

An Investigation of the Structure of Furfuryl Alcohol Polycondensates with Infrared Spectroscopy*

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INTRODUCTION

Limpricht¹ in 1873 and Wissel and Tollens² in 1893 reported that furfuryl alcohol on treatment with acidic reagents forms a resinous product. It is interesting that this is about the same time that Baeyer³ made his initial observations on the reaction between phenol and aldehydes, also producing, now familiar, resinous phenol-aldehyde polycondensates. Erdmann⁴ studied the resinification of furfuryl alcohol under acidic conditions and postulated the formation of an unsaturated open-chain aldehyde. Many acidic reagents, including mineral acids⁵⁻⁸ and catalysts of the Friedel-Crafts type,⁹ were investigated for use in the formation of furfuryl alcohol polymers. The application of amine salts¹⁰⁻¹² active at elevated temperatures has been reported in recent years. Dunlop and Peters¹³ investigated the effect of pH on the resinification process; it was found that, at least during the early stages of the reaction, the rate of polymerization is a simple function of pH. Most recently, Nielson¹⁴ has reported the polymerization of furfuryl alcohol with the use of a neutral promotor, α -alumina, at temperatures between 100 and 260°C.

The changes in the physical properties of furfuryl alcohol upon long exposure to air, high temperatures, acidic reagents, or combinations of these factors, have been reported by many investigators. Under these widely divergent conditions, furfuryl alcohol converts to a water-insoluble resin which, on further reaction, forms a high polymer.

The Status of Structural Knowledge

Pummerer and Gump¹⁵ concluded that the so-called water-insoluble resin from furfuryl alcohol is not a single species, does not show any aldehyde reactions, and has a higher carbon content than the parent alcohol, indicating water is eliminated during the polymerization. Dunlop and Peters¹⁶ treated furfuryl alcohol under a wide variety of polymerization conditions, to obtain the water-insoluble resin—in each case, however, in

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differing amounts. The resin was separated into three fractions by vacuum distillation after the unreacted furfuryl alcohol was removed. Chemical tests indicated that the materials distilling from the resin mixture up to 210°C. at 4 mm. Hg contained no aldehyde, ketone, or acid functional groups. In a similar study, Hachihama and Shono¹⁷ concluded that the viscous liquid resin obtained by polymerizing furfuryl alcohol with acidic reagents consisted of 2-oxymethyl-5-furfuryl furan, 2-oxymethyl-5-(5'-furfuryl)-furfuryl furan, difuryl ether, di-2-furylmethane, formaldehyde, and levulinic acid.

The present knowledge concerning the structure of these resins can be summarized, as in Figure 1. The extent of terminal methylol groups depends upon the temperature of the polymerization process and the reaction time. The furfuryl alcohol acts as a bifunctional monomer and, in the early stages of condensation, gives rise to linear products.

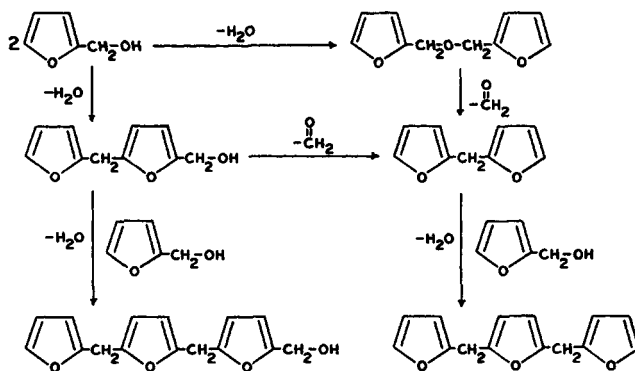


Fig. 1. Commonly accepted mode of polymerization of furfuryl alcohol.

It was of interest to investigate the structure of furfuryl alcohol polycondensates at various stages of the resinification process by means of infrared spectrophotometric techniques for the purpose of following any functional group changes during the polymerization process. It was also of interest to examine the extended polymerization occurring during the curing of the resin in inert atmospheres, for some insight into the reactions taking place and the structural parameters of the cured high polymer.

EXPERIMENTAL

All infrared spectra were obtained with a Baird Model AB-2 double-beam recording spectrophotometer equipped with sodium chloride optics. All viscometric data was determined with a Brookfield Synchro-Lectric viscometer, Model LVF. The pH values reported were determined with a Beckman Glass Electrode pH meter, Model M-2. The furfuryl alcohol used in all experiments contained a maximum furfural contaminant of 0.5% as determined by vapor phase chromatography with a Perkin-Elmer Model 154-C vapor phase chromatograph equipped with a Perkin-Elmer Type

R column. At 175°C. and a column pressure of 30 psig with a 56-ml./min. flow rate of helium carrier gas, the retention times for furfuryl alcohol and furfural were 6.2 and 3.6 min., respectively.

