

3 THE EFFECTS OF MOLECULAR STRUCTURE ON THE THERMOCHEMICAL
PROPERTIES OF PHENOLICS AND RELATED POLYMERS

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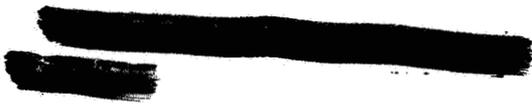
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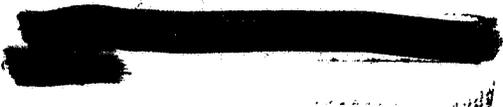
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INTRODUCTION

The particular combination of thermophysical and thermochemical properties needed for major components of reentry heat shields for manned space vehicles are characteristic of char-forming polymers. The thermal degradation of simple phenolic resins, and structurally related aromatic polymers, can protect the substructure of space vehicles from aerodynamic heating encountered during reentry. A schematic representation of the char-forming pyrolysis of an ablative heat shield of this kind is shown in figure 1. A char cap forms and covers the front surface as indicated by the shaded area. It is characterized in part by a surface temperature, T_s , and a thickness, X_c , which in the absence of surface removal reactions, increases with the time of exposure to the incident heat flux. (Part of this heat is radiated from the surface by the hot char.) The gaseous species, depicted as flowing counter current to the direction of the applied heating, are first formed by the pyrolysis of the polymer within the narrow decomposition zone as indicated. Lateral flow of these gases is restricted by the surrounding material. Convective heat transfer to the surface of the vehicle is partially blocked by the diffusion of the pyrolysis gases from surface. Under steady-state ablation, the pyrolysis zone is bounded by two definite isotherms indicated as T_D , the polymer decomposition temperature, and T_C , the lowest temperature required to form a stable char residue of a definite density and composition. Usually



these isotherms proceed into the pyrolyzing heat shield at uniform rates. The rapid thermochemical reactions which take place in this zone and which yield primary char are essentially anaerobic ones. Oxygen and other reactive gas species diffusing from boundary layer to the char surface are scavenged by surface combustion before reaching the decomposing polymer. The direction of flow and the boundary-layer combustion of pyrolysis vapors also prevent oxygen from reaching the pyrolyzing virgin material. It is clear that reaction mechanisms leading to primary yields of ablative char proceed in the absence of an oxidizing environment. This fact is of key importance in selecting experimental conditions to use for determining the thermochemical properties of interest to heat shield designers.

The primary char yield is one of the most important thermochemical properties of polymers when considered for use in ablative heat shields. It is defined here as the mass of stable carbonaceous residue formed by the complete thermal decomposition of unit mass of polymer in the absence of any secondary cracking reactions. It is this yield which basically controls the ratio of the rate of vapor production to char formation, which in turn determines the relative thermal efficiency of an ablative material in a particular heating environment.

It is the primary purpose of this paper to present an analysis of the structure of phenolic resins and related polymers by which it is possible to predict the primary char yields obtained under

specific thermogravimetric analysis conditions. Finally it will be shown how the analysis can account for the ablative char yields obtained from composites formulated from these resins, under simulated reentry heating conditions.

THERMOCHEMICAL REACTION MECHANISM

To develop the analysis, a mechanism is proposed which postulates that the formation of stable chars occurs as the result of a series of consecutive and noncompetitive pyrolysis reactions, which retain only those carbon atoms which were present in the virgin polymer as multiply bonded phenolic rings. Pendant aromatic rings and aliphatic side chains are lost as vapor products. It is suggested that in the absence of oxygen or preoxidized structures, the initiation step for the pyrolysis of simple phenolic resins is the rupture of the carbon-carbon bond connecting the aromatic pendant groups to the main chain as shown in figure 2. To be sure this process occurs along the main chain as well, but when it occurs on either side of a terminal methylene bridge a phenol or cresol radical is created. These species eliminate aromatic carbon atoms by abstraction of hydrogen, as indicated, to form volatile phenol and cresol as vapor products. It has been observed that both of the parent ions of phenol and cresol are formed in about equal amounts when a phenolic novolac resin is decomposed at 300^o C in the inlet of a time of flight spectrometer at 10⁻⁷ torr.

These reactions may be expected to produce free radical main chain intermediates with structures typified by II and V. To account for the formation of the new diaryloxy and keto groups produced in the formation of a definite, thermally cross-linked intermediate over a temperature range of 300°-500° C, a rearrangement of these primary scission products as given in figure 2 is suggested.

The formation of this key thermally cross-linked intermediate (VIII) is clearly evident in the kinetic analysis of thermograms obtained for variously cross-linked phenolic novolacs reported by Winkler (ref. 1). The maximum rate of weight loss observed during the formation of this cross-linked intermediate at 375° C varies proportionally with the observed sol fraction which in this case is proportional to the total weight fraction of polymer containing pendant aromatic rings. The amount of VIII formed was found to vary, as expected, with the initial concentration of the pendant groups. This thermal cross-linking reaction is essential to retain the multiply bonded aromatic rings as char. Structurally similar polymers like polybenzyl, which do not form cross-linked intermediates during pyrolysis, do not produce carbonaceous chars.

The thermally cross-linked intermediate, VIII, loses methane and carbon dioxide above 500° C as shown in figure 2. Scission and recombination produce the unstable char (IX) observed to form at 500° C. As can be seen IX, obtained as a black brittle solid, is in effect a highly cross-linked diphenyl ether polymer. Over a temperature range from 500° to 800° C, thermally stable char networks

are depicted as forming by continued cross-linking of the aromatic rings present in IX with elimination of both hydrogen and water. These gaseous species and the temperatures at which they are produced are consistent with the mass spectrometric data of Madorsky (ref. 2) for simple phenolic resins.

PHENOLIC NOVOLACS

To test this mechanism, and determine the exact relationship between molecular structure and char yield, a series of variously cross-linked phenolic novolacs were prepared by reacting different amounts of hexamethylenetetramine with an acetone-soluble phenolic novolac with a molecular weight of 837, containing eight phenolic rings per molecule. These cured polymers were characterized by elemental, infrared and sol gel analysis. A series of seven polymers ranging in sol content from 100 to 9 percent, and average molecular weight of repeat unit from 837 to 882 were prepared. These polymers were pyrolyzed under anaerobic conditions, that is, using argon as a transpirational gas at heating rates of 3° C per minute. Typical thermograms for these phenolic novolacs are shown in figure 3. Here the remaining weight fraction, Y, is plotted as a function of the programmed temperature. These thermograms were started at room temperature, and finally terminated at 800° C when the weight loss rates of the char residues became less than 1 percent per minute. It can be seen that the remaining stable char residue, Y_c , varies with the degree of cross-linking expressed as the measured

sol fraction. A char yield of 64.0 percent is obtained from the most highly cross-linked polymer prepared. The uncross-linked oligomer gives a char yield of 43.2 percent.

