

Analysis of Phenol-Formaldehyde Resols by Gel Permeation Chromatography

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Synopsis

The chromatographic analysis of resol solutions in tetrahydrofuran solvent, by means of a set of columns packed with crosslinked polystyrene gels, has been carried out with adequate resolving power for a clear-cut qualitative or semiquantitative differentiation between various types of resols to be practicable. The resulting chromatograms, which show the distribution of different constituents by molecular size, could be interpreted by the use of reference substance and by calibrating the system with a number of compounds of known structures. The method has been used to investigate the way in which various reaction parameters (nature of catalysts, proportion of starting material, treatments undergone by the resols) affect the composition of resols. Different commercial products have been thus characterized. It has also afforded an insight into the progress of the polycondensation reaction as a function of time and helped to state the reactivity of different groups and unblocked ring positions. Thus, an hydroxymethyl group appears to be more reactive in the para than in the ortho position. Otherwise the reactivity of unblocked ring positions would be enhanced by an hydroxymethyl group in the ortho rather than para position.

INTRODUCTION

The chemistry of phenol-formaldehyde polymers is much more complex than that of other types of condensation polymers such as polyamides, polyesters, etc. This is due to the two kinds of polydispersities that occur in resols with regard to molecular weights, as well as to the many types of chemical structures of molecules. Thus, for example, one may expect 13203 linear isomeric structures in a polymer having only ten phenolic units, bound together at ortho or para ring position by methylene links.¹ Of course, this type of linkage is not the only possible one. The molecular weights of an average resol may be included between that of water and 7000.²

Many fractionation methods have been recommended. Paper partition chromatography of phenolic mixtures indicates the following:

1. The single-ring compounds: the two monohydroxymethylphenols (2-HMP and 4-HMP), the two dialcohols (2,4-DHMP and 2,6-DHMP), and the trialcohol (2,4,6-THMP)

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2. Among the two-ring compounds: the three dihydroxydiphenylmethanes (2,2'-DPM; 2,4'-DPM; 4,4'-DPM); only one monohydroxymethyl-DPM (HMDPM) out of the six theoretically possible; three polyhydroxymethyl-DPM out of the 19 possible (with two, three, or four alcoholic functions)

3. Among the three-ring compounds: four compounds only, besides less easily detectable

4. The preferential formation of some of these compounds has been shown to be a function of resin preparation conditions.

The related results of Reese,³ Finn and James,⁴ and Yeddanapali,⁵⁻⁸ who achieved the most important studies on the subject, are divergent, among other things, about the presence of HMDPM and dibenzyl ether, and about the relative importance of addition and condensation reactions.

The formation of acetylated, silylated, or urethane derivatives stabilizing the resin by blocking off the —OH groups have made it possible to use gas-liquid chromatography⁹ for estimating the single-ring compounds. Resuming this method, Zavitsas,¹⁰ in opposition to Yeddanapali,^{5,6} is of the opinion that ortho substitution increases the reactivity of unblocked ring positions.

In the case of the most condensed parts of a resol, one was limited to isolating the mixtures with a few individual compounds as possible, mainly by means of precipitation and dissolution fractionation methods. However, these methods are very long and rather unreliable, owing to the lack of stability of resol constituents.

Some authors have shown it possible to analyze by gel permeation chromatography (GPC) the simplest resins that is, prepared in acidic media, and usually called "novolak." The phenol and the DPMs¹¹ and the three-ring compounds¹² have been separated by GPC of a novolak resin, and a "picture" of molecular weight distribution has been obtained.¹³

The problem of fractionating the more complex resins prepared with an alkaline catalyst (resols) has just been outlined inconclusively.¹⁴ Yet the GPC technique could be quite useful in this case, as it allows in situ fractionation of compounds in solution which could not be separated by gas-liquid chromatography because of their great instability or their high boiling point. This is true for resol constituents.

EXPERIMENTAL

Preparation of Products

The methods described by Kohn¹⁵ and d'Alelio¹⁶ were used for preparing, in alkaline or acidic media, the different resins that will be discussed here. The initial mixture of phenol and formaldehyde, maintained during the reaction at constant temperature under inert atmosphere, is finally distilled for removing water in a rotary vacuum evaporator.

Several individual reference constituents were synthesized according to the literature. Because of the difficulty of obtaining well-crystallized

compounds because of small quantities of isomers or impurities, starting materials were first purified and synthesis was performed under inert atmosphere. The purity of obtained compounds was controlled by gel permeation chromatography (GPC) and gas-liquid chromatography (GLC) when possible. The latter method was developed following Higginbottom.⁹ Reaction control and absence of any oxidation was checked by infrared spectral analysis in the phenolic ring substitution region (600–1100 cm^{-1}), according to the data of Bender,¹⁷ Burke,¹⁸ and Richards and Thompson.¹⁹ The identification was completed by comparing boiling points and paper-chromatogram R_F values to those given in the literature. The chromatograms were prepared according to the method of Freeman²⁰ as modified by Reese,²¹ and were studied for various types of commercial papers in this laboratory by Omnes and Doussin.²² The method consists of two-dimensional chromatography. The first development, by water saturated with carbon dioxide, separates compounds according to the number of rings; the second one, with a butanol/ammonia mixture (4:1), separates the same compounds according to the number of hydroxymethyl groups per ring. Table I lists the chemical formulas and characteristics of the compounds that have been thus synthesized and identified.

