

Laser Raman Spectral Study of Resol Formation

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Synopsis

Laser Raman spectroscopy was used to monitor changes in the substitution pattern during the formation of a phenol-formaldehyde resin (resol). The substitution-sensitive bands were identified and their relative intensities related to molecular weight of the resol. Results of this study are similar to those obtained by previous workers in the field using paper chromatography. The absorbance ratio of 784-cm⁻¹ to 998-cm⁻¹ bands was found to be linearly related to the molecular weight of the resol.

INTRODUCTION

Resol, a base-catalyzed, water-soluble phenol-formaldehyde resin, is one of the most important industrial adhesives. Although modern instrumentation methods will permit the analysis of some chemical and physical properties of the resin in the course of resin formation, a more direct and rapid method for characterization, particularly during the initial polymerization process, remains to be found. Freeman^{1,2} developed a paper-chromatographic technique for separation of phenolic compounds related to phenol-formaldehyde resin. Later, Freeman and Lewis³ reported the appearance and disappearance of individual methylophenols in the resol reaction system using this chromatographic method. Most recently, gas-liquid-chromatographic (GLC) techniques^{4,5} have been developed to separate the phenolic compounds in a resol. Using the GLC techniques, Zavitsas et al.⁶ studied the kinetics of the base-catalyzed hydroxymethylation reactions, and Troughton⁷ studied the condensation reactions in a resol system.

Infrared (IR) spectroscopy is an effective instrument to study polymer structures. It is also a powerful tool to monitor the progress of reactions quantitatively.⁸ However, because water exhibits strong IR absorption, dehydration of samples from resol condensation reactions is mandatory prior to spectral determinations. Inevitably, such steps cause further chemical reactions and irreversibly alter the chemical and physical properties of the resol.

Raman spectroscopy can circumvent the dehydration step and allows a direct spectral determination of a resol condensate.^{9,10} Technically, how-

ever, prelaser Raman spectroscopy encountered serious problems from fluorescence which, in turn, demands a high-purity sample.¹⁰ Advent of more advanced Raman spectroscopy using a laser source greatly eliminates the above difficulties and offers a powerful tool for monitoring of reactions in aqueous systems.^{11,12} In view of the fact that Raman spectroscopy is complementary to IR spectroscopy, we have investigated the potential of its application using a resol system as a model.

EXPERIMENTAL

Material. A resol was prepared by reacting a 1.5 molar ratio of formaldehyde (40% solution with about 1% methanol content) to phenol with 8% (w/w) of sodium hydroxide as catalyst, at 85°C under a nitrogen atmosphere. In a preliminary experiment, the samples obtained from the reaction of resin under an oxygen atmosphere were found to show strong fluorescence effects which contributed to high background in the low-wavenumber region of the spectrum. About 10 ml of each sample was withdrawn from the reaction vessel at time intervals of 0, 15, 30, 40, 50, 75, 90, 120, 140, 160, and 180 min. A 1 ml portion of the sample was immediately examined by Raman spectroscopy while the rest was retained in a refrigerator for molecular weight and bromination studies.

p-Cresol (100 g) was also reacted under the same conditions as described above. Additional samples were taken at 5 and 10 min. The *p*-cresol system was intended for the observation of the effect of 2, 4, or 2, 4, 6 substitutions, a linear polymer system, on the change of Raman spectra for comparison with phenol-formaldehyde reactions.

Raman Spectroscopy. The Raman spectra were recorded with a Cary Model 81 Raman spectrophotometer equipped with a Spectra-Physics Model 125 CW helium-neon laser (6328 Å). Solution samples were placed in a capillary (1 mm o.d. × 0.6 mm i.d. × 60 mm) Pyrex liquid-sample cell. The solid samples, including a number of model compounds, were pelletized using a 10-ton load. The neutralized samples described below were also pelletized and examined by Raman spectroscopy.

Molecular Weight Determination. A sample (3 ml) was neutralized with aqueous HCl (1*N*), filtered, and the filtrate extracted with diethyl ether. The ether extract and any precipitated resin were combined for each sample, evaporated under reduced pressure, and then dried under high vacuum to constant weight. The number-average molecular weight was determined with a Mechrolab Model 301-A vapor pressure osmometer. Acetone was used as solvent, and bis-2-hydroxyphenyl methane was used as a calibration standard.

