# A Study of Thermal Degradation and Oxidation of Polymers by Infrared Spectroscopy. Part II. Polybenzyl

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INTRODUCTION

The synthesis and properties of polybenzyl have been described by Haas and co-workers.[1] The structural arrangement is generally considered to be a few centrally located highly substituted aromatic rings onto which are substituted a number of monosubstituted benzyl groups. The infrared spectra are in agreement with this point of view, as may be seen from Figures 1 and 2, which show the marked similarity in spectra of polybenzyl and diphenylmethane. The absorption pattern in the long-wavelength region is indicative of monosubstitution. As the molecular weight of the polymer increases, the number of singly substituted aromatic groups present should approach a limiting value of 75% if it is assumed that the maximum number of substituents on the internal aromatic rings is four. The polymer is believed to be globular, and its structure may be represented as
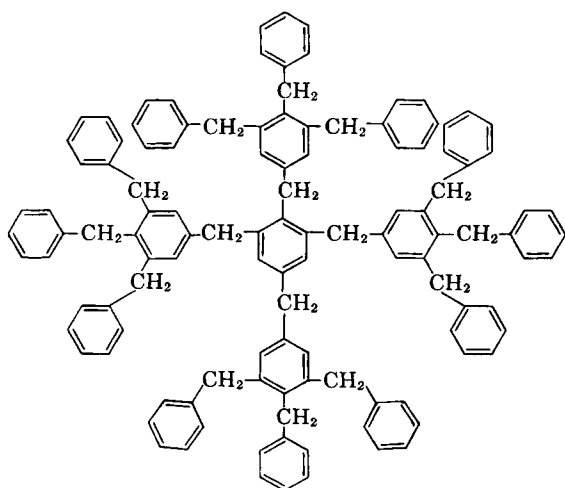
For the purpose of this study, however, it suffices to represent the polymer as
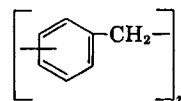
It is believed that the information derived from the study of this and other relatively simple polymers may be of considerable aid in interpreting and evaluating the data previously obtained on the considerably more complicated phenolic and novolac resins. The methylene bridge in phenolics
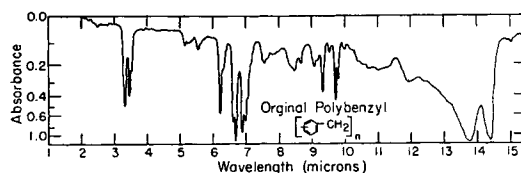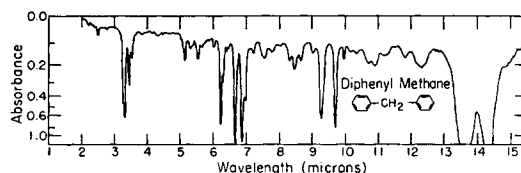

Fig. 1. Infrared spectrum of polybenzyl.

Fig. 2. Infrared spectrum of diphenylmethane.

and novolacs has also been found to be highly susceptible to oxidation and is oxidized to the keto group fairly rapidly at temperatures as low as 150°C.

A quantitative study of phenolic systems is complicated by the heavy —OH absorption bands which overlap the relatively weak aromatic and aliphatic hydrogen-stretching bands and by the multiplicity of the carboxyl —C=O stretching vibration apparently generated by the oxidation of residual methylol groups to carboxyl groups (in addition to those formed by oxidation of the methylene bridge). Hydrogen bonding between the

phenolic —OH and the acid and keto groups further complicates the study of phenolics, because this bonding has considerable influence on the band frequencies. The simultaneous depletion of hydroxyl groups as a result of ether linkage formation and the generation of hydroxyl by oxidation of methylene groups to acid makes the monitoring of the —OH concentration somewhat uncertain. From the position of the various bands generated in the phenolics by oxidation we can get at present only a qualitative idea of the course of the oxidation. It appears that a quantitative picture of this system can be obtained only by first examining somewhat more simple, related systems. Polybenzyl is considered in this part of the study, as it is a fairly simple and straightforward system as compared to the more complicated polymers. It is our intention in this particular study to consider mainly the oxidative attack made on the methylene bridge.