I. Polymerization Studies

Acid-Catalyzed Polymerization

The catalysts used in these studies, together with the properties of the resins produced, are summarized in Table I. The polymerizations were

TABLE I
Effect of Acid Catalyst on Furfuryl Alcohol Resin
Properties

Catalyst	Wt.-%	Dis-til- late, ml.	pH	Vis- cosity, cpoise	H ₂ O, %
C ₆ H ₅ SO ₃ H	0.08	66	3.8	9360	1.0
FeCl ₃ ·6H ₂ O	0.50	68	—	gel	—
FeCl ₃ ·6H ₂ O	0.25	74	—	gel	—
FeCl ₃ ·6H ₂ O	0.12	62	—	gel	—
H ₂ SO ₄ ^a	3.75	75	—	gel	—
H ₂ SO ₄ ^a	2.50	71	—	gel	—
H ₂ SO ₄ ^a	1.25	62	3.7	238	1.1
H ₂ SO ₄ ^a	1.75	68	3.6	1638	1.1
(COOH) ₂	0.30	39	5.6	15	1.0
(COOH) ₂	0.90	60	5.2	54	0.6
p—CH ₂ —C ₆ H ₄ — SO ₃ H	0.10	58	5.2	331	0.8

^a The sulfuric acid used in these experiments was prepared by mixing 2.2 g. concd. H₂SO₄ with 97.8 g. water.

carried out in a 1-l. three-necked flask fitted with a sealed stirrer unit, thermometer, and condenser. The catalyst, dissolved in 15 ml. of water, was added to 400 g. of purified furfuryl alcohol. The desired polymerization temperature was maintained either by heating or cooling, depending on the extent of the exothermic reaction taking place. The experiments were conducted under reduced pressure (460 mm.) in a nitrogen atmosphere (0.05 cu. ft./hr.). After 140 min., the acid was neutralized with a 20% aqueous sodium hydroxide solution. The brownish-black liquid was heated for 40 additional min. During the first 20 min. of the distillation period, the pressure was reduced to 160 mm. The distillation was continued at that pressure for the remaining 20-min. period. The total polymerization and distillation process was completed in 3 hrs. The resin obtained was used directly, without further treatment, for spectral studies and other physical-property determinations. The infrared spectra were determined on samples prepared by depositing a thin film of resin on polished sodium chloride plates. The viscosity was checked after 24 hrs.

Determination of Water in the Furfuryl Alcohol Resins

The resin (50 ml.) was mixed with 50 ml. of anhydrous benzene and refluxed under a Dean-Stark water separator and condenser system. After 1 hr. no further water separated and the volume of the aqueous layer was recorded.

Determination of pH in the Furfuryl Alcohol Resins

The resin (50 ml.) was vigorously shaken for 1 min. with 50 ml. of distilled water. After 30 min. the top layer was decanted and filtered. The filtrate was used for the pH determinations.

Use of Nonaqueous Media for Polymerization

With the apparatus previously described for aqueous solution polymerization, 400 g. of purified furfuryl alcohol and 100 ml. of the solvent medium were heated at reflux. The catalyst, either dissolved in 50 ml. of solvent or suspended in the solvent, was added slowly to the furfuryl

TABLE II
Nonaqueous Polymerization of Furfuryl Alcohol

Catalyst	Wt.-%	Atm.	Solvent	Viscosity, cpoise	pH	H ₂ O, %
C ₆ H ₅ SO ₃ H	0.08	N ₂	Cellosolve	7270	4.3	0.6
C ₆ H ₅ SO ₃ H	0.08	N ₂	Benzene	240	5.2	0.6
C ₆ H ₅ SO ₃ H	0.08	N ₂	1:1 Benzene- toluene	140	5.6	0.6

alcohol-solvent mixture. In experiments with benzene-toluene mixture as polymerization medium, the water produced in the reaction was continuously separated by means of a Dean-Stark water separator. After 140 min. the reaction mixture was diluted with 100 ml. of water and the acid neutralized with 20% aqueous sodium hydroxide. The distillation was carried out after initial stripping of the solvents, as previously described. The resulting resins, solvent systems, and conditions are summarized in Table II.

TABLE III
Effect of Nitrogen Atmosphere and Reaction Time

Catalyst	Wt.- %	Atmos- phere	Time	Vis- cosity, cpoise	pH	H ₂ O, %
C ₆ H ₅ SO ₃ H	0.08	N ₂	140	4,480	4.3	1.0
C ₆ H ₅ SO ₃ H	0.08	N ₂	160	100,000	4.7	1.0
C ₆ H ₅ SO ₃ H	0.08	Air	140	6,100	4.5	1.0
C ₆ H ₅ SO ₃ H	0.08	Air	160	100,000	4.3	1.0

Effect of Nitrogen Atmosphere and Reaction Time

The apparatus used in these experiments was identical with that previously described for the study of acid catalysis on the polymerization. The reaction conditions and resulting polymer properties are summarized in Table III.

Thermal Polymerization of Furfuryl Alcohol

Furfuryl alcohol (2000 g.) was slowly distilled through a 36-cm. Vigreux column. After 3 hrs. of distillation, 800 g. of brown liquid remained in the still pot. From this liquid, 180 g. of furfuryl alcohol was removed at reduced pressure (10 mm.). The viscous liquid which remained in the flask had a viscosity of 2200 cpoise and a pH of 3.4. This resin was identical in physical properties and infrared spectrum with the resin obtained by the procedure described by Nielson,¹⁴ in which α -alumina was used as polymerization catalyst at the boiling point of furfuryl alcohol.

Structural Studies*Distillation Procedures*

A. Vacuum Distillation of a Typical Acid-Catalyzed Resin. By means of a semimicro Vigreux column and fraction collection system, 50 g. of benzene sulfonic acid-catalyzed furfuryl alcohol resin (9360 cpoise) was fractionated at 1.5 mm. The volatile portion of the resin was separated into four fractions and a residue. Each of the five parts was examined spectrally. The results are summarized in Table IV.

B. Vacuum Distillation of Thermally Produced Resin. The resin (50 g.) produced by thermal polymerization was prefractionated at 1.5 mm. The distillate, b.p. 25–130°C., was separated in four fractions, as shown in Table V. The residue from prefractionation (63.5%) was identical with the residue obtained by fractionation of the acid-catalyzed resin and the spectrum of original resin with the disappearance of the band at 5.72 μ .

