EFFECTS OF CROSS-LINK DENSITY AND POLYMER STRUCTURE ON THERMAL ANALYSIS OF PHENOL-FORMALDEHYDE POLYMERS

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ABSTRACT

The course of the pyrolysis process for cross-linked polymers is greatly influenced by the cross-link density. The usual path for pyrolysis of these classes of polymers is elimination of pendant groups and rearrangement followed by thermal cross-linking to form a highly cross-linked intermediate. Chemical cross-linking can lead to similar structures. Further pyrolysis leads to a thermally stable char. The reactions occurring during these pyrolyses are consecutive and overlapping.

A mechanism has been proposed for the pyrolysis of a phenolic novolak through a set of concerted reactions following the general mechanism for cross-linked polymers (1). This mechanism is different from that proposed by Jackson and Conley (2) for a resol type of phenol-formaldehyde polymer. These mechanisms are consistent for the kind of polymer to which they are applied. Examination of the pyrolysis products for novolaks and resols, and comparison of their infrared spectra led to the conclusion that the structures of resols and novolaks are different.

Cross-link density in a phenolic novolak was varied over a broad range by varying the quantity of hexamethylenetetramine used in the cure. By using this technique, the rearrangement and cross-linking reactions were sufficiently separated to determine the thermokinetic parameters for each reaction by thermogravimetry. When these kinetics were combined with those for the pyrolysis of nylon, a thermogram was constructed for the composite and it agrees well with experiment. It is suggested that variations of the method are applicable to a broad class of cross-linked polymers.

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NOMENCLATURE

A = Pre-exponential factor

C^i = Chance for adding i pendant groups

E^* = Activation energy

H = Number of equivalents of cross-linking reagent

i = Number, either 0 or 1

M = Average molecular weight of repeating mer unit

M' = Number average molecular weight of prepolymer

N = Number of groups in molecule

$\overline{N}$ = Number of groups in average molecule

P = Present number of pendant groups

P_o = Initial number of pendant groups

S_1 = Present number of type 1 functional sites

$S_{1(o)}$ = Initial number of type 1 functional sites

S_2 = Present number of type 2 functional sites

$S_{2(o)}$ = Initial number of type 2 functional sites

S_o = Initial number of all functional sites

$S_{r(1)}$ = Number of reacted type S_1 functional sites

$S_{r(2)}$ = Number of reacted type S_2 functional sites

S_T = Present number of all functional sites

α = Branching coefficient

Π_N^{P+i} = Probability for existence of a molecule with $P + i$ pendant groups

$$\phi_1 = \frac{P}{P_o} = \frac{S_1}{S_{1(o)}} = \left(1 - \frac{H}{S_o}\right)^2$$

$$\phi_2 = \frac{S_2}{S_{2(o)}}$$

X_S = Sol fraction

INTRODUCTION

The primary char yield of the resins used in ablative heat-shield composites is uniquely determined by the degree of aromaticity and the cross-link density. This has been shown in reference 1 as being typical of a broad class of polymers when they are pyrolyzed in an anaerobic environment. This environment was chosen as being most typical of the conditions existing in depth in an ablative heat shield during the entry of a space vehicle into a planetary atmosphere (3). These conditions are different from those used in studies (2 and 4) where films of similar resins were exposed to accelerated oxidizing conditions prior to pyrolysis.

The present paper shows how the structure of an average phenolic novolak prepolymer molecule can be inferred by statistical methods and how cross-linking affects the pyrolysis process when the prepolymer is cured with hexamethylenetetramine. The methods are demonstrated by comparing the calculated results with experiment. Char yield for a cross-linked phenolic novolak prepolymer is correlated with the inferred structure, and a method of using variation in cross-link density to resolve the pyrolysis reactions occurring in the polymer during thermogravimetry is presented.

