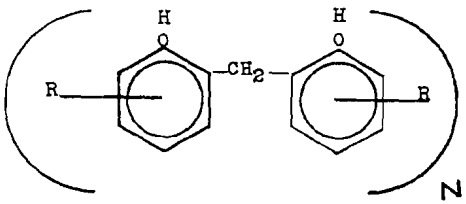
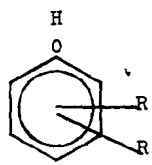
The resin discussed previously serves as a typical example for this solvent system. As indicated earlier it was not possible to obtain extracts from this resin with the usual solvents. Using KOH-$SbCl_3$ an extract was obtained which yielded an excellent infrared and PMR spectra. These spectra will be shown and the analysis of bands presented.

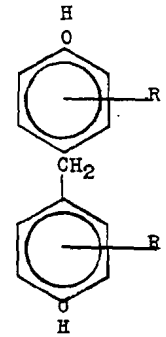
The author would like to suggest the use of the KOH-$SbCl_3$ as a solvent for polymers other than phenol-formaldehyde. He has previously(1) reported these which are soluble in $SbCl_3$ and $AsCl_3$ and presumably all of these will be also soluble in the KOH system. At present he is working on the solution of various cellulose materials in this solvent.

The second part of this paper will be concerned with the identification of monomers and polymers that are extracted from resins. The discussion will be limited to the kinds of phenol derivatives which may occur in resins and how each can be identified by using PMR spectroscopy. It has been found that each give a unique pattern. As solvents, $AsCl_3$, $SbCl_3$ or KOH-$SbCl_3$ can be used. The author has found the extract yield is larger with these rather than conventional solvents and the spectra are quite sharp.

The compounds which have been examined are as follows. All give unique patterns or positions which allows one to distinguish one from the others.







R = H, CH_2OH, $CH(CH_3)_2$, C $(CH_3)_3$ etc.

(1) Polymer Letters Vol. 3, PP. 81-82 (1965)

MOLECULAR WEIGHT DISTRIBUTION MEASUREMENTS OF PHENOLIC RESINS

John J. Gardikes and Fred M. Konrad

INTRODUCTION

It has long been recognized that novolak resins are composed of a spectrum of molecules made of phenolic nuclei joined by methylene bridges at the ortho and para positions. Many of the "average" properties of novolaks are dependent upon the distribution of these various molecular species. Two methods were developed to quantitatively measure the molecular weight distribution of phenolics: (1) the classical fractional precipitation, and (2) the Gel Permeation Chromatography techniques.

DISCUSSION

Fractional Precipitation

Resolution of the molecular weight distribution of a phenolic novolak by fractional precipitation required a preliminary separation of the "non-resinous" components. All of the phenol and a portion of the dihydroxydiphenylmethanes were removed from the resin by precipitation of an ethanol solution in a large volume of water acidified with oxalic acid to a pH of 3-5. The precipitation was repeated a second time to insure complete phenol removal. This preliminary separation was necessary because phenol interfered with the subsequent fractional precipitation. [1]

A 2.5% solution of the "water insoluble" resin in an acetone-water solvent was separated into narrow molecular weight bands by preferential evaporation of the acetone with a stream of nitrogen. The solution was adjusted to pH 3.0 with oxalic acid to facilitate separation of the precipitated fraction from the supernatent liquor. The temperature of the solution was maintained at 30.00 $\pm$ .02°C in a constant temperature water bath. The resolution was further improved by refractionation of the first four fractions, representing about 20% of the original solids, from a second acetone-water solution. As each secondary fraction was removed another fraction from the primary separation was added. The solvent-swollen secondary fractions were recovered by precipitation into water, or by removing the solvent by vacuum evaporation. Molecular weights of the fractions were measured by vapor pressure osmometry (VPO).

Fractionation data for a typical novolak resin are shown in Table I. This includes 14 fractions resolved by fractional precipitation, the bisphenols removed by water washing, and the free phenol determined directly on the resin.

Integral and differential distribution curves constructed from the data are shown in Figure 1. It will be noted that 60% of the resin had molecular weight species of less than 2000 and the remainder tailed out to over 7400.

