Gel Permeation Chromatographic Analyses of Resole Phenolic Resins

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Synopsis

Tetrahydrofuran solutions of resole polymers were analyzed by gel permeation chromatography (GPC) on crosslinked polystyrene gel packings. The best separation was obtained with low solvent flow rates in low porosity columns. Irregular elution volumes were observed, but the effects of this erratic behavior can be eliminated by referencing retention times to that of a marker compound such as benzene or phenol. A calibration and data analysis method are presented which utilizes hydrodynamic volumes. Phenolic polymers vary in shape and ability to form hydrogen bonds with solvent; hence their molecular weights cannot be estimated from GPC data. Separation of the constituent species of resole samples is shown to be incomplete, because of aggregation between the various phenol derivatives. Particular peaks in the GPC chromatogram could generally not be assigned to individual species. Despite these limitations, GPC is a useful tool for characterizing phenolics, and several applications are reviewed here.

INTRODUCTION

Phenol–formaldehyde polymers are among the oldest known thermosetting materials.[1] Despite this antiquity, the significant developments which have been made in phenolics technology have been derived largely from empirical or intuitive insights. This is because the soluble prepolymers, which are formed as the initial products of the condensation of phenol and formaldehyde, comprise a complex mixture of different species and because the subsequent crosslinking reactions and structures that occur in the solid state have not been amenable to chemical analysis. Modern techniques are changing this situation, for ex- the study of curing reactions of phenolics.[2]

Gel permeation chromatography (GPC) is currently the most widely used method for characterizing molecular weight distributions of polymers, and this article explores the application and limitations of this analytical technique with soluble resole phenol–formaldehyde polymers. Complete characterization of resoles by GPC is very difficult. The low molecular weight region of the GPC chromatogram consists of a number of overlapping peaks,[3] while the higher molecular weight region gives the appearance of a single peak. Despite these difficulties, GPC analyses have been used to provide qualitative pictures of the distribution of molecular sizes in samples[4] and to investigate the general effects of various reaction parameters on the composition of resole prepolymers.[3,5,6]

In this article we explore the effects of variables in the GPC technique on the

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efficiency and limitations of this analytical method for phenolic polymers. Improved calibration and data handling procedures are described, and a quantitative method for summarizing details of the size distribution of these materials is presented. Several applications of this technique are summarized briefly.

EXPERIMENTAL

Analyses were performed on a Waters ALC 100 gel permeation chromatograph. The solvent was tetrahydrofuran (THF) which was purified by distillation after refluxing for at least 24 h over potassium. The solvent used boiled at 65°C at 1 atm pressure. "Styragel" polystyrene gel columns were used for separations. Samples were introduced through the 2-mL sample loop injector supplied with the chromatograph. Resolution was observed to deteriorate with faster flow rates through the columns. The best compromise between resolution and analysis time appeared to be at 1.5 mL/min flow rate, and this was the condition used in this study. Different flow rates may be expected to be better suited to other packing types and porosities.

Resole concentration in injected samples was about 4 mg/mL. Elution volumes were not affected by phenolic concentrations over the range (1–4 mg/mL) which was studied. This is as expected for low molecular weight species found in these phenolic prepolymers.

The concentrations of species in the eluting solvent was measured with a Waters differential refractometer. The response of this detector may not be strictly proportional to the concentration of different compounds because the specific refractive index increment may change with the number of phenolic nuclei in the material.[6,7] This may be a minor source of error compared to other difficulties such as incomplete resolution, which is described below.

Ultraviolet (UV) detection is not as sensitive as the refractive index technique, and the UV extinction coefficient varies with size of the phenol formaldehyde derivative.[8] This detector was therefore not used in this investigation.

GPC Column Arrangements

The effects of column configuration on GPC separation were studied. Styragel columns were available with nominal pore sizes of 10^6, 10^5, 10^4, 500, 200, and 60 Å. Use of all columns in series separated the high molecular weight species but gave poor resolution of lower molecular weight components. Similar results were obtained with 10^6-, 10^4-, and 10^3-Å columns in series.

The best separation was achieved with a configuration consisting of 10^3-, 500-, 200-, and 60-Å columns. This arrangement gave the best resolution of low molecular weight species, with some loss of separation of the very largest components in the sample. In all cases, resolution improved with slower flow rates, down to 1.5 mL/min.