Bromine Substitution Determination. To 2 ml of the aqueous resol solution in an Erlenmeyer flask (250 ml), bromine-saturated water (150 ml) was added slowly with stirring. After standing for 12 hr, the mixture was filtered and thoroughly washed with water. The sample was dried to constant weight under vacuum, pulverized, and the fraction between mesh size 180–200 was retained for analysis.

A pellet was prepared by pressing a mixture containing 100 mg of the sample with 1 g Whatman CF 11 cellulose powder in a laboratory press using a 10-ton load.

The percentage bromine content of the resin was determined by x-ray spectrometry. The x-ray beams were generated with a gold target tube at 45 kV and 34 mA in a Sieman x-ray spectrometer. LiF was used as the analyzing crystal. The counts were taken with a proportional counter at the bromine K_{α} ($29.8^{\circ}:2\theta$) peak with a baseline of 10 V, window width of 20 V, and a counting time of 12 sec. A standard calibration curve was prepared from standard samples by mixing different concentrations of tri-bromoanisole (180–200 mesh size) with 1 g cellulose powder and pelletized as described above.

RESULTS AND DISCUSSION

The increase in number-average molecular weight (MW) and the decrease of the bromine content of the resol in relationship to reaction time is

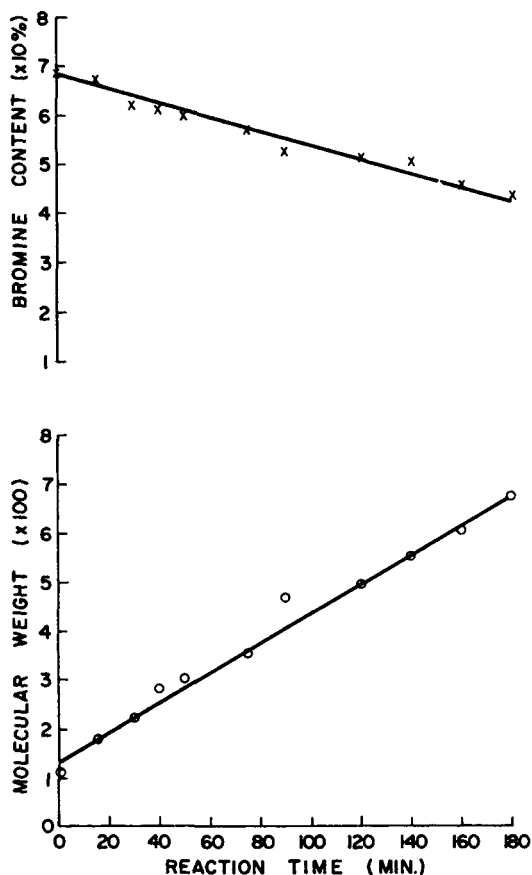


Fig. 1. Relationship between bromine content, number-average molecular weight, and reaction time of resol.

shown in Figure 1. Within the experimental range, their relationship with reaction time is linear. The per cent Br content is therefore linearly related to molecular weight of the sample. When the number of the bromine substituents per mole of the resin, calculated by use of the equation

$$\frac{[(\% \text{Br content})/80]}{[(100 - \% \text{ Br content})/\text{number-average molecular weight}]}$$

where 80 is the atomic weight of bromine and expressed as a molar ratio, was plotted against the molecular weight, a curvilinear relationship was found, as shown in Figure 2. The amount of bromine substitution is interpreted as the number of the substitutable sites that remain unreacted in the aromatic rings during the condensation. This number of substitutable sites per mole of resin increases as the molecular weight increases and levels off at a molecular weight of about 500. As the pattern and extent of aromatic substitution is expected to be reflected in the Raman spectrum, the qualitative relationships of these factors, with respect to molecular weights of resol, can be extracted from a series of the spectra recorded for a kinetic run.

