Finally, the *total* volume of overlap, i.e., sum of the two above expressions, is

$$\Delta V = (2\pi/3)(R_-^3 + R_+^3) - \pi[R_-^2x^* + R_+^2(x_0 - x^*)] + (\pi/3)[(x^*)^3 + (x_0 - x^*)^3] \quad \text{(A3)}$$

which is eq 5 of the text.

Registry No. H_2O, 7732-18-5; Nafion, 39464-59-0.

References and Notes

(1) Helfferich, F. "Ion Exchange"; McGraw-Hill: New York, 1962.

(2) Marinsky, J. A. "Ion Exchange"; Marcel Dekker: New York, 1966; Vol. I.

(3) (a) Gregor, H. P. *J. Am. Chem. Soc.* **1948**, *70*, 1293. (b) Gregor, H. P. *J. Am. Chem. Soc.* **1951**, *73*, 642. (c) Lazare, L.; Sundheim, B. R.; Gregor, H. P. *J. Phys. Chem.* **1956**, *60*, 641.

(4) (a) Katchalsky, A.; Lifson, S.; Eisenberg, H. *J. Polym. Sci.* **1951**, *7*, 571. (b) *Ibid.* **1952**, *8*, 476. (c) Katchalsky, A.; Lifson, S.; Mazur, J. *J. Polym. Sci.* **1953**, *11*, 409. (d) Katchalsky, A.; Michaeli, I. *J. Phys. Chem.* **1955**, *15*, 69.

(5) (a) Harris, F. E.; Rice, S. A. *J. Chem. Phys.* **1956**, *24*, 1258. (b) Rice, S. A.; Harris, F. E. *Z. Phys. Chem.* (*Wiesbaden*) **1956**, *8*, 207. (c) Rice, S. A.; Nagasawa, M. "Polyelectrolyte Solutions"; Academic Press: New York, 1961; p 461.

(6) Eisenberg, A.; King, M. "Ion-Containing Polymers"; Academic Press: New York, 1977.

(7) "Surlyn" and "Nafion" are registered trademarks of E. I. du Pont de Nemours and Co.

(8) Eisenberg, A. *Macromolecules* **1970**, *3* (2), 147.

(9) Mauritz, K. A.; Hora, C. J.; Hopfinger, A. J. In "Ions in Polymers"; Eisenberg, A., Ed.; American Chemical Society: Washington, DC, 1980; Adv. Chem. Ser. No. 187, p 123.

(10) (a) Hsu, W. Y.; Gierke, T. D. *Macromolecules* **1982**, *15*, 101. (b) Gierke, T. D.; Munn, G. E.; Wilson, F. C. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1687.

(11) Lowry, S. R.; Mauritz, K. A. *J. Am. Chem. Soc.* **1980**, *102*, 4665.

(12) Komoroski, R. A.; Mauritz, K. A. In "Perfluorinated Ionomer Membranes"; Eisenberg, A., Yeager, H. L., Eds.; American Chemical Society: Washington, DC, 1982, ACS Symp. Ser. No. 180, p 113.

(13) Mauritz, K. A.; Gray, C. L. *Macromolecules* **1983**, *16*, 1279.

(14) Starkweather, H. W., Jr. *Macromolecules* **1982**, *15*, 320.

(15) Mauritz, K. A.; Hopfinger, A. J.; In "Modern Aspects of Electrochemistry"; Bockris, J. O'M., et al., Ed.; Plenum Press: New York, 1982; No. 14, p 425.

(16) See ref 1, Chapter 5.

(17) Gent, A. N.; Lindley, P. B. *Proc. R. Soc. London, Ser. A* **1958**, *249*, 195.

(18) Bjerrum, N. *Mat-Fys. Medd.-K. Dan. Vidensk. Selsk.* **1926**, *7*, No. 9.

(19) (a) Diebler, H.; Eigen, M. *Z. Phys. Chem.* (*Wiesbaden*) **1959**, *20*, 299. (b) Eigen, M.; Tamm, K. *Z. Elektrochem.* **1962**, *66*, 93, 107.

(20) Reference 15, p 449.