EXPERIMENTAL

Preparation of a Phenolic Novolak

Two hundred grams of reagent grade phenol was mixed with 53-1/4 gm of formaldehyde as an uninhibited 37 percent solution and 2 gm of oxalic acid. This mixture was refluxed for two hours at 100°-101°C when a dinitrophenylhydrazine test for formaldehyde showed negative. Water and excess phenol were distilled off and the yield was 213 gm of a water white, glassy solid. Theoretical yield was 221 gm. This corresponded to a loss of 8 gm of phenol. The resultant resin was completely soluble in acetone and the molecular weight determined by ebuloscopic methods was 794.

Curing of the Phenolic With Hexamethylenetetramine

Portions of the phenolic novolak were mixed with hexamethylenetetramine at hexa/phenol equivalency ratios of 0.07, 0.14, 0.21, 0.29, 0.36, 0.43, 0.50, and 0.65. The mixtures were cured in an atmosphere of pure nitrogen at 157°C for 1 hour. A hard brittle polymer resulted.

Extraction of the Cured Polymer

Portions of each of the cured polymer specimens were crushed to 100 mesh and extracted with acetone in a Soxhlet extractor for 4 hours. The ratio of the loss in weight to the initial weight yielded the sol fraction.

Pyrolysis of the Cured Polymer

Portions of each of the cured polymer specimens were crushed to 80 mesh and pyrolyzed in a transpirational thermogravimetric balance at a heating rate of 3°C/min. The atmosphere was purified dried nitrogen, and the peak temperature was 800°C.

RESULTS AND DISCUSSION

The char yield resulting from the pyrolysis of phenolic novolak resins can be determined through use of the empirical equation

$$Y_C = \left[\frac{N}{M} - \left(\frac{N}{M} - \frac{N - P}{M'}\right) X_S\right] \qquad (1)$$

N, M, and M' can be determined independently from char yield. Heretofore X_S has been determined by extraction of the partially cured resin with acetone. P has been determined by application of equation (1) to the char yield for the uncured prepolymer. However, methods of predicting the char yield through use of parameters determined from the quantities of reactants used in the formulation of the heat shield are highly desirable.

Fig. 1 shows the generalized structure of a phenolic novolak prepolymer produced by reacting phenol and formaldehyde with an acid catalyst. In this structure N phenol molecules are linked through N-1 methylene bridges. P represents the number of singly bonded phenolic units. The remaining N-P units are multiply bonded. In the derivation of equation (1) it was assumed that the carbon in the multiply bonded units is retained in the primary char structure; the pendant units are eliminated as a vapor in the pyrolysis process.

The number of repeating mer units for the average prepolymer molecule can be calculated from the quantities of reactants consumed through use of equations IX-1 and IX-32 of reference 5. These equations were used to calculate $\overline{N}$ for the prepolymer used in the experiment from the quantities of reactants actually consumed. A correction for the loss of phenol was applied. The calculated result was that $\overline{N} = 7.58$ and the calculated molecular weight for this average molecule is 791 compared with the measured number average molecular weight of 794 quoted by the manufacturer of the resin.

The conformation of the average prepolymer molecule was inferred through an application of the Bernoulli distributions of chance events as applied to the reaction of a trifunctional reactant (6). This analysis yielded a value of 8.8 percent of unreacted phenol. From these results it was calculated that 2.74 of the 7.58 units were singly bonded and therefore pendant. This approach is based on a pure chance analysis and does not account for steric effects caused by the conformation of the growing molecule. The method is open to question. However, since no experimental method of verification is known to the authors, a second method of determining the number of pendant groups will be outlined.

Fig. 2 illustrates a method for calculating the number of pendant groups in any conformation containing N repeating trifunctional mer units. This method is based on the probability for existence of a molecular configuration and the chance for adding either a pendant group or a chain extending group when one trifunctional group is added. The following equations were developed.

$$\Pi_N^{P+i} = \Pi_{N-1}^{P} C^i , \qquad i = 0,1 \tag{2}$$

$$C^1 = \frac{N - 2P + 2}{N + 2} , \qquad C^0 = \frac{2P}{N + 2} \tag{3}$$

$$\overline{P}_N = \sum \Pi_{N-1}^{P} C^i (P + i) \tag{4}$$

This set of recursion equations yields the average number of pendant groups for all configurations containing N groups. When these results were combined with the number average molecular weight distribution for polymers of this kind for N ranging from 2 to 20 (5) the results showed that

$\overline{P} = 2.68$, which compares favorably with the Bernoulli value of $\overline{P} = 2.74$. The Bernoulli value is used because in the present method, if N is extended to infinity, P will approach the Bernoulli value. The calculated values for N and P specify the conformation of the average molecule, which is shown in Fig. 3.