EXPERIMENTAL

General Considerations

The experimental techniques and instrumentation used have been described previously in Part I of this series of papers.[2] The continuous scanning technique was used in this study.

The infrared absorption bands of principal interest in this study are tabulated in Table I. These bands are also labeled in Figures 3, 4, and 5, which are examples of spectra as they are obtained during the course of the oxidation. The arrows with heads pointing down (i.e., toward higher absorbance values) indicate the functional group is being generated, and arrows pointing up indicate the func-

TABLE I
Infrared Absorption Bands

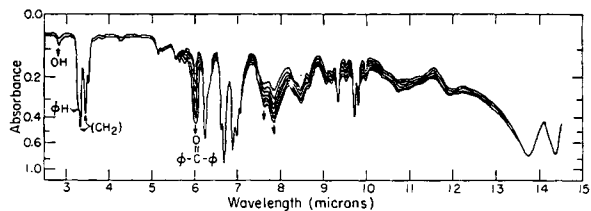| Functional group	Wavelength, μ
—OH (nonhydrogen-bonded)	2.8
—OH (hydrogen-bonded)	2.9–3.0
—C—H (aromatic carbon-hydrogen stretching)	3.28
—CH₂ (aliphatic carbon-hydrogen stretching)	3.44
—C=O (diaryl ketone)	6.0
$\overset{O}{\overset{\|}{-C}}-O-\overset{O}{\overset{\|}{C}}-$ and $-\overset{O}{\overset{\|}{C}}-OR$	5.64, 5.77[a]
—C—O—C—	ca. 8[b]
Aromatic ring	6.8

[a] Band pair.
[b] Broad band.

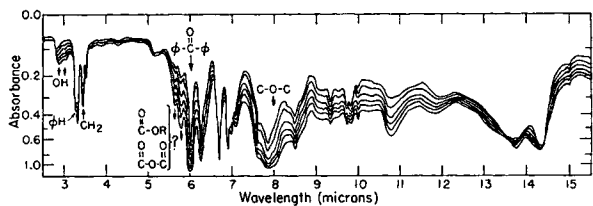Fig. 3. Infrared spectra showing the initial stages of oxidation.

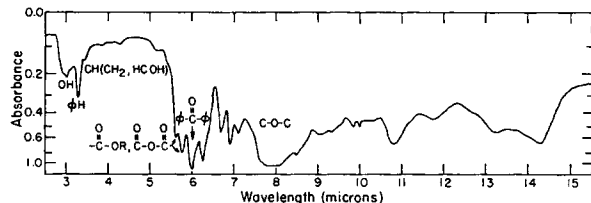Fig. 4. Infrared spectra showing intermediate stages of oxidation.

Fig. 5. Infrared spectra showing final stages of oxidation.

tional group is decreasing. The —OH first appears as the nonhydrogen-bonded form and gradually becomes more and more hydrogen-bonded as the oxidation progresses. Benzyhydrol exhibits both bonded and nonhydrogen-bonded hydroxyl bands as may be seen in Figure 7, which is the spectrum of a mixture of benzhydrol and polybenzyl. The position of the —OH band depends on the degree of hydrogen bonding and therefore on the concentration of the hydroxyl groups or presence of other groups, such as the keto group, which also contribute to hydrogen bonding. The keto group generated by oxidation is in exactly the position in which it would normally be expected to occur for the production of the diaryl ketone. This is shown by Figure 6, which is a spectrum of a mixture of benzophenone and polybenzyl and may be verified by consulting any standard reference source such as Bellamy.[3] The two sharp bands initially developed near 7.6 and 7.8 micron are also present in benzophenone and are to be expected. In the final stages of oxidation a broad band developed near 8 microns which blanks out the bands at 7.6 and 7.8 microns. Broad bands of this type are
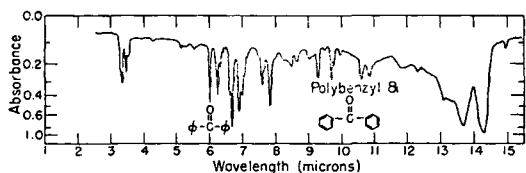
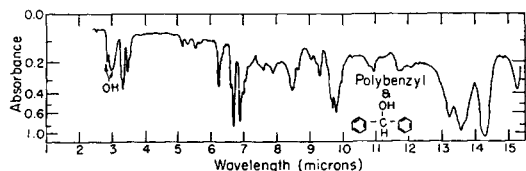Fig. 6. Infrared spectrum of a mixture of polybenzyl and benzophenone.

