On the Dissolution of Novolak in Aqueous Alkali

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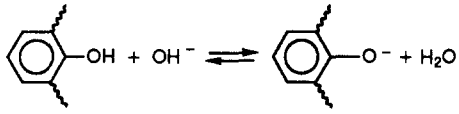
ABSTRACT: A model for the dissolution of novolak in aqueous alkali (the developer) is proposed. It is based on the notion that dissolution is controlled by the diffusion of developer through a thin penetration zone into the solid matrix of the novolak resin. The penetration zone is formed by the entry of developer base and deprotonation of some of the phenol groups of novolak. The polymer-bound phenolate ions attract water, and their negative charge is compensated by the arrival of the cations. The penetration zone constitutes a distinct phase with sharp boundaries separating it from the developer solution and from the solid matrix. When a certain degree of conversion to phenolate is reached, the structure of the penetration zone unravels and the multiply ionized macromolecules are transferred into the developer. At that point a mobile stationary state is established in which the penetration zone propagates identically in the direction of the concentration gradient. The existence of a minimum base concentration below which dissolution does not occur, the supralinear dependence of dissolution rate on base concentration, and the effect of cation size on dissolution can be derived from the diffusional properties of the stationary state. On a molecular level diffusion of base in novolak proceeds by a succession of hydrophilic sites, namely, the OH groups of the phenol units of the material. These sites define a pathway that acts like a hydrophilic diffusion channel. Suitably designed hydrophobic molecules can block some of these channels and in this way alter the dissolution rate of the resin. Hydrophilic additives can introduce additional channels into the system and promote dissolution. The concept of hydrophilic diffusion channels allows a unified intepretation of a number of commonly observed resist phenomena.

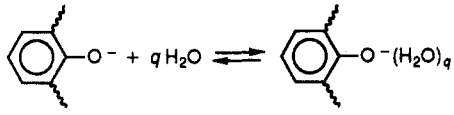
Because of the importance of novolak–diazoquinone resists in the manufacture of semiconductor devices the system has received considerable attention. In spite of this, the dissolution mechanism of novolak resists is still not fully understood.

It is generally accepted that the dissolution of novolak involves the deprotonation of phenol groups to polymer-bound phenolate ions.



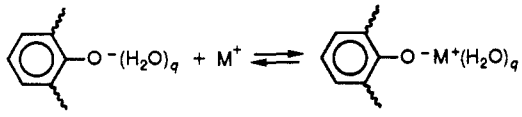
(1)

Phenolate ions are solvated by water



(2)

and their negative charge is compensated by the cation of the base.



(3)

This is followed by the rearrangement of the multiply ionized polymer chains, their detachment from the body of the matrix, and eventual transfer into solution.

Two major models of novolak dissolution have been proposed in the literature. In the model of Arcus[1] the interface between the polymer matrix and the developer solution is viewed as a membrane that "...can differentiate between the ions of aqueous basic developers due to variations in size, composition and charge... The membrane properties can be modified by chemical treatments, changes in concentration ...and most importantly by the photochemistry of the included naphthoquinonediazide." The membrane model implies that the dissolution process is controlled by the rate of entry of developer into the polymer film. The model is intuitively appealing, and it covers a great many aspects of the behavior of novolak resists.

In the model developed by Templeton, Szmanda, Trefonas, Daniels, Garza, and others formerly at the Monsanto Laboratories,[2,3] the rate of dissolution is thought to be determined by the secondary structure of the novolak chains in the matrix, in particular by the relative configurations of the OH groups of the phenols. The Monsanto model allows for large differences in dissolution rate between resins that differ little in primary structure. It assumes that the rate-limiting step in novolak dissolution is a chemical reaction, namely the deprotonation of the hydroxyl groups, and it describes the dissolution process by a chemical rate equation in the form

$$R = k[M^+]^m[OH^-]^n \quad (4)$$

where the exponents m and n are interpreted as true kinetic reaction orders. Hinsberg and Guttierez[4] have taken a similar view.

There is much truth in both models. Phenol deprotonation is certainly a crucial step in novolak dissolution as Arcus has emphasized, and the Monsanto group have the merit of having recognized the importance of the secondary structure of the polymer. Nonetheless, the "chemical" approach of the Monsanto model[3] cannot explain the dependence of the dissolution process on the thermal history of the film, as well as other aspects of the system, and Arcus' model[1] is rather nonspecific. This paper is concerned with a model that specifies the properties of the penetration zone in more detail. We hope to show that most aspects of novolak dissolution can be derived from the diffusional properties of the penetration zone.