Since there is little literature available for band assignment of Raman spectra of compounds related to phenol-formaldehyde resins, some spectra

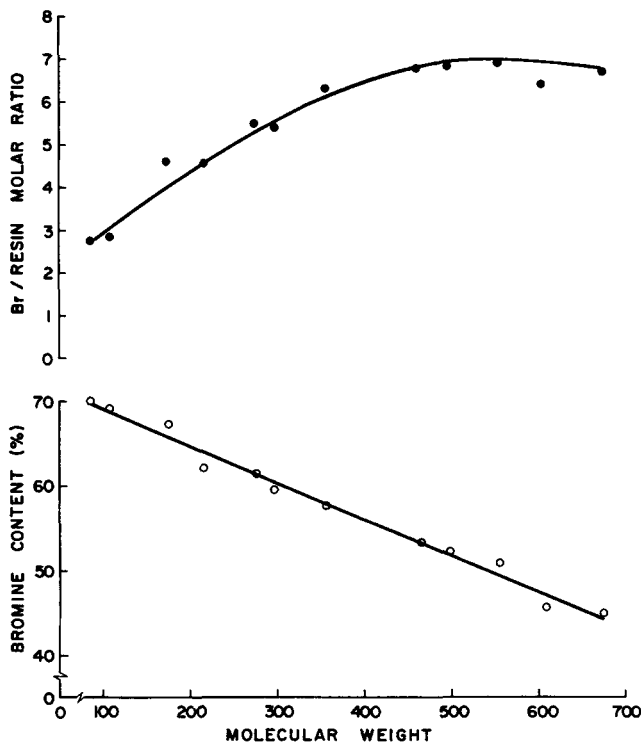


Fig. 2. Relationships between bromine content, bromine-resin molar ratio, and number-average molecular weight of resol.