Fig. 7. Infrared spectrum of a mixture of polybenzyl and benzhydrol.

generally associated with C—O—C vibration and generally occur in esters and anhydrides.

The band pair at 5.64 and 5.77 microns presents a problem, in that the generation of two different functional groups might give rise to these bands. The first possibility is formation of linear anhydrides similar to benzoic anhydride. Anhydrides exhibit two C=O frequencies, generally approximately 0.2 micron apart and differing in intensity. (The position of these two bands is about that of the benzoic anhydride pair; however, the relative intensity is not similar.) The ratio of the intensities of these two bands were found to remain fairly constant throughout the course of the oxidation, which suggests that they may arise from the same functional group. However, it is not inconceivable that they are arising from two different functional groups which are being generated at approximately the same rate. It should also be noted at this point that peroxides of the type

$$R—\overset{\overset{O}{\|}}{C}—O—O—\overset{\overset{O}{\|}}{C}—R'$$
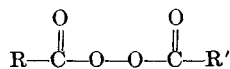
also exhibit C=O absorption at two frequencies; however, these are generally never separated by more than 0.1 micron; also, such peroxides are very unstable and would in all probability not exist at 200°C.

The second possibility is formation of an ester (C=O at 5.77), with the simultaneous formation of a cyclic anhydride similar to phthalic anhydride, which would account for the band at 5.64 microns. Cyclic anhydrides of this type generally have a strong C=O frequency at near 5.6 micron and a considerably weaker C=O band near 5.4 microns.

There is actually some indication of the formation of a weak band at 5.44 microns which is in support of this possibility. The formation of an ester would well account for the band at 5.77 microns, since esters generally exhibit C=O frequencies near 5.8 microns.

The polymer is rendered thermosetting by oxidation, which indicates that crosslinking is produced by this mechanism. The formation of either esters or linear anhydrides would produce this effect. The formation of ether linkages by splitting out of water from two adjacent hydroxyl groups could also produce crosslinking. The appearance of a band corresponding to an ether group is not observed, but, the presence of a low percentage of ether groups could easily go undetected by infrared since this band is not a particularly intense one.

Apparently no significant concentration of carboxyl groups is built up, as indicated by the absence of the acid hydroxyl band at 3.8 microns and the acid carboxyl band at 5.9 microns. This indicates that the carboxyl groups are converted to ester or anhydride at a rate significantly faster than that at which they are produced. It is also significant that the ester and/or anhydride develops only after the hydroxyl and keto groups have been generated to a considerable degree, indicating that a second oxidation step probably occurs at the hydroxyl or keto group to produce the acid group which is subsequently converted to an ester or anhydride. The two possibilities are presented below in equation form.

If the initial oxidation is assumed to occur by the initial formation of hydroperoxide which subsequently decomposes to form the hydroxyl and keto groups:
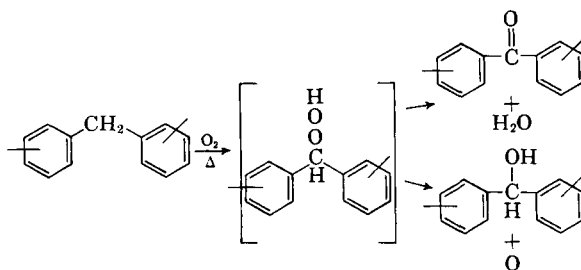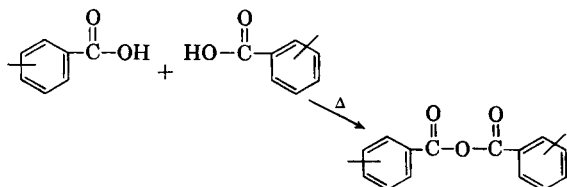