Penetration Zone

The penetration zone is formed by the diffusion of developer into the solid polymer matrix. At the onset of development, water and OH^- ions enter the matrix simultaneously and a small number of phenol groups of the resin are converted to phenolate ions. Cations of the developer base follow to maintain electroneutrality. In a thin layer of the resin adjacent to the interface with developer solution a low concentration of polymer-bound phenolate and mobile cations will accumulate. Initially the concentration of phenolate salt is low enough to form a solid

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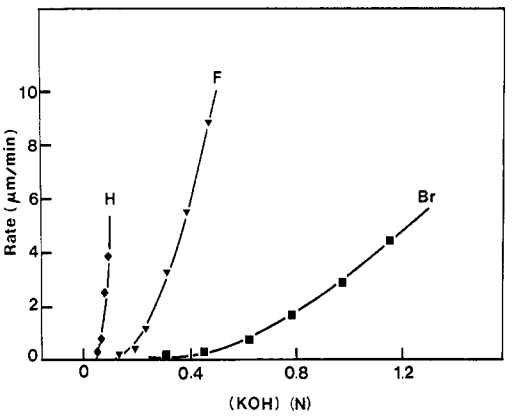

Figure 1. Dissolution rates of three para-substituted phenol novolaks plotted as a function of base concentration in developer.

solution in the matrix. As more base enters, the solubility limit of phenolate in the matrix is reached and a new phase is formed, which we shall call the penetration zone. The penetration zone is the equivalent of the gel layer that forms in the dissolution of solid polymers in thermodynamically good solvents.[5]

The formation of the new phase occurs only if the base concentration in the developer is higher than a critical minimum concentration below which dissolution does not occur. Figure 1 documents the existence of such a critical concentration. An equilibrium is established between the developer components at the interface between the resin matrix and the developer solution where the activities of the mobile components of the developer are the same on both sides of the interface.

$$a_s = a_o \tag{5}$$

$$c_s\gamma_s = c_o\gamma_o \tag{6}$$

Here, the subscript s refers to the solid matrix and the subscript o to the developer solution, and the activities are those of the cations of the base.

The solubility of phenolate salt in the solid matrix, indicated by c_s^* is linked to the critical value of base concentration in the developer, c_o^*.

$$c_o^* = c_s^*(\gamma_s/\gamma_o) \tag{7}$$

An estimate of the activity coefficient ratio between the matrix and the developer solution could be obtained by measuring the distribution coefficient of a neutral salt of the base cation between a phenolic liquid and the corresponding aqueous equilibrium phase. In general, the activity coefficient of cations in the phenolic solid is expected to have much higher values than in the developer solution, the critical base concentration can therefore be substantial, even if the solubility of phenolate salts in the solid matrix is low. The interpretation of the critical base concentration expressed in eq 7 agrees with the observed fact (see Figure 1) that the critical concentration is higher for more hydrophobic materials where the activity coefficient of cations is expected to be higher than in the more hydrophilic resins.

The phenolate–cation pairs which are in equilibrium with the developer base are located in the novolak matrix at or just behind the interface with the developer solution. Base will diffuse only very slowly into the bulk of the solid phase, but, if sufficient time is allowed, the phenolate concentration will eventually spread throughout the depth of the matrix and eventually the novolak film will dissolve even in developers that contain less than the critical concentration of base. The process will be several orders of magnitude slower than regular development. We have observed this slow dissolution process and have found that at a base concentration corresponding to half the critical value dissolution occurs after a couple of days in the developer.

Growth of the Penetration Zone

If the base concentration in the developer exceeds the critical value, the penetration zone separates from the matrix as a distinct phase. The system consists now of three adjoining phases: The developer solution (subscript o), the penetration zone (no subscript), and the solid novolak matrix (subscript s).

The nature of the penetration zone as a separate phase is indicated by sharp boundaries with discontinuities of the refractive index. Reflections of probe light from both boundaries are observed in laser interference experiments. We refer to the work of Arcus[1] and of Rodriguez et al.[21]

If the diffusion of water and base within the zone is significantly slower than the rate of transfer from the developer solution into the zone, water will accumulate in the first slice of the zone and the transfer will slow down. In contrast, the concentration of base (OH^- ions) is kept low as a result of its reaction with the phenol groups of the resin. The influx of base into the first slice will therefore continue almost unchanged while the influx of water will decrease. If the rate of outflow from the slice can be ignored in a first approximation, the quantity of water accumulated in the first slice will equal the quantity (moles) of water in the same volume of developer solution when 6.4 molecules of water/monomer unit of novolak are present in the zone. If we take into account that the influx of water is driven by the difference of activities rather than concentrations, the equality of the activities of water in both phases will occur when some 4 or even fewer molecules of water/phenol unit are present in the zone. An approximate calculation indicates that at the point of water saturation only some 10% of phenol in the slice have been converted to phenolate. As more base flows in, the concentration of unconverted phenol in the first slice diminishes, the probability that base is not captured in the first slice increases and phenolate will gradually be formed in a second, a third, a fourth slice, etc.

As the zone continues to grow, a critical degree of conversion of phenol to phenolate is eventually reached at which the structure of the first slice collapses and the novolak chains dissolve in the developer solution. At this point a steady state is established in which the zone propagates identically in the direction of the concentration gradient. As Arcus[1] envisioned, in the stationary state the penetration zone can be regarded as a membrane through which the developer must pass in order to reach the polymer matrix. The rate of travel of the moving membrane is the rate of dissolution of the resist film.

