Effect of Hydrogen Acceptors on pK_a of Phenolic Resins: Link to Dissolution Inhibition

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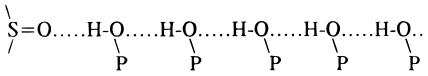
ABSTRACT: Dissolution inhibition in positive resists is brought about by an inductive polarization effect of strong hydrogen acceptors, which creates hydrogen-bonded strings of OH groups. The acidity of the OH groups bound in the strings is considerably lower than that of phenols in the bulk of the system. It is the reduction in the concentration of protons in equilibrium with the various parts of the resin that lowers the rate of phenol deprotonation and with it the rate of resin dissolution. Here we describe changes in the pK_a of the resin in the presence of hydrogen acceptors (dissolution inhibitiors) and we demonstrate the existence of a quantitative link between acidity changes and inhibition factors.

Introduction

It is now generally accepted that dissolution inhibition in phenolic resins is linked to hydrogen bonding between the acceptor groups (S═O or C═O) of the inhibitor and the polymer-bound OH groups of the resin.[1] We had shown earlier that the interaction of the acceptor group of the inhibitor with the hydroxyls of the resin leads to the formation of "phenolic strings" of hydrogen-bonded OH groups.[1]



While the real existence of such phenolic strings had been convincingly established,[1,4,5] it was by no means clear how phenolic strings can bring about the phenomenon of dissolution inhibition. At the time we thought that the coming together of phenols in strings or clusters produces in their vicinity areas of low (OH) site density. That would reduce the overall connectivity of the percolation field and lower the dissolution rate of the resist film.

Since then we have gained a clearer understanding of the dissolution process. A recent deuterium isotope experiment[6] persuaded us that the rate-determining step of dissolution is the deprotonation of phenol by developer base.

$$POH + OH^- = PO^- + H_2O$$

In the solid environment of the resist film the deprotonation process can be described as follows: When an ion pair of base appears in the vicinity of the phenolic OH group, the proton of the phenol may transfer to the OH^- ion of the base.[7] The probability of that event depends not only on the average distance between base ions and OH groups, i.e., on the concentration of base, but also on the concentration of the protons that are in equilibrium with the local phenols. The protons of those phenols that are part of a string are thought to be more strongly bound than the protons of free phenols; their concentration will be lower. This slows down the progress of base into the matrix and lowers the dissolution rate. We are not the first to come to this conclusion; Willson and his colleagues[2,3] perceived clearly that the reduced availability of phenolic protons is the fundamental cause of dissolution inhibition. In support of this thesis, McAdams and others in Willson's group at Austin[8,9] have titrated Novolak samples and samples of poly(4-hydroxystyrene) and have interpreted the observed acidity differences as the source of the lithographic behavior of the two resins. We have taken a different route. Using a potentiometer and a glass electrode, we determined directly the pK_a of phenolic resins in the absence and in the presence of dissolution inhibitors. The acidity of the resins decreased and their average pK_a increased, as inhibitors were added to the solution.

Experimental Section

The average pK_a of a resin can be determined by measuring the pH of a known solution of the polymer in a suitable solvent, using an electrochemical cell calibrated for that solvent. From the definition of the dissociation constant of the phenolic units

$$K_a = \frac{[H^+][PO^-]}{[POH]}$$

follows a relation between pH and pK_a,[10]

$$pK_a = 2\ pH + \log c_{OH} \qquad (1)$$

where c_{OH} is the overall concentration of phenol.

The medium used in our experiments was a mixture of 95 vol % acetonitrile and 5% water. Our resins as well as the inhibitors dissolved in this mixture. The pH of the solutions was determined with a Tagamet 1006 pH meter from Fischer Scientific, using a combination glass electrode with a double junction Ag/AgCl reference electrode and a temperature sensor to correct for changes in temperature between measurements. The experiments were carried out at 25 °C. The instrument was calibrated with solutions of acetic acid in water/acetonitrile mixtures. The pK_a of acetic acid in pure water is 4.75; in pure acetonitrile[11] it is 22.3. The pK_a of acetic acid in the intermediate mixtures is indicated in Figure 1.

