Analysis of the Formation and Curing Reactions of Resole Phenolics

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Synopsis

The chemical compositions and molecular size distributions of a series of soluble resole phenolics was studied by high resolution ^{13}C NMR, IR, GPC, and viscosity techniques. The curing reactions were then followed by IR and solid state ^{13}C NMR techniques. The ultimate degree of cure increases with curing time and temperature. The molecular weight of the precursor resole can be increased with increasing formaldehyde/phenol mole ratio and increased condensation reaction time and temperature. The degree of cure achieved under given conditions is directly proportional to the molecular weight of the precursor resole. The condensation catalyst has a great effect on resole composition and molecular size. It also influences preferential methylolation at the para position to the phenolic OH group in the following increasing order $Ba(OH)_2$, NaOH, Na_2CO_3. The curing pH affects the degree of cure as well as the type of linkages formed. Methylene bridges are almost exclusive at high or very low pH's, while dibenzyl ether bridges predominate at neutral pH. High resolution ^{13}C NMR spectroscopy is the most powerful tool to study soluble resoles. Infrared spectroscopy supplies qualitative results. Solid state ^{13}C NMR is useful to study polymers during the curing process but there are inherent limitations and potential errors in this method.

INTRODUCTION

Phenol-formaldehyde thermosetting resins have many industrial applications.[1] The chemistry of prepolymers such as resoles has been very well studied in the past decades by conventional analytical techniques like proton and carbon-13 nuclear magnetic resonance spectroscopy,[2-5] infrared spectroscopy (IR),[6,7] and gel permeation chromatography (GPC).[2,8,9] A few good reviews on the chemistry of phenolic resins are available.[10-12]

Phenolic prepolymers become insoluble and infusible as they are cured, making conventional techniques less useful in the study of curing reactions. Although IR spectroscopy can be applied to solid state polymers, it has had only limited success with phenolics and is confined to qualitative work only. Thus, conclusions about the curing reactions and structure of the final, cured products are often inferred from the chemistry of the resole prepolymers.

It would be of scientific and practical interest to be able to study and characterize phenolic resins as solids, since this is the form in which they are most useful. Carbon-13 CP-MAS NMR spectroscopy techniques[13] can characterize structural changes that occur during the curing and thermal decomposition reactions of solid resole phenolics.[14-16] Recently, we have reported a quantita-

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tively reliable procedure to follow the degree of cure of resole phenolics from the ratios of CH_2 to aromatic carbons.[17]

The objectives of the present study were to characterize the chemical compositions and molecular size distributions of different kinds of soluble resoles by high resolution solution ^{13}C NMR, IR, GPC, and viscosity techniques. The curing reactions were then followed by IR and solid state ^{13}C CP-MAS NMR techniques. Resoles were made with different kinds of alkaline catalysts, different formaldehyde-phenol (F/P) mole ratio, and different reaction times. The effect of curing time, curing temperature, and curing pH were also investigated.

EXPERIMENTAL

Phenolic Prepolymers

All resoles were prepared by small scale (0.191 moles phenol) condensation of phenol, formaldehyde, and an alkaline catalyst in appropriate amounts for specified reaction times at 70°C in a water bath. The reaction was timed once the mixture reached 70°C. Crystal phenol, 37% formalin solution, and catalysts were all analytical reagents. The formalin contained methanol as a preservative. Distilled water was used. After the condensation reaction, as much water as possible was removed from the resole solution at water aspirator pressures and temperatures up to 45°C. The pH of the finished resole prepolymers was measured at room temperature.

Three resoles were made with different formaldehyde-phenol (F/P) mole ratios: 1.37, 1.70, and 2.03. The catalyst here was barium hydroxide and its mole ratio to phenol was 0.015.

With 1.37 F/P and 0.015 barium hydroxide to phenol mole ratios, two more resoles were made at $3\frac{1}{2}$ and $5\frac{1}{2}$ h reaction times. Furthermore, with 1.37 F/P mole ratio, 2 h reaction time, and catalyst to phenol mole ratio of 0.015, two other resoles were made. One was catalysed with sodium hydroxide and the other with sodium carbonate.

The above resoles were also made with ^{13}C enriched formaldehyde. The procedures that were followed were exactly those used to prepare the nonenriched resoles except that the normal formalin solution (1.1% atom ^{13}C) was mixed with ^{13}C enriched formalin to given desired degrees of ^{13}C enrichment. For instance, 1.2 g of 17.5% formalin with 90% atom ^{13}C mixed with 55.2 g of 37% formalin gives an ^{13}C enrichment factor about 2, with a formaldehyde net weight of 20.6 g.

Gel Permeation Chromatography

A gel permeation chromatograph (GPC) with a differential refractometer detector was used to analyse the resoles at room temperature. Procedures reported earlier[9] were followed with several modifications. The GPC column packing materials were polystyrene gels with nominal pore sizes 1000, 500, 200, and 60 Angströms. The column length for each pore size packing was 2 × 61 cm. Analytical grade, filtered THF was used as solvent without further distillation. Different flow rates (1.5, 1.0, and 0.8 mL/min) were tried with one

resole sample. It was found that better resolution resulted from slower rates but that there was no significant resolution improvement between the two slower rates. Therefore, a flow rate of 1.0 mL/min was used throughout these experiments. The concentration of injected resoles was about 1 mg/mL. Phenol was used as an internal standard to calculate the elution volume index (*EI*) as follows:

$$EI = \frac{\text{elution volume of species } i}{\text{peak elution volume of phenol}} \quad (1)$$

(Phenol was always present in all the low molecular weight resoles that were prepared. Hence, it could serve as an internal standard.) Small amounts of phenol were added to serve as markers in the GPC traces of other compounds that were used for calibration of the apparatus.

The universal size calibration curve for the GPC columns was constructed using compounds with molecular sizes close to those of the resoles. These compounds were chlorobenzene, phenol, phenolphthalein, and polystyrene standards with molecular weights of 480, 1050, 2000, and 4000. Calibration was in terms of size in solution, rather than molecular weight because the hydrodynamic sizes of resole prepolymers are a function of molecular architecture as well as of molecular weight.[9]

Viscosity

The viscosities of different neat resoles were measured with a Rheometrics Mechanical Spectrometer (Model 605) equipped with a 10 g cm–100 g cm torque transducer. The sample was placed between cone and plate fixtures having a diameter of 50 mm and a cone angle of 0.04 radian. All measurements were carried out at ambient temperature in steady rotation.

Infrared Spectroscopy

All IR spectra were recorded on a Beckman Acculab 10 spectrophotometer. One drop of resole prepolymer was spread onto two NaCl plates for examination. For cured resins, 1 mg of resin was ground with 10 mg of dried KBr using a dental amalgamator. A small amount of the mixture was then pressed with 10 tons force under vacuum for 10 min to provide a transparent disk for examination. The percentage transmittance was plotted against wave number (cm^{-1}) in all IR spectra.

High Resolution Solution ^{13}C NMR

A series of solutions of different resoles were prepared for ^{13}C NMR analyses at about 50/50 (v/v) concentrations in DMSO.

All ^{13}C NMR spectra were obtained at ambient temperature using either a Bruker WH-400 spectrometer at 100.6 MHz or a Bruker AM-250 spectrometer at 62.9 MHz. Both machines were operated with a 90° pulse width, proton broad-band decoupling without Nuclear Overhauser Effect (NOE), data file of 16K points and 10 mm o.d. tubes. Most aliphatic carbons of the resole were fully relaxed at a pulse delay of about 2 s. Different pulse delay times such as

5, 10, 30, 60, and 85 s were tried. The intensities of some aromatic carbons increased slightly with delay times up to 85 s. A delay time of 120 s, which was close to the fully relaxed state for all carbons, was, therefore, used in all solution ^{13}C NMR analyses, unless otherwise stated. The error involved in using delay times of 60 and 120 s for the intensity measurements was estimated to be no higher than 2%.

After the baseline of each ^{13}C NMR spectrum was optimumly phased, the peak intensities were integrated by the spectrometer. The maximum instrumental error was about 5%. The number of scans for each spectrum was from 220 to 720. DMSO-d6 was served as an internal field-frequency lock signal and an internal chemical shift standard (39.5 ppm of the highest peak with reference to TMS). Results from the two spectrometers were comparable because they gave very much the same resolution.

The ^{13}C NMR spectra of three model compounds (o-, m-, and p-methylolphenol) were obtained with similar procedures as mentioned except that the pulse delay was 90 s and the number of scans was 80. Similarly, the ^{13}C NMR spectra of other model compounds (α-phenyl-o-cresol, 4-hydroxyl diphenyl methane, and benzyl phenyl ether) were obtained in deuterated chloroform with pulse delays of 15 s and 159 scans.

To determine the ^{13}C enrichment factor, a delay time of 5 s was sufficient to fully relax all aliphatic carbons. Seven hundred and twenty scans was chosen for each ^{13}C NMr run here. More details are given in the section on Results and Discussion.

Solid State ^{13}C-MAS NMR

(i) CP-MAS Procedures in General

A Kel-F poly(chlorotrifluoroethylene) spinner was used in our preliminary study.[17] In the later stage of the study, the spinner was found to wear out very rapidly at 3 kHz spinning rate. The worn spinner could still reach about 2 kHz spinning rate without any mechanical vibration, but this was its limit. However, a spinning rate of at least 3 kHz is required to move the spinning sidebands away from desired isotropic carbon peaks for resole phenolics. It is obviously impractical to use a new spinner for each solid state ^{13}C CP-MAS NMR experiment. The next choice of spinner material was Delrin (polyoxymethylene) which has a huge background peak at 88.4 ppm. This interference is less troublesome, for phenolics, than the background peaks of other available materials. Delrin spinners can reach a 4 kHz spinning rate easily at moderate, workable air pressures.