The proposed overall reaction mechanism can be tested by applying it to see if it accounts for the observed variation in char yield with structure of these phenolic novolacs. This can be done most conveniently by expressing the number of singly bonded phenolic groups present in polymer as a function of the sol fraction X_s , and the number of pendant groups of this kind initially present in the polymerizable oligomer. For six carbon aromatic rings and for any number of pendant phenolic rings initially present in the parent oligomer, the char yield is given by the equation shown in figure 4 where

N = total number of aromatic rings per average mer unit

M = average molecular weight of repeating mer unit

P = average number of pendant or singly bonded aromatic
rings in oligomer

M' = average molecular weight of oligomer.

The proposed mechanism can be applied to the oligomer by this equation to calculate the number of pendant phenolic end groups present in this resin with a sol fraction of 1.00 and a char yield of 43.2 percent. These observations require that the parent phenolic novolac possess an average of three pendant groups.

The observed thermogravimetric char yields for the six phenolic novolacs prepared has been plotted as a function of the measured sol fraction in figure 5. It can be seen that, as required by the mechanism, the char yield decreases linearly with increasing sol fraction of polymer. The line in figure 5 was obtained by use of the equation, the structural parameters, and the measured sol fraction. The observed char yields are in excellent agreement with those predicted from this equation.

DIPHENYL OXIDES

To generalize this pyrolysis mechanism for other classes of phenolic derived polymers, series of diphenyl oxide modified phenolics and anhydride cured epoxy novolacs were investigated. These polymers were chosen in such a way as to permit a wider variation in the number of aromatic groups per gram of polymer, cross-link density, and the number and kinds of pendant side chains than is possible with the simple phenolics and consequently a corresponding wider range of char yield.

The diphenyl oxide modified phenolics were prepared from combinations of monomers given in figure 6. The polymers were obtained by condensing the tetramethylol derivative and its higher homologs with the diphenyloxide diphenol, its isomers, and tertiary butyl substituted derivatives. These monomers were polymerized at different mol ratios. Elementary analysis, with exception of polymers from the tertiary butyl derivative, indicated that for every four

reactive diphenol sites, about 3.2 have reacted to form effective cross-links. From this characterizing information it was possible to calculate an effective equivalency ratio for each polymer system, that is, the ratio of number of methylol equivalents reacted to the number of reactive diphenol sites at completion of polymerization.

These polymers, like the simple phenolic novolacs, gave finite yields of stable primary char in thermogravimetric tests by the time a temperature of 800° C was attained. It was found it was possible to correlate these observed char yields with the information given for monomer structure, the effective equivalency ratio, and the general reaction mechanism proposed for simple phenolics. The results of this correlation are given in figure 7. Here the char yield is given as a function of equivalency ratio, r . It can be seen that the observed char yields lie close to the lines predicted by the equation, and go through a maximum at $r = 1.00$ as expected. Isomeric (ortho para) differences do not seem to be important in controlling the char yields. Application of this analysis to the t-butyl derivatives shows that this derivative is present in polymers as an unreacted diluent.

ANHYDRIDE CURED EPOXY NOVOLACS

A third class of phenolic derivatives was investigated by polymerizing Nadic Methyl Anhydride with the glycidyl ethers given in figure 8. The functionality of the glycidyl ether moiety with the structures given here was varied by reacting them individually

or as mixtures at a fixed equivalency ratio of 0.85 with respect to the anhydride. Nine polymers were obtained by polymerizing mixtures of the two glycidyl ethers (A) and (C) with (B) at the fixed equivalency ratio of 0.85. The resulting polymers were characterized by infrared, elementary, and swelling volume analysis.

These polymers also gave stable char yields in thermogravimetric tests by the time a temperature of 800° C was attained. It was found that the char yield of these polymers varied linearly with the swelling volume. As the concentration of the glycidyl ethers with higher functionality increases in the polymer, there is a corresponding increase in phenolic rings multiply bonded through methylene groups and a proportionate decrease in swelling volume. According to the general mechanism, these are the only aromatic rings in these polymers which should be expected to contribute to char yield.

If one applies the analysis given for the simple phenolics to these polymers, the calculated values for the observed char yields are consistently low. The differences observed in each case are exactly and uniquely equal to the contribution that would be made by the three carbons of each epoxy group in the polymers.

An analytical expression is given which takes into account the contribution of these oxirane carbons in figure 9. The notation N, M, and P have the same definition as given above, and S is the total number of epoxy carbons per average mer unit. The observed thermogravimetric char yields for the nine epoxy novolacs prepared

are plotted here as a function of those calculated by applying this equation to the structural parameters of these resins. This agreement is sufficiently close to lend considerable support to general application of the proposed mechanism to complex derivatives of phenol systems.

COMPOSITES

To compare the ablative char yields under one-dimensional heating at high flux rates, simulating reentry heating, two types of composites were fabricated from the model polymers. It was necessary to obtain the polymers in composite form to prevent thermally induced stress cracking and severe spalling of these brittle resins when pyrolyzed at high heating rates.

The hexa cured phenolic novolac which gave a sol fraction of 0.51 and a char yield of 51.2 percent was formulated with 6-6 nylon and phenolic microspheres as given in figure 10. This composition was fabricated by procedures described by Keller (ref. 2) and thermochemically characterized as given in reference 3. As indicated here, the nylon component functions as a vapor producer only and does not contribute to char formation. It has been shown by Winkler (ref. 1) that there are no thermochemical interactions between the vapor products of the nylon component and the phenolic resins by observing the char yields as a function of the weight fraction of nylon in a series of polyblends with the hexa cured phenolic resin. This fact

permits one to estimate the expected thermogravimetric char yield for this composite from a knowledge of the char yield of the individual components and their weight fraction.

Two of the Nadic Methyl Anhydride cured epoxy novolacs, which gave 11.0 and 23.1 percent thermogravimetric char yields, respectively, were mixed and cured with 5 percent chopped pure quartz fiber. This amount of fiber was sufficient to obtain well-behaved ablation performance.

Reentry heating was simulated by use of an arc-imaging furnace. It was possible to obtain applied heating rates in range of 20 to 150 cal cm⁻² sec⁻¹ and surface temperatures between 1700° and 3000° K. These conditions correspond to heating rates of decomposing polymer of 5°-8000° C per minute as compared with 3° C per minute as employed in thermogravimetric tests.

The ablation char yields were determined by removing the char cap at pyrolysis zone. The results obtained are compared with thermogravimetric char yield in figure 11.

It can be seen for the phenolic-nylon composite that up to heating rates of approximately 25 cal cm⁻² sec⁻¹ there is good agreement between the thermogravimetric char yields and arc furnace char yields. There is observed an increase in char yield at the high heating rate condition of about 9 percent. This higher heating rate produces a surface temperature of about 3000° K. The increase in char yield is believed to be due to the cracking of carbon bearing vapor species on the hot char matrix formed as primary char.

This increase in char yield can be accounted for by assuming that the nylon vapors contribute exactly four atoms of carbon for every mer unit decomposed by secondary cracking.