Materials. A sample of a commercial Novolak resin was graciously provided by the Clariant Co. It was dissolved in acetone and the solution shaken with a 5% solution of aqueous sodium bicarbonate to remove all traces of acid. It was three times washed with water, precipitated, and dried. Poly(4-hydroxystyrene) was obtained from Polysciences and was used as received.

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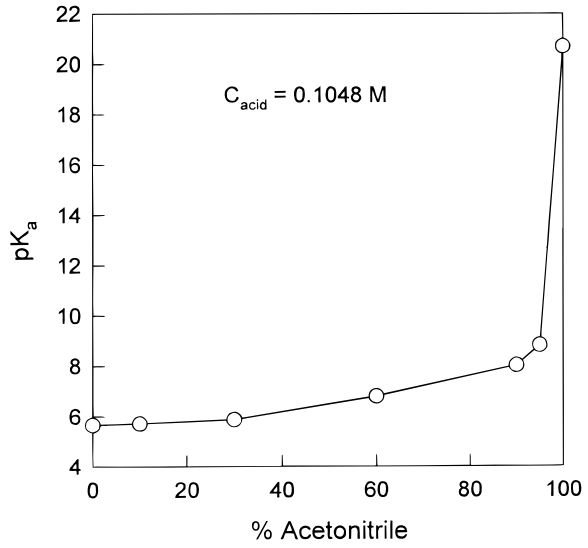


Figure 1. pK_a of acetic acid in mixtures of acetonitrile/water (acid concentration = 0.1048 M).

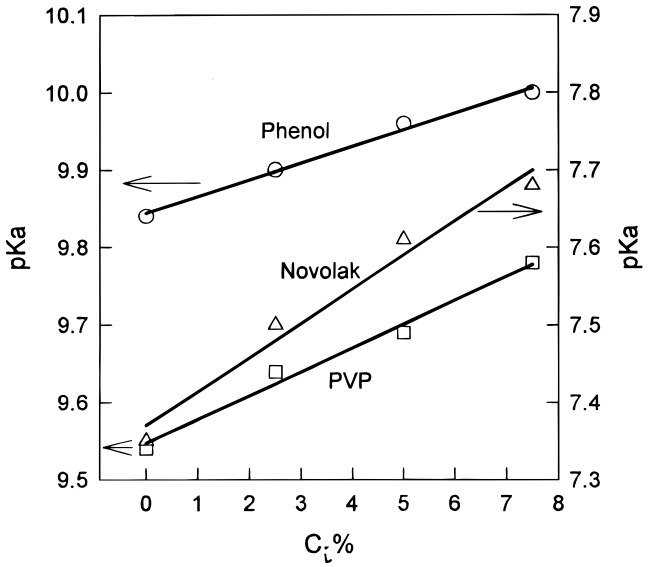


Figure 2. Effect of the inhibitor flavone on 1 M solutions of Novolak, of poly(4-hydroxystyrene), and of phenol in 95% actonitrile/5% water mixtures. The inhibitor concentration is in weight %.

A standard commercial diazoquinone inhibitor (the 4-*tert*-butyl phenyl ester of 2,1-naphthodiazoquinone-5-sulfonic acid) was freed of acidic impurities by dissolving it in dichloromethane and shaking the solution with 3% aqueous sodium bicarbonate. After washing with water, the inhibitor was precipitated and dried. A nonphotoreactive inhibitor, naphthalene-1-sulfonic acid phenyl ester, was prepared in this laboratory. The three pyrones, flavanone, flavone, and α-naphthoflavone, were obtained from Aldrich and were used as received.

Solutions of Novolak or poly(4-hydroxystyrene) with 0−10 wt % of an inhibitor were prepared in the mixed solvent, and their pH was measured. From the value of pH and from the concentration of phenol in the solution, the pK_a of the resin was calculated.