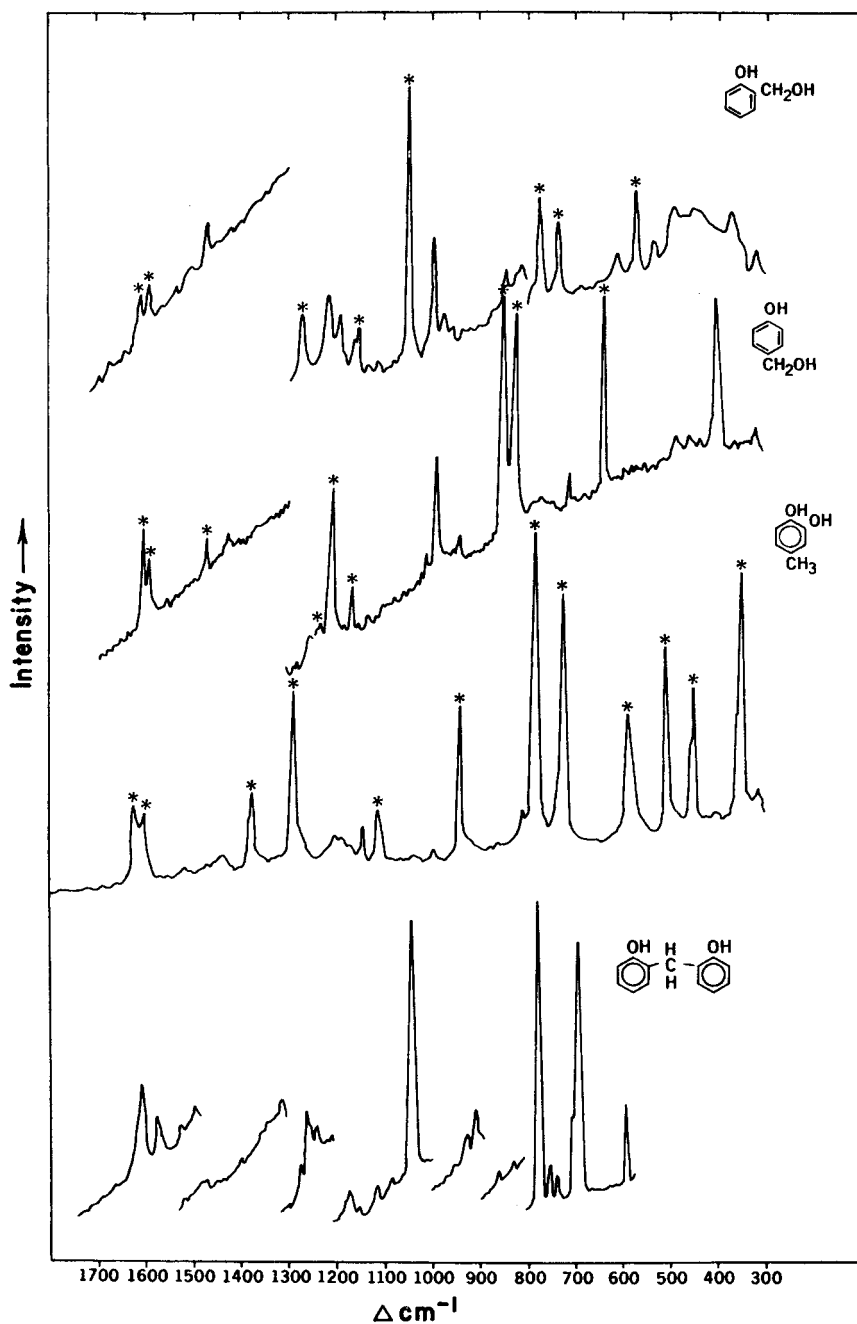


Fig. 3. Raman spectra of model compounds. Asterisks indicate common absorption bands of other model compounds with same ring substitution pattern.

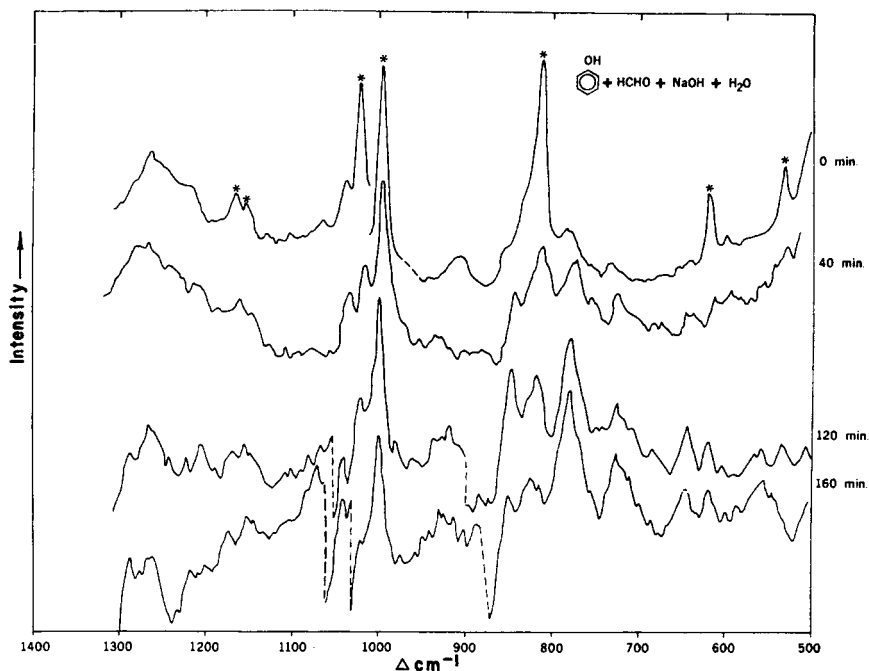


Fig. 4. Raman spectra of resol at different stage of cooking. Asterisks indicate common bands with phenol.

of model compounds were recorded in order to identify their substitution-sensitive bands. Some spectra of the relevant compounds are shown in Figure 3. In Figure 4, the spectrum for the 0 minute of phenol-formaldehyde reaction indicates the phenol absorption bands. On the basis of the correlation in these reference spectra, tentative assignments for the useful bands are as follows: phenol, 998 and 814 cm^{-1} ; 2-substituted phenol, 1042 and 784 cm^{-1} ; 4-substituted phenol, 850 and 645 cm^{-1} ; 2,4-disubstituted phenols, 570 cm^{-1} ; a superimposed absorption of 2-substituted, 2,4-disubstituted, and 2,4,6-trisubstituted phenols, 784 cm^{-1} .

