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Studies of the Stability of Condensation Polymers in Oxygen-Containing Atmospheres

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Studies of the Stability of Condensation Polymers in Oxygen-Containing Atmospheres

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Synopsis

The stability of polymeric substances in oxidizing atmospheres is almost always quite different from that observed in nonoxidizing media. The methods and techniques applicable to studies of the chemical changes taking place in a number of complex condensation polymers have been examined in detail in an effort to draw from the resultant data fundamental information regarding the mechanisms of thermooxidative degradation processes. In general terms, it has been of interest to examine condensation polymers at various stages of curing in both oxidizing and inert atmospheres in order to elucidate the chemical transformations that contribute to the over-all stability of these polymers. The use of structural modifications in specific polymer systems together with model-compound studies, solid-phase monitoring of functional-group changes, and gaseous-product analysis are exemplified as they pertain to an investigation of detailed degradation reactions. The results of these investigations and the mechanistic conclusions that can be drawn offer a ready source of information pertaining to the effects of processing upon the thermal life of particular polymers in oxygen-containing atmospheres and, in addition, they offer data concerning the effect of specific linkages within the polymer unit upon the over-all stability of the polymer. Such information is extremely valuable from a viewpoint of new polymer synthesis and stabilization methods for existing complex polymer systems.

In recent years the chemistry of complex condensation polymers, such as phenol–formaldehyde polycondensates and epoxy resins, has become the focal point of a large number of experimental investigations. In the past it has been commonplace to follow gross physical changes of a formed polymer piece or a composite molding during various stages of "degradation." In practice this approach has been highly successful in evaluating changes in materials that potentially exhibit desirable properties from a stability viewpoint. Unfortunately, detailed structural specification of polymers for high-temperature application has not been clearly defined with the utilization of this approach. There are numerous, rather obvious, reasons for this failure. Paramount among these reasons are two facts that seem to outweigh all other considerations. First, and in most cases, the physical property change being measured has not been, or cannot be, related to detailed physical and chemical changes taking place within the polymer mass. Second, and even more fundamental, the chemist simply does not have detailed information concerning the structure of the polymeric substance termed the "cured polymer." That is to say, we have not been highly successful in characterizing these complex substances from a functionality viewpoint, such that we know precisely the reaction species involved in curing and degradation of the polymer mass. These materials, once partially cured, are usually insoluble, infusible substances, which do not lend themselves readily to a detailed evaluation of structural parameters with the use of even the most sophisticated of the modern instrumental techniques available.

It would seem quite clear that if we are to attack a problem such as the stability of a particular resinous mass, a wide variety of information regarding the structural features and relative changes possible within the system must be evaluated. Any such evaluation must necessarily involve the application of numerous physical and chemical methods of analysis, utilized at as many stages of the curing and degradation sequence as possible. Most desirable, of course, would be the continous analysis of individual reactions taking place within the polymer mass. In addition, it would be of the utmost importance to investigate the structural features of the initial polymer. The literature concerning the structures of most complex condensation polymers is limited to those functional groups forming the repeat unit. Thus, structural moieties present other than those characteristic of the major course of the condensation process must be ascertained, since these by-product units may well be the sites within the resin that "trigger" the degradation sequence. In so far as possible it was deemed most advantageous to study the structural aspects of such polymer systems and the chemistry of degradation simultaneously.

Experimental Procedures (*1–6*)

The specific techniques must be numerous, since any single technique is suspect until corollary data obtained via other techniques confirm any specific single observation. This is particularly true when the observations concerning degradation behavior seem contrary to sound mechanistic principles established for model-compound systems. The bulk polymer phase can best be evaluated for chemical changes by monitoring specific changes in composition. To accomplish this such techniques as infrared spectrophotometric analysis at degradation temperature, to establish functional-group changes, ultraviolet spectral detection of the incorporation of chromophoric groups during degradation, electron spin resonance spectroscopy for the detection of radical species produced during degradation, nuclear magnetic spectroscopy as a means of obtaining specific data concerning changes in the number and environment of hydrogens in the degrading polymer and the analysis of changes in elemental composition as a function of extent of the degradation, allow the chemist to gain extensive data relating to specific chemical changes taking place during thermal and oxidative degradation.

Simultaneously, volatile fragments resulting from the degradation process can be measured qualitatively and quantitatively by means of vapor-phase chromatography coupled with infrared or mass spectrometric identification of the volatile components. Mass spectrometric thermal analysis of the volatiles produced and continuous infrared monitoring of solid-phase changes allow kinetic evaluation of specific reactions.

Such techniques, when coupled with gross changes in the resin system as measured by thermogravimetric analysis and differential thermal analysis, lead to a rationale concerning the resin being examined and generally allow the formulation of a mechanistic postulate describing the most likely course of the degradation under the conditions investigated. In each case the proposals reflect the application of several of the above-mentioned techniques, which gives sufficient information to allow the postulation of a reasonable route describing the degradation and, where necessary, information concerning the structure of the resin being investigated.

Recently we have described the experimental methods and details of a series of initial studies concerned with the degradation chemistry of phenol–formaldehyde polycondensates (*1*), polybenzyl (*2*), furfuryl alcohol resins (*3*), butylated melamine and urea–formaldehyde polycondensates (*4*), poly(phenylene ether) polymers (*5*), and epoxy resin systems (*6*). This report summarizes and extends these reports with typical examples of the application of both physical and chemical methods to the study of the degradation of several typical complex condensation polymers.

Approach to Degradation Problems

Considering the experimental procedures already delineated, the method of attack necessary to obtain definitive information seems worthy of some brief discussion. The following outline delineates the methods found to be most applicable to such studies. The reader will, of course, recognize that the categories cited are for discussion purposes only and that considerable overlap between them always occurs.

Polymerization Studies. In all fundamental studies that attempt to establish a structure-reaction relationship "pure" polymer(s) are required for investigation. Although such a comment outwardly seems unnecessary, the literature is replete with reports of degradation studies carried out on "off-the-shelf" materials of unknown composition and prior history. In many cases the interpretation of the data resulting from such studies is purely speculative. The use of broadly modified polymers in many cases aids in the confirmation of a particular mechanistic pathway for resin degradation. In most cases the particular materials required are only available via direct syntheses.

Fractionation and Molecular Weight Studies. The examination of the effect of molecular weight on the course of degradation is necessary in the evaluation of the role of end group(s), the role of curing agent, and the intervention of cross-linking reactions potentially taking place simultaneously with both curing and degradation. Fractionation into narrow-molecular-weight ranges of several widely varying molecular weights generally offers the potential for such evaluations.