Effect of Inhibitors on Resin pK_a

Figure 2 shows a test of the basic idea. The pH of a 1 M solution of a Novolak resin increased markedly in the presence of increasing quantities of flavone, and similar results were obtained in solutions of poly(vinylphenol) and even of phenol. The linear increase in pK_a can be understood as the result of an increase in the fraction of phenols bound in phenolic strings. If the concentration of inhibitor is increased further, a point is reached when almost all phenols are captured in strings, whereupon the pK_a of the system stabilizes at the mean pK_a of bound phenols. Figure 3 shows this behavior in a 1 M solution of Novolak, to which increasing quantities of a representative sulfonate inhibitor (naphthalene-1-sulfonic acid phenyl ester) were added. In Figure 4 we have plotted the evolution of the pK_a of solutions of three pyrones that have similar structures but differ markedly in acceptor strength.[12] Both the slope of the plots and the mean pK_a of the bound phenols depend on the acceptor strength of the inhibitor.

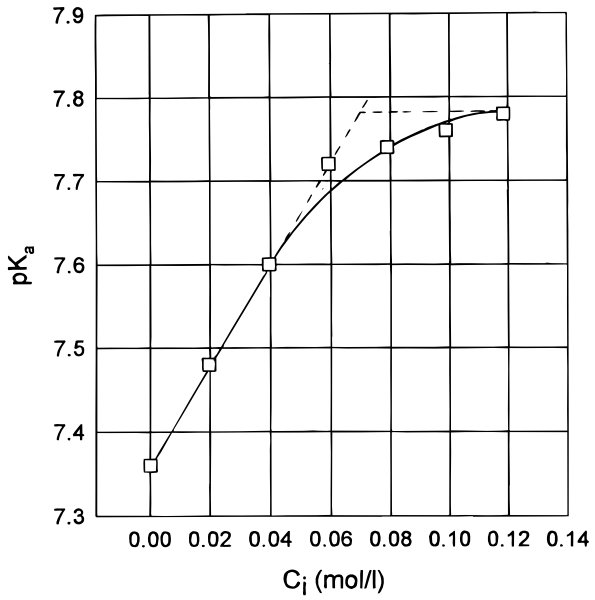
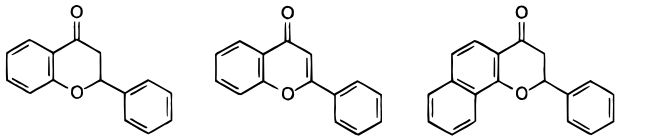


Figure 3. Saturation curve (pK_a vs c_i) of the sulfonic acid inhibitor mentioned in the text, in a 1 M solution of Novolak in 95% acetonitrile/5% water. The inhibitor concentration is in terms of molarity, i.e., moles of inhibitor in 1 L.



Flavanone f = 0.68 Flavone f = 1.8 α-Naphthoflavone f = 4.9

While the pK_a of the resin solutions changes from the pK_a of free phenols, [pK_a(a)], to the mean pK_a of phenols bound in strings, [pK_a(b)], the pK_a at intermediate concentrations of inhibitor may be viewed as that of a mixture of free and of bound phenols.

$$\mathrm{p}K_a(c_i) = \left(1 - n\frac{c_i}{c_{OH}}\right)\mathrm{p}K_a(a) + n\frac{c_i}{c_{OH}}\mathrm{p}K_a(b)$$

$$= \mathrm{p}K_a(a) + n\frac{c_i}{c_{OH}}[\mathrm{p}K_a(b) - \mathrm{p}K_a(a)] \qquad (2)$$

Here c_{OH} is the overall concentration of OH groups in the system, c_i is the concentration of inhibitor, and n is