Extraction Procedures

A. Sodium Hydroxide Extraction of a Typical Acid-Catalyzed Resin. In a 125-ml. Erlenmeyer flask, 10 g. of acid-catalyzed resin and 50 ml. of 5% aqueous sodium hydroxide solution were thoroughly blended. After 72 hrs. at room temperature the mixture was heated for 1½ hrs. on a steam bath. On cooling, the mixture was extracted five times with equal volumes of benzene. The benzene extracts were combined and evaporated, yielding 8.3 g. (83%) of base-insoluble resin. The resin isolated had the same spectral properties as the original resin, but the intensity of the hydroxyl stretching vibration at 2.94 μ was much less intense.

The alkaline solution was acidified with 10% aqueous sulfuric acid. The acidified solution (pH 1) was extracted three times with 100-ml. portions of diethyl ether. The ether solution was filtered, for removal of suspended solids, dried over anhydrous magnesium sulfate, filtered, and

TABLE IV
Distillation of a Typical Acid-Catalyzed Resin

Fraction no.	B.p., °C.	Weight, g.	Resin, %	Spectral data
1	24-30.5	7.72	15.4	Identical with furfuryl alcohol spectrum
2	66-77	2.53	5.1	In addition to typical furan-alcohol spectrum, a band at 5.86 μ is present
3	106-113	2.81	5.6	Same as fraction 2
4	115-121	1.01	2.0	Same as fraction 2
Residue ^a	Gel	35.02	70.0	Same as fractions 2, 3, and 4, except the hydroxyl band at 2.94 μ is decreased in intensity

^a The spectrum of the distillation residue was practically the same as that of the original resin prior to distillation, with the exception that the residue had a markedly decreased hydroxyl vibration at 2.94 microns.

TABLE V
Distillation of Thermally Produced Resin

Fraction no.	B.p., °C.	Weight, g.	Resin, %	Spectral data
1	26-30	3.57	7.1	Identical with furfuryl alcohol spectrum
2	56-64	3.61	7.2	Same as fraction 1, except the 2.94 μ band was decreased in intensity
3	85-87.5	2.86	5.7	Typical spectrum of a lactone with a strong carbonyl absorption band at 5.72 μ
4	80-92	2.10	4.2	Same as fraction 3
Residue	Gel	5.02	10.0	Same as residue from prefractionation

evaporated, and yielded 0.1 g. (1%) of an amber liquid identified by its infrared spectrum as levulinic acid.

B. Sodium Hydroxide Extraction of Thermally Produced Resin. With the above procedure, 10 g. of the resin produced thermally yielded 7.5 g. (75%) of base-insoluble resin. The alkaline solution yielded 1.2 g. (12%) of a black mobile liquid, on acidification and extraction. Microdistillation of the liquid gave 0.9 g. (9%) a light yellow liquid, b.p. 86–92°C., which was spectrally identical with the lactone isolated in 9.9% yield by vacuum distillation of the original resin. This lactone was identical in all respects with the lactone prepared from furfuryl alcohol in 10% yield by the procedure described by Boeseken.¹⁸

Fractional Precipitation Studies

The acid-catalyzed resin (10 g.) was dissolved in 40 g. of benzene. To this solution, 20 ml. of diethyl ether was added and the mixture set aside for 2 hrs. at room temperature. The solid powderlike precipitate was filtered and dried, yielding 0.64 g. (6.4%) solid resin which was spectrally identical with the starting liquid and had approximately equal intensity bands at 2.94 and 5.86 μ .

The addition of 120 ml. of ether resulted in the formation of resinous precipitate. After decantation of the benzene-ether solution and vacuum evaporation of the residual solvent, 0.96 g. (9.6%) of viscous residue was obtained. This fraction was also identical with the original resin.

Further addition of ether (240 ml.) caused no further precipitation. Vacuum evaporation of the solvents yielded 8.4 (84%) of the remaining viscous resin. This was examined spectrally and again found identical with the original resin.

All three fractions showed the same ratio of hydroxyl (2.94 μ) to carbonyl (5.86 μ) absorptions.

III. Resin Curing Studies

The furfuryl alcohol resin used for these studies was the base-insoluble resin isolated from the sodium hydroxide extraction of the acid-catalyzed resin. This material was used because it was free from acid contaminants such as levulinic acid.

Benzenesulfonic acid (1 g.) was dissolved in a mixture of 80 g. of benzene and 20 g. of methanol. To 1 g. of the catalyst solvent mixture, 2 g. of resin was added and the solution was thoroughly mixed. The resulting resin solution was used to cast five films of equal thickness on polished sodium chloride disks. The solvents were evaporated in air and then *in vacuo* at room temperature and left a thin polymer film on each plate. The polymer-coated plates were clamped in asbestos holders and the infrared spectrum of each was recorded. The samples were then placed in a specially constructed curing oven.¹⁹ The oven was thoroughly flushed with nitrogen and each sample was cured under a positive flow of nitrogen (0.08 cu. ft./hr.). The curing times and temperatures are shown in Table VI. After curing, each sample was allowed to cool in the nitrogen atmosphere.

TABLE VI
Nitrogen Curing Conditions of Furfuryl Alcohol Resins

Sample	Temperature (°C.)	Time (hrs.)	Total Curing Time (hrs.)
1	100	1	1
2	100	1	
	200	2	3
3	100	1	
	150	2	
	200	1	4
4	100	1	
	150	2	
	200	2	5
5	200	17	17

After cooling, the spectrum of each sample was determined. In each case, a condensate collected in the outlet tube of the oven. This condensate was found to be water. No volatile organic materials were detected under the curing conditions shown in Table VI.