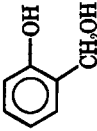

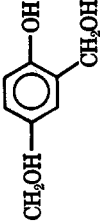
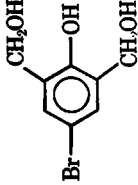
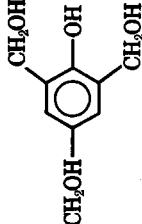
It could be interesting, in addition, to dispose of higher molecular weight resin fractions. Precipitation and dissolution fractionation techniques appeared to be very tedious and inefficient. The related gradient elution chromatographic method, used for fractionating fuel oils, is fast and shows no fraction recuperation problems.²³ Thus, we tried to apply the method to phenolic resin: a small quantity of polymer was dissolved in an appropriate solvent (tetrahydrofuran, THF) and the solution was brought to the precipitation point with a nonsolvent (cyclohexane). Then this solution was poured on top of a column packed with a support medium inert with respect to solution (Fluoropack 80) and filled with the same solvent-nonsolvent mixture.

The solution was allowed to diffuse in the column and eluted with a mixture of increasing solvent power. Thus, the most soluble parts were eluted first, then the more insoluble ones. About 3 g of polymer was used for a total elution volume of 600 cc, at a liquid flow rate of 5 ml per minute. The molecular weights of the fractions were measured, when possible, by means of a Mechrolab 301 A vapor pressure osmometer.

Gel Permeation Chromatography (GPC)

Separations have been performed on a Recomat apparatus (distributed by Waters Associates), with tetrahydrofuran (THF) as solvent. THF is a good solvent for phenolic resins. Injected samples had an average concentration of 0.5 wt-%. Compounds separated on the columns were detected by means of a Waters differential refractometer, measuring the refractive index difference between solution and pure solvent. Columns were 4 ft long, $\frac{3}{8}$ in. in diameter, and were packed with Styragel, a Waters crosslinked polystyrene.

TABLE I
Phenol Formaldehyde Resin Constituents

Compound	Formula	Boiling pt., °C	R_f values water/ ammonia	GPC peak (K)	Preparation method (reference)
2-HMP				0.67	commercial
4-HMP		120	0.72/0.65	0.62	(38)
2,4-DHMP		101	0.72/0.43	0.54	(40) (41)
4-Br-2,6-DHMP		163		0.57	(42)
2,4,6-THMP		75	0.73/0.24	0.52	(43)

<p>3,3',5,5'-THM 4,4'-DPM</p>		<p>0.65/0.27</p>	<p>0.52</p>	<p>(43)</p>
<p>2,2'-DPM</p>		<p>0.52</p>	<p>(44)</p>	
<p>2,4'-DPM</p>		<p>0.52</p>	<p>(6)</p>	
<p>4,4'-SPM</p>		<p>0.52</p>	<p>commercial</p>	
<p>Triphenol</p>		<p>0.41</p>	<p>(17)</p>	

There is no definite rule for choosing, with certitude, the optimal gel porosity for a given type of mixture to be separated. In principle, low molecular weight compounds will be more easily separated with gels of lower porosity. Nevertheless, it appeared that adding a column of slightly higher porosity (700 or 500 Å, for example) gave more efficiency than that obtained by increasing the number of low-porosity columns (60 Å). Furthermore, adding more columns, whatever their porosity limit, did not increase separation above a given level. The best combination of columns for separating phenolic resins was finally the following: 700, 500, 250, 60, 60, and 60 Å.

Miscellaneous

Free phenol in resins was analyzed by a gas-liquid chromatographic method derived from that of Stevens,²⁴ with 2,5-dimethylphenol as internal standard. Free formaldehyde was analyzed chemically with hydroxylamine hydrochloride.²⁵

RESULTS AND DISCUSSION

GPC of Phenol-Formaldehyde Resin Compounds

GPC is a liquid-phase chromatographic technique able to fractionate molecules according to their size or to a related parameter.²⁶ In order to correlate the elution volume of a compound with its size by a calibration curve, one must first choose the most suitable method of measuring molecular size. It is an easy problem for a homologous series of compounds; in this case, molecular weight is quite suitable. Otherwise, two specific measurements of dimension of small molecules have been suggested: the effective chain length, in carbon atoms units,^{27,28} and the molar volume, the ratio of molecular weight to density at a given temperature.²⁹⁻³¹ These