Figure 1 shows a typical chromatogram of a phenolic prepolymer. The rather steep rise at elution volumes greater than 18 counts indicates that high molecular weight species are excluded from the columns without differentiation. The lowest elution volumes in these chromatographs are slightly less than that corresponding to a 9000 molecular weight anionic polystyrene in THF.

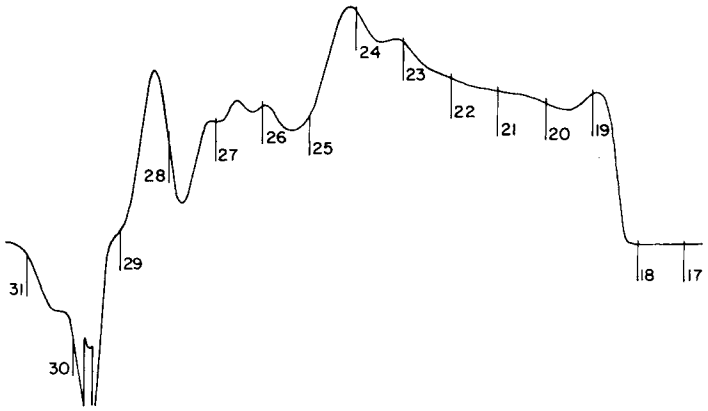

Fig. 1. Typical GPC chromatogram of a resole prepolymer. The numbers on the curve correspond to 5-mL siphon dumps.

The peak between 28 and 29 counts in Figure 1 is that of phenol and the negative peak betwen 29 and 30 counts (off-scale in this case) is due to formaldehyde and water. These identifications were made by comparing GPC chromatograms of phenolic resins before and after addition of phenol and aqueous formaldehyde to the sample. The assignments agree with those of previous workers.[4]

GPC Operation

It has been reported that elution volumes of phenolic samples are erratic because of adsorption and periodic release of material from the column packing.[9] This behavior was confirmed in the present work, where elution volumes of replicate samples varied and where even the elution volumes of anionic polystyrene standards were observed to differ between repeated trials in column sets that were being used to analyze resoles.

The effects of this erratic operation can be eliminated by referencing each elution volume to that of benzene, which was added to each sample as a marker.

Benzene appears at a higher elution volume than the negative water/formaldehyde peak and does not mask any part of the spectrum of the phenolic resin. Figure 2 shows a chromatogram of a resole prepolymer with the benzene peak appearing between 31 and 32 counts. With this procedure, each elution volume is recorded as an R_F value, where

$$R_{Fi} = \frac{\text{elution volume of species } i}{\text{peak elution volume of benzene}} \quad (1)$$

Although the elution volume of the benzene standard varied between trials R_F values were reproducible in our apparatus to $\pm$ 0.001. It is strongly recommended that the procedure described or a similar method be used for phenolics in preference to the usual technique of measuring elution volumes alone.

In retrospect, it would probably be feasible to use the phenol peak itself as an internal standard and to dispense with the added marker.

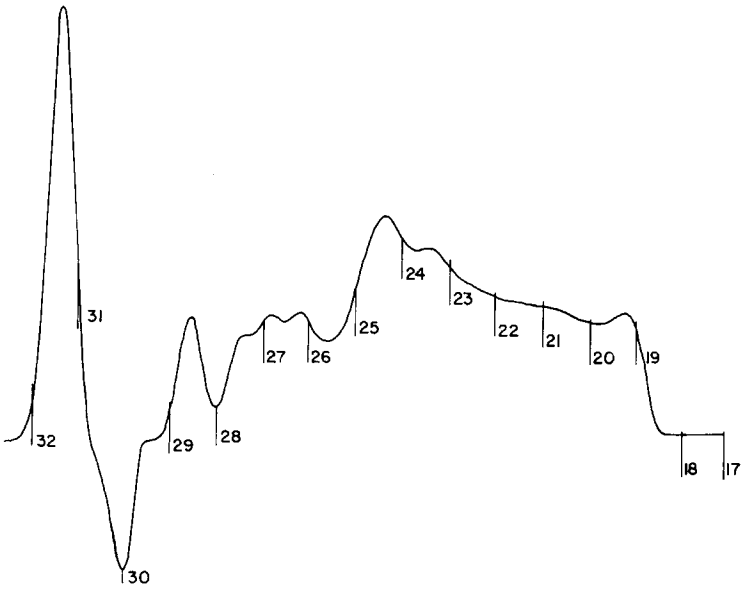

Fig. 2. GPC chromatogram of resole phenolic resin with benzene marker peak at extreme left.