Degradation Studies. The detailed assessment of both physical and chemical changes occurring during thermal and oxidative sample exposure (including exposure of samples during preparation and curing), with the use of both solid-phase and volatile monitoring of changes in the polymer systems, is the framework around which all other studies are correlated. It is necessary to establish, if oxidative reactions are being evaluated, for example, the surface nature of the reaction as well as the fact that the particular processes being followed are indeed oxidative rather than simple thermal processes characteristic of the polymer in the absence of oxygenated atmospheres (i.e., initial chain scission to radical ends via thermal bond rupture, followed by oxygen scavenging of the radical ends.

Model-Compound Studies. The use of model compounds, including model polymers of two to five units, is one of the most valuable aids to the investigator interested in degradation studies. Model compounds may be used in several ways for specific evaluations. The addition of models of projected degradation units to nondegraded polymer and the comparison of the functional characteristics of the composite to the degraded polymer mass are probably the most valuable techniques for the confirmation of the presence of a particular degradation unit. Often differences between the composite and degraded polymer allow an assessment of other species formed during the degradation, by substraction, for example, of the characteristic absorptions in the infrared spectrum of the composite from those in the spectrum of the degraded polymer. A second useful technique is to use a model compound that is unreactive to the resin-curing process and possesses a particular functionality suspected of being present in the resin in minor amounts. After degradation the remaining model unit is extracted from the polymer mass and examined for structural changes. Such models are usually tagged with either an isotopic atom or a characteristic substituent that has no effect upon the reactivity of the model compound.

Synthesis of Partially Degraded Polymers. The incorporation of those functional groups known to be "produced" during degradation into the polymer mass represents an excellent method both of authenticating structural change and of examining gross property changes. The difficulty is that such syntheses are often quite involved and require conditions markedly different from those utilized in preparing the original polymer, thus failing to yield the ultimate in structure proof as commonly the criteria for low-molecular-weight compound structural elucidation. Such synthetic samples, however, are extremely useful in cases in which they can easily be prepared.

It is the purpose of the present report to draw on examples from a variety of studies to exemplify the application of each of the above described methods to the degradation of condensation polymers in oxygen-containing atmospheres. The polymers to be discussed here will include two systems: the phenol-formaldehyde polycondensates and related polymers and the poly(phenylene ether) polymers.

DISCUSSION

Oxidative Degradation of Phenol–Formaldehyde Polycondensates and Related Polymers

Figure 1 summarizes the phenol-formaldehyde resins chosen for investigation (*1*). The acid-catalyzed condensation product (novolac) contains only diphenylmethane linkages, denoted by —CH_2— in the figure. The thermally polymerized samples contained in addition to the methylene bridged structure both methylol and ether linkages, as indicated. The based-catalyzed resinous product (resole) contained both the methylene and methylol linkages. It should be noted that both in the case of the thermal

	Acid	Thermal	Base
pH	Below 4	~4-5	Above 8
	$-CH_2-$ (ALMOST QUANT.)	$-CH_2-$ $-CH_2-OH$ (Dependent on F/P ratio) $-CH_2-O-CH_2-$ (Small amount ~5%)	$-CH_2-$ $-CH_2-OH$

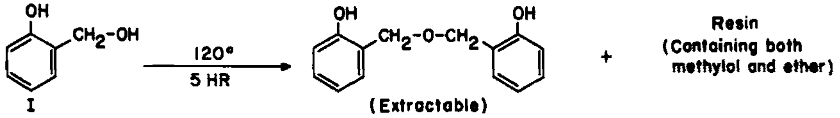


FIG. 1. Summary of the phenol-formaldehyde resins studied, indicating the key structural features in each resin system.

resin and in that of the base resin the methylene-to-methylol ratio varied as a function of the formaldehyde-to-phenol ratio. For comparison saligenin (I) in Fig. 1 was converted via thermal polymerization (120°C for 5 hr) to an ether-containing resin. Figure 2 summarizes the possible reactions occurring during base-catalyzed condensation.

Before a discussion of the results of oxidation studies is undertaken, it is advantageous to consider the over-all process of oxidative degradation, as determined by the infrared method. When a resole (base-catalyzed) condensate is thermally set and hardened in an inert atmosphere such as nitrogen at 120°C for 3 hr, little or no volatilization of organic materials is detected. Therefore, on examining the cured resin, the nonvolatile, solid phase of the polymer system is being monitored. The course of the degradation, exclusive of volatile fragments produced during oxidation, can therefore be detected from changes observed in the functional-group bands in the infrared region.

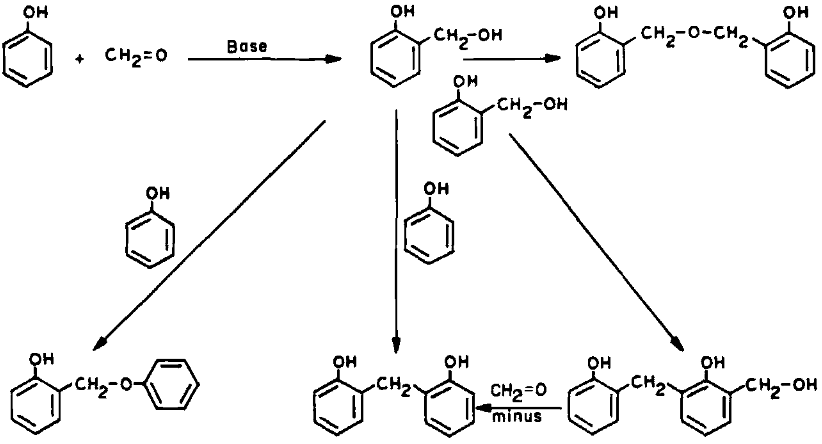


FIG. 2. Typical reactions possible in the base-catalyzed condensation of phenol with formaldehyde.

Several observations concerning the structure of cured phenolic resins of this type can be made from initial examination of the infrared spectrum of the resin film sample. If a polymer consisting of phenol rings connected by methylene linkages in the *ortho* and *para* positions is assumed, then all the absorption bands appearing in the 2-to-16-μ region can be assigned to the various vibrational modes expected for a structure of this type. After heating the phenolic resin film in vacuo (0.05 mm) for 50 hr at temperatures between 100 and 200°C no carbonyl bands appeared in the spectrum. Therefore, under these conditions of aging quinone methide structures cannot be supported in the infrared examination of the film specimens. If present, these moieties make up only a small concentration of the resin system.

