

An Investigation of the Polymerization of Furfuryl Alcohol with Gel Permeation Chromatography

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Synopsis

Several series of furfuryl alcohol resins, made by the polymerization of furfuryl alcohol with a variety of catalysts and having viscosities as high as 7×10^6 cpoise, were characterized by gel permeation chromatography (GPC). A series-by-series comparison of the GPC curves of the resins was made, to determine the effects of catalyst type and concentration on resin molecular structure as elucidated by GPC. Furfuryl alcohol resins were produced not only by thermal polymerization but also by catalysis with maleic anhydride, 86% phosphoric acid, γ alumina, and anhydrous magnesium sulfate. The gel permeation chromatograms of the resins made by catalysis with maleic anhydride were found to be nearly identical with those catalyzed with 86% phosphoric acid. Moreover, catalyst concentration did not affect the GPC curves of the resins catalyzed by maleic anhydride. These observations are consistent with an initial reaction mechanism, of which the rate-controlling step is a function of pH. The chromatograms of the resins made by catalysis with γ alumina showed a shift of the peak maximums of the lower molecular weight species to lower elution volumes, indicating that esterification of the free hydroxyl groups with levulinic acid and other related acids may have taken place. The resins polymerized by thermal catalysis and by catalysis with anhydrous magnesium sulfate exhibited GPC curves that fell between those of the resins catalyzed by acids and those of the resins made by catalysis with γ alumina.

INTRODUCTION

For a number of years furfuryl alcohol polymers have been used for a wide variety of applications in the resin and coating industries.¹ Recently furfuryl alcohol resins have been shown to have thermal and structural properties suited to their use as binder materials in the manufacture of nuclear-grade graphites.² There is continual searching in this latter area for improved methods of characterizing furfuryl alcohol resins in an effort to correlate binder resin properties with graphite properties.

The chemical heterogeneity of furfuryl alcohol resins made past attempts to determine their molecular size or weight distributions by any of the usual methods difficult. In a previous paper gel permeation chromatography (GPC) was shown to be a fast, convenient method of determining the molecular distributions of these resins³ (the hydrodynamic, molecular volumes of the individual species appear to be the universal separation factor in GPC, giving rise to molecular volume distributions;^{4,5} however, for brevity and lack of an exact description, the term molecular

distribution is used here to describe the GPC curves). The mode of molecular separation of the GPC technique ideally depends only on the physical sizes of the molecules and not on the chemical homogeneity of the polymer, making it an advantageous method for this purpose. This paper describes the use of GPC in a study of the effects of reaction variables on the molecular distributions of furfuryl alcohol resins.

BACKGROUND

Furfuryl alcohol resins are made by the thermal or catalytic polymerization of furfuryl alcohol. Previous studies of them have concentrated mainly on two areas; the isolation and identification of the initial reaction products and the kinetics of resin formation. A knowledge of the chemistry of furfuryl alcohol resins is most useful to the interpretation of the GPC data.

