Oxidative Degradation of Polybenzyl*

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Synopsis

The primary steps involved in the degradation of polybenzyl at temperatures between
140 and 220°C. in the presence of air or pure oxygen has been found to be an attack at the
methylene linkages to give benzhydrol and benzophenone linkages.   Kinetic evaluation
of the rate of benzophenone-type carbonyl ingrowth indicated an apparent initial activa-
tion energy for the oxidation process of 14.5 ± 3.5 kcal.   Vapor-phase chromato-
graphic analysis of the volatile products of the reaction indicate that the formation of
benzoic acid and benzophenone are the major products of oxidation, along with smaller
amounts of benzene, toluene, water, and carbon dioxide.   It must be concluded that the
initial oxidation of polybenzyl closely parallels the oxidation of phenolic resins and other
closely related activated methylene polymers.   Secondary degradation reactions which
produce chain scission are generally equitable to further oxidation at both the benzhydrol
and benzophenone linkages.   The appearance and spectral substantiation of the forma-
tion of benzoic anhydride linkages from thermal dehydration of benzoic acid most ade-
quately accounts for the formation of the secondary reaction products giving new but
minor infrared bands in the early and intermediate stages of the degradation.

Introduction

In a series of previous articles,[1-5] the oxidation chemistry of phenol–
formaldehyde and furfuryl alcohol polycondensates was described.   In
both of these systems, it was shown that the primary oxidation step was at
the methylene linkage between the aromatic rings.   This step was found
to best describe the major course of degradation in highly cured samples.
In systems containing residual methylol groups, competitive oxidation of
these groups also was observed.   By using infrared spectrophotometric
techniques coupled with vapor phase chromatographic methods, reasonable
routes for these oxidative degradations could be proposed.   Substantiation
by using model compounds strongly supported the observed infrared spec-
tral changes and volatile product formation.   During the course of these
studies it was shown that the infrared spectrophotometric method could be
adapted to study the kinetic details of the primary oxidation process in the
phenol–formaldehyde system, namely the oxidation of the methylene
bridges to ketonic carbonyl species.   However, due to the complexity of
the resin system, competitive reactions at the early stages of oxidation were
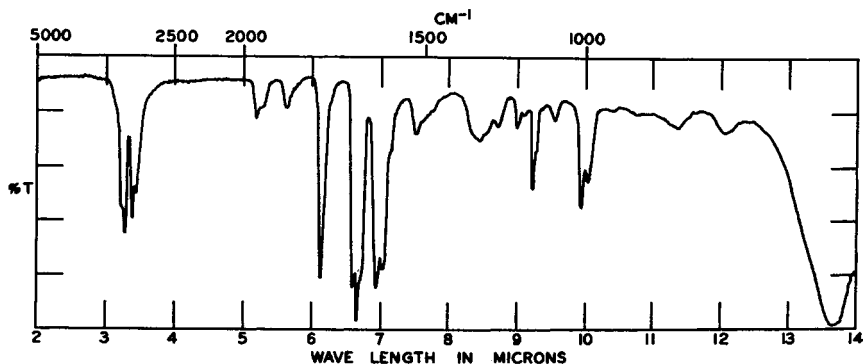not detected or at best only indicated by questionable spectral assignments.

Fig. 1. Spectrum of polybenzyl.

In order to gain further data on competitive reaction processes, a number of model systems were considered. The present report delineates the results obtained from one such model, namely, linear polybenzyl. The data obtained here are also of interest from a correlative viewpoint, since they add additional evidence to the activated methylene oxidation route proposed for phenol–formaldehyde and furfuryl alcohol polycondensates. Since resins of both types are of interest as ablative thermal protection systems in the aerospace industry, the fundamental chemistry of these systems, as well as closely related model compounds, offers on approach to understanding their utility in high temperature applications.