Similarly, ether linkages are absent in the cured base-prepared phenolic resin. The structures obtained from multisubstituted phenolic rings and formaldehyde cannot be analogously applied to simple phenol–formaldehyde condensation products. In view of these initial facts the starting material used for the degradation studies was considered to consist predominantly of phenol rings connected by methylene groups substituted at the 2, 4, or 6 positions, or any combination of these substitutions.

If the phenolic resin, after it has been cured by being heated in nitrogen, is heated further in either nitrogen or vacuum, no apparent degradation occurs, since no changes are observed in the successive infrared spectra taken to follow any possible chemical change, but if the resin is heated in air, a number of spectral changes occur. If the air-heated resin is then transferred to an inert atmosphere system for further degradation, the chemical changes as manifested in changes in the infrared region slowly cease. It can be concluded that the initial degradation is dependent on the presence of oxygen and that the products of degradation are oxygenated species.

When a base-catalyzed phenolic resin is heated at temperatures

TABLE 1

Observed Functional-Group Changes in Resole and Novolac Resins at 200°C

Frequency, cm^{-1}	Assignment	Change	Time of appearance, hr
3300	—OH	Decrease	18th
3200	—COOH(OH)	Increase	4th
1650	C═O	Increase	4th
1720	—COOH	Increase	4th
1480	—CH—	Decrease	1st
875, 820	1,2,4-trisubstituted aromatic ring	Decrease	18th

between 100 and 200°C, a number of changes take place in the polymer system, which can be detected by infrared analysis. The over-all reaction is basically the same at temperatures between 100 and 200°C. Only the rate of oxidation changes with increasing temperature, as would be expected from consideration of the Arrhenius equation. By measuring the intensity of the carbonyl groups produced on oxidation a general relationship concerning the rate of oxidation at different temperatures was obtained.

A number of significant changes take place in the spectra of various resin samples during the course of oxidative aging. A series of bands attributed to the ingrowth of carbonyl groups are observed in the 5.5-to-6.5-μ region. Concurrent with the ingrowth of these bands a number of other changes appear in these spectra. The over-all changes in the polymer structure upon being heated in air at 200°C, detected by infrared spectral analysis, are summarized in Table 1.

The course of degradation of an acid-catalyzed phenolic resin (novolac) is essentially the same as that of a base-catalyzed phenolic resin (resole) as evidenced in the changes in the infrared spectrum. The same carbonyl groups appear at the same frequencies in the identical order of appearance. Therefore, it is convenient to speak of phenolic resins in general when discussing the course of the degradation, since no differentiation can be made by infrared analysis.

The first new band to appear in the resin spectrum is the carbonyl band at 1650 cm^{-1} (6.05 μ). Since oxidation at a methylene linkage has been assumed to be reasonable by Hall (7), this initial carbonyl absorption was tentatively assigned to a dihydroxy-substituted

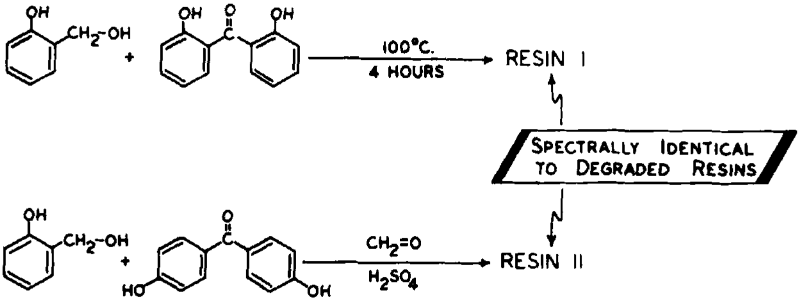


FIG. 3. Preparation of model polymers containing oxidized methylene linkages for spectral comparison with oxidized phenol-formaldehyde polymers.

benzophenone structure. It then became necessary to confirm this by independent syntheses of ketone-containing polymers. The 2,2′- and 4,4′-di-hydroxybenzophenones were prepared. Both these ketones exhibited carbonyl frequencies at 1625 cm^{-1}, but when they were incorporated in the polymer chain by copolymerization with phenol and formaldehyde, the carbonyl absorption band was observed at 1650 cm^{-1}, see resins I and II, Fig. 3. These data confirm the initial assignment of the primary oxidation band to a carbonyl group arising from methylene oxidation. The frequency of the monomeric compounds compared to that of the polymers might well be expected on the basis of steric considerations in the polymer unit.

This mode of oxidation agrees with previous evidence of the spontaneous oxidation of phenolic resins (7). Although peroxide intermediates were not detected in the infrared spectrum, their existence was proved by chemical analysis. In addition, resin samples fully cured in high vacuum at 400 to 450°C, which showed no oxidative degradation, were carefully examined by the spectral methods just described. It was concluded that the hydroperoxidic intermediate decomposed to dihydroxybenzhydrol linkages and also to carbonyl linkages during the initial stages of degradation, since the ingrowth of hydroxylic species was readily detected during the continuous monitoring of the degrading films at reaction temperatures between 100 and 225°C.

Further, it was shown by the inclusion of a substituted phenolic methylol-containing compound in the resin mass that (resin IV, Fig. 4), at least to some small degree (not detectable by infrared

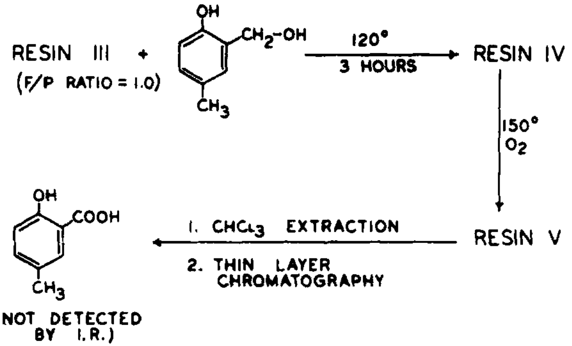


FIG. 4. Typical model compound evidence for methylol oxidation as an initial step in phenolic resin oxidation.

methods), some initial oxidation of methylol groups to carboxylic acids also occurs in competition with the curing process (further condensation of methylol to diphenylmethane linkages). Therefore, the primary steps in the oxidative degradation can be visualized as shown in Fig. 5.