In the stationary regime the diffusional flux F through the zone is the product of the rate of travel, R, of the moving boundary, and the mean base concentration, $\bar{c}$, in the zone.

$$F = R\bar{c} \tag{8}$$

To find the dissolution rate, we need to estimate the diffusional flux.

Diffusion in the Penetration Zone

The diffusional flux through the penetration zone is the product of the overall concentration gradient across the zone and the mean value of the diffusion coefficient.[7]

$$F = \frac{c'' - c'}{\delta}\,\frac{1}{c'' - c'}\int_{c'}^{c''} D(c)\,dc \tag{9}$$

Here δ is the thickness of the zone, and c'' and c' are the concentrations of the diffusant (i.e. developer base) at the boundaries of the penetration zone. The thickness of the zone is linked to, but probably larger than, the mean radius of gyration of the macromolecules.

If the integral in eq 9 is to be evaluated, the function $D(c)$ has to be known. To derive it from first principles would mean to quantitatively describe the transient phase of the system prior to the establishment of the stationary state. This requires the solution of three simultaneous integro-differential equations for the time-dependent distributions of phenolate, of water, and of base. In addition, the distribution coefficients of all components between adjoining phases would have to be known.

We propose a different approach to the description of the stationary state. The effect of the concentration dependence of the diffusion coefficient will be introduced into the description of the diffusion process in general terms, and then a function $D(c)$ will be sought such that it correctly reproduces the experimentally observed concentration dependence of the dissolution rate.

It can be shown that a function that fulfills these requirements has the form

$$D(c) = \alpha(c - c')^n \tag{10}$$

where α is a proportionality constant that signifies the somewhat ficticious diffusion coefficient at the concentration $c = c' + 1$. When expression 10 is used, the diffusional flux in eq 9 can be written in the form

$$F = \frac{\alpha}{\delta}\int_{c'}^{c''}(c - c')^n \, dc = \frac{\alpha}{\delta}\frac{1}{n+1}(c'' - c')^{n+1} \tag{11}$$

The rate of dissolution can now be found from eq 8 by introduction of a mean value for the base concentration in the zone that can be shown (see eq 20) to be given by

$$\bar{c} = \frac{n+1}{n+2}(c'' + c') \tag{12}$$

This leads to the following expression for the rate of dissolution.

$$R = \frac{\alpha}{\delta}\frac{n+2}{(n+1)^2}\frac{(c'' - c')^{n+1}}{(c'' + c')} \tag{13}$$

In the stationary state, the base concentration c'' at the boundary with the developer solution is proportional to the base concentration c_0 in the developer solution

$$c'' = ac_0 \tag{14}$$

The concentration c' at the boundary with the solid matrix is related to the critical minimum concentration of base in the developer, c^*, as defined in eq 7. This is a characteristic of the novolak resin and is independent of developer concentration. Equation 13 can then be written in the form

$$R = \frac{\alpha a^n}{\delta}\frac{n+2}{(n+1)^2}\frac{(c_0 - c^*)^{n+1}}{(c_0 + c^*)} \tag{15}$$

which describes the dependence of dissolution rate on the base concentration in the developer.

The dependence of dissolution rate on base concentration is often expressed by an empirical scaling law of the form[3,4,6]

$$R = \text{constant } c^n \tag{16}$$

where the exponent n has been reported with values in the range from 2 to 10. Figure 2 shows that eq 16 does indeed fit experimental data for base concentrations well above the critical minimum concentration. However, nearer the critical minimum concentration eq 16 is clearly not satisfactory. Equation 15, which is derived from a purely diffusional model, represents the data over a much wider concentration range as can be seen in Figure 3 where the product $R(c_0 + c^*)$ is plotted logarithmically against the concentration difference $(c_0 - c^*)$.

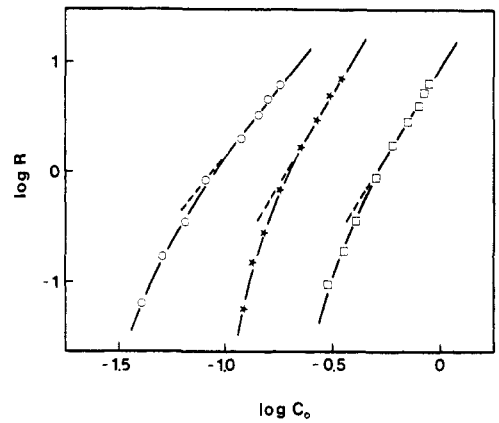

Figure 2. Logarithm of dissolution rate plotted against the logarithm of base concentration in the developer for the following resins: (○) *p*-Cl–PHMP, (*) poly(bisphenol)-1, (□) poly(bisphenol)-2.