(21) (a) Bernal, J. D.; Fowler, R. H. *J. Chem. Phys.* **1933**, *1*, 515. (b) Latimer, W. M.; Pitzer, K. S.; Slansky, C. M. *J. Chem. Phys.* **1939**, *7*, 108. (c) Verwey, E. J. W. *Recl. Trav. Chim. Pays-Bas* **1942**, *61*, 127. (d) Vasilev, V. P.; et al., *Russ. J. Phys. Chem.* **1960**, *34*, 1763. (e) Dzidic, I.; Kebarle, P. *J. Phys. Chem.* **1970**, *74*, 1466.

(22) Wiklander, P. *Lantbrukshoegsk. Ann.* **1946**, *14*, 1–171.

(23) Reference 15, p 447.

(24) Gurney, R. W. "Ionic Processes in Solution"; McGraw-Hill: New York, 1953; p 4.

(25) Hopfinger, A. J. "Conformational Properties of Macromolecules"; Academic Press: New York, 1973.

(26) Reference 1, p 117.

(27) Gregor, H. P.; Sundheim, B. R.; Held, K. M.; Waxman, M. H. *J. Colloid Sci.* **1952**, *7*, 511. See also ref 1, p 105.

(28) Geil, P. H. "Polymer Single Crystals"; Wiley: New York, 1963.

(29) Treloar, L. R. G. "The Physics of Rubber Elasticity"; Oxford University Press: London, 1949.

(30) Kyu, T.; Eisenberg, A. In ref 12, p 92.

(31) Grot, W. G. F.; Munn, G. E.; Walmsley, P. N. 141st National Meeting, Electrochemical Society, Houston, 1972.

(32) Hsu, W. Y.; Barkley, J. R.; Meakin, P. *Macromolecules* **1980**, *13*, 198.

Modeling Phenolic Resins and Their Thermolysis

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ABSTRACT: A simple interpretation of the structure of phenolic resins permitted development of a mathematical model for their thermolysis. The resin was viewed as an ensemble of single-ring aromatics linked into a polymer by diphenylmethane (DPM) bonds. The rate of thermal fission of the polymer's DPM bonds was used to deduce the rate of evolution of single-ring products. Previous pyrolyses of related model compounds provided the reaction pathways and kinetics for the polymer's DPM bond fissions. Simple probability concepts allowed calculation of six individual product identities and yields. Experimental pyrolyses of an actual phenolic resin permitted evaluation of these model predictions.

Introduction

The prediction of a polymer's pyrolysis pathways and rates is of interest in such areas as polymer thermal stability,[2] polymer recycle,[5] and coal liquefaction.[14] Unfortunately, these fundamental pathways and kinetics are usually obscured in the complexity of both the polymer's structure and its pyrolysis product spectra. Predictions and correlations based on observations of actual polymer pyrolysis can thus be difficult. In contrast, the comparatively simple structure and product spectra of model compounds[1,6,11,13] permit resolution of reaction fundamentals. This motivated the present development of a mathematical model of phenolic resin pyrolysis that is based on the pathways, kinetics, and mechanisms of a model compound's pyrolysis.

This paper describes the development, execution, and analysis of the pyrolysis model. We begin with a simple analysis of phenolic resin structure. This is combined with model compound pyrolysis information and elementary probability concepts into the polymer pyrolysis model. A delineation of experimental techniques, model predictions, and experimental results follows. We then compare experimental results and model predictions, and conclude by considering the utility and limitations of the present modeling approach.

Model Development

The analysis of a phenolic resin's thermolysis is complicated by its large and distributed molecular weight and apparently randomly branched structure. We thus con-

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sider the fate of an average aromatic ring within an averaged polymer in a model of not only pyrolysis but also of the structure of the polymer itself.

Synthesized through the acid- or base-catalyzed condensation of phenol and formaldehyde,[8,9,16] thermally cured phenolic resins comprise monohydroxyl phenolic rings linked together by, substantially, diphenylmethane (DPM) bonds. In the analysis to follow we neglect the occurrence of less prevalent ring substituents such as ether linkages and methylol groups.[10] An averaged cured phenolic resin will have α DPM substituents on each of its 2-, 4- and 6-ring positions where $0 \le \alpha \le 1$ and the 1-position is defined to contain the hydroxyl substituent. Assuming that every formaldehyde molecule is incorporated into the resin as a DPM bond, which serves as a DPM substituent to two rings, the number of DPM substituents per ring will be 2/PFR, where PFR is the phenol to formaldehyde molar ratio during synthesis. This must also be equal to 3α since a single α describes each of the three ring positions. The globally averaged polymer thus contains phenolic rings with α (=2/(3 PFR)) DPM substituents on each of its 2-, 4- and 6-ring positions.

