The Mechanism of Phenolic Polymer Dissolution: A New Perspective

Pavlos C. Tsiartas,[†] Lewis W. Flanagin,[†] Clifford L. Henderson,[†] William D. Hinsberg,[‡] Isaac C. Sanchez,[†] Roger T. Bonnecaze,[†] and C. Grant Willson^{*,†}

Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712 and IBM Almaden Research Center, 650 Harry Road, San Jose, California 95126

Received May 29, 1997; Revised Manuscript Received June 2, 1997®

ABSTRACT: The function of common, positive tone photoresist materials is based on radiation-induced modulation of the dissolution rate of phenolic polymer films in aqueous base. The process through which novolac and other low molecular weight phenolic polymers undergo dissolution is examined from a new perspective in which the "average degree of ionization" of the polymer is regarded as the principal factor that determines the rate of dissolution rather than a diffusive, transport process. This perspective has been coupled with a probabilistic model that provides an explanation for the dependence of the dissolution rate on molecular weight, base concentration, added salts, residual casting solvent, and the addition of "dissolution inhibitors". It predicts the observed minimum base concentration below which dissolution is no longer observed, and it predicts a molecular weight dependence of that phenomenon. A series of experiments was designed to test this predicted molecular weight response. The results of these experiments are in good agreement with the predicted response.

Introduction

The continuing race to shrink the circuit elements of microelectronic devices has captured the interest of both the technical world and the general public. This race to miniaturize provides both improved performance and decreased cost. One of the key elements in this race is the lithographic process that is used to define the patterns of conductor, semiconductor, and insulator materials that make up the devices. The lithographic process, in turn, is based on radiation-induced changes in the dissolution rate of thin photoresist films that are formulated from phenolic polymers such as novolac or poly(p-hydroxystyrene). It surprises many to learn that the dissolution process upon which the multibillion dollar microelectronics industry is based is very poorly understood. Scientists and engineers understand Brillouin zones, band gaps, and signal propagation, and they have accurate models based on fundamental understanding that allow them to predict accurately the performance of devices before they are constructed. However, there is no molecular level model with predictive capability for the dissolution of phenolic polymers in aqueous base, the process that is the key to their fabrication.

There are actually several different regimes of polymer dissolution, each of which demands a separate model. The mechanism whereby polystyrene dissolves in a good solvent is clearly very different than that which controls the dissolution of poly(methyl methacrylate), and both of these are different from the dissolution of phenolic polymers in aqueous base. Of these processes, only the first, dissolution of glassy polymers like polystyrene, is reasonably well understood.

Peppas and co-workers have recently applied scaling concepts¹ to the description of the dissolution of polystyrene.² Their theory proposes the initial formation of a gel layer at the polymer–solvent interface that is generated as the solvent diffuses into the film. Once this gel layer is formed, it is propagated at constant thickness through the polymer film as it dissolves. The dissolution rate and the thickness of the gel layer are dependent on the molecular weight of the polymer, and the dependence can be accurately described by reptation theory.² Experiments in which polystyrene of high but differing molecular weights was dissolved in methyl ethyl ketone show excellent correlation between theory and measurement. This description that works so well for polystyrene fails when applied to poly(methyl methacrylate). Ouano and Carothers have shown that poly-(methyl methacrylate) dissolves without formation of a significant gel layer except for the case of very high molecular weight samples.³⁻⁶

It is tempting to apply the scaling approach to the description of the dissolution of phenolic polymers in aqueous base, but this is inappropriate for two reasons. First, the material of greatest engineering interest, novolac, has a degree of polymerization of about 10 and a $M_{\rm w}$ of the order of 1000, far below the entanglement molecular weight. Therefore, reptation models and scaling theory do not apply to these materials.¹ Secondly, and more importantly, when phenolic polymers dissolve in aqueous base, they undergo a chemical reaction. The substance in solution, a polyion, is very different from the polymer in the glassy film, a polyol. The "dissolution" of novolac films may be best described as "etching" in the sense that this term is used to describe the "dissolution" of copper in nitric acid or the "dissolution" of quartz in hydrofluoric acid. In these examples, the starting material is essentially insoluble in the solvent (water) but is converted into a soluble species through a chemical reaction. We believe that the dissolution of novolac in aqueous base is more like the dissolution of copper in nitric acid than it is like high molecular weight polystyrene dissolving in methyl ethyl ketone.

The dissolution of phenolic polymers in aqueous base is obviously a fairly complex process, the rate of which depends on a number of variables. The influence of a number of variables on dissolution rate has been quantified, and any really useful model of the process must account for at least the sense or trends of the

^{*} Author to whom correspondence should be addressed.

[†]The University of Texas at Austin.

[‡]IBM Almaden Research Center.

[®] Abstract published in *Advance ACS Abstracts,* July 15, 1997.