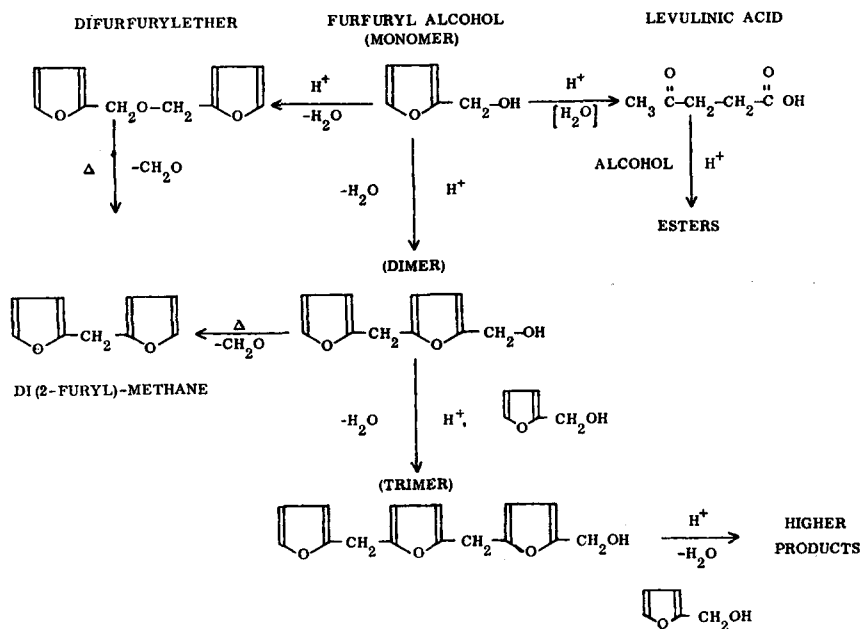


Fig. 1. Initial reaction scheme of the polymerization of furfuryl alcohol in acidic medium.

Many of the initial reaction products of the acid-catalyzed polymerization of furfuryl alcohol were identified by the early work of Roberti and Dinelli⁶ and Dunlop and Peters.⁷ Later studies made by Hachihama and Shono,⁸ Takano,⁹ and Conley and Metil¹⁰ have added to the knowledge of this reaction. The generally accepted initial reaction profile of the polymerization of furfuryl alcohol, resulting from these studies, appears in Figure 1. The actual distribution of products is dependent on reaction conditions.

In the study mentioned above, Conley and Metil¹⁰ found evidence of ketonic species in the infrared spectrum of the polymerization products. They attributed this to a degree of ring cleavage that took place during resinification.

Boquist and his co-workers,¹¹ following the procedures outlined in the patent of Nielsen,¹² studied the composition of the products from the γ alumina-catalyzed polymerization of furfuryl alcohol. Infrared analysis showed the presence of carbonyl groups and the absence of hydroxyl groups. The alumina condensation of furfuryl alcohol was found to produce relatively large amounts of levulinic acid and related acids, causing most of the free hydroxyl groups to be complexed as esters of these. In addition, difurfurylether was found to be a main product. Resins produced by the thermal catalysis of furfuryl alcohol have been reported to be identical in composition with those made by polymerization with alumina.¹³

Mention is made in the patent literature^{14,15} of the polymerization of furfuryl alcohol with anhydrous magnesium sulfate, but little appears to be known about the compositions of these resins.

Several groups have studied the acid-catalyzed polymerization of furfuryl alcohol from a mechanistic standpoint.¹⁶⁻¹⁸ There appears to be essential agreement that the initial reaction rate follows a pH-dependent course.

In this study furfuryl alcohol was polymerized in the presence of several types of catalysts, including maleic anhydride, phosphoric acid, γ alumina, and anhydrous magnesium sulfate. These cover three major classes of catalysts commonly used to polymerize furfuryl alcohol: organic acids, inorganic acids, and dehydrating agents. In addition, furfuryl alcohol was thermally polymerized in the absence of any added catalysts. For each of these a series of resins was made, ranging in viscosity from approximately 50 to 5×10^5 cp. The variation of the molecular distributions of these resins with the type of polymerization catalyst used was investigated by the GPC technique.

EXPERIMENTAL

Procedures

The resin molecular distributions were determined with a Waters, Model 200, Gel Permeation Chromatograph at room temperature in tetrahydrofuran. The sample system consisted of a series of three columns, packed with crosslinked polystyrene gels, which had maximum permeabilities of 8×10^3 , 250, and 50 A. The resin samples (1% by weight in tetrahydrofuran) were injected for a period of 30 sec. A solvent flow rate of 1 ml./min. was used.

The sample column system was calibrated with respect to molecular weight by first noting the elution positions of a series of narrow molecular weight distribution polyethylene and polypropylene glycols. Then the

average molecular weights of these were plotted against their peak elution volumes, resulting in an approximate measure of molecular weight at each increment of elution volume.