The average ring of this averaged polymer will thus contain a hydroxyl substituent at its 1-position, a hydrogen substituent at its 3- and 5-positions, and α DPM substituents at each of its 2-, 4-, and 6-positions; hence $\beta = 1 - \alpha$ nonbonded (hydrogen) substituents will also be present at the 2-, 4-, and 6-positions. This suggests that for polymers with $\alpha < 1$, i.e., synthesized at PFR > $^2/_3$, a finite number of the polymer rings will not be bonded to any other ring. Since an aromatic ring is defined by the substituents at each of its six ring positions, simple probability theory suggests that phenol should be present in fraction β^3 of all aromatic rings. In this calculation, hydrogen substituents were required to occur simultaneously at the 2-, 4-, and 6-positions of the aromatic ring that always contains a hydroxyl substituent at its 1-position and hydrogen at its 3- and 5-positions. It is interesting that Knop and Scheib[8] reported that a resin prepared in hydrochloric acid at a PFR of 2 contained 28 wt % phenol. The present analysis suggests that, at PFR = 2, $\alpha = {}^1/_3$ (and hence $\beta^3 \cong 0.30$), which corresponds to 28.3 wt % (see below) phenol.

Our interest is in the yield and identity of single aromatic ring pyrolysis products (SRP) since these are experimentally observable. Quantitation of multiring carbon-rich products is more challenging and not considered here. Formation of a SRP during pyrolysis requires the fragmentation of any DPM substituent present on each of the 2-, 4-, and 6-positions on any ring. The reactions of the DPM substituents and, hence, the temporal variations of $\alpha(t)$ and $\beta(t)$, chronicled the resin thermolysis. We thus recognize the values of α and β that described the initial resin (before pyrolysis) to be the limiting values $\alpha_0 = \alpha(t = 0)$ and $\beta_0 = \beta(t = 0)$. The functions $\alpha(t)$ and $\beta(t)$ were inferred from the reactions of pure diphenylmethane as follows.

Our simple interpretation of the fragmentation of DPM to its major single-ring products benzene and toluene[1,4,7,13] is illustrated in Figure 1. The stoichiometrically balanced reaction of 2 mol of DPM to 1 mol each of benzene, toluene, and fluorene satisfies the hydrogen requirement for the formation of the single-ring products. Note that symmetry requires the transformation of a given one of the two DPM aromatic rings to benzene or toluene to be equally likely. As regards the actual resin, the reaction of a DPM substituent on a given ring will thus leave a hydrogen or methyl substituent with equal probability; i.e., half of the nonbonded β substituents that form from pyrolysis will be hydrogen and half will be methyl.

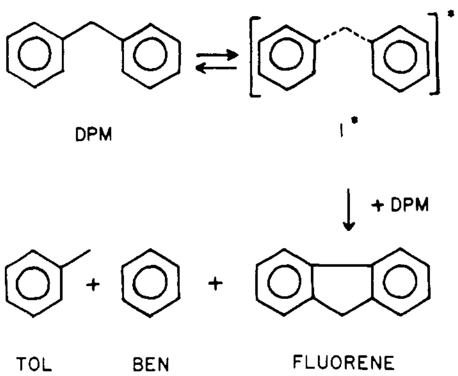

Figure 1. Interpretation of diphenylmethane pyrolysis pathway and kinetics.

The mechanism advanced in Figure 1, based on the observations that the initial rate of DPM pyrolysis is very nearly first order in DPM and that the apparent pyrolysis order increases with conversion,[13] admits derivation of an analytical rate expression. Pseudo-steady-state analysis of (i) slow bond fission through a hypothetical stretched DPM species I*, (ii) collapse of I* to DPM, and (iii) reaction of I* with DPM to yield benzene, toluene, and fluorene yields eq 1 and 2 for the rate of reaction of DPM and the rate of formation of benzene and toluene, respectively.

$$-\mathrm{d(DPM)}/\mathrm{d}t = k_1(\mathrm{DPM})^2/[1 + K(\mathrm{DPM})] \quad (1)$$

$$\mathrm{d(BEN)}/\mathrm{d}t = \mathrm{d(TOL)}/\mathrm{d}t = 0.5k_1(\mathrm{DPM})^2/[1 + K(\mathrm{DPM})] \quad (2)$$

Values for k_1 and K of eq 1 and 2 were estimated from the pyrolyses of DPM,[4,13] o- and p-hydroxyl-DPM,[1,7] and phenolic resins.[12] The latter substrates allowed estimation of the electronic activation of the DPM bond by the hydroxyl substituents that are always present in the phenolic resins. Arrhenius parameters were not fully available and thus product yield temperature dependence was not modeled.