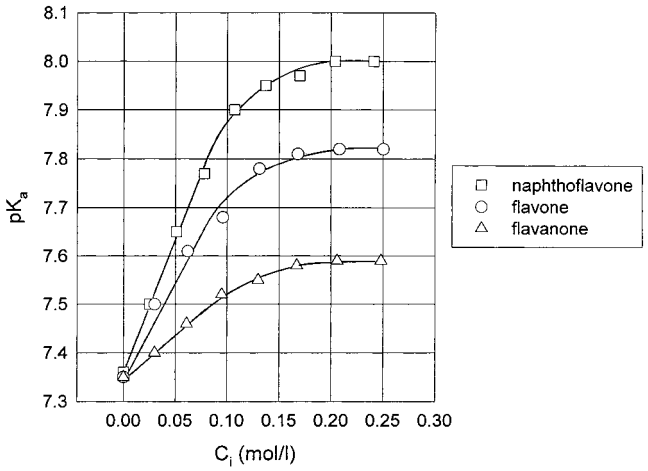


Figure 4. Saturation curves (pK_a vs c_i) of the three pyrones of Table 1 in 1 M solutions of Novolak in 95 wt % acetonitrile/5 wt % water. The inhibitor concentration is in terms of molarity, i.e., moles inhibitor in 1 L.

Table 1. String Length and Mean pK_a of Free and of Bound Phenols in 1.0 M Novolak Solutions in 95% Acetonitrile/5% Water

	n	pK_a(a)	pK_a(b)
flavanone	14.5	7.35	7.59
flavone	15.0	7.37	7.83
α-naphthoflavone	16.8	7.37	8.00
sulfone inhibitor	14.3	7.37	7.77

the string length, i.e., the average number of OH groups in a string. pK_a(c_i) is in principle a linear function of c_i up to the point of saturation, as indicated in Figure 3. The deviations from linearity in Figures 3 and 4 stem from the inability of the inhibitor in the almost saturated solution to find all still available OH groups.

The length of the phenolic strings may be estimated from the initial slope of a pK_a vs c_i plot.

$$\frac{(\mathrm{d}pK_a)}{\mathrm{d}c_i} = \frac{n}{c_{OH}}[pK_a(b) - pK_a(a)] \qquad (3)$$

Using eq 3 with the data for the sulfonic acid ester, one finds a string length of $n = 14.3$. String lengths and the pK_a values for this inhibitor and for the three pyrones shown above are listed in Table 1.

The inhibitor is characterized here by the length of the phenolic string that it creates and by the mean pK_a of the bound phenols within these strings.

Link between pK_a and Inhibition

In Figure 5 we have plotted the pK_a of Novolak solutions and of solutions of poly(4-hydroxystyrene) as a function of the concentration of the inhibitor naphthalene-1-sulfonic acid phenyl ester. We have also included in the figure the logarithm of the dissolution rate of films containing similar concentrations of the same inhibitor. In agreement with the findings of Willson's group at Austin, the conformity between these plots suggests a link between the increase in pK_a of the solutions and the change in dissolution rate of the films. Initially, this was merely an intuitive interpretation of the data. To establish a causal correspondence between resin pK_a and dissolution rate, we have attempted to calculate the (kinetic) inhibition factor from the (thermodynamic) electrochemical data.

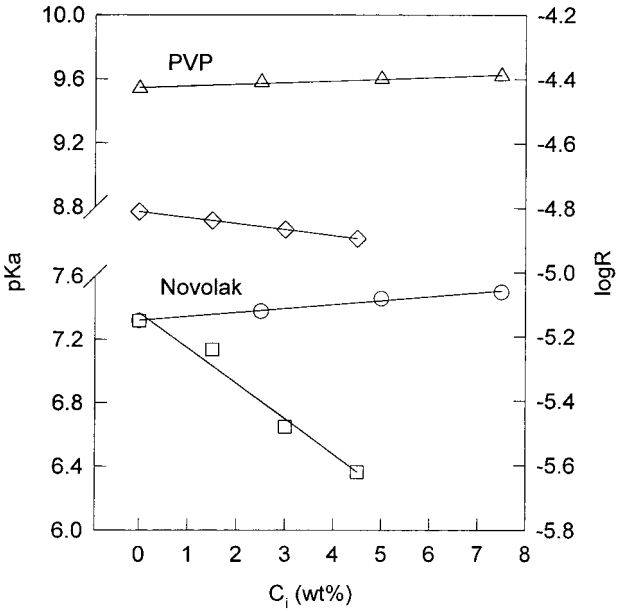


Figure 5. 1 M solutions of Novolak or of poly(vinylphenol) containing the indicated concentration of a naphthalene-1-sulfonic acid phenyl ester inhibitor in 95% acetonitrile/5% water. In accordance with lithographic practice the inhibitor concentration, c_i, is given here in wt %, i.e., grams of inhibitor in 100 g of resin. The descending lines and the right-hand scale refer to the dissolution rate (cm/s) of films cast from 25 wt % coating solutions in isobutyl acetate The films were dissolved in 0.2 M aqueous KOH.