The experimental procedures for CP-MAS experiments reported elsewhere[17] were followed except for the following modifications. Only ^{13}C enriched resins were studied by CP-MAS experiments. All ^{13}C enriched resoles (e.g., those prepared with different catalyst, mole ratio, and reaction times) were cured for 4 min in a press at 160°C with 157 kg/cm^2 pressure, unless otherwise stated. The cured resoles are then referred to as "resins" in this article.

The spinners which were machined from Delrin had an internal capacity of 0.27 cm^3. The magic angle must be readjusted for Delrin spinners after the resolution, Hartmann-Hahn cross-polarization, and the magic angle settings

have been determined with sucrose, adamantane, and KBr, respectively, in a Kel-F spinner. This is because the magic angle settings for these two spinners are very different. For fine adjustment of the magic angle, a small amount of KBr was packed with the sample into the Delrin spinner. The spinning rate for each sample in a run was adjusted to 3.65 kHz (driven by air) with a maximum deviation of ± 0.05 kHz between separate runs.

Two different methods were used to determine the optimum conditions (Hartmann-Hahn contact time and delay time between sequences) for CP-MAS analyses of all ^{13}C enriched resins:

(a) In method (a), the optimum contact time was determined with a mixed delay time of 3 s by varying the contact time in increments of 0.5 ms. Then the optimum delay time was determined similarly in 1 s increments with the optimum contact time. The minimum number of scans to give sufficient signal/noise balance was 100 for each run. This procedure was repeated for another sample.
(b) The second procedure was the same as the first method with the addition that the optimum contact time was redetermined using the measured optimum delay time.

These two methods gave two different optimum contact times for some samples. Method (b) was the procedure used in this study, for reasons that are noted in the Results section.

(ii) Effect of Curing Time and Temperature

The ^{13}C enriched and $Ba(OH)_2$-catalysed resole, made with 1.37 F/P mole ratio and 2 h reaction time, was cured for different times (i.e., 2, 4, 6, 8, 16, and 35 min) at 160°C, and at different temperatures (i.e., 140°C, 160°C, 180°C, 200°C, and 220°C) for 4 min. The pH of this resole was 8.3. A similar ^{13}C enriched resole made with 2.03 F/P mole ratio was also cured at different temperatures for 4 min.

(iii) Effect of Curing pH

Aliquots of the above resole were adjusted to pH 9.5 with concentrated sodium hydroxide solution, and to pH 6.5 with dilute sulphuric acid. Then, these resoles with pH's of 9.5, 8.3, and 6.5 were cured at 160°C for 4 min. In addition, some of the resole was adjusted to pH's 5, 3, and 1 with concentrated sulphuric acid. Only the resole with pH equal to 1 cured spontaneously. This particular pinkish resin was ground and neutralized with concentrated sodium hydroxide solution before being analyzed in the CP-MAS experiment. This neutralization step is essential because traces of acid can catalyze degradation of the Delrin spinner and cause it to explode inside the probe.

(iv) General

All CP-MAS spectra of ^{13}C enriched resins shown were obtained with the same line broadening setting, spinning rate of 3.65 kHz, number of scans of 500, contact time of 1.5 ms, and delay time of 8 s, unless otherwise stated.

Since ^{13}C enriched resins were used in all CP-MAS analyses for better sensitivity, it is necessary to convert the CH_2/Ar results back to their equivalents

for nonenriched resins. The ^{13}C enrichment factor for each resin was determined by comparing the intensities of aliphatic carbons of one ^{13}C NMR spectrum of the enriched resole to another spectrum of the same, nonenriched resole made under exactly the same experimental conditions. All the CH_2/Ar ratios shown in the Results section are, therefore, converted to nonenriched values.

A corresponding CP-MAS spectrum of the Delrin spinner packed with KBr was obtained under the same experimental conditions (e.g., contact time, delay time, spinning rate, and number of scans) as for the corresponding resin. This background spectrum was used to make peak intensity corrections for overlapping of spinning sidebands of the Delrin peak with the desired resin peaks.

Each peak area was measured with a planimeter on an expanded spectrum. There were 10 to 20 measurements, depending on the particular peak size. The average measurement error here was about 1%. The quoted uncertainty in the Results section reflects errors due to replicate measurements and different baselines drawn on one CP-MAS spectrum.

RESULTS AND DISCUSSION

GPC and Viscosity

Rudin et al.[9] have indicated the limitations of GPC analyses in their study of resole prepolymers. These include problems of aggregation, overlapping of peaks, and unresolved baselines. Therefore, we do not attempt to give assignments for individual GPC peaks. Despite these limitations, GPC is still a useful technique to characterize and compare different resoles.

Figure 1 shows GPC traces of resole prepolymers made with different F/P ratios. The concentration of each injected resole was slightly different so the absolute intensity of an individual peak is not comparable between spectra. However, the peak intensity relative to that of the phenol peak, which occurs at about 30 counts, can provide useful information. Figure 1 shows that the relative intensities of the two peaks between 29 to 27 counts increase with formaldehyde concentration. These two peaks are probably due to polyoxymethylene oligomers, dibenzyl ether bridges, and other substituted methylolphenols. More importantly, there is little variation of apparent hydrodynamic volumes with F/P mole ratio. So far as GPC analyses can determine, the F/P ratio does not affect the molecular size of resole prepolymers made under standard condensation conditions. (Recall that molecular size increases from right to left in these GPC chromatograms.)

Figure 2 shows the effect of the duration of the formaldehyde-phenol condensation reactions. The peak located between 27 and 28 counts decreased with increasing reaction time while the other peak, at higher apparent hydrodynamic volume, increased with reaction time. This indicates the expected result that some constituents of the resole are converted to larger volume species as the reaction time is prolonged.

Figure 3 indicates that the sizes of the constituents of resoles made with different catalysts are very different. It can be seen that NaOH-catalysed resole has more species with smaller apparent hydrodynamic volumes than other resoles. The NaOH-catalysed resole was very soluble in water, probably because it consisted mainly of mono-nuclear methylolphenols. Resoles catalysed with

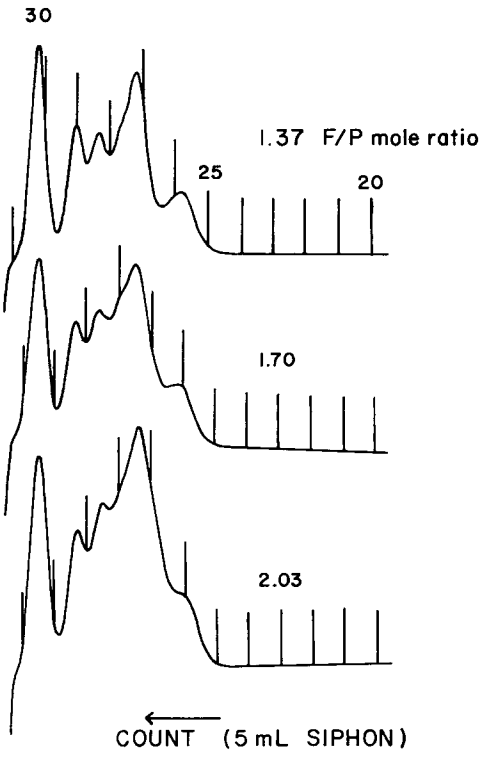

Fig. 1. GPC traces of resole prepolymers made with the indicated F/P ratios. The catalyst here was $Ba(OH)_2$ with catalyst/phenol mole ratio = 0.015.

$Ba(OH)_2$ and Na_2CO_3 had very similar size ranges although the particular constituents evidently differed.

Molecular weight averages cannot be computed from GPC analyses for reasons given above and elsewhere.[9] Molecular volumes are accessible, however, in terms of apparent hydrodynamic volumes (H) that can be calculated from the relation between GPC elution volume and hydrodynamic volumes of calibration substances. Table I lists such parameters for the samples of present interest.

Under standardized reaction conditions the molecular size of the resole prepolymer increases in the order $NaOH < Na_2CO_3 = Ba(OH)_2$ catalysts, but the total variation is very small. There is no significant effect of formaldehyde/phenol mole ratio on the molecular size of the resole. As expected, increasing the time of the condensation reaction produces larger resole molecules.

All resoles exhibited Newtonian viscosity at least over the shear rate range from 0.4 to 16 s^{-1}. The viscosity data in Table II (at 6.31 s^{-1} shear rate) show more differences between the various resoles than are apparent in the GPC chromatograms. Viscosity values fall in the order $NaOH < Ba(OH)_2 < Na_2CO_3$ catalysis, with large differences between the different products. The condensation reaction is further advanced (as judged by resole viscosity) when the formaldehyde/phenol mole ratio is raised form 1.37 to 1.70, but no further advantage is apparent from an increase to 2.03. Increased reaction time results in significant higher resole viscosity, all other conditions being equal.

