# Mechanism of Phenolic Polymer Dissolution: Importance of Acid–Base Equilibria

# Lewis W. Flanagin,<sup>†</sup> Christopher L. McAdams,<sup>†</sup> William D. Hinsberg,<sup>‡</sup> Isaac C. Sanchez,<sup>†</sup> and C. Grant Willson<sup>\*,†</sup>

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

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ABSTRACT: The dissolution phenomena that are the basis of microlithography are largely dependent on the acid-base equilibrium of phenolic polymers in aqueous base. Fundamental equations are derived to relate the probabilistic quantities of the critical-ionization model to experimentally measurable acidbase properties in such polymer systems: solution pH, polymer  $pK_a$ , degree of polymerization, and average degree of ionization. Model predictions for the dependence of the dissolution rate on these properties support previous experimental observations. A method for estimating the  $pK_a$  of phenolic polymers as a function of the average degree of ionization is developed, and the results of this approach for novolac and poly(hydroxystyrene) agree with the observed differences in the dissolution rates of these two species. These results also corroborate the hydrogen-bonding dissolution inhibition model previously reported. The change in dissolution rate accompanying the substitution of deuterium for hydrogen in the phenol group is interpreted in terms of the deuterium isotope effect on  $pK_a$ .

#### Introduction

Improved photoresists have enabled extraordinary advancements in photolithography and rapid growth in the semiconductor industry. The enhanced performance of photoresists arises from modifications to all component polymer and organic materials that make up resist formulations. Nearly every commercially available photoresist operates on the principle of a photoinduced change in the rate at which the photoresist dissolves in aqueous base. The most widely used photoresists employ a base-soluble phenolic resin, novolac, and a photoactive  $additive, \ diazonaphthoquinone.^1 \ The \ diazonaphtho$ quinone reduces the rate at which novolac dissolves in aqueous base. Exposure to 365 nm radiation photochemically converts diazonaphthoquinone to a basesoluble indenecarboxylic acid that accelerates dissolution

The drive toward ever-smaller features inspired the development of more sensitive, "chemically amplified" resists that operate at wavelengths of 248 and 193 nm.<sup>2</sup> Like novolac-based photoresists, most chemically amplified resists also contain acidic polymers that provide solubility in aqueous-base developers. The majority of chemically amplified resist systems utilize poly(hydroxystyrene), another phenolic polymer. Although novolac and poly(hydroxystyrene) are both phenolic polymers, they dissolve in aqueous base at substantially different rates. Difficulties encountered in the transition to new photoresists manifest the value of understanding the dissolution kinetics of acidic polymers in aqueous base.

According to the critical-ionization model that we described in 1997,<sup>3</sup> a critical fraction of acidic sites on the polymer chain must ionize for the chain to dissolve in aqueous base. In the first stage of developing the critical-ionization model, the dissolution rate was ex-

plained in terms of the probability that an individual polymer chain meets the solubility criterion.<sup>3</sup> This approach offers qualitative insight into the dissolution behavior of these phenolic polymer systems, but a fully quantitative understanding of the dissolution rate requires a clear, mathematical expression relating the parameters of the probabilistic model to precise, fundamental, and experimentally measurable quantities. The current paper addresses this need by considering the acid-base equilibria between the phenolic polymer and the developer solution. Because knowledge of the  $pK_a$  of the polymer is crucial to such an approach, a method for estimating the  $pK_a$  of phenolic polymers is developed, and the  $pK_a$  is analyzed as a function of the degree of ionization. Finally, the experiment of Kim and Reiser<sup>4</sup> that quantifies the effect of substituting deuterium for hydrogen on the phenol group is discussed in terms of the deuterium isotope effect on polymer  $pK_a$ and the critical-ionization model.