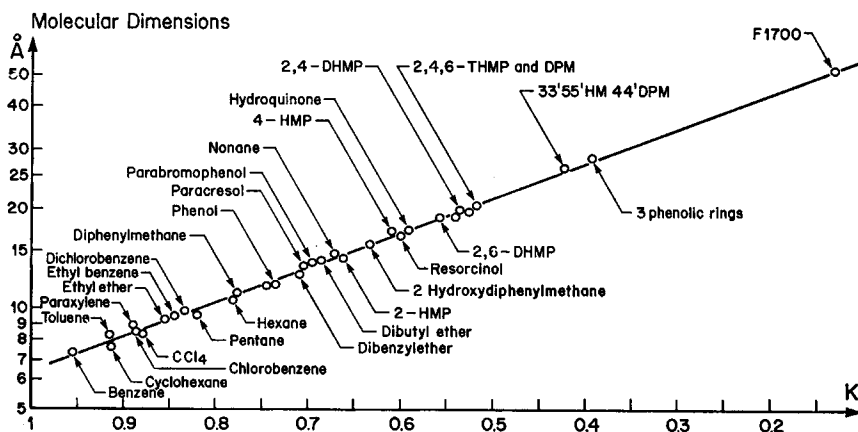


Fig. 1. Calibration curve.

TABLE II
Molecular Dimensions and Elution Volumes of Various Compounds

Compound	Length (calculated), Å	GPC peak (<i>K</i>)	Compound	Length (calculated), Å	GPC peak (<i>K</i>)
Calibration Compounds					
Pentane	9.5	0.830	Diphenylmethane	11.2	0.781
Hexane	10.6	0.785	Chlorobenzene	8.7	0.891
Heptane	11.9	0.748	Dichlorobenzene	9.9	0.839
Nonane	14.5	0.672	Trichlorobenzene	9.9	0.840
Cyclohexane	7.5	0.915	Carbon tetrachloride	8.5	0.885
Benzene	7.2	0.956	Ethyl ether	9.1	0.865
Toluene	8.2	0.916	Dibutyl ether	14	0.690
Ethylbenzene	9.4	0.860	Dibenzyl ether	12.5	0.712
Paraxylene	9.2	0.891			
Mono- and Polyphenols					
Phenol-1 THF	12	0.740	2-Hydroxy-DPM.1 THF	15.4	0.638
Paracresol-1 THF	13.4	0.710	Hydroquinone.2 THF	17.8	0.604
Parabromophenol-1 THF	13.9	0.700	Resorcinol.2 THF	16.8	0.611
Phenol-Formaldehyde Compounds					
Ortho-HMP-2 THF	14.2	0.670	4,4'-DPM.2 THF	21	0.525
Para-HMP-2 THF	18	0.608	2,4'-DPM.2 THF	20.8	0.525
2,4-DHMP-2 THF	20	0.540	3,3',5,5'-HM 4,'- DPM.6 THF	26	0.455
6-Cl-2,4-DHMP-2 THF	20	0.540	3-Ring para-THF	27.5	0.397
4-Br-2,6-DHMP-2 THF	18.5	0.562	4-Ring para-THF	33	—
2,4,6-THMP-24 THF	20.4	0.525	6-Ring para-THF	39	—
			Fraction with $M_n =$ 1700	—	0.139

two methods themselves have appeared questionable or unpracticable when applied to phenolic compounds able to display in solution nonlinear conformations and associations with solvent, or unobtainable in a pure state.

For this reason it was preferred here to measure molecular dimensions directly, by means of a molecular model set and molecular lengths and configuration tables.³² A calibration curve was first built with a nonhomologous series of compounds but having well-known conformation in solution in THF: short-chain (thus linear) *n*-alkanes and *n*-ethers,³³ and rigid aromatic or cyclic derivatives. This calibration curve is given in Figure 1. The position (V_e) of GPC peaks is represented by the distribution coefficient *K* calculated with respect to two internal standards, nitrogen (V_e) and

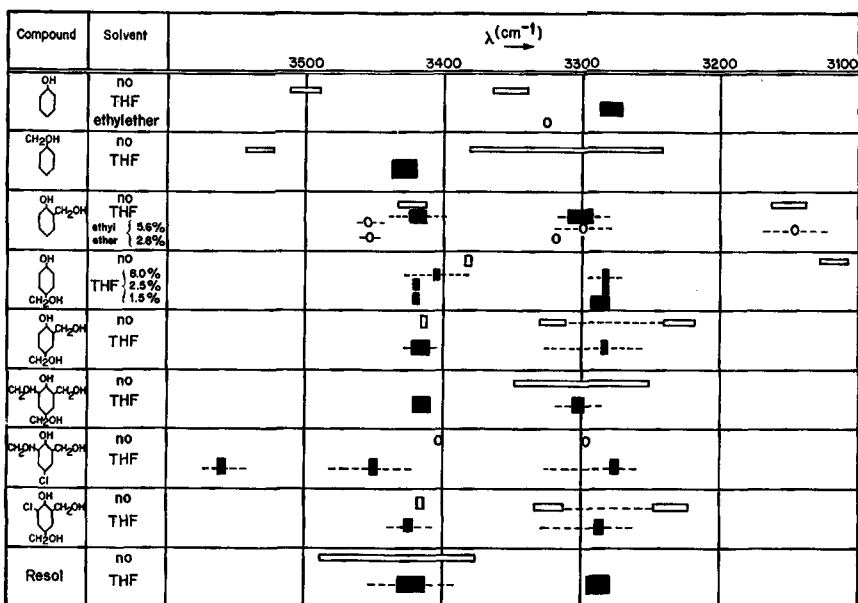


Fig. 2. Infrared absorption bands of reference compounds, in the pure state and in a solvent (THF or ethyl ether).

a polystyrene with a very high molecular weight (V_0), V_t and V_0 being the extreme values of elution volumes:

$$\left(K = \frac{V_e - V_0}{V_t} \right).$$

K is independent of any variations due to the apparatus or aging of columns. The lengths and K values of the calibration compounds, as well as those of other compounds studied here, are given in Table II.