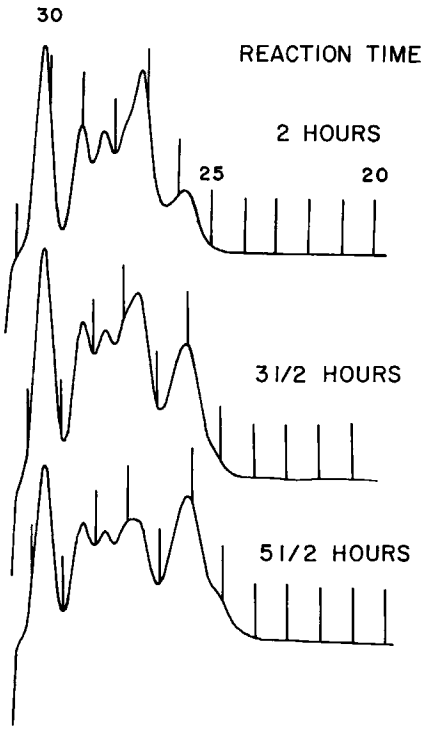

Fig. 2. GPC traces of resole prepolymers made with the indicated condensation reaction times at 70°C. The catalyst here was $Ba(OH)_2$ with a catalyst/phenol ratio of 0.015 and the F/P ratio was 1.37.

Evidently, GPC and viscosity measurements do not provide parallel indications of the state of advancement of the phenol-formaldehyde condensation. Both methods agree on the effects of more prolonged reaction times but differ on the results of choice of catalyst and phenol/formaldehyde ratio. The viscosity technique is the more attractive of the two because of its simplicity and relative sensitivity. In addition, the viscosity response to changing reaction variables is the more plausible, from a chemical point of view. As mentioned above, GPC analyses of complicated structures like resoles may be comprised by the varying effects of intermolecular shape as the condensation reaction proceeds.

Infrared

In principle, IR spectra should reveal information particularly on methylol groups ($-CH_2OH$) and the dimethylene ether bridges ($-CH_2OCH_2-$). However, most peaks in the IR spectra of resoles are overlapped and are not resolved to a clear baseline. Therefore, quantitative analysis of peak areas is not reliable and may provide misleading results. Nevertheless, IR technique can provide some valuable qualitative information. The IR absorption bands are assigned according to earlier reports.[7,15] The useful bands (see Figure 4) reflect the existence of different kinds of substituted aromatic rings (1480 to 1520 cm^{-1}), the phenol ring double bond stretching (about 1600 cm^{-1}), and $-CH_2O-$ units,

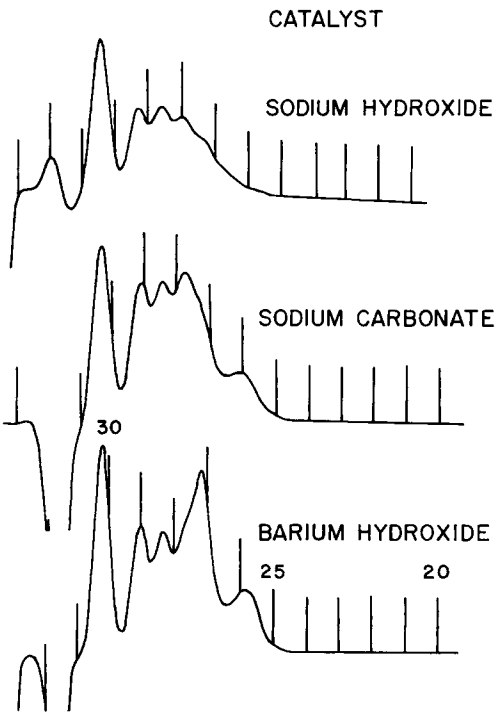

Fig. 3. GPC traces of resole prepolymers catalyzed with the indicated bases. The F/P ratio is 1.37. The reaction time at 70°C was 2 h and the catalyst/phenol mole ratio was 0.015.

including methylols around 1000 to 1050 cm^{-1} and ether bridges around 1050 to 1070 cm^{-1}. Figure 4 shows that peaks corresponding to methylols and ether bridges are not resolved. It is possible to compare peaks from different spectra qualitatively by taking the relative intensity of any peak with respected to the phenol peak at 1600 cm^{-1}. For instance, it can be seen that the extent of substitution on the phenol ring is greater with Na_2CO_3- and $Ba(OH)_2$-catalysis than in NaOH- catalysed resole (see Figure 4 (a), (b), and (c)), and that the amount of $-CH_2O-$ units decreases slightly with reaction time (Figure 4 (f), (g), and (h)). Moreover, the amount of $-CH_2O-$ units increases significantly with F/P mole ratio (Figure 4 (c), (d), and (e)). As a whole, all these resoles were shown to have large amounts of methylols.

High Resolution Solution ^{13}C NMR

The chemical shifts of most peaks in the ^{13}C NMR spectra of resoles were assigned based on the information from the literature[4,5] and from the six model compounds. The assignment of peaks in a typical resole ^{13}C NMR spectrum is depicted in Figure 5.

Peaks around 55 to 67 ppm are due to various kinds of ether and methylol carbons, and it is not possible to integrate such individual peak areas with accuracy. Nevertheless, it is feasible to calculate the amount of ortho and para substituted methylols through the well-resolved free ortho and para aromatic carbon peaks. Some valuable information can be calculated as follows:

TABLE I
Summary of GPC Results on Resoles

Sample	H_N $\times 10^{23}$ cm³/mol.	H_w $\times 10^{23}$ cm³/mol.	H_Z $\times 10^{23}$ cm³/mol.	$H_{(z+1)}$ $\times 10^{23}$ cm³/mol.	S_W[a] $\times 10^{23}$ cm³/mol.	SK_W[b]
Effect of catalyst (1.37 F/P mole ratio, 2 h reaction time)						
Catalyst						
NaOH	30.6	34.0	38.7	45.0	12.6	1.84
Na_2CO_3	34.1	39.2	46.5	56.4	17.0	1.81
$Ba(OH)_2$	34.7	40.4	48.4	58.2	18.0	1.54
	(0.2%)*	(0.5%)	(1.0%)	(2.0%)	(2.2%)	(3.2%)
Effect of mole ratio ($BaOH)_2$-catalysed, 2 h reaction time)						
F/P						
1.37	34.7	40.4	48.4	58.2	18.0	1.54
1.70	35.3	41.2	49.2	58.9	18.1	1.49
2.03	36.8	42.8	50.3	58.9	17.9	1.26
Effect of reaction time ($Ba(OH)_2$-catalysed, 1.37 F/P mole ratio)						
Reaction time						
2 h	34.7	40.4	48.4	58.2	18.0	1.54
$3\frac{1}{2}$ h	36.5	44.9	56.7	70.1	23.0	1.36
$5\frac{1}{2}$ h	40.0	52.4	69.8	88.6	30.2	1.34

[a] Standard deviation of the weight distribution of hydrodynamic volumes in THF.
[b] Skewness of weight distribution of hydrodynamic volumes in THF.
* Error % on replicate experiment.
Universal calibration curve was established with chlorobenzene, phenol, phenolphthalein, and polystyrene of 480, 1050, 2000 and 4000 molecular weights.

The extent of para-substituted methylols per phenol unit

$$= 1 - \text{free para aromatic carbons per phenol unit.}$$

The extent of ortho-substituted methylols per phenol unit

$$= 2 - \text{free ortho aromatic carbons per phenol unit}$$

$\therefore$ Total percentage of methylolation per phenol unit

$$= \frac{3 - (\text{free ortho and para aromatic carbons per phenol unit})}{3} \times 100\%$$

The above calculation assumes that the amount of methylene bridges formed by coupling one methylolphenol to a phenol is very small. For the resoles of this study, this assumption is probably justified.

Values of the ratio of ortho/para substituted methylol carbons greater than, less than, and equal to two indicate preferential methylolation at ortho positions, para position, and both para and ortho positions, respectively. Furthermore, the number of oxymethylene carbons per phenol unit which is indicated from

TABLE II
Summary of Resole Viscosities

Sample	Viscosity[ab] (poise)
Catalysed with (1.37 F/P mole ratio, 2 h reaction time)	
Sodium hydroxide	6.8
Barium hydroxide	12.9
Sodium carbonate	23.3
F/P mole ratio ($Ba(OH)_2$-catalysed, 2 h reaction time)	
1.37	12.9
1.70	19.9
2.03	18.7
Reaction time ($Ba(OH)_2$-catalysed, 1.37 F/P mole ratio)	
2 h	12.9
$3\frac{1}{2}$ h	34.6
$5\frac{1}{2}$ h	40.6

[a] All resoles show Newtonian behaviour over the range of shear rates from 0.4 to 15.9 s^{-1}.
[b] Quoted at 6.31 s^{-1} shear rate at ambient temperature.

polyoxymethylene oligomers (trimers to pentamers)[5] can be measured with accuracy.

One of the methylene bridge carbon peaks (i.e., p,p'-at about 41 ppm in Fig. 5) is partially overlapped with the DMSO-d6 solvent peaks. To see if a peak was covered totally by the solvent peaks, one ^{13}C NMR spectrum ($Ba(OH)_2$ catalysed resole made with 1.37 F/P mole ratio and 2 h reaction time) was measured in pyridine-d5. Conditions here included a pulse delay of 120 s, 660 scans, and no NOE. This spectrum (not shown) indicates no significant p,p'-methylene bridge carbons for this sample.

