2, and addition of further sodium hydroxide causes increase in peak 1. The function of the catalyst presumably is to affect the

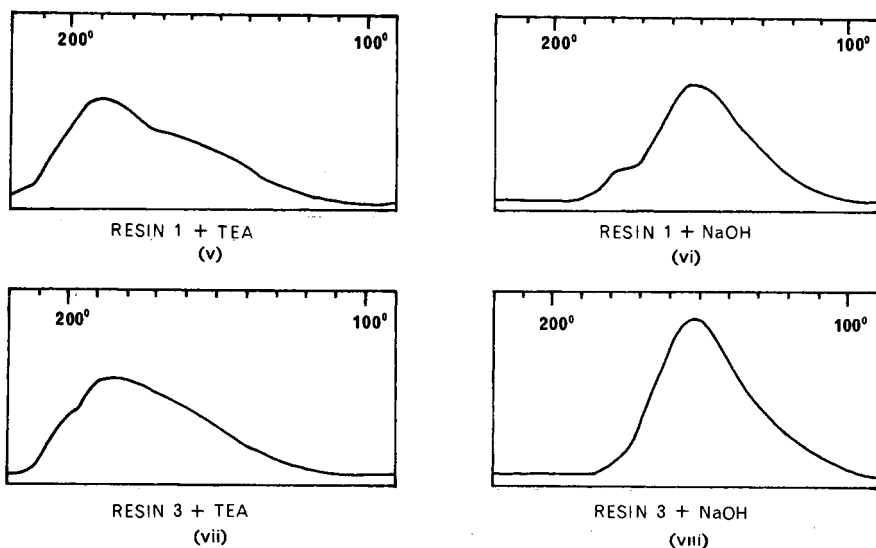


Fig. 7. DSC traces of resins with added catalyst.

relative numbers of sites available for the two processes which must have different activation energies.

The crosslinking reactions which can occur in the thermal cure of phenolic resins, leading to methylene or methylene ether bridges have already been outlined. Previous work has indicated that although methylene and methylene ether linkages may be formed simultaneously, ether formation is very largely eliminated under alkaline conditions.⁹ Under mildly acidic or neutral conditions, evidence for ether bridge formation has been presented.^{10,11}

A further factor expected to influence the ratio of methylene to ether bridges formed is the number of free ring positions in the resin. Ether formation becomes increasingly probable with a resin of high methylol content or with few free ortho and para ring positions. Evidence for the relative tendency for ether or methylene formation with increasing temperature is not well established.¹¹ Some authors state that at temperatures up to 150°, ether formation is the primary reaction, whereas other work has shown that in some systems, dibenzyl ether formation in maximum quantities occurs at temperatures higher than this.¹² Many of the conclusions have been drawn from work on model compounds with deliberately blocked para positions, and they may therefore not be valid for commercial resin systems.

In view of the foregoing comments, therefore, it is proposed that DSC peaks 1 and 2 broadly correspond to the two main types of crosslinking reaction, peak 1 arising from the crosslinking reaction of a single methylol group to form a methylene bridge and peak 2 arising from the condensation of two methylol groups to give a dibenzyl ether bridge. It is proposed that the latter reaction is favored at higher temperatures. The catalyst will determine which reaction will predominate, and the relative extents of

reaction in each case will also be influenced by the number of aromatic protons and free methylol group actually available for reaction.

In the case of resin 4, only peak 1 occurs, and this is consistent with the strong tendency for sodium hydroxide as a catalyst to favor methylene bridge formation. With resin 2, however, methylene bridge formation is again favored by the presence of the caustic catalyst, but some self-condensation of methylol groups can take place giving rise to peak 2 because of the favorably high probability for this reaction to occur. The ratio $E/(C + D)$ in Table IV, which gives a measure of the free methylol content in relation to the total number of bridging links and thus to molecular size, is greater for resin 2 than for any of the other three materials examined. This ratio has its lowest value for resin 4, making it much less likely that peak 2 would occur in this case.

The amine catalyst allows both reactions to occur, although peak 2, ether bridge formation, is preferentially catalyzed. Traces (v) and (vii), which result from the addition of extra amine to resins 1 and 3, demonstrate this clearly. The addition of further sodium hydroxide to resin 1 gives trace (vi), which is very similar to that of resin 2, whereas its addition to resin 3 gives trace (viii), which is very similar to that of resin 4. Again, this demonstrates that for a particular F/P ratio, it is the catalyst present at the curing stage which is the important factor determining curing behavior.

It is usually stated that in the cure of phenolic resoles, molecular enlargement reactions predominate at temperatures up to around 170°C and that above this temperature more complex reactions start to occur involving dibenzyl ethers and still unreacted phenol alcohols.¹¹ In relation to the DSC traces, however, several points must be noted: (a) the peak temperatures are dependent on scan speed; (b) the DSC measurements are made under pressure; and (c) the time scale of the experiment is limited to a few minutes only.

In fact, all the traces were only recorded up to approximately 200°C. Above this temperature, further peaks occur which undoubtedly correspond to degradation reactions and include a contribution from the widely accepted reaction whereby dibenzylether linkages eliminate formaldehyde to form methylene linkages. This proposal is consistent with the findings of Kurachenkov and Igonin¹³ who observed exothermic peaks at 220°C during differential thermal analysis under pressure of various para-substituted polybenzyl ethers. They quoted infrared evidence which supported identification of the peak as arising from the elimination of formaldehyde from ether linkages to form methylene crosslinks. Linked with other techniques, DSC is obviously a valuable technique for the study of thermosetting resin curing.

CONCLUSIONS

The object of this work was the study of the effects of F/P ratio and catalyst type on resin structure and reactivity. With respect to the three analytical techniques studied, NMR and GPC tended to divide the four resins into two groups according to F/P ratio, whereas DSC divided them

according to catalyst. In fact, despite the basic structural differences between the pairs of resins 1 and 2, and 3 and 4, as shown by NMR and DSC, it is interesting that the shapes of their DSC curing curves are largely determined by the type of catalyst used. Thus, it would appear that the type of species formed and the resultant molecular weight distribution of the products of preparation are determined largely by the ratio of formaldehyde-to-phenol starting materials, although these effects are obviously modified by the reaction conditions which were slightly varied in these experiments. It also follows that the catalyst present in the resin system is the most important factor in controlling the way in which the preparation products go on to give more fully crosslinked structures in the process of thermal cure. The main conclusions of the work may therefore be summarized as follows:

1. MnO_2 has been successfully used to selectively oxidize phenolic methyloxy groups to aldehydes, allowing quantitative determination of ether bridge structures in phenolic resoles to be made by NMR.

2. Typical molecular structures in any given resole depend to a great extent on the F/P ratio used. However, triethylamine as a catalyst tends to favor the formation of ether bridges, whereas sodium hydroxide favors methylene bridges.

3. The direction and rate of thermal cure of resoles depend to a marked degree on the catalyst present during the curing stage.

4. The molecular weight distribution of a resole depends heavily on the F/P ratio. However, sodium hydroxide does tend to increase the proportion of high molecular weight material, relative to triethylamine, at a particular F/P ratio.

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