Fig. 4 illustrates the result of a mathematical study of the reactions that occur when a multifunctional, branched structure is cross-linked. In this study, it is assumed that the reactivity of all functional sites is equal and that sufficiently large numbers of molecules are present to allow the methods of statistical mechanics to be applied. Functional sites are labeled as to type, whether on pendant or doubly bonded groups.

When a differential amount of cross-linking reagent is added, the reaction can be written

$$dS_r = -dH \tag{5}$$

Due to the assumption of equal reactivity

$$dS_{r(1)} = -\frac{S_1}{S_1 + S_2}\,dH \tag{6a}$$

$$dS_{r(2)} = -\frac{S_1}{S_1 + S_2}\,dH \tag{6b}$$

However, when an S_1 functional site is reacted, the companion site changes label to become an S_2 site. Thus

$$dS_1 = 2\,dS_{r(1)} \tag{7}$$

and equation (6a) becomes

$$dS_1 = -\frac{2S_1}{S_1 + S_2}\,dH \tag{8}$$

However, $S_1 + S_2 = S_T = S_o - H$ and

$$\frac{dS_1}{S_1} = -\frac{2\,dH}{S_o - H} \tag{9}$$

and the solution is

$$\frac{S_1}{S_{1(o)}} = \left(1 - \frac{H}{S_o}\right)^2 \tag{10}$$

It is obvious that the fraction of functional sites on pendant groups is affine to the fraction of pendant groups remaining so that equation (10) can be written

$$\frac{P_1}{P_o} = \left(1 - \frac{H}{S_o}\right)^2 \tag{11}$$

This equation is compared with experiment; the fraction of pendant groups remaining and the sol fraction are presented as they vary with the equivalency ratio H/S_o. This figure shows that (a) cross-linking to produce an insoluble gel occurs mostly through pendant groups and pendant groups are rapidly multiply bonded in the process, and (b) the sol fraction or extent of cross-linking may be expressed as

$$X_S = \left(1 - \frac{H}{S_o}\right)^2 \tag{12}$$

Equation (1) then becomes

$$Y_c = 72.06\left[\frac{\overline{N}}{M} - \left(\frac{\overline{N}}{M} - \frac{\overline{N} - P}{M'}\right)\left(1 - \frac{H}{S_o}\right)^2\right] \tag{13}$$

This theoretical equation is compared with experiment in Fig. 5 where the char yield is plotted as a function of the equivalency ratio H/S_o for the phenolic novolak previously characterized. Note that M' and M can be calculated from

$$\overline{N} = f(\alpha) \tag{14}$$

$$M' = 94\overline{N} + 12(\overline{N} - 1) \tag{15}$$

$$M \approx M' + 12P \tag{16}$$

The effect of variation in cross-link density is graphically illustrated in Fig. 6 where the rate of conversion with time is presented as a function of temperature for the pyrolysis of three samples with different extent of cross-linking. In this case the extent of cross-linking is expressed in terms of the sol fraction. A notable effect shown in this figure is the small variation in temperature range over which the major reactions occur when the extent of cross-linking is varied. This implies that only the magnitude of the reaction is altered by cross-linking: the thermokinetic processes occurring during the pyrolysis do not change. The first peak occurring at 350°-400°C can be related to the pendant group elimination and thermal cross-linking reactions proposed in reference 1. The second reaction occurring at temperatures above 450° is a char forming reaction.

Pyrolysis reactions occurring in plastics are usually described in terms of the rate and Arrhenius equations. However, it is not always possible to resolve the reactions sufficiently to determine the kinetic parameters entering these equations. The variation in magnitude of the reactions with extent of cross-linking suggests that altering the extent of cross-linking can be used to determine these parameters when the reactions cannot normally be resolved. Table 1 lists the kinetic parameters for the two reactions as determined by the methods of references 7 and 8. No information indicates failure of the method.