Figure 1. Structures of aryl 1-Oxo-2-diazonaphthoquinonesulfonate (**I**), Medrum's diazo compound (**II**), and aryl naphthoquinone sulfonate (**III**). **I** is the sort of structure commonly used as a photoactive compound and dissolution inhibitor in resist formulations. Compound **I** undergoes base-catalyzed azocoupling with activated aromatics to yield azobenzene derivatives. Meldrum's diazo compound (**II**) does not form azo linkages to phenols under the conditions used in photoresist development, but Meldrum's diazo compound is a functional dissolution inhibitor. Compound **III**, an aryl ester of α -naphthalenesulfonic acid, is equivalent to **I** as an inhibitor but lacks the diazo functionality required for the "stone wall" model.²³

measured responses. For example, the dissolution rate is inversely related to the logarithm of the molecular weight, and the slope of this relationship is always negative but varies from -0.3 to about -3.0, depending on the experimental conditions and the exact nature of the polymer.^{7–11} The rate is strongly dependent on the pH of the developer, increasing nonlinearly with increasing pH,¹² and there is a "critical", nonzero base concentration (c_0) below which the rate is essentially zero.¹³ The effect of added salts is particularly complex; the influence as a function of added salt concentration can essentially be divided into two parts: a fairly linear region in which dissolution rate increases with the initial addition of salt and a nonlinear, decreasing dissolution rate region at higher salt concentrations.¹⁴ The influence of residual casting solvent is to increase markedly the dissolution rate of phenolic polymer films,¹⁵⁻¹⁸ and the rate can be drastically retarded by the addition of certain monomeric substances appropriately called dissolution inhibitors.^{19,20} All of these response functions must be captured by a useful model for the dissolution process.

Several models have been proposed to describe the dissolution of novolac in aqueous base. Hanabata and co-workers at Sumitomo Co.²¹⁻²⁵ have conducted detailed studies on the influence of changes in novolac structure on dissolution. On the basis of these studies, they proposed the "stone wall model" for the function of novolac-based photoresists.²³ The photoresists studied were all formulated from novolac and a diazonaphthoquinone dissolution inhibitor. The model invokes the formation of a base-catalyzed azo-coupling between the diazoquinone and the phenolic resin which occurs in the unexposed areas of the resist film. This coupling reaction causes increases in molecular weight and thereby creates a "stone wall" that is resistant to dissolution in base. Ultraviolet radiation "destroys" the diazoquinone and thereby prevents the coupling reaction in the exposed areas of the film, which therefore dissolve rapidly. This model describes many aspects of photoresist dissolution response, but it has fallen from favor because many compounds have been demonstrated to have a powerful dissolution inhibition response that do not undergo azo-coupling. The 1,3diacyl-2-diazo compounds described by Grant et al.²⁶ are functional examples, and the dissolution inhibition of the naphthalene sulfonate of hydroxybenzophenone is essentially equal to that of the corresponding diazonaphthoquinone (Figure 1).

Arcus' studies of the dissolution of phenolic polymers in aqueous base led him to propose the "membrane model" for positive photoresist development.¹⁰ This model is based on data derived from the study of high molecular weight phenolic polymers and involves the presence of a gel layer of the sort described by Peppas.² Arcus presents some experimental evidence for the formation of a gel layer in his samples. Arcus' work is excellent, but the materials used in his study are in a very different molecular weight regime than that of the novolac used to formulate photoresists. They are, for example, well above the entanglement molecular weight. If a gel layer is formed during the dissolution of novolac, it is very, very thin.²⁷

The most promising current picture of novolac dissolution is based on an adaptation of percolation theory by Reiser and co-workers at the Polytechnic University.²⁸⁻³² Percolation theory was originally developed by the physics community to describe a number of phenomena ranging from the spread of forest fires to the gelation of polymers and the formation of infinite networks.³³ Reiser has adopted and adapted this theory to the description of the dissolution of phenolic polymers in aqueous base with considerable success. His theory has provided good agreement with experiment for many of the variables that influence dissolution rate. Reiser's work is most impressive and is continuously being refined. However, it does not account for the effect of some of the key variables on rate. Chief among these is the influence of molecular weight. The existence of a minimum base concentration below which development does not occur is not currently explained by Dr. Reiser's theory, and it is not clear that the percolation theory can account for the complex influence of added salts and changes in ionic strength on the rate.

The common element of all these models is an assumption that the rate-controlling step in the dissolution process is the diffusion of base through some barrier to the acidic hydroxyls of the novolac. Reiser's model, in particular, does not deal with the question of how the novolac, once ionized, is transported through the "transport layer" into solution. Presumably, this process is fast compared to the rate-controlling transport of base to the hydroxyl groups.

Our model is very different than these and is derived from careful analysis of the complex and counterintuitive influence of changes in developer concentration and composition on the rate of dissolution of novolac and low molecular weight poly(*p*-hydroxystyrene). It was influenced by our "etching" picture of the dissolution process, and it should be emphasized that it applies only to phenolic polymers below the entanglement molecular weight.

In our study of developer effects,¹⁴ novolac films were dissolved in a series of solutions of constant hydroxide ion strength (0.07 N) derived from different alkali metal hydroxides (LiOH, NaOH, KOH, RbOH, CsOH), in which their corresponding chloride salts (LiCl, NaCl, KCl, RbCl, CsCl) were added in increasing amounts. For all the salts studied, the dissolution rate curve can essentially be divided into two parts: a fairly linear region in which the dissolution rate increases with increasing amounts of added salt at constant hydroxide ion concentration and a nonlinear, decreasing dissolution rate region at higher salt concentrations (Figure 2).

We feel that an explanation for this behavior, and novolac dissolution in general, can be realized if the deprotonation reaction, which transforms a phenol group from the novolac matrix into a phenolate ion pair, is considered in greater detail. During the dissolution



Figure 2. Fit of the model in eq 5 to experimental data for the effect of added salt on development rate.¹⁴

process, some fraction of the OH sites on the (insoluble) novolac chains are converted to (soluble) phenolate sites by means of an acid-base deprotonation reaction. We hypothesize that the onset of dissolution occurs only after the polymer has attained some critical fraction F of deprotonated (phenolate) sites. In the extreme case the polymer chain is insoluble for all the deprotonation steps prior to this critical step; once the polymer is soluble, subsequent deprotonation steps have no bearing on the dissolution process. Let us first consider the simplest case, the acid-base equilibrium reaction of a crystalline or glassy monomeric phenol compound dissolving in an aqueous base solution.



