

Oxidative Degradation of Phenol-Formaldehyde Polycondensation Initial Degradation Reactions

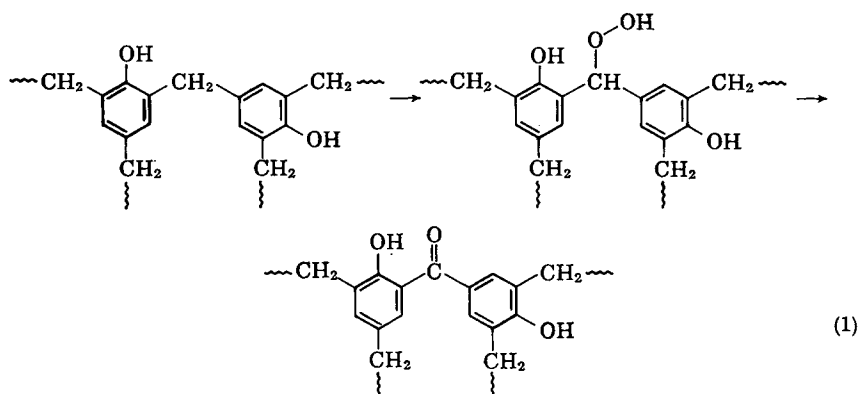
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Synopsis

The initial degradation of phenol-formaldehyde polycondensates has been found to follow two distinct pathways. Oxidation of the dihydroxydiphenylmethane unit to substituted dihydroxybenzophenone and dihydroxybenzhydrol species has been observed and substantiated using model compounds to support the characteristic infrared spectral changes. The ingrowth of ketonic species has been evaluated kinetically on phenol-formaldehyde polymers which have been cured fully to remove residual methylol groups. The rate constants have been found to be a factor of 33 times slower than those observed earlier for partially cured resins having relatively large numbers of residual methylol groups present. The activation energy for the initial ketonic carbonyl was found to be 15.6 ± 3.9 kcal. This value compares favorably with other values obtained for phenolic oxidation. The potential oxidation of methylol groups to substituted salicylic acid moieties could not be substantiated spectrally. However, a polymer containing 2-methylol-*p*-cresol on oxidation gave a small quantity of 5-methylsalicylic acid, thus substantiating methylol oxidation in competition with the further curing reaction which produces new diphenylmethane linkages. The secondary oxidation resulting in chain scission can be separated on a time scale from oxidations of the methylol type. The present study therefore significantly extends the initial oxidative degradation chemistry of phenol-formaldehyde polycondensates.

INTRODUCTION

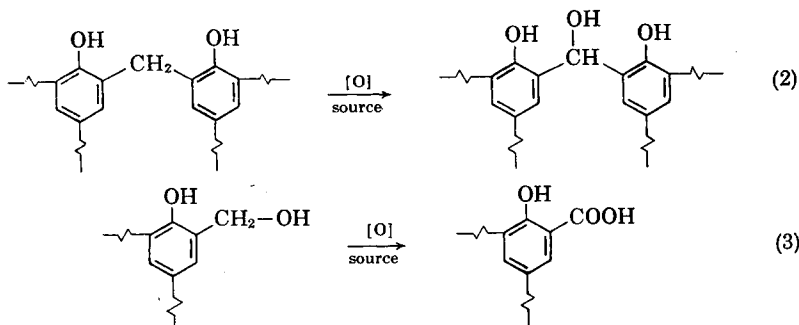
In several previous articles,¹⁻³ the oxidative degradation of phenol-formaldehyde polycondensates was reported over the temperature range 140-1000°C. From the lower temperature studies,^{1,2} the course of degradation was found to be primarily oxidation at the bridging methylene linkages. This proposal was substantiated by synthesis of polymers containing the resulting carbonyl moiety, delineation of the rate of oxidation as a function of surface methylene species, and by analysis of the infrared spectral changes observed during the oxidation process. More recent work⁴ on a nonhydroxylated model and the phenolic resin system, itself,³ indicated that several additional reactions may be occurring simultaneously with the observed methylene oxidation. This initial oxidation route for the formation of dihydroxybenzophenone species is shown in eq. (1).