We did not make further attempts to characterize methylene bridge carbons in soluble resoles in this study. If this were to be of interest we suggest measuring the ^{13}C NMR spectra in DMSO-d6 and in acetone-d6 to quantify all the methylene bridge carbons accurately. If acetone-d6 is used as solvent, the aromatic peaks will be freed from the solvent peaks, enabling measurement of the peak area per phenol unit. Thus, the acetone results would be comparable to those obtained in different solvents. This is not the case for pyridine-d5, where solvent peaks interfere slightly with the Ar_1 peaks.

The ^{13}C NMR data on all resoles are summarized in Table III. All peak intensities were measured relative to that of aromatic carbons attached to the hydroxyl group (Ar_1). In other words, the intensities measured are values per phenol unit (p.p.u.).

The NaOH-catalyzed resole has a lower degree of substitution per phenol unit than the soluble polymers catalyzed with Na_2CO_3 or $Ba(OH)_2$. This is consistent with the smaller molecular sizes of the NaOH-catalyzed product as shown by GPC and viscosity measurements.

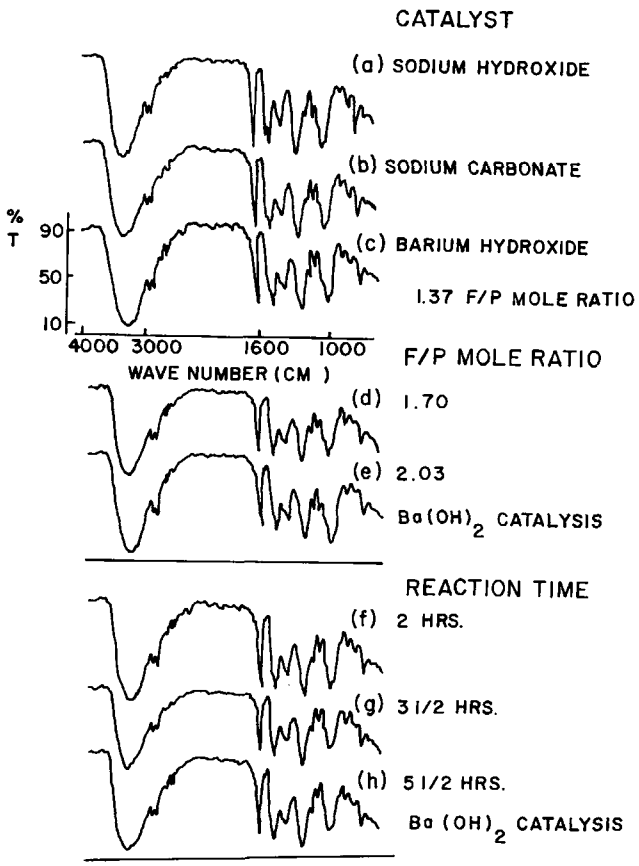

Fig. 4. Infrared spectra of resoles.

Another important piece of information from this catalyst study is that methylolation is always preferentially at the ortho positions. This is consistent with the results of Werstler, for NaOH-catalysed resoles, in which the para position was reported to be favored for condensation over the ortho position on a per site but not on a total basis (there being twice as many ortho as para sites).[18] The ratio of ortho/para substituents increases with a decrease in the basicity of the alkaline catalyst, as has been reported earlier by others.[19] Also, as is well known, $Ba(OH)_2$ is more ortho-directing than NaOH, presumably because of chelation in the transition state in the reaction between formaldehyde and ortho sites on phenolic residues.[19]

Higher F/P mole ratios promote a higher methylol content, more polyoxymethylene oligomers and more dibenzyl ether bridges, as recorded in Table III. These are all potential sources of formaldehyde in subsequent curing reactions. The effects of reaction time indicate that some of these formaldehyde sources are converted to methylene bridges with longer reaction times, to gives resoles with higher molecular weights. The GPC traces in Fig. 2, the viscosity data in Table II and the IR spectra in Fig. 4 (f), (g), and (h) all support this indication.

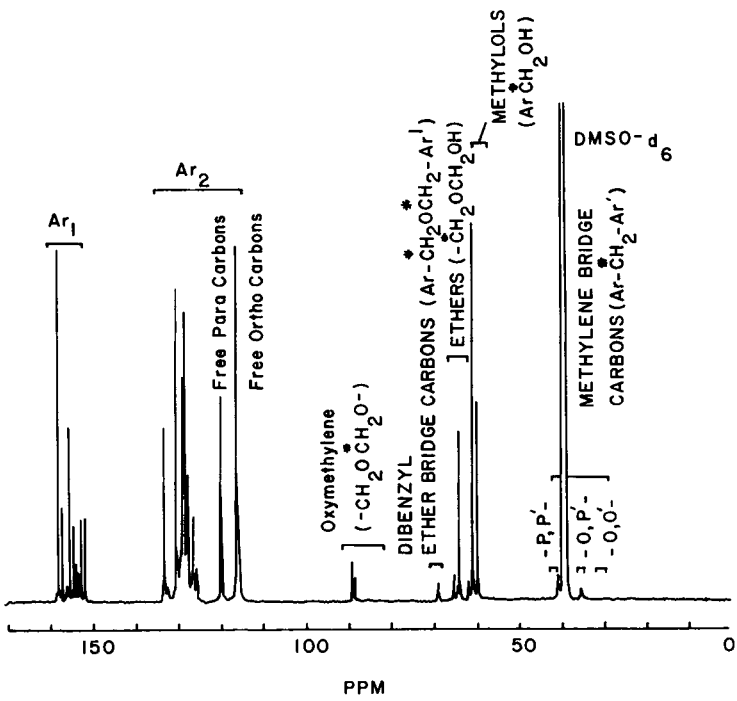

Fig. 5. A typical ^{13}C high resolution NMR spectrum of a resole. This spectrum was obtained with 535 scans at 100.6 MHz. Ar_1 is the aromatic carbon attached to the OH group and Ar_2 represents the remaining aromatic ring carbons. The particular carbon that corresponds to a given peak is marked with an asterisk.

Also, as shown in Table III, an increase in reaction time increases para methylolation. Changes in formaldehyde/phenol ratio have no effect on the relative amounts of substitution at ortho and para positions.

At these very early stages of curing, there is no significant content of o,o-methylene bridge carbons (peak around 31 ppm) except for the Na_2CO_3-catalysed resole, where only a minute peak was detected.

High resolution ^{13}C NMR technique is a very powerful tool to characterize the chemical structures of phenolic prepolymers, and as a basis for the detailed analysis of the curing process, which is discussed in the following section of this article.

CP-MAS Qualitatively Reliable Results

We have reported a quantitatively reliable procedure for measuring the desired CH_2/Ar_1 ratio in a cured resole-type phenolic resin. The CH_2/Ar_1 ratios measured in the CP-MAS (2 ms contact time and 8 s delay time) spectra (both with 3 kHz spinning rate in a Kel-F spinner) were 0.63 ± 0.06 and 0.65 ± 0.06, respectively.[17]

In the present study, the CP-MAS experimental conditions were slightly modified and a different spinner material was used. Therefore, an ^{13}C enriched resin (made with 1.37 F/P mole ratio, 2 h reaction time, barium hydroxide as

TABLE III
Summary of High Resolution ^{13}C NMR Data on Resoles

Sample	Para-subs. methylol carbons (ppu)[a]	Ortho-subs. methylol carbons (ppu)	Total methylol carbons (%)	Ortho-subs. para-subs. methylol carbons	Oxymethylene carbons (ppu)	Dibenzyl ether bridge carbons (ppu)	Methylene bridge carbons[b] (ppu)	Other ether and active methylol carbons (ppu)	pH[c]
Catalyst effect (13.7 F/P mole ratio, 2 h reaction time)									
NaOH	0.36	0.63	33.0	1.75	0.28	0.080	0	0.57	8.4
Na_2CO_3	0.42	0.69	37.0	1.64	0.21	0.070	0.025	0.92	8.6
$Ba(OH)_2$	0.45	0.88	44.3	1.96	0.14	0.040	0.012	1.05	8.3
F/P mole ratio ($Ba(OH)_2$-catalysed, 2 hours reaction time)									
1.37	0.45	0.88	44.3	1.96	0.14	0.040	0.012	1.05	8.3
1.70	0.52	1.01	51.0	1.94	0.25	0.080	0.013	1.14	—
2.03	0.58	1.12	56.7	1.93	0.36	0.130	0.013	1.11	—
Reaction time effect ($Ba(OH)_2$-catalysed, 1.37 F/P mole ratio)									
2 hours	0.45	0.88	44.3	1.96	0.14	0.040	0.012	1.85	8.3
3½ hours	0.50	0.93	47.7	1.86	0.12	0.036	0.085	1.11	—
5½ hours	0.59	1.07	55.3	1.81	0.06	0.019	0.130	1.05	—

[a] ppu represents number per phenol unit.
[b] Estimated values; less accurate than the other data quoted here.
[c] pH of resole solution after excess water removed.

catalyst, and then cured) was used in a Delrin spinner with 3.65 kHz spinning rate to recheck the reliability of the technique.

The optimum CP-MAS conditions determined by method (a) (see Experimental) were the same as before,[17] but those determined by method (b) were different. These involved 1–5 ms contact time and 8 s delay time. The relative intensity of the aliphatic to aromatic peaks was found to be more affected by the contact time than by the delay time. For instance, if the contact time is increased at values greater than 1.5 ms, the intensities of the aromatic peaks grow slightly while that of the methylene carbons decrease. The intensities of both aromatic and methylene carbon peaks decrease rapidly at contact times around 3 ms. This indicates that the cross-polarization time for the aromatic and aliphatic carbons is different. For some resins, it is difficult, then, to determine the optimum contact time without ambiguity.