then the carboxyl group necessary for the formation of esters and anhydrides may be formed by oxidation of part of the hydroxyl groups:
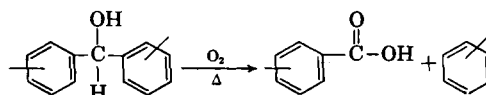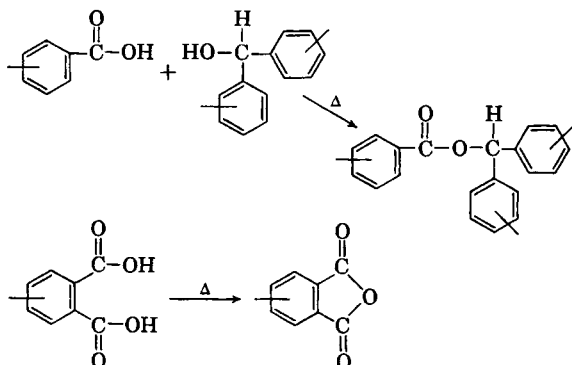
This provides the necessary carboxyl groups for the two alternative possibilities described above which may be represented as follows.

(*1*)   Linear anhydride formation:

(*2*)   A combination of ester formation with a considerably smaller amount of cyclic anhydride formation:

It should be recalled at this point that the polymer is not a linear polymer but is considered to be more or less spherical or globular in structure and contains some highly substituted aromatic rings surrounded on the outside edges by a majority of monosubstituted aromatic rings. The straight lines as shown in the equation above indicate connection to the polymer unit. Consequently the number of sites available for cyclic anhydride formation are not large because the polymer actually consists primarily of monosubstituted groups.

DISCUSSION AND CONCLUSIONS

As indicated above, Figures 3, 4, and 5 are only examples of portions of the data. The overall picture of the growth and decay of the various bands are shown in Figure 8. This is a plot of the absorbance, and, since different bands have different molar extinction coefficients, these plots as such do not represent the amount of each functional group present (a plot showing the actual amounts is shown in Figure 9). Significant points to note in Figure 8 are as follows.

(*1*)   The number of aromatic rings remain essentially constant, showing only approximately 7% volatilization loss, as indicated by the 6.8-micron band.

(*2*)   The methylene band decreases markedly.

(*3*)   The bands at 5.75 and 5.63, microns parallel each other to a close degree, indicating that they may arise from the same group.

(*4*)   The diaryl keto band at 6.0 microns is considerably more intense than the other bands and essentially goes off scale on the plot. (This resulted in having to make a separate determination on the C=O as shown in the subsequent quantitative discussion regarding Figure 9). The 7.8-micron band is also present in diaryl keto compounds.

(*5*)   The hydroxyl band increases initially and then levels off; however, this is a band of relatively low intensity and actually represents a considerable amount of hydroxyl groups.

Figure 9 gives a plot of the fraction or percentage of methylene groups converted to the various other forms by oxidation. This is on a molar basis and a point of 20% on the hydroxyl curve, for example, indicates that 20% of the methylene groups have been converted to hydroxyl groups.
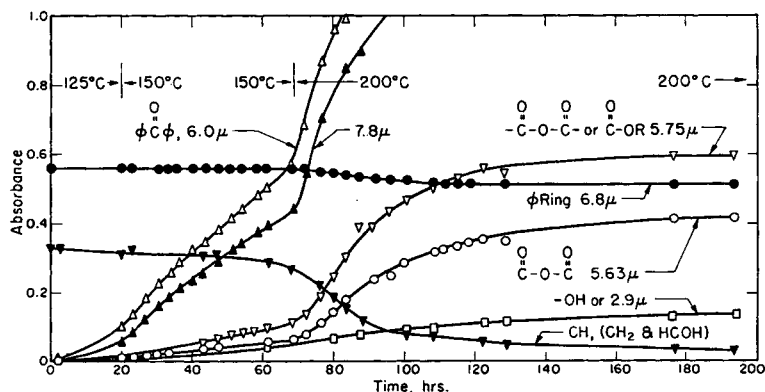