One can write an equilibrium constant for such a reaction as

$$K = \frac{a_{\rm A} - a_{\rm H_2O}}{a_{\rm HA} a_{\rm OH^-}} \tag{1}$$

where a_i are the activities of the species indicated. It should be stressed that it is very important for the activity coefficients of the species in the solution to be taken into consideration, especially when the concentrations in the solution are high (beyond the limits of the Debye–Hückel regime).

Substituting $a_i = [i]\gamma_i$ in the above equation, where the quantities in brackets are concentrations and γ_i is the mean activity coefficient for species *i*, gives

$$K = \frac{[A^{-}] \gamma_{A^{-}}}{[HA][OH^{-}]\gamma_{OH^{-}}}$$
(2)

where the activity of water and the activity coefficient of HA have been set equal to unity. Equation 2 can be rearranged to the form

$$\frac{[\mathrm{A}^{-}]}{[\mathrm{HA}]} = \frac{K[\mathrm{OH}^{-}]\gamma_{\mathrm{OH}^{-}}}{\gamma_{\mathrm{A}^{-}}}$$
(3)

It is this ratio, the ratio of ionized to unionized phenolic sites, that we hypothesize is related to the dissolution rate of this type of phenolic material into basic solutions. It will be shown later in this paper that there is a formal connection between this ratio and the dissolution rate of novolac films in aqueous base. Thus far, we have considered the simplest case of a monomeric species, while our real interest lies in polymer chains of these phenolic groups. If one assumes that the pK_a of the phenolic hydroxyls is independent of the degree of ionization, then one can assume that the same type of expression can be used to estimate the overall ratio of phenolic to deprotonated sites on the polymer chain. We propose that the dissolution rate of the films is directly and simply related to this quantity. The following sections of this paper show how this simple concept, coupled with a stochastic analysis, can be used to explain the results of the added salts study14 and provide an explanation for all of the key factors that have been shown to influence the dissolution rate of novolac films.

Explanation of Added Salt Effects on Novolac Dissolution

Equation 3 provides a functional form for analyzing the data from the salt study.¹⁴ However, in order to use this expression to fit the dissolution rate data, a model for the activity coefficient, γ_A- , is needed. A widely used model for activity coefficients in solutions of high ionic strengths is due to Bahe^{34,35} and is based on the premise that the dielectric constant of the surrounding medium changes when an electrolyte is added to a solution containing that medium. The final result of Bahe's analysis, after some mathematical manipulation, is

$$\log \gamma_+ = -Ac^{1/3} + Bc \tag{4}$$

where γ_{\pm} is the mean activity coefficient of an ion pair in a solution containing an electrolyte of concentration *c*. For the reaction of interest (eq 1) the concentration of the equilibrium constituents is negligible in comparison to the electrolyte concentration. Thus, the concentration c in eq 4 can be approximated solely by the electrolyte concentration in the solution. For a pure electrolyte solution in water under standard conditions, the constant A, which follows from the structural theory of solutions, has a universal value of 0.288 94 for 1:1 electrolytes and 0.641 00 for 2:1 electrolytes, 34,35 and B is an experimentally determined parameter specific to the electrolyte. Since the solutions in our salt study¹⁴ contained a mixture of aqueous base, salt, and polyion, the value for A is expected to be different from the reported values given above for pure electrolyte solutions. Therefore, we allow both A and B to be determined through fitting the experimental data. The Madelung constants A and B are used to relate the physical forces in the electrolyte solution to the activity

Table 1. Fit Parameters for Data Presented in Figure 2Using the Model in Eq 5

	0		-	
salt added	k	Α	В	correl coeff
LiCl	0.5628	3.869	1.703	0.99
NaCl	0.3236	3.869	1.470	0.98
KCl	0.2359	3.869	1.483	0.97
RbCl	0.0904	3.869	1.474	0.96

coefficients of the ionic species. The constant A is a scaling factor for the Coulombic forces, and the constant B is a scaling factor for the forces resulting from a lowering of the dielectric constant in close proximity to the ions. The constant A should depend only on the charges of the ionic species present, whereas B should vary directly with the size of the hydrated ions.³⁴ Consequently, in our parametrization of the data, we choose a single value for A, which represents all of the data well, and allow the parameters k and B to vary.

Substituting γ_{\pm} from eq 4 for γ_{A} – in eq 3 yields

$$R = k \cdot 10^{Ac^{1/3} - Bc} \tag{5}$$

where *R*, the dissolution rate, is taken to be proportional to the ratio of ionized to unionized sites on the polymer chain and the constant k is a lumped parameter that scales with the base activity and the degree of polymerization. Figure 2 shows the fit of the model in eq 5 to the rate data for a number of different added salts presented in our earlier paper.¹⁴ The values for the model parameters A, B, and k, which were extracted from these data, are displayed in Table 1. Note that the *B* parameter varies directly with the hydrated ionic radii of the cations, as predicted.³⁴ The radius of the hydrated lithium ion is significantly larger than those of the other hydrated alkali metal cations, which are nearly all the same size.¹³ The model successfully represents the dissolution rate data for each of the salts with high correlation coefficients (Table 1).