DISCUSSION

Acid-Catalyzed Resins

For the preparation of a furfuryl alcohol resin, free from possible by-products, the condensation reactions were conducted in an inert atmosphere (nitrogen) and at reduced pressure. The nitrogen atmosphere protected the furfuryl alcohol mixture from air oxidation during the polymerization, while the low temperatures possible at the reduced pressures protected the system from any thermally induced degradative reactions. By using the low pressure it was also possible to remove the water immediately after it was formed during the condensation process. This procedure also prevented the formation of excessive amounts of levulinic acid and inhibited the formation of large amounts of formaldehyde that usually accompany the elevated temperatures used in such polymerization.

Among the catalysts chosen for the polymerization, benzenesulfonic acid, p-toluenesulfonic acid, oxalic acid, sulfuric acid and ferric chloride were studied in varying amounts. The reaction conditions in each experiment were kept constant and, by varying the catalyst concentrations, resin mixtures of widely varying viscosities were obtained. It could be concluded after examination of the infrared spectral properties of each resin, that the polymers produced differed only in the furfuryl alcohol content of the mixture. Removal of the excess furfuryl alcohol by vacuum distillation yielded resins which were spectrally identical in all respects regardless of the catalyst used. The resin spectrum had strong similarities with the spectrum of furfuryl alcohol. Below 7 μ all polymers had characteristic bands at 3.21, 3.45, 5.86, and 6.10 μ , which were independent of the resin viscosity. The band at 2.94 μ attributed to hydroxyl stretching (hydrogen bonded)

decreased as the viscosity increased. The band at 3.21 could be assigned to the carbon-hydrogen stretching vibrations of the hydrogens attached to the furan nucleus. The 3.45-band was typical of aliphatic carbon-hydrogen vibrations, while the 6.10-band could be assigned to the stretching vibrations of the unsaturations in the furan ring. The strong absorption band at 5.86 indicated the presence of carbonyl species. The absence of aldehydic carbon-hydrogen at 3.65-3.7 negated the possibility that the 5.86-band was due to aldehydic carbonyl. The absence of typical acidic type hydroxyl at 3.0-4.0 suggested the absence of carboxylic acids. However, it remained plausible that some contribution to the 5.86 band might be due to some levulinic acid and that the major portion was probably due to ketonic species.

Since the band at 5.86 μ was present in every polymer, regardless of the conditions used, such as catalyst or solvent, and since the band was always present in the same relative intensity when compared with the 6.21 and the 6.45 μ bands, it had to be assumed that it was present in the polymer unit. This assumption was supported in distillation and precipitation experiments which, again, indicated no separation or change in relative intensity of this band. Definite support that the functional group was ketonic rather than acidic was obtained from the alkaline extraction of the resins, effected to remove any acidic or possible ester contaminants. On reisolation of the base-insoluble resin, the 5.86 μ band was present without change in this resin portion. An effort to isolate the ketonic material as a dinitrophenylhydrazone derivative, although inconclusive as a chemical test, added additional weight to the postulation of ketonic materials in the polymer chain. On reaction with this reagent, a black resinous mass precipitated. However, the spectrum of the resinous material was so complex that no definite proof of reaction could be made.

It must be concluded from these data, however, that, regardless of the technique used to prepare furfuryl alcohol polymers, appreciable amounts of ketonic species are formed. Since the formation of the ketonic portion of the resin occurs early in the polymerization and the concentration remains the same regardless of the molecular weight, there is strong suggestion that the polymerization is a two-step process in which the condensation reaction must be coupled with a certain amount of ring cleavage to γ -diketone structures. Since the amount of water in the polymer systems was varied over a wide range in this study, the ring cleavage process is most probably due to protonation of the furan ring oxygen in a rate-controlling process, followed by the rapid attack of water and the formation of the diketone system. These reactions are summarized in Figure 2.

It can be concluded from this study that furfuryl alcohol resinification is more complex than originally postulated.¹⁶⁻¹⁷

Thermal Furfuryl Alcohol Polymerization

Since furfuryl alcohol at its boiling point polymerizes slowly, the polymer thermally produced was investigated. The resin produced by heat alone was spectrally the same as that produced on acid-catalyzed polymerization,

with the exception that an additional carbonyl absorption at 5.72μ was present in the crude resin (viscosity 2260 cpoise). It is of interest to note that this resin is spectrally identical with the resin prepared according to Nielson,¹⁴ i.e., with the use of γ -alumina as neutral catalyst. Both resins showed strong carbonyl absorption at 5.72μ .

To determine whether the 5.72μ carbonyl absorption, which is indicative of an ester or lactone, was a portion of the resin or simply a monomeric by-product, the resin was vacuum distilled and extracted with sodium hydroxide. In each case, when the resin portion was reexamined, the

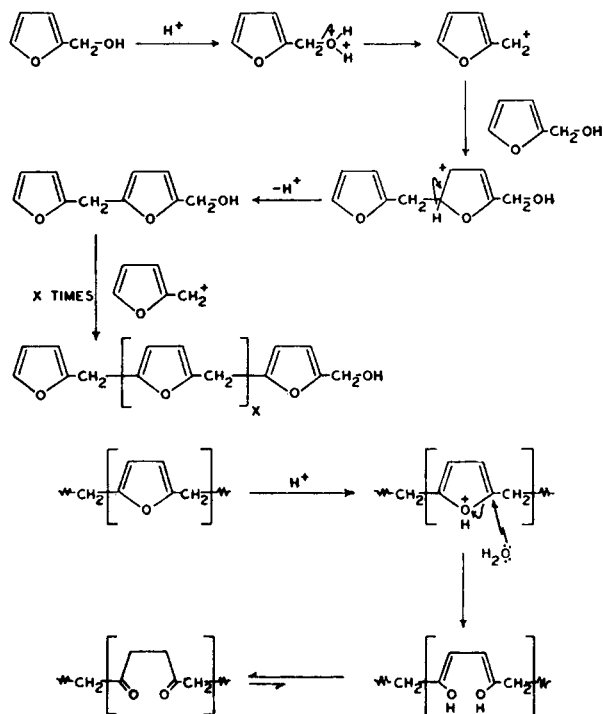


Fig. 2. Polymerization of furfuryl alcohol with acid catalysis (I), and competitive ring cleavage of furfuryl alcohol resin (II).