The order indicated for the char forming reaction is an estimate which gave the best fit for the data when the integral method (8) was used. The tabulated values for order n, activation energy E, and pre-exponential factor A show no significant change in the kinetic parameters when the extent of cross-linking is altered. Furthermore, it is evident that altering the extent of the cross-linking can resolve the pyrolysis reactions in these kinds of polymers.

CONCLUDING REMARKS

1. This investigation has shown that it is possible to determine the structure and configuration of the "average" molecule of a phenolic novolak prepolymer by the application of well-known statistical methods. These methods predict the number of structural units composing the average molecule, the fraction of these which are singly bonded and therefore pendant, and the molecular weight of the average molecule. Furthermore, the fraction of pendant units remaining and the molecular weight of the average repeating mer unit can be calculated from the equivalency ratio when the prepolymer is cured with hexamethylenetetramine. These parameters can be combined to predict the char yield when the cured resin is pyrolyzed under anaerobic conditions.

2. The reactions during the anaerobic pyrolysis of cured phenolic novolak resins are sequential and overlapping. However, these reactions may be resolved by altering the extent of cross-linking. The thermokinetic parameters for pyrolysis may then be determined by usual methods.

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FIGURE LEGENDS

Fig. 1 Generalized structure of a phenolic novolak.

Fig. 2 Molecular model for calculating number of pendant units.

Fig. 3 Conformation of the phenolic prepolymer.

Fig. 4 Variation in cross-link density with equivalency ratio.

Fig. 5 Variation of thermochemical yield with cross-link density.

Fig. 6 Mass loss rate from thermograms of hexa cured phenolic novolak at different cross-link density.

REACTION	THERMAL CROSSLINKING				CHAR FORMING	
SOL FRACTION	1.00		.54	.09	.09	
ANALYTICAL TECHNIQUE	F–C	$\int$	$\int$	$\int$	F–C	$\int$
ORDER, n	2	2	2			2
ACTIVATION ENERGY, E*	39.9	42.1	41.2			43.5
PRE–EXPONENTIAL FACTOR, A	5.1×10^{11}	6.6×10^{11}	5.3×10^{11}			8.2×10^{9}

Table 1.

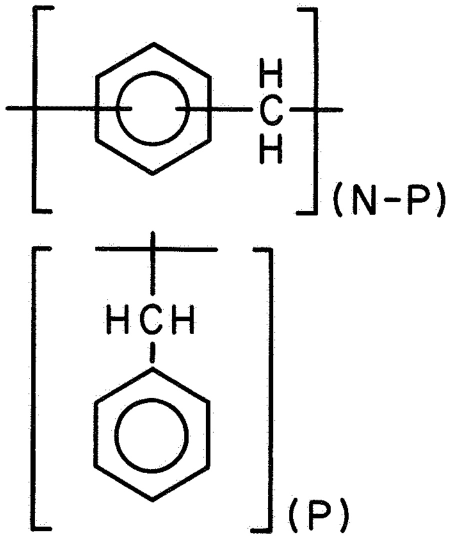
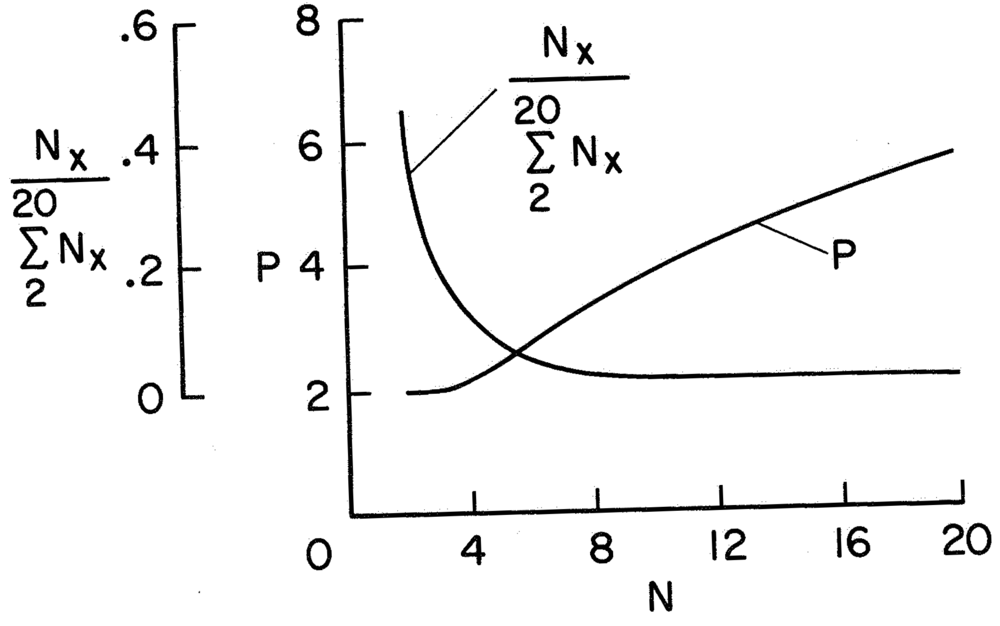