Haas, Livingston, and Saunders[6] have described the synthesis and properties of polybenzyl. For the sake of discussion we shall consider the structural arrangement as a linear aromatic–methylene system. The reason for this assumption is based on the fact that highly branched polybenzyl can be synthesized and the degree of "crosslinking" controlled.[7] It must be noted, however, that the structural arrangement originally proposed[6] was considered to be a few centrally located, highly substituted aromatic rings of which are a number of monosubstituted benzyl groups.[8] For spectral purposes, the structure I represents the pertinent portion of polymer under study and exemplified by the spectrum of a typical film sample shown in Figure 1.

I
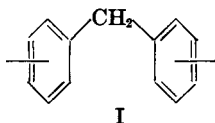
Experimental

The experimental techniques and instrumentation utilized to study the oxidative degradation have been described in detail in previous reports.[1-5,9] For purposes of comparison with previously reported studies in this area by Lady, Kesse, and Adams,[8] as well as to determine some aspects of the
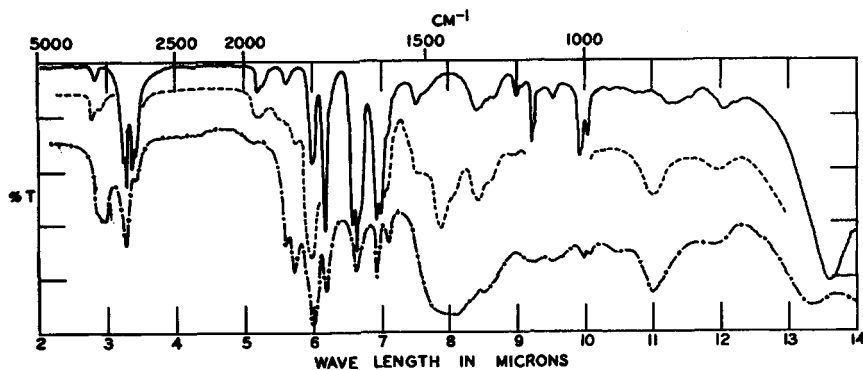
Fig. 2. Oxidation of polybenzyl at 200°C.: (——) initial oxidation, spectrum recorded after 1 hr. of exposure in air; (—) intermediate stages, spectrum recorded after 5 hr. of exposure in air; (— —) final stages, spectrum recorded after 20 hr. of exposure in air.

overall changes in the spectrum with time, a series of samples were examined as thin films deposited on salt plates in a heated cell[9] at temperatures of 140, 150, 170, 180, 200, and 220°C. The general changes in the spectrum of polybenzyl can best be visualized as shown in Figure 2. For correlation and band assignment, the more important spectral changes are summarized at a single temperature (170°C.) in Table I. It should be

TABLE I
Observed Functional Group Changes in Polybenzyl Oxidation at 170°C.[a]

Frequency, cm.$^{-1}$	Assignment	Change	Time of appearance, hr.
3560	—OH (not hydrogen-bonded	Increase	1
		Decrease	2
3400	—OH (hydrogen-bonded)	Increase	2
3050	=CH (aromatic carbon hydrogen stretching	Decrease (slow)	30
2800	—CH$_2$ (aliphatic carbon-hydrogen stretching	Decrease	4
1660	C=O (diaryl ketone)	Increase	1
1730	$\overset{O}{\overset{\|}{-C}}-O-\overset{O}{\overset{\|}{C}}-$ (linear anhydride,		
1780	band pair)	Increase	10
1260	C—O—C (diaryl ketone and linear C—O anhydride, broad band complex)	Increase	1
1450	Aromatic ring	Decrease (slow)	30

[a] Other bands, also indicative of these functional groups, are changing with oxidation but these are not summarized, for convenience (see Fig. 2).

noted that within the temperature region studied (140–220°C.), the overall changes at each temperature were identical and differed only in rate of change.