The conformation of hydroxylated compounds, alcoholic or phenolic, in solution in THF is far less known. One must take into account the solute-solvent associations. It is known that THF is likely to give a hydrogen bond with the mobile hydrogen of the OH group.³⁴ Indeed (Table II), the monophenols (*p*-cresol, *p*-cromaphenol, *p*-chlorophenol) and polyphenols (resorcinol, hydroquinone) display an elution behavior related to the formation of a bond between THF and the OH group. Their length, calculated by means of molecular models, with one THF molecule per OH group, is identical with that deduced from elution volume in the preceding calibration curve.

On the basis of this solvent-OH group association, it is now possible to explain the behavior of hydroxymethylated phenols and other reference compounds that have been synthesized during this work. The problem of calculating apparent lengths is complicated here by the possible formation of strong intramolecular bonds between hydroxymethyl ($-\text{CH}_2\text{OH}$) and $-\text{OH}$ groups in the ortho position, even in polar solvents.³⁵ But there are

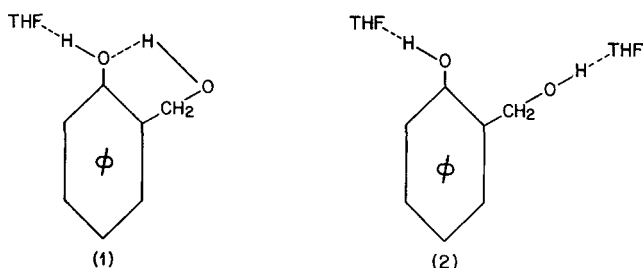


Fig. 3. Conformations of 2-HMP.

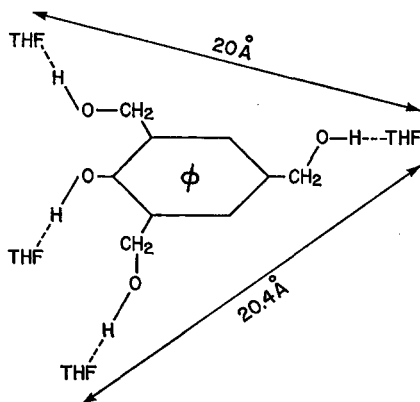


Fig. 4. Conformations of 2,4-DHMP and 2,4,6-THMP.

no definite data in the literature with regard to intramolecular bonds in hydroxymethylated phenols in THF. Therefore, infrared spectra of these compounds have been recorded in the $3100\text{--}3600\text{ cm}^{-1}$ region, in the pure state and in solution in THF. Results are given in Figure 2. It shows that bands corresponding to bonding between THF and, respectively, phenolic and alcoholic OH groups, appear at $3280\text{--}3300\text{ cm}^{-1}$ and $3420\text{--}3430\text{ cm}^{-1}$ (as seen on phenol and benzyl alcohol spectra in THF). The intramolecular bond band appears at 3420 cm^{-1} on spectra of saligenin and 2,4-DHMP in the solid state, which is confirmed elsewhere.¹⁹ Thus, it may be masked, in solution in THF, by the THF-alcoholic OH group bond band. To measure the length of the saligenin molecule, one has thus to choose between the two conformations (1) and (2) of Figure 3, as the saligenin spectrum in THF shows two bands at 3300 and 3420 cm^{-1} .

On the other hand, the eventual intramolecular hydrogen bond should involve the more acidic phenolic hydrogen. So, conformation (1) has a lower probability to occur, and otherwise its length does not fit the calibration curve. Thus conformation (2) would be the actual conformation of saligenin in THF. In addition, Figure 2 shows that 4-HMP and 2,4,6-THMP do not show intramolecular bonding in the solid state as 2,4-DHMP and 6-chloro-2,4-DHMP do. In THF solution bonding with the solvent appears. But the THF-phenolic OH group bond band of 2,4-