Probabilistic Approach to Describing Phenolic Polymer Dissolution

The analysis presented above suggests that the dissolution rate is not diffusion-limited but, rather, is somehow dependent on the ratio of ionized to protonated phenolic hydroxyl sites on the surface of the film. It is therefore possible to visualize the dissolution process as a layer-by-layer "etching" of the phenolic sites on the surface by hydroxide ions. A cartoon comparing this process to the percolative dissolution process is provided in Figure 3. In the limit of a crystal of the monomer, each molecule that is ionized is switched from the insoluble to the soluble state and is quickly transported into solution. The layer is thus etched away just as a copper surface is etched by nitric acid. One does not need to invoke a gel layer to describe either process. When the degree of polymerization is greater than one, some certain proportion of the phenol sites on a single chain must be ionized in order for the chain to be converted from the insoluble to the soluble state; i.e., the dissolution rate is controlled by an imposed solubility criterion and depends on the degree of ionization.

In mathematical terms, a given phenolic polymer becomes soluble when a certain fraction F of its phenol groups are deprotonated. First, for the sake of simplicity, we will make several obviously inaccurate and oversimplifying assumptions. We will return to the importance of these assumptions later. For simplicity then, we assume that all phenol groups have equal probability of being ionized; i.e., the pK_a is constant and



Figure 3. Schematic comparison of (a) the stochastic "surfaceetching" model and (b) the percolation model. In both models, the cubes represent ionizable sites on the phenolic polymers, and the top surface of the solid is in contact with the developer. In the stochastic model for the case of tetramers (a), those chains that include at least two ionized sites (filled cubes) go rapidly into solution. The etching rate is determined by the length of the polymer and the fraction of the surface that is ionized. In the percolation model (b), the rate of dissolution depends upon the formation of an interconnected, percolative pathway from the developer surface through the penetration zone and the transport of ionic species along that pathway.

independent of the degree of ionization. The issue of "solvent accessibility" is neglected, which essentially implies that all of the monomer units of a particular chain are in the same layer of the film. A monodisperse polymer sample is also assumed.

The model system under consideration can then be imagined as composed of a thin, solid layer of *m* phenolic polymer chains, each having *n* phenol groups or sites, immersed in a bath of aqueous base. If we assume that the acid—base equilibria are fast relative to the dissolution rate and that the ratio $[A^-]/[HA]$ is the same on the surface as in the equilibrium boundary layer that is in contact with the surface, then the deprotonated fraction ϕ of all *nm* phenol groups on the surface and in the boundary layer may be assumed to be constant. Define $x_1, x_2, ..., x_m$ for each of the *m* chains such that x_i may have one of two values: 1 (soluble) if at least *Fn* of the sites on chain *i* are ionized and 0 (insoluble) otherwise. The fraction *y* of polymer chains that meet the solubility criterion is then given by

$$y = E(\sum_{i=1}^{m} x_i)/m = \frac{1}{m} \sum_{i=1}^{m} E(x_i)$$
(6)

where E(z) is the expectation value for *z*. Because of the identical nature of the polymer chains, $E(x_i)$ should be the same for all the chains, so the product $mE(x_1)$ may be substituted for the sum in eq 6, leaving the following result:

$$y = E(x_1) = P(x_1=1)$$
 (7)

where P(z) is the probability of *z*. Thus, for our simplified boundary conditions, the fraction of polymer chains that are soluble is merely the probability that the first chain is soluble.



Figure 4. Plot of the dimensionless dissolution rate for a number of phenolic oligomers of varying length as a function of base strength for a solubility criterion F = 0.5.

If, in the first chain, *k* of the *n* phenol groups are ionized, then the number of ways of distributing these ionized sites independently from the other polymer chains in the system is given by the combinatorial expression n!/[k!(n - k)!]. In the remaining m - 1 chains, which have a total of n(m - 1) sites, there are $\phi nm - k$ ionized phenol groups and $(1 - \phi)nm - (n - k)$ unionized sites. The number of ways that it is possible to arrange the *m* polymer chains for any given value of *k* is thus

$$C = \frac{n!}{k!(n-k)!} \frac{(nm-n)!}{(\phi nm-k)![(1-\phi)nm-(n-k)]!}$$
(8)

The number of ways that it is possible to arrange the *m* polymer chains with *k* unspecified is

$$T = \frac{(nm)!}{[(1 - \phi)nm]!(\phi nm)!}$$
(9)

Therefore, the fraction of chains which meet the solubility criterion is

$$y = \frac{1}{T} \sum_{k=Fn}^{n} C \tag{10}$$

with *C* and *T* defined by eqs 8 and 9.

Systems of interest in this work have an extremely large number of polymer chains on the surface that are in contact with the developer. Consequently, a more useful quantity is the limit of *y* as *m* approaches infinity, which we shall designate *Y*, which in the limit simplifies to

$$Y = \sum_{k=Fn}^{n} \frac{n!}{k!(n-k)!} \phi^{k} (1-\phi)^{n-k}$$
(11)

This expression is the well-known binomial distribution function. The dissolution rate of a phenolic polymer film is proportional to *Y*. In addition, ϕ scales with the difference between the pH of the developer and the p K_a of the phenolic polymer. Consequently, we can refer to *Y* as the *dimensionless dissolution rate* and relate ϕ to the base strength at constant polymer p K_a .