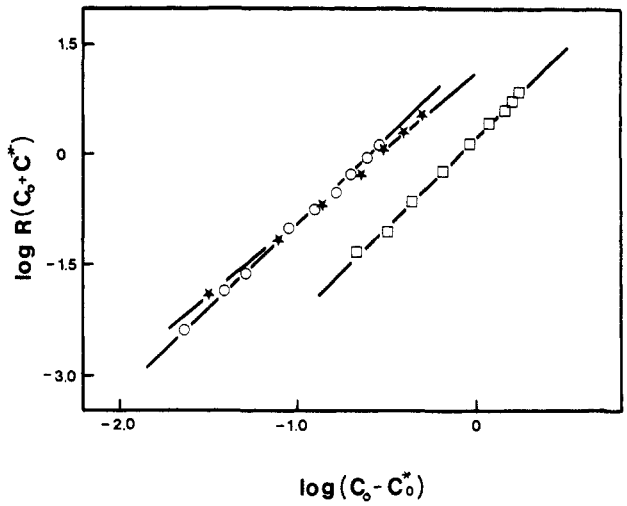

Figure 3. Test of eq 15. The logarithm of the product $R(c_0 + c^*)$ is plotted against the logarithm of $(c_0 - c^*)$ for the novolak resins referred to in the caption to Figure 2.

Profiles of Concentration and of Diffusion Coefficient

Given the concentration dependence of the diffusion coefficient, it is possible to derive the stationary profile of base concentration in the penetration zone. For the case of a planar membrane, Barrer[8] has derived the following expression.

$$\frac{\int_{c'}^{c''}D(c)\,dc - \int_{c'}^{c}D(c)\,dc}{\int_{c'}^{c''}D(c)\,dc - \int_{c'}^{c'}D(c)\,dc} = \frac{x}{\delta} = x' \tag{17}$$

Here x is the depth in the zone and x' is the relative depth given by the ratio of x/δ. Since $\int_{c'}^{c'}D(c)\,dc$ is zero by definition, the Barrer expression can be adapted for our purpose in the form

$$\int_{c'}^{c}D(c)\,dc = [1 - x']\int_{c'}^{c''}D(c)\,dc \tag{18}$$

which, on substitution of eq 10 for $D(c)$, leads directly to

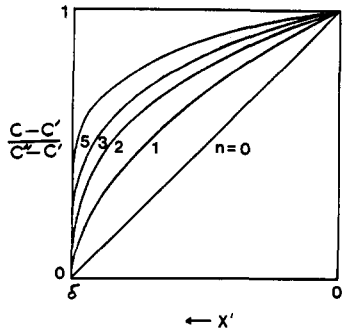

Figure 4. Dimensionless plot of concentration profiles in the penetration zone calculated from eq 19 for a few values of the exponent n.

an expression for the concentration profile $c(x)$ of base in the penetration zone.

$$\frac{(c - c')}{(c'' - c')} = [1 - x']^{1/(n+1)} \tag{19}$$

The mean base concentration, $\bar{c}$, in the zone can be derived from eq 19 in the form

$$\bar{c} = (c'' + c') \int_1^0 [1 - x']^{1/(n+1)} = \frac{n+1}{n+2}(c'' + c') \tag{20}$$

Equation 19 generates the concentration profiles shown in Figure 4 for several values of the exponent n. It can be seen that for $n = 0$ the diffusion coefficient is constant and Fick's first law is obeyed but that for $n = 1$ there are significant deviations from a linear concentration profile and that these become more pronounced as n increases.

To calculate the gradient profile across the penetration zone, eq 19 is differentiated with respect to x. The result is expressed in the dimensionless eq 21.

$$\frac{\delta}{c'' - c'} \frac{dc}{dx} = -\frac{1}{n+1} \frac{(c'' - c')^n}{(c - c')} \tag{21}$$

Equation 21 represents the concentration gradient of base as a function of the local base concentration c. The gradient as a function of relative depths x' in the penetration zone is obtained by inserting eq 19 into eq 21.

$$-\frac{(n+1)\delta}{c'' - c'} \frac{dc}{dx} = [1 - x']^{-n/(n+1)} \tag{22}$$

A knowledge of the concentration gradient profile is of interest here because it is linked to the diffusion coefficient.

$$D(x)\frac{dc}{dx}(x) = D(0)\frac{dc}{dx}(0) \tag{23}$$

By combining eq 22 and eq 23, one obtains an expression for the profile of the diffusion coefficient of base in the penetration zone.

$$\frac{D(x)}{D(0)} = [1 - x']^{n/(n+1)} \tag{24}$$

Profiles of diffusion coefficient derived from eq 24 are plotted in Figure 5 for a few values of the exponent n.

The significant feature in Figure 5 is that the diffusion coefficient decreases gradually in the direction of the concentration gradient but drops precipitously near the interface of the zone with the solid matrix. It appears that the rate-limiting step in novolak dissolution occurs at the interface.