#### Acid-Base Equilibria of Phenolic Polymers

For a solid film consisting of an acidic polymer with X protons that can be ionized per molecule in contact with an aqueous solution of hydroxide ion, the following set of deprotonation steps can occur at the liquid-solid interface:

$$OH^{-} + P_{x}H_{x} \stackrel{K_{1}}{\rightleftharpoons} P_{x}H_{x-1}^{-} + H_{2}O$$

$$OH^{-} + P_{x}H_{x-1}^{-} \stackrel{K_{2}}{\rightleftharpoons} P_{x}H_{x-2}^{2-} + H_{2}O$$

$$\vdots$$

$$OH^{-} + P_{x}H_{x-i+1}^{(i-1)-} \stackrel{K_{i}}{\rightleftharpoons} P_{x}H_{x-i}^{i-} + H_{2}O$$

$$\vdots$$

$$OH^{-} + P_{x}H_{1}^{(X-1)-} \stackrel{K_{x}}{\longleftarrow} P_{x}H_{0}^{X-} + H_{2}O$$

$$(1)$$

Here,  $P_x H_{x-i}^{i-}$  represents the polymer chain, which

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<sup>\*</sup> Author to whom correspondence should be addressed.

<sup>&</sup>lt;sup>†</sup> The University of Texas at Austin.

<sup>&</sup>lt;sup>‡</sup> IBM Almaden Research Center.

began with X ionizable protons per chain but now has X - i ionizable protons remaining on the chain. An equilibrium constant

$$K_{i} = \frac{[P_{X}H_{X-i}]^{I-}}{[P_{X}H_{X-i+1}]^{(i-1)-}][OH^{-}]} = K_{a}/K_{w}$$
(2)

can be written for each reaction in eq 1. Under the conditions of interest, the OH<sup>-</sup> concentration can be considered to be constant. Having a single equilibrium constant,  $K_i$ , for each degree of ionization implies that the equilibrium constant of ionization is the same regardless of the particular arrangement of ionized and un-ionized sites on a given polyion.

The set of constants,  $K_1$ , ...,  $K_X$ , can be related to one another by a statistical factor. The statistical factor arises from a difference in the number of pathways for protonation and deprotonation for each equilibrium expression.<sup>5</sup> If  $\overline{K}$  is defined as the geometric mean of the constants,  $K_1$ , ...,  $K_X$ , then these constants are related by the following expression:

$$K_i = (X - i + 1)\overline{K}/i \tag{3}$$

By material balance, the sum of the surface concentrations of all polymer species is a constant equal to the initial polymer surface concentration,  $[P_XH_X]_0$ , prior to contact with the liquid:

$$\sum_{i=0}^{X} [P_X H_{X-i}^{i-}] = [P_X H_X]_0$$
(4)

If the initial surface concentration of polymer, the values of  $K_1$ , ...,  $K_X$  (calculable from the  $pK_a$  of the polymeric species), and the OH<sup>-</sup> concentration are all known, the surface concentrations of all polymer species can be calculated:

$$[\mathbf{P}_{X}\mathbf{H}_{X-i}^{i-}] = [\mathbf{P}_{X}\mathbf{H}_{X}][\mathbf{O}\mathbf{H}^{-}]^{i}\prod_{j=1}^{i}K_{j}$$
(5)

Using eq 3, eq 5 may be simplified to the form

$$[P_{X}H_{X-i}^{i-}] = [P_{X}H_{X}][OH^{-}]^{i}\binom{X}{i}\bar{K}^{i}$$
(6)

where

$$\binom{X}{i} = \frac{X!}{i!(X-i)!} \tag{7}$$

Combining eq 4 with eq 6 results in

$$[P_{X}H_{X-i}^{i-}] = \frac{[P_{X}H_{X}]_{0}[OH^{-}]^{i}\binom{X}{i}\bar{K}^{i}}{\prod_{j=0}^{X}[OH^{-}]^{j}\binom{X}{j}\bar{K}^{j}}$$
(8)