Figure 1.



$$\pi_N^{P+i} = \pi_{N-1}^{P} C^i \quad i = 0, 1$$

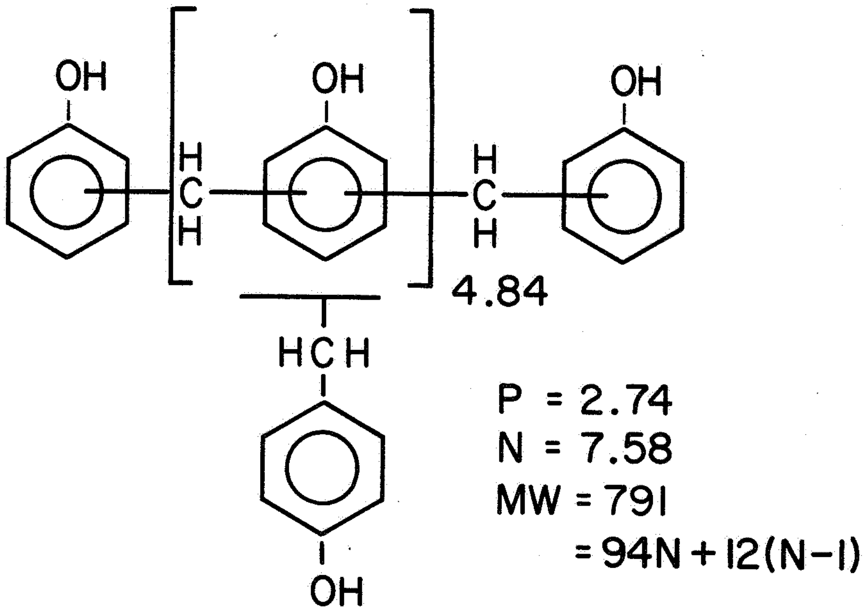
$$C^1 = \frac{N-2}{N+2}\,\frac{P+2}{} \qquad C^0 = \frac{2P}{N+2}$$

$$\bar{P}_N = \sum \pi_{N-1}^{P} C^i (P+i)$$

$$\bar{P}_{calc} = 2.68$$

$$\bar{P}_{ber} = 2.74$$

Figure 2.



$P = 2.74$

$N = 7.58$

$MW = 791$

$= 94N + 12(N-1)$

Figure 3.