Cation Size Effect and Absolute Values of the Diffusion Coefficients

Dissolution rates are affected by the size of the cation of the developer base.[1,3,4] Figure 6 shows dissolution curves

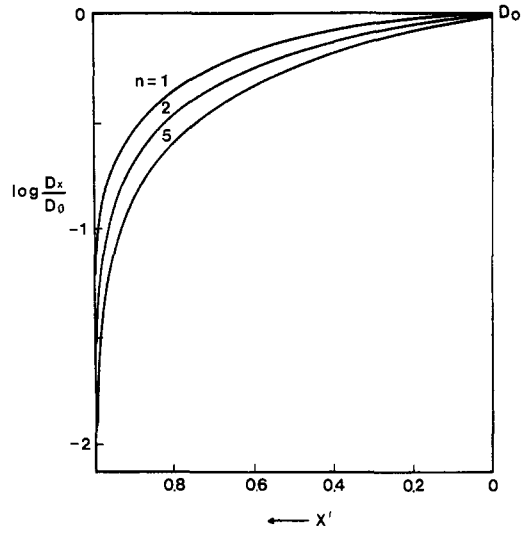

Figure 5. Logarithmic plot of the relative diffusion coefficient $D(x)/D(0)$ as a function of relative depth x' in zone calculated for three values of the exponent n. $D(0)$ is the diffusion coefficient at the interface with the developer solution.

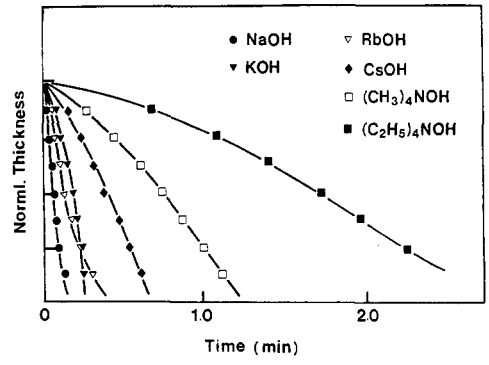

Figure 6. Dissolution curves of a p-nitro-substituted novolak developed in hydroxide solutions of different cations (0.08 N, 27.5 °C).

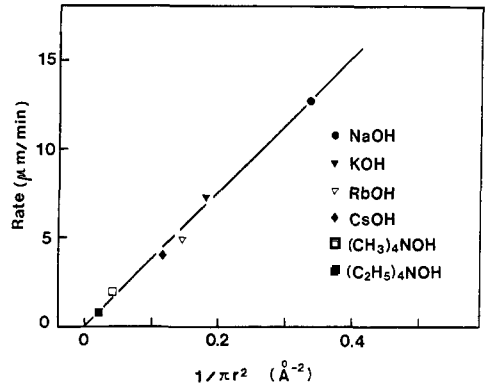

Figure 7. Dissolution rates derived from the data in Figure 6 plotted against the reciprocal of the cross section of the cations as calculated from crystallographic data.

Table I
Radii of Hydrated and Unhydrated Alkali Ions[7] (Å)

	Li^+	Na^+	K^+	Rb^+	Cs^+
crystallographic radii	0.68	0.98	1.33	1.48	1.67
radii of hydrated ions	3.40	2.76	2.32	2.28	2.28

obtained in this laboratory with a para-substituted phenol novolak. The rates correlate with the crystallographic radii of the cations, not with the sizes of the solvated ions (see Table I). This indicates that in the rate-limiting step of the dissolution process the cations leave their hydration

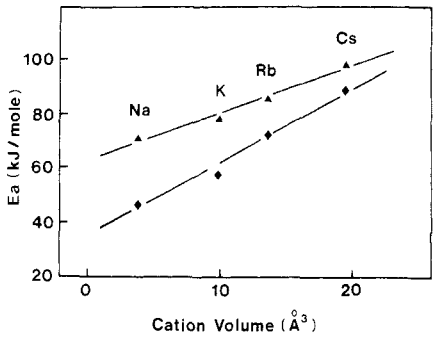

Figure 8. Activation energies plotted as a function of cation volume. The lower data points are derived from our dissolution measurements on novolak films. The upper data points refer to conductivity measurements on cellulose films containing low concentrations of chlorides of the ions indicated.[12]

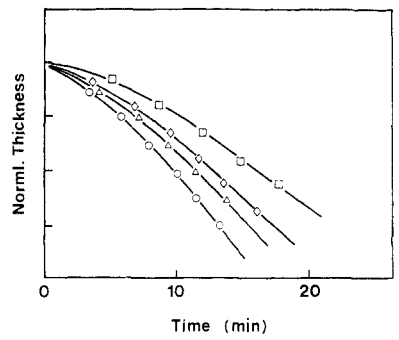

Figure 9. Dissolution in 1 N KOH at 30.0 °C of blends of novolak Varcum-2217 with 10% by weight of copolymers of methyl methacrylate (MMA) and methylstyrene (MS): (○) PMMA, (▲) 89 mol % MMA and 11 mol % MS, (◇) 79 mol % MMA and 21 mol % MS, (□) 67 mol % MMA and 33 mol % MS.

shell behind. It can be seen from Figure 7 that the rate of dissolution, determined from the linear part of the dissolution curves is a linear function of the reciprocal ionic cross section $(4\pi r^2)^{-1}$.

