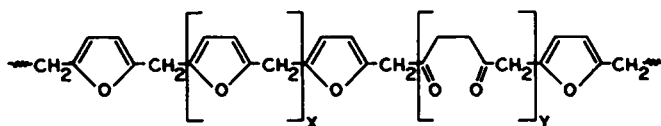


A Study of the Oxidative Degradation of Furfuryl Alcohol Polycondensates by Infrared Spectroscopy*

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INTRODUCTION

In a previous paper,¹ the structure of furfuryl alcohol polycondensates was reported. The examination of the polymerization reactions producing an initial liquid resin and the curing of the liquid resin to high polymer with infrared spectrophotometric techniques led to the formulation of the polymer structure as shown in (I).



(I)

The polymerization reaction was postulated to consist of methylol interaction with open alpha positions on neighboring furan rings to form a methylene bridged polycondensate. In addition, competitive ring opening was proposed to account for the nonacidic carbonyl formation evidenced by chemical reactions and infrared spectral characteristics. The formation of water during the initial condensation and ring oxygen protonation could be extended to account for the ring opening reaction to form gamma-diketone moieties incorporated into the resin chain. The extended polymerization, the resin curing cycle, was observed to follow the same reaction course as the initial polymerization process.

Since this furan polymer system is a heterocyclic ring analog of phenol formaldehyde polycondensates, it was of interest to examine the oxidative degradation chemistry of this system in an effort to correlate the oxidative degradation processes in both polymers. Oxidative degradation in the phenolic resin system has recently been investigated by means of infrared spectroscopy, both qualitatively² and kinetically.³ The initial oxidation

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of the methylene bridge groups to ketonic species and the oxidative chain scission reaction are rather firmly established.

From the above studies, it seemed logical to extend the oxidative chemistry of furfuryl alcohol polymers in an attempt to establish a parallel degradation route. Oxidation of the furan methylene bridge to a carbonyl group as the initial process, followed by ring tautomerization to an exocyclic olefin, would be consistent with the phenolic resin secondary degradation reaction. Chain scission of the enolic double bond would quite adequately account for the oxidative decomposition in the furan resin system. Since the formation of the enol would be expected to control the formation of acid fragments it was of interest to compare the relative stabilities of these two systems. To gain the necessary data, the furan resin was cured oxidatively on one hand and compared with the oxidation of nitrogen (nonoxidative) cured polymer on the other. Each system was examined for changes occurring in the infrared spectrum at 2 to 16 μ .

EXPERIMENTAL

All infrared spectra were obtained with a Baird Model AB-2 or a Beckmann IR-4 double-beam recording spectrophotometer equipped with sodium chloride optics. Resin viscosity was determined with a Brookfield Synchro-Lectric viscometer, model LVF. The furfuryl alcohol used in all experiments contained a maximum furfural contaminant of 0.5% determined, as previously described,¹ by vapor phase chromatography.

Preparation of the Furfuryl Alcohol Resin

The furan resins used in this study were prepared as described previously.¹ The polymerization was catalyzed with benzenesulfonic acid to yield an initial liquid polymer of 9360 cpoise viscosity. The crude resin was thoroughly extracted with 10% sodium hydroxide solution. The benzene-soluble portion of the base-insoluble resin was isolated by evaporation of the solvent at reduced pressure. The excess furfuryl alcohol was removed by vacuum fractionation. The resulting resin was then used as a benzene-methanol solution in preparing thin films for infrared examination.

Oxidative Curing Studies

Benzenesulfonic acid (1.0 g.) was dissolved in a mixture of 80 g. of benzene and 20 g. of methanol. To 2.0 g. of purified furfuryl alcohol resin, 2.0 g. of the catalyst-solvent mixture was added and thoroughly mixed. Aliquot portions of the resin-solvent mixture were applied to the surface of polished sodium chloride discs. The solvents were allowed to evaporate at room temperature, leaving a thin film of resin on the plates. The resin films were evaporated further *in vacuo* at room temperature to remove all possible solvent impurities. The infrared spectrum was determined and the samples were cured and aged in air. The curing cycle was carried

out on 5 individual samples at temperatures and times as follows: Sample I, 1 hr. at 100°C.; Sample II, 1 hr. at 100°C. followed by 1 hr. at 200°C.; Sample III, 1 hr. at 100°C., 2 hrs. at 150°C., and 1 hr. at 100°C.; Sample IV, 1 hr. at 100°C., 2 hrs. at 150°C. followed by 2 hrs. at 200°C.; Sample V, cured at 200°C. for 5 hrs. Each film was examined spectrally after each hour of curing and each spectrum compared with the starting resin spectrum. Sample IV was further aged at 200°C. for 40 hrs.

