1966 *Macromolecules* **1992,** *25,* 1966-1969

The Novolak Synthesis Reaction: A Description Based on Reactivities[†]

Leonard E. Bogan, Jr.

Rohm and Haas Company, 727 Norristown Road, Spring House, Pennsylvania 19477

Received September 16, 1991; Revised Manuscript Received December 17, 1991

ABSTRACT: A kinetic model is proposed for the acid-catalyzed condensation of *m*- and *p*-cresol with formaldehyde. It differs from previous models in that, rather than considering the two reaction steps separately, it describes them together using relative reactivities of the reactive ring positions. These reactivities can be measured, and the model requires no adjustable parameters. Calculations based on this model accurately predict the amount of unreacted cresol at the end of a reaction, the fraction of *m*-cresol rings in the polymer that are substituted at both the 2- and 4-positions, and the composition of *m,p*-cresol copolymer novolaks. The results of these calculations and others describing branch density and end-group compositions are reported. According to the model, incorporation of a phenolic monomer into a polymer chain does not change the reactivities of the unreacted sites on the ring. Due to its poor reactivity, *p*-cresol functions to a first approximation as an unreactive diluent and ultimately as a capping monomer. The result is that copolymers prepared with a large fraction of *p*-cresol in the monomer charge look like *m*-cresol homopolymer novolaks made with a higher formaldehyde/phenol ratio and then end-capped with *p*-cresol.

Introduction

A major objective in the advancement of electronics technology is the miniaturization of integrated circuits. The limiting factor in this miniaturization is and has been imaging technology, or microlithography. Advances in microlithography will come from better optics, which are designed by engineers, and better photoresists, which are designed by chemists.

Exposure of a resist to actinic radiation induces a chemical change (usually production of acid) in the exposed area which, either on its own or by catalyzing a chemical reaction, changes the rate at which the resist dissolves in developer solution (usually aqueous base). Accurate transfer of a pattern to the resist, and ultimately to the substrate, requires a clear and sharp differentiation of dissolution rates at the border between exposed and unexposed resist. The major component of a photoresist is a polymer, and the dissolution properties of that polymer greatly affect the ability of the resist to resolve small images. Novolak copolymers of *m*-cresol and *p*-cresol find wide use in photoresists for microlithography because they exhibit the necessary differentiation of dissolution rates.

The importance of *m,p*-cresol novolak resins to photoresist formulation makes the supply of a range of copolymer compositions and molecular weights useful. In novolak resin synthesis, the growing polymer chains compete with cresol monomer for formaldehyde. As conversion increases, the polymer competes better than the monomer, so that the supply of phenolic monomer is never exhausted, and the amount of unreacted monomer changes with extent of reaction. Since different monomers react at different rates, copolymer composition will not be the same as the charge ratio of the monomers, and it will change over the course of the reaction. We describe the use of relative monomer reactivities to predict copolymer composition.

The acid-catalyzed condensation of phenols with formaldehyde proceeds in two steps. In the first step, a hydroxymethyl cation attacks a phenolic ring at a position ortho or para to the hydroxyl, forming a (hydroxymethyl)phenol. In a faster step, the (hydroxymethyl)phenol condenses with another phenolic ring to give a methylene bridge between two rings.[1] Earlier attempts at the simulation of this reaction were made complex by the consideration of these steps separately.[2] This is necessary if one wants to describe the methylene (bridge) environment (i.e., *o,o*′, *o,p*′, etc.). A simpler approach can be used if one describes only the substitution pattern of the phenolic rings. In this case, both steps are considered at once, and the pair of steps is characterized by a set of site reactivity ratios. The resulting simple, kinetic model of the novolak synthesis reaction requires knowledge of the relative reactivities of the phenolic monomers and, optionally, of the different reactive sites on those monomers. Competition experiments have recently made this information available.[3] We have simulated the novolak synthesis reaction using these measured reactivities, considering the synthesis of a *m*-cresol novolak homopolymer and of *m,p*-cresol novolak copolymers at 70:30 and 50:50 charge ratios.