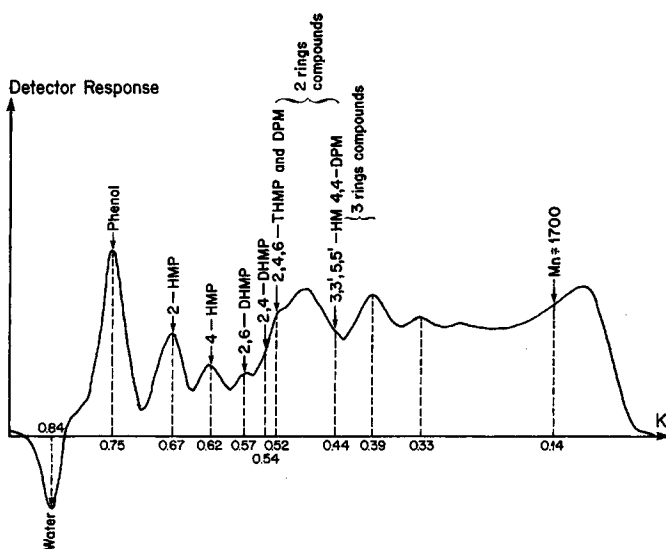


Fig. 5. Peak identification of a resol.

DHMP is very weak, which could be explained by formation of an intramolecular bond. This might explain the little difference between di- and trialcohol elution volumes (Fig. 4). The 4,4'-DPM molecule is symmetrical, with its rings bent to an angle of 52° . This conformation fits the calibration curve and was kept for calculating the lengths of the other phenolic compounds of Table II, the probable elution volume of which is deduced from the calibration curve. The elution volume of a phenolic fraction of molecular weight 1700, obtained by means of elution chromatography, has been recorded. Extrapolating the calibration curve to this value suggests a length of about 50 Å.

The complete identification of the peaks of a resol is obtained by means of this calibration curve and, with reference to the individual compounds, by means of paper chromatography. To this end, the fraction of solution corresponding to one single peak is removed at the end of the apparatus. If the K value of the peak maximum and the R_F value of the main compound in the removed sample correspond with the K and R_F values of the same reference compound, this peak may be assigned to this compound. The GPC spectrum of thus identified resol is shown in Figure 5. It is to be noted that peak heights corresponding to pure substances are increasing functions of injected substance quantity. It will thus be possible to compare, semiquantitatively, the heights of each respective peak, by superposing different resol spectra, provided that solutions be injected at constant temperature and volume.

Characterization of Various Resol Preparations

Influence of Physical Treatments on Final Composition. Distilling water does not change the nature and proportion of other compounds (Fig. 6).

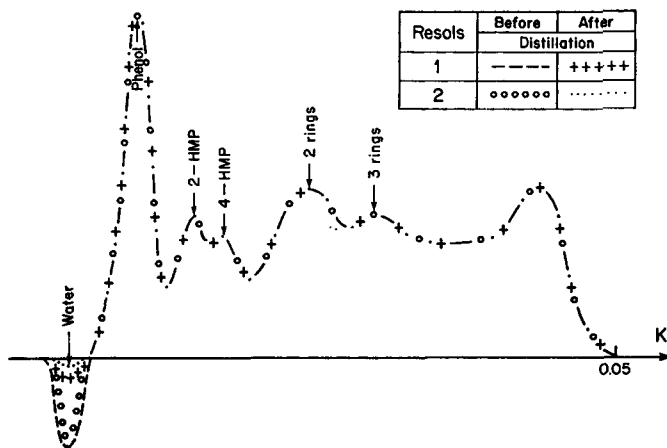


Fig. 6. Distillation of a resol.

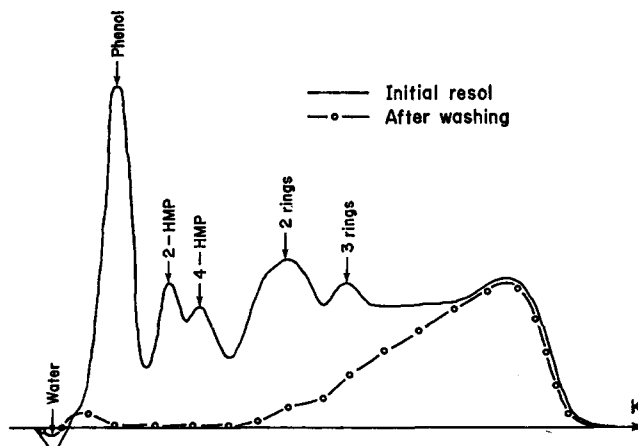


Fig. 7. Precipitation with oxalic water of a solution in acetone of an ammonia-catalyzed resol.

Similarly, washing with oxalic water removes lighter fractions without any further polycondensation (Fig. 7). Finally, fractionating by elution chromatography leads to relatively definite but still polydisperse fractions (Fig. 8). The latter figures clearly show the superiority of GPC as an efficient tool for the analysis of phenolic resols.

Analysis of Commercial Resols. One of the goals of this laboratory is to synthesize thermostable resols. Comparing the GPC spectra of some commercial resols and referring to their thermal stabilities inferred from thermogravimetry, they may be classified in two families (Fig. 9):

1. The first type of resols display a rather regular distribution of compounds of any molecular weight, including those with one and two rings. Their weight loss is less than 20% at 500°C and 8% above 600°C. This first type includes the following commercial resins: Monsanto SC 1008, Ironsides 1111, and Phenora.