Calibration and Size Calculations

Gel permeation chromatography separates on the basis of hydrodynamic volumes of solvated species. Universal calibration methods are essentially in terms of hydrodynamic volumes of the calibration standards.[10,11] Molecular weights can be estimated from calibration curves if a single-valued, known relation exists between the molecular weight of the eluting material and its hydrodynamic volume in the GPC solvent. This is not possible in the case of phenolic resins because the extent of solvation of different species of condensed phenolics will vary with their ability to form hydrogen bonds with the THF[3] and because the sizes of different multinuclear species with the same molecular weight depend on the architecture of the molecules.

For this reason, most workers have chosen not to attempt to summarize GPC chromatograms quantitatively but rather to rely on the shape of the chromatogram itself to provide a "picture" of the distribution of molecular species.[3,4]

Although summarizing parameters, such as averages, standard deviations, and so on, cannot convey all the information which is contained in the full array of GPC data, they are very convenient for the storage of information and comparison of size distributions of different samples. Since molecular weights cannot be estimated reliably for complicated mixtures such as those in resole polymers molecular sizes must be described in terms of hydrodynamic volumes in the GPC solvent. This was accomplished in the following manner.

Calibration of the GPC columns was in terms of hydrodynamic volumes of standards with appropriate sizes in THF. Apparent molar volumes of micromolecular species in THF are estimated from partial specific volume data by a standard technique.[12] For convenience in our calculations, these data are recorded as apparent hydrodynamic volumes per molecule. The compounds used

and molecular volumes (cm^3/molecule) were as follows[13]: benzene (14.8×10^{-23}); chlorobenzene (16.61×10^{-23}); *p*-dichlorobenzene (18.84×10^{-23}); and phenolphthalein (61.44×10^{-23}). The hydrodynamic volume V_h of a polymer molecule in solution at concentration c ($g \cdot cm^{-3}$) is given by[10,14]

$$V_h = \frac{4\pi K M^{(a+1)}}{9.3 \times 10^{24} + 4\pi N_0 c (KM^a - K_\theta M^{0.5})} \tag{2}$$

where K and a are the appropriate Mark–Houwink constants for the polymer in THF, N_0 is Avogadro's constant, and K_θ is the Mark–Houwink pre-exponential constant for theta solutions. The appropriate polymeric standards for calibration of soluble resole prepolymer analyses are all in the oligomeric molecular weight range and their solutions will be close in behavior to theta solutions. In that case, the second term in the denominator of eq. (2) goes to zero ($KM^a = K_\theta M^{0.5}$ in theta solutions), and this expression reduces to

$$V_h = \frac{4\pi K M^{a+1}}{9.3 \times 10^{24}} \tag{3}$$

Anionic polystyrenes with molecular weights 2100, 4000, and 9000 were used as calibration standards. For these oligomers in THF $K = 0.1$ $cm^3 \cdot g^{-1}$ and $a = 0.5$.[15]

A sample of poly(ethylene oxide) with nominal molecular weight 400 amu was also used to calibrate the GPC column set. Under theta conditions the Mark–Houwink constants of oligomers should be independent of solvent.[15] The poly(ethylene oxide) values used in this study were $K = 129 \times 10^{-3}$ $cm^3 \cdot g^{-1}$ and $a = 0.5$.[16] The particular sample employed in this calibration had a bimodal gel permeation chromatogram, but the calibration curve drawn between the two peaks seemed to produce a good curve joining R_F values of the micromolecular standards and larger, anionic polystyrene oligomers.