#### **Dissolution Rate of Phenolic Polymers**

The overall process of dissolution is composed of three steps: base transport (diffusion) into the polymer film, equilibration of the acid-base reactions, and polymer transport into aqueous solution. All models for the dissolution of phenolic polymers in aqueous base assume that one of these steps determines the observed dissolution rate. Some of the earliest of these models (e.g., models by Hinsberg and Gutierrez<sup>6</sup> and by Garza et al.<sup>7</sup>) proposed that the ionization of the phenolic groups at the interface between the solvent and polymer limits the rate of dissolution. In the membrane model of Arcus, "the formation and stabilization of the phenolate anion is the major chemical reaction for the dissolution of photoresist films."8 Arcus suggested that ionization occurs within a thin boundary layer, or membrane, between the polymer and solvent, and that "the only way for this [ionization] to occur is for the base in the developer to be transported into the membrane via some mechanism such as diffusion or infiltration into voids."8 Reiser and co-workers<sup>9,10</sup> developed this concept of a boundary layer further by using percolation theory to describe the diffusion of developer base into the film through a thin penetration zone. The percolation model originally defined the rate-determining step in the dissolution process as the "phenolate-phenol transfer [of base] which occurs at the front of the penetration zone."10 More recently, the critical-ionization model,<sup>3</sup> which assumes that the ionization step determines the solubility of the polymer, has demonstrated very interesting and useful predictive capabilities. After the critical-ionization model had been introduced, Kim and Reiser<sup>4</sup> conducted an important study of the effect of the base cation on the dissolution rate. The results of this study led the authors to shift the emphasis of the percolation model from base transport to the ionization step. Kim and Reiser concluded, "the rate-determining step of Novolak dissolution is not the diffusion of base within the penetration zone but the deprotonation step at the interface of the zone with the virgin matrix."<sup>4</sup> An alternative approach is taken in the chain disentanglement model of Peppas and co-workers,<sup>11</sup> which is an excellent description of the dissolution of polystyrene and other high molecular weight polymers. The chain disentanglement model, however, is inappropriate for describing novolac, which has a  $M_{\rm w}$  on the order of 1000, far below the entanglement molecular weight. The real rate-determining step is, in all likelihood, dependent on the molecular weight of the polymer. For low-molecularweight polymers, ionization probably controls the dissolution rate, while for high-molecular-weight polymers, polymer disentanglement is the limiting step.

The dissolution rate of the polymer film can be related to the rate at which each polymer species dissolves. The transfer of each ionized species,  $P_XH_{X-i}$ , from the solid state to aqueous solution is now assumed to be an irreversible first-order process characterized by a rate constant  $k_{d,i}$ .

$$[\mathbf{P}_{X}\mathbf{H}_{X-i}^{i-}] \xrightarrow{k_{\mathrm{d},i}} \mathbf{P}_{X}\mathbf{H}_{X-i(\mathrm{aq})}^{i-};$$

$$r_{i} = \frac{\mathbf{d}[\mathbf{P}_{X}\mathbf{H}_{X-i(\mathrm{aq})}^{i-}]}{\mathbf{d}t} = k_{\mathrm{d},i}[\mathbf{P}_{X}\mathbf{H}_{X-i}^{i-}] \quad (9)$$

The polymer film dissolves on a molecular basis at a rate R given below:

$$R = \sum_{i=0}^{X} k_{\mathrm{d},i} [\mathrm{P}_{X} \mathrm{H}_{X-i}^{i-}]$$
(10)

While the values for  $\bar{K}$  and the rate constants,  $k_{d,1}$ , ...,  $k_{d,X}$ , are not yet determined for the phenolic polymer systems of interest here, this description can be used to test the hypothesis that film dissolution kinetics are

controlled by the degree of surface ionization. This hypothesis is reasonable in the molecular weight regime of engineering interest for both novolac and poly-(hydroxystyrene). It may not be accurate for higher molecular weight polymers. The dissolution rate constant,  $k_{d,i}$  is assumed to depend on the extent of ionization but not on the chain length. The rate constant  $k_{d,i}$  is assumed to be zero unless the fraction of phenolate groups on the chain exceeds a critical value *F*. For all chains in which the phenolate fraction is greater than *F*, the rate constant  $k_{d,i}$  is assumed to have a singular, nonzero value,  $k_d$ . Under these assumptions, the rate equation reduces to the following:

$$R = k_{\rm d} \sum_{i=FX}^{X} [P_X H_{X-i}^{i-}]$$
(11)

Earlier, the dissolution rate of phenolic polymers was described by the probability of satisfying a criterion for solubility based on the degree of ionization.<sup>3</sup> In this work, a similar criterion is invoked in an analysis of the thermodynamics and kinetics of polymer dissolution. The probabilistic and thermodynamic/kinetic approaches, although different, are complementary. Both models rest on the premise of a critical degree of ionization required for solubility.