In working with a nonhydroxylated model polymer, polybenzyl, the decomposition of the initially formed hydroperoxide was observed to follow two distinct reaction routes.⁴ The typical oxidation of the methylene linkages to ketonic species, observed in a number of activated methylene polymers, including furfuryl alcohol polycondensates,⁵ urea-formaldehyde resins,⁶ and melamine resins,⁶ as well as the phenolic polymer systems, was found to be the predominant process. However, a second reaction was also observed in which hydroxylated species (in polybenzyl these would be substituted benzhydrols) were formed at the initial stages of oxidative degradation. This latter reaction was of interest, since it may also occur during oxidation of other activated methylene polymer systems.

Further a third process, unrelated to the oxidation of the methylene bridges, must also be considered as a definite possibility during the initial oxidation,⁵ namely, the oxidation of residual methylol groups to acidic species rather than their further condensation to new methylene bridges. Initial investigation^{1,2} indicated that although such a reaction route is possible, it must be of minor consequence in the phenolic resin system after curing at 120°C. This conclusion was based upon the fact that the appearance of acidic species in the spectrum of oxidized phenol-formaldehyde resins occurred only after extended periods of time and at the expense of the carbonyl group attributed to benzophenone-type linkages; it was, therefore, a secondary reaction.

However, the relative insensitivity of the spectrophotometric method to minor reactions in this system, led us to study these specific processes in greater detail. This report, therefore, details the results obtained in an attempted examination of (a) hydroperoxide decomposition to dihydroxybenzhydrol species as well as benzophenone linkages [eq. (2)] and (b) methylol oxidation to acidic components; namely, substituted salicylic acids and related hydroxybenzoic acids [eq. (3)].



EXPERIMENTAL

Hydroperoxide Decomposition Studies

The base-catalyzed resin utilized in this study was prepared as previously described.² The resin was prepared such that the phenol-formaldehyde ratio was 0.77. For comparison of the degree of curing of the sample, one film was cured in nitrogen at 120°C. for 3 hr. in the curing oven system reported earlier;⁷ the remaining samples were cured in high vacuum at 400°C. for 1 hr.³ The actual curing time was approximately 3 hr., since the temperature was slowly increased to 400°C. As reported earlier,³ this extreme curing procedure, although difficult to control, resulted in a nonoxidized, completely cured resin system. In Figure 1, spectrum 1 indicates the 3 hr., 120°C. nitrogen-cured polymer; spectrum 2 was obtained from one of the samples subjected to the extreme curing procedure.

The oxidative degradation studies were carried out on the nonoxidized, fully cured resin films on sodium chloride plates. The infrared spectrum was monitored continuously at the reaction temperature over the 2-15 μ region. This series of data was used for interpretative purposes. Kinetic data were obtained for carbonyl band ingrowth at 1650 cm^{-1} by using the

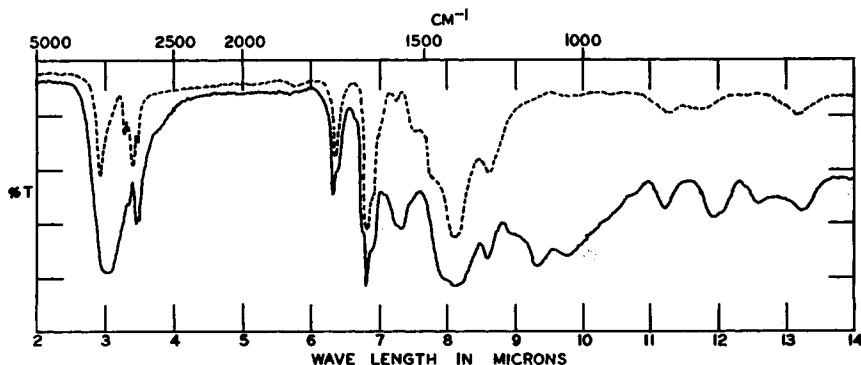


Fig. 1. Spectra of (—) resin cured for 3 hr. at 120°C. in nitrogen (spectrum 1); (---) resin cured for 1 hr. at 400°C. *in vacuo*. Baselines are staggered for clarity.