Gel Permeation Chromatography

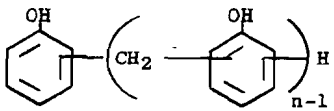
Resolution of the molecular weight distribution of polymers by Gel Permeation Chromatography [2] is based on the principle that the degree of permeation of a molecule into a solvent-swollen, cross-linked polystyrene gel is dependent on its

size. Small molecules permeate more readily than large. Hence, a polymer solution when passed through a column of appropriate pore size gel will elute in order of decreasing molecular weight.

The molecular weight distribution studies with phenolics were done on a Waters Associates[3] Gel Permeation Chromatograph. A dilute resin solution sample was injected into a carrier solvent stream which flowed through a series of four 3/8" x 48" polystyrene gel columns with pore size ratings of 40A°, 100A°, 800A° and 1000A°. Tetrahydrofuran was used as the solvent at a flow rate of one milliliter per minute at 30°C. A differential refractometer and recorder measured and recorded continuously the difference in refractive index between the sample stream and a reference stream. This difference is a direct measure of the concentration of the polymer species eluted from the columns.

The chromatograph was calibrated for phenolics by determining the volume of tetrahydrofuran required to elute a series of phenolic fractions of narrow molecular weight distribution. Additional calibration data were obtained with several linear polymer fractions and some pure aliphatic hydrocarbons. The calibration data are summarized in Tables II and III.

Infrared structural studies in our laboratories have shown that for novolaks and fractions similar to those used in our present studies, 75% of the end hydroxyls were para-substituted and 25% ortho-substituted.[4] In addition, 15 to 20% of the phenolic nuclei were trisubstituted or branched. The amount of branching was a linear function of the molecular weight with the obvious exception of the low molecular weight species. In calculating the chain lengths of the phenolic fractions, it was assumed that the novolak resin structure (I) was linear and composed of phenolic nuclei joined only by methylene groups at the ortho and para positions.



I

The calibration curves shown in Figure 2 were obtained by plotting the elution volume of each standard against the log of the calculated chain length. The elution volume is expressed in counts, each count representing five milliliters of eluent. It will be noted that the phenolic fractions eluted sooner than comparable size non-phenolic standards. This deviation indicated the phenolic molecules were larger than calculated. Branching was ruled out as the cause since the deviation was also observed at the low molecular weight range.

Table IV lists the phenolic and non-phenolic chain lengths for the complete range of elution volumes. It will be noted that the difference between the phenolic and non-phenolic chain length values increased with an increase in chain length. If the difference is divided by the number of phenolic nuclei in the novolak chain, a number which averaged 3.53A° was obtained.

This value of 3.53A° was attributed to association of one molecule of tetrahydrofuran per phenolic nucleus. Hendrickson and Moore[5] reported a value of 3.54A° for one hydrogen bonded

TABLE I

ACETONE-WATER FRACTIONAL PRECIPITATION DATA

Fraction	Wt. %	Σ Wt. %	Mi
Phenol	4.78	4.78	94
Bisphenol	9.31	14.09	200
14	3.02	17.11	383
13	5.96	23.07	410
12	5.47	28.54	561
11	5.55	34.09	675
10	5.58	39.67	882
9	8.67	48.34	1130
8	7.25	55.59	1470
7	8.92	64.51	1840
6	8.20	72.71	2470
5	7.75	80.46	3450
4	9.84	90.30	4440
3	6.57	96.87	7260
2	2.39	99.26	7400
1	0.74	100.00	7400 (est.)

molecule of tetrahydrofuran. Thus, the addition of n x 3.53A° (where n is the number of phenolic nuclei in the chain) to the previously calculated phenolic chain lengths brings all calibration data within very good agreement, Figure 3.

These results further suggest that our chain length calculations were correct and the phenolic branches, if present, merely added their effective chain lengths to the main chain length of the resin.

A typical gel permeation chromatogram for a phenolic resin is shown in Figure 4. From this curve and the calibration curve of Figure 2 for phenolics, the number average, $\overline{Mn}$, and weight average, Mw, molecular weights of the resin were calculated, Table V.

Figure 5 shows the good agreement of the integral distribution curves for the same resin obtained by the fractional precipitation and Gel Permeation Chromatographic techniques. The number average molecular weights, $\overline{Mn}$, as calculated by these two methods, was 603 and 670, respectively. The vapor pressure osmometry value was 571.

Gel Permeation chromatography promises to be a rapid method for determining the average molecular weights and molecular weight distributions of phenolics. It may be used in conjunction with other analytical techniques to follow the changes in molecular distribution during the course of a phenol/formaldehyde condensation reaction and correlate such changes with time or raw material consumption.