Oxidative Degradation Studies

By the procedure described above for film preparation, 5 samples of resin film were prepared and the solvents removed *in vacuo*. The samples were cured in nitrogen for 1 hr. at 100°C. The oven temperature was increased to 150°C. for 2 hrs. and the temperature again increased to 200°C. for 2 hrs. more. The samples were slowly cooled in the nitrogen atmosphere. An infrared examination was undertaken at 200°C. for 40 hrs. The spectrum was determined intermittently by removing the film from the oven and desiccating the sample until cool. The spectrum was determined and the sample returned to the aging oven.⁴

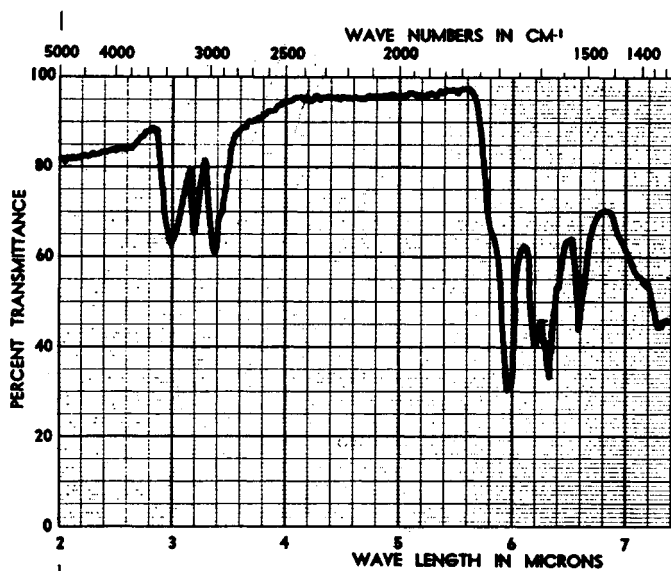
RESULTS AND DISCUSSION

As observed previously,¹ the samples cured in nitrogen showed a general decrease in the hydroxyl content of the polymer, as evidenced by the decreased intensity of the hydroxyl stretching vibration at 2.94 μ . The infrared spectrum of all polymers below 7 μ had a strong similarity with the spectrum of furfuryl alcohol, exhibiting characteristic bands at 3.21, 3.45, 5.86, 6.21, 6.45, and 6.70 μ in addition to the 2.94 μ hydroxyl stretching vibration. On curing the spectrum exhibited changes in the carbon-hydrogen portion of the resin. The band at 3.21 μ , indicative of the carbon-hydrogen stretching vibration of furan ring hydrogens, decreased slightly along with a decreased intensity of the 13.6 μ band and an increased intensity of the 12.6 μ band. These changes on curing could be attributed to the formation of 2,5-disubstituted furan ring moieties.

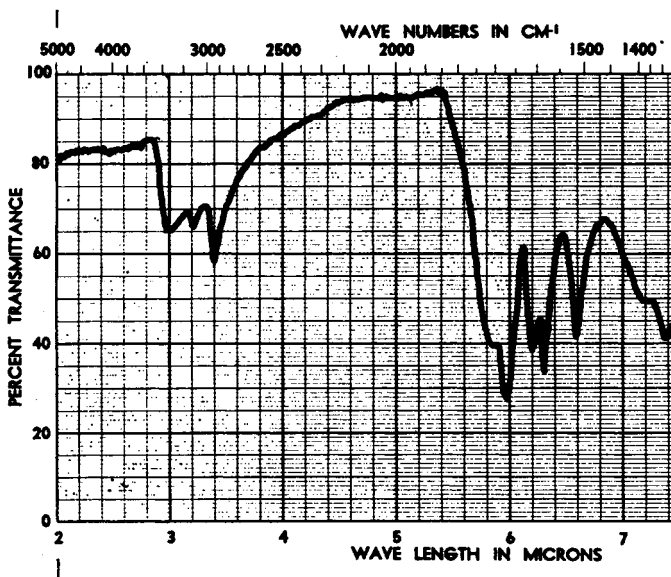
Oxidative Curing

Since the nonoxidative curing is consistent with extended polymerization, it was of interest to follow resin curing in air. If it is assumed that any oxidation which occurs is a surface phenomenon, then the oxidation reactions will be superimposed spectrally upon the normal curing reactions taking place in the bulk of the resin. Spectral monitoring of the resin after various time intervals (see under Experimental) at elevated temperatures, 100–200°C., indicated that the new bands were appearing in the spectrum of the resin and surprisingly little, if any, material was being lost from the bulk of the resin sample. The 3.21 and 3.45 μ bands for the aromatic and aliphatic carbon-hydrogen stretching vibrations, respectively, were observed to change owing to a broad complex band

growing in throughout the 3.0 to 4.0 μ region. Bands of this type are typical for the carboxylic acid group. In addition, a carbonyl band at 5.85 μ , superimposed upon the 5.86 carbonyl vibration, also appeared to