same procedure, only changes between 5.6 and 6.4 μ being recorded, however. The data were analyzed in a manner identical to that reported for the kinetic study of phenol-formaldehyde polycondensates cured at 120°C.² The temperatures at which the data were collected were 180, 200, and 220°C.

Methylol Oxidation Studies

The resin was prepared as described previously for hydroperoxide decomposition studies (P/F ratio 0.77). The samples were filmed from acetone or propylene oxide solution and cured in a nitrogen atmosphere at 150°C. Samples were cured at intervals of 3, 6, 12, and 24 hr. The hydroxyl group band at 3.0 μ due to both hydrogen-bonded, methylol, and phenolic hydroxyl group vibrations and the 9.5 μ band due to the C-O vibration was used to relate the change in methylol content with curing time. Figure 2 summarizes the changes observed on curing samples for extended time intervals in the 2.5–4.0 μ region and in the 8–10 μ region. These samples were then oxidized in air at 170°C. for 90 min. The spectrum was recorded at 20 min. intervals at the reaction temperature as previously described.²

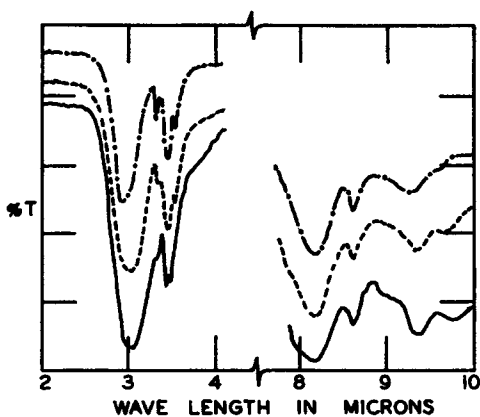


Fig. 2. Effect of nitrogen curing on the spectral characteristics of the methylol group: (—) 3 hr. at 120°C.; (---) 12 hr. at 120°C.; (-·-) 24 hr. at 120°C. Baselines are staggered for clarity.

Model Compound Studies

Nonoxidized, fully cured phenol-formaldehyde polycondensate was mechanically ground, and a potassium bromide pellet of 0.1% polymer in potassium bromide was prepared for a reference spectrum. For comparison with the reference spectrum a sample was oxidized at 170°C. for 120 min., and a pellet of similar concentration was prepared.

Samples of nonoxidized, fully cured polymer admixed with 10% benzhydrol or 10% *p,p'*-dihydroxybenzophenone-10% benzhydrol were pre-

pared for comparison with both oxidized and nonoxidized polymer spectrum obtained from potassium bromide pellets.

For methylol oxidation studies, 10.0 g. of 2-methylol-*p*-cresol was added to 50.0 g. of liquid phenolic resin (P/F ratio, 0.77). The resin was cured at 120°C. for 3 hr. in nitrogen as a thin film on sodium chloride for spectral comparison. For chemical analysis, a second portion was cured on aluminum foil in a similar manner. Both samples were oxidized at 170°C. for 1 hr. The spectral changes were monitored continuously over the 60-min. period. The material on the aluminum foil was oxidized at 170°C. for the same period of time, removed from the foil, and thoroughly ground to a fine powder. The powdered resin sample was thoroughly extracted in a Soxhlet apparatus for 2 days with boiling chloroform as a solvent. The extracted material was isolated by evaporation of the solvent. The crude product, 0.42 g., was recrystallized twice from hot water. The infrared spectrum of the purified material was identical to that obtained from 5-methylsalicylic acid. The purified compound melted at 150–151°C. and when admixed with an authentic sample, no depression in melting point was observed, m.p. 150–151°C.