Experimental Section

The calculations were carried out on an Apple Macintosh II computer using a Microsoft Excel 3.0 spreadsheet written for this purpose. The model keeps track of the number of cresol rings in the reaction mixture which have a given substitution pattern. In each iteration of the calculation, 0.001 equiv of formaldehyde was allowed to react with all of the available sites according to their relative reactivities. The number of reactions at each site was normalized to a total of 0.002 equiv (0.001 equiv of CH_2O × 2 sites/CH_2O molecule), and the number of rings with each substitution pattern was adjusted for the number which had reacted and the number which had formed during that iteration.

Novolak Synthesis. In a typical reaction, *m*-cresol (296.9 g, 2.75 mol), oxalic acid dihydrate (29.9 g, 0.24 mol), and diglyme (290.1 g) were mixed to dissolve and heated under nitrogen to 99 °C. A solution of formalin (159.0 g × 36.3% w/w CH_2O = 57.72 g, 1.92 mol) in diglyme (57.5 g) was added at once. The solution was stirred under nitrogen at 99 °C for 3 h, and then the volatile components were distilled. During the distillation, the temperature was gradually increased and the pressure was gradually decreased until final conditions of 215 °C/10 mmHg were achieved. Throughout the reaction, the reaction vessel was equipped with a Friedrich condenser which was, in turn, connected to two dry ice traps in series. The reaction vessel was filled with nitrogen and cooled in solid dry ice. The solid polymer was removed and weighed (271.9 g). The material collected from the distillation and from the dry ice traps was weighed (539.5 g).

[†] For Shipley Co., 2300 Washington St., Newton, MA 02162.

0024-9297/92/2225-1966$03.00/0

Mass Balance Calculations. The mass not accounted for is assumed to be formaldehyde which distilled but did not condense. Thus, for the experiment described above, the total mass charged was 833.4 g, and the total collected was 811.4 g. The difference between the mass charged and the mass condensed represents the mass of unreacted formaldehyde as well as CO and CO_2 formed in the thermolysis of the oxalic acid. The amount of unreacted formaldehyde is then 833.4 g − 811.4 g − 17.08 g = 4.92 g. The amount of carbon in the polymer which was derived from formaldehyde is then

$$(57.72\text{ g} - 4.92\text{ g})[(12.011\text{ g/mol})/(30.03\text{ g/mol})] = 21.12\text{ g}$$

and the amount of cresol in the polymer is obtained by difference; 271.9 g − 21.1 g = 250.8 g. At low pH, (hydroxymethyl)phenol groups are unstable with respect to further condensation, so a polymer chain involves the condensation of n moles of cresol with $n - 1$ moles of formaldehyde. The mean chain length, or degree of polymerization of the polymer (DP_n), can be expressed as

$$1/\left(1 - \frac{(21.12/12.011)\text{ mol of CH}_2\text{O carbon}}{(250.8/108.14)\text{ mol of cresol}}\right) = 4.14$$

This method assumes that unreacted formaldehyde, once distilled, does not condense in the same traps with the water, diglyme, and cresol. The validity of this assumption cannot be tested by determining the weight loss at zero time because, under the conditions necessary for distillation, some reaction of formaldehyde with cresol is inevitable even in the absence of catalyst. The validity of the assumption can be tested in the following manner. One can calculate DP_n and the amounts of (un)reacted formaldehyde and cresol by setting up independent equations based separately on the weight of novolak resin and the weight of distillate. At a single value of DP_n, both equations generate the same value for the amount of unreacted formaldehyde. The agreement of this calculation of the amount of formaldehyde in the polymer with the amount determined by assuming that the mass unaccounted for was distilled formaldehyde validates that assumption.

Substitution Pattern at *m*-Cresol. We have previously shown that the upfield (ca. 16 ppm relative to TMS) methyl resonance in ^{13}C NMR spectra of *m*-cresol novolak resins corresponds to rings which are substituted at both the 2- and 4-positions.[3] Since the model tells us about ring substitution, we can compare the experimentally determined fraction of all rings which have this substitution pattern with the prediction of the model.