5.72μ band had disappeared and could be isolated as a clear mobile liquid in the distillate or isolated from the acidified alkaline extracts of the resin. The position of the carbonyl and its solubility characteristics suggested the formation of a hydroxylactone. This assumption was substantiated by preparing the lactone from furfuryl alcohol polymerization with peracetic acid by the method described by Boeseken et al.,¹⁵ which yielded a spectrally identical product, 5-hydroxy-3-pentenoic lactone.

It should be noted that the residual resin produced thermally was identical in every respect with the acid-catalyzed resins previously described.

Despite the fact that the utilization of furan resins in high-temperature

binding applications up to 1000°C. has been reported,²⁰ the reactions which take place on furan resin curing for high polymers have not entailed serious investigation.

Curing of Furan Resins

In the present study, a sulfuric acid-catalyzed resin was examined by infrared techniques. To be sure that only the condensed furan resin system was giving results, all base-soluble components were removed prior to curing of the resin sample. The furfuryl alcohol resin was catalyzed with benzenesulfonic acid and filmed on polished sodium chloride plates. The samples were then cured in a nitrogen atmosphere, as summarized in Table VI. In each case, only water was detected in the off-gas stream from the curing ovens. Further substantiation that little or no organic material was lost was given by the infrared spectrum of the cured resins. The majority of bands in the spectrum of the solid phase showed little or no change in intensity when compared with the uncured samples.

The sample cured in nitrogen for 1 hr. at 100°C. showed only a slight decrease in the hydroxyl stretching frequency at 2.94 μ . However, as the curing temperature was increased and the time lengthened, increasingly smaller absorption was noted at 2.94 μ . In addition, a band attributable to the hydrogen out-of-plane bending vibration of the furan ring hydrogens at 13.6 μ began slowly to decrease. A second similar vibration at 12.6 μ , however, showed a small increase in intensity. In addition, the furan ring carbon-hydrogen stretching frequency at 3.2 μ showed a slightly decreased intensity when compared with the 3.45- μ aliphatic carbon-hydrogen stretching frequency, which showed no apparent change in intensity.

These spectral changes indicate that the nitrogen curing of furfuryl alcohol resins is, for the most part, a further polymerization through the removal of water, as observed in the initial polymerization. Since Hachihama and Shono¹⁷ have shown that, during early stages of the condensation, removal of the hydrogen at the 5 position of the furan ring occurs, the appearance of the 12.6- μ band in the original resin can be attributed to the out-of-plane bending of the hydrogens attached to the 3 and 4 positions on the ring. The decrease of the 13.6- μ band and the increase of the 12.6- μ band can be attributed to the further formation of 2,5-disubstituted furan ring moieties, as indicated in Figure 3.

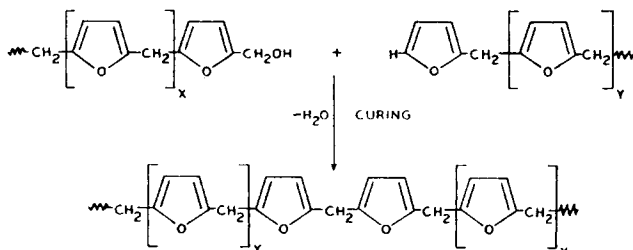


Fig. 3. Proposed curing reaction (extended polymerization) of furfuryl alcohol resin.