RESULTS AND DISCUSSION

Hydroperoxide Decomposition Studies

The phenol-formaldehyde polycondensate cured at 400°C. was, indeed, a unique material. As can be seen from Figure 1, the methylol content has been reduced to the level where spectrophotometric observation is impossible. The phenolic and methylol hydroxyl vibration at 3.0 μ has been significantly reduced in intensity. In addition, it can be seen that the aliphatic methylene vibration can readily be distinguished, whereas, in the 120°C. cured sample, this vibration is only a shoulder on the intense hydrogen bonded hydroxyl vibration. Figure 3 indicates the

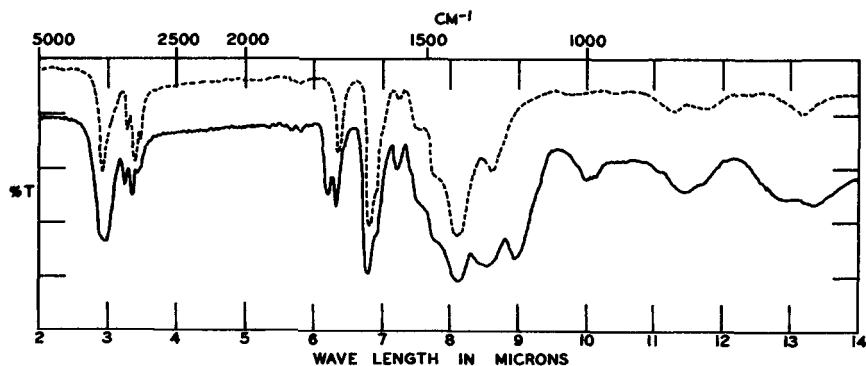


Fig. 3. Effect of air oxidation on the spectrum of fully cured, phenol-formaldehyde polycondensates: (--) nonoxidized, fully cured polymer; (—) after oxidation at 180°C. in air for 2 hr. Baselines are staggered for clarity.

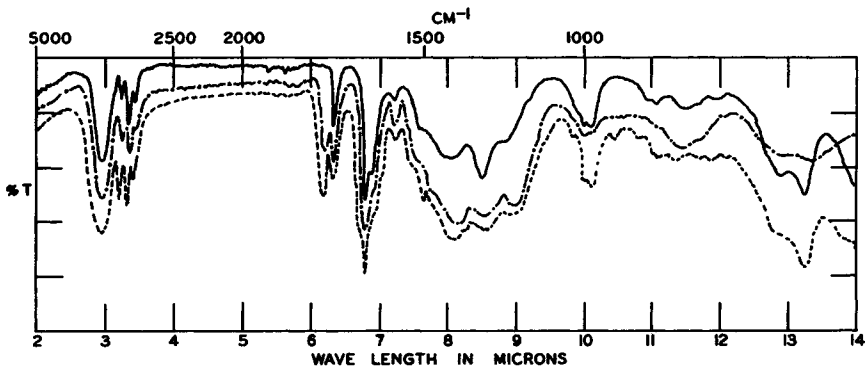


Fig. 4. Comparison spectra of: (---) oxidized, fully cured polymer; (—) nonoxidized, fully cured polymer admixed with benzhydrol; (-·-) nonoxidized, fully cured polymer admixed with *p,p'*-dihydroxybenzophenone and benzhydrol. Baselines are staggered for clarity.