A direct, quantitative correspondence exists between the microscopic quantities that appear in the probabilistic model and the macroscopic observable properties that appear in the acid-base equilibria model. The fraction *Y* of polymers meeting the solubility criterion may be expressed in terms of polymer concentrations as

$$Y = \frac{\sum_{i=FX}^{X} [P_X H_{X-i}^{i-}]}{[P_X H_X]_0}$$
(12)

Combining eq 12 with eq 11 yields the following relation between the observable dissolution rate, R, and the probabilistic quantity Y:

$$Y = \frac{R}{k_{\rm d}[{\rm P}_{\rm X}{\rm H}_{\rm X}]_0} \tag{13}$$

According to this result, Y may be viewed appropriately as a dimensionless dissolution rate. The function  $\alpha$  is defined as the deprotonated fraction of phenol groups (i.e., the ratio of phenolate concentration to the initial phenol concentration);  $\alpha$  may be expressed in terms of polymer concentrations as

$$\alpha = \frac{\sum_{i=1}^{X} i[\mathbf{P}_{X}\mathbf{H}_{X-i}^{i-}]}{X[\mathbf{P}_{X}\mathbf{H}_{X}]_{0}}$$
(14)

Substitution of eq 8 into eq 14 leads to

$$\alpha = \frac{\sum_{i=1}^{X} i \binom{X}{i} z^{i}}{X \sum_{j=0}^{X} \binom{X}{j} z^{j}}$$
(15)



**Figure 1.** Degree of ionization ( $\alpha$ ) vs pH – p $K_{a}$ .



Figure 2. Dimensionless dissolution rate as a function of pH –  $p{\it K}_{a\cdot}$ 

where  $z = [OH^{-}]\bar{K}$ . When one recognizes that  $\sum_{j=0}^{X} {\binom{X}{j}} z^{j}$ =  $(1 + z)^{X}$  and from this that  $\sum_{i=1}^{X} i {\binom{X}{i}} z^{i} = Xz(1 + z)^{X-1}$ , this seemingly complex expression for  $\alpha$  reduces to the relatively simple result

$$\alpha = \frac{z}{1+z} = \frac{10^{\mathrm{pH-p}\bar{K}_{a}}}{1+10^{\mathrm{pH-p}\bar{K}_{a}}}$$
(16)

(By recalling that  $\overline{K} = \overline{K}_a/K_w$ , it is clear that log  $z = pH - p\overline{K}_a$ .) Equation 16 is a slightly modified form of the well-known Henderson–Hasselbalch equation.<sup>12,13</sup> From eq 16,  $\alpha = 0.5$  when pH =  $p\overline{K}_a$ ,  $\alpha > 0.5$  when pH >  $p\overline{K}_a$ , and  $\alpha < 0.5$  when pH <  $p\overline{K}_a$ . The function  $\alpha$  is also independent of polymer chain length, as expected. A plot of  $\alpha$  vs pH –  $p\overline{K}_a$  is shown in Figure 1.

In ref 3 it was shown that the fraction (*Y*) of chains meeting the solubility criterion (*F*) is related to the surface degree of ionization ( $\alpha$ ) by

$$Y = \sum_{i=FX}^{X} {\binom{X}{i}} \alpha^{i} (1-\alpha)^{X-i}$$
(17)

Substituting eq 13 and eq 16 into eq 17 leads to

$$R = \frac{k_{\rm d}[{\rm P}_{\rm X}{\rm H}_{\rm X}]_0}{(1+10^{{\rm p}{\rm H}-{\rm p}\bar{K}_{\rm a}})^X} \sum_{i=FX}^X {X \choose i} (10^{{\rm p}{\rm H}-{\rm p}\bar{K}_{\rm a}})^i \quad (18)$$

The dimensionless dissolution rate,  $R/k_d[P_XH_X]_0$ , is plotted vs pH –  $p\bar{K}_a$  in Figure 2 and vs polymer chain length, *X*, in Figure 3.