Figures 4 and 5 show the Raman spectra of the resol solution samples, taken at various time intervals during condensation of formaldehyde with phenol and *p*-cresol, respectively. The spectra of the neutralized resol samples in the form of solid pellets are virtually identical to the solution spectra, with the exception of the 1250- cm^{-1} band which may be assumed to the aromatic O-Na absorption mode. This indicates that neutralization can be used as a convenient means of sample preparation, since it retains intact the original chemical structure of the resin. It is fortunate that an aqueous solution of formaldehyde gives only a weak band at 910 cm^{-1} in the range under study (500–1600 cm^{-1}).

Examination of Figure 5 indicates that in the *p*-cresol reaction a spectral change was very sudden, within 10 min, with the rapid appearance of the new bands confirming the validity of the band assignments based on model

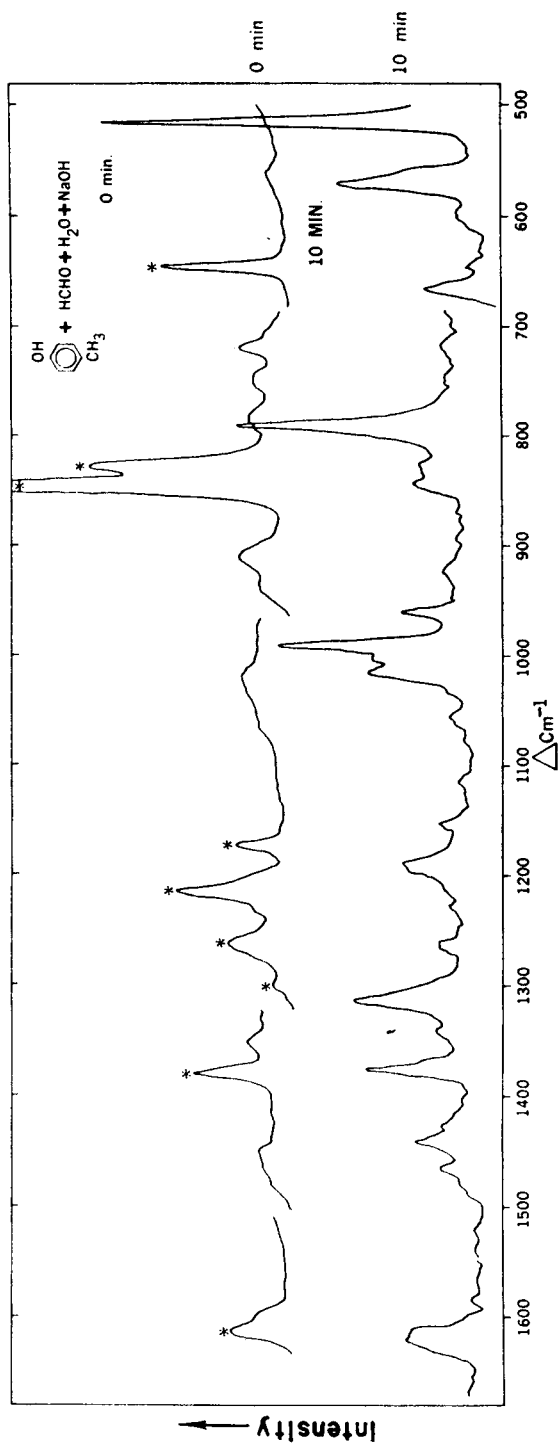


Fig. 5. Spectra showing reaction of resol using *p*-cresol as basic material. Spectrum for 180-min reaction time is identical to that for 10 min. Asterisks indicate common bands with *p*-cresol.

compounds. As the spectra of the samples taken at 10 min are very similar to those taken at 180 min of reaction, the condensation reactions in the linear polymer system must have been substantially completed in the first 10-min period.