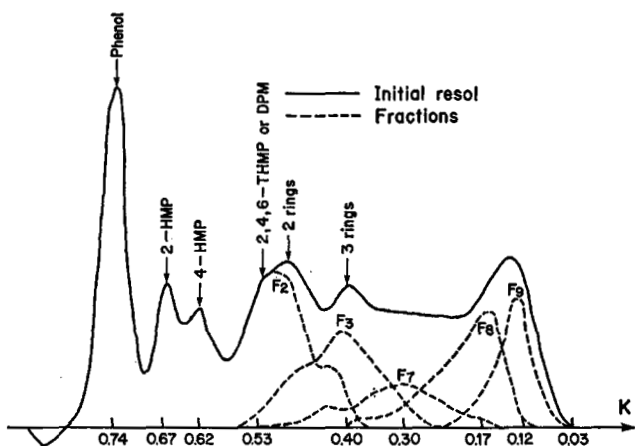


Fig. 8. Fractionation of a resol by gradient elution chromatography.

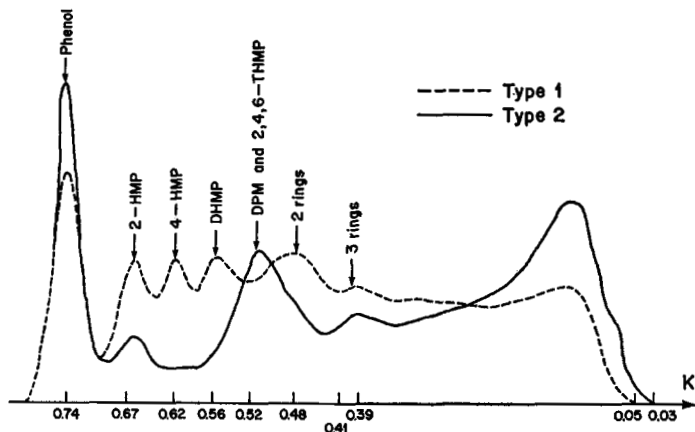


Fig. 9. Commercial resols.

2. In the second type of resols, there is a relatively more important quantity of free phenol and highly condensed compounds, at the expense of other intermediates (especially those with one ring). At 500°C, their weight loss is very important (about 35%) but less important above 600°C (6%). The Ironsides 91LD and Durez 22 323'S are of this type.

The stability (up to 500°C) of the crosslinked lattice might thus be extremely improved by a regular repartition of intermediate compounds and lowered by too many compounds of higher molecular weight in the uncured resol.

Influence of Nature of Catalyst on Distribution. Resins were prepared with the following catalysts: hydrochloric acid, ammonia, and sodium, lithium, barium, and zirconium hydroxides. The spectrum of novolak (HCl catalyst) is distinctly different from that of alkaline resols (Fig. 10). The absence of hydroxymethyl substitutions on the single- and double-ring

TABLE III
 Number of —CH₂— per Ring as a Function of Catalyst and Initial Molar Ratio (F/P)

	HCl		NH ₄ OH		NaOH
Initial molar ratio					
<i>F/P</i>	0.92	0.92	1.22	2.50	1.37
Free formaldehyde, %	15	8	12	54	5
Free phenol, %	6.5	27	20.5	16.5	13
Number of —CH ₂ — per ring (calculated)	0.84	1.18	1.33	1.37	1.50

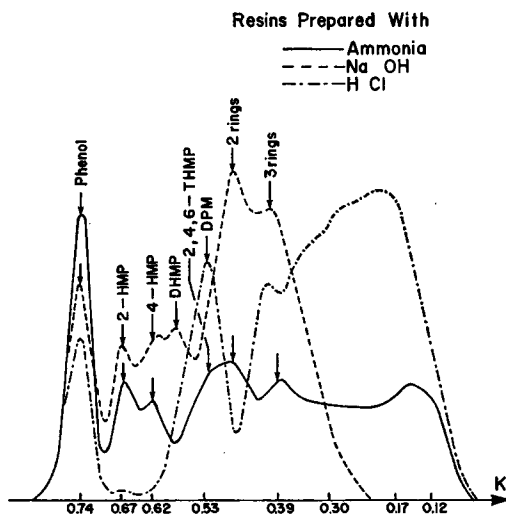


Fig. 10. Comparison of resins prepared with ammonia, sodium hydroxide (resols), and hydrochloric acid (novolak).

phenolic compounds, and the presence of a very definite peak of DPM ($K = 0.525$) are noticeable. The number of phenol and formaldehyde molecules having effectively reacted together have been calculated independently, which provides the number of [—CH₂— + —CH₂OH) groups per phenolic ring (Table III). In the case of novolaks, this ratio is equal to 0.84, which actually means very few —CH₂OH substitutions. Definitely, a zirconium hydroxide-catalyzed resin is not a resol, as could be expected, but a novolak (Fig. 11).