Turning now to the temporal variations of α and β, the DPM pathway of Figure 1 requires that every transformation of two α substituents be attended by the formation of one nonbonded β substituent (either H or CH_3) and one fused ring substituent akin to the moiety in fluorene. The rate of change of α was estimated by replacing DPM molar concentrations in eq 1 with the number concentration of α substituents; likewise β replaced BEN (or TOL) in eq 2.

$$-\mathrm{d}\alpha/\mathrm{d}t = k_1\alpha^2/(1 + K\alpha) \quad (3)$$

$$\mathrm{d}\beta/\mathrm{d}t = 0.5k_1\alpha^2/(1 + K\alpha) \quad (4)$$

$$\alpha - \alpha_0 = -2(\beta - \beta_0) \quad (5)$$

$$\alpha_0 = 2/(3\ \mathrm{PFR}) \quad (6)$$

$$\beta_0 = 1 - \alpha_0 \quad (7)$$

Equations 2–7 thus described the temporal variations of DPM and nonbonded substituents.

The pyrolytic formation of SRP required the simultaneous occurrence of three nonbonded (β) substituents on a given ring. Akin to the calculation for phenol in the initial resin (before pyrolysis), the number concentration of SRP was estimated as illustrated in eq 8. In eq 8, β

$$N(\mathrm{SRP}) = \beta^3 \quad (8)$$

Table I
Predicted Product Identities and Yields

comb. no.	substituent at ring position 2	4	6	implied SRP	product yield,[a] wt %
1	CH_3	CH_3	CH_3	2,4,6-trimethylphenol	$N(\mathrm{SRP})P(\mathrm{CH_3})^3 136/M_{\mathrm{AR}}$
2	CH_3	CH_3	H	2,4-xylenol (=4,6 xylenol)	$2N(\mathrm{SRP})P(\mathrm{CH_3})^2 P(\mathrm{H}) 122/M_{\mathrm{AR}}$
3	CH_3	H	CH_3	2,6-xylenol	$N(\mathrm{SRP})P(\mathrm{CH_3})^2 P(\mathrm{H}) 122/M_{\mathrm{AR}}$
4	CH_3	H	H	*o*-cresol	$2N(\mathrm{SRP})P(\mathrm{CH_3})P(\mathrm{H})^2 108/M_{\mathrm{AR}}$
5	H	CH_3	CH_3	4,6-xylenol (=2,4 xylenol)	see comb. 2
6	H	CH_3	H	*p*-cresol	$N(\mathrm{SRP})P(\mathrm{CH_3})P(\mathrm{H})^2 108/M_{\mathrm{AR}}$
7	H	H	CH_3	*o*-cresol	see comb. 4
8	H	H	H	phenol	$N(\mathrm{SRP})P(\mathrm{H})^3 94/M_{\mathrm{AR}}$

[a] $N(\mathrm{SRP}) = \beta^3$, $P(\mathrm{H}) = (\beta_0 + {}^1/_2\Delta\beta)/(\beta_0 + \Delta\beta)$, $P(\mathrm{CH_3}) = ({}^1/_2\Delta\beta)/(\beta_0 + \Delta\beta)$, and $M_{\mathrm{AR}} = 94 + 18\alpha_0$.

represents the sum of hydrogen and methyl substituents. Once again a SRP was required to have a hydroxyl substituent at its 1-position and hydrogen substituents at its 3- and 5-positions.