The composite derived from the anhydride cured epoxy novolac ENC-1 also gave ablation char yields in good agreement with the calculated primary char yield. An increase of about 4 percent is observed at the high heating rate. This increase is also attributed to cracking and secondary char deposition. It appears that the aromatic species also evolved as vapor products are not cracked by this secondary process at the high heating rate. This conclusion is indicated by the result obtained with the low char yield composite ENC-2. Here the principal vapor products are aromatic species. In this figure it can be seen that the ablative char yield of this composite agrees fairly well with the primary char yield from thermogravimetric analyses at both the low and high heating rate. It can be concluded that the formation of secondary char depends on both the char surface temperature and the chemical constitution of the vapor products produced by the primary char-forming processes.

SUMMARY AND CONCLUSIONS

It has been possible to account for the char-forming reactions of these phenolic derived resins in terms of a general pyrolysis mechanism for these classes of polymers. An analysis based on this mechanism has been developed which predicts, from molecular

structure, the observed thermogravimetric char yields accurately over a range from 11 to 65 percent yield. Application of this analysis makes it possible to control the primary rates of vapor to char production required for a particular heat shield application.

Composites have been developed from these polymers and have been tested under one-dimensional pyrolysis simulating reentry ablation. Up to applied heating rates of about $25 \text{ cal cm}^{-2} \text{ sec}^{-1}$, the observed char yields agree quite closely with those obtained in thermogravimetric tests or calculated from analysis. It is tentatively concluded that the primary char-forming processes with these classes of materials are independent of polymer heating rate over a range of temperature rise rates varying from 2° to 5000° C per minute. With certain composites and at heating rates greater than $25 \text{ cal cm}^{-2} \text{ sec}^{-2}$ an additional amount of char is formed due to secondary pyrolysis of vapor products within the char matrix induced by high char temperatures. These secondary processes seem to depend on surface temperature, pressure, and the chemical nature of the vapor products. It should be possible to elucidate the mechanisms involved in these secondary processes from experimental studies under one-dimensional heating and the information presented here about the primary ones.

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2. Keller, L. B.: Development of Characterized and Reproducible Syntactic Foam of Phenolic Nylon for Heat Shields. Hughes Aircraft Report, P-66-49, Dec. 1965 (CR-73041).
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PYROLYSIS MECHANISM OF CHAR FORMING ABLATORS UNDER UNIDIRECTIONAL HEATING

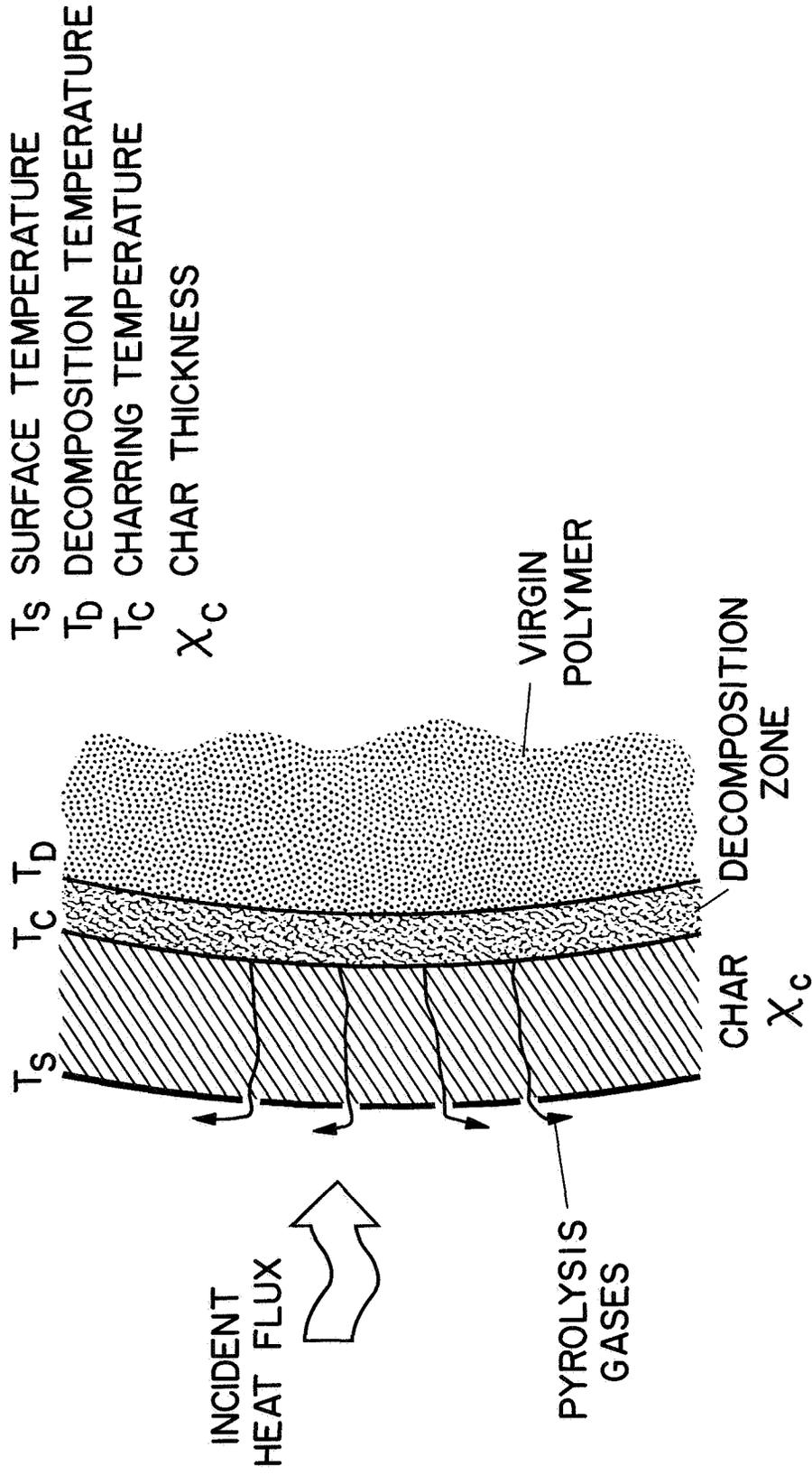


Figure 1.