The resins catalyzed with maleic anhydride were made in a 1000-ml. three-necked round-bottomed flask equipped with a water-cooled reflux condenser, a motor-driven paddle-type stirrer, and a thermometer. Heating was provided with a heating mantle controlled by a variable transformer and, when needed, cooling was obtained by immersion of the flask into a container of ice-water. The usual reaction mixture consisted of furfuryl alcohol (560 g.), maleic anhydride (1 g.), and water (200 g.). These were added to the flask and heated with stirring at 400 rpm to reflux temperature (92°C.). The reactants were refluxed for periods of 30–150 min., depending on the desired viscosity. (A series of resins made with 10 g. of maleic anhydride required only 5–30 min. to reach the desired degrees of polymerization.) The polymerization was terminated by cooling the products to 50°C. and neutralizing the catalyst with 5% sodium hydroxide solution. If necessary, saturated salt water was added to the mixture, to effect phase separation. After separation of the aqueous phase the residual water was stripped from the resins by heating under house vacuum in a rotary evaporator.

The resins catalyzed with phosphoric acid were made in apparatus identical with, and under experimental conditions similar to, those used for the resins catalyzed by maleic anhydride. For these 2 ml. of 86% phosphoric acid was initially added to the reaction flask with the water (200 g.) and furfuryl alcohol (560 g.). The reflux periods varied from 30 to 120 min.

The γ alumina-catalyzed resins were made in a 500-ml. three-necked round-bottom flask fitted like that mentioned above. The alumina (30 g.) and furfuryl alcohol (225 g.) were added directly to the flask. The mixture was stirred and uniformly heated to the final reaction temperature, which varied from 140 to 220°C. The resin was then cooled to 100°C., and the alumina was separated by decanting or by filtering of the resin through glass wool. The small amount of lower molecular weight material that escaped with the water through the reflux condenser was not collected.

The thermally polymerized resins were made in a 500 ml. three-necked round-bottom flask equipped with a motor-driven stirrer, a thermometer, and a 24 in. Vigreux column topped with a distilling head, water-cooled condenser, and receiver. The furfuryl alcohol (usually 340 g.) was added to the flask and heated with stirring, to maintain slow distillation of the lower molecular weight products into the receiver. After several hours of reaction the residual polymer was heated to 170 or 180°C., until the desired final viscosity was reached. The resins were cooled to 50°C. before being removed from the flask.

The furfuryl alcohol resins catalyzed with anhydrous magnesium sulfate were made much as were the thermally polymerized resins. In this case, however, polymerization was more quickly achieved and less volatiles were removed during the reaction, allowing a more uniform approach to the final

temperature. The usual proportions of reactants were 285 g. of furfuryl alcohol and 75 g. of anhydrous magnesium sulfate. Terminal reaction temperatures of 160–200°C. were required to give the viscosities needed.

The resin viscosities were measured at 25°C. with a MacMichael-Fisher Viscosimeter. Prior to measurement the resins and sample cups were suspended in a constant-temperature bath at 25°C. for 1 hr. Spindle wires of 18–34 gauge were used, and the sample cup was rotated at 20 rpm.

Chemicals and Materials

The poly(ethylene glycol) and poly(propylene glycol) calibration standards were distributed by either the Baker Chemical Co. or Waters Associates. The GPC solvent was du Pont commercial-grade tetrahydrofuran. Eastman White Label furfuryl alcohol, MCB standard-quality maleic anhydride, Baker and Adamson reagent-grade anhydrous magnesium sulfate, and Baker and Adamson reagent-grade 86% phosphoric acid were used for this study. The alumina (grade F-10) was manufactured by Alcoa. Other standard laboratory chemicals and apparatus were also used.

The γ alumina was prepared by heating the alumina, 8–14 mesh, F-10 grade, for 1 hr. at 1,000°F. All other chemicals and materials were used as received from the manufacturers.

RESULTS AND DISCUSSION

GPC Calibration

For the purposes of this study only a general knowledge of the molecular weight ranges of the resins involved was needed. The interpretation of the experimental results was based solely on comparisons between the GPC curves of the individual resins, which required little prior knowledge of the resin molecular weights. However, it is desirable from the standpoint of general information to have a rough molecular weight calibration for the specific column set used.