We have estimated the value of the rate-limiting diffusion coefficient from the product of the dissolution rate and the width of the penetration zone.

$$F \cong D(c_0/\delta) \cong Rc_0$$

$$D \cong R\delta \tag{25}$$

Using the dissolution rates observed (R = 200 Å/s) and reasonable values for the thickness of the penetration zone (δ = 20 Å), diffusion coefficients of the order of

$$D = 4 \times 10^{-13}\ \text{cm}^2/\text{s}$$

are obtained. These are some 7–8 orders of magnitude smaller than the diffusion coefficients of alkali ions in water or in ion-exchange gels.[11] However, values of this order are not inappropriate for the transfer of ions into a solid polymeric phase. Barker and Thomas[12] have measured the mobility of alkali ions in solid cellulose films and found values corresponding to diffusion coefficients of the order of 10^{-18} cm^2/s. Figure 8 shows the activation energies for ionic migration in cellulose films from the data of Barker and Thomas (upper line) and the activation energies for novolak dissolution in bases of different cations as measured in this laboratory. There are clearly similarities between the two processes.

In the foregoing sections it was demonstrated that many aspects of novolak behavior can be described quantitatively in terms of the diffusion of developer base into the solid polymer matrix. The molecular mechanism of this diffusion process will now be considered.

Molecular Mechanism of Diffusion

Novolak is essentially a hydrophobic material that contains some hydrophilic moieties. When a novolak film is immersed in an aqueous developer, water and OH^- ions will enter the matrix preferentially at hydrophilic sites and the cations of the base will follow. In the subsequent diffusional random walk the developer components will spend more time at hydrophilic sites than at others. A diffusion path will thus be defined by a succession of hydrophilic sites, and the developer will effectively proceed as if through a set of diffusion channels. Several observations support the concept of hydrophilic diffusion channels.

It is a common observation that the effect of diazoquinone inhibitors on the dissolution rate of novolak is quite out of proportion to the volume fraction of the inhibitor in the overall system: the addition of some 20% of inhibitor can slow down the dissolution of the resin by 2 orders of magnitude.[13] It is not easy to justify such a large change in terms of thermodynamics, but one can envision that a small number of inhibitor molecules may be able to block some of the diffusion channels and in this way have a large effect on the dissolution rate.

The Monsanto group have shown[2] that the secondary structure of novolak strongly affects the rate of dissolution. The model based on hydrophilic diffusion channels requires an unbroken succession of hydrophilic sites for fast dissolution. That is precisely the situation prevailing in poly(vinylphenol) where the hydroxyl groups form a continuous spiral around the polyvinyl backbone. Poly(vinylphenol) has indeed very high dissolution rates. In contrast, the hydroxyl groups of ortho–ortho linked *p*-cresol novolak aggregate in "nests" leaving large regions of the matrix without hydrophilic sites. These resins dissolve much more slowly.[3]

Our model predicts that dissolution inhibitors will be effective only if they are located in the hydrophilic diffusion pathways. The sulfonyl groups, which are contained in almost all commercial resists, appear to anker the inhibitors in the hydrophilic channels by interacting with the OH groups of the resin. Purely hydrophobic molecules are expected to locate exclusively in the hydrophobic regions of the matrix and may not have much effect on the dissolution rate. Such behavior has been observed by Koshiba et al.[14] who found that unsubstituted diazonaphthoquinone did not act as dissolution inhibitor of novolak but that, e.g., diphenyl sulfone, which contains the sulfonyl anker group, is as effective as the sulfonyl-substituted diazonaphthoquinone of a popular commercial inhibitor.

With a given type of secondary structure, the dissolution rate will be controlled by the overall content of hydrophilic moieties in the resin. The hydrophilic–hydrophobic balance of a resin can be subtly altered by blending with resins of different hydrophobicity and that should have an effect on the dissolution rate. Figure 9 shows the dissolution curves of a novolak blended with copolymers of methyl methacrylate (MMA) and methylstyrene (MS). As the content of the more hydrophobic methylstyrene increases, the dissolution rate of the blend decreases proportionally. The opposite strategy was followed in a second set of experiments where novolak was blended with copolymers of methyl methacrylate and the more hydrophilic component hydroxyethyl acrylate (HEA). It can be seen in Figure 10 that here the dissolution rate steadily increases with increasing content of the hydrophilic component.