changes in the infrared spectrum when the fully cured polymer was oxidized at 180°C. Most notable among the band changes is the increase in the 3.0 μ hydroxyl vibration together with the competitive ingrowth of the carbonyl group at 6.05 μ already established as ketonic carbonyl ingrowth. These data are strongly suggestive of the observations made on the polybenzyl model compound⁴ as reported earlier. In order to confirm the hydroxyl group formation during the initial stages of degradation, oxidized polymer was removed from the sodium chloride disc and thoroughly pulverized. From this material, a potassium bromide wafer was prepared. Its spectrum was contrasted with the spectra obtained from nonoxidized polymer admixed with benzhydrol and from a second sample containing benzhydrol together with *p,p'*-dihydroxybenzophenone. These spectra are shown in Figure 4. From these data there is doubt that the decomposition of the hydroperoxide precursor in phenol-formaldehyde polycondensates follows a twofold pathway, forming both benzophenone linkages and benzhydrol species. The oxidized, fully cured phenolic polymer sample spectrum and the nonoxidized sample admixed with *p,p'*-dihydroxybenzophenone and benzhydrol spectrum are strikingly similar throughout the functional group region of the spectrum.

For comparison with the phenolic resin cured at 120°C. in nitrogen, a kinetic evaluation was undertaken using the techniques reported earlier.² Table I summarizes the rate constants obtained from the two phenolic resins of widely different methylol concentrations and polybenzyl over the same temperature range.

The activation energies of the reactions in each case are remarkably similar for the methylene oxidation process as determined from carbonyl ingrowth. The partially cured phenolic resin although possessing reaction rates approximately 33 times faster than either the fully cured phenolic or polybenzyl gave an activation energy of 19.5 kcal. by graphic analysis of the plot of $-\log k$ versus the reciprocal of the absolute tem-

perature. Polybenzyl and the fully cured phenolic activation energy values were determined computationally. The data for polybenzyl were analyzed by a linear regression analysis whereas those for the fully cured phenolic were calculated by the least squares method. The difference in choice of methods rested simply in the fact that data was only obtained over a narrow temperature range in the present study. All calculations were carried out with standard programs on an IBM 1620 computer. For polybenzyl the

TABLE I
Comparison of Rate Constants Determined for the Ingrowth of Ketonic Carbonyl in Methylol-Containing Phenolic Resin, Fully Cured Phenolic Resin, and Polybenzyl

Temp., °C.	Rate constant $k \times 10^{-2}$, min. ⁻¹		
	Phenolic resin, 120°C., N ₂ cured	Phenolic resin, 400°C., vacuum cured	Polybenzyl
180	6.88	0.22	0.21
	7.67	0.28	0.27
200	17.5	0.61	0.66
	17.8	0.56	0.52
220	37.6	1.12	1.16
		1.44	1.36

calculated activation energy was found to be 14.5 ± 3.5 kcal., and the fully cured phenol-formaldehyde system gave an activation energy of 15.6 ± 3.9 kcal.

Methylol Oxidation Studies

The resin samples cured at various time intervals were oxidized in the heated infrared cell at 170°C. The infrared spectrum was monitored as rapidly as possible from 2 to 7 μ (approximately every 7 min.). In none of the samples was the ingrowth of acidic moieties apparent in the spectra regardless of the degree of cure. These data indicate that if the methylol groups are competitively oxidized, the concentration of acidic components are of sufficiently low level that the spectral determination is not significantly sensitive enough to indicate their presence. In order to gain some further information, two techniques were attempted. The first method was to compare the spectrum of a nonoxidized cured sample with an oxidized, cured sample spectrum of similar thermal exposure. To effect this, a sample was cured for 4 hr. in inert atmosphere, (3 hr. at 150°C., 1 hr. at 170°C.) and compared differentially with a sample cured for 3 hr. in inert atmosphere followed by 1 hr. of oxidation at 170°C. The oxidized sample was placed in the sample beam of the spectrophotometer, the non-oxidized sample in the reference beam. The difference in the spectrum, so produced, generally reflects the differences between the two samples. Small, but definite differences were observed in the hydrogen-bonded,