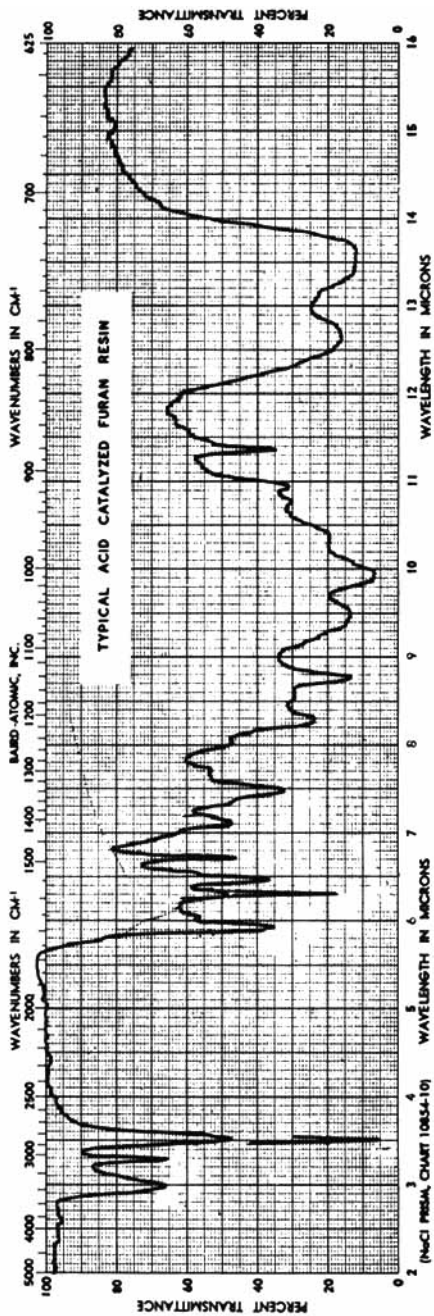
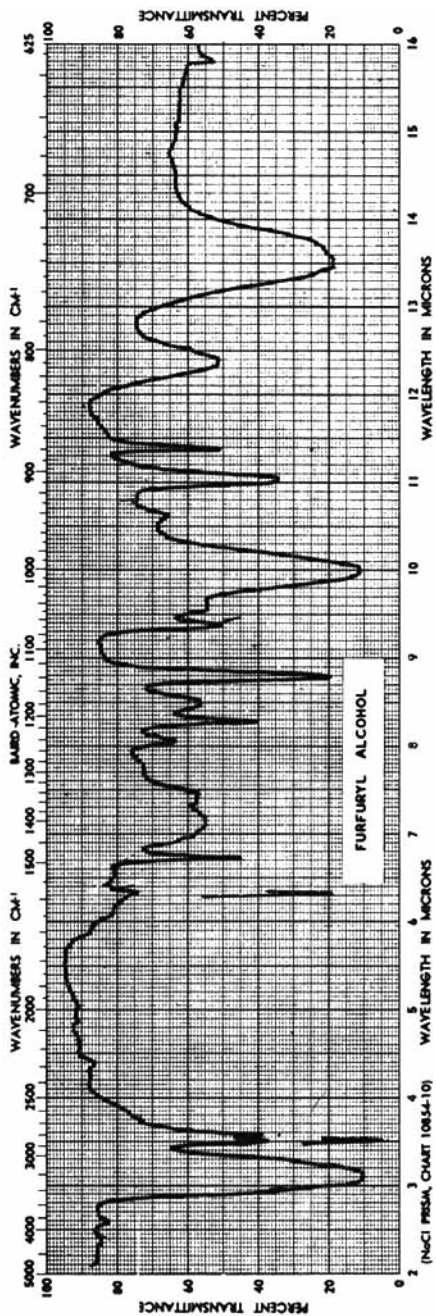
In addition, curing reactions which might be proposed to proceed through condensation at the 3 and 4 positions (β -condensation) of the furan ring must be of only minor consequence. It is well known that the β -furan ring positions are much less reactive than the α positions. Therefore, it would be expected that this crosslinking reaction occurs only after the majority of the 5 positions are substituted. Since in the curing process almost all the hydroxyl has been lost, with only minor decrease in the 3.21- μ carbon-hydrogen stretching vibration as well as the appropriate bending vibrations, β -condensation seems unlikely.

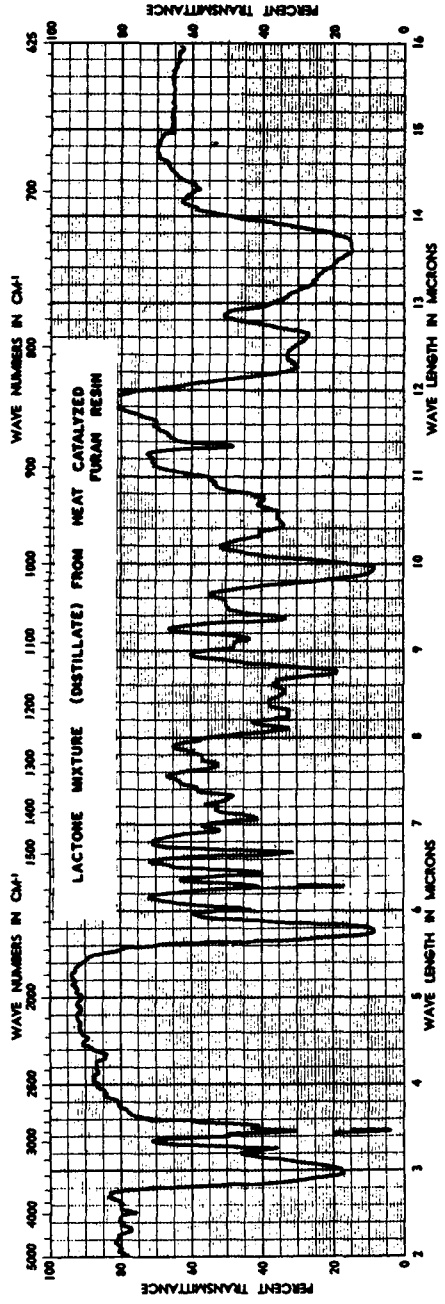
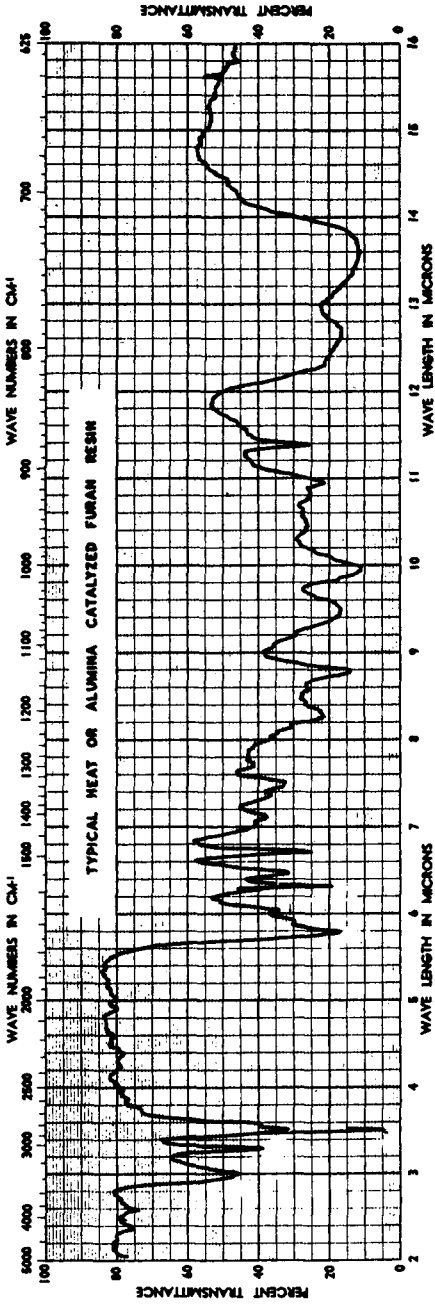
Condensation through attack of a methylol group on the activated methylene linkage unfortunately can be neither negated nor substantiated from this study. On the basis of the physical changes, such as increased brittleness occurring in the solid phase of the resin, it seems reasonable to assume that crosslinking does occur. Then crosslinkages formed at the methylene bridges seem most likely, from the present study. Typical spectra of various stages of furan resin polymerization are shown in Figure 4.

