Percolation View of Novolak Dissolution. 9. Deuterium Isotope Effect on Dissolution Rate

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ABSTRACT: A commercial Novolak resin was partially (OH groups) deuterated, and the dissolution rate of the deuterated material in 0.1 N solutions of KOD, NaOD, and LiOD in D_2O was measured. The dissolution of the deuterated systems is considerably slower than that of the corresponding protonated systems. In both cases the dissolution rate depends on the nature of the base cation, and it is in fact a linear function of the reciprocal cross section of the ions. These results are compatible with the view that the rate-determining step in Novolak dissolution is the deprotonation of phenol groups at the interface of the penetration zone with the resin matrix. The dissolution of deuterated Novolak in deuterated developers is strongly affected by the presence of salts of the base cations, in a manner similar to that of the protonated systems investigated in refs 1 and 2.

Introduction

Henderson et al.[1] in C. G. Willson's group at the University of Texas at Austin have investigated the effect of salts on the dissolution rate of Novolak films in aqueous bases. Subsequently, we were able to show that the observed behavior can be accounted for by the effect of salt on the diffusion of the hydroxyl ions of the base.[2]

It appears from our results that the effective diffusion coefficient of OH^- ions in Novolak films is an order of magnitude larger than that of other ions.

The size of hydroxyl ions is not very different from that of the halogenide anions of the salts used in these experiments, and the large differences in ionic mobility seemed to indicate that the hydroxyl ions migrate through the system by a mechanism different from the free volume diffusion of other ions. We suggested in our earlier communication[2] that the base function may propagate in the Novolak film by a sequence of proton-transfer steps, similar to the Grotthus conduction mechanism in aqueous acids and bases.[3,4] While this suggestion seemed plausible, it was felt that more direct experimental evidence for proton transfer would be desirable. In this context we have looked for a deuterium isotope effect in Novolak dissolution. The self-dissociation constant of D_2O ($pK_w = 15.13$) is an order of magnitude smaller than that of H_2O ($pK_w = 14.16$).[5,6] Deuteron transfer in D_2O is therefore expected to be slower than proton transfer in water. If the dissolution rate of deuterated Novolak in a deuterated developer (e.g. KOD in heavy water) was slower than the dissolution rate of the corresponding protonated system, that would be an indication that the rate-determining process involves a proton transfer step.

Experimental Part

The only protons involved in the dissolution of Novolak are the protons of the phenolic OH groups, and it was assumed that within the time frame of our experiments these do not exchange with the other protons of the polymer. If that is true, it will be sufficient for the purpose of our experiments to deuterate the phenolic protons of the resin. We have tested this assumption by deuterating the phenolic protons of a Novolak sample and then monitoring its proton NMR spectrum over a span of 2 weeks. In that time the trace of the phenolic protons did not reappear in the NMR spectrum.

Deuteration of Novolak Resins. Six grams of a commercial microlithography Novolak were dissolved in 100 g of D_2O and 7.2 g of KOD (40 wt % solution in heavy water) in a 250 mL round-bottom flask purged with nitrogen. The solution was dark brown in color. After 24 h at room temperature the reaction mixture was filtered to remove unreacted material, and then 4 mL of DCl (37 wt % solution) were added to the filtrate, whereupon the deuterated resin precipitated. The precipitate was washed with heavy water to neutrality and then filtered off. The filtered material was dried at room temperature in a vacuum for 4 days. All operations were carried out in an AtmosBag under flowing nitrogen to protect the deuterated material from moisture. The final product is a brown powder (yield 91%). The deuteration process was monitored by taking the NMR spectrum of Novolak in acetone-d_6, using tetramethylsilane as an internal reference. As deuteration progressed the NMR peak of the protons of the phenolic OH group disappeared from the spectrum (see Figure 1).

The Novolak resin made from a mixture of *p*-cresol and *m*-cresol was supplied to us graciously by Hoechst Celanese Corporation. Deuterium oxide (99.9 atom % D), potassium deuteroxide (40 wt % solution in D_2O), sodium deuteroxide (40 wt % solution), lithium deuteroxide (40 wt % solution), deuterium chloride (37 wt % solution), and 2-butoxyethanol-(ol-d) (98 atom % D) were purchased from Aldrich Chemical Co.

Preparation of Novolak Films and Dissolution Rate Measurements. Deuterated Novolak (D-Novolak) was dissolved in 2-butoxyethanol(ol-d) to a concentration of 27 wt %. This solution was spin-coated at 3000 rpm onto 1 in. diameter silicon wafers (Virginia Semiconductor, Inc.). The coated wafers were baked on a Corning hot plate for 5 min at 90°. All these operations were carried out in a drybox under nitrogen.