Oxidation Rate Studies

The polybenzyl film samples were monitored continuously at the desired reaction temperature. The spectrum was recorded continuously between 5.0 and 7.0 μ at approximately 3 min. intervals at the early stages of the degradation. After each 15 min. interval (5 data points) a complete spectrum was obtained between 2 and 16 μ. At the lower temperatures (140–170°C.) and at longer time intervals (after 2 hr.) at the elevated temperatures, spectra were obtained less frequently from the sample. In order to eliminate pre-oxidation, a flow of dry, oxygen-free nitrogen was passed over the polymer film until the desired reaction temperature was attained. A single sample was oxidized in air, a mixture of 30% oxygen–70% nitrogen and pure oxygen at 170°C. Since the reaction rates were found to be identical in the three aging atmospheres, only the data recorded in air appears here. It should be noted that this observation parallels the findings previously reported for phenolic resin systems.[2] The absorbance data was obtained by the baseline method described by Wright.[10] The recorded absorbance values were corrected, however, because a portion of the polymer was lost due to volatilization during the oxidation study. This correction was made by assuming the aromatic ring vibration at 6.8 μ (1450 cm.$^{-1}$) was constant throughout the course of the rate measurement period. Since the data were collected over the very early portion of the degradation, this assumption seems justified. In order further to insure that the observations were only made at the early stages of degradation, benzophenone was used as a limiting standardized sample for comparison with the oxidation mixture. A sample of 10% benzophenone in poly-
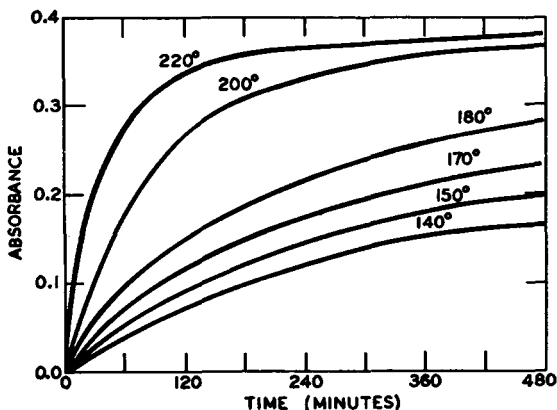

Fig. 3. Typical plots of polybenzyl oxidation expressed as increasing absorbance of the 1660 cm.$^{-1}$ band (6.0 μ) vs. time at temperatures between 140 and 220°C.

benzyl was used as a limiting absorbance value on the 1660 cm.$^{-1}$ carbon–oxygen double bond stretching frequency. In applying these limitations, it was felt the maximum validity could be placed on the recorded spectral data. Rate constants were obtained by using the method described by Gugenheim[11] and in the same manner as described earlier for phenolic resin oxidation.[2] This method is particularly adaptable for oxidation studies of this type, since the reactions are pseudo first-order due to oxygen excess during the primary oxidation reaction period being studied. The absorbance data obtained are plotted graphically in Figure 3, and the rate data are summarized in Table II.

TABLE II

Rate Constants Determined for the Ingrowth of the 1660 cm.$^{-1}$ Carbonyl Stretching Frequency in Polybenzyl at Various Temperatures

Temp., °C.	$1/T \times 10^{-3}$, °K.$^{-1}$	Rate constant k $\times 10^{-2}$, min.$^{-1}$	$-\log k$
140	2.42	0.03	3.523
150	2.36	0.07	3.155
		0.06	3.222
170	2.25	0.16	2.796
180	2.21	0.21	2.678
		0.27	2.569
200	2.12	0.66	2.180
		0.52	2.284
220	2.03	1.16	1.935
		1.36	1.866