REFERENCES

1. Work done by E. A. Barr and V. Auerbach
2. Moore, J. C., J. Polymer Sci., A2, 835 (1964)
3. Waters Associates, Framingham, Massachusetts
4. Work done by S. M. Rugg and J. J. Smith
5. Hendrickson, J. G. and Moore, J. C., "Gel Permeation Chromatography III, Molecular Slopes vs. Elution", published by Waters Associates, Framingham, Massachusetts

TABLE II

CALIBRATION DATA FOR LINEAR STANDARDS

Fraction	Chain Length, A°	Elution Counts*
122,000 NBS Polystyrene	2945	19.4**
4000 polyglycol	247	22.0
2000 polyglycol	138	23.3
C28 aliphatic	37.2	26.4
C12 aliphatic	17.1	30.0
o-dichlorobenezene	7.7	34.4

*One elution count equals 5 ml. of eluent.
**Interstitial volume in counts.

TABLE III

CALIBRATION DATA FOR PHENOLIC FRACTIONS

Fraction	Molecular Weight	Chain Length, A°	Elution* Counts	Phenolic Nuclei
phenol	94	7.6	32.45	1.00
2,4-oisphenol-F	200	12.4	29.3	2.00
14	383	21.4	26.9	3.72
12	561	29.6	25.6	5.40
10	882	44.5	24.5	8.42
8	1470	71.9	23.4	14.00
6	2470	123	22.5	23.42
4	4440	209	21.4	42.00
3	7260	341	21.0	68.60
2	7390	347	20.3	69.90

*One elution count equals 5 ml. of eluent.

TABLE IV

CORRELATION OF CHAIN LENGTHS OF LINEAR STANDARD WITH PHENOLIC FRACTIONS

Elution Counts	Length Phenolic Chain (A_P°)	Length Linear Chain (A_L°)	$A_L^\circ - A_P^\circ$	Phenolic Nuclei, ni	$(A_L^\circ - A_P^\circ)/ni$	$A_P^\circ + 3.53ni$
32.45	7.6	10.9	3.3	1.00	3.30	11.1
32	8.1	11.9	3.8	1.03	3.77	11.7
31	9.5	14.2	4.9	1.32	3.55	14.2
30	11.1	17.0	5.9	1.65	3.58	16.9
29	13.2	20.6	7.4	2.07	3.57	20.5
28	16.0	25.3	9.3	2.64	3.52	25.3
27	19.9	31.9	12.0	3.43	3.50	32.0
26	25.9	42.5	16.6	4.65	3.57	42.3
25	36.1	61.6	25.5	6.82	3.74	60.2
24	54.5	94.0	39.5	10.46	3.77	91.5
23	89.0	150	61	17.45	3.50	150.6
22	154	247	93	30.60	3.05	262