### pK<sub>a</sub> Estimation

Several investigators have measured the acidity of phenolic compounds in nonaqueous solvents. Sprengling<sup>14</sup> was the first to conduct potentiometric titrations on a series of oligomeric, phenolic compounds. His results showed that *ortho–ortho*-linked bis(hydroxyphenyl)methanes contain "hyperacidic" hydroxyl groups, i.e., their first ionization constants are much higher than those of their corresponding isomers. Similarly *ortho–* 



**Figure 3.** Dimensionless dissolution rate plotted as a function of polymer chain length.

*ortho*-linked trimers and tetramers demonstrate even greater hyperacidity, but *ortho*–*para*-linked compounds are less acidic.<sup>14</sup> The apparent reason for the hyperacidity of the *ortho*–*ortho*-linked compounds is their ability to form hydrogen bonds and to distribute the anionic charge efficiently over several atoms.

Böhmer et al.<sup>15</sup> measured the first dissociation constants of ortho-ortho-linked oligomeric phenolic compounds. In each of these compounds, the researchers incorporated a *p*-nitrophenol unit, which is much more acidic than the remaining alkylphenol units. They were thus able to assign the first dissociation unequivocally to the nitrophenol group. Substituent effects on the acidity of the nitrophenol group were studied rigorously and systematically. The first dissociation constant increases (i.e., the  $pK_1$  decreases) as the number of ortho-linked alkylphenol units increases from 0 to 3. This result provides evidence that a chain of up to three intramolecular hydrogen bonds stabilizes the monoanion and that this effect grows as the number of phenolic units participating in the distribution of charge increases. Böhmer et al. found that those compounds having their dissociating unit in the middle of the chain are more acidic because the monoanion is stabilized by a second intramolecular hydrogen bond to the negatively charged oxygen.<sup>15</sup> The UV spectra of the monoanions show that the absorption coefficient and wavelength of the absorption maximum related to the nitrophenol unit decrease as the strength of the intramolecular hydrogen bond increases.<sup>15</sup>

Over the course of about 20 years, Chatterjee and coworkers performed a systematic and thorough study of ortho-ortho-linked phenolic compounds through potentiometric and conductometric nonaqueous titrations. The initial study demonstrated that intramolecular hydrogen bonding and ion association between the base cation and the partially neutralized polyphenol strongly influence the titration curves.<sup>16</sup> The potentiometric titration curves of pentameric phenolic compounds in pyridine with sodium methoxide as titrant showed four inflections, the first of which was very sharp, and the conductometric titration curves for the same compounds displayed five breaks.<sup>17</sup> Each inflection or break coincides with the neutralization of a hydroxyl group. The first, sharp inflection, therefore, corresponds to the neutralization of a hyperacidic hydroxyl group. Hydrogen bonding, electrostatic interactions, and ion association all evidently play a role in the stepwise neutralization of the hydroxyl groups. The ability to distinguish between hydroxyl groups was demonstrated further in mixtures of dimeric and trimeric phenolic compounds.<sup>18</sup> Titrations of oligomers containing six to eight phenolic





groups showed as many distinct breaks in the conductometric curves as there were hydroxyl groups on the compound.<sup>19</sup> The potentiometric curves, however, showed only two to three inflections, indicating that some of the hydroxyl groups on each chain are hyperacidic, while others have roughly the same acidity. A similar study of a nonameric phenolic compound showed as well that the hydroxyl groups are neutralized in mostly a stepwise manner in the conductometric titration, whereas they are lumped together in the potentiometric titration.<sup>20</sup> Chatterjee attributes this difference to homoconjugation, which potentiometry cannot detect. Later studies considered the influence of additional functional groups on the acidity of novolac-like oligomers.<sup>21,22</sup>