The chemical identities of individual SRP were determined by considering allowed combinations of β substituents on the 2-, 4-, and 6-positions. Since hydrogen and methyl substituents formed from DPM substituent fragmentation in equal likelihood, the number concentrations of hydrogen and methyl substituents were given by eq 9 and 10, respectively. Given that a SRP had formed (from

$$N(\mathrm{H}) = \beta_0 + {}^1\!/_2(\beta - \beta_0) = \beta_0 + {}^1\!/_2\Delta\beta \qquad (9)$$

$$N(\mathrm{CH_3}) = {}^1\!/_2\Delta\beta \qquad (10)$$

eq 8), the normalized probabilities of the occurrence of hydrogen and methyl substituents were given by eq 11 and 12. The number concentration of an individual SRP was

$$P(\mathrm{H}) = N(\mathrm{H})/[N(\mathrm{H}) + N(\mathrm{CH_3})] = (\beta_0 + {}^1\!/_2\Delta\beta)/(\beta_0 + \Delta\beta) \qquad (11)$$

$$P(\mathrm{CH_3}) = {}^1\!/_2\Delta\beta/(\beta_0 + \Delta\beta) \qquad (12)$$

thus calculated as the product of the number concentration of SRP and the three probabilities of its implied substituents [either $P(\mathrm{H})$ or $P(\mathrm{CH_3})$] on the 2-, 4-, and 6-positions. Product yields in (wt product)/(wt resin) (wt %) were determined by multiplying the number concentration of a given product by the ratio of its molecular weight to the molecular weight of the average ring in the averaged resin. The latter was a function of α_0 and was determined by eq 13. This information is summarized in Table I, which also

$$M_{\mathrm{AR}} = M_{\mathrm{C_6H_2}} + M_{\mathrm{OH}} + {}^3\!/_2\alpha_0 M_{\mathrm{CH_2}} + 3(1 - \alpha_0)M_{\mathrm{H}} = 94 + 18\alpha_0 \qquad (13)$$

lists the six predicted products, namely, 2,4,6-trimethylphenol, 2,4-xylenol, 2,6-xylenol, *o*-cresol, *p*-cresol, and phenol.

Prediction of the identity and temporal variations of the yield of individual products from phenolic resin thermolysis thus amounted to solution of eq 3 and 4 for the time dependence of α and β, respectively. Analytical solution of eq 3 for $\alpha(t)$ is represented as eq 14. Equation 5 hence

$$\frac{1}{\alpha} - \frac{1}{\alpha_0} + K \ln \frac{\alpha}{\alpha_0} = -k_1 t \qquad (14)$$

provided $\beta(t)$, eq 8 provided the number of SRP, and the calculations summarized in Table I provided the yield of individual products. The total yield of multiring carbon-rich products is thus determined as 1.0 minus the sum of the yields of SRP.

Experimental Section

Pyrolysis of an actual phenolic resin permitted scrutiny of the model. The resin was an acid-catalyzed novolac supplied by Rogers Corp. (E46-0018, lot L4B-439). Micro batch tubing bomb reactors of 0.6-cm^3 internal volume were used as described elsewhere.[13] Loaded reactors were immersed in a fluidized sand bath held constant at 400 °C for the desired reaction time and then quenched in a room-temperature fluidized sand bath. Quenched reactors were then opened, and a measured amount of 4-propylphenol was added to each to serve as a standard for gas chromatographic (GC) analysis. The contents of each reactor were then mixed in acetone, which effectively dissolved SRP. Injection of aliquots into an HP5880 GC equipped with an SE-54 capillary column and flame ionization detector allowed quantitation of SRP yields. Details are available.[12]

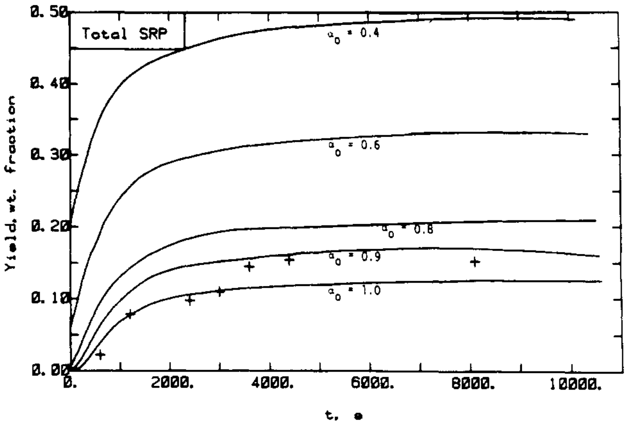

Figure 2. Predicted (curves) and experimental (+) temporal variations of the total yield of SRP at various values of the initial DPM substituent concentration α_0.