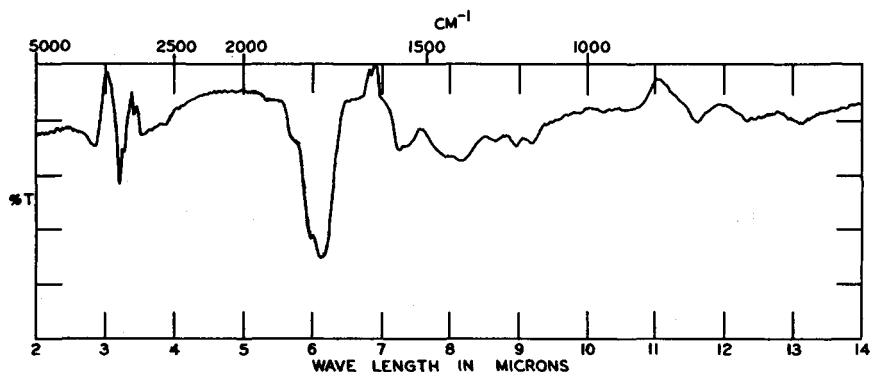


Fig. 5. Difference spectrum obtained from oxidized resin (oxidation 1 hr. at 170°C.) (120°C., nitrogen cured) vs. nonoxidized material.

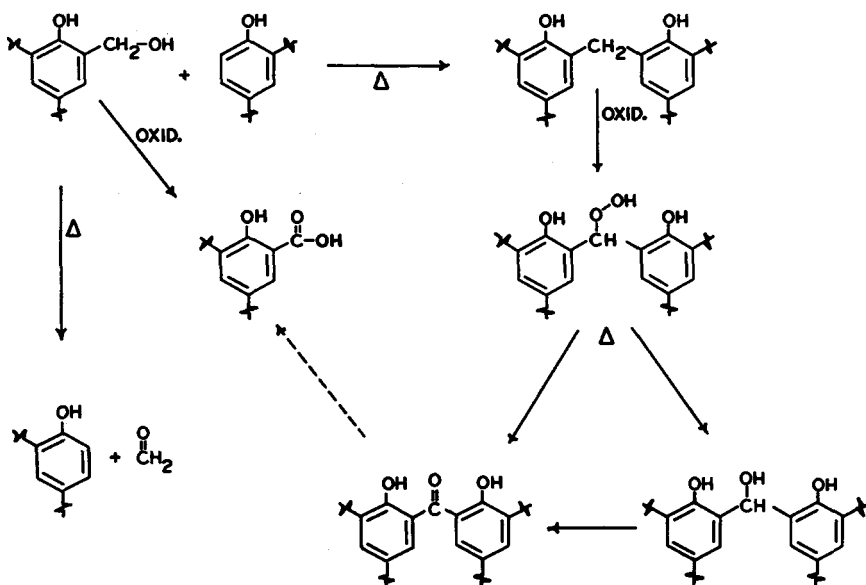


Fig. 6. Summary of initial degradation reactions and competitive curing reactions for phenol-formaldehyde polycondensates.

acid type hydroxyl region (3–4 μ) and the carbonyl region (5.5–6.5 μ) as shown in Figure 5.

The spectral evidence is far from satisfactory. Therefore, an effort was made to strengthen the spectral argument with a definite chemical isolation technique. The resin (50 g.) prepared from purified phenol and formaldehyde solution (P/F ratio 0.77) was contaminated with 10 g. of 2-methylol-*p*-cresol. The resin was cured in the usual fashion but both on sodium chloride and a large sample on aluminum foil. The sample on sodium chloride was examined spectrally at 170°C. for 1 hr. The coated

foil sample was oxidized at the same temperature in an oven. No spectral evidence was obtained for the initial oxidation of methylol groups to acidic fragments. However, the foil sample was worked up chemically for soluble acidic components as described in the experimental section. From the extractable substances a small amount (less than 1%) of crude 5-methylsalicylic acid was obtained. The isolation of a methylsalicylic acid from the oxidized resin system clearly supports the postulation of methylol oxidation to salicylic acid moieties as an initial degradation process in competition with the further curing process of the methylol linkage to diphenylmethane bridges.