PRINCIPAL STEPS IN NONOXIDATIVE THERMAL DEGRADATION
OF PHENOLIC - NOVOLAC RESINS (I)

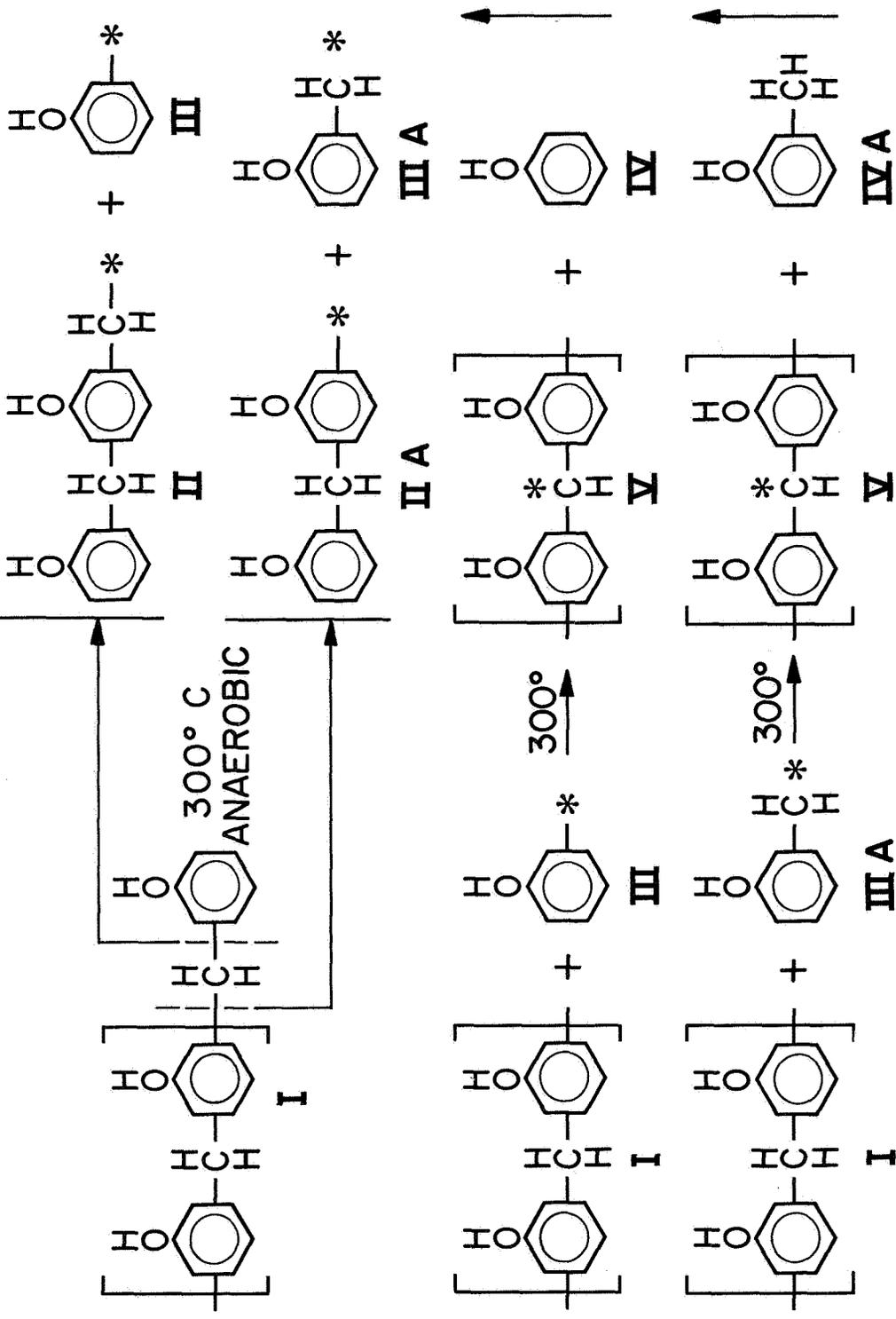


Figure 2.

TERMINATION REACTIONS FORMING STABLE THERMALLY
CROSS-LINKED INTERMEDIATES

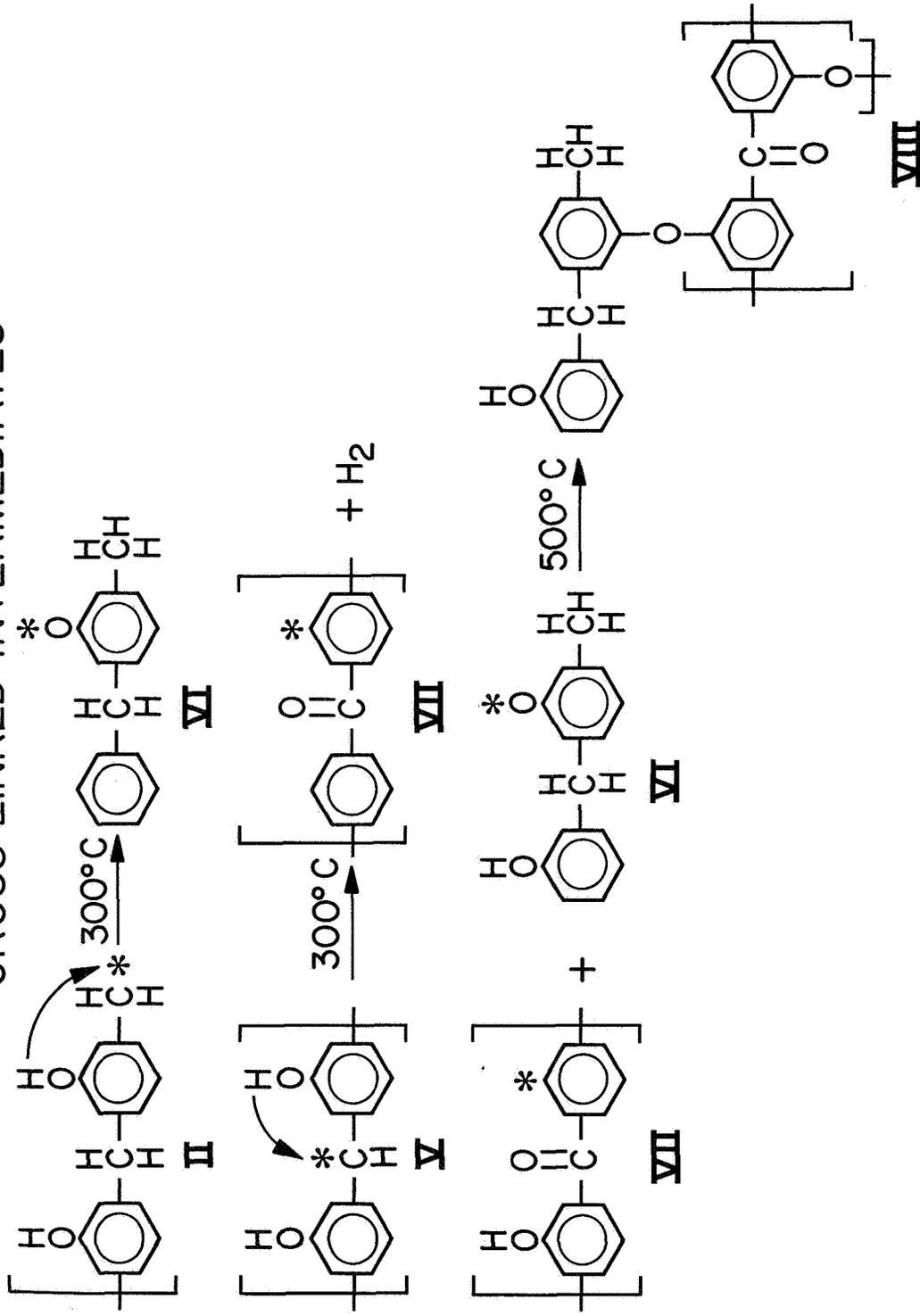


Figure 2.- Continued.