The dissolution rate of the coated samples in 0.1 N KOD in D_2O was measured at 20 °C with the single-channel laser interferometer described earlier.[7] This was also done in a drybox under nitrogen.

Dissolution Rate of Deuterated Novolak

We have measured the dissolution rate of deuterated Novolak in 0.1 N solutions of KOD, NaOD, and LiOD in heavy water, and under the same conditions we have determined the dissolution rate of protonated Novolak in 0.1 N aqueous KOH, NaOH, and LiOH. The results are listed in Table 1. It can be seen that the dissolution rate of the deuterated systems is only about half that of the protonated materials, and that supports the view that base migrates through the system by a proton-

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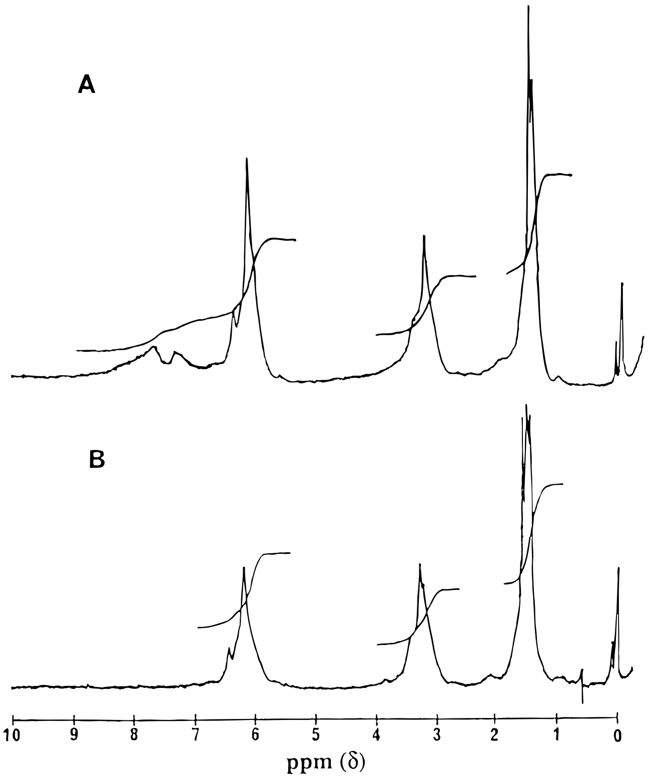

Figure 1. Proton NMR spectrum of Novolak (A) and of deuterated Novolak (B).

Table 1. Dissolution Rate of Novolak in Deuterated and in Protonated Bases (0.1 N Solutions)

	$R_{\mathrm{exp}}°$ (nm/s)		
	OD^- [a]	OH^- [b]	r_i^{-2} (Å^{-2})
K^+	7.1	14.4	0.57
Na^+	10.2	21.5	1.11
Li^+	15.9	30.3	2.78

[a] Coated from 2-butoxyethanol solution. [b] Coated from isoamyl acetate solution.

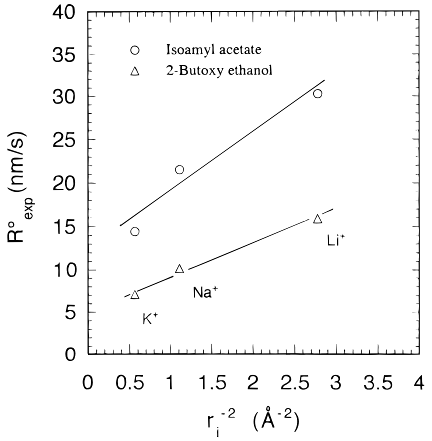

Figure 2. Dissolution rate of protonated (○) and of deuterated (△) Novolak in 0.1 N solutions of KOH, NaOH, and LiOH and of KOD, NaOD, and LiOD, respectively, plotted against the reciprocal square of the ionic radii of the cations.

transfer mechanism. At the same time, the dissolution rate depends also on the nature of the base cation (Figure 2). This, we believe, is incompatible with the assumption that the dissolution of Novolak is controlled by the diffusion of base *through or across* the penetration zone of the dissolving film. This statement becomes clearer when we consider the genesis of the penetration zone.