The nonaqueous titrations reviewed thus far provide clear evidence for the stepwise neutralization of phenolic polymers, but they are unable to produce precise values for the  $pK_a$  of phenolic polymers in aqueous base. The  $pK_a$  of novolac and poly(hydroxystyrene) in aqueous solution can be estimated using the acidity function for phenol given by Biggs et al.<sup>23</sup> and Perrin et al.<sup>5</sup> This approach allows one to estimate the  $pK_a$  of phenolic oligomers and polymers by the following equation:

$$pK_{a} = 9.92 - 2.23 \sum \sigma - \log(A/B)$$
 (19)

Here  $\Sigma \sigma$  is the sum of all Hammett sigma constants, which account for substituent effects, and log(A/B) is the statistical correction needed for polybasic acids. The constant A is the number of energetically equivalent ways to deprotonate a given polybasic acid, and the constant *B* is the number of reverse protonation pathways. Thus, a dibasic acid, such as bis(2-hydroxyphenyl)methane (Figure 4), has two equivalent protons that may be deprotonated, but the reverse protonation may occur at only one location. In this case, the statistical factor is equal to log(2/1), or  $\sim$  0.3. For the second ionization  $(pK_2)$  the statistical factor is log(1/2). If substituent effects are ignored, then  $pK_1$  and  $pK_2$  are calculated to be 9.62 and 10.22, respectively. The measured values<sup>24</sup> (Figure 4) of  $pK_1$  (7.5) and  $pK_2$  (11.6) show that substituent effects in this case are very large and cannot be ignored. Perrin<sup>5</sup> has calculated the Hammett *ortho*  $\sigma$  constant ( $\sigma_{ortho} = 0.95$ ) for the effect of a (2-hydroxyphenyl)methyl group on a phenol. Since the p $K_2$  is known to be 11.60,  $\sigma_{ortho}$  for the phenolate is calculated to be -0.62.

If one assumes that only nearest neighbor effects need to be considered for novolac and that substituent effects



#### Oxygen: , Carbon: O, Hydrogen: O

**Figure 5.** Optimized gas-phase structures of (a) *ortho*–*ortho* linked *p*-cresol novolac trimer, (b) poly(4-hydroxystyrene) trimer, and (c) the trianion of the novolac trimer depicted in part a. Energies calculated using the HyperChem PM3 self-consistent field are (a) -5459, (b) -6005, and (c) -5224 kcal/mol, respectively. The distances between nearest oxygen atoms are (a) 2.75, (b) 10.59, and (c) 5.58 Å, respectively.

are additive, then one may use this acidity function (eq 19) to estimate the  $pK_a$  of any *ortho–ortho*-linked novolac oligomer or polymer (Figure 5). Nonnearest-neighbor effects may be ignored because the energy of the electrostatic, Coulombic interaction varies inversely with the square of the distance between the ions.<sup>25</sup> Additivity of substituent effects is essentially the basis of linear free-energy relationships.

Assuming additive substituent effects, the acidity function (eq 19) predicts that the  $pK_a$  of a phenolic compound decreases as the number of neighboring phenolic groups increases. However, the  $pK_a$  of a phenol group vicinal to an already existing phenolate group is larger than the  $pK_a$  of an unsubstituted phenol because like charges repel.

Consider, for example, the phenolic pentamer shown in Figure 6. Each of the three energetically "equivalent", ionizable phenols in the middle of the pentamer has two nearest-neighbor hydroxyl groups ( $\Sigma \sigma = 1.90$ ). Each terminal group, however, has only one adjacent phenol group ( $\Sigma \sigma = 0.95$ ) and subsequently requires more energy to deprotonate. Thus, the first deprotonation is most likely to occur at any of the three middle phenol groups (A = 3). After the first deprotonation, only one reverse pathway is possible (B = 1). For the second deprotonation, with which  $pK_2$  is associated, only one hydroxyl group with two adjacent phenols remains ( $\Sigma \sigma$ = 1.90, A = 1, B = 2). The most likely candidate for the third deprotonation, associated with  $pK_3$ , is a terminal group adjacent to a phenolate ( $\Sigma \sigma = -0.62, A = 2, B =$ 1). The fourth ionization, associated with  $pK_4$ , occurs at the other end group, and either end group may reaccept a proton ( $\Sigma \sigma = -0.62$ , A = 1, B = 2). The final ionization, associated with  $pK_5$ , can occur at only one