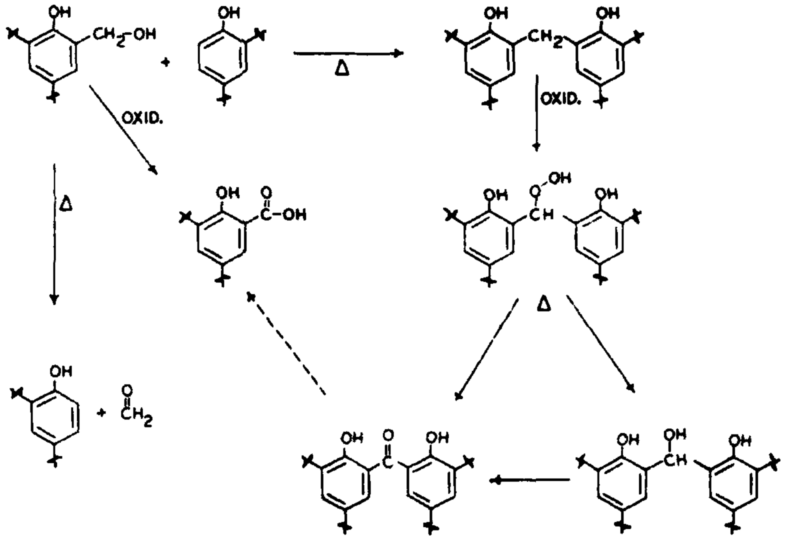


FIG. 5. Summary of the initial steps in the oxidative degradation of phenol-formaldehyde polycondensates.

On further oxidation a shoulder on the initial carbonyl band grows in at a frequency of 1680 cm^{-1}. A consideration of the chemistry of this system led to the general deduction that only two chemical processes that would lead to the formation of carbonyl-containing fragments are possible. One is the cleavage to acid fragments and the other is rearrangement to quinoid-type structures. The band at 1680 cm^{-1} is far too low in frequency to be assigned to an acid moiety. Therefore, it is postulated that it is due to the formation of quinone-type structures. Examination of a large number of quinones has shown that the general region in which these systems exhibit absorption is from 1660 to 1690 cm^{-1}, which is in good agreement with the observed frequency for the second carbonyl frequency appearing on oxidation.

Oxidative degradation does not stop at this stage but proceeds further. A third absorption band grows in at 1720 cm^{-1} and is accompanied by a broad band at 3100 to 3300 cm^{-1}. By using the difference-spectrum technique it is possible partially to resolve this band. The changes occurring indicate that the phenolic hydroxyl band is decreasing and an acid hydroxyl is appearing. Therefore, the final stage of the secondary oxidation can be formulated as shown in Fig. 6.

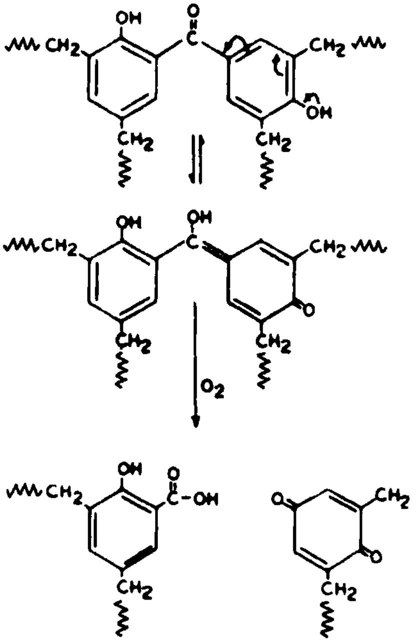


FIG. 6. Proposed chain scission process in phenol-formaldehyde resin oxidation: the major secondary reaction.

After the appearance of acid fragments no further changes occur that are detectable by infrared analysis. After many hours of continued heating the spectrum slowly diminishes to a few broad bands of no real analytical value. Sufficient data were obtained, however, to postulate and substantiate experimentally a sound working hypothesis for the oxidative degradation in phenolic resins.

Kinetic Studies

The oxidative reaction of the phenolic resins studied was expected to be first-order with respect to methylene concentration at the surface of the film sample. From data obtained on examination of the filmed resin in air, 30% oxygen, and pure oxygen it was apparent that the rate of oxidation was independent of the amount of oxygen over the sample. The rate of oxidation is dependent only on the available methylene groups at the polymer surface. The rate constants for the oxidation of the dihydroxydiphenylmethane group to the dihydroxybenzophenone system are summarized in Table 2. Plotting these data (−log *k* versus $1/T$) gives a straight line, whose slope, when multiplied by $2.303R$, yields an activation energy of 19.5 kcal.

TABLE 2

Rate Constants for the Initial Oxidation Reaction in Phenolic Resins at Various Temperatures

Temp., °C	$1/T$, $\times 10^{-3}$, °K	Rate constant, $\times 10^{-2}$ min^{-1}	$-\log k$
140	2.42	0.90	2.046
150	2.36	1.40	1.854
160	2.31	2.06	1.686
		2.37	1.625
170	2.25	4.94	1.306
180	2.21	6.88	1.162
		7.67	1.115
200	2.12	17.5	0.757
		17.8	0.750
220	2.03	37.6	0.425

A similar set of data based upon this initial oxidation reaction of a series of resins having regularly varying ratios of phenol to formaldehyde indicated that on oxidation at 160°C there was a good correlation between the rate of oxidation and the "P/F" ratio of the resin samples. Since there is a marked change in the reaction rate compared with the number of available methylene linkages, the postulate that the primary mode of oxidation is methylene oxidation is firmly established.

An insight into the secondary oxidation process can also be gained from a comparison of a bisphenol A modified resin and the standard resin used in this study. Since it is postulated that the ingrowth of the band at 1680 cm^{-1} is a measure of the quinoid structure prior to chain scission, a comparison of the two systems was made with the use of data obtained at 180°C. The rate constants for quinoid-type structure formation were found to be 2.58×10^{-2} min^{-1} for the phenolic resin but only 1.48×10^{-2} min^{-1} for the bisphenol-modified resin. The rate is approximately one half as great in the bisphenol resin. This data is in good agreement with the proposed mechanism, since the formation of quinoid species depends on the formation of oxidized methylene linkages.

The third step in the proposed oxidation mechanism is the formation of acidic functional groups by further oxidation of the quinoid intermediate. The rate constant determined by analysis of the ingrowing band at 1720 cm^{-1}, due to acid formation, was found to be 5.7×10^{-3} min^{-1} at 200°C. Compared to the rate constant for primary oxidation of methylene groups, this reaction is only 1/40th as fast. It might be thought that, once chain scission occurs and acid fragments are produced, extensive volatilization would take place, but this was found not to be the case.