Of the phenol bands as shown in Figure 4, the 998-cm^{-1} band, which may have some contribution from other reaction products, remained relatively constant as the reaction progressed, whereas the 814-cm^{-1} band intensity decreased greatly. The 998-cm^{-1} band was therefore used as common denominator for other bands. On the basis of the previous band assignments, the ratios of these bands to the 998-cm^{-1} band was plotted versus molecular weights in the resol system (Fig. 6).

The profile of the hydroxymethylation and condensation reactions in the resol system is shown in Figure 6. The relative intensity variation of the 814-cm^{-1} band indicated that the rapid disappearance of phenol in the early stages of the above reactions slowed with the increase of 2- and 4-substituted phenol bands and reoccurs after attaining a molecular weight of about 550. The rate of disappearance of phenol slowed down considerably at a MW of about 200, which coincided with the advent of the 570-cm^{-1}

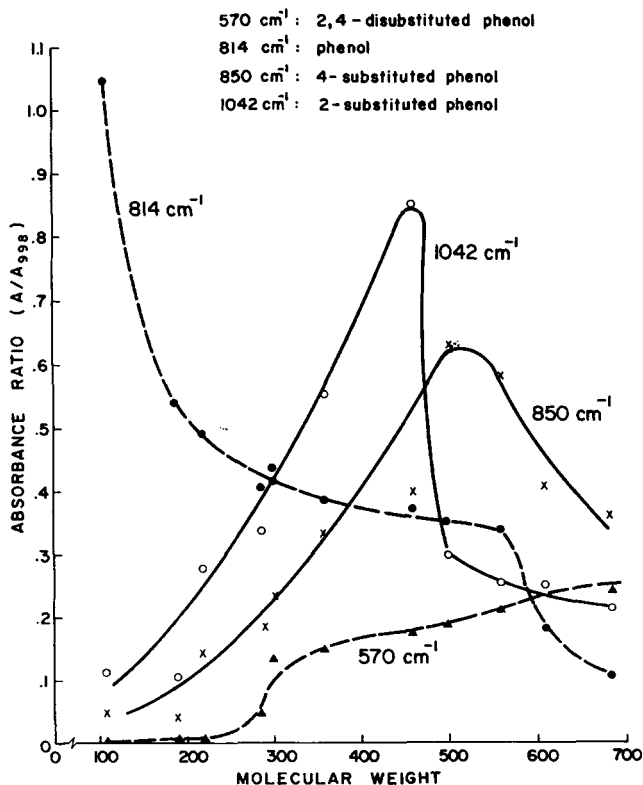


Fig. 6. Absorbance ratio between different substitution-sensitive bands and intensity of 998-cm^{-1} band in respect to number-average molecular weight of resol.

2,4-disubstituted phenol band. The rapid disappearance of the remaining phenol, starting at about MW 500, cannot be interpreted with certainty. The relative intensity of the 2-substituted phenol found at 1042 cm^{-1} increased to about MW 460 and then decreased sharply as the reaction proceeded to higher MW. The relative intensity of the 4-substitution sensitive band at 850 cm^{-1} , although its rate of increase is slower than the 1040-cm^{-1} band, increased up to MW 560 and then decreased similarly to the 1042-cm^{-1} band. The molecular weight (500) at which the profiles of these two bands reached the maximum is similar to that for the leveling-off point of the number of available sites shown by the bromination results (Fig. 2). These results indicated that 2-substitution is favored over 4-substitution in the initial stages of the resol reactions and agrees with the kinetic results measured by Zavitsas et al.⁶

The relative intensity of the 570-cm^{-1} band (Fig. 6), which is mainly contributed by 2,4-disubstituted phenol, started to appear at MW 200, showed an inflection upward at about MW 300, and increased approximately linearly thereafter. A convincing explanation for this inflection is not available. The relationships shown in Figure 6 are very similar to those of Freeman and Lewis,³ who studied the initial phenol-formaldehyde reaction at 30°C over a long period of reaction time (1000 hr) by paper-chromatographic techniques. However, the Raman spectroscopic technique is much more sensitive to the concentration changes of the components at the initial phase (0-3 hr) of resol condensation at 85°C using phenol as starting material. At the later stage, no doubt complexity of the reac-