It is of interest to note in this connection that the introduction of hydrophilic moieties has a much greater

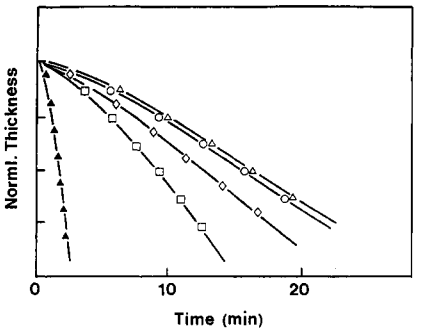

Figure 10. Dissolution in 1 N KOH at 30.0 °C of blends of novolak Varcum-2217 with 10% by weight of copolymers of methyl methacrylate (MMA) and hydroxyethyl acrylate (HEA): (▲) pure novolak, (△) with PMMA, (○) with copolymer 95 mol % MMA and 5 mol % HEA, (◇) with copolymer 90 mol % MMA and 10 mol % HEA, (□) with copolymer 80 mol % MMA and 20 mol % HEA.

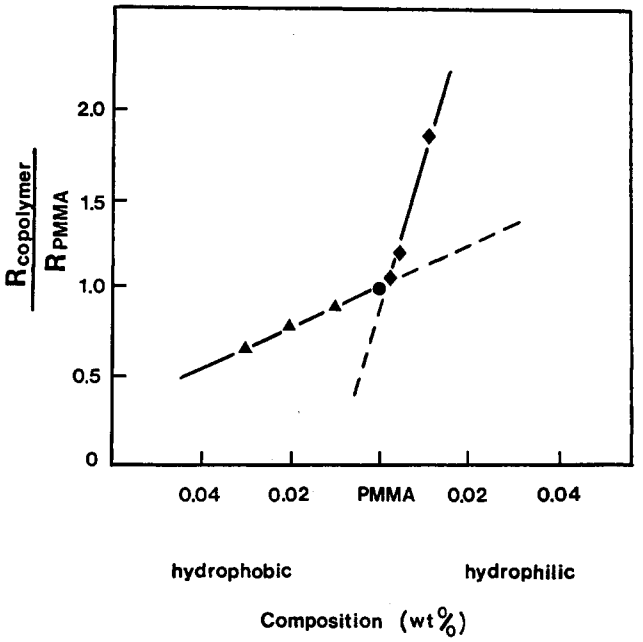

Figure 11. Dissolution rates of novolak as shown in Figures 9 and 10 plotted as a function of the fraction of added hydrophobic and hydrophilic components.

effect on the dissolution rate than the introduction of hydrophobic components (see Figure 11). We believe that this is because the hydrophobic components affect the dissolution rate only if they interact with the hydrophilic sites, while additional hydrophilic moieties always increase the number of hydrophilic sites, irrespective of their location in the matrix.

Hydrophilic sites can be introduced into the resin also by substitution. This is shown in Figure 12 where the dissolution rate of some para-substituted phenol novolaks is plotted as a function of base concentration. The large difference in the behavior of the methyl-substituted and the methoxy-substituted resins should be noted. The two substituents are very similar in their electronic effects and in their steric requirements, but the introduction of a large number of hydrophilic sites in the form of the methoxy groups dramatically increases the dissolution rate of the resin.

Another example of the effect of hydrophilic additives to the novolak matrix is the observation by Blum and others[15] of a large dissolution rate enhancement brought about by the indenecarboxylic acid photogenerated from diazoquinone. See, however, Hinsberg et al.[16]

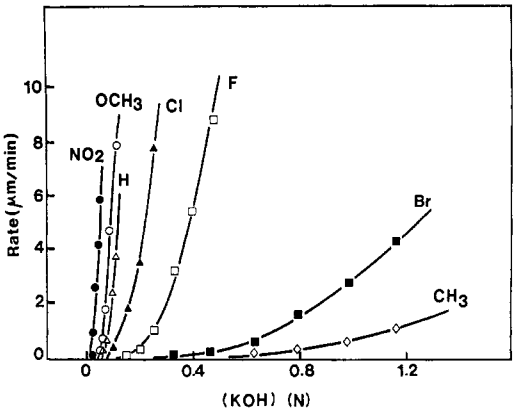

Figure 12. Dissolution rates of a group of para-substituted phenol novolaks in aqueous KOH at 20.0 °C, plotted as a function of base concentration.

Table II
Molecular Weight and T_g of Polymers

polym	M_n	T_g, °C
PHMP	1000	92
p-F-PHMP	1000	113
p-Cl-PHMP	820	84
p-Br-PHMP	1300	108
p-NO_2-PHMP	900	125
p-OCH_3-PHMP	900	67
p-CH_3-PHMP	670	99
p-*t*-Bu-PHMP	1000	101
Varcum-2217	890	89
PMA	30700[a]	10
PMMA	350000[a]	124
PEMA	340000[a]	72
PBMA	320000[a]	
PHMA	300000[a]	

[a] Weight average molecular weight of commercial sample. PHMP is poly(hydroxymethylenephenylene).

Experimental Section

Materials. Methyl methacrylate and *p*-methylstyrene (Aldrich) were distilled under reduced pressure at 60 °C. The purified monomers were sealed and stored in a refrigerator before use. Hydroxyethyl acrylate (Aldrich) was used without further purification.