Rate Determining Step in Novolak Dissolution

Arcus[8] discovered the penetration zone as early as 1986. He showed that when a Novolak film is immersed in aqueous base, the ions of the base enter the film matrix and deprotonate the phenols of the resin in a thin layer adjacent to the interface of the film with the base solution. This layer is now termed the penetration zone. At each step of the deprotonation process a hydroxyl ion disappears and is replaced by a molecule of water. Each of the resin-bound phenolate ions is associated with its counter-cation (say K^+) and with one molecule of water. The next ion pair of base entering the zone associates itself temporarily with the phenolate$^-$/K^+ ion pair. When a further ion pair enters, the first pair moves forward in the direction of the virgin matrix while the second pair takes its place. This move is accomplished by proton transfer with the local water molecule.

$$H_2O + OH^-, K^+ = OH^- + H_2O, K^+ = OH^-, K^+ + H_2O \quad (1)$$

In the next step, the now supernumerary base deprotonates the next layer of phenols, and this process is repeated many times, being driven by the activity gradient of base at the interface of the zone with the developer solution. At some point, most of the phenol groups near the back of the zone are ionized and the Novolak chains start to float off into the developer solution. When the rate of the loss of material at the back of the zone equals the rate of progress into the virgin matrix of the front of the zone, a stationary regime is established and the zone moves forward at a constant rate. The rate of progress of the zone is identical with the dissolution rate (loss of thickness) of the resin film.

In the stationary regime the penetration zone is a fully continuous phase of constant composition, the unit cell of the zone containing one resin-bound phenolate ion accompanied by its counter-cation, one molecule of water, and one ion pair of base. The movement of base which is implied in the movement of the zone is fueled by the entry of base ion pairs at the back of the zone. Every arriving base pair sets in motion a series of proton-exchange steps which result in the appearance of an OH^- ion at the front interface of the zone with the virgin matrix. The proton-exchange steps within the zone are those of the classic Grotthus conduction mechanism.[3,4]

$$H_2O + OH^- = OH^- + H_2O \quad (2)$$

The point to be made here is that inside the penetration zone the anions of the base and the counter-cations move together, the rate of movement being that of the slower component. If the protons in the system are replaced by deuterons, either the OD^- or the counter-cations can be the slower component. In the first case, the dissolution rate of the deuterated material would be slower than that of protonated Novolak, but the dissolution rate would not any more depend on the nature of the base cation. If the cation of the base was the slower component, the dissolution rate of the deuterated resin would depend on the cations of the base, but it would be substantially the same as that of the protonated resin. Neither of these alternatives seems to apply. We conclude that 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.

The rate-determining event can now be described as follows: The ion pair of base that has arrived at the front of the penetration zone positions itself in a way that minimizes the electrostatic potential of the system. The base cation will be located adjacent to the "last" phenolate ion of the zone; the OH^- ion will position itself ahead of the base cation in the direction of the nearest phenol group in the matrix, influenced by the field of its $O^-{-}H^+$ dipole. With the appropriate reaction frequency, the hydroxyl ion will abstract the proton of the phenol. This changes the electrostatic potential in the region; the base cation is now in the attractive field of *two* phenolate anions, the newly created anion being the stronger attractor, because it is not yet interacting with (or shielded by) all the other ions in the polyelectrolyte of the zone. Given appropriate thermal activation, the base cation will transfer from a location near the original phenolate ion to one adjacent to the newly created negative center. This center contains already one molecule of water, and with the arrival of the cation (K^+) it will be ready to accommodate one more ion pair of base. The zone has now made one step forward into the resin film.

This two-step mechanism is compatible with the experimental results: The deprotonation step

$$POH + OH^- = PO^- + H_2O \qquad (3)$$

sets the time frame for the whole process, and as expected, that is slower in the deuterated system. However, deprotonation is not completed until the base cation has moved from its original location to its new position next to the newly created phenolate ion. The rate of this move depends on the (electrostatic) binding energy between the phenolate ions and the base cation, and as we have shown in the preceding paper,[8] this depends on the ionic radii. The two-step mechanism allows for the slower dissolution rate in the deuterated system and at the same time has the dissolution rate depend on the nature of the base cation.

Another argument supporting the view that the rate-determining step occurs at the front of the penetration zone is the fact that negative activation energies of dissolution are observed with the larger base cations in Novolak dissolution as well as in the dissolution of poly(4-hydroxystyrene).[9] Garza et al.[10] have shown that this is only possible if the rate-determining step is coupled to an exothermic chemical reaction. In our case this reaction is the deprotonation step of eq 3. Negative activation energies of dissolution could not have been observed if the rate was controlled by the diffusion of base through the zone. That type of diffusion is linked to proton exchange within the zone, as described by eq 2, and that is an athermal process, ($\Delta H° = 0$).