(a)

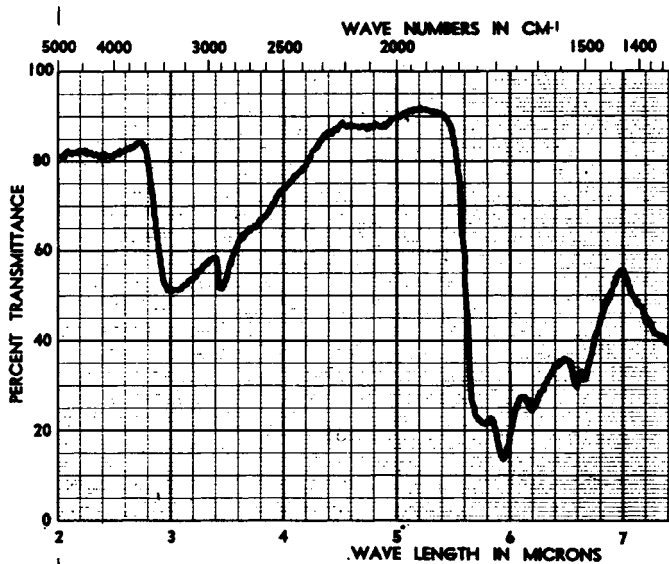


(b)

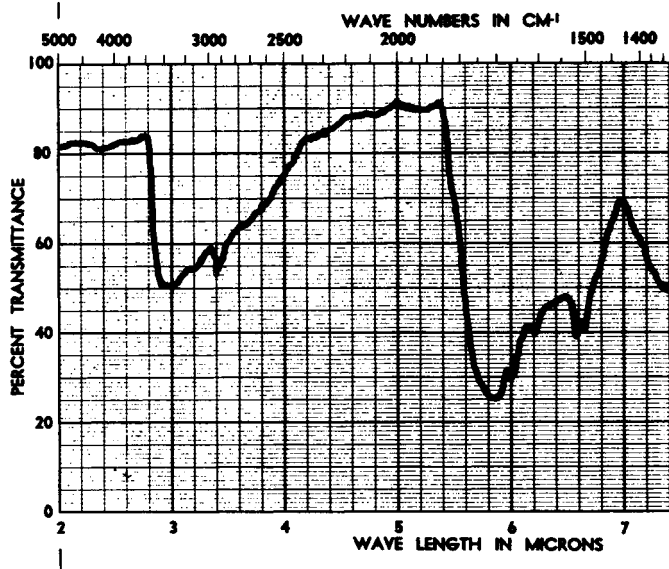
Fig. 1. (a) Oxidation of a nitrogen-cured typical furfuryl alcohol resin: spectrum after 3 hrs. of air oxidation at 200°C. (b) Oxidative curing of typical furfuryl alcohol resin: spectrum of 3 hrs. of air oxidation at 200°C.

be growing in along with the acid hydroxyl. A second carbonyl vibration also appeared at 5.96μ and its ingrowth was parallel to ingrowth observed in the 6.21μ band.

These changes are consistent with the formation of both acid fragments



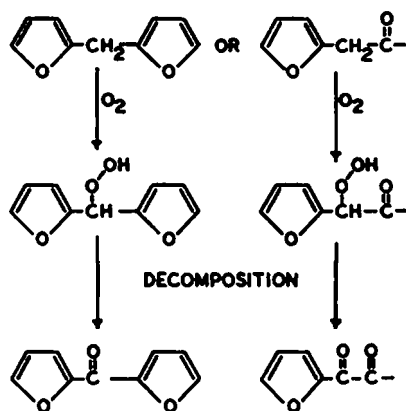
(a)



(b)