DECARBONYLATION AND CHAR FORMATION REACTION 3

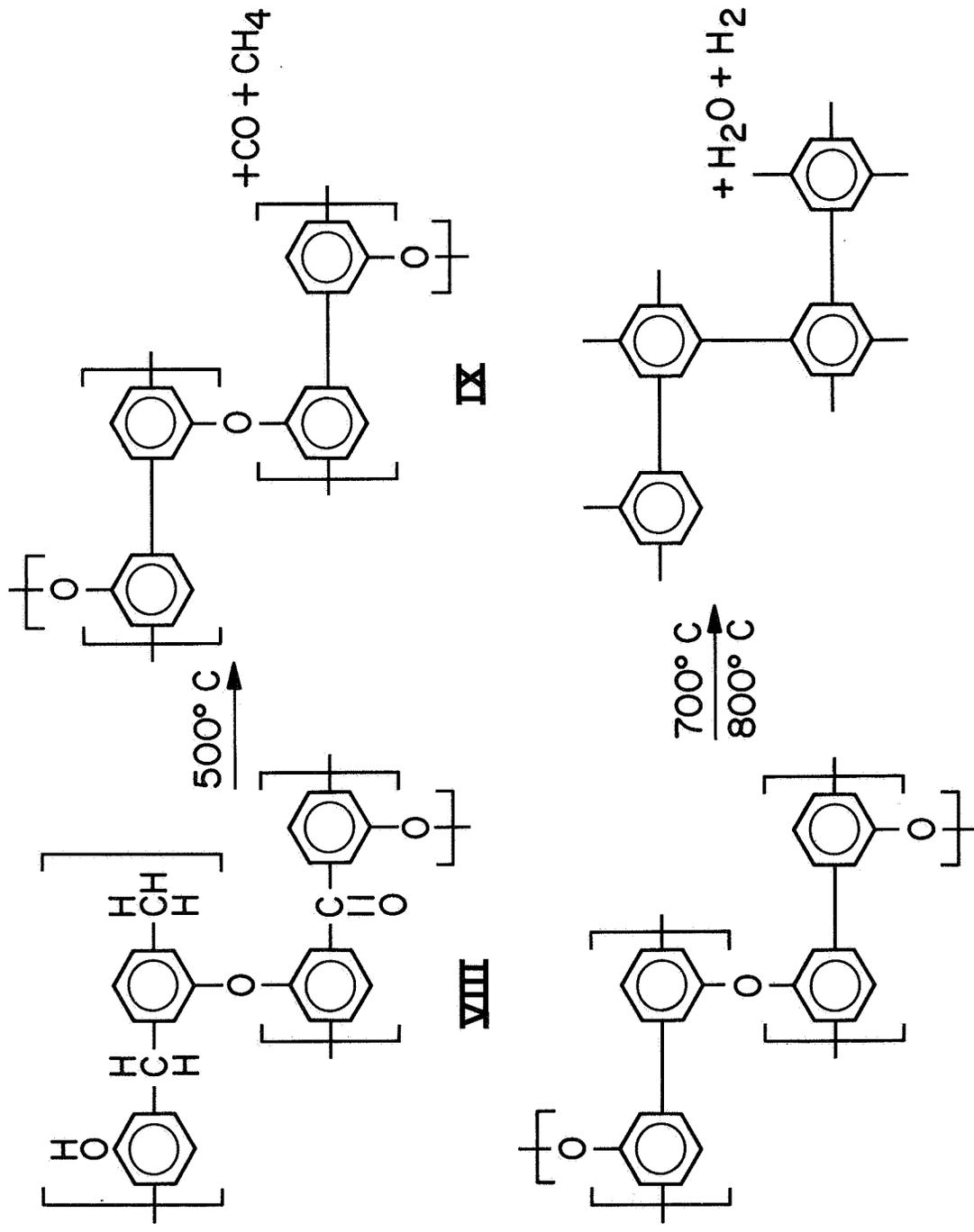


Figure 2.- Concluded.