Molecular weight calibrations of this type are usually accomplished by determining the elution volumes of a series of narrow molecular weight distribution polymers of known average molecular weights and with molecular geometries similar to those of the unknown resins. An extension of a line drawn through the points on a semilogarithmic plot of the number-average molecular weights versus the peak elution volumes of a series of polyglycols (Fig. 2) corresponds reasonably well to the elution positions of the lower molecular weight species of the furfuryl alcohol resins. (Because of incomplete separation the elution positions of the higher molecular weight species of the furfuryl alcohol resins are not known.) The limited molecular weight range of polyglycols available (approximately 300–4000) makes the establishment of a calibration curve with these species covering the entire molecular weight range of interest difficult. However, a straight line extended from the available points gives a rough molecular weight

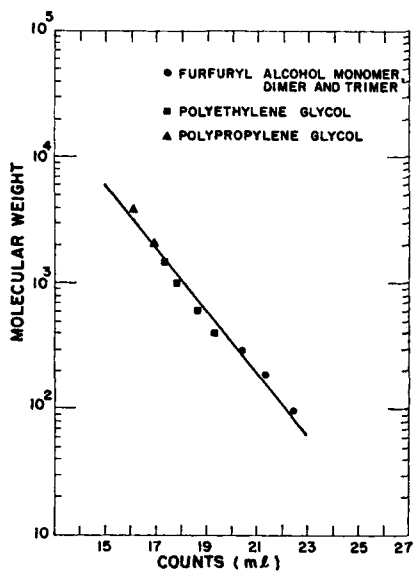


Fig. 2. Semilogarithmic plot of number-average molecular weights versus peak elution volumes (given as 5 ml. increments called counts) of the GPC calibration materials.

calibration in the 15- to 23-count span, provided the elution volumes of the higher molecular weight species of furfuryl alcohol resins do not exhibit gross deviations from the linear relationship with the logarithm of molecular weight, as indicated in Figure 2.

Furfuryl Alcohol Resin Characterization

Maleic Anhydride Catalyst. The gel permeation chromatograms of the furfuryl alcohol resins catalyzed with maleic anhydride were used as standards with which to compare those synthesized by other methods. Owing to the large number of resins needed it was desirable to find a set of reaction conditions under which the exothermic polymerization could be easily controlled and which would require a minimum of run-time attention. In 500–1000 ml. batches the ratio of reactants stated above under "Experimental" was found to be optimal for this purpose. These conditions gave controllable reactions, requiring no external cooling, the desired resin viscosities being attained over reasonable periods of time. Resins made by this process were completely soluble in tetrahydrofuran and were reproducible within the experimental error of the GPC method.

The standard series of furfuryl alcohol resins catalyzed by maleic anhydride has been discussed in a different context elsewhere,³ but a short review is in order here. Figure 3 shows the GPC curves of three members of this series of resins, illustrating the changes of molecular distribution with resin viscosity. The ordinate Δn is a relative measure of refractive-index difference, which in turn is proportional to the concentration of species at

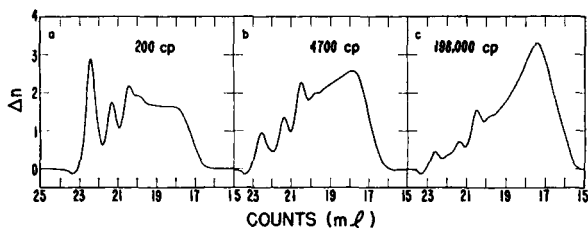


Fig. 3. GPC curves of furfuryl alcohol resins catalyzed with 1 g. of maleic anhydride.

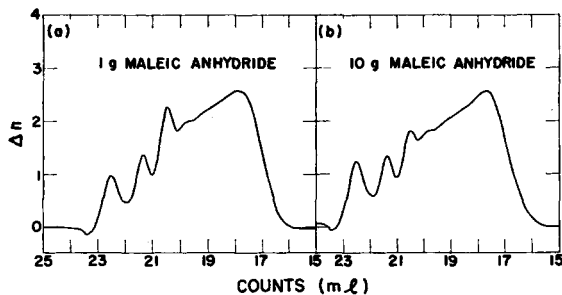


Fig. 4. GPC curves of furfuryl alcohol resins made with 1 g. and 10 g. of maleic anhydride, having viscosities of approximately 4700 cp.

each elution volume. The elution volume is given in counts, each count equal to 5 ml. of solvent passed through the column system. As shown in Figure 3, the species of lower molecular weight (i.e., monomer at 22.4, dimer at 21.3, and trimer at 20.3 counts) are particularly resolved. Reference to the calibration curve (Fig. 2) shows the molecular weights of these resins to vary from monomer weight up to 4000 or 5000. Because the furfuryl alcohol resins contain a number of distinct chemical species (Fig. 1), the terms "dimer" and "trimer" refer to all the species with approximately those molecular weights. Therefore, Δn at each elution volume is the total refractometer response due to the collective responses of all the species appearing at that volume.