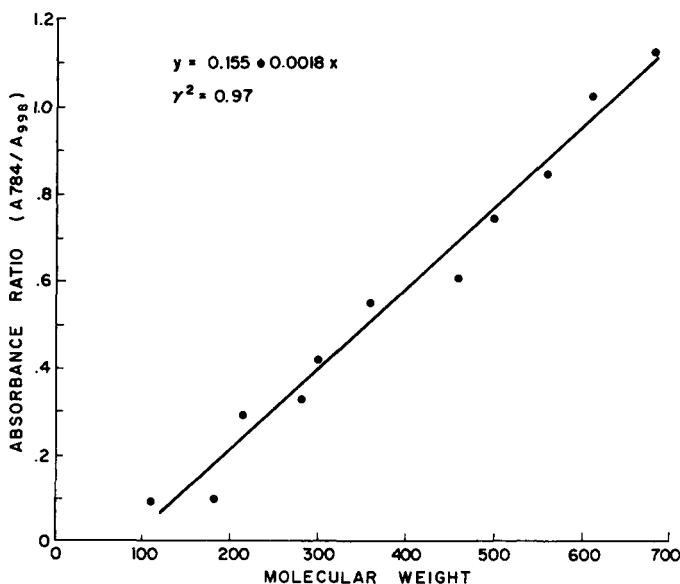


Fig. 7. Linear relationship between absorbance ratio (A_{784}/A_{998}) and number-average molecular weight of resol.

tion mixture causes a difficulty in spectral resolution and renders a spectral comparison unrealistic. Indeed, it should be pointed out that in the present resol condensation at 85°C, a Raman spectral change is nearly imperceptible after 180 min of reaction. The consistent results obtained from the Raman spectral and paper-chromatographic techniques suggest that Raman spectrometry can be efficiently applied for studying the complex resol reactions and that the two techniques complement each other.

When the relative intensity of the 784-cm⁻¹ band, which is a combined absorption of the major substituted phenolic compounds of the resin, was plotted against the molecular weight, an excellent linear relationship was obtained, as shown in Figure 7. This further demonstrated that Raman band intensity can be a single and rapid indicator for molecular weight determination of phenolic resins in aqueous solution. A similar correlation between the number-average molecular weight and signals of proton magnetic resonance spectrum of phenol-formaldehyde resin was reported by Woodbrey and co-workers.¹³

References

1. J. H. Freeman, *Anal. Chem.*, **24**, 955 (1952).
2. J. H. Freeman, *Anal. Chem.*, **24**, 2001 (1952).
3. J. H. Freeman and C. W. Lewis, *J. Amer. Chem. Soc.*, **76**, 2080 (1954).
4. G. E. Troughton and L. Rozon, *Wood Sci.*, **4**(4), 219 (1972).
5. H. P. Higginbottom, H. M. Culbertson, and J. C. Woodbrey. *Anal. Chem.*, **37**, 1021 (1965).
6. A. A. Zavitsas, R. D. Beaulieu, and J. R. LeBlanc. *J. Polym. Sci. A-1*, **6**, 2544 (1968).
7. G. E. Troughton, *Holzforschung*, **26**(5), 170 (1972).
8. L. J. Bellamy, in *The Infrared Spectra of Complex Molecules*, Methuen, London, 1954.
9. J. C. Evans, in *Infrared Spectroscopy and Molecular Structure*, Mansel Davis, Ed., Elsevier, Amsterdam, 1936, p. 212.
10. R. N. Jones, J. B. D'Giorgio, J. J. Elliott, and B. A. A. Nonnenmacher, *J. Org. Chem.*, **30**, 1822 (1964).
11. A. Weissberger, in *Technique of Organic Chemistry*, Vol. IX, Interscience, New York, 1956.
12. T. R. Gilson and P. J. Hendra, in *Laser Raman Spectroscopy*, Wiley-Interscience, New York, 1970, p. 266.
13. J. C. Woodbrey, H. P. Higginbottom, and H. M. Culbertson. *J. Polym. Sci. A*, **3**, 1079 (1965).

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