Results and Discussion

It was expected that the oxidative degradation of polybenzyl should follow quite consistently with similar observations made during the oxidation of phenol–formaldehyde polycondensates. Indeed, this was found to be the case for the general aspects of the degradation process. Examination of the spectral changes in the 2–15 μ range indicated that the ingrowth of carbonyl groups at 6.0 μ (1660 cm.$^{-1}$), typical of benzophenone type linkages was the major oxidation reaction. This was further substantiated by the appearance of a 7.6 and 7.8 μ doublet, typical of benzophenone linkages as the oxidation progressed. As the carbonyl ingrowth continued a very weak hydroxyl vibration (nonbonded) at 3560 cm.$^{-1}$ appeared. Since this absorption shifts to the hydrogen-bonded, hydroxyl vibration region after a short time (3400 cm.$^{-1}$) and the higher frequency vibration begins to disappear, there is no doubt that this is due to a benzhydrol type linkage. Since the hydroxyl vibration (nonbonded) is a weak absorption, it is not unexpected that it remains undetected at the very early stages of the oxidation. It is interesting to note that similar changes generally cannot be noted in the hydroxyl region of phenol–formaldehyde systems due to overlapping absorption from phenolic hydroxyl groups and residual methylol linkages, thus posing an interesting (but difficult to solve)
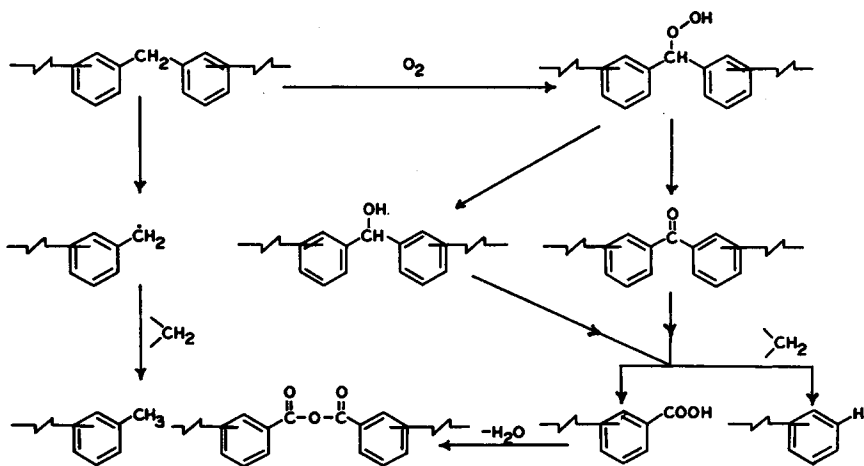
Fig. 4. The primary oxidation route of polybenzyl in which the diphenylmethane unit is converted to benzhydrol and benzophenone linkages and, as well, the chain scission reactions proposed to account for both spectral changes and vapor-phase chromatographic data.

problem regarding the similarities in decomposition of the intermediate hydroperoxide in the two systems. As the initial oxidation phase continues, the hydroxyl band shifts to 3.0 μ (hydrogen-bonded). After extended periods of oxidation the hydroxyl vibration broadens and extends beyond 4.0 μ as a broad diffuse band. This suggests the formation of a small amount of acidic component during the terminal stages of oxidation. It should be pointed out in this regard that the methylene stretching vibration at 3.45 μ (2800 cm.$^{-1}$) is virtually absent at this point in the oxidative degradation. At carbonyl concentration levels of approximately 5%, a doublet appears at 5.64 μ (1730 cm.$^{-1}$) and 5.77 μ (1780 cm.$^{-1}$), respectively. This band has been attributed to ester and/or anhydride by previous investigators.[8] By admixing benzophenone, benzoic anhydride, and polybenzyl, these bands can be assigned with a high degree of certainty to linear anhydride formation. The change in relative intensities of these bands when compared to those of the pure anhydride can be attributed to the effect of the adjacent ketonic carbonyl overlapping the 5.77 μ anhydride band. It should also be noted that the relative rate of band ingrowth of this doublet remains quite constant until acid formation is observed in the 3.0 μ region. At this time the 5.77 μ band broadens and grows at the expense of the 5.64 μ vibration. This is consistent with the formation of acids in the later stage of oxidation from the anhydride linkages. With these observations in mind, the oxidation route may be proposed with some degree of certainty as shown in Figure 4.