Estimation of Error. Experimental error was calculated by assuming measurement accuracies of ±0.5 g (ca. 0.25%) for novolak weights and ±2.0 g (ca. 0.25%; this is a reasonable estimate of possible "hang-up" in the condenser) for distillate weights and then solving for *F:P*, amount of unreacted cresol, and DP_n at these limits. Measurement errors for NMR determinations of copolymer composition and *m*-cresol 2,4-disubstitution were assumed to be 0.01, as determined in our earlier work.[3] It is worth noting that a large error in the measurement of the amount of formaldehyde reacted would render comparisons useless, since this is the independent variable for all of the calculations.

The parameter χ^2/η was calculated from the following formula, which convolutes the error estimate for the independent variable with the error estimate for the dependent variable:

$$\chi^2/\eta = \frac{\sum[(y_{obs} - y_{pred})^2/(S_y^2 + S_x^2 \times \text{slope}^2)]}{(\text{no. of points}) - 1}$$

Results and Discussion

The results of a simulation are only as good as the model, and the credibility of the model can be assessed only by comparing its predictions with experimentally measured quantities. Analysis of actual resins by NMR spectroscopy gives the amount of 2,4-substitution of *m*-cresol rings, and for the copolymers, monomer composition.[3] We were able to quantify three additional properties by carrying out a careful mass balance of the reaction. Careful experimentation gives the weight of novolak resin formed in the reaction as well as the weight of material distilled from the resin after reaction. Consideration of the weights of materials charged and the chemistry of the reaction enables an accounting for the weights recovered. From these measurements, one can calculate the amount of cresol reacted, the amount of formaldehyde reacted, and the number-average degree of polymerization.

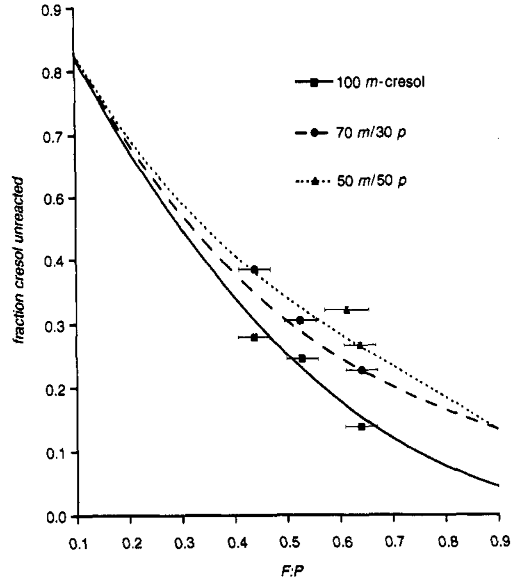

Figure 1. Experimental points and calculated curve for amount of unreacted cresol as a function of formaldehyde/phenol (*F:P*) ratio for novolak resins prepared from charge ratios of 100 *m*-cresol, 70 *m*-cresol/30 *p*-cresol, or 50 *m*-cresol/50 *p*-cresol.

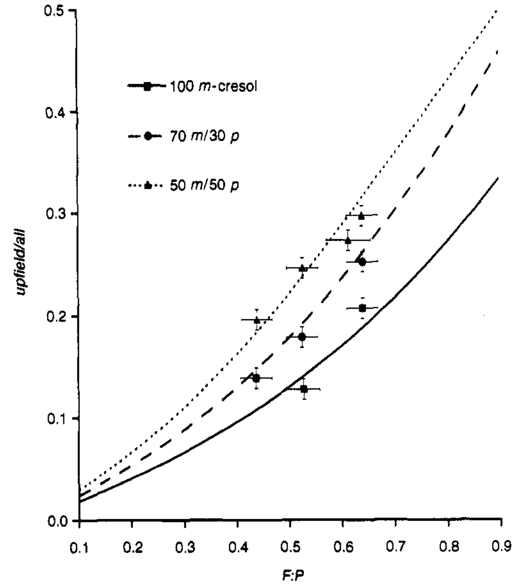

Figure 2. Experimental points and calculated curve for fraction of all rings which are 2,4-disubstituted *m*-cresol as a function of formaldehyde/phenol (*F:P*) ratio for novolak resins prepared from charge ratios of 100 *m*-cresol, 70 *m*-cresol/30 *p*-cresol, or 50 *m*-cresol/50 *p*-cresol.