**Figure 6.** Calculations of  $pK_1$  through  $pK_5$  for an *ortho–ortho*-linked phenolic pentamer.

Table	1.1	Expressi	ions fo	or tł	1e p <i>l</i>	K <sub>a</sub> of	Novo	lac
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i	$\mathbf{p}K_i$
<x 2<="" th=""><th><math>9.92 - 2.23(1.90) - \log((X - 2i)/i)</math></th></x>	$9.92 - 2.23(1.90) - \log((X - 2i)/i)$
X/2 (for even X)	$9.92 - 2.23(0.95) - \log(1/1)$
(X+1)/2 (for odd X)	$9.92 - 2.23(-0.62) - \log(2/1)$
X/2 + 1 (for even X)	$9.92 - 2.23(-0.62) - \log(1/1)$
(X+3)/2 (for odd X)	$9.92 - 2.23(-0.62) - \log(1/2)$
>(X+3)/2	9.92 - 2.23(-1.24) -
	$\log((X - i + 1)/(2i - X - 2))$

site, which is adjacent to two ionized sites ( $\Sigma \sigma = -1.24$ , A = 1). Three equivalent choices for the reverse protonation exist (B = 3). In each of the above steps, the actual phenolic site that ionizes may be different from the one indicated, but in this case, the molecule would quickly rearrange to the lowest-energy configuration by the classic Grotthuss proton-transfer mechanism.<sup>26</sup>

For completely *ortho–ortho*-linked novolac systems with degree of polymerization X, it is possible to calculate the  $pK_i$  (*i*th  $pK_a$ ) using the same logical steps (Table 1).

Conformations available to poly(hydroxystyrene) allow the hydroxyl groups to be separated much further in space (Figure 5);<sup>27</sup> thus, nearest-neighbor effects can be ignored, and all of the acidic sites can be treated as energetically equal. However, the alkyl-substituent effect ( $\sigma = -0.15$ ) is included (eq 20).

$$pK_i = 9.92 - 2.23(-0.15) - \log((X + 1 - i)/i)$$
 (20)

The degree of ionization for a single polymer chain is defined as the number of ionized sites divided by the number of total sites ( $\alpha = i/X$ ). In Figure 7,  $pK_i$  is plotted vs  $\alpha$  (Figure 7 is the example for X = 20). Clearly, as the degree of ionization increases, the  $pK_i$  also increases. However, our model for *ortho–ortho*-linked novolac predicts a sharp change in the slope at  $\alpha = \sim 0.5$ , where for the first time, deprotonation creates adjacent anions. This type of behavior has been observed in other polyelectrolytes. For example, Kitano et al.<sup>28</sup> observed that the  $pK_a$  has this sharp increase as a function of the degree of ionization for poly(maleic acid) but not for poly(acrylic acid) (Figure 8). The increased distance



**Figure 7.** Predicted  $pK_a$  vs degree of ionization ( $\alpha$ ) for poly-(hydroxystyrene) and *ortho–ortho*-linked novolac.



Figure 8. Poly(maleic acid) (left) and poly(acrylic acid) (right).



**Figure 9.** Predicted degree of ionization ( $\alpha$ ) vs pH for poly-(hydroxystyrene) and *ortho–ortho-*linked novolac.

between the nearest neighbors in poly(acrylic acid) results in a lower charge density.

Honda et al.<sup>29</sup> demonstrated that adding *ortho–ortho*linked diad and triad phenolic moieties to poly(hydroxystyrene) lowers the  $pK_a$  significantly during the early stages of neutralization. At later stages of neutralization, the  $pK_a$  finally reaches the same value as that of unmodified poly(hydroxystyrene). In agreement with our model, these results indicate that *ortho–ortho*linkages initially facilitate proton dissociation through intramolecular hydrogen bonding, but eventually electrostatic repulsion dominates.