In order to support at least a portion of the proposed route, a sample was oxidized at 200°C. in a closed system[12] and the condensable, volatile products collected. The trapped materials represented a small amount (29%) of the total weight loss but were deemed significant, since on vapor-
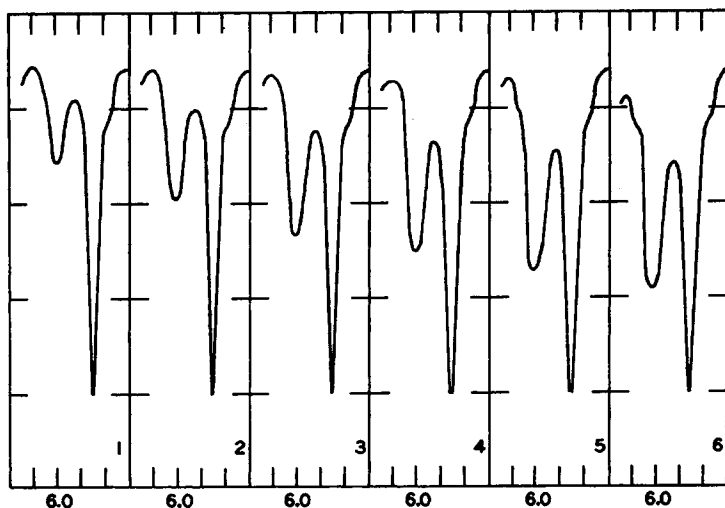
Fig. 5. Representative spectrum between 5.6 and 6.6 μ indicating the ingrowth of the 1660 cm.$^{-1}$ band (6.0 μ) on air oxidation at 180°C.: (*1*) at 30 min. of oxidation; (*2*) after 60 min.; (*3*) after 90 min.; (*4*) after 120 min.; (*5*) after 150 min.; (*6*) after 18 min.

phase chromatographic separation, benzene (12%), toluene (4%), benzoic acid (58%), and benzophenone (26%) could be identified. The formation of the very small amount of toluene (approximately 1% of the total weight loss) indicates that thermal chain rupture processes seem to be of minor consequence in this temperature region. Benzene, benzoic acid, and benzophenone are all consistent with the observed oxidative degradation mechanism (Fig. 4). Water and carbon dioxide were also detected but not determined quantitatively.

For purposes of comparison with the phenol–formaldehyde systems previously reported,[1,2,5] the oxidation rates of polybenzyl were determined by the procedures described in the experimental section. Figure 5 graphically represents a typical set of curves indicating the ingrowth of the 6.0 μ (1660 cm.$^{-1}$) ketonic carbonyl group. From data of this type, the absorbance versus time plots (Fig. 3) were constructed for each temperature and the rate constants derived (Table II).

The oxidative degradation of polybenzyl, if parallel to phenol–formaldehyde polycondensate degradation,[2] was expected to be pseudo first-order with respect to the available, surface methylene groups. Since the rate was found to be invariant when the aging atmosphere was changed from air to pure oxygen, a swamping effect of oxygen, even in air, occurs. Therefore the rate of oxidation was found to be dependent only upon the available methylene groups at the polymer surface.

In Figure 6, $-\log k$ is plotted versus the reciprocal of the absolute temperature to give a straight line whose slope, when multiplied by 2.303R, gives an activation energy of 16.8 kcal. From the values of $-\log k$, the best curve through the data points (Table II) was determined by a step-
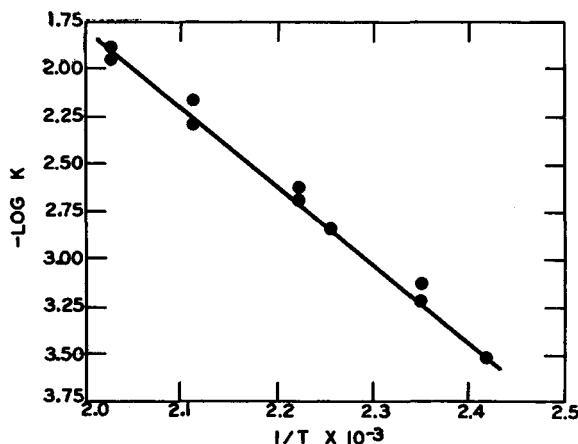
Fig. 6. Graphic representation of the change in rate constant vs. the reciprocal of the absolute temperature for estimation of the activation energy of methylene oxidation in polybenzyl.

wise linear regression analysis. All calculations were carried out using a standard program on an IBM 1620 computer. The slope so obtained when multiplied by $2.303R$ gave an activation energy of 14.5 ± 3.5 kcal/mole. This value corresponds favorably with the value for methylene oxidation obtained using similar procedures in phenolic resin systems, and is in particularly good agreement with the data obtained from a fully cured phenol–formaldehyde polycondensate[5] in which complete removal of the methylol groups was accomplished.