We have approached this task by noting that in the solid environment of the resist film the base ions are bound by electrostatic forces to the ions of the penetration zone and that, consequently, it is the protons that move in the transfer step. As a result, the reaction probability, r, of any phenol unit in the system is proportional not only to the local concentration of base, c_B, but also to the concentration, c_{H^+} of the free protons in equilibrium with that phenol. The reaction probability at any given site can thus be expressed in the form shown below.

$$r = kc_Bc_{H^+} \qquad (4)$$

The overall dissolution rate of the film is the sum of the local deprotonation probabilities. It takes the form of a sum of two terms, one referring to free phenols, the other to phenols bound in the strings.

$$R = \sum r = \left[1 - n\frac{c_i}{c_{OH}}\right]kc_Bc_{H(a)} + \left[n\frac{c_i}{c_{OH}}\right]kc_Bc_{H(b)} \qquad (5)$$

The expression in the first bracket is the fraction of free phenols in the ensemble, the second bracket is the fraction of bound phenols, and $c_{H(a)}$ and $c_{H(b)}$ are the (mean) proton concentrations in equilibrium with free and bound phenols, respectively. In the absence of inhibitor, i.e., in the pure resin, the dissolution rate is given by

$$R_o = kc_Bc_{H(a)} \qquad (6)$$

and with that eq 5 takes the form

$$\frac{R}{R_o} = 1 - n\frac{c_i}{c_{OH}c_{H(a)}}[c_{H(a)} - c_{H(b)}] \qquad (7)$$

Table 2. Inhibition Factors Calculated from Electrochemical Data via Eq 9 and Values Obtained from Dissolution Experiments

	n	$1-(c_{H(b)}/c_{H(a)})$	f_{calc}	$f_{experiment}$
flavanone	14.5	0.223	0.67	0.68
flavone	15.0	0.414	1.24	1.8
α-naphthoflavone	16.8	0.617	2.09	4.9
sulfonic acid inhibitor	14.3	0.369	1.10	0.93

For small values of c_i the logarithm of eq 7 may be approximated by the first term of an expansion formula

$$\ln \frac{R}{R_o} = -n\frac{c_i}{c_{OH}}\left[1 - \frac{c_{H(b)}}{c_{H(a)}}\right] \tag{8}$$

Equation 8 is essentially a statement of Meyerhofer's rule,[13] which says that in a limited concentration range the logarithm of the dissolution rate is a linear function of the inhibitor concentration, c_i. Differentiation of eq 8 and substitution of decadic logarithms leads to an expression for the inhibition factor f in terms of string length and bound and free proton concentrations.

$$f \equiv -\frac{(\mathrm{d}\log R)}{\mathrm{d}c_i} = n\frac{\log e}{c_{OH}}\left[1 - \frac{c_{H(b)}}{c_{H(a)}}\right] \tag{9}$$

The proton concentrations needed in eq 9 can be obtained via the pK_a values determined in the electrochemical experiments (see Table 1).

$$c_{H^+} = 10^{-pH} = 10^{1/2(pK_a - \log c_{OH})} \tag{10}$$

Using eq 9 we have calculated inhibition factors for the sulfonic acid inhibitor and for the three pyrones of Table 1. In Table 2 we compare the calculated f values with those obtained from dissolution experiments. The inhibition factors are expressed here in reciprocal moles per liter.

The fit between the two sets of values is good for flavanone and for the sulfonic acid inhibitor and poor for flavone and α-naphthoflavone. This discrepancy may be caused by the fact that the electrochemical measurements were conducted in a medium that contains water, while the films for the dissolution rate measurements were cast from aprotic solvents. We note at this point that eq 9 does not contain any adjustable parameters. In view of this, even the qualitative correspondence between calculated and experimental f numbers is strong support for the idea that the lowering of the acidity of the phenolic protons in the strings of the inhibitor brings about dissolution inhibition.