The molecular-size distribution is more regular with ammonia than with sodium hydroxide, the latter leading to an increased formation of one- and two-ring compounds (Fig. 10). At last, lithium hydroxide leads to a resol different from all the other ones, with no phenol, monoalcohols, and highly condensed compounds, in contradiction to other observations.¹⁰

Influence of Initial Formaldehyde-to-Phenol (F/P) Ratio. A comparison of spectra of ammonia-catalyzed resols with initial *F/P* ratios equal to 0.92, 1.22, and 2.50 shows (Fig. 12):

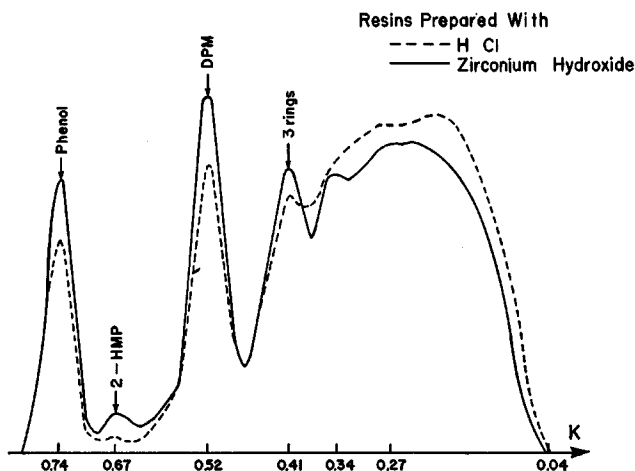
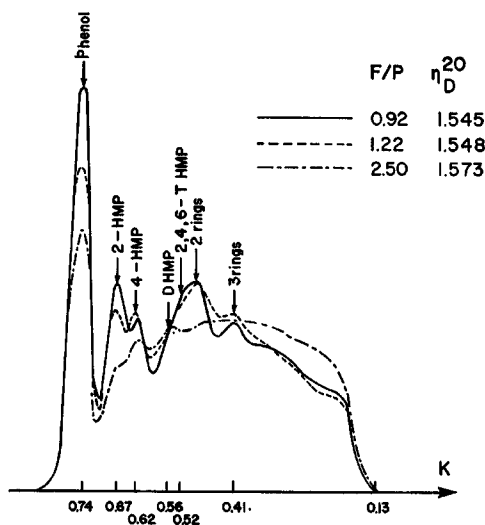


Fig. 11. Resols catalyzed by HCl and zirconium hydroxide.

Fig. 12. Influence of initial F/P ratio on resol composition.

1. A reciprocal variation of peak height ratio of 2-HMP and 4-HMP, with initial F/P ratios. Thus, 2-HMP would disappear faster than 4-HMP with formaldehyde, implying that 2-HMP would be more reactive than 4-HMP with respect to formaldehyde addition.

2. A shift toward higher molecular sizes, a flattening of one- and two-rings compounds, implying formation of compounds with more hydroxymethyl substitutions. Indeed, Table III shows the increase in the number of $(-\text{CH}_2\text{OH} + -\text{CH}_2-)$ groups per phenolic ring with increasing initial F/P ratio.

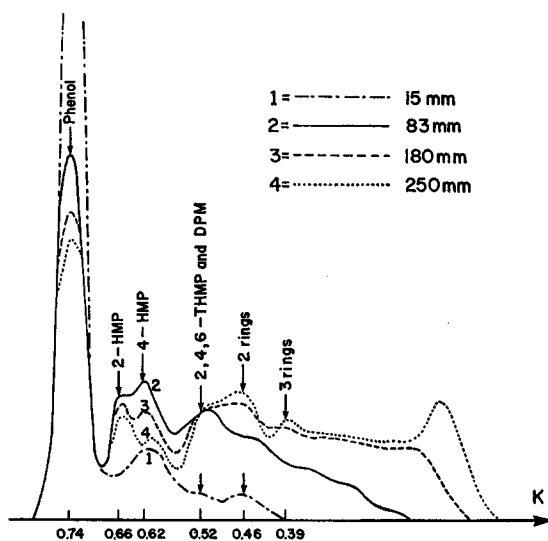


Fig. 13. Ammonia-catalyzed resol composition as a function of time.

Evolution of a Polycondensation Reaction with Time. An ammonia-catalyzed resol at 97°C and sodium hydroxide resols at 80°C, 89°C, and 97°C were synthesized. Samples were taken during reaction, strongly cooled to block any further reaction, and analyzed by GPC.

In the case of ammonia resol (Fig. 13), there is an exclusive initial formation of 4-HMP (spectrum 1), the quantity of which increases in the mixture up to a maximum value and then decreases near the end of the reaction. Condensation compounds appear before any 2-HMP formation. Thus, 4-HMP would be more reactive than 2-HMP with respect to formaldehyde addition, and 4-HMP condensation with phenol would also be fast. As soon as 2-HMP appears, the ratio of 4-HMP to 2-HMP keeps decreasing with time. The *para*-CH₂OH group would thus be more reactive. On the other hand, we have already seen that 4-HMP reacted with phenol, prior to any 2-HMP formation. To summarize, the —CH₂OH group would react faster on the *para* position of phenol and subsequently would itself be more reactive than the *ortho* position, with respect to further reactions.