Now we can compare amount of unreacted cresol, degree of 2,4-substitution, calculated resin composition, and resin DP_n with experiment. These comparisons are shown in Figures 1–7. The amount of unreacted cresol remaining after polymerization depends on the competition between free monomer and growing chains for formaldehyde. The simplest version of our model assumes that site reactivities are unchanged when a phenolic ring is part of a polymer chain. The relative reactivities of monomer and

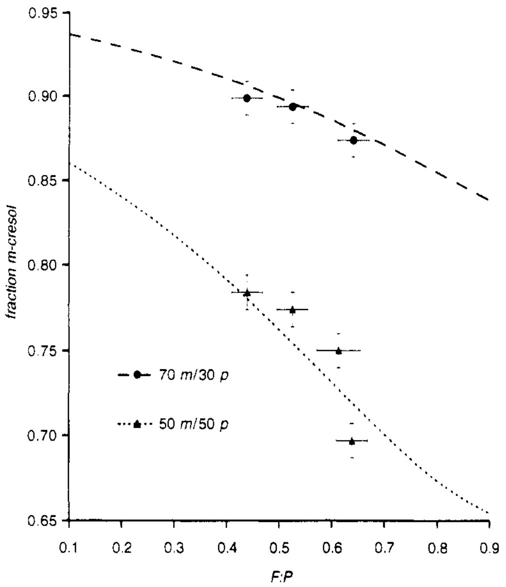

Figure 3. Experimental points and calculated curve for fraction of *m*-cresol in the polymer as a function of formaldehyde/phenol (*F*:*P*) ratio for novolak resins prepared from charge ratios of 70 *m*-cresol/30 *p*-cresol or 50 *m*-cresol/50 *p*-cresol.

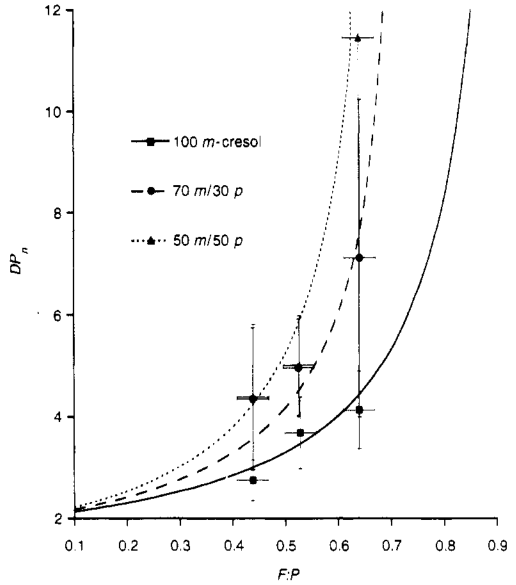

Figure 4. Experimental points and calculated curve for DP_n of the polymer as a function of formaldehyde/phenol (*F*:*P*) ratio for novolak resins prepared from charge ratios of 100 *m*-cresol, 70 *m*-cresol/30 *p*-cresol, or 50 *m*-cresol/50 *p*-cresol.

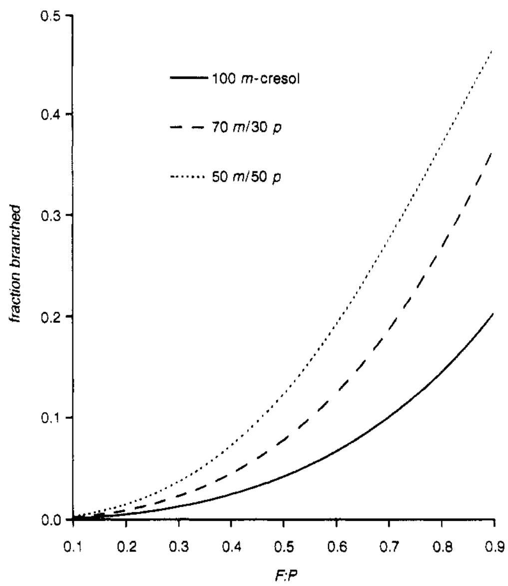

Figure 5. Calculated branch density (as fraction of all rings which are branch sites) as a function of formaldehyde/phenol (*F*:*P*) ratio for novolak resins prepared from charge ratios of 100 *m*-cresol, 70 *m*-cresol/30 *p*-cresol, or 50 *m*-cresol/50 *p*-cresol.