Results

Model Predictions. The pyrolysis model logic illustrated in Table I emphasizes the profound influence of α_0 on both total SRP yield and also the yields of individual SRP. The total weight fraction of all SRP, obtained by summing the yields of individual SRP, is plotted against pyrolysis time in Figure 2 for parametric values of α_0. Asymptotic yields in Figure 2 increased from 0.1 at α_0 = 1 to 1.00 at the trivial case where α_0 = 0; the latter yield simply reflects the thermal stability of phenol that was incorporated into the model.

The temporal variations of the predicted yields of the individual SRP phenol, cresols, xylenols, and trimethylphenol are shown in Figure 3a–d, respectively, for parametric values of α_0. Inspection of Figure 3a shows that phenol increases in prevalence as α_0 decreases. Note also the nonzero prepyrolysis yields of phenol predicted as 0.006, 0.057, and 0.20 at α_0 = 0.8, 0.6, and 0.4, respectively. The predicted behavior of cresols was more interesting. Ultimate yields increased from 0.06 at α_0 = 0.1 to about 0.15 at α_0 = 0.4 before decreasing to 0.04 as α_0 approached 1.0. Yields of xylenols increased from 0 at α_0 = 0 to about 0.001 at α_0 = 0.1 and 0.05 at α_0 = 0.8. The predicted trimethylphenol ultimate yield was less than 0.004 at α_0