Ether Linkages

When polymers containing ether linkages, by synthesis or by incorporation of 2,2′-dihydroxydibenzyl ether as a model com-

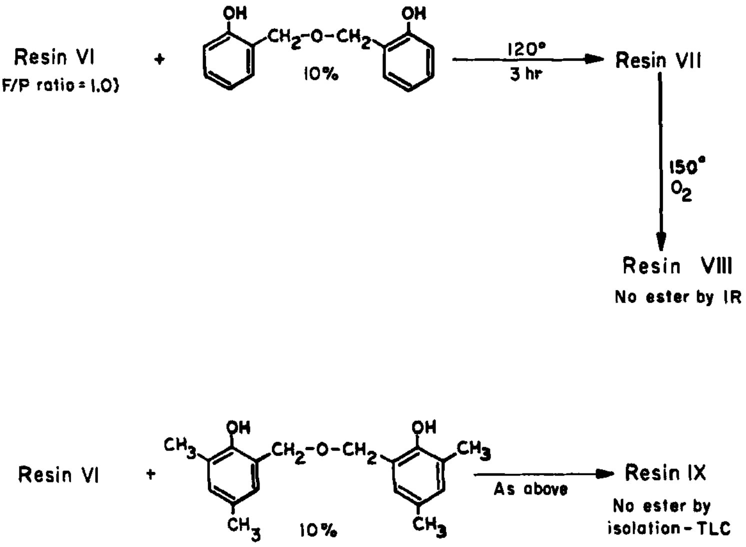


FIG. 7. Typical model compound studies in possible oxidations at ether linkages in phenolic resin systems.

pound into a resole (resin VI, Fig. 7, giving resin VII), were subjected to oxidation at 150°C in air, no evidence of ester formation (i.e., as shown in Fig. 8) was obtained. A further study with 3,3′,5,5′-tetramethyl-2,2′-dihydroxydibenzyl ether in resin VI also failed to give any trace of ester by direct isolation. In both cases, however,

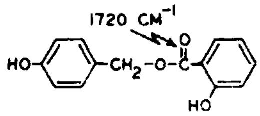


FIG. 8. Spectral characteristics and the typical structural unit from ether oxidation.

small amounts (approximately one percent) of the corresponding diphenylmethanes could be detected. These data indicate that the ether linkage is at least partially destroyed during the 120-to-150°C heating sequence but is not oxidized to the corresponding ester linkage (Fig. 9).

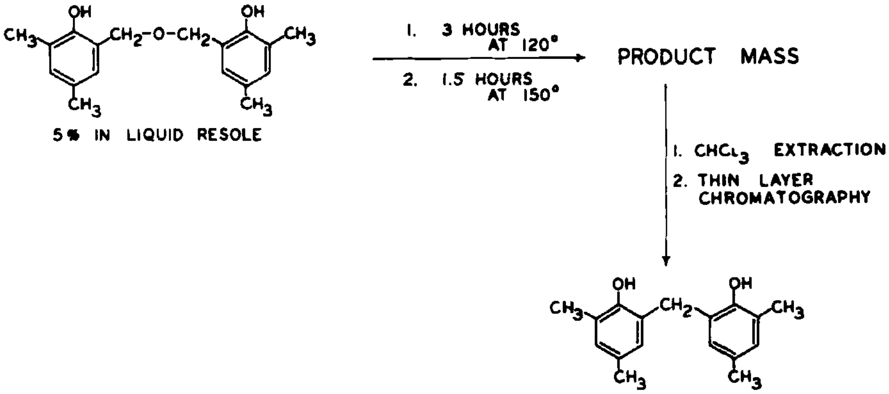


FIG. 9. The fate of the ether linkage during thermooxidative degradation of phenolic resins.

Effect of Extended Curing on Oxidation Rate

Postcuring the resole sample at 450°C in vacuo, followed by a study of its oxidative stability, yielded unexpected and interesting results. The postcured polymer has been shown to have a higher oxidative stability than the nonpostcured and partially oxidized resin. For example, it has been shown that the rate constants, as determined by infrared spectrophotometric monitoring of the ingrowth of benzophenone carbonyl groups, are quite large. By contrast, rate constants obtained from nonoxidized samples in this study (with the same method), cured at 450°C in high vacuum, are considerably smaller (by a factor of roughly 33). This comparison is summarized in Table 3.

TABLE 3

Comparison of Rate Constants Obtained for the Initial Oxidation Reaction of Phenolic Resins As a Function of Curing Temperatures

Temp., °C	$1/T$, $\times 10^{-3}$, °K	Rate constant $\times 10^{-2}$ min^{-1} at resin-curing temp., °C	
		120°	450°
180	2.21	6.88	0.22
		7.67	0.28
200	2.12	17.5	0.61
		17.8	0.56
220	2.03	37.6	1.12
			1.44

Plotting $-\log k$ versus the reciprocal of the absolute temperature gives a straight-line plot whose slope, when multiplied by $2.303R$, gives an activation energy of 16.7 kcal. This value corresponds favorably with the value for the same oxidation reaction obtained earlier on the resins cured at 120°C. It is also interesting that the rate constants obtained on the postcured resin (450°C) and the activation energy determined are almost identical with those obtained in a study of the oxidative degradation of polybenzyl.

Polybenzyl: A Nonhydroxylated Model Polymer

It was of interest to extend these and related studies to other activated methylene systems, to determine whether this mode of oxidation was common to polymeric materials bearing activated methylene substituents. In these studies model polymers and also the more complicated substituted systems have been and are being scrutinized both qualitatively and quantitatively.

Table 4 summarizes the observed spectral changes, and Table 5

TABLE 4

Observed Functional-Group Changes in Polybenzyl Oxidation at 170°C

Frequency cm^{-1}	Assignment	Change	Time of appearance, hr
3560	—OH (non-hydrogen-bonded)	Increase Decrease	1st 2nd
3400	—OH (hydrogen-bonded)	Increase	2nd
3050	═CH (aromatic ring CH)	Decrease (slow)	30th
2800	—CH_2 (aliphatic CH)	Decrease	4th
1660	C═O (diaryl ketone)	Increase	1st
1730 1780	C═O (linear anhydride, band pair)	Increase	10th
1260	C—O—C and C—O (diaryl ketone and linear anhydride, broad-band complex)	Increase	1st
1450	Aromatic ring	Decrease (slow)	30th

TABLE 5

Rate Constants for the Initial Oxidation Reaction in Polybenzyl at Various Temperatures

Temp., °C	$1/T$, $\times 10^{-3}$, °K	Rate constant, $\times 10^{-2}$ 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

indicates the rate constants obtained for polybenzyl oxidation by the infrared method. Analysis of the rate data yields an activation energy for the oxidative degradation, as manifested by the ingrowth of ketonic carbonyl, of 16.8 kcal.