Figures 4 and 5 show how the dimensionless dissolution rate (*Y*) of phenolic oligomers of varying degrees of polymerization (*n*) varies as a function of base strength (ϕ). For Figure 4, the imposed solubility criterion is that at least half of the sites per chain must be ionized for



Figure 5. Plot of the dimensionless dissolution rate for a number of phenolic oligomers of varying length as a function of base strength for a solubility criterion F = 0.25.

the polymer to be soluble (i.e., F = 0.5 in eq 6), whereas for Figure 5 a more relaxed solubility criterion (F = 0.25) is assumed. One may easily and correctly deduce from these graphs that higher molecular weight polymers display nearly a step-function dependence of dissolution rate on base strength, but the oligomeric novolac polymers, which are crucial to lithographic applications, have a steep dependence of dissolution rate on the degree of polymerization for base strengths below the condition at which, on average, a fraction F of the phenolic sites are ionized. The curves in these figures demonstrate that $\phi = F$ represents a base strength corresponding to a turning point in solubility. From this point on, we will use a solubility criterion of F = 0.5 for convenience.

The dissolution rate decreases rapidly with molecular weight for $\phi < F$. For $\phi > F$, the analysis predicts a counterintuitive reversal in molecular weight dependence. This reversal is one artifact of our simplifying assumptions. The higher the molecular weight, the worse is the assumption that the process is two-dimensional. As the degree of polymerization increases, we expect the process to change until, at high molecular weight, it approaches the situation studied and described by Arcus.¹⁰ Note that in the limit where the entire surface is occupied by a single chain, there is a phase-transition-like behavior at $\phi = F$.

Examination of Figure 4 provides insight into another important variable, the critical base strength below which dissolution stops. In the probabilistic model, we may refer to a critical value of ϕ , which we designate ϕ_0 , for which $Y \approx 0$. Recalling that ϕ scales with the pH of the solution, we recognize that ϕ_0 is directly related to the critical base concentration, c_0 , and represents a critical fraction of surface phenolic sites which must be ionized in order for dissolution to occur at an observable rate. For practical purposes, we will define ϕ_0 as the base strength for which $\hat{Y} = 0.0004$. Figure 6 is a magnification of Figure 4 in the region of low dissolution rates. In Figure 6, the horizontal dotted line represents the low dissolution rate (Y = 0.0004) we have somewhat arbitrarily selected as the point at which "no observable" dissolution occurs, and thus the intersection of each *n*-curve with this line yields the critical base strength ϕ_0 for a given *n*-length polymer chain. In Figure 7, ϕ_0 is plotted versus the degree of polymerization, *n*. The critical base strength rises sharply with *n* for low molecular weight polymers, but the slope of the



Figure 6. Magnification of Figure 4 in the region of low dimensionless dissolution rates. The dotted line through Y = 0.0004 represents the defined basis for the critical base strength, ϕ_{0} .



Figure 7. Critical base strength (ϕ_0) from Figure 4 plotted as a function of the polymer chain length (*n*).

Table 2. Molecular Weights and Polydispersities for PHSFractions Used in Determining the Molecular WeightDependence of the Critical Base Concentration

Hoechst Celanese PHS fractions			Nippon Soda PHS fractions				
fraction	Mn	$M_{ m w}$	PD	fraction	$M_{ m n}$	$M_{ m w}$	PD
7E01	3 230	6 700	2.074	VP3000	3 600	4 170	1.158
8E01	5 920	11 100	1.875	VP5000	5 160	5 780	1.120
15E01	8 450	16 700	1.976	VP8000	8 770	9 740	1.111
20E01	9 250	18 400	1.989	VP15000	14 500	17 100	1.179
30E01	13 000	29 300	2.254	VP30000	29 700	33 100	1.114

curve decreases for higher degrees of polymerization. From Figure 4, it may be predicted that ϕ_0 should approach an asymptotic value of 0.5 for very high molecular weight polymers. We have conducted a series of experiments designed to test these predictions.

Experimental Procedure

A series of low-polydispersity poly(hydroxystyrene) (PHS) fractions of varying molecular weights were used for investigating the molecular weight dependence of the critical base concentration. These PHS fractions were supplied by Hoechst Celanese and Nippon Soda for the purpose of this study. Table 2 lists the molecular weights and polydispersities of the samples, as determined by SEC relative to polystyrene standards. Solutions of these resins (approximately 20 wt % in PGMEA) were spin-coated (2500 rpm for 30 s) on 4 in. silicon wafers using a Headway Research PM101DT spinner. The resulting films were then soft-baked for 2 min at 90 °C on a temperature-controlled Thermolyne HP1151B hot plate fitted with a vacuum chuck. Film thicknesses for these samples ranged from about 1 to 1.8 μ m, as measured on a SC Technologies INS800 multiwavelength interferometry instrument. Developer solutions were prepared using Shipley MF-501, a 0.262 N (nominal) tetramethylammonium hydroxide (TMAH) solution, which was diluted to provide a range of concentrations. The hydroxide ion concentration was determined by titration against an acid standard. Dissolution rates were measured at room temperature using the SC Technologies INS800 multiwavelength interferometry instrument op-



Figure 8. Dissolution rates of the poly(hydroxystyrene) samples from Hoechst Celanese shown as a function of base concentration.



Figure 9. Dissolution rates of the poly(hydroxystyrene) samples from Nippon Soda shown as a function of base concentration.

erating in Dissolution Rate Monitor (DRM) mode. Dissolution of the PHS films was carried out in puddle mode, and rate data used for comparisons were measured at the film halfthickness.