The optimum conditions determined by method (b), above, were chosen for CP-MAS analyses because the procedure is believed to be less ambiguous. The average CH_2/Ar_1 ratios measured in the CP-MAS and fully relaxed MAS (120 s delay time) spectra were 1.02 ± 0.05 and 1.00 ± 0.06, respectively. Clearly, this indicates that the CP-MAS technique can be used to follow the extent of curve of resole phenolics quantitatively. Furthermore, the optimum contact time for most resins was found to be 1.5 ms.

A typical CP-MAS spectrum of ^{13}C enriched cured resole phenolic is shown in Figure 6 (a). Ar'_1 is the isotropic peak of the aromatic carbon carrying the hydroxyl group and Ar'_2 is the sum of isotropic peaks of all other aromatic ring

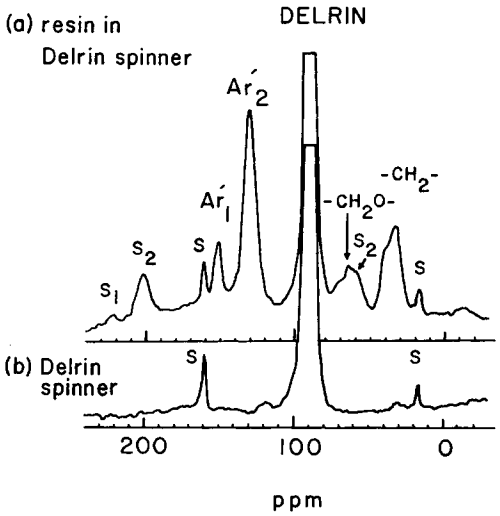

Fig. 6. Typical ^{13}C CP-MAS spectra of ^{13}C CP-MAS spectra of ^{13}C enriched cured resole phenolic and Delrin spinner.

carbons. A shoulder around 120 ppm, which is absent in this particular resin, reflects the presence of free ortho and para aromatic carbons. S, S_1, and S_2 are the spinning sidebands of Delrin, Ar'_1 and Ar'_2, respectively. The spinning sidebands corrections can be made by running a CP-MAS spectrum of only the Delrin spinner under the same experiment conditions and this typical spectrum is shown in Figure 6 (b). These two spectra are for illustration purposes; the intensities of peaks should not be compared directly because the scales are slightly different.

The formation of spinning sidebands has been explained.[20-22] The intensities of spinning sideband pairs are often not the same, but the spinning sideband pairs are symmetrically placed and separated by the spinning frequency. Therefore, the total intensity of a particular carbon peak (e.g., Ar_1) will be the sum of the isotropic peak (Ar'_1) and all the significant spinning sideband pairs (S_1 pair). One of the S_1 pair is hidden at about 75 ppm and can be estimated as follows:

$$\text{Area of } S_1 \text{ at about 75 ppm} = \frac{\text{area of S at 18 ppm} \times \text{area of } S_1 \text{ at 222 ppm}}{\text{area of S at 160 ppm}} \quad (2)$$

Subsequently, the intensity of Ar_1 can be obtained.

The $-CH_2O-$ units (mainly dibenzyl ether bridges and a small concentration of methylols) could be seen clearly in Fig. 6 (a), if they existed. This provides another useful, qualitative piece of information about the nature of the curing reactions of resole phenolics and will be discussed further in a later section. The CH_2/Ar_1 ratios of various kinds of resins are shown in Table IV. The measurement errors were $\pm$ 0.04 for all CP-MAS results.

TABLE IV
Effect of Catalyst on State of Cure

Resin catalysed with	CH_2/Ar_1
Na_2CO_3	1.20
$Ba(OH)_2$	1.03
NaOH	1.01
	0.89*

* Measured with 2.5 ms contact time in CP-MAS.

(i) Effect of Catalyst and Curing pH

The CP-MAS results shown in Table IV indicate that the degree of crosslinking is in the following order of catalyst type: $Na_2CO_3 > Ba(OH)_2 > NaOH$. The Na_2CO_3-catalyzed resole had the highest pH, and this may have contributed to the higher methylene bridge/phenol ratio observed with this catalyst. A series of resins was cured at different pH using the $Ba(OH)_2$-catalysed resole. CP-MAS results (see Figure 7) show the degree of crosslinking increasing strongly with curing pH. At very low curing pH (i.e., 1), the resole cured spontaneously without application of heat or pressure. This resin had a relatively high extent of crosslinking, as shown. The data clearly illustrate that the curing pH is an important parameter determining the ultimate degree of cure of resole phenolics.

When allowance is made for pH differences, our CP-MAS results appear to agree with those of Fukuda and coworkers, who studied the curing reactions of resoles by measuring the viscosity of the resole as it reacted in a mold.[23]

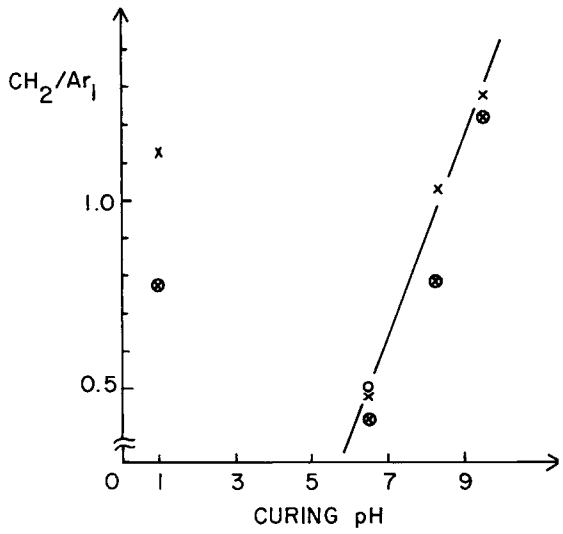

Fig. 7. Effect of curing pH × data obtained with 1.5 ms contact time, 8 s delay time, 500 scans and 3.65 kHz spinning rate; ⊗ data obtained with 2.0 ms contact time, 3 s delay time, 3000 scans and 3.5 kHz spinning rate; O data obtained with 1.0 ms contact time, 8 s delay, 740 scans and 3.65 kHz spinning rate.

(ii) Effect of F/P Mole Ratio

Viscosity, GPC, and solution ^{13}C NMR results cited above have indicated that resoles made with higher F/P mole ratios have slightly higher molecular weights, larger molecular sizes in the GPC solvent, more methylol groups, and more potential formaldehyde sources such as polyoxymethylene oligomers and dibenzyl ether bridges. Therefore, the extent of cure of the resin resole would be expected to be higher the higher the F/P ratio used in the preliminary condensation reaction. The CP-MAS results (Figure 8) confirm this speculation.

(iii) Effect of Reaction Time During Resole Synthesis

The results of GPC, viscosity and high resolution ^{13}C NMR analyses indicate that a longer reaction time during the resole synthesis would produce a prepolymer that cures to a higher extent under given conditions. The reasoning here parallels that just presented for the effects of F/P ratio in the resole synthesis. CP-MAS data are plotted in Figure 9.

(iv) Effect of Curing Time and Curing Temperature

The optimum curing time and curing temperature can be determined by following the CH_2/Ar_1 ratios, as illustrated in Figures 10 and 11.

It is interesting to notice that even for resoles made with a high F/P mole ratio the ultimate degree of cure decreases at curing temperatures higher than the optimum. During curing, it was observed that gases escaped from the press to the atmosphere. The observed decrease in CH_2/Ar_1 ratio might be due to the loss of formaldehyde from the dibenzyl ether linkages, the polyoxymethylene oligomers, or even from the methylol units. At lower temperatures (e.g., below 160°C), the formaldehyde evolved would presumably be available for curing. Moreover, there is evidence[16] that thermal and oxidative decomposition of the resin, which can destroy some methylene bridges, occurs at curing temperature of 180°C or above to form minor amounts of oxidized products with characteristic carbonyl functions. The CP-MAS spectra obtained in this study cannot

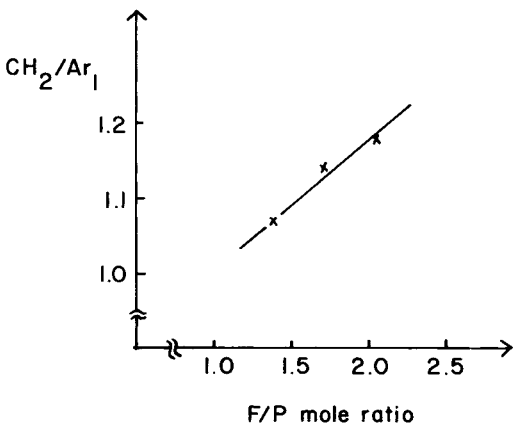

Fig. 8. Effect of resole formaldehyde/phenol mole ratio on subsequent state of cure.