At the initial stages of oxidation the major spectral change at all of the temperatures studied was the ingrowth of a ketonic carbonyl group at 6.0 μ (1660 cm^{-1}). Concurrently with this change two bands at 7.6 and 7.8 μ (typical or benzophenone) also show a steady increase in absorption with the time of oxidation. A very weak hydroxyl absorption (nonbonded) appears after the concentration of carbonyl has reached approximately an absorbance level corresponding to 2% of benzophenone linkages (estimated from the standard mixtures). This data should not be interpreted as excluding the presence of the hydroxyl absorption prior to this time but, rather, since in its nonbonded form it has a relatively weaker absorption compared to the strong carbonyl, this species is not spectrally detected. As the initial oxidation process continues, the hydroxyl band shifts to 3.0 μ (hydrogen-bonded). After extended periods of oxidation the hydroxyl vibration broadens and extends

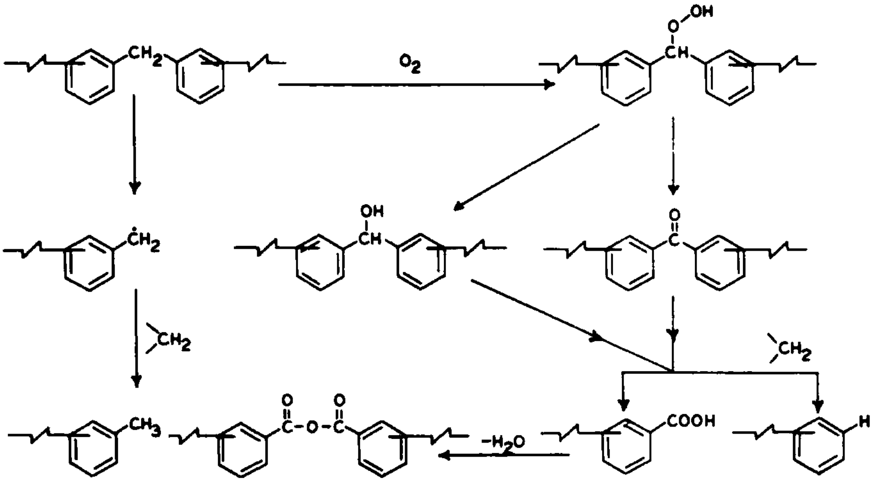


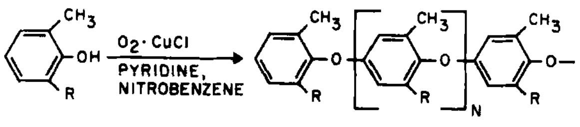
FIG. 10. Summary of the primary reactions in the thermooxidation of polybenzyl.

beyond 4.0 μ as a broad diffuse band. This suggests the formation of a small amount of acidic components during the terminal stages of oxidation. It should be pointed out in this respect 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 5% a doublet appears at 5.64 μ (1730 cm^{-1}) and 5.77 μ (1780 cm^{-1}). 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 absorption. This is consistent with the formation of acids in the later stages of oxidation from the anhydride linkages.

With these observations in mind the oxidation route similar to that proposed for phenolic resins may be proposed with some degree of certainty, as shown in Fig. 10.

Thermooxidative Degradation of Poly(phenylene ether) Polymers (8)

It was of interest to us to investigate the course of oxidative degradation of poly(phenylene ether) polymers, since it might be expected that exposure to oxygen-containing atmospheres would enhance the stability of the polymer via oxidative cross-linking reactions. If such was the case, extensive investigations in these systems would be well justified, since few polymers exhibit reasonable flexibility at low temperatures and high thermal stability in oxygen-containing atmospheres at elevated temperatures. In this regard, it was deemed most desirable to study the oxidative degradation of poly(2,6-dimethyl-1,4-phenylene ether) and poly(2-methyl-6-isopropyl-4-phenylene ether) (Fig. 11). Solid-phase changes were followed via continuous infrared examination at reaction temperatures between 150 and 300°C. Volatile products from degradation in air were examined by means of gas chromatographic separation techniques, trapping of effluent fractions, and chemical and physical evaluation of individual product structures. The over-all thermal changes were contrasted in both air and inert atmospheres by means using both differential thermal analysis and thermogravimetric analysis techniques. Short-term experiments in oxygen were followed by solubilization of the polymer and studies of the changes in viscosity or gel content, or both, with time of exposure. Inert-atmosphere degradation was followed by mass spectrometric techniques. It was hoped that by using this



WHERE: R = $-CH_3$, N = 390, M.W. = 45,100

R = $-CH(CH_3)_2$, N = 75, M.W. = 10,100

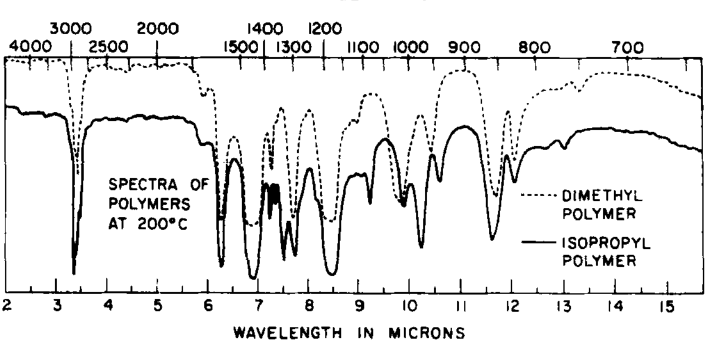


FIG. 11. The poly(phenylene oxide) polymers investigated and their infrared spectral characteristics.

combination of techniques a reasonable evaluation of the degradation process could be gained for alkyl-substituted poly(phenylene ether) polymers.