TABLE V

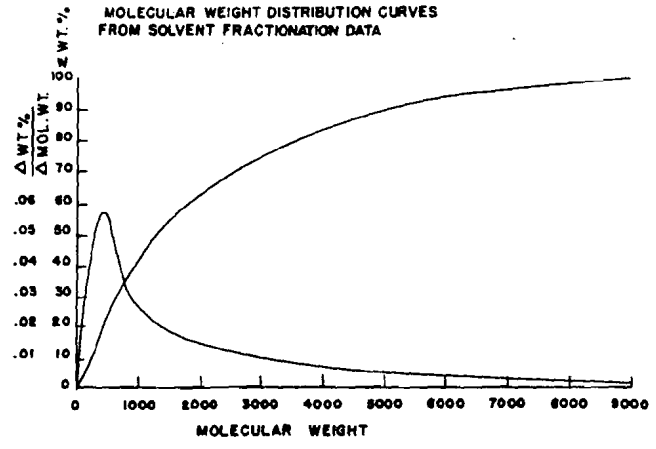
CALCULATION OF THE NUMBER AVERAGE AND WEIGHT AVERAGE

MOLECULAR WEIGHTS FROM GEL PERMEATION CHROMATOGRAPHY

Elution Counts	Wi	Mi	Wi/Mi	Mi Wi	Wt. %	ΣWt. %
32	31	105	.2952	3,255	1.44	1.44
31	4	130	.0308	520	0.45	1.89
30	64	166	.3855	10,624	3.78	5.67
29	117	212	.5519	24,804	4.38	10.05
28	112	277	.4043	31,024	5.11	15.16
27	166	365	.4548	60,590	7.21	22.37
26	218	490	.4449	106,820	9.57	31.94
25	286	720	.3972	205,920	12.38	44.32
24	346	1160	.2983	401,360	14.77	59.09
23	398	1900	.2068	746,700	16.16	75.25
22	366	3250	.1126	1,189,500	14.09	89.34
21	248	5600	.0443	1,388,800	8.39	97.73
20	86	10,000	.0086	860,000	2.26	99.99
	2437		3.6353	5,029,917		

$\overline{Mn} = \Sigma Wi / \Sigma (Wi/Mi) = 2437/3.6353 = 670$; $\overline{Mw} = \Sigma(Wi/Mi)\,\Sigma Wi = 5029917/2437 = 2064$

FIG. 1



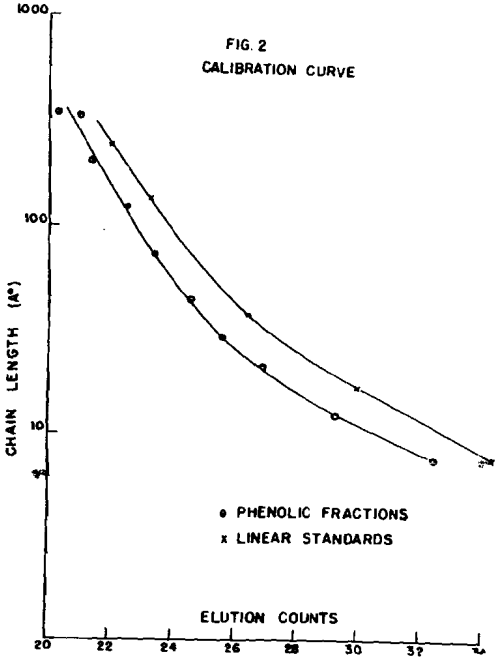


FIG. 2
CALIBRATION CURVE

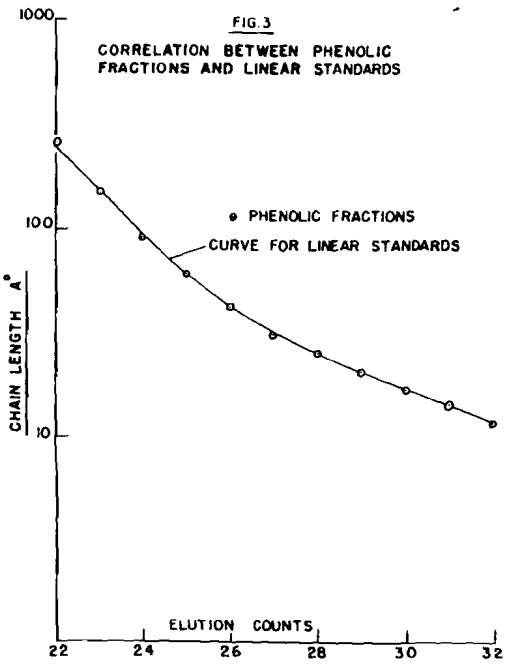


FIG. 3
CORRELATION BETWEEN PHENOLIC FRACTIONS AND LINEAR STANDARDS

FIG. 4

GEL PERMEATION CURVE

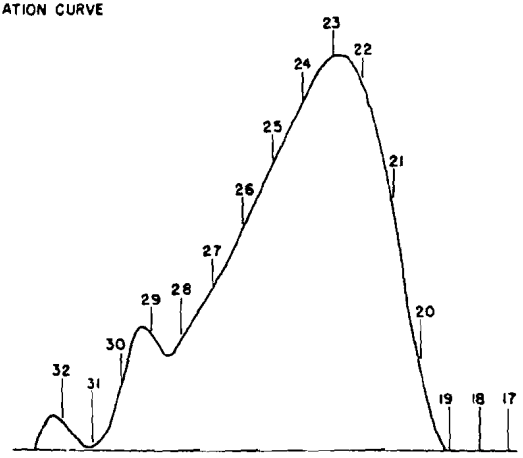


FIG. 5

COMPARISON OF INTEGRAL DISTRIBUTION CURVES