Experimental Results: Poly(hydroxystyrene) Dissolution Rates

The measured dissolution rates of the poly(hydroxystyrene) samples are shown as a function of base concentration in Figures 8 and 9 and, in the customary fashion, as a function of the number-average molecular weight in Figures 10 and 11. Dissolution rates obtained in this study are shown in Tables 3 and 4 for the PHS fractions from Hoechst Celanese and Nippon Soda, respectively. Critical base concentration data extracted from this study are shown in Table 5. As can be seen from the semilog plots of Figures 8 and 9, the base concentration dependence of the dissolution rate is, as predicted, very accurately represented by an exponential form. Extrapolation of these expressions to a rate of 1 Å/s yields a critical base concentration, c_0 , the molecular



Figure 10. Dissolution rates of the poly(hydroxystyrene) samples from Hoechst Celanese shown as a function of the number-average molecular weight. Note that these data are shown on a customary log-log plot.



Figure 11. Dissolution rates of the poly(hydroxystyrene) samples from Nippon Soda shown as a function of the number-average molecular weight.

weight dependence of which may be compared to that of the critical base strength, ϕ_0 , described earlier. In Figure 12, c_0 for the poly(hydroxystyrene) samples is plotted versus the number-average molecular weight. The critical base strength is seen to increase with



Figure 12. Experimental results for the critical base concentration vs number-average molecular weight for both samples. The plot follows the general form predicted from the probabilistic theory (Figure 7).

Table 3. Dissolution Rate Data at Varying BaseConcentrations for Nippon Soda PHS Fractions

		rate (Å/s)			
sample	$M_{\rm n}$	0.109 N	0.122 N	0.134 N	0.161 N
VP3000	3 600	112	318	572	
VP5000	5 160	37	107	212	
VP8000	8 770	11	31	74	435
VP15000	14 500	5	15	24	119
VP30000	29 700	1	5	12	50

 Table 4. Dissolution Rate Data at Varying Base

 Concentrations for Hoechst Celanese PHS Fractions

		rate (Å/s)			
sample	$M_{ m n}$	0.108 N	0.122 N	0.131 N	0.156 N
7E01	3 230	107	260	440	
8E01	5 920	37	75	120	532
15E01	8 450	11	29	47	200
20E01	9 2 5 0	11	21	42	174
30E01	13 000	2	10	17	77

Table 5. Critical Base Concentration Data for the PHS Fractions

sample	Mn	c₀ for HoechstCelanese PHS (N)	<i>c</i> ₀ for Nippon Soda PHS (N)
7E01 8E01 15E01 20E01 30E01	3 230 5 920 8 450 9 250 13 000 2 600	0.032 0.043 0.066 0.069 0.094	0.027
VP5000 VP8000 VP15000 VP30000	5 160 5 160 8 770 14 500 29 700		0.037 0.056 0.075 0.085 0.101

molecular weight, and the rise in c_0 is steeper for samples having a molecular weight less than 10 000 than the rise in c_0 for higher molecular weight samples. In addition, if these data points are extrapolated to even lower molecular weights than those measured, the extrapolation intersects the concentration axis very close to the origin.

Thus, the probabilistic model for ϕ_0 exhibits qualitatively all of the trends observed experimentally. No other model for phenolic polymer dissolution predicts all of these behaviors. This leads us to conclude that this primitive probabilistic model captures the important physical elements affecting the dissolution process that are absent from models based solely on diffusion or percolation theory. While the probabilistic model is successful at capturing the qualitative behavior of the molecular weight effect on the critical base concentration, some of the crude assumptions employed in the model must be modified in order to produce quantitative agreement with the experimental data. We are now exploring the details of the relationship between ϕ , the



Figure 13. Surface of the film envisioned as a matrix of phenolic sites, one of which is occupied by an embedded, soluble solvent molecule (shaded). The solvent dissolves rapidly, leaving a surface with fewer phenolic sites, and therefore increases the dissolution rate.

pH, and the ion concentration of the developer and the pK_a of the phenolic polymers. It is clear that the first and second ionization constants for a phenolic dimer are not identical. The dependence of the ionization constant on the degree of ionization must be taken into account in order to describe accurately the dependence of ϕ on pH. We are also working on approaches that allow inclusion of the third dimension into the dissolution analysis, which serve to increase the order of the rate dependence on molecular weight and may provide some insight into the edge roughness phenomenon.

Residual Casting Solvent Effects

The effect of residual solvent on the dissolution rate of phenolic films has been studied by several laboratories. Researchers have employed a variety of experimental methods to quantify the amount of residual solvent present in phenolic films after the so-called softbake step. These methods range from basic mass balance¹⁷ to FT-IR³⁶ to quartz crystal microbalance³⁷ to radiolabeling.^{16,38} All of the studies report that the bulk dissolution rate is substantially increased with increasing amount of residual solvent. Our model described above can account for this observation by noting that the incorporation of casting solvent in the polymer film displaces ionizable sites on the surface with intrinsically soluble sites, since the solvent has finite solubility in water without ionization. By extending the definition of ϕ to incorporate all sites within the matrix, including residual solvent, the presence of residual solvent amounts to an increase in ϕ , which results in accelerated dissolution.

Figure 13 provides a pictorial representation of this concept. Since the solvent molecules are already soluble in the developer and do not require the phenolic deprotonation reaction, their addition to the phenolic matrix amounts to the removal of one cell from the surface without the need for ionization and thereby increases the dissolution rate.