Initial weight-loss experiments were carried out with samples degraded in oxygen at 250°C for 1.5 hr. The differences between the poly(2,6-dimethyl-1,4-phenylene ether) and the poly(2-methyl-6-isopropyl-1,4-phenylene ether) samples were quite startling. After 1.5 hr at 250°C the dimethyl-substituted polymer showed weight losses averaging approximately 46%. The residues were badly charred. On the other hand, the isopropyl polymer, although darkened in color, lost only 1.8% of its original weight. Further examination of the reaction of the dimethyl polymer with oxygen indicated that a vigorous reaction took place between 3 and 10 min of exposure to oxygen at 250°C, depending upon the flow rate of oxygen through the apparatus. This exothermic reaction was also examined by means of differential thermal analysis. A comparison of the two polymers is shown in Figs. 12 and 13. At about 210°C a vigorous, highly exothermic reaction commences

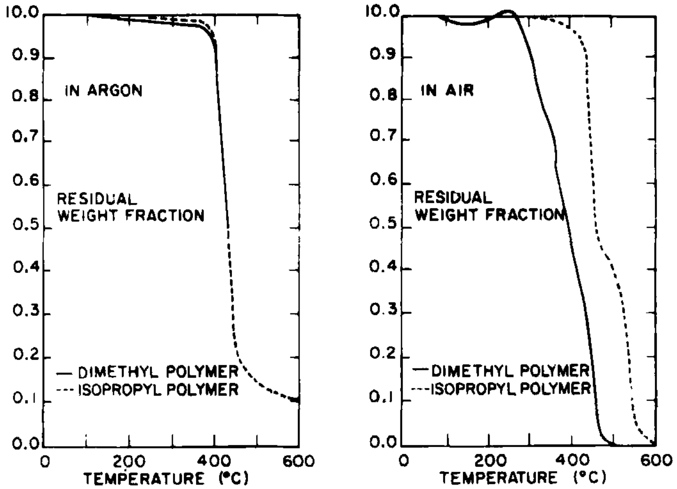


FIG. 12. Thermogravimetric-analysis data for the weight-loss characteristics of poly(2,6-dimethylphenylene oxide) and poly(2-isopropyl-6-methyl-phenylene oxide) in argon and air atmospheres.

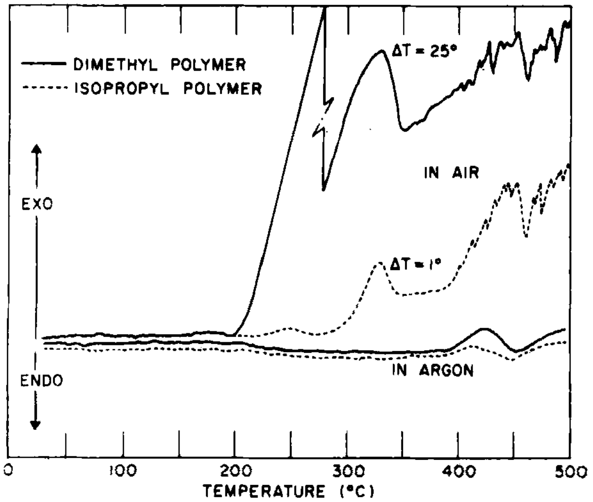


FIG. 13. Typical differential-thermal-analysis data for the poly(phenylene oxides) in both air and argon atmosphere.

for the dimethyl polymer. A much milder reaction is observed, however, for the isopropyl-substituted polymer. These data suggested to us that a peroxidic species was formed, which decomposed rather vigorously in the 200-to-300°C temperature region.

Indeed, in several experiments on small samples in glass apparatus the sample was observed to burn with such violence that the pressure build-up in the apparatus caused rupture of exit-tube connecting joints. In argon, however, no such decomposition was observed for either material. In air the weight losses from film samples were quite interesting. At 200°C the dimethyl polymer lost 10.1% of its weight in 574 min, whereas the isopropyl polymer lost only 4.7% of its weight in the same time period. Examination of the infrared spectra obtained from the films indicated that the initial changes in functional groups in the solid phase were the same for both samples (Fig. 14). Carboxylic acids were detected spectrally, and so was the formation of quinoid-type linkages. Collection of volatiles from the oxidation process at 250°C indicated a vastly different route of volatilization of products from the two polymers. Spectrally, the ingrowth of bands paralleled the weight-loss data (i.e., the dimethyl degraded significantly faster than the

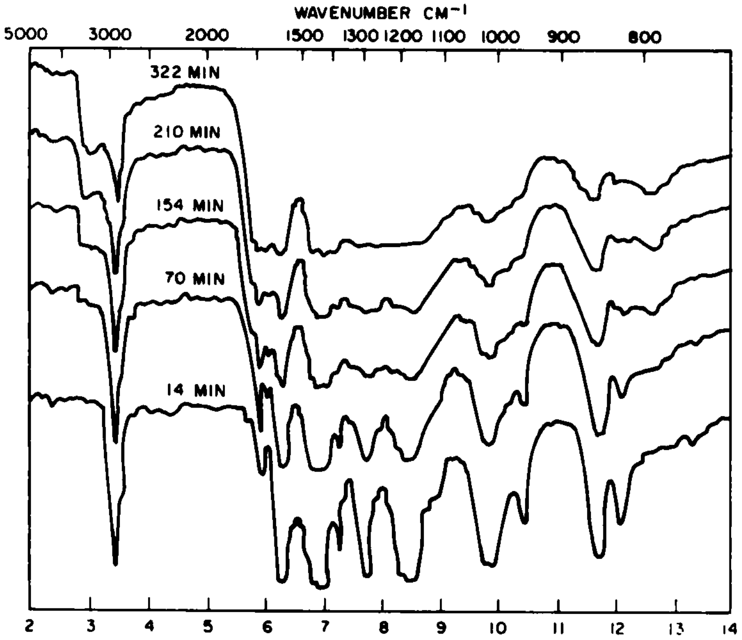


FIG. 14. Typical infrared spectral changes in the dimethyl polymer as a function of time during heating in air at 250°C.

isopropyl polymer). The volatiles from the isopropyl polymer were predominantly water and acetone. From the dimethyl polymer some sixteen different components have been detected by gas-liquid chromatography (Fig. 15). Of the sixteen components four have been isolated and amount to approximately 80% of the total volatile products; two of these four are alkyl-substituted phenols, one is a quinone, and one is an ester. The formation of these

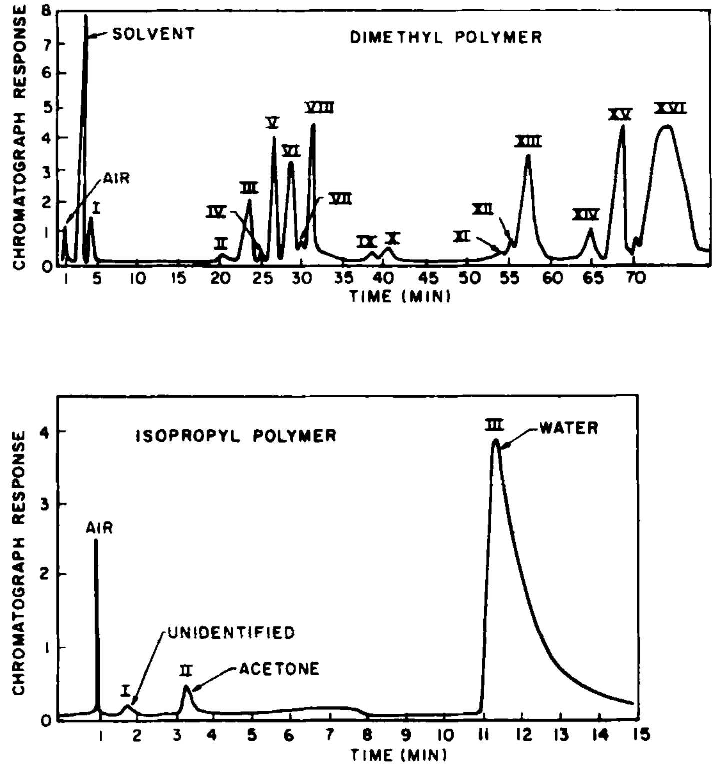


FIG. 15. Gas chromatographic data summarizing the volatile degradation products formed on the oxidation of the poly(phenylene oxides).