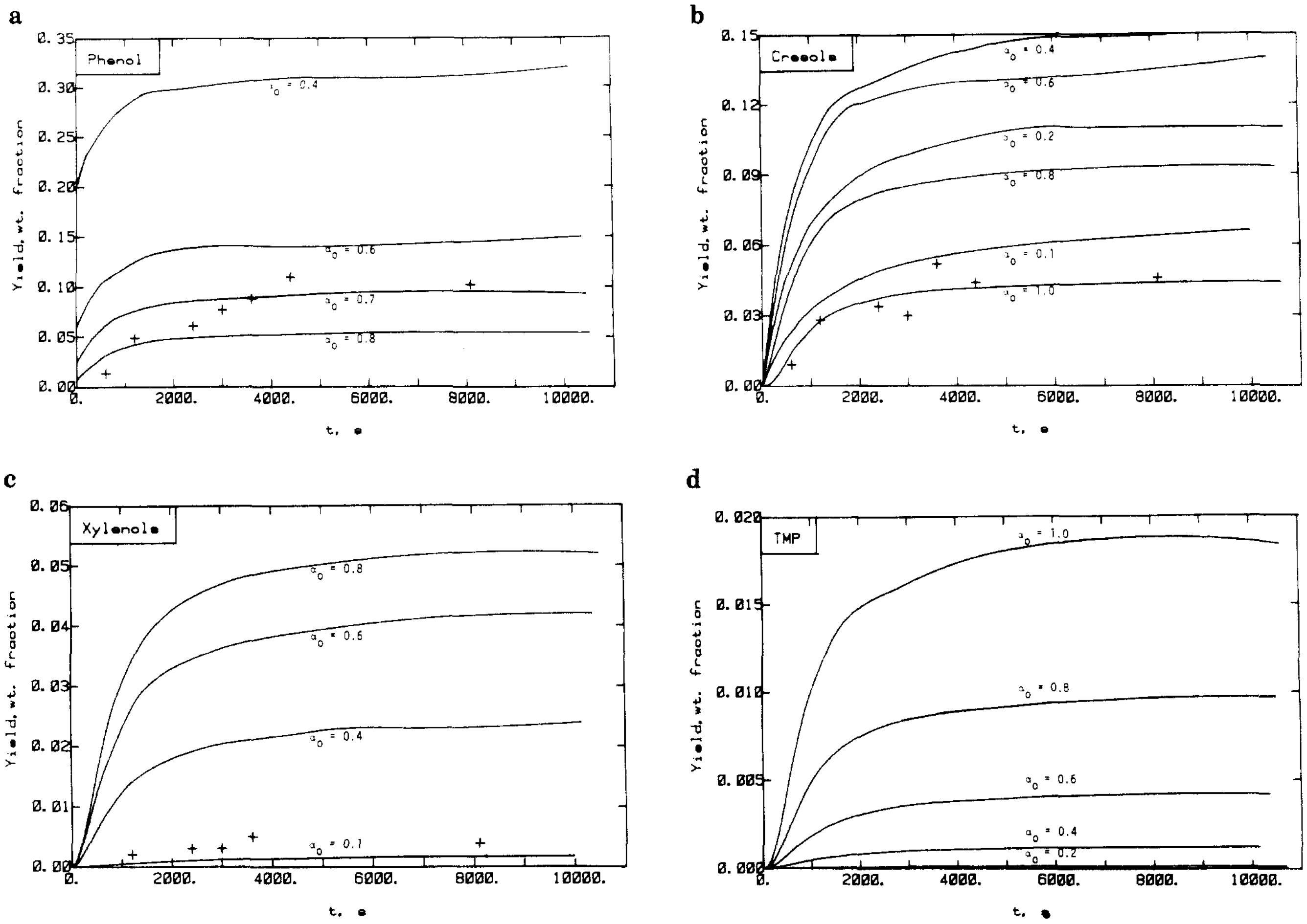

Figure 3. Predicted (curves) and experimental (+) temporal variations of the yield of individual products at various values of the initial DPM substituent concentration α_0: (a) phenol; (b) cresols; (c) xylenols; (d) trimethylphenol.

= 0.6, where phenol and cresols were the dominant products, and increased to 0.018 for α_0 = 1.0.

Experimental Results. Single-ring products observed from the pyrolysis at 400 °C of the sulfuric acid catalyzed novolac resin were, in order of descending prevalance, phenol, cresols, and xylenols. This is in qualitative accord with previous experimental pyrolyses of phenolic resins.[3,9,15,17] Trimethylphenol was not observed. The temporal variations of these product yields are illustrated in Figure 3a–c. Ultimate yields in Figure 3a–c were approximately 0.11, 0.05, and 0.01 for phenol, cresols, and xylenols, respectively. The product proportions illustrated in Figure 3a–c thus suggested a value of α_0 consistent with that expected from less condensed acid-catalyzed novolac. However, a single GC analysis of the acetone extract from the unreacted polymer revealed only trace amounts of phenol and no other SRP to be present initially.

Discussion

Our comparison here of the accord of model predictions and experimental results allows scrutiny of the utility of the modeling approach. We phrase this comparison in terms of the α_0 that best aligns the two sets of results, in spite of the fact that the conditions of the resin synthesis, and thus α_0, were not available pieces of information. However, since the same resin was used in all pyrolyses, its single α_0 should certainly characterize all experimentally observed products and, in principle, describe each of the model's predictions accurately. In what follows we thus might consider α_0 as a single deduced parameter that minimizes either the deviation between the experimental and predicted value of a single yield (e.g., total SRP) or some function that accounts for each of the total SRP, phenol, cresol, xylenol, and trimethylphenol yields.

The predicted and experimentally observed temporal variations of product yields are compared in Figures 2 and 3. Predicted and experimental yields of total SRP accord best for α_0 = 0.9. This value seems unusually high for a typical acid-catalyzed phenolic resin where PFR ~ 1 and $\alpha_0 \cong 0.67$. The model thus seems to overpredict the observations expected from typical acid resins. A likely cause of this overprediction is the mechanistically motivated DPM pyrolysis stoichiometry illustrated in Figure 1. An overall stoichiometry where 2 mol of DPM react to fewer than 2 mol of single-ring products (i.e., benzene and toluene) and greater than 1 mol of carbon-rich products (e.g., fluorene) is thus suggested as being more reasonable. However, no a priori reason for altering the stoichiometry from that in Figure 1 is evident presently.

Predicted and experimental yields of phenol align best for α_0 = 0.7, which is slightly higher than that expected of a novolac but certainly in closer accord than that deduced from the total SRP yields. Note that the implied prediction of only 1.73 wt % phenol being present in the initial resin is in agreement with our observation of only trace amounts of phenol in the novolac extract. Predicted and experimental yields of cresols best agree for values of α_0 = 0.1 and 1. The former is clearly unrealistic for a polymeric material since it predicts 73 wt % phenol to be present in the initial resin. The latter value of α_0 is inconsistent with the information that the resin was the result of an acid-catalyzed synthesis. However, it is worthwhile to note that overpredictions in the total SRP yield would propagate linearly into the prediction of cresol yield. Agreement between predicted and experimental yields of xylenols was poor, as an $\alpha_0 \sim 0.1$ provided a best fit. Certainly this aspect of both the model predictions and the experimental analyses requires further investigation. For example, pyrolysis of several better characterized resins would be useful. Finally, the experimental paucity of trimethylphenol products suggests indeed that the acid-catalyzed novolac had an α_0 no greater than 0.6.