Further studies of the curing of furfuryl alcohol resins in air and the mode of oxidative degradation of furan resins are in progress, and will be reported at a later date.

References

1. Limpricht, H., *Ber.*, **3**, 90 (1870).
2. Wissel, L. V., and B. Tollens, *Ann.*, **272**, 291 (1893).
3. Baeyer, A., *Ber.*, **25**, 280 (1872).
4. Erdmann, E., *Ber.*, **35**, 1855 (1902).
5. Trickey, J. P., and C. S. Miner, U.S. Pat. 1,665,235 and 1,665,366 (1928).
6. Heberer, A. J., and W. R. Marshall, U.S. Pat. 2,095,250 (1937).
7. Dinelli, D., and G. B. Marini-Bettolo, *Gazz. chim. ital.*, **71**, 117 (1941).
8. Meiler, J. G., U.S. Pat. 2,243,481 (1941).
9. Lieber, E., and M. E. Thorner, U.S. Pat. 2,274,864 (1942).
10. The British Thomson-Houston Co., Ltd., Brit. Pat. 549,515 (1944); *Chem. Abstr.* **38**, 814 (1944).
11. Fiedler, E. F., and G. D. Holmberg, U.S. Pat. 2,345,966 (1944).
12. Nordlander, B. W., U.S. Pat. 2,399,055 (1946).
13. Dunlop, A. P., and F. N. Peters, *The Furans*, Reinhold, New York, 1953.
14. Nielson, E. R., U.S. Pat. 2,681,896 (1954).
15. Pummerer, R., and W. Gump, *Ber.*, **56**, 999 (1923).
16. Dunlop, A. P., and F. N. Peters, *Ind. Eng. Chem.*, **34**, 814 (1942).
17. Hachihama, Y., and T. Shono, *Studies on the Furfuryl Alcohol Resin. I.*, *Tech. Repts. Osaka Univ., Japan* (1954).
18. Boeseken, J., C. O. G. Vermij, H. Bunge, and C. Van Meeuwen, *Rec. trav. chim.*, **50**, 1023 (1931).
19. Conley, R. T., and J. F. Bieron, *J. Appl. Poly. Sci.*, to be published.
20. Watt, W., R. L. Bickerdike, A. R. G. Brown, and W. Johnson, *Nuclear Power*, **86** (1959).