products indicates a complex route for the degradation of the dimethyl polymer. Viscosity measurements indicate that the viscosity of the isopropyl polymer increases significantly during the early stages of the oxidation (from an intrinsic viscosity of 0.380 to 0.487 after 5 min of oxidation). Unfortunately, after comparable periods of time the dimethyl polymer could only be examined via changes in gel content. Apparently, however, cross-linking had occurred. On the basis of volatile components, however, it must be concluded that oxidation at the isopropyl group, although expected to be faster than attack at the methyl group, results in the formation of a polymer that does not readily undergo further degradation to volatile components at the temperature of degradation. No phenolic or quinoid species could be detected from samples of the isopropyl-substituted polymer exposed to 250°C for 1.5 hr. These data, when contrasted with the significant formation of chain-ruptured products from the dimethyl polymer and coupled with

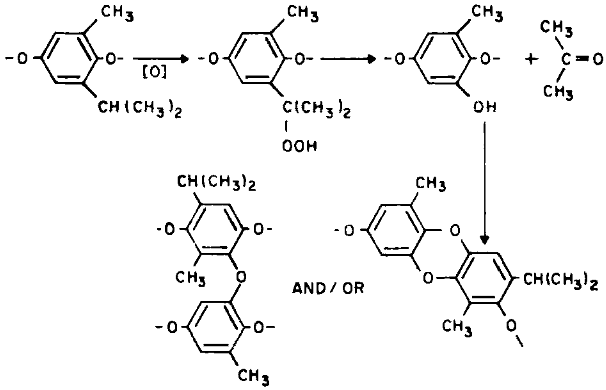


FIG. 16. Postulated initial degradation reactions at the isopropyl group on oxidation.

nonidentical solid-phase changes observed in the infrared spectral changes of both materials, strongly suggests the oxidative cross-linking of the isopropyl polymer. Since the samples widely varied in initial molecular weight (40,000 for the dimethyl polymer versus 10,000 for the isopropyl methyl polymer), these results can best be interpreted by using a cross-linking postulate to account for the observed solid and volatile composition changes. Since both polymers exhibit cross-linking behavior, it must be concluded that the dimethyl polymer linkage formed oxidatively is unstable or at least of poor thermal stability, whereas the linkage formed in the isopropyl system exhibits stability at least as satisfactory as the ether linkage itself.

Oxidative changes at the isopropyl group are best accounted for in the diagrammatic representation shown in Fig. 16. Attack at the isopropyl group to give acetone and an appendaged oxygen for further ether cross-linking seems likely from these initial studies. Infrared studies indicate an appreciably greater loss in aliphatic carbon-hydrogen groups in the isopropyl polymer than in the dimethyl polymer. Moreover, the aromatic substitution region

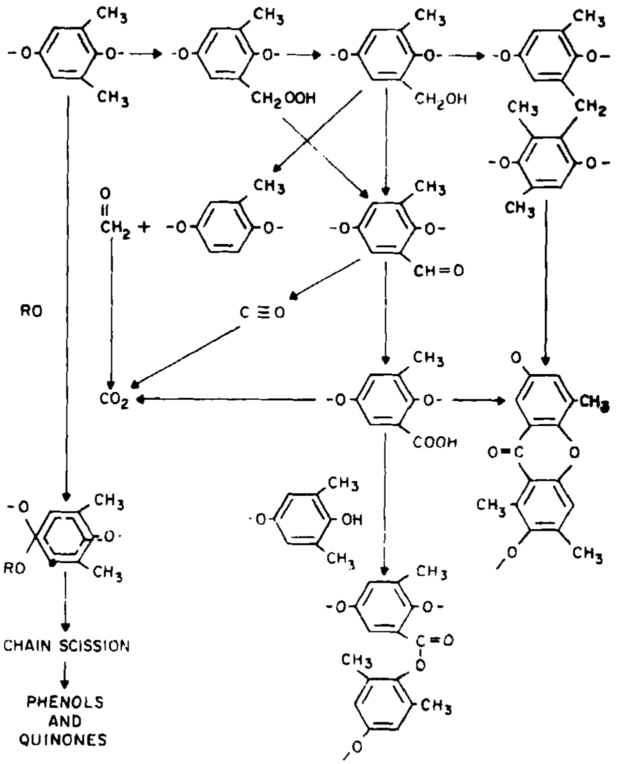


FIG. 17. Postulated initial degradation reactions at the methyl group on oxidation.

shows significant changes in band intensities of the aromatic carbon-hydrogen bending absorptions, suggestive of cross-linking via the formation of an additional ether linkage. The dimethyl polymer degrades more severely via a rapid chain-scission process after the uptake of an appreciable amount of oxygen, presumably as the hydroperoxide or peroxide linkage, as suggested in the sequence shown in Fig. 17. Apparently, on exposure to oxygen-containing atmospheres the polymer rapidly builds up large amounts of peroxidic species, which decompose concurrently with chain scission rather than cross-linking. These observations suggest that the differences in the course of the degradation of the two polymers lies in the relative stabilities of the peroxidic intermediates and their potential modes of decomposition. Volatiles from the product trapping studies indicate extensive oxidation of the methyl groups to carbon dioxide at 250°C. These data seem consistent with the reaction sequence shown in Fig. 17.

The cross-linking process observed in these studies for the isopropyl-substituted aromatic ring seems significant. A polymer containing such a group attached to an aromatic ring could well be employed for improving heat stability and residue yield by delaying the thermal loss of aromatic fragments via the formation of a series of new ether cross-links. Thus, a polymer system exhibiting high flexibility at reasonably low temperatures may, on exposure to oxygen-containing atmospheres at elevated temperatures, cross-link to a material of high thermal stability.

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