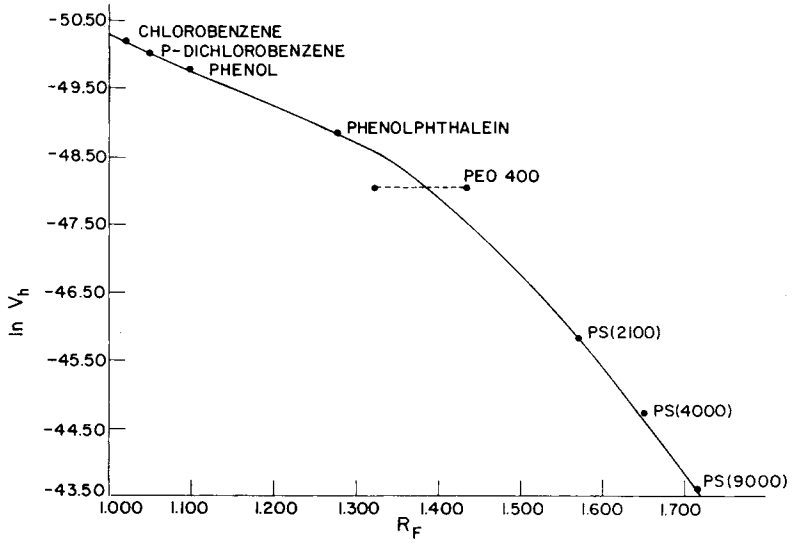

Fig. 3. Calibration curve in terms of the natural logarithm of molecular hydrodynamic volume and R_F (PS = polystyrene).

The calibration curve obtained is shown in Figure 3. The plot is in terms of ln V_h vs. R_F, where R_F is defined by Eq. (1). The calibration line bends towards the abscissa at higher elution volumes, suggesting that the exclusion limits of the columns were not much higher than the hydrodynamic volume of polystyrene with molecular weight 9000. A calibration equation was obtained by fitting the observed ln V_h − R_F data to a second-order equation to obtain:

$$\ln V_h = 9.8334R_F^2 - 17.6587R_F - 42.3070 \quad (4)$$

with the multiple correlation coefficient equal to 0.9994 in this case.

The GPC chromatograms of phenolic resins were normalized on peak heights as is usual in this technique. The molecular hydrodynamic volume was calculated at each elution volume from eq. (4), and the parameters of the volume distribution were calculated by standard statistical techniques. Number-, weight-, and z-average hydrodynamic volumes were produced by computer-assisted calculations, along with estimates of the breadth and skewness of the number and weight distributions of molecular hydrodynamic volumes. Examples of such data are given below.

Separation of Species of GPC

The resole prepolymers produced in this study appeared at elution volumes between 18 and 31 counts in our GPC apparatus. In order to investigate the efficiency of separation, the eluant from a particular phenolic sample was collected in three fractions: 18–22 counts, 23–26 counts, and 27–31 counts. Figure 4 shows the chromatogram of the initial, whole resole. The three fractions obtained were injected separately into the same set of GPC columns, with the results shown in Figure 5. Clearly, all three cuts contained phenol, although this compound would have been present only in the fraction taken at 27–31 counts if the separation in the GPC columns had been strictly on the basis of size.

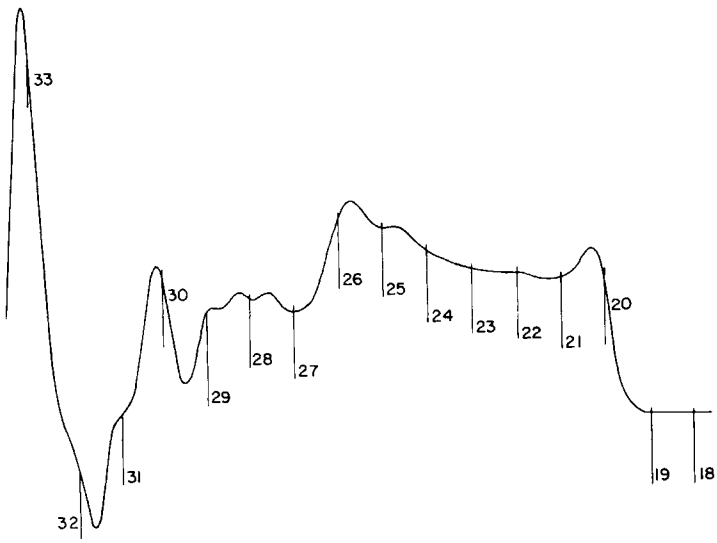

Fig. 4. GPC chromatogram of resole polymer for which eluant was collected in the intervals 18–22, 23–26, and 27–31 counts.