Equation 16, which expresses the degree of ionization in terms of the difference between pH and  $p\bar{K}_{a}$ , was derived under the assumption that each  $K_i$  differs from  $\bar{K}_a$  by only a statistical factor (eq 3). The following equation, which is a general form of eq 16 that allows for differences such as substituent effects, may be used to calculate a predicted degree of ionization at any pH ( $\alpha$  vs pH in Figure 9) when individual values for  $pK_i$ are known:

$$\alpha = \frac{\sum_{i=1}^{X} 10^{\sum_{j=1}^{i} pH - pK_j} i}{X[1 + \sum_{j=1}^{X} 10^{\sum_{j=1}^{j} pH - pK_j}]}$$
(21)

Note that the pH of the 0.26 N OH<sup>-</sup> solution is drawn in as a reference to the strength of standard developer solution. In this model,  $\alpha$  is only about 0.75 in the developer solution. The model predicts that, in this pH range, novolac is not completely ionized. Since the dissolution rate is a function of  $\alpha$ , the prediction is in agreement with the observation that higher molecular weight poly(hydroxystyrene) dissolves more quickly than lower molecular weight novolac in 0.26 N tetramethylammonium hydroxide.

It should be noted in this discussion that the results in Figures 7 and 9 pertain only to *ortho–ortho*-linked novolac systems. Because novolacs used in photolithography are synthesized from a combination of *m*-cresol and *p*-cresol monomers, both *ortho–para* and *ortho– ortho* linkages exist in these systems. Because *ortho– para* linkages disrupt the hydrogen-bonded network and distribute the charge density differently, the  $pK_a$  for complex novolacs probably changes more gradually than the  $pK_a$  for completely *ortho–ortho*-linked novolac.

The concept that the dissolution rate depends on the  $pK_a$  of the polymer helps in explaining the function of dissolution inhibitors. Our previous work<sup>30</sup> has shown that "a primary mode of dissolution inhibition is a strong polarization of the intramolecular hydrogen bonding clusters found in novolac. The polarization increases the effective  $pK_a$  of novolac [by stabilizing the acid form of the phenol] and decreases the ratio of ionized to unionized phenolic sites." The higher  $pK_a$  induced by the dissolution inhibitor decreases the rate of dissolution (Figure 2). Because poly(hydroxystyrene) does not have a high degree of intramolecular hydrogen bonding, the effect of dissolution inhibitors is much weaker on poly-(hydroxystyrene) than on novolac. The hydrogen-bonding interaction between the inhibitor and the polymer can be strengthened by introducing resonance-stabilizing electron donating groups or by substituting sulfonyl esters in place of carbonyl esters in the inhibitor.<sup>30</sup>

# **Deuterium Isotope Effect**

Recent experimental data<sup>4</sup> for the effect of isotopic substitution on the dissolution rate of novolac support the assumption of the critical-ionization model that the  $pK_a$  of a polymer controls the dissolution rate. Kim and Reiser<sup>4</sup> found that the dissolution rate of deuterated novolac in deuterated base developer is about a factor of 2 less than the dissolution rate of the corresponding protonated system. This observation is consistent with the solvent isotope effect on pK<sub>a</sub> as stated by Lowry:<sup>31</sup> "Weak acids are stronger in H<sub>2</sub>O than in D<sub>2</sub>O by about 0.5 pK unit." If the  $pK_a$  of novolac in deuterated developer is approximately 0.5 pK units higher than in protonated developer, Figure 2 implies that the deuterated system dissolves at a slower rate than the protonated system because each rate curve is shifted right by 0.5 p*K* units.

# Conclusions

Through equations describing the acid—base equilibria of phenolic polymers in aqueous base, the predictions of the critical-ionization model can now be understood in terms of experimentally measurable properties: solution pH, polymer  $pK_a$ , degree of polymerization, and average degree of ionization. The model has been used to predict the dependence of the dissolution rate on each of these properties. The faster rate at which poly-(hydroxystyrene) dissolves compared to novolac is attributed to its greater acidity, whereas the function of dissolution inhibitors is explained as an effective decrease in the polymer acidity. Finally, the change in dissolution rate accompanying the substitution of deuterium for hydrogen in the phenol group has been interpreted in terms of the deuterium isotope effect on рK<sub>a</sub>.

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