EFFECT OF CONVERSION ON PYROLYSIS OF PHENOLIC RESIN

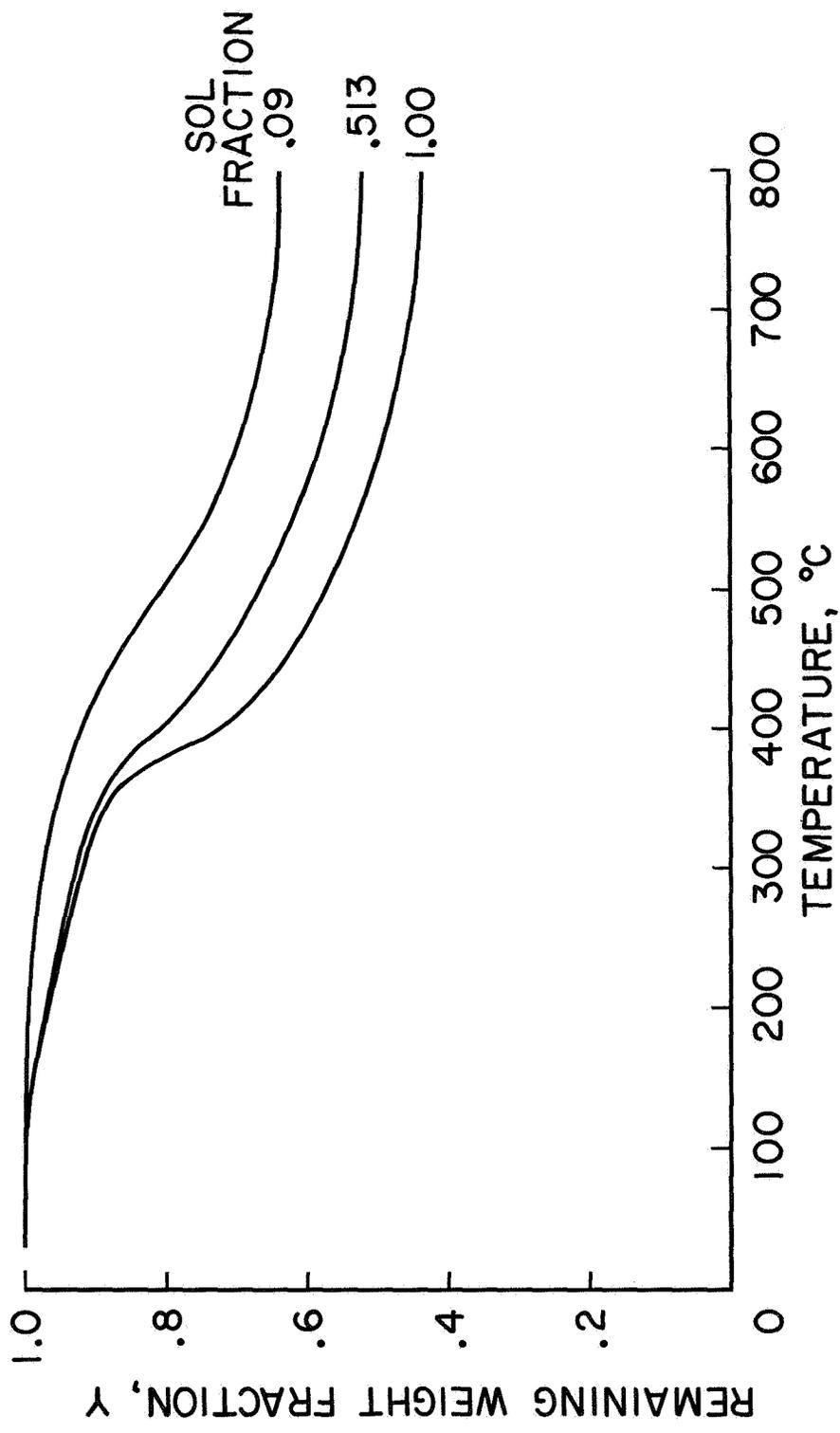


Figure 3.

CHAR YIELD FOR PHENOLIC POLYMERS

$$Y_c = 72.06 \left[\frac{N}{M} - \left(\frac{N-P}{M'} \right) X_s \right]$$

N - NUMBER OF AROMATIC RINGS PER
AVERAGE MER UNIT

M - AVERAGE MOLECULAR WEIGHT OF THE
REPEATING MER UNIT

P - AVERAGE NUMBER OF PENDANT
END GROUPS

M' - MOLECULAR WEIGHT OF THE OLIGOMER

X_s - SOL FRACTION

Figure 4.

VARIATION OF THERMOCHEMICAL YIELD WITH SOL FRACTION

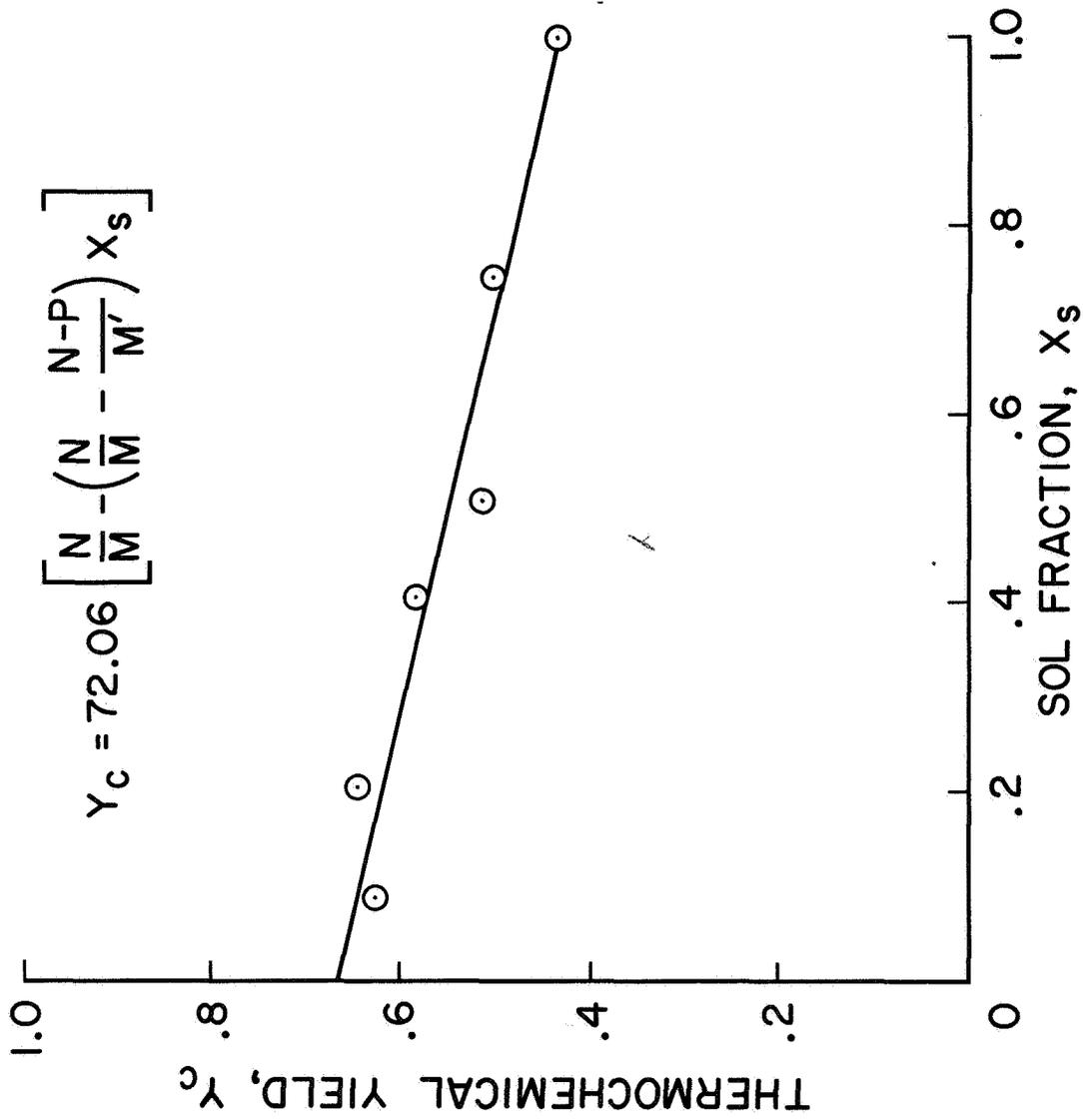
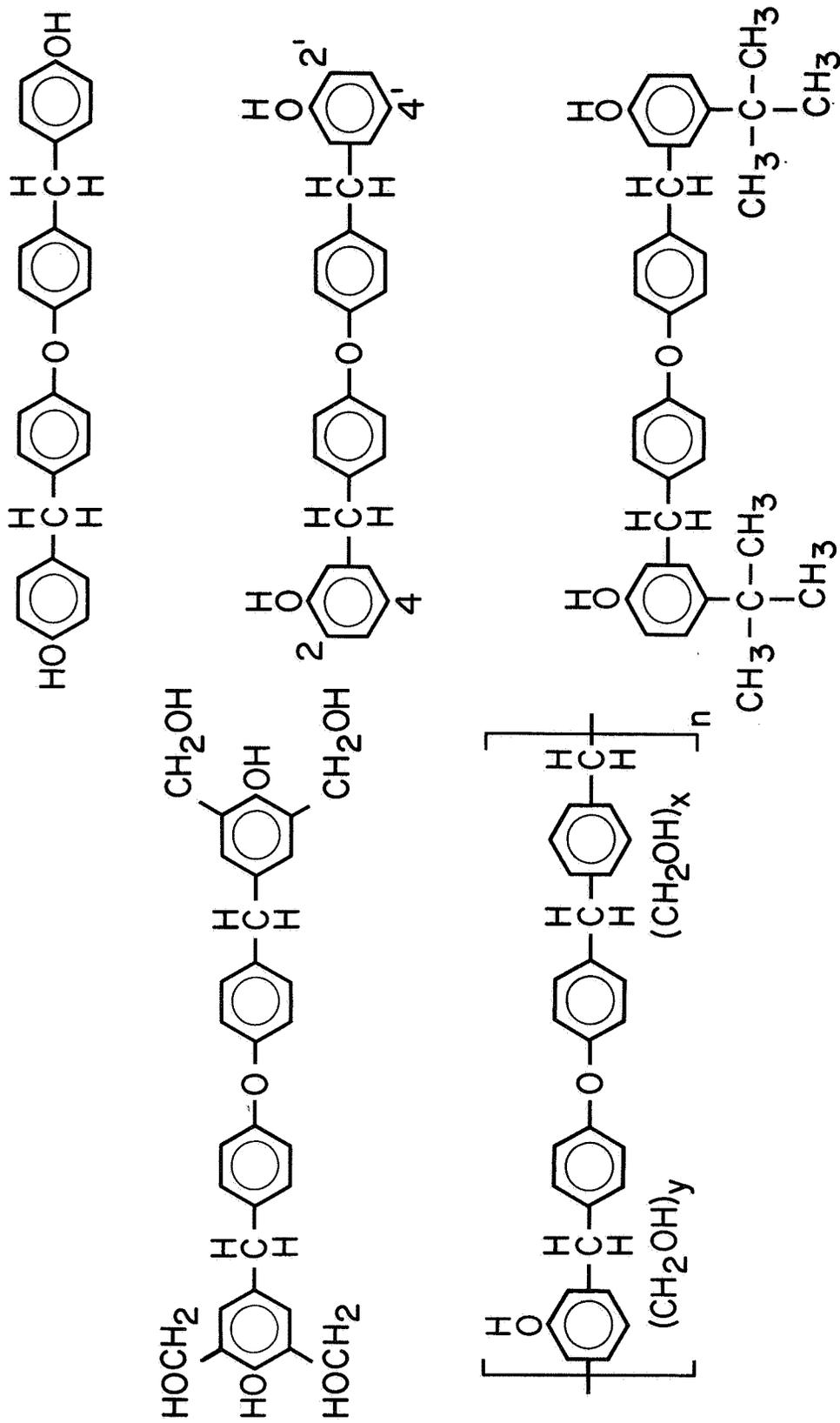