Para-substituted phenol novolaks based on poly(1-hydroxy-2,6-methylenephenylene) (PHMP) were prepared according to the procedures given in ref 17. The novolak Varcum-2217 was supplied by BTL Specialty Resins Corp.; poly(bisphenol) resins were supplied by the Mead Corp.; poly(methyl acrylate) (PMA), poly(ethyl methacrylate) (PEMA), poly(butyl methacrylate) (PBMA), and poly(hexyl methacrylate) (PHMA) were supplied by Aldrich; poly(methyl methacrylate) was supplied by Polysciences. The average molecular weights and the glass transition temperatures of the polymers are listed in Table II.

Copolymers of methyl methacrylate with hydroxyethyl acrylate and with methylstyrene were prepared from the monomers by free-radical-initiated copolymerization in ethanol.[18-20] The initiator was AIBN at 0.3% of the weight of monomer. The reactions were conducted at 70 °C under nitrogen and terminated at a conversion of about 10%. The copolymers were worked up by the usual procedure.

Dissolution Measurements. Solutions of the resists in mixtures of isoamyl acetate/cyclohexanone/methyl isobutyl ketone (90:5:5 by vol) were spin coated onto silicon wafers at about 2000 rps. The coated wafers were prebaked in a convection oven at 90 °C for 1 h and then stored in a desiccator. Film thickness was about 2 μm. Resist dissolution was measured by laser interferometry with a He–Ne laser. During measurement the coatings were kept at an accurately controlled constant temperature.

Acknowledgment. Financial support by IBM is gratefully acknowledged.

Registry No. (MMA)(MS) (copolymer), 28429-02-9; (MMA)(HEA) (copolymer), 27756-39-4; PHMP, 9003-35-4; p-F-PHMP, 26045-02-3; p-Cl-PHMP, 26045-03-4; p-Br-PHMP, 26045-04-5; p-NO_2-PHMP, 27322-28-7; p-OCH_3-PHMP, 38639-99-5; p-CH_3-PHMP, 25053-88-7; Varcum 2217, 121674-18-8; KOH, 1310-58-3; NaOH, 1310-73-2; RbOH, 1310-82-3; CsOH, 21351-79-1; $(CH_3)_4NOH$, 75-59-2; $(C_2H_5)_4NOH$, 77-98-5.

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On the Physical Meaning of the Kwei Equation for the Glass Transition Temperature of Polymer Blends

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ABSTRACT: Poly(vinyl cinnamates) substituted with electron-donor or -acceptor groups in the para position of the phenyl ring and similar vinyl polymers where the substituted cinnamoyl groups are separated from the main chain by $(CH_2)_3$ and $(CH_2)_6$ spacers were prepared. The glass transition temperatures of 12 miscible pairs of these polymers were determined as a function of composition, and the T_g versus composition curves were approximated by an empirical equation proposed earlier by Kwei:[2] $T_g = (w_1T_{g1} + kw_2T_{g2})/(w_1 + kw_2) + qw_1w_2$. By classifying the systems according to the values of the constants k and q, certain regularities of behavior became apparent, which led to a physical interpretation of this equation. It is suggested that, in the important class of systems where $k = 1$, the constant q represents the stabilization energy of the backbone in the blend in excess of the weighted mean of the stabilization energies of these components. This interpretation is supported by the results of photoreactivity measurements. Systems where $k \neq 1$ and $q \neq 0$ have S-shaped T_g versus w curves. These are characteristic of incipient phase separation.

In a study of the photosensitivity of substituted poly(vinyl cinnamates), a series of blends of electron-donor with electron-acceptor-substituted polymers was prepared.[1] To test the compatibility of the polymers with each other and detect the possible appearance of a second phase, the glass transition of the blends was monitored as a function of composition. The experimental data were fitted by an equation proposed in 1984 by Kwei.[2] Certain regularities observed in the T_g versus composition curves invited further investigation, which led finally to a qualitative interpretation of the characteristic constants of the Kwei equation.

The thermodynamic criterion for compatibility is a negative value of the free energy of mixing of the components:

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (1)$$

Since the entropy of mixing of high polymers is always small, the coexistence of two polymers in the same phase is predicated by a negative enthalpy of mixing, $\Delta H_m < 0$, corresponding to an attractive interaction between the components. This has been understood for a long time[3] and miscible polymer blends have been formulated on the basis of various secondary interaction forces, such as hydrogen bonding,[2,4] ion–dipole forces,[5] and electron-donor–acceptor interactions.[6,7] In this study we had available a series of polymer blends in which the strength of electron-donor–acceptor interactions in the side chains had been systematically varied, while keeping the basic structure of the backbone constant. It was found in preliminary experiments that the glass transition was affected by these interactions, we have therefore undertaken a systematic mapping of the T_g of the blends of these polymers. To estimate the nature and the degree of side-chain interaction, we have also determined the photoreactivity of the blends and have tried to understand the relation between the two phenomena.

Because of the link of the glass transition with the mechanical and thermal properties of polymer blends, the dependence of the glass transition temperature on composition has received much attention. Several equations are available to describe this relationship in empirical

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