There are other arguments in favor of the location of the rate-determining step at the front of the zone, and these will be presented in a forthcoming paper on the effect of resin molecular weight on the dissolution rate.

Salt Effects in Deuterated Systems

We have investigated the effect of salts on the dissolution rate of deuterated Novolak in deuterated bases by measuring the dissolution rate in the presence of increasing concentrations of salts of the developer base. The direct results of these experiments are shown in Figure 3, where the data for KCl in a 0.1 N solution of KOD in D_2O are compared to those for the protonated resins with KCl in 0.1 N solutions in water. The data are plotted in Figure 3 against the salt-to-base ratio y = [KCl]/[KOD] or [KCl]/[KOH]. As in the protonated resins, there is clearly a strong salt effect in the deuterated systems. To characterize it quantitatively by the diffusional parameters used in the earlier paper,[2] we needed to linearize the experimental data as we had done before.[2] The method is condensed in eq 26 of ref 2. To eliminate the scaling constant from this expression, we have normalized the linearized dissolution rates with respect to the dissolution rate in 0.1 N solutions of the pure base.

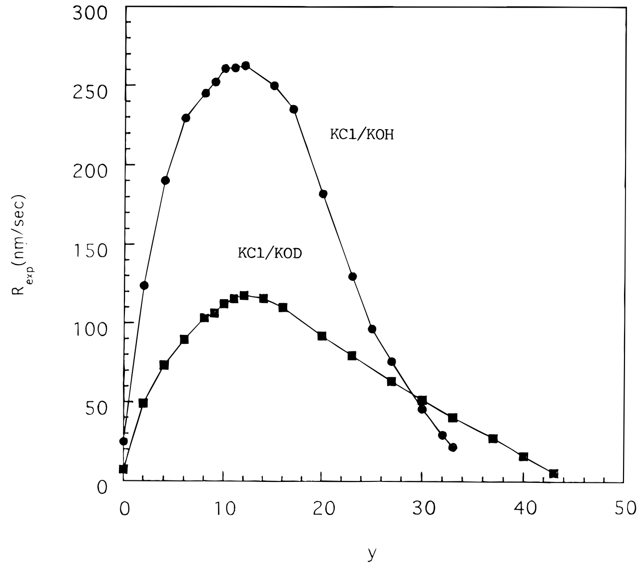

Figure 3. Experimental dissolution rate of Novolak and deuterated Novolak in 0.1 N solutions of KOH and KOD, respectively, in the presence of increasing concentrations of KCl. The data are plotted as a function of the salt-to-base ratio y = [KCl]/[KOH] or [KCl]/[KOD].

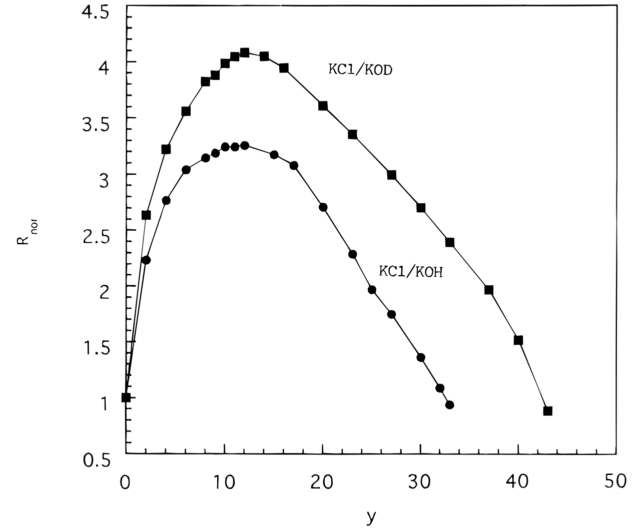

Figure 4. Normalized dissolution rates of protonated and of deuterated Novolak in 0.1 N solutions of KOH and KOD, respectively, in the presence of increasing concentrations of KCl. The data are plotted as functions of the salt-to-base ratio y.

$$R_{norm} = (1/\sqrt{R_{exp}°})\sqrt{R_{exp}} \qquad (4)$$

In Figure 4 the normalized dissolution rates of KOH and of KOD are plotted against the salt-to-base ratio, y. From these data the diffusional parameters α and

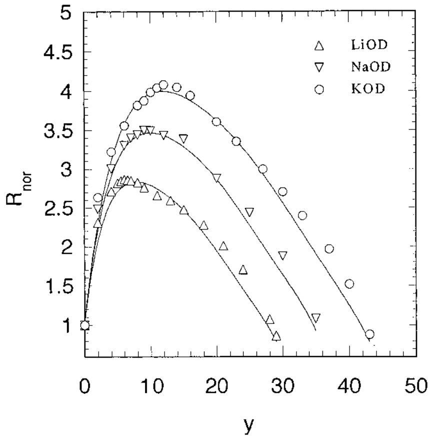

Figure 5. Salt effect plots of the normalized dissolution rate of deuterated Novolak in 0.1 N solutions of LiOD, NaOD, and KOD in heavy water.