As mentioned above, the initial polymerization rates of furfuryl alcohol are reasonably well known to be pH-dependent; however, the kinetics of the latter stages of reaction may be more complicated, because of the formation of a heterogeneous system by the separation of a layer of higher molecular weight polymer from the main bulk of solution. This observation necessitated a test of the dependence of the resin molecular distributions on catalyst concentration.

Another series of furfuryl alcohol resins was synthesized with maleic anhydride; in this series the viscosity range of the first series was duplicated, but in which ten times the original amount of catalyst was utilized. On the basis of viscosity no catalyst concentration effects could be noted from the GPC curves. Figure 4 shows chromatograms of two resins, one

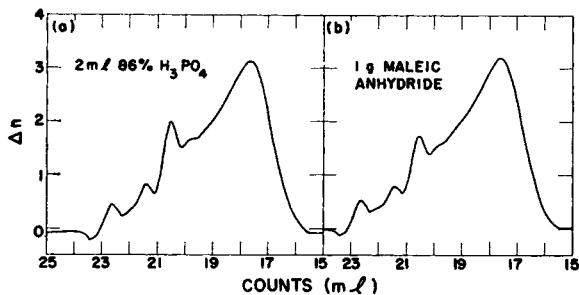


Fig. 5. GPC curves of furfuryl alcohol resins made by catalysis with 86% phosphoric acid (91,000 cp.) and maleic anhydride (96,000 cp).

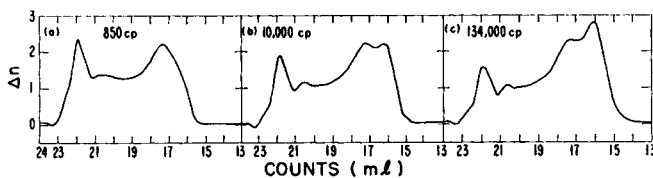


Fig. 6. GPC curves of furfuryl alcohol resins made by catalysis with γ alumina.

made at each catalyst concentration, having approximately equal viscosities. The slight differences between the two curves is due to the fact that resin 4b was at a slightly higher degree of polymerization than resin 4a. Small differences of this type, although detectable by GPC, are not manifested by the viscosity values. This is due mainly to the relatively large error (approximately 5%) involved in the viscosity measurements, attributed in large part to the extremely high temperature coefficients of viscosity of these resins.¹⁹

Phosphoric Acid Catalyst. A series of furfuryl alcohol resins catalyzed with 86% phosphoric acid was synthesized for a comparison with the resins catalyzed with maleic anhydride. Here also the reaction conditions were chosen such that resins of high viscosities could be produced in several hours, requiring little attention during the time of production. A comparison of the gel permeation chromatograms of these with those of resins catalyzed with maleic anhydride having similar viscosities showed little difference between the two series of resins. Two resins, one from each of these series, having approximately equal viscosities, are represented in Figure 5. In this instance the small apparent difference in the degree of polymerization between resin 5a and 5b is reflected in their viscosities.

The near identity of the molecular distributions of resins made with maleic anhydride and those made with phosphoric acid holds little consequence of its own. However, this evidence supports a conclusion that the mode of reaction followed in the two cases is similar. This, coupled with the lack of a catalyst concentration effect, supports the postulation that these reactions are dependent on the concentration of active hydronium ions in solu-

tion and not on the specific acid used. It appears that within the areas studied any complication of the rate law during the latter stages of reaction is independent of the catalyst type or concentration used.

Alumina Catalyst. An additional purpose of this study was to determine whether the reported chemical differences between alumina-catalyzed furfuryl alcohol resins and those catalyzed by acids were detectable by GPC. A number of resins condensed by γ alumina were made and their molecular distributions determined.