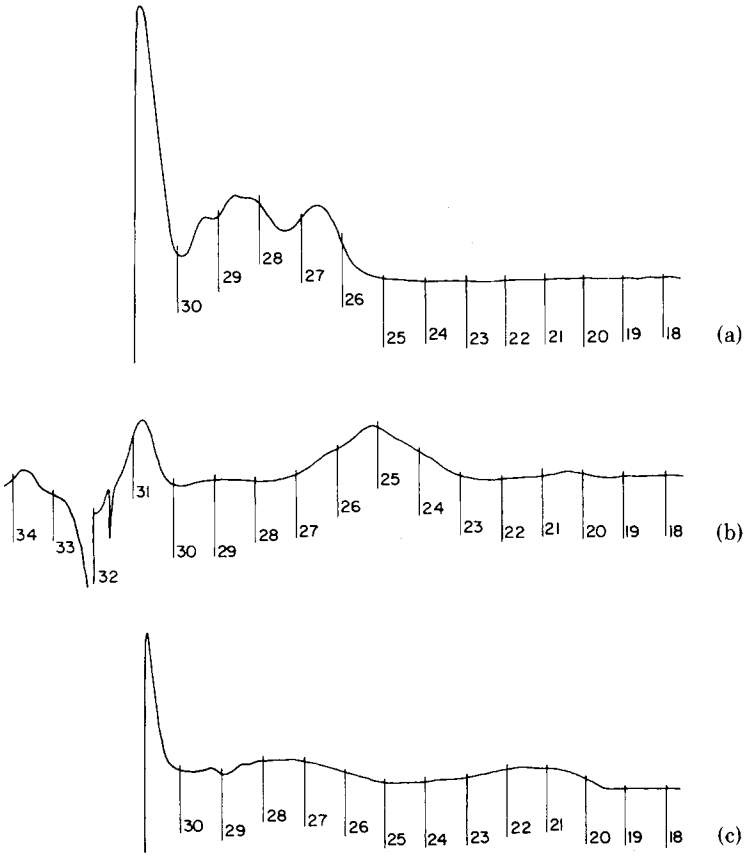

Fig. 5. (a) Eluant at 27–31 counts in chromatogram of Figure 4; (b) eluant at 23–26 counts in chromatogram of Figure 4; (c) eluant at 18–22 counts in chromatogram of Figure 4.

It appears that aggregation between the various phenolic species occurs to a significant extent, possibly because of hydrogen bonding between the different phenolic and alcoholic residues. As a result, the material eluting at a given R_F is not only a mixture of different compounds with the same size and different architecture but also of phenolic entities with different sizes. This seems to be a function of the relative magnitudes of solvent–solute and solute–solute attractions. It sets an obvious limit to the reliability of size calculations.

Identification of Low Molecular Weight Species

Previous workers have attempted to identify the species responsible for the various peaks seen in the high elution volume region of the GPC chromatogram.[3,4,8] Our study produced results in qualitative agreement with these prior studies, but we do not conclude that particular peaks in the GPC chromatograms can be assigned to specific compounds because of the overlapping and aggregation phenomena which have been mentioned above.

The following model compounds were studied in this work: *o*-, *m*-, and *p*-methylol phenol, α-phenyl-*o*-cresol, 4-hydroxyl diphenyl methane, *p*-phenyl

benzyl alcohol, and benzyl phenyl ether. Not all these compounds would be expected to be produced in the condensation reactions of phenol and formaldehyde. Their structures are, nevertheless, close enough to those of phenolic condensates for testing of the separation efficiency of the GPC unit.

The three methylol phenol isomers all appeared in a single peak when they were mixed in THF and a mixture of the seven materials listed above with phenol produced a chromatogram with three overlapping peaks.

None of the peaks in the present chromatograms or those of the cited earlier reports[3,4,8] are resolved to the baseline, and the assignment of specific entities to each peak and calculation of their concentrations appears to be of dubious validity.

A sample of NaOH-catalyzed phenol formaldehyde resin was centrifuged, and the water layer was concentrated and dissolved in D_2O for ^{13}C NMR spectral analysis. The NMR spectrum suggested the presence of phenol, *o*- and *p*-methylene-substituted phenol, paraformaldehyde, benzyl ether, and some methylene bridges between aromatic nuclei. These compounds are all consistent with the reaction schemes which have been postulated for early stages of the condensation of phenol and formaldehyde. Ortho- and para-hydroxylbenzyl alcohols were shown to be present by adding authentic specimens to this solution.

Applications of GPC

This article has focussed to this point on details of the analytical method and limitations of the reliability of GPC in the study of phenolics. Despite the problems that have been mentioned, this technique remains a powerful tool for the characterization of soluble phenol formaldehyde polymers. Several examples are reviewed briefly here.