Table 2. Dissolution Rate and Diffusional Characteristics of Deuterated Novolak in Deuterated Alkali Metal Bases (0.1 N Solutions in D_2O)

	R_{exp}° (nm/s)	R_{lin}° (nm/s)	α	y_c
Li^+	31.1	15.9	0.18	29
Na^+	21.5	10.2	0.14	36
K^+	14.4	7.1	0.12	43

y_c can be obtained. The diffusivity ratio α is defined as the ratio of the effective diffusion coefficients of chloride ions to those of hydroxide ions (or deuteroxide ions).

$$\alpha = D_{Cl}/D_{OH} \quad \text{or} \quad D_{Cl}/D_{OD} \tag{5}$$

The critical salt-to-base ratio y_c is that number of chloride ions that on average must surround a hydroxyl ion in order to force it to migrate with the speed of the chloride ions.

It is found that, for the deuterated resin in KOD solution, α = 0.12; for the protonated resin in KOH under the equivalent conditions, α = 0.15. This means that the diffusion of chloride ions has been slowed down in the deuterated system even more than the proton-transfer process.

To gain further insight into this situation, we measured the effect of KCl in other deuterated bases, LiOD and NaOD. The normalized dissolution rate curves of these experiments are in Figure 5, and their affine shape speaks for the consistency of the measurements. The diffusional characteristics of the three systems are listed in Table 2.

As we had found before in the protonated systems,[2] α and as y_c do not depend on the nature of the cations but rather are functions of the ionic flux and depend therefore on R_{exp}°. Figure 6 shows this dependency. From the extrapolation of y_c to zero flux one finds that it requires 55 chloride ions to suppress the independent movement of OD^-. The value of α extrapolated to zero flux is α = 0.07, indicating that in the deuterated system the (Grotthus) mobility of the OD^- ion is about 14 times higher than the diffusional mobility of chloride. The slowing down of ionic (free volume) diffusion in deuterated systems, as exemplified by the diffusion of chloride ion, is not without precedent. The conductivity of KCl and of NaCl in D^2O is 20% lower than that in water.[11] In a rigid medium such as the penetration zone (it is *below* its glass transition temperature[12]) the deuterium effect is expected to be more significant, as is indeed observed.

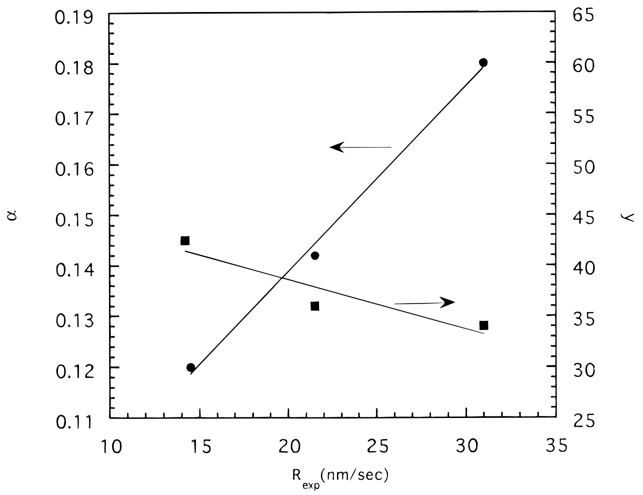

Figure 6. Diffusivity ratio α and the critical retardation parameter y_c plotted as a function of the experimental dissolution rate for deuterated Novolak dissolving in 0.1 N solutions of KOD in heavy water.

In summary: Deuterated Novolak dissolves in deuterated bases in D_2O with about half the rate of the dissolution of protonated Novolak in aqueous bases. In both systems the dissolution rate depends on the size of the base cations and is in fact a linear function of the reciprocal cross section of the ions. Like their protonated counterparts, the deuterated systems show a strong salt effect. It appears from the results that the diffusion coefficient of chloride ion is lowered in the deuterated systems even more than the rate of proton transfer by which OD^- ions migrate through the resin film.

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References and Notes

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