The dissimilarity of the GPC curves of the alumina-condensed resins and the acid-catalyzed resins can be seen by a comparison of Figures 3 and 6. The most noticeable difference is in the positions and spreading of the lower molecular weight elution bands. The band containing monomeric material peaks here at 22.0 counts, as compared to 22.4 for the acid-catalyzed resins. The dimer band is indistinct and is shifted down to about 20.8 counts. The trimer band can no longer be distinguished. Further comparison also reveals differences in the manner of conversion of the lower molecular weight products to those of higher molecular weights as the polymerization progresses. The lower molecular weight species of the alumina-catalyzed resins (22-count region) appear to remain in considerably higher concentration throughout the polymerization than do those of the acid-catalyzed resins. Thus, the alumina-catalyzed resins at high degrees of polymerization contain a greater amount of low molecular weight materials than do the acid-catalyzed resins. However, when alumina is used, the relative proportions of species do appear to be dependent on the particular heating rate used during polymerization.

A partial explanation of these observations can be found in the aforementioned work of Boquist et al.¹¹ The formation of high amounts of levulinic acid and other acids during the alumina catalysis of furfuryl alcohol facilitates complexing of many of the available free hydroxyl groups as esters. Therefore, the band in the alumina resin GPC curves peaking at 22.0 counts is probably made up of unesterified monomer and dimer species as well as of esterified monomer, accounting for the broadening of the band as well as the downward shift of the position of the peak maximum. The corresponding shifts of the other bands probably are due to similar circumstances. However, the presence of large amounts of difurfurylether and low molecular weight polymers derived from it could also account for the band shifts and broadening mentioned above.

The large amounts of low molecular weight products contained in the higher-viscosity alumina-catalyzed resins probably reflects an inability of some of these species to polymerize further. This may be due to the presence of relatively large amounts of difurfurylether or complexing agents such as levulinic acid and related acids.

The alumina-catalyzed furfuryl alcohol resins were found to be somewhat unlike the acid-catalyzed resins in bulk physical properties. At equal viscosities the alumina-catalyzed resins were darker in color and had a slightly burned odor; at the higher viscosities they contained small amounts

of insoluble materials, indicating that some crosslinking may have taken place. The latter characteristics probably reflect the high reaction temperatures to which they were subjected. Moreover, the alumina-catalyzed resins reflected a more complex internal state by exhibiting a higher degree of plasticity than did the acid-catalyzed resins.

Anhydrous Magnesium Sulfate Catalyst and Thermal Catalysis. Several batches of resins were made by the polymerization of furfuryl alcohol by catalysis with anhydrous magnesium sulfate and by thermal catalysis, and their CPC curves were compared with those of the resins discussed above. Unfortunately, conclusions were difficult to draw, because the most definitive peaks found in the lower molecular weight regions (20-23 counts) were small and indistinct. This was the result of the removal of much of the lower molecular weight material by distillation during the polymerization processes, required to achieve the high reaction temperatures needed to produce resins of desired viscosities in reasonable periods of time. The general shapes of the GPC curves of the resins made by either of these processes appeared intermediate between those of resins polymerized by catalysis with acids and those made with γ alumina. At low resin viscosities (below 3000 cp.) the GPC curves appear, with respect to both shapes and positions, to be similar to those of acid-catalyzed resins, with the exception of the presence of larger amounts of materials at 22 and 20.8 counts. At higher resin viscosities (above 50,000 cp.) the chromatographic curves appear very similar to those of alumina-catalyzed resins.

There are apparent similarities between the higher-viscosity resins produced from furfuryl alcohol by thermal catalysis or catalysis with anhydrous magnesium sulfate and the alumina-catalyzed resins. However, neither of these methods appears feasible for the production of large amounts of furfuryl alcohol resins without the accompanying removal and reuse of the lower molecular weight materials.

The synthesis of many of the resins used for this study was carried out by Tomas G. Sanchez, and the γ alumina was prepared by S. D. Stoddard of the LASL Group CMB-6, Ceramic Section. The help of these persons is sincerely appreciated.

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