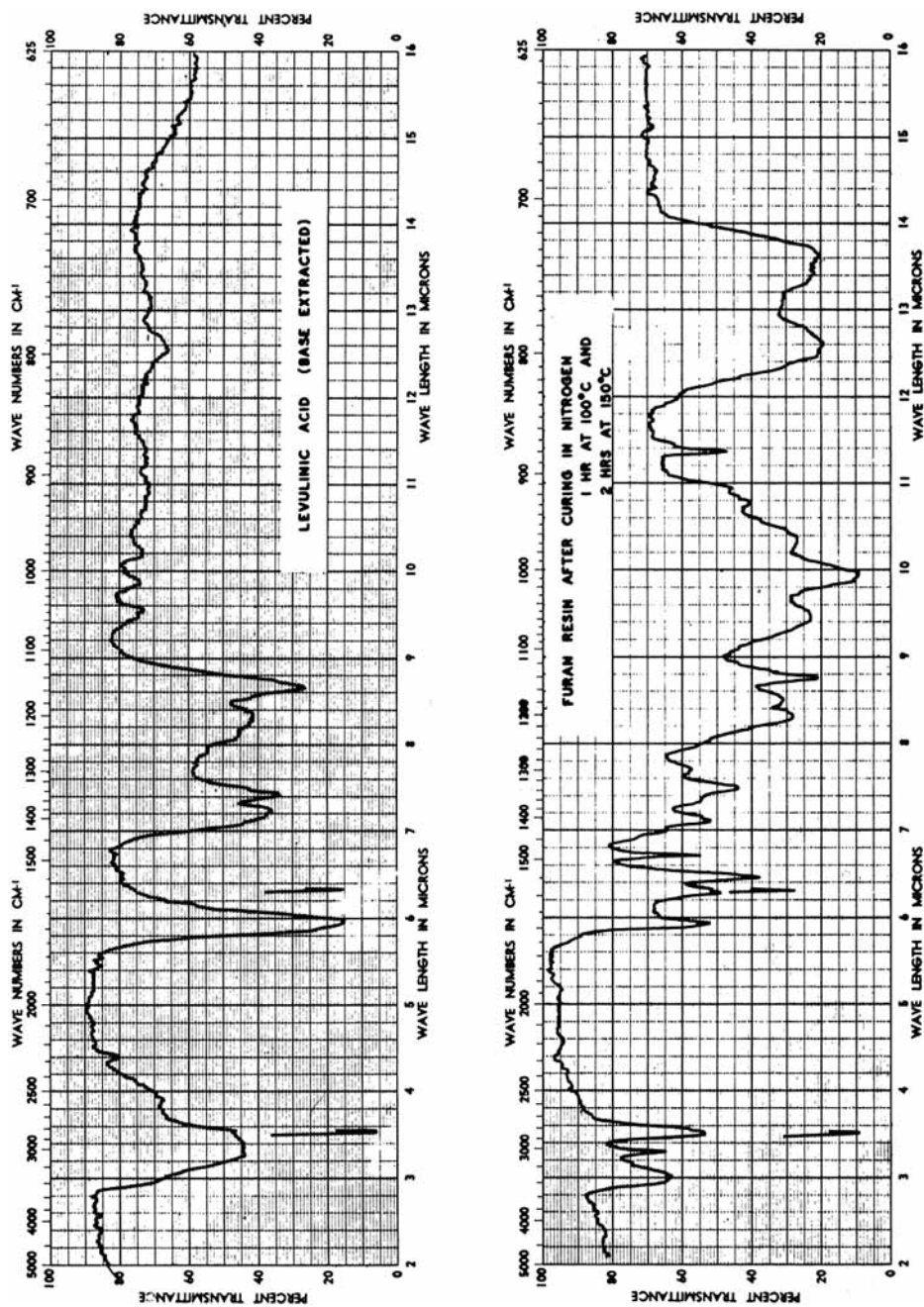


Fig. 4. Typical spectra of various stages of furan resin polymerization.

Synopsis

Furan resins were prepared by the polymerization of furfuryl alcohol with either acid or thermal catalysis. The effect of catalysts, solvents, polymerization time, and atmosphere were studied for their effects upon the chemical structure of the polymer produced. It has been found that, regardless of the technique employed, the resins contained appreciable amounts of ketonic species. Examination of the infrared spectrum of these resins indicated that the relative amount of ketonic material to furan ring-containing species was the same, regardless of the resin viscosity. It is proposed that the ketonic species arise during the polymerization by ring-opening of the furan unit, forming γ -diketone functional systems as part of the polymer unit. The resins were separated into crude fractions by vacuum distillation, base extraction, and fractional precipitation. From heat-catalyzed resins a lactonic component identified as 5-hydroxy-3-pentenoic γ -lactone was isolated. The curing of furan resins in nitrogen was shown to proceed through further condensation of furan methylol groups with furan rings having an available α -hydrogen. β -Hydrogen crosslinking reactions were not supported by infrared examination of the curing process.

Résumé

On a préparé des résines furanniques par polymérisation de l'alcool furfurylique par catalyse acide ou thermique. On a étudié l'influence des catalyseurs, des solvants, de la durée de polymérisation et de l'atmosphère sur la structure chimique des polymères formés. On a trouvé que, quelque soit la technique employée, les résines contiennent d'appréciables quantités de groupes cétoniques. L'examen de spectres infra-rouges de ces résines révèle que le rapport cétonesfurannes restait constant quelque soit la viscosité de la résine. Les unités cétoniques seraient formées durant la polymérisation par ouverture d'une unité furannique et formation d'une gamma-dicétoone faisant partie d'une unité polymérique. Les résines ont été séparées en fractions brutes par trois techniques: distillation sous vide, extraction par les bases, et précipitation fractionnée. Des résines formées thermiquement, on a isolé une lactone identifiée comme étant le 5-hydroxy-3-penténoïque gamma-lactone. On a démontré que le traitement des résines furaniques sous atmosphère d'azote consiste en la condensation des groupes méthylols des unités furaniques avec les cycles furaniques ayant un hydrogène en alpha. De l'examen des spectres infra-rouges on peut exclure les réactions de pontage par condensation avec les hydrogènes bêta.

Zusammenfassung

Furanharze wurden durch säurekatalysierte oder thermische Polymerisation von Furfurylalkohol dargestellt. Der Einfluss von Katalysatoren, Lösungsmitteln, Polymerisationsdauer und der verwendeten Atmosphäre auf die chemische Struktur des entstehenden Polymeren wurde untersucht. Es wurde gefunden, dass, unabhängig vom verwendeten Verfahren, die Harze beträchtliche Mengen von Ketogruppen enthalten. Das Infrarotspektrum der Harze zeigte, dass das Verhältnis von Ketogruppen zur Zahl der Furanringe, unabhängig von der Viskosität der Harze, das gleiche war. Es wird angenommen, dass die Ketogruppen durch Öffnung des Furanringes während der Polymerisation zu einem γ -Diketonsystem als Teil der Polymereinheit gebildet werden. Die Harze wurden durch drei Verfahren in rohe Fraktionen zerlegt, nämlich Vakuumdestillation, basische Extraktion und fraktionierte Fällung. Aus den thermisch polymerisierten Harzen wurde eine als 5-Hydroxy-3-pentenoat- γ -lacton identifizierte Lactonkomponente isoliert. Die Härtung von Furanharzen unter Stickstoff verlief über eine weitere Kondensation von Furanmethylolgruppen mit Furanringen mit freiem α -Wasserstoff. Die Infrarotuntersuchung des Härtungsprozesses lieferte keine Hinweise auf Vernetzungsreaktionen mit β -Wasserstoff.

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