The agreement between each of the model's predictions and their associated experimental observation is not quantitative. However, modeled and experimental yields of total SRP, phenol, and trimethylphenol suggest approximately $0.7 < \alpha_0 < 0.9$, which is a reasonable range for the novolac used here. This qualitative agreement encourages further investigation along the present lines. Certainly the notion that a polymer's reactions can be inferred from the reactions of its simple chemical models is appealing.

Summary and Conclusions

A model of phenolic resins and their thermolysis was developed. A single parameter, α_0, which represented the fraction of all 2-, 4- and 6-ring substituents on an average aromatic ring that was DPM substituted, provided the initial conditions for the pyrolysis model; α_0 was related to the PFR during synthesis and can be deduced independently of pyrolysis experiments. An interpretation of the pyrolysis of diphenylmethane provided the pathways and kinetics for the rate of reaction of the polymer's DPM substituents; this rate combined with simple probability arguments to chronicle the rate of the polymer's pyrolysis.

Phenol, cresols, xylenols, and trimethylphenol were the products predicted of resin thermolysis. Agreement between model prediction and experimental results was most favorable for total SRP, phenol, and trimethylphenol yields. The agreement between predicted and experimental yields of cresols and xylenols was poor.

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Nomenclature

α	fraction of a 2-, 4-, or 6-aromatic ring position substituent that is a bonded DPM substituent
α_0	$\alpha(t = 0)$
β	fraction of a 2-, 4-, or 6-aromatic ring position substituent that is a nonbonded substituent (e.g., H or CH_3)
DPM	diphenylmethane (substituent or pure compound)
BEN	benzene
TOL	toluene
β_0	$\beta(t = 0)$
I*	hypothetical intermediate in the pyrolysis of DPM
k_1	rate constant (L/(mol·s))
K	ratio of rate constants L/mol
PFR	phenol to formaldehyde ratio during resin synthesis
SRP	single aromatic ring product
$N(i)$	number fraction of species i
$P(i)$	probability of substituent i (either H or CH_3)
Δ	change
M_i	molecular weight of species or fragment i
t	time (s)

References and Notes

(1) Benjamin, B. M.; Maupin, P. H.; Brown, L. L.; Collins, C. J.; Raaen, V. F. *Fuel* **1978**, *57*, 69.
(2) Conley, R. T. "Thermal Stability of Polymers"; Marcel Dekker: New York, 1970; Chapter 11.
(3) Fischer, G. E.; Neerman, J. C. *Ind. Eng. Chem. Prod. Res. Dev.* **1966**, *5*, 3, 288.
(4) Kamiya, Y.; Yao, T.; Oikawa, S. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1979**, *24*, 116.
(5) Katti, M. R.; Thampy, R. T. *Plast. Age* **1977**, *28* (2), 121–8.
(6) Klein, M. T.; Virk, P. S. *Ind. Eng. Chem. Fundam.* **1983**, *22*, 35.
(7) Klein, M. T.; Virk, P. S. MIT Energy Lab Report No. MIT-EL81-005, 1981.
(8) Knop, A.; Scheib, W. "Chemistry and Application of Phenolic Resins"; Springer-Verlag: Berlin, 1979.
(9) Korshak, V. V. "The Chemical Structure and Thermal Characteristics of Polymers"; Israel Program for Scientific Translations, Ltd.: Jerusalem, Israel, 1971.
(10) Maciel, G. E.; Chuang, I. S.; Gollob, L. *Macromolecules* **1984**, *17*, 1081.
(11) Orzeszco, A.; Kolbrecki, A. *J. Appl. Polym. Sci.* **1980**, *25*, 2969.
(12) Ozer, R. B.Ch.E. Thesis, University of Delaware, Newark, DE, 1984.
(13) Petrocelli, F. P.; Klein, M. T. *Macromolecules* **1984**, *17*, 161.
(14) Shah, Y. T. "Reaction Engineering in Direct Coal Liquefaction"; Addison-Wesley: Reading, MA, 1981.
(15) Sharifi, N.; Tirgan, M. R. *J. Appl. Polym. Sci.* **1973**, *17*, 4, 1113.
(16) Tewarson, A. "Pyrolysis Properties of Polymeric Materials"; *Gov. Rep. Announce. Index* (*U.S.*), 1981.
(17) Voorhees, K. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 213.