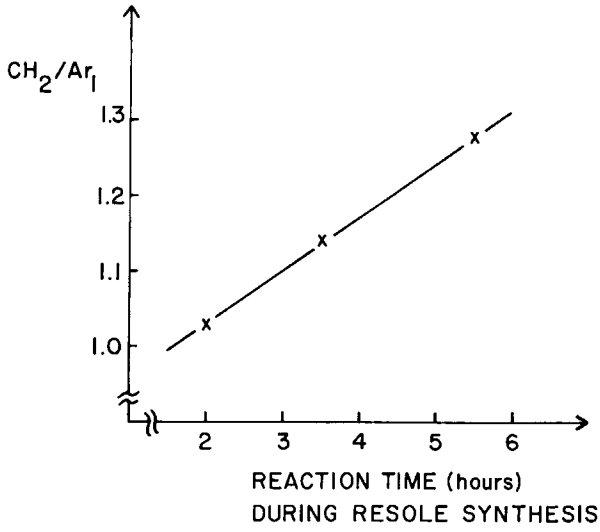

Fig. 9. Effect of reaction time during resole synthesis on subsequent state of cure.

reveal such carbonyl carbons since these are obscured by the spinning sidebands. Nevertheless, the IR spectra of these resins, shown in Figure 12, indicate that there are such carbonyl group at about 1750 cm^{-1}. These bands are absent in

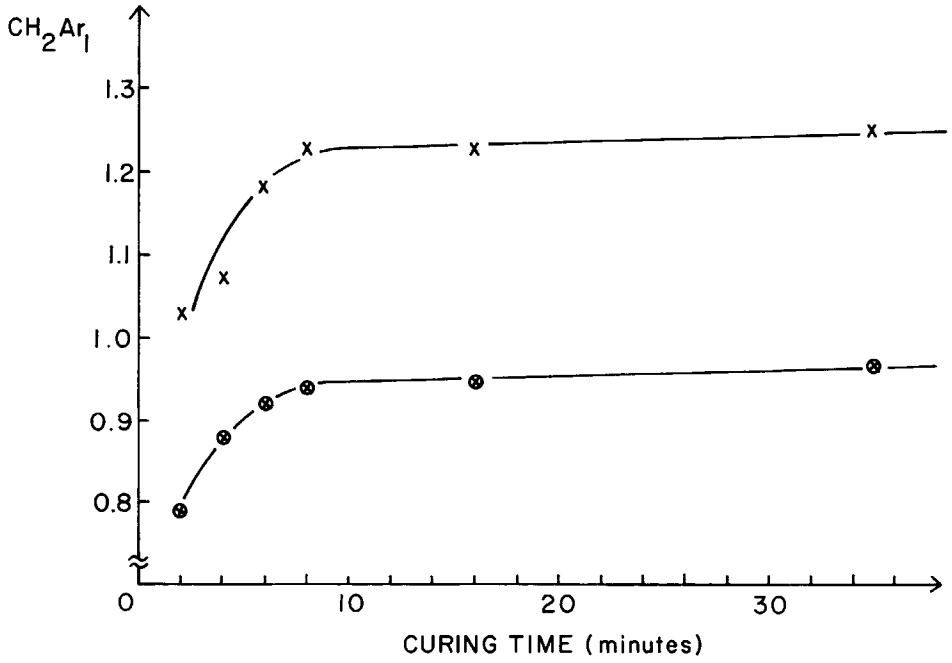

Fig. 10. Effect of curing time × obtained with 1.5 ms contact time, 8 s delay time, 500 scans and 3.65 kHz spinning rate; ⊗ obtained with 2.0 ms contact time, 3 s delay time, 3000 scans and 3.5 kHz spinning rate.

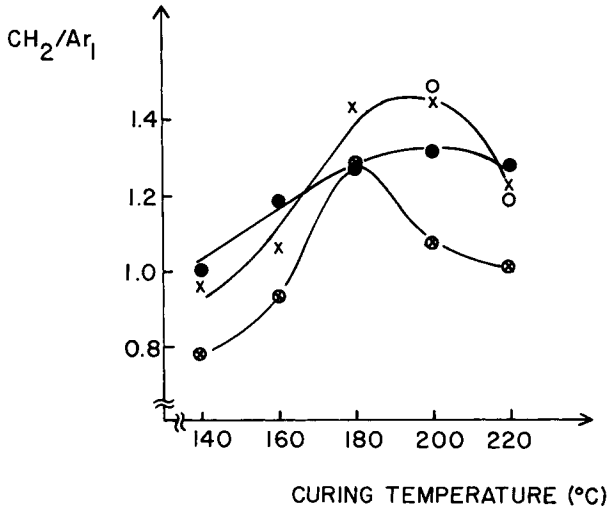

Fig. 11. Effect of curing temperature × obtained with 1.37 F/P mole ratio, 1.5 ms contact time, 8 s delay time, 500 scans and 3.65 kH_3 spinning rate; ○ obtained with 1.37 F/P mole ratio, 1.0 ms contact time, 8 s delay time, 500 scans and 3.65 kH_3 spinning rate; ⊗ obtained with 1.37 F/P mole ratio, 2.0 ms contact time, 3 s delay time, 3000 scans and 3.4 kHz spinning rate; ● obtained with 2.03 F/P mole ratio, 1.5 ms contact time, 8 s delay time, 500 scans and 3.65 kHz spinning rate.

the IR spectra of uncured resoles. Decomposition starts at 180°C for the 1.37 F/P mole ratio resin and the carbonyl content increases with curing temperature. A similar observation is also seen for the higher F/P mole ratio resin, but these events occurred at a higher curing temperature (Figure 10 (f) and (g)).

Furthermore, there is no evidence of thermal and oxidative decomposition for resins cured at 160°C for very long curing times (Figure 12 (i) and (j)). Another feature of these IR spectra in comparison to those of the parent resoles (Fig. 4) is that there are significant increases of the amount of the ortho and para substituted aromatic sites ($\sim$ 1450 cm^{-1}) and a significant decrease of the -CH_2O- units ($\sim$ 1000 cm^{-1}). This is another piece of evidence to indicate an increase of crosslinking.

Technical Limitations and Accuracy of CP-MAS Experiments

The CP-MAS results obtained with different contact times are different. Some of them differ slightly (e.g., Figs. 7 and 11), while others (Table III) differ more. Deliberately, some of the CP-MAS experiments were repeated with shorter delay times (3 s) with the alternative possible "optimum" contact time (2 ms). In order to obtain an acceptable signal/noise balance, which is usually worse for shorter delay times, a larger number of scans was used in these experiments. The difference in delay time merely affects the overall intensities of all peaks to similar extent. The relative peak intensities are not affected as much by different contact times. It can be seen from Figs. 7, 10, and 11 that the CH_2/Ar_1 ratios are different and smaller. Nevertheless, the trend of the results are unchanged. Experimentally, when the contact time is slightly longer

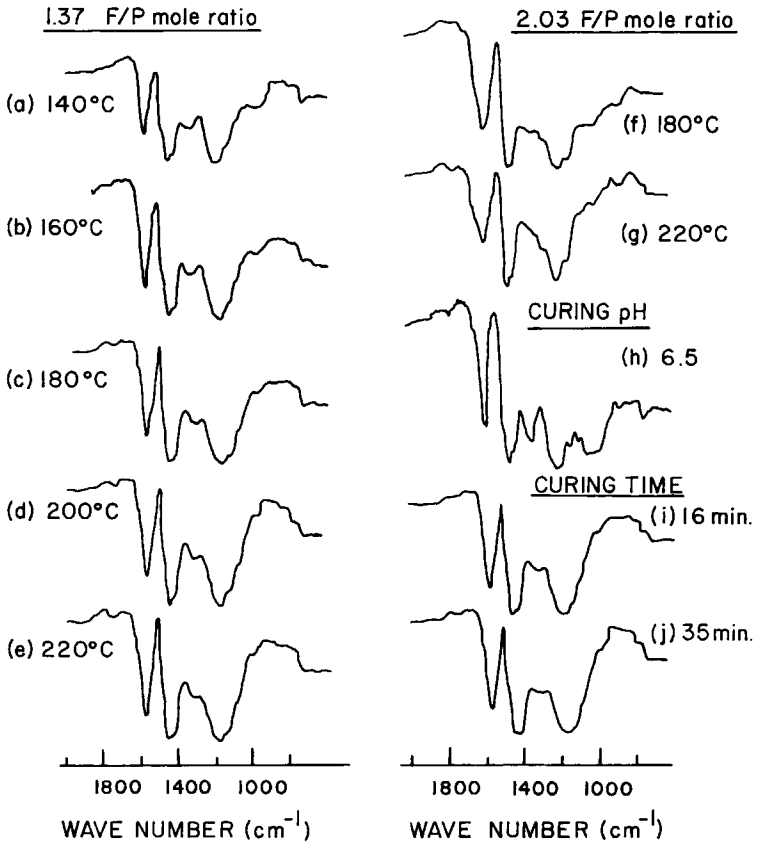

Fig. 12. Infrared spectra of cured resoles.

than the optimum value, the $-CH_2-$ peak starts to decrease slightly while the $-Ar_1-$ peak still increases slightly. This results in a smaller CH_2/Ar_1 ratio. Another example which has been mentioned previously can illustrate this point. The CH_2/Ar_1 was 0.63 for experimental conditions of 2 ms contact time and 8 s delay time. On the other hand the ratio was 1.02 for 1.5 ms contact time with the same delay time.

The other sources of errors reflect problems in reproducing the instrument settings for resolution, Hartmann-Hahn matching, the magic angle, the Delrin background and spinning sidebands corrections and the determination of base lines in the spectra.

In this study, the resins which are to be compared were all analyzed in the same experimental campaign, in order to have internally consistent results. For instance, in the same experimental sequence, the $Ba(OH)_2$-catalysed resin made with 1.37 F/P mole ratio was analyzed at the beginning and at the end of the session; the corresponding CH_2/Ar_1 ratios are 1.03 and 1.07.

