Percolation View of Novolak Dissolution. 10. Effect of Resin Molecular Weight

Hsiao-Yi Shih,[†,‡] Huifang Zhuang,[†,§] Arnost Reiser,[*,†] and Iwao Teraoka[||]

Institute of Imaging Sciences and Department of Chemistry, Polytechnic University, Brooklyn, New York 11201

Jonathan Goodman

Courant Institute of Mathematical Sciences, New York University, New York, New York 10012

Paula M. Gallagher-Wetmore

Phasex Corporation, Lawrence, Massachusetts 01843

Received October 21, 1997; Revised Manuscript Received December 17, 1997

ABSTRACT: An interpretation of the effect of resin molecular weight on the dissolution of Novolak is offered. It is based on Eyring's transition state theory and on the percolation model of Novolak dissolution. The rate-determining step of Novolak dissolution is the deprotonation of phenol by base at the front edge of the penetration zone. In order for this reaction to occur at a particular site, an ion pair of base must appear there, and to make this possible, all base ions of the corresponding percolation channel have to move forward in synchronism. That requires the simultaneous thermal activation of all the sites of the channel. At this point the mechanism of energy transport intervenes: In a system of polymer chains, thermal (vibrational) energy propagates much faster along the chains than between them, and the critical energy fluctuations needed for the activation of a site will reach this site almost exclusively via the chain to which the site belongs. It can be shown that the probability that a particular site will receive an activating quantum is inversely proportional to chain length. The probability that all sites of a percolation channel will be activated simultaneously is inversely proportional to chain length to a power that is the number of sites involved in the move. The probability of this event decreases steeply with chain length, as is observed. These principles lead to a quantitative description of the dissolution of Novolak films as a function of the molecular weight of the resin.

A Preliminary Note

When this manuscript was complete, an important paper by Willson and his group at the University of Texas, Austin, appeared (*Macromolecules* **1997**, *30*, 4642). It deals, among other things, with the effect of resin molecular weight on the dissolution of Novolak, but it approaches the problem very differently from us. At first sight it may appear that the two papers, Willson's and ours, are not compatible, but that is not the case. On the contrary, they complement each other in a very necessary way. The following is an attempt to show how.

The dissolution of Novolak in aqueous bases involves a chemical reaction, the deprotonation of phenols to phenolate