Figure 5.

MONOMERS AND PREPOLYMERS OF DIPHENYLOXIDE MODIFIED PHENOLICS



TETRAMETHYLOL DERIVATIVES DIPHENYL OXIDE DERIVATIVES

Figure 6.

EFFECT OF EQUIVALENCY RATIO ON THERMOGRAVIMETRIC CHAR
YIELD OF DIPHENYLOXIDE MODIFIED PHENOLICS

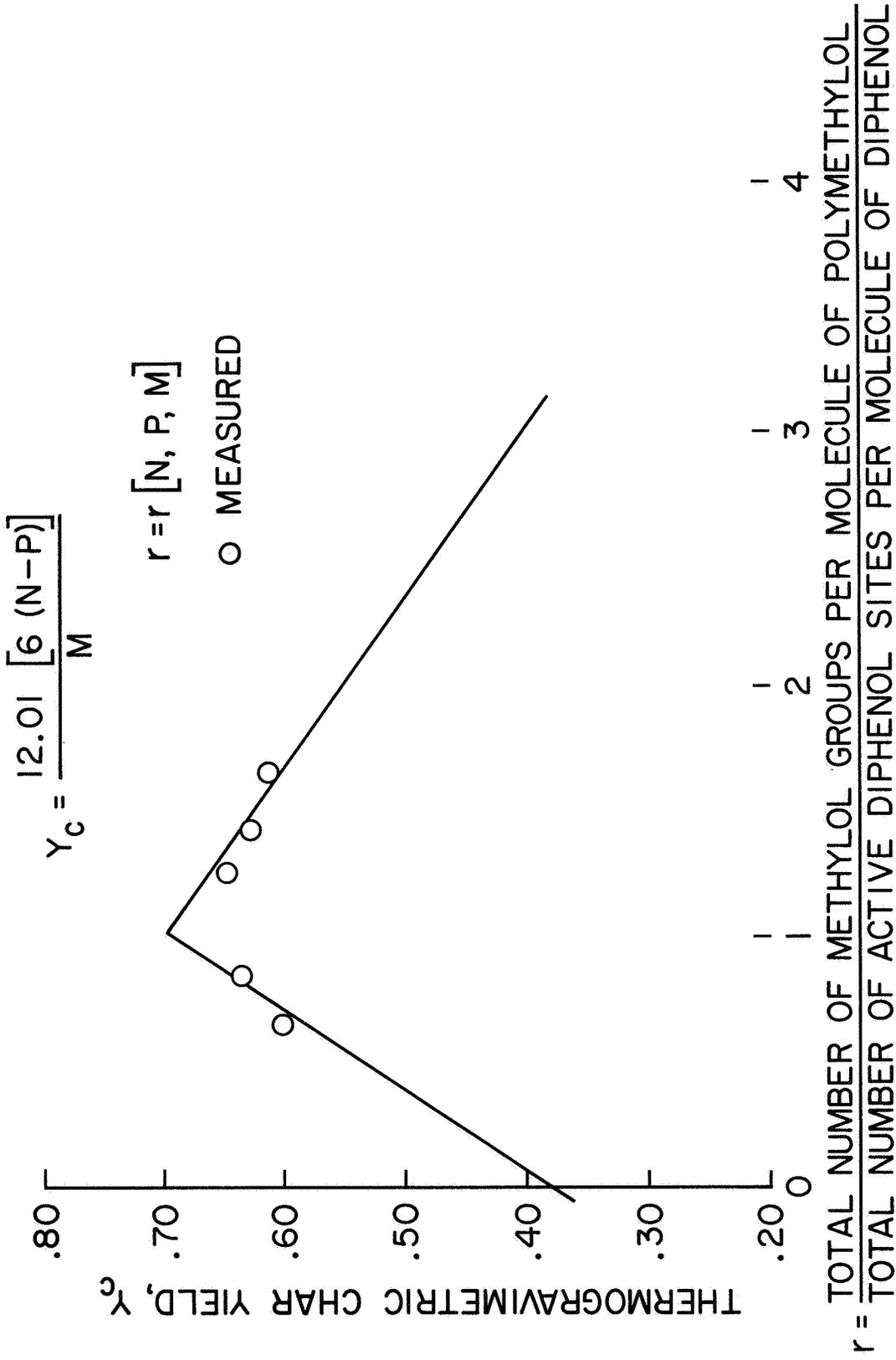
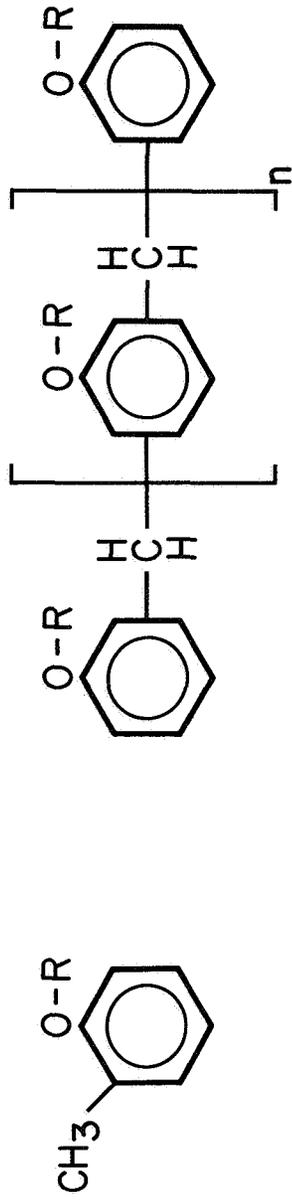