The GPC chromatograms of two versions of the same NaOH-catalyzed phenol formaldehyde condensate are shown in Figures 6(a) and (b). The resin in Figure 6(a) is as made, while the sample of Figure 6(b) is the former material after a very low degree of acid curing. It is obvious from the chromatograms that the condensation has advanced much further in the second sample. Quantitative features of these data are summarized in Table I. For comparison, the hydrodynamic volume of phenol is 2.5×10^{-22} cm^3/molecule in THF. Thus the number average size of the condensed species in sample 6(a) is a little more than double that of phenol. The corresponding parameter of sample 6(b) is 15 times as large as phenol.

GPC analysis can also be used to follow the condensation reactions of phenolic resins during storage. Figure 7 shows GPC chromatograms of a NaOH-catalyzed resole after storage for 6 days at room temperature [Fig. 7(a)] and in a refrigerator [Fig. 7(b)]. The GPC chromatogram of the polymer which had been stored cold was essentially the same as that of the freshly made resin while the product stored at room temperature shows the presence of a slightly more pronounced high molecular weight tail to the size distribution.

Another useful application of GPC is in the blending of resole prepolymers. When the GPC data have been summarized, as in Table I, the proportions of blending resins required to produce a given mixture can be calculated by a straightforward method analogous to that used in molecular weight estimations.

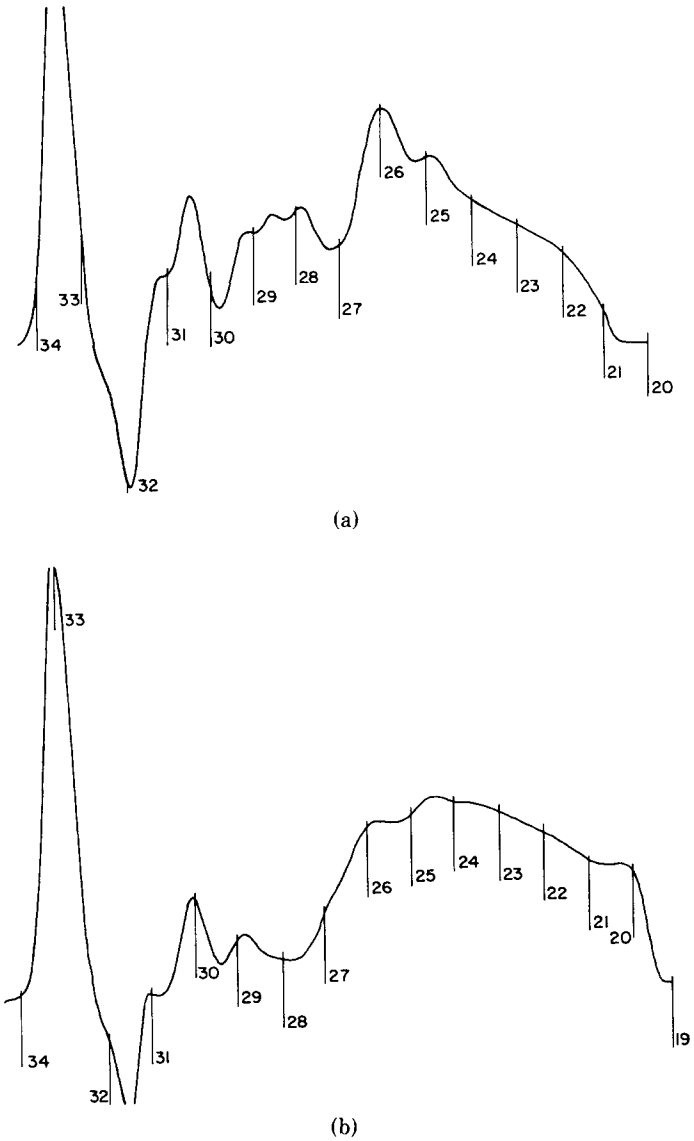

Fig. 6. (a) GPC chromatograms of resole resin, as made; (b) GPC chromatogram of resin 6(a) after slight acid catalyzed crosslinking.

In the case of phenolics, however, the desired properties of the final blend must be specified in terms of average hydrodynamic volumes in THF. Some experience will be needed in correlating such parameters with more conventional properties of resoles, like viscosity, residual activity, and so on.