All the peak areas were measured in expanded CP-MAS spectra by adopting similar base and boundary lines to improve the precision of the measurement. The measurement errors are mostly $\pm$ 0.04 of the CH_2/Ar_1 values.

Because of the limitations mentioned, we feel that the CH_2/Ar_1 ratios obtained from the present solid-state ^{13}C CP-MAS analyses are reliable but semi-

quantitative only. To this time, in fact, most CP-MAS studies of curing reactions of thermosets seem not to be quantitative enough to derive curing kinetics reliably.

Qualitative Information

The extent of cure of resole phenolics has also been examined by monitoring the ratio of peak areas of CH_2/CH_2O.[14,15] We were unable to follow the -CH_2O- peak quantitatively from the CP-MAS spectra in this study because of overlapping with the spinning sidebands of other isotropic carbon peaks. It is possible, however, to follow the changes in the -CH_2O- peak qualitatively to give some insights about the nature of the curing reactions.

In the figures that follow, the ^{13}C enrichment factors for most resins were not always the same (they vary from 1.90 to 2.25). The Delrin background spectra were slightly different, too, so that the peak intensities cannot be compared directly.

(i) Effect of Catalyst

Figure 13 shows that the resins made with different catalysts have basically the same kind of chemical compositions (e.g., with noticeable -CH_2O- units

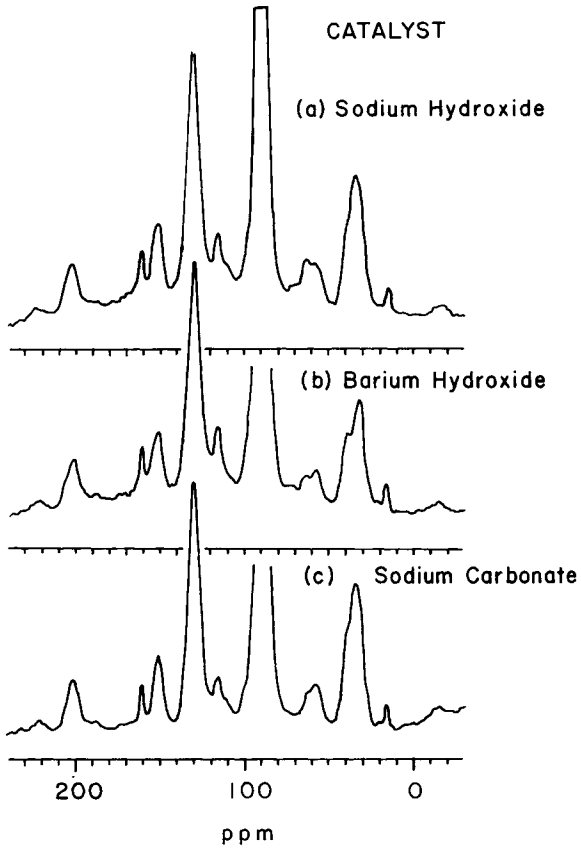

Fig. 13. Effect of catalyst type on chemical composition of cured resoles.

(~ 65 ppm) and free ortho and para aromatic sites (~ 118 ppm)). These particular resins are not highly cross-linked.

(ii) Effect of F/P Mole Ratio

The effect of F/P mole ratio on the curing reaction is clearly shown in Figure 14. Solution ^{13}C NMR results indicated that methylol groups and other potential formaldehyde sources increase greatly with F/P mole ratio in the resole, and there are still some significant amounts of free ortho and para sites left. The free sites after curing clearly decrease the higher the initial F/P ratio of the resole. At the same time, of course, the concentration of $-CH_2O-$ units increases. This suggests that the resole made with a higher F/P mole ratio can be further methylolated when it is cured at the expense of available, excess polyoxymethylene oligomers. This resin has a reasonably high degree of crosslinking (i.e., from methylene bridges) as well as a significant amount of dibenzyl ether linkages and with possibly a small amount of methylol units left.

(iii) Effect of Reaction Time

The effect of reaction time during resole synthesis on the subsequent curing reaction is shown in Figure 15. High resolution ^{13}C NMR analyses of resole

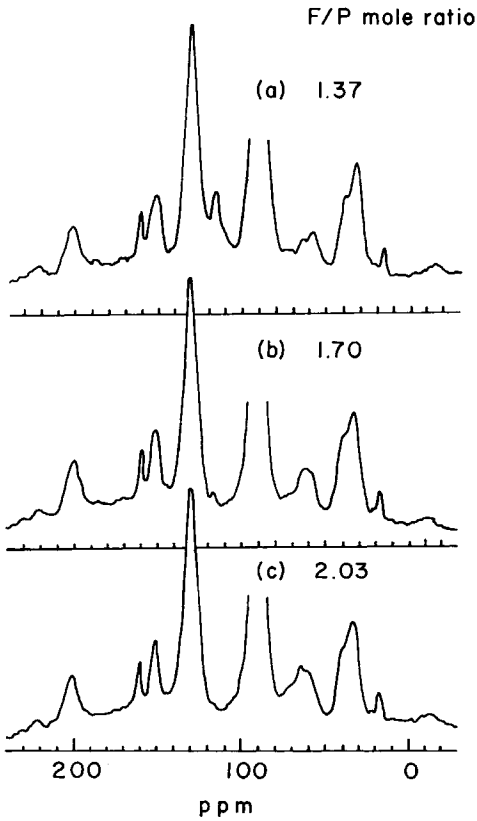

Fig. 14. Effect of formaldehyde/phenol ratio on chemical composition of cured resoles.

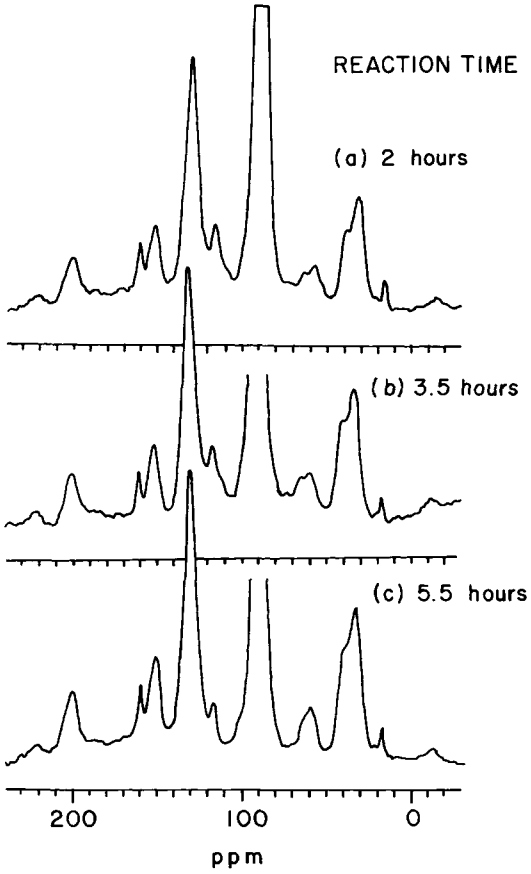

Fig. 15. Effect of duration of F/P condensation reaction on chemical composition of cured resoles.

solutions indicate that methylolation and the production of methylene bridges increase with duration of the F/P condensation reaction. Surprisingly, there is little change of the free ortho- and para-sites after cure. The resin has predominantly methylene bridges and possibly a very small amount of dibenzyl ether bridges. Apparently, the amount of free ortho and para sites left after cure would, therefore, not reflect the degree of crosslinking directly.

(iv) Effect of Curing Time

A series of CP-MAS spectra of resins from the same resole cured for different times at 160°C is shown in Figure 16. The gradual disappearance of the -CH_2O- linkage is seen to be complete after about 8 min cure. The CP-MAS results have indicated that there is no significant change of the CH_2/Ar ratio for longer curing times (Fig. 10). This suggests that all the -CH_2O- units (methylols and dibenzyl ether bridges) are eventually converted to methylene bridges. The formaldehyde evolved during cure has likely escaped instead of condensing with phenols with free ortho and para sites. This conclusion follows because

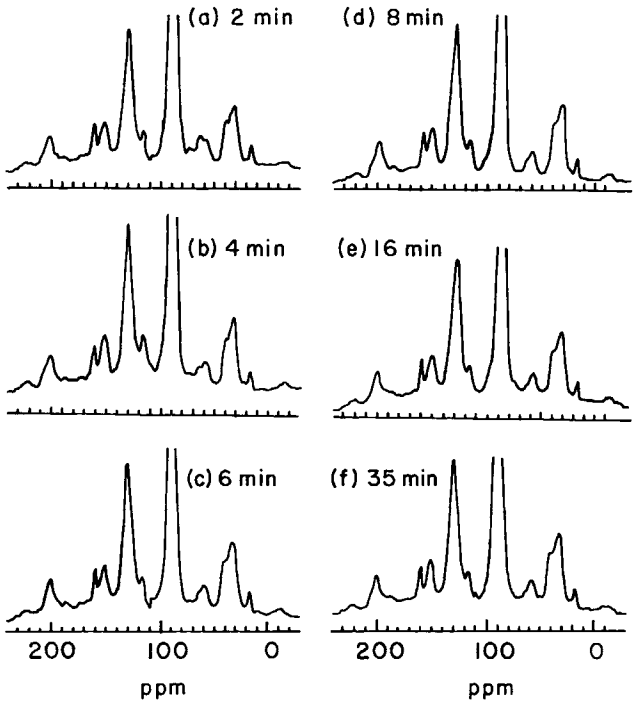

Fig. 16. Effect of time of cure on chemical composition of resole resins.

the shoulder peak at around 118 ppm, which characterizes the free sites, is basically unchanged.