The fact that f depends more on the binding strength of the phenols in the strings than on string length (see Table 2) has interesting practical consequences: The concentration of inhibitor needed to absorb a given fraction of incident radiation will be the same for weak as for strong inhibitors, and as a result, the optical and absorptive properties of films made with inhibitors of different strength will be almost the same. The two coatings will differ only in the strength of inhibition.

Structure of Phenolic Strings

Phenolic strings owe their existence to an inductive polarization effect. The dipole of the acceptor (inhibitor) forms a hydrogen bond with the nearest OH group and in so doing polarizes it. The oxygen atom of this hydroxyl carries now an excess negative partial charge, which attracts and polarizes another hydroxyl etc. etc., thus forming a phenolic string.[1] This implies that the members of a phenolic string differ in acidity. The first phenol that interacts directly with the acceptor will be highly polarized and its proton will be strongly bound; the pK_a of this phenol will be high. The second member of the string will be less polarized and its pK_a will be somewhat lower than that of the first. This continues throughout the length of the string, until the last member will be almost indistinguishable from a free phenol, its pK_a being almost that of the pure resin. If we assume that the degree of polarization decreases in the string by a constant fraction from one member to the next, the pK_a values of the individual members form a geometric progression characterized by a decay factor, q, which is the ratio between the pK_a values of any two consecutive members of the string.

Table 3. String Length, Polarization Decay Factor, and pK_a Values of First and Last Members of Strings

	n	q	pK_a(1)	pK_a(n)
flavanone	14.5	0.995	7.86	7.33
flavone	15.0	0.991	8.39	7.29
α-naphthoflavone	16.8	0.990	8.66	7.37

$$\frac{pK_a(x)}{pK_a(x-1)} = q \tag{11}$$

The pK_a of any member, x, of a string can then be expressed in the form

$$pK_a(x) = pK_a(1)q^{x-1} \tag{12}$$

The mean pK_a of the members of the string averaged over the whole string, which is pK_a(b), is given by the sum of the members of the progression[14] divided by their number, namely the string length n.

$$pK_a(b) = pK_a(1)\frac{1-q^n}{(1-q)n} \tag{13}$$

Using eq 13 and an appropriate value of q, we have calculated pK_a for the first member of the string, namely pK_a(1), and pK_a for the last member, which is pK_a(n). These data for the strings of flavanone, flavone, and α-naphthoflavone are listed in Table 3. It can be seen that the pK_a of the last member of the strings approaches the pK_a of pure Novolak (Table 1).

Conclusions

Dissolution inhibition in resist films is based on the formation of strings of hydrogen-bonded, polarized OH groups. The acidity of the phenol units that are part of such strings is significantly lower than the acidity of free phenols in the bulk of the system. The lower acidity (higher pK_a) means that the concentration of protons in equilibrium with the phenols of the string is lower than that in the bulk of the solution. That leads to a decreased rate of phenol deprotonation and consequently to a lower dissolution rate.

There is a direct link between the electrochemical characteristics of the inhibitor (string length and the mean pK_a of bound phenols) and the lowering of the dissolution rate that the inhibitor causes in the corre-

sponding resist films. It appears that differences between inhibitors reflect principally differences in the acidity (pK_a) of bound phenols. Differences in string length between inhibitors are fairly small.

This inhibition mechanism has consequences for the exposed resists: it removes the difficulty of the limited range of the thermal pulse of the photolyzing DNQ. If inhibition is caused by the stronger bonding of protons to the phenolic strings, it is enough to affect the hydrogen bond between the inhibitor and the first phenol of the string to sever the whole string from its "anchor". As soon as the string is separated from the inhibitor, it loses its polarization and becomes simply a succession of phenols bound to each other no more strongly than other phenols in the bulk of the resin. This explains how the effect of even the longest strings observed in our experiments is completely suspended on exposure, although the range of the thermal pulse is smaller than the radius of gyration of the string.

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