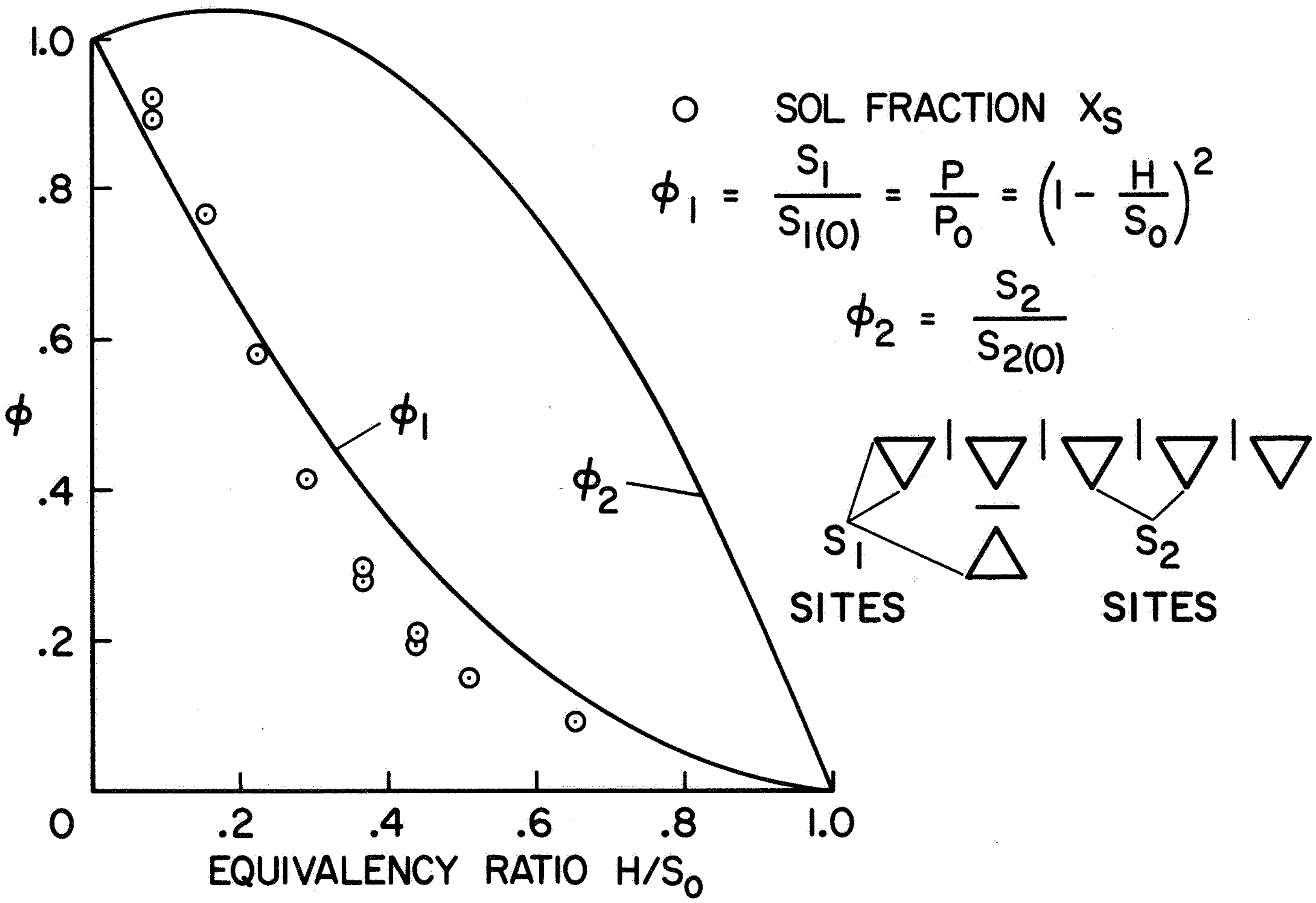

1.0
.8
.6
.4
.2
0
ϕ
.2
.4
.6
.8
1.0
EQUIVALENCY RATIO H/S_0
ϕ_1
ϕ_2
○ SOL FRACTION X_S
$\phi_1 = \frac{S_1}{S_{1(0)}} = \frac{P}{P_0} = \left(1 - \frac{H}{S_0}\right)^2$
$\phi_2 = \frac{S_2}{S_{2(0)}}$
S_1 SITES
S_2 SITES

Figure 4.