Novolac/Inhibitor Interactions

The function of photoresists depends on the dissolution inhibition phenomenon and the ability to modulate this effect through photochemical transformations. Reiser's percolation model for novolac dissolution describes base transport as a percolation process in which ions of the base migrate through a thin penetration zone by stepping from one hydrophilic site (phenol or phenolate) to the next.^{28–32} Reiser's model deals with the issue of inhibition in a very insightful way. In Reiser's model, dissolution inhibitors function by forming novolac "clusters" that concentrate the hydrophilic sites, effectively preventing access to these sites by the attacking base and thereby inhibiting the dissolution rate.^{29,30} Reiser presents data that show that up to 16 such ionizable sites can be clustered per inhibitor molecule by an

efficient photoactive dissolution inhibitor such as an aryl diazonaphthoquinone sulfonate²⁹ (Figure 1). Our model does not contradict this basic thesis. Percolation pictures a field that traverses through the thickness (or along the z-axis) of the film, and movement of the hydroxide ions along this axis is the rate-controlling step in the dissolution process. Our model proposes that the rate is simply proportional to the fraction of chains on the surface that have a number of ionized sites (Y) that meets or exceeds that fraction (F) required to render them soluble in the developer solution. When the solubility criterion F has been reached, dissolution of the chain occurs, and by this process the surface layer is successively etched away. This process is repeated for all the subsequent layers until the full thickness of the film is dissolved away. In our model, dissolution inhibitors function by simply reducing the probability of deprotonation at those sites that are proximate to the inhibitor molecule. The effect of the hydrogen bonding interaction between the dissolution inhibitor and the phenolic polymer that has been described by Reiser's group^{29,30} and by ours¹⁹ serves to stabilize the acid form of the phenol and thereby effectively to increase the pK_a of the sites affected. Hence, our view of the interaction is much like that of Reiser's except that it is acting in a plane that is rotated 90° with respect to Reiser's (Figure 3).

Conclusions

A new probabilistic model for novolac dissolution based on the phenolic deprotonation reaction has been developed. Even though the model is simplistic in nature, and primitive in its current state, it provides for the first time an explanation for all of the critical and complex dependencies of the dissolution rate of novolac on material and process variables. In particular, it provides an explanation for the critical base concentration phenomenon and for the dependence of rate on molecular weight, phenomena that are not readily explained by other models. The model is in agreement with experimental results for the dependence of critical base concentration on molecular weight. It has thereby demonstrated the most important characteristic of any useful model, a predictive capability.

Acknowledgment. The authors gratefully acknowledge the support of SRC under contract 95-LP-409 and the National Science Foundation for Graduate Research Fellowships (C.L.H. and L.W.F.). We also thank Dr. Ralph Dammel and Professors Arnost Reiser and Miguel Arcones for valuable technical discussions. We thank Dr. Michael Sheehan of Hoechst Celanese and Dr. Andrew Jasper of Nippon Soda for their generous donation of polymer samples.

References and Notes

- de Gennes, P. G. Scaling Concepts in Polymer Physics; Cornell University Press: Ithaca, NY, 1979.
- (2) Peppas, N. A.; Wu, J. C.; von Meerwall, E. D. *Macromolecules* **1994**, *27*, 5626–5638.
- (3) Ouano, A. C.; Carothers, J. A. Polym. Eng. Sci. 1980, 20, 160– 166.
- (4) Ouano, A. C.; Carothers, J. A. In Science and Technology of Polymer Processing; Suh, N. P., Sung, N.-H., Eds.; MIT Press: Cambridge, MA, 1979; pp 755-769.
- (5) Ouano, A. C.; Tu, Y. O.; Carothers, J. A. In *Structure-Solubility Relationships in Polymers*; Harris, F. W., Seymour, R. B., Eds.; Academic: New York, 1977; pp 11–20.
- (6) Ouano, A. C.; Tu, Y. O.; Carothers, J. A. Polym. Prepr. 1976, 17, 329-334.