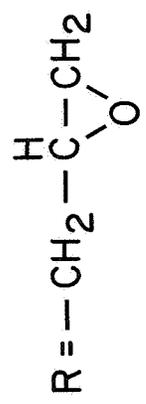
Figure 7.

STRUCTURE AND ANALYSIS OF EPOXY NOVOLAC MONOMERS



A

B & C



GLYCIDYL ETHER	n	MOLECULAR WEIGHT	FUNCTIONALITY
A		164	2.0
B	1.8	604	7.6
C	5.7	1226	15.3

Figure 8.

COMPARISON OF MEASURED AND CALCULATED CHAR YIELDS FOR ANHYDRIDE CURED EPOXY NOVOLACS

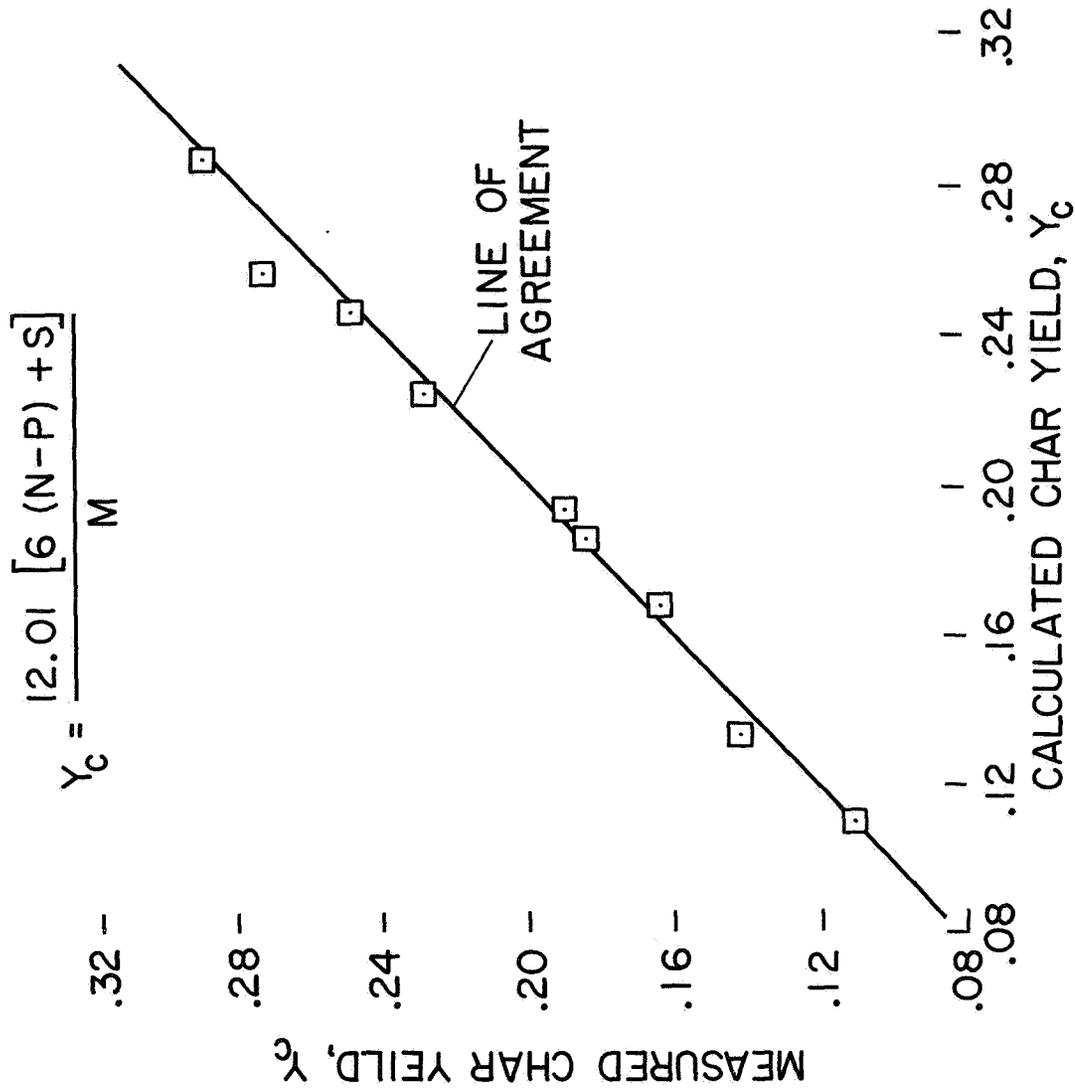


Figure 9.

TYPICAL LOW DENSITY PHENOLIC NYLON
HEAT SHIELD COMPOSITE

COMPONENT	FUNCTION	WEIGHT, %	Y_c , %
NYLON	VAPOR PRODUCER	40	0
HEXA-CURED PHENOLIC NOVOLAC RESIN	CHAR FORMER AND BINDER	37	51.2
PHENOLIC MICROSPHERES	CHAR FORMER AND DENSITY REDUCER	23	55.0

Figure 10.

A COMPARISON OF THERMOGRAVIMETRIC CHAR YIELDS WITH
ARC FURNACE CHAR YIELDS

COMPOSITE	CALC CHAR YIELD, Y_c	TGA CHAR YIELD, Y_c	ARC FURNACE CHAR YIELD	
			$25 \frac{\text{cal}}{\text{cm}^2 \text{ sec}}$	$150 \frac{\text{cal}}{\text{cm}^2 \text{ sec}}$
LDPN	.314	.291	.292	.381
EN C-1	.225	.231	.240	.280
EN C-2	.110	.110	.090	.090

Figure 11.