Fig. 8. The variation in absorbance of the bands arising from various functional groups with oxidation.
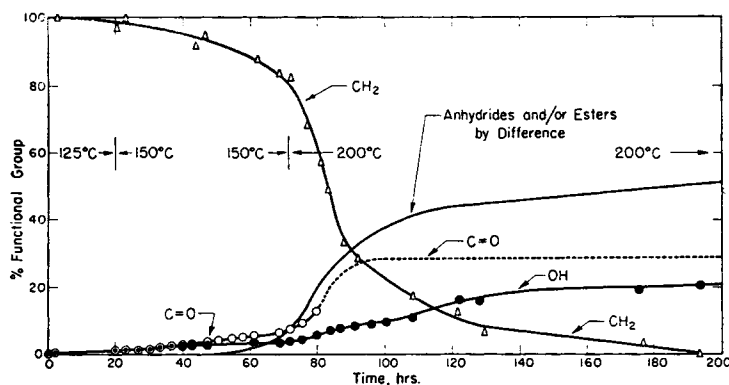
Fig. 9. Percentage of functional groups generated or remaining during the course of oxidation.

The values plotted in Figure 9 were produced by comparison with standards which were prepared by the addition to known quantities of benzophenone and benzhydrol to the polymer. The aromatic ring vibration at 6.8 microns was used as a reference point in the analysis. The data were computed in such a manner as to compensate for volatilization losses. The dotted line portion of the carboxyl curve represents estimated values of the diaryl keto group. As indicated above the high intensity of this band prevents a simultaneous determination of its concentration above approximately 12%. The determination of the keto group was therefore made independently on a much thinner specimen, the results of which are shown in Figure 10. It was assumed in Figure 9 that the keto group approached approximately the same final concentration, namely 30%. The solid line without points was calculated
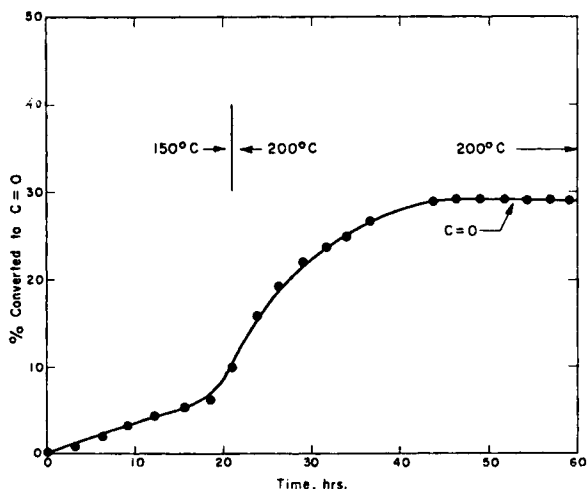

Fig. 10. Percentage of methylene groups oxidized to C=O (thin film).

by difference and thus represents all other constituents not otherwise accounted for by direct analysis. The bands developed, as indicated above, suggest that this curve represents primarily linear anhydrides and/or ester groups accompanied by the formation of some cyclic anhydride. It is possible that some ether groups are formed and they would also be included in this curve; however, the spectra do not indicate the formation of appreciable amounts of ether groups, as indicated by the absence of an ether band in the 9–10 micron region. The background in the spectra is fairly heavy in this region and a small percentage of ether could easily go undetected. Some specific points of note in Figure 9 are the following.

(1) The methylene group is totally depleted by oxidation at 200°C.

(2) The difference curve representing mainly anhydrides and/or esters does not appear until approximately 5% hydroxyl and carbonyl are generated. This, as mentioned earlier, may indicate a second step in the oxidation process which converts these groups to acids which immediately react to form either anhydrides or esters. It may be recalled that no significant or detectable quantity acid was indicated by the spectra.