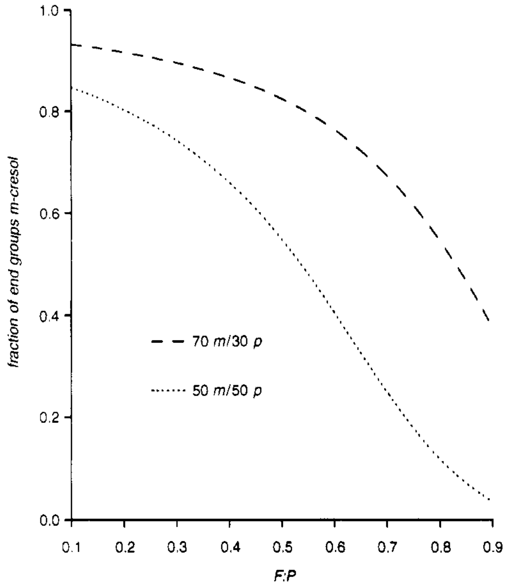

Figure 6. Calculated fraction of the polymer end groups which are *m*-cresol rings as a function of formaldehyde/phenol (*F*:*P*) ratio for novolak resins prepared from charge ratios of 70 *m*-cresol/30 *p*-cresol or 50 *m*-cresol/50 *p*-cresol.

growing chain were parametrized to test the assumption, but we found that this offered no improvement in the fit to experimental data, so we do not use a parameter. Calculation of the amount of unreacted cresol in a copolymerization of *m*- and *p*-cresol is also sensitive to the relative reactivities of the monomers. We relied primarily on calculated composition but also on the amount of unreacted cresol to choose the best value for this reactivity. For all three polymer systems considered together (a total of 10 experimental points) and for equal reactivity of free monomer and growing chain, the best fit to the observed amount of unreacted cresol gave a χ^2/η of 1.09.

The most important attributes for determining the relative site reactivities are the calculated and observed amounts of 2,4-substitution. One unexpected benefit of modeling is that it enables us to reduce the uncertainty in the measurement of relative reactivities. To measure these numbers, the amount of each dimer formed by reaction of excess *m*-cresol with formaldehyde was measured by ^{13}C NMR. The reactivities were calculated from the product distribution to be 0.12 ± 0.06, 0.54 ± 0.07, and 0.34 ± 0.06 for the 2-, 4-, and 6-positions, respectively.[4] The best fit to experimental data (10 experimental points) used values of 0.17, 0.52, and 0.31, respectively, giving a χ^2/η of 0.94.

The calculated resin composition depends primarily on the relative reactivities of the two cresols. Just as the calculated amount of 2,4-substitution helped to define relative site reactivities with less error than the measurement, this calculation helps to define relative monomer reactivities more accurately than the measurement. The reactivity of *p*-cresol with formaldehyde was measured to be 0.09 ± 0.03 relative to that of *m*-cresol. The best fit of the model to experiment (seven experimental points) used a value of 0.07, giving a χ^2/η of 1.27.

The calculated DP_n depends on the relative reactivities of the monomers. The measurement error increases with

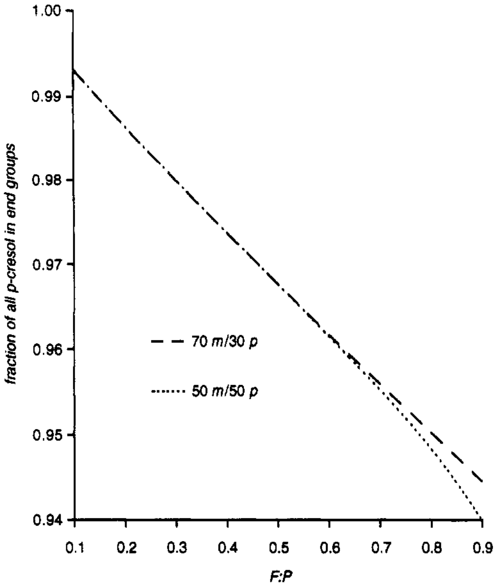

Figure 7. Calculated fraction of the polymer *p*-cresol which is present in the end groups as a function of formaldehyde/phenol (*F*:*P*) ratio for novolak resins prepared from charge ratios of 70 *m*-cresol/30 *p*-cresol or 50 *m*-cresol/50 *p*-cresol.