- (7) Barclay, G. G.; Hawker, C. J.; Ito, H.; Orellana, A.; Malenfant, P. R. L.; Sinta, R. F. In Advances in Resist Technology and Processing XIII; Kunz, R. R., Ed.; Proc. SPIE, Vol. 2724; SPIE Press: Bellingham, WA, 1996; pp 249-260.
- Tsiartas, P. C.; Simpson, L. L.; Qin, A.; Willson, C. G.; Allen, (8) R. D.; Krukonis, V. J.; Gallagher-Wetmore, P. M. In *Advances* in *Resist Technology and Processing XII*; Allen, R. D., Ed.; Proc. SPIE, Vol. 2438; SPIE Press: Bellingham, WA, 1995; pp 261-271.
- (9) Long, T.; Rodriguez, F. In Advances in Resist Technology and Processing VIII; Ito, H., Ed.; Proc. SPIE, Vol. 1466; SPIE Press: Bellingham, WA, 1991; pp 188–198. (10) Arcus, R. A. In Advances in Resist Technology and Processing
- III; Willson, C. G., Ed.; Proc. SPIE, Vol. 631; SPIE Press: Bellingham, WA, 1986; pp 124–131. (11) Nonogaki, S.; Hashimoto, M.; Iwayanagi, T.; Shiraishi, H. In
- Advances in Resist Technology and Processing II; Thompson, L. F., Ed.; Proc. SPIE, Vol. 539; SPIE Press: Bellingham,
- (12) Hinsberg, W. D.; Gutierrez, M. L. In *Advances in Resist Technology*, Willson, C. G., Ed.; *Proc. SPIE*, Vol. 469; SPIE Press: Bellingham, WA, 1984; pp 57–64.
 (12) Marcellingham, WA, 1984; pp 57–64.
- (13) Huang, J.-P.; Kwei, T. K.; Reiser, A. Macromolecules 1989, *22*, 4106–4112.
- (14) Henderson, C. L.; Tsiartas, P. C.; Simpson, L. L.; Clayton, K. D.; Pancholi, S.; Pawloski, A. R.; Willson, C. G. In Advances in Resist Technology and Processing XIII; Kunz, R. R., Ed.; Proc. SPIE, Vol. 2724; SPIE Press: Bellingham,
- (15) Batchelder, T.; Piatt, J. Solid State Technol. 1983, 211–217.
 (16) Rao, V.; Hinsberg, W. D.; Frank, C. W.; Pease, R. F. W. In Advances in Resist Technology and Processing X, Hinsberg, W. D. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. D. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. D. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. 2017 Advances in Resist Technology and Processing X, Hinsberg, W. 2017 Advances in Resist Technology Advances in Resist Tec W. D., Ed.; Proc. SPIE, Vol. 1925; SPIE Press: Bellingham, WA, 1993; pp 538–551.
 (17) Ouano, A. C. In *Macromolecular Solutions: Solvent-Property*
- Relationships in Polymers, Seymour, R. B., Stahl, G. A., Eds.; Pergamon Press: New York, 1982; pp 208-217.
- (18) Ouano, A. C. In Polymers in Electronics; Davidson, T., Ed.; ACS Symposium Series, Vol. 242; American Chemical Society: Washington, DC, 1984; pp 79-90.
- (19) McAdams, C. L. Structure-Function Correlation Studies of Dissolution Inhibitors for Novolac-Based Photoresists. Masters Thesis, The University of Texas at Austin, 1996. (20) Lin, C.-C.; Yeh, T.-F.; Reiser, A.; Honda, K.; Beauchemin, B.
- T. In Advances in Resist Technology and Processing X; Hinsberg, W. D., Ed.; *Proc. SPIE*, Vol. 1925; SPIE Press: Bellingham, WA, 1993; pp 647–656.

- (21) Furuta, A.; Hanabata, M.; Uemura, Y. J. Vac. Sci. Technol. B 1986, 4, 430-436.
- (22) Hanabata, M.; Furuta, A. In Advances in Resist Technology and Processing VII; Watts, M. P. C., Ed.; Proc. SPIE, Vol. 1262; SPIE Press: Bellingham, WA, 1990; pp 476-482.
- (23) Hanabata, M.; Uetani, Y.; Furuta, A. In Advances in Resist Technology and Processing V, MacDonald, S. A., Ed.; Proc. SPIE, Vol. 920; SPIE Press: Bellingham, WA, 1988; pp 349– 354.
- (24) Hanabata, M.; Furuta, A.; Uemura, Y. In Advances in Resist Technology and Processing IV; Bowden, M. J., Ed.; Proc. SPIE, Vol. 771; SPIE Press: Bellingham, WA, 1987; pp 85-92.
- (25) Hanabata, M.; Furuta, A.; Uemura, Y. In Advances in Resist Technology and Processing III; Willson, C. G., Ed.; Proc. SPIE, Vol. 631; SPIE Press: Bellingham, WA, 1986; pp 76-79.
- (26) Grant, B. D.; Clecak, N. J.; Twieg, R. J.; Willson, C. G. IEEE Trans. Electron Devices 1981, ED-28, 1300-1305.
- Rodriguez, F.; Krasicky, P. D.; Groele, R. J. Solid State (27)Technol. 1985, 125-131.
- (28) Shih, H.-Y.; Reiser, A. Macromolecules 1996, 29, 2082-2087.
- (29) Shih, H.-Y.; Reiser, A. Macromolecules 1995, 28, 5595-5600.
- (30) Shih, H.-Y.; Yeh, T.-F.; Reiser, A.; Dammel, R. R.; Merrem, H. J.; Pawlowski, G. Macromolecules 1994, 27, 3330-3336.
- (31)Yeh, T.-F.; Reiser, A.; Dammel, R. R.; Pawlowski, G.; Roeschert, H. Macromolecules 1993, 26, 3862-3869.
- (32) Yeh, T.-F.; Shih, H.-Y.; Reiser, A. Macromolecules 1992, 25, 5345-5352.
- (33) Stauffer, D.; Aharony, A. Introduction to Percolation Theory, Taylor and Francis: London, 1992.
- (34)Bahe, L. W.; Parker, D. J. Am. Chem. Soc. 1975, 97, 5664-5670.
- (35) Bahe, L. W. J. Phys. Chem. 1972, 76, 1062-1071.
- (36) Beauchemin, B. T., Jr.; Ebersole, C. E.; Daraktchiev, I. In Advances in Resist Technology and Processing XI; Nalamasu, O., Ed.; Proc. SPIE, Vol. 2195; SPIE Press: Bellingham, WA, 1994; pp 610-623.
- (37) Mueller, K. E.; Koros, W. J.; Wang, Y. Y.; Willson, C. G. Proc. SPIE, in press.
- Gardiner, A. B.; Qin, A.; Henderson, C. L.; Pancholi, S.; Koros, W. J.; Willson, C. G.; Dammel, R. R.; Mack, C.; Hinsberg, W. D. Proc. SPIE, in press.

MA9707594