(v) Effect of Curing Temperature

Another two series of CP-MAS spectra of resins with different F/P mole ratio cured at different temperature for 4 minutes are shown in Figure 17. For the lower F/P mole ratio resin (i.e., 1.37), all the -CH_2O- units disappear at curing temperature about 180°C. For the higher F/P mole ratio (i.e., 2.03), the -CH_2O- units essentially disappear at 220°C. One striking feature of these spectra is that there is no significant change of the relative intensity of free ortho and para peaks with curing temperature for both low and high F/P mole ratio resins. This suggests that further full methylolation is possible only in the presence of a large excess of potential formaldehyde sources (i.e., in higher F/P mole ratio resins). This has been demonstrated previously (see Fig. 14) in the effect of F/P mole ratio. These spectra (Fig. 17 (f) to (j)) also suggest that methylolation occurs and is complete at very low curing temperatures, and that the formaldehyde evolved during cure essentially escapes (a similar observation to the effect of curing time). As the curing temperature is increased, the curing reaction is merely converting the -CH_2O- units into the more thermodynamically stable methylene bridges, to reach the ultimate degree of cure.

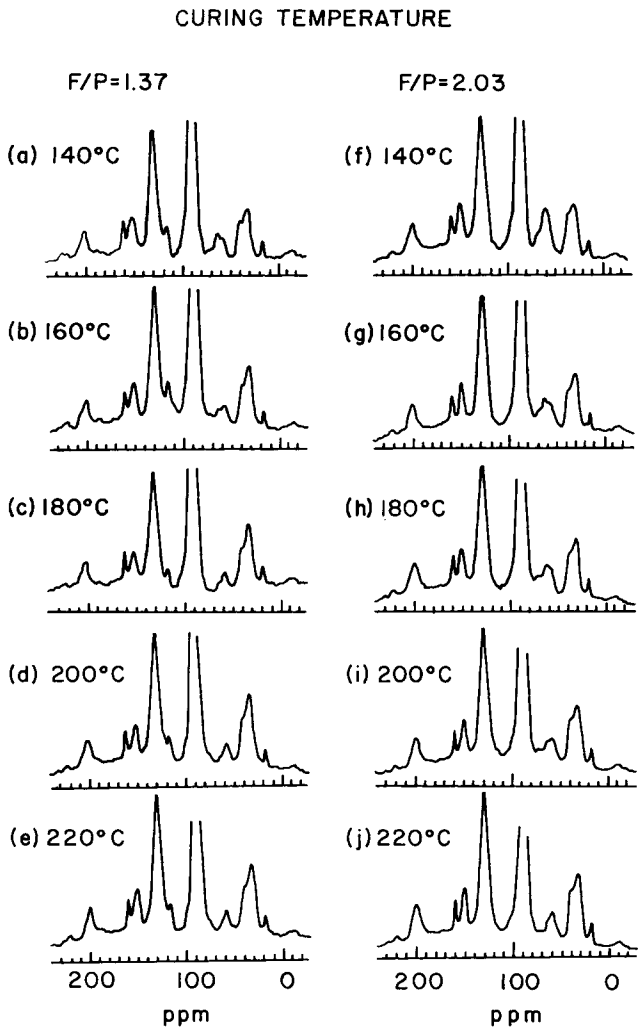

Fig. 17. Effect of curing temperature on the chemical composition of resole resins.

(vi) Effect of Curing pH

The CP-MAS spectra of a series of resins from a given resole composition cured at different pH's are shown in Figure 18. The effect of curing pH on the ultimate degree of crosslinking has been discussed. These spectra provide more qualitative information than just the CH_2/Ar_1 ratios about the curing reactions. As the curing pH is increased from 6.5 to 9.5, the amount of -CH_2O- units and free ortho and para peak decrease significantly. This suggests that most of the -CH_2O- units (mainly dibenzyl ethers bridges) are converted to methylene bridges while others (mainly methylols) are forming methylene bridges by crosslinking with other phenols on the free ortho and para sites. However, under such experimental conditions, there is still a small amount of -CH_2O- units left in the resins after cure.

At curing pH equal to 1, the resin has virtually no -CH_2O- units left but still has a few free ortho and para sites. The resole crosslinks spontaneously at this

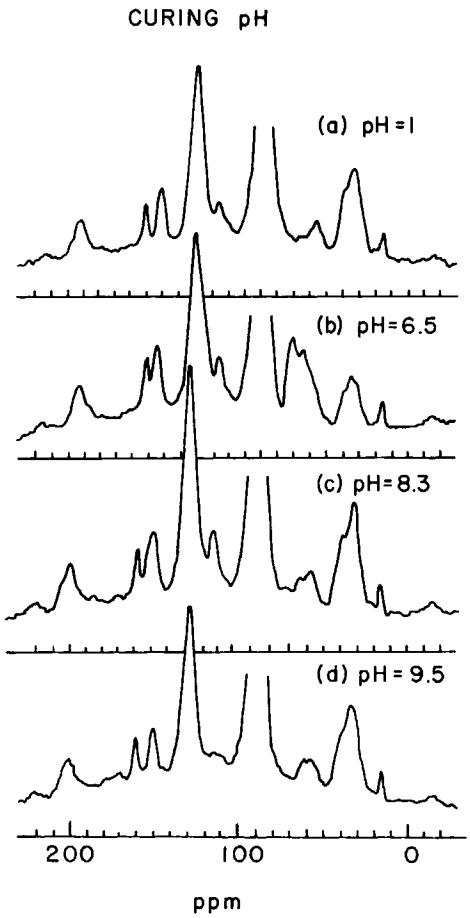

Fig. 18. Effect of curing pH on the chemical composition of resole resins.

pH. Therefore, the curing reaction would be expected to be different from that of resins cured at pH's higher than 6.5, with external heat and pressure.

In summary, under neutral pH, dibenzyl ether bridges are formed preferentially and co-exist with methylene bridges. This is further supported by the IR spectrum of the resin cured at pH of 6.5 (see Fig. 12 (h)). At high pH (alkaline) and at very low pH (acidic), the methylene bridges prevail, since this is the more stable linkage, and higher extents of cure are subsequently expected.

As a whole, this qualitative information implies that the conversion of dibenzyl ether bridges to methylene bridges is an important pathway to obtain higher degrees of crosslinking for resole phenolics.

CONCLUSIONS

The chemical structures of resole prepolymers and their intermediates are very complex because of the many closely related isomers available. Nevertheless, the chemical reactions for the curing are basically divided into three stages.

Firstly, a mixture of simple mono-nuclear methylolphenols are formed by the initial substitution reactions between formaldehyde and phenol.

Secondly, higher molecular weight prepolymers are formed by condensation reactions between methylolphenols themselves and with phenol in many possible ways. These prepolymers contain many active methylol groups. Dibenzyl ether bridges and methylene bridges co-exist and polyoxymethylene oligomers and different kinds of benzyl-type hemiformals are also formed. The extent and proportion of these species in the resole depend on the ratio of reactants (i.e., formaldehyde, phenol, alkaline catalyst) and reaction conditions (i.e., temperature, time, concentration, and type of catalyst).

Thirdly, as curing proceeds, further methylolation takes place by unzipping the existing potential formaldehyde sources, and further condensation occurs at the expense of the available active methylols. The dibenzyl ether bridges and methylene bridges still co-exist. At curing temperatures around 160°C, the former bridges are less stable and are converted into methylene bridges with the loss of formaldehyde and water. However, at curing temperatures above 180°C, the proportion of methylene bridges starts to decrease due to thermal and oxidative decomposition of the resin.

For resin being cured in a press with sufficient pressure to prevent foaming, the ultimate degree of cure depends on the resole composition, the curing time, and the curing temperature. The molecular weight of the resole can be increased with increased F/P condensation reaction time, reaction temperature, and F/P mole ratio. This would increase the subsequent degree of cure under given curing conditions.

The kind of catalyst used has great effect on the resole composition and its molecular size, and also determines the preferential methylolation at the para-position in the following increasing order: $Ba(OH)_2$, NaOH, Na_2CO_3.

The curing pH affects the degree of crosslinking as well as the type of linkages formed. At high or very low pH, methylene bridges are almost exclusive, while at neutral pH, dibenzyl ether bridges are predominant. The degree of cure increases with curing pH (from pH = 6.5 onwards). Resins cured at high pH, neutral pH, and very low pH are dark reddish, milky white, and pinkish respectively. It is a common practice in industry to make "colourless" resin by neutralizing the alkaline resole before further curing. It should be understood that the amount of methylene bridges will be reduced because dibenzyl ether bridges are predominant at this curing pH. This may affect the mechanical and thermal properties and chemical stability of the resole phenolics.

High resolution solution ^{13}C NMR spectroscopy is the most powerful analytical tool to characterize the chemical composition of soluble resoles. It is advantageously used in conjunction with GPC and viscosity techniques. Because of poor resolution, IR spectroscopy is a suitable technique only for qualitative information. Solid state ^{13}C CP-MAS NMR spectroscopy is another powerful technique to allow study on the solid state polymers. Due to the technical limitations and potential errors, the data from this technique are semi-quantitative only.

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