F:*P*, and for the copolymers it renders this attribute useless for calibration of the model. This comparison is not used to judge the accuracy of the model.

All of these comparisons of calculation with observation show good agreement. Because the model accurately predicts four different properties, the calculation of which depend on the entire group of kinetic variables used in the model, we believe that the model is a good description of the system and we place some trust in its other predictions.

In addition to the data presented, the calculations provide two pieces of information: the branch density (i.e., the amount of 2,4,6-substitution) and the composition of end groups. Since the growing chain competes better for formaldehyde at higher conversion, branch density increases with increasing molecular weight. Since *p*-cresol is so much less reactive than *m*-cresol, a higher fraction of *p*-cresol in the initial charge gives not only higher molecular weights but also higher branch density at a given *F*:*P*.

As *F*:*P* (which is equivalent to extent of reaction) increases, more *p*-cresol is found in the end groups. The majority of the *p*-cresol (≥95%) is always contained in the end groups. In other words, the relatively low reactivity of *p*-cresol makes it act as a capping monomer, to a first approximation.

Conclusions. The acid-catalyzed condensation of *m*- and/or *p*-cresol with formaldehyde is described well by a model in which chain growth occurs in a statistical manner characterized by constant, relative reactivities of the reactive ring positions. These reactivities can be measured, and the model requires no adjustable parameters. Calculations based on this model accurately predict the amount of unreacted cresol at the end of a reaction, the fraction of *m*-cresol rings in the polymer which are substituted at both the 2- and 4-positions, and the composition of *m*,*p*-cresol copolymer novolaks.

According to the model, incorporation of a phenolic monomer into a polymer chain does not change the reactivities of the unreacted sites on the ring. Due to its poor reactivity, *p*-cresol functions to a first approximation as an unreactive diluent and ultimately as a capping monomer. The result is that copolymers prepared with a large fraction of *p*-cresol in the monomer charge look like *m*-cresol homopolymer novolaks made with a higher formaldehyde/phenol ratio and then end-capped with *p*-cresol.

The accurate predictions of copolymer composition which are made by the model enable rational synthesis of new *m*,*p*-cresol novolak resins. The other predictions made by the model lead to a better understanding of copolymer structure. Both the rational synthesis of these copolymers and an understanding of their structure are important in the design of photoresists for microlithography.

References and Notes

(1) Knop, A.; Pilato, L. A. *Phenolic Resins*; Springer-Verlag: New York, 1985.

(2) McLaughlin, H. S.; Nauman, E. B. *Polym. Mater. Sci. Eng.* **1988**, *59*, 558. Williams, R. J. J.; Adabbo, H. E.; Aranguren, M. I.; Borrajo, J.; Vazquez, A. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1983**, *24* (2), 169. Kumar, A.; Gupta, S. K.; Kumar, B.; Somu, N. *Polymer* **1983**, *24*, 1180. Kumar, A.; Gupta, S. K.; Kumar, B. *Polymer* **1982**, *23*, 1929. Kumar, A.; Phukan, U. K.; Gupta, S. K. *J. Appl. Polym. Sci.* **1982**, *27*, 3393. Kumar, A.; Phukan, U. K.; Kulshreshtha, A. K.; Gupta, S. K. *Polymer* **1982**, *23*, 215. Ishida, S.-I.; Tsutsumi, Y.; Kaneko, K. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1609.

(3) Bogan, L. E., Jr. *Macromolecules* **1991**, *24*, 4807.

(4) Bogan, L. E., Jr.; Wolk, S. K. *Macromolecules* **1992**, *25*, 161.