The case of sodium hydroxide resols is more complex (Fig. 14). They are more reactive and all the compounds appear faster. The 4-HMP goes on building up as 2-HMP and dialcohols quantities decrease (spectra 1 and 2). Then the relative quantities of phenols, 2-HMP, 4-HMP, decrease regularly to the benefit of one and two ring compounds only, but without any more condensed compounds, as in the case of ammonia. Temperature influences the rate of compound formation rather than their actual nature and final composition. Nevertheless, to find the individual reactivities, we tried to add some additional formaldehyde to the resol and to let it "age:"

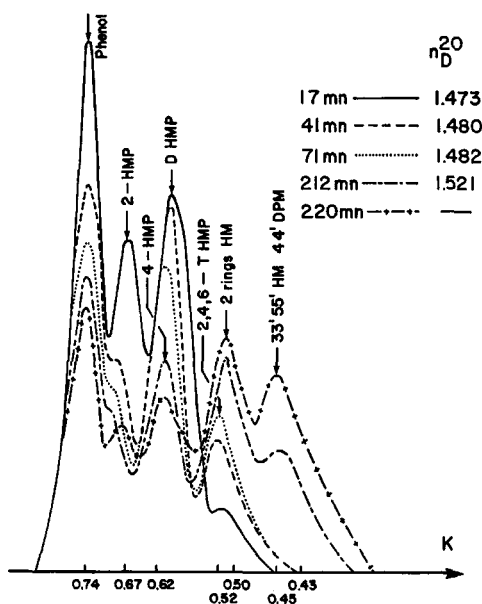


Fig. 14. Sodium hydroxide-catalyzed resol composition as a function of time.

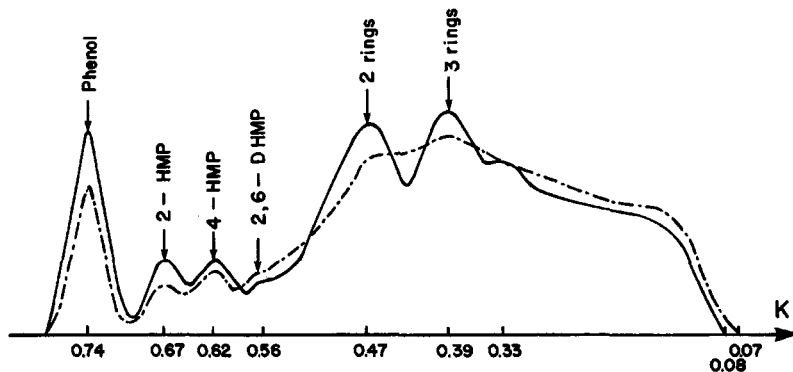


Fig. 15. Addition of formaldehyde to a resol.

1. A sodium hydroxide resol was prepared at 80°C; 12% formaldehyde was added to the resol, which was then heated for 140 min at 80°C. Figure 15 shows an increase of the 4-HMP-to-2-HMP ratio. The condensation that could occur during that time would induce the opposite variation, as will be seen further. This would imply that formaldehyde addition is faster on 2-HMP. The ortho alcoholic group would enhance reactivity of unblocked ring positions, which agrees with the results of Zavitsas et al.¹⁰ and contradicts those of Yeddanapali⁵ and Freeman.³⁸ This agrees with the conclusions above.

2. There is only very little formaldehyde left in a resol at the usual termination of the reaction. Thus, further evolution, or aging, will in-

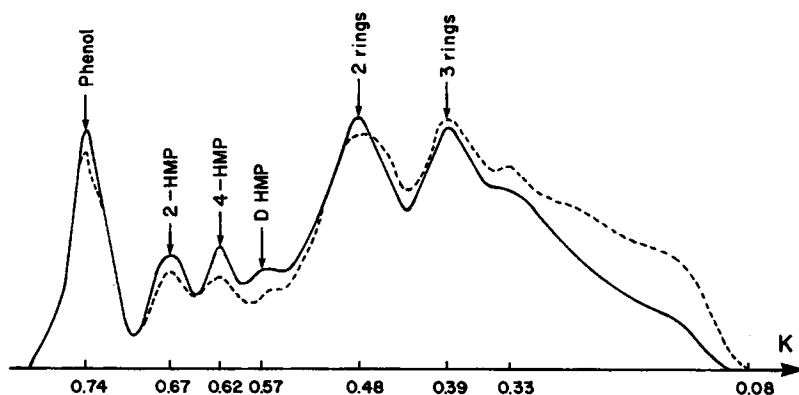


Fig. 16. Aging of a resol.

volve condensation reaction between different species rather than their addition reactions with formaldehyde. After aging three months at ambient temperature, the resol shown in Figure 16 has lost relatively more 4-HMP than 2-HMP. Thus, 4-HMP condenses more easily. As unblocked ring positions are less reactive, (see above), condensation would involve the hydroxymethyl group. This group would then be more reactive in the para rather than in the ortho position, which agrees with conclusions about the ammonia catalyst.

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