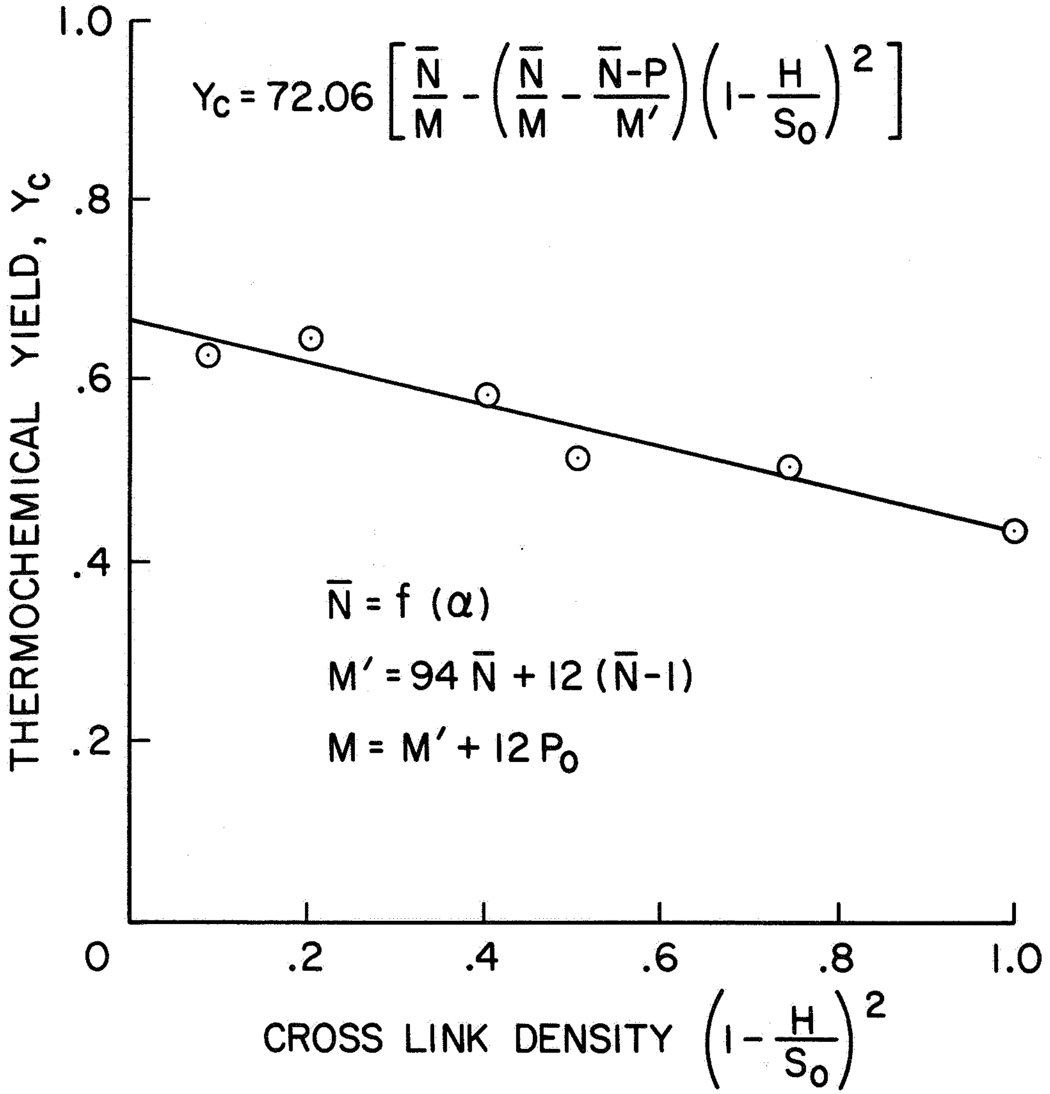
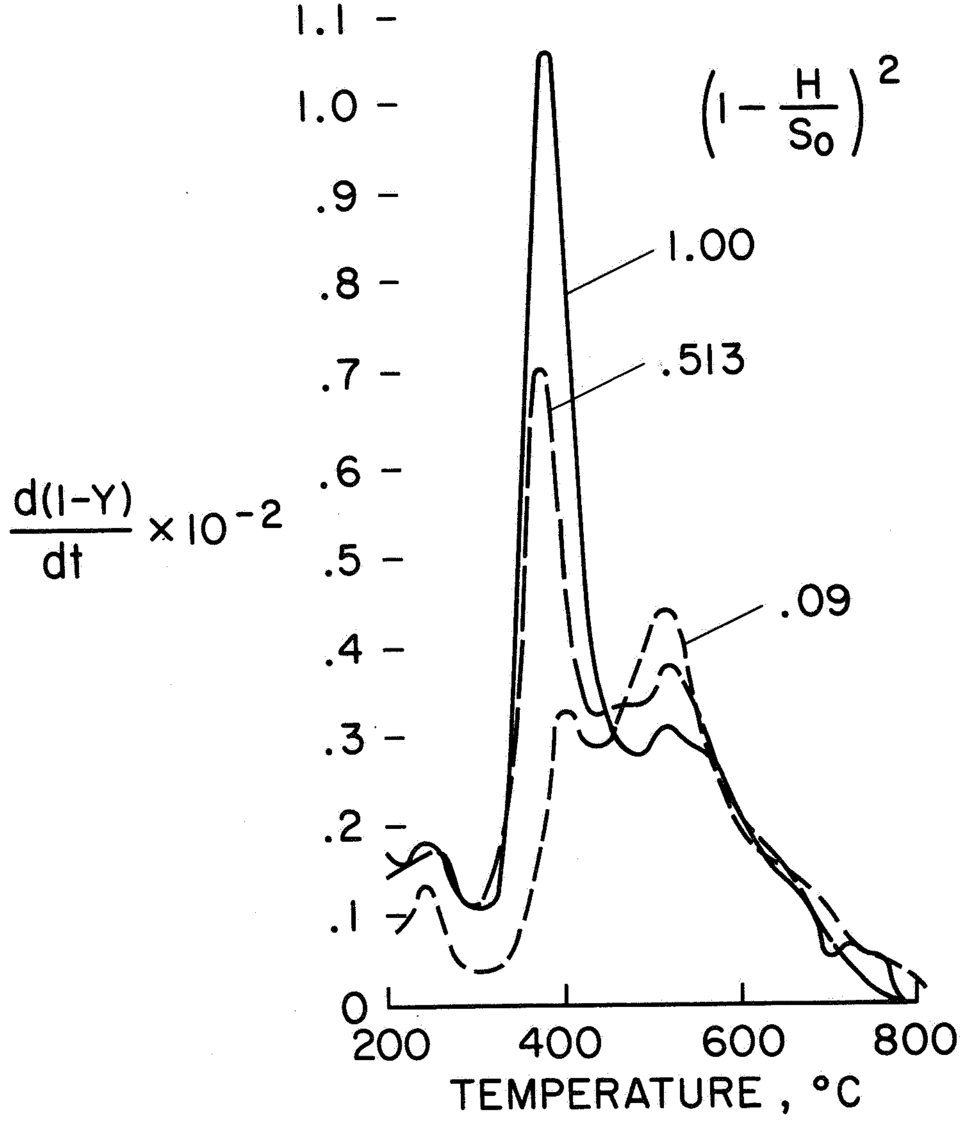

$Y_c = 72.06 \left[\frac{\bar{N}}{M} - \left(\frac{\bar{N}}{M} - \frac{\bar{N}-P}{M'} \right) \left(1 - \frac{H}{S_o} \right)^2 \right]$
$\bar{N} = f(\alpha)$
$M' = 94\bar{N} + 12(\bar{N}-1)$
$M = M' + 12P_o$
THERMOCHEMICAL YIELD, Y_c
1.0
.8
.6
.4
.2
0
.2
.4
.6
.8
1.0
CROSS LINK DENSITY $\left(1 - \frac{H}{S_o}\right)^2$

Figure 5.



$\frac{d(1-Y)}{dt} \times 10^{-2}$
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
200
400
600
800
TEMPERATURE , °C
$\left(1-\frac{H}{S_0}\right)^2$
1.00
.513
.09

Figure 6.