(3) The rate of oxidation is quite appreciable even at 150°C. and is greatly accelerated at 200°C. As a rough approximation, the slope of the methylene decay curve in the initial phase of the oxidation at 200°C. is approximately ten times as great as the slope of the same curve in the 150°C. region.

This study indicates, as well as other studies we have conducted on phenols, novalacs, and other polymers, that the methylene bridge is extremely susceptible to oxidation at elevated temperatures. In phenols, for example, the oxidation of this group

occurs quite rapidly at temperatures as low as 150°C. In general, it appears that the methylene bridge may well be the weak link in many polymeric chains at elevated temperatures under oxidizing conditions.

The authors are indebted to Dr. J. H. Freeman for supplying the polymer used in this study.

References

1. Haas, H. C., D. I. Livingston, and M. Saunders, *J. Polymer Sci.*, **15,** 503 (1955).

2. Lady, J. H., R. E. Adams, and I. Kesse, *J. Appl. Polymer Sci.*, **3,** 65 (1960).

3. Bellamy, L. J., *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1956.

Synopsis

The primary mode of degradation of polybenzyl at elevated temperatures in the presence of air has been found to be an oxidative attack on the methylene bridge. Initially the methylene bridge is oxidized to keto and hydroxyl groups. Later substantial amounts of acid anhydride and/or ester are formed. Extensive oxidation has been found to oxidize approximately 30% of the methylene bridge to keto groups and 20% to hydroxyl groups. This leaves approximately 50% not quantitatively accounted for specifically; however, the data indicate that the residual methylene groups are consumed primarily by the formation of anhydride and/or ester. While the polymer is initially thermoplastic, it becomes thermosetting as a result of oxidation. The course of the oxidation is followed by observing the growth of the infrared absorption bands arising from the various functional groups being generated as well as following the simultaneous decrease of the methylene absorption band.

Résumé

On a trouvé que le mode primaire de dégradation de polybenzyle à température élevée, en présence d'air consiste en une attaque oxydante sur le pont méthylène. Initialement, le pont méthylène est oxydé en groupements cétones et hydroxyles. Ensuite d'importantes quantités de groupements anhydrides et/ou esters sont formées. On a trouvé qu'une oxydation poussée, oxydait approximativement 30% de la liaison méthylénique en groupements cétoniques et 20% en groupements hydroxylés. Cela laisse approximativement 50% de ponts méthylènes qui ne sont pas déterminés quantitativement; cependant, les données indiquent que les groupements méthyléniques résiduels sont consommés d'abord par la formation de groupements anhydrides et/ou esters. Le polymère est initialement thermoplastique, bien qu'il devienne ensuite thermodurcissable, comme si cela résultait de l'oxydation. L'avancement de l'oxydation est suivi en observant la croissance des bandes d'absorption infra-rouge provenant des différents groupements fonctionnels qui sont formés, aussi bien qu'en suivant la diminution simultanée de la bande d'absorption du méthylène.

Zusammenfassung

Es wurde gefunden, dass der erste Schritt beim Abbau von Polybenzyl bei höheren Temperaturen in Gegenwart von Luft ein oxidativer Angriff auf die Methylenbrücke ist. Anfänglich wird die Methylenbrücke zu Keto- und Hydroxylgruppen oxidiert. Später werden wesentliche Mengen von Anhydrid- und Estergruppen oder einer davon allein gebildet. Bei weitgehender Oxydation werden etwa 30% der Methylenbrücken zu Ketogruppen und 20% zu Hydroxylgruppen oxidiert. Diese Bilanz gibt keine Rechenschaft über etwa 50%, die Ergebnisse sprechen aber dafür, dass die restlichen Methylengruppen in erster Linie durch die Bildung von Anhydrid- und Estergruppen verbraucht werden. Das Polymere zeigt anfänglich thermoplastisches Verhalten, wird aber dann als Folge der Oxydation wärmehärtend. Der Verlauf der Oxydation wird sowohl durch Beobachtung des Anwachsens der Infrarotabsorptionsbanden verfolgt, die den verschiedenen entstehenden funktionellen Gruppen zuzuordnen sind, als auch durch die der gleichzeitigen Abnahme der Methylen-Absorptionsbande.