It must be concluded from these results and those data previously reported[1-5] for phenolic and furan resin that methylene oxidation is the initial degradation reaction in activated methylene polymer systems of this type. The major secondary degradation reactions which produce chain scission and other concurrent physical changes in the polymer are generally equitable to further oxidation at the carbonyl linkage. It must also be concluded from this study that the possibility of hydroperoxide decomposition to occur, in part, to give diphenylmethanol linkages as well as benzophenone-type linkages in activated methylene systems, warrants consideration and further investigation. Studies are in progress in phenol–formaldehyde systems which we anticipate will confirm this initial competitive route for hydroperoxide decomposition. We hope to report the details of this study in the near future.

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Résumé

On a trouvé que les étapes primaires de la dégradation du polybenzyle en présence d'air ou d'oxygène pur entre 140° et 220°C sont des attaques des groupes méthylènes avec formation de groupes benzhydrols et benzophénones. L'étude cinétique de la vitesse d'incorporation de groupes carbonyles du type benzophénone indique une énergie d'activation apparente initiale du processus d'oxydation égale à 14.5 ± 3.5 Kcal. L'analyse par chromatographie en phase gazeuse des produits de réaction volatils indique que l'acide benzoique et la benzophénone sont les produits formés les plus importants, tandis que de petites quantités de benzène, de toluène, d'eau et d'anhydride carbonique se forment également. On peut conclure que l'oxydation initiale du polybenzyle est très semblable à l'oxydation des résines phénoliques et autres polymères à méthylène actif. Les réactions de dégradation secondaire dues à des oxydations ultérieures et qui entraînent une scission de chaîne intéressent généralement aussi bien les groupes benzhydrols que ceux de la benzophénone. L'apparition et la preuve spectrale de la formation de liens d'anhydride benzoique par déshydration thermique de l'acide benzoique expliquent suffisamment la formation de produits de réactions secondaires qui donnent de nouvelles mais plus petites bandes d'absorption dans l'infra-rouge au début et au cours de la dégradation.

Zusammenfassung

Den primären Schritt beim Abbau von Polybenzyl bei Temperaturen zwischen 140 und 220°C in Gegenwart von Luft oder reinem Sauerstoff bildet ein Angriff an den Methylenbrücken unter Bildung von Benzhydrol- und Benzophenonbrücken. Die kinetische Auswertung der Geschwindigkeit der Bildung von Carbonyl vom Benzophenontyp lieferte eine scheinbare Anfangsaktivierungsenergie für den Oxydationsprozess von 14,5 ± 3,5 kcal. Gaschromatographische Analyse der flüchtigen Reaktionsprodukte zeigt, dass als Hauptprodukte der Oxydation Benzoesäure und Benzophenon zusammen mit kleineren Mengen von Benzol, Toluol, Wasser und Kohlendioxyd gebildet werden. Man kommt zu dem Schluss, dass die Anfangsoxydation von Polybenzyl parallel zur Oxydation phenolischer Harze und eng verwandter aktivierter Methylenpolymerer verläuft. Sekundäre Abbaureaktionen, welche zur Kettenspaltung führen, können im allgemeinen einer weiteren Oxydation der Benzhydrolund Benzophenonbrücken zugeschrieben werden. Das Auftreten und der spektrale Nachweis der Bildung von Benzoesäureanhydridbrücken durch thermische Dehydratisierung von Benzoesäure kann die Bildung der sekundären Reaktionsprodukte, die in den frühen und Zeischenstadien des Abbaus nur unbedeutende Infrarotbanden liefert, am besten erklären.