DISCUSSION

Use of a marker material as an internal reference for calibration is infrequent in gel permeation chromatography. Such procedures are, however, standard

TABLE I
Characterization of Phenolic Resins in Terms of Molecular Hydrodynamic Volume Parameters

Sample	No. average hydrodynamic volume $(\overline{V_h})_n \times 10^{22}$ (cm^3/molecule)	Wt average hydrodynamic volume $(\overline{V_h})_w \times 10^{22}$ (cm^3/molecule)	z average hydrodynamic volume $(\overline{V_h})_z \times 10^{22}$ (cm^3/molecule)	Number distribution		Weight distribution	
				Standard deviation $\times 10^{22}$ (cm^3/molecule)	Skewness[17]	Standard deviation $\times 10^{22}$ (cm^3/molecule)	Skewness[17]
6(a)	5.9	17.9	62.9	8.4	8.7	28.4	0
6(b)	38.5	102.6	130.8	49.7	1.4	53.8	0.1

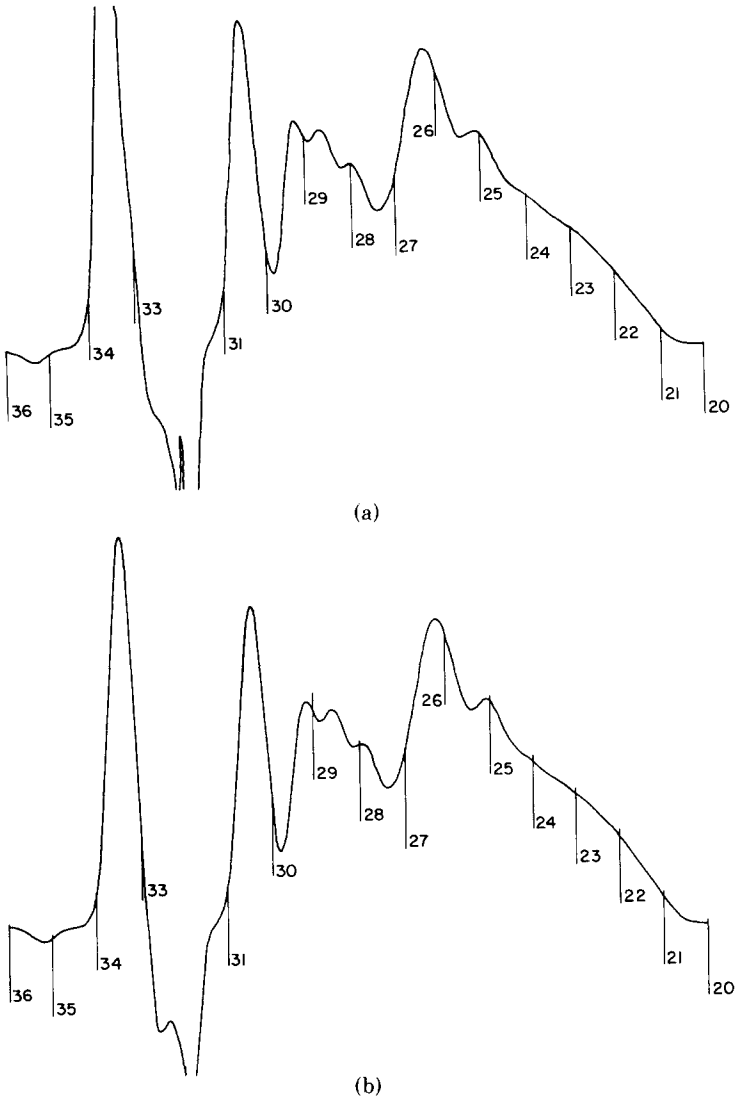

Fig. 7. (a) GPC chromatogram of an NaOH catalyzed resole, as made; (b) GPC chromatogram of sample (a) after 6 days storage at room temperature.

good practice in chromatographic separations in which retention times may vary because of causes such as fluctuating flow rates or changes in column characteristics. As mentioned, the latter may be a factor in the separation of role polymers on polystyrene gel columns.

The hydrodynamic volume treatment presented here appears to be valid for analysis of GPC data of compositionally heterogeneous polymers. It cannot, of course, account for any selective adsorption of eluting species. Such selective adsorption appears to be quite unlikely in this case, however, because of the compositional similarity of the major components in resole prepolymers.

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