From the two-part study reported here it is apparent that the initial changes of phenol-formaldehyde polycondensates on exposure to air can best be summarized as shown in Figure 6. Both secondary oxidations² and methylol oxidation give rise to salicylic acid species, however, at markedly different time intervals during the oxidation. Early acid formation, although undetected spectrally, takes place in competition with the further curing process. Observable acid formation only occurring from the rupture of the polymer after significant ketonic species have been formed. Hydroperoxide formation, although the primary step, leads to two species, hydroxylated benzophenones and benzhydrols at the initial phases of the degradation.

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Résumé

On a trouvé que la dégradation initiale des résines de condensation phénol-formaldéhyde s'effectuait de deux façons. On a observé l'oxydation de l'unité dihydroxydiphénylméthane en dihydroxybenzophénone substitué et en dihydroxybenzhydrol, ce qui est confirmé en employant des composés modèles pour évaluer les changements caractéristiques dans le spectre infra-rouge. La formation de cétone a été évaluée d'une façon cinétique sur des polymères phénol-formaldéhyde traités à fond en vue d'enlever les fonctions méthylol résiduelles. On a trouvé que les constantes de vitesse étaient 33 fois plus petites que celles observées antérieurement pour des résines partiellement traitées et contenant encore un grand nombre de fonctions méthylols résiduelles. L'énergie d'activation pour le carbonyle cétonique initial était de $15,6 \pm 3,9$ Kcal. On peut comparer cette valeur avec d'autres obtenues pour l'oxydation des phénols. On n'a pas pu prouver par spectroscopie l'oxydation possible des fonctions méthylols en acide salicylique substitué. Cependant, un polymère contenant du 2-méthylol-*p*-crésol donne, après oxydation, un peu d'acide 5-méthyle salicylique, prouvant ainsi que l'oxydation des méthylols est en compétition avec la réaction ultérieure qui produit des liaisons diphenylméthanes nouvelles. L'oxydation secondaire, provoquant une rupture de chaîne, peut être séparée dans le temps des oxydations du type méthylol. Cette étude

élargit cependant la chimie de la dégradation oxydante initiale des polycondensats phénol—formaldéhyde.

Zusammenfassung

Das Anfangsstadium des Abbaues von Phenolformaldehydpolykondensaten kann auf zwei verschiedenen Wegen vor sich gehen. Oxydation der Dihydroxydiphenylmethaneinheit zu substituiertem Dihydroxybenzophenon- und Dihydroxybenzhydrogruppen wurde beobachtet und durch Verwendung von Modellverbindungen zur Bestätigung der charakteristischen Veränderungen im Infrarotspektrum erhärtet. Die Bildung von Ketongruppen wurde an Phenolformaldehydpolymeren, welche zur Entfernung der restlichen Methylolgruppen voll ausgehärtet worden waren, kinetisch verfolgt. Die Geschwindigkeitskonstante erwies sich als um einen Faktor von 33 langsamer als die früher an partiell gehärteten Harzen mit einer relativ grossen Zahl noch vorhandener Methylolgruppen beobachtete. Die Aktivierungsenergie für die Bildung des ketonischen Carbonyls wurde zu $15,6 \pm 3,9$ kcal bestimmt. Dieser Wert ist durchaus mit anderen bei der phenolischen Oxydation erhaltenen Werten vergleichbar. Die potentielle Oxydation von Methylolgruppen zu substituierten Salyzilsäureeinheiten konnte spektroskopisch nicht nachgewiesen werden. Ein Polymeres, das 2-Methylol-*p*-cresol enthielt, lieferte jedoch bei der Oxydation eine kleine Menge von 5-Methylsalyzilsäure, was zeigt, dass Methyloloxydation kompetitiv mit der weiteren Härtingsreaktion auftritt, die neue Diphenylmethanbrücken bildet. Die zur Kettenspaltung führende Sekundäroxydation kann auf der Zeitskala von den Oxydationen des Methyloltyps getrennt werden. Die vorliegende Studie führt somit zu einer wichtigen Erweiterung der Chemie des Anfangsstadiums der oxydativen Abbaues von Phenolformaldehydpolykondensaten.

Received May 11, 1964