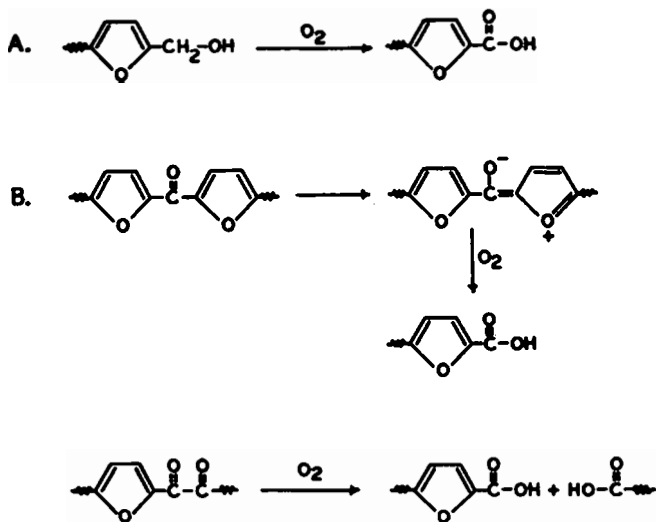
Fig. 2. (a) Nitrogen-cured resin sample after 17 hrs. of air oxidation at 200°C .
(b) Oxidative curing of resin sample after 17 hrs. of air oxidation at 200°C .

and α,β -unsaturated ketone formation. The formation of unsaturated ketonic species is in agreement with the expected oxidation of methylene linkages activated by two adjacent furan nuclei. This reaction may be visualized as shown in (II).



(II)

The formation of acidic species curing in air, however, could arise from either of two reactions: (1) methylol groups that have not yet undergone further condensation with a neighboring furan nucleus might be expected to oxidize to carboxyl groups, a reaction process which would be expected to give substituted furoic acids, or (2) the bifuryl ketone linkages produced by methylene oxidation might be oxidatively cleaved to produce, as one of the chain scission products, substituted furoic acids. These reactions are exemplified in (III).

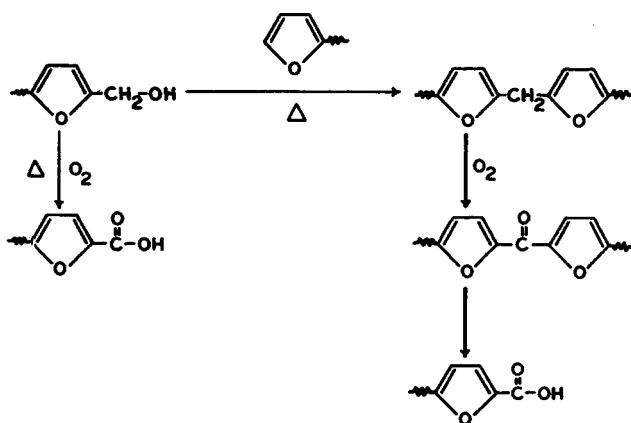


(III)

Since both of these reactions would be expected to give the same product, at least in part, and since the resin had appreciable species present which might have served as the necessary starting materials for such processes, attention was turned to the examination of the nonoxidatively cured resin in an effort to obtain data which would clarify the oxidative curing chemistry of the furfuryl polycondensate.

Oxidative Degradation

A series of samples were cured in a nitrogen atmosphere to prevent oxidation at methylol positions. After curing for 5 hrs. with stepwise increases in temperature from 100 to 200°C. (Sample IV, see Experimental), the cured resins were oxidized at 200°C. in air, and after each successive hour of exposure the infrared spectrum was examined. It was immediately discerned from these data that the initial oxidation was proceeding via a different route from that of oxidative curing. A typical spectral comparison is shown in Figure 1. For convenience, only the 2-7 μ region is shown, for 3 hrs. of oxidative curing in air versus 3 hrs. of oxidative degradation of a nitrogen-cured resin sample in air at 200°C. The initial oxidation of the cured resin sample shows a slight amount of acid formation but the most uniquely different observation lies in the comparison of the 5.96 and 6.21 μ band ingrowth, indicative of the formation of bifuryl ketonic species. When the oxidation is continued for 17 hrs. at 200°C. the spectral changes become almost identical in that the presence of acid fragments is discernible in each sample regardless of whether or not it has been precured in nitrogen, as shown in Figure 2. These data, therefore, lead one to the conclusion that the oxidative degradation of cured furfuryl alcohol polymers proceeds in a fashion closely allied to that reported for phenolic resin oxidation.^{2,3} The initial oxidative reaction is the formation of substituted bifuryl ketonic species followed by a secondary oxidation step involving chain scission producing substituted furoic acids.



In contrast, the oxidative chemistry of air curing in furfuryl alcohol polycondensates proceeds via a series of competitive reactions. The behavior of the methylol groups on oxidative curing can be summarized as shown in (IV).

This mechanism is consistent with earlier observations by Hachihama and Shono,⁵ who investigated the degradation of cured furfuryl alcohol resins under rather strenuous conditions. The degradation of the resin with hydrogen peroxide and alkali was reported to yield acetic acid, furoic acid, and dehydromucic acid. If one extends the mechanism proposed in this study, the products of these drastic degradation conditions can be correlated with the observed products of oxidative curing and degradation in air.

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Synopsis

The oxidative curing and oxidative degradation of cured furfuryl alcohol polycondensates was examined, with infrared spectroscopy, by following the functional group changes occurring in the solid phase of the resin. It has been found that the oxidative degradation of nitrogen-cured resins initially proceeds through the oxidation of methylene linkages to bifuryl ketonic species activated by adjacent furan rings. The second stage of oxidation is the scission of the bifuryl ketonic chain positions to produce substituted furoic acids. The process is postulated to proceed in a manner analogous to that observed in phenolic resin systems. The curing of furfuryl alcohol resin in air is shown to be a multistep process in which the initial oxidation of methylol groups to carboxylic acids is competitive with further polymerization through methylol condensation at adjacent furan ring alpha hydrogen positions. In addition, the oxidation of already formed methylene linkages to the bifuryl ketones is a competitive process removing methylene linkages after they are produced during further condensation (curing reactions). These routes of degradation are in good agreement with observed oxidations of furfuryl alcohol resins under more drastic conditions and offer a reasonable mechanism for resin degradation consistent with observations in analogous polymer systems.

Résumé

On a étudié l'oxydation et la dégradation oxydante de polycondensats de l'alcool furfurylique en suivant par spectroscopie infra-rouge le changement des groupes fonctionnels dans la phase solide de la résine. On a trouvé que la dégradation oxydante des résines traitées sous azote résulte de l'oxydation initiale des groupes méthylènes en donnant des composés cétoniques bifuryliques par suite de l'activation due aux cycles du furanne voisins. La seconde étape de l'oxydation est la scission aux endroits de la chaîne bifuryl-cétonique, avec production d'acides furoïques. On postule que le processus se passe d'une façon analogue à celle observée dans le cas des résines phénoliques. On démontre que le traitement de l'alcool furfurylique à l'air est un processus à plusieurs étapes dans lequel l'oxydation initiale des groupes méthylols en acides carboxyliques, est en compétition avec la polymérisation ultérieure par la condensation des

groupes méthylols avec les hydrogènes en alpha du cycle furannique voisin. En outre, l'oxydation des liaisons méthylènes déjà formées en cétones bifuryliques est un processus compétitif éliminant les liaisons méthylènes, après qu'elles aient été produites pendant la condensation ultérieure (réaction de traitement). Ces voies de dégradation sont en bon accord avec les oxydations observées sur les résines de l'alcool furfurylique, dans des conditions plus drastiques et fournit un mécanisme raisonnable de la dégradation de résines, comparable avec les observations effectuées sur des systèmes analogues de polymères.

Zusammenfassung

Die oxydative Härtung und der oxydative Abbau von gehärteten Furfurylalkohol-Polykondensaten wurde durch infrarotspektroskopische Verfolgung der in der festen Harzphase auftretenden Änderung der funktionellen Gruppen untersucht. Es wurde festgestellt, dass der oxydative Abbau von unter Stickstoff gehärteten Harzen anfänglich in einer durch die benachbarten Furanringe aktivierten Oxydation von Methylenbrücken zu Bifurylketonverbindungen besteht. Das zweite Oxydationsstadium ist die Spaltung der Bifurylketongruppierung in der Kette unter Bildung substituierter Furancarbonsäuren. Es wird angenommen, dass der Vorgang in ähnlicher Weise wie in Phenolharzen verläuft. Die Härtung von Furfurylalkoholharzen unter Luft ist ein vielstufiger Prozess, bei welchem die anfängliche Oxydation von Methylolgruppen zu Carbonsäuren kompetitiv zur weiteren Polymerisation durch Methylolkondensation am α -Wasserstoff eines benachbarten Furanrings verläuft. Zusätzlich bildet die Oxydation schon gebildeter Methylenbrücken zu Bifurylketonen einen kompetitiven Prozess, der Methylenbrücken nach ihrer Bildung durch weitere Kondensation (Härtungsreaktionen) wieder entfernt. Diese Abbauege stehen in guter Übereinstimmung mit der unter drastischeren Bedingungen beobachteten Oxydation von Furfurylharzen und bilden einen brauchbaren, mit Beobachtungen in analogen Polymersystemen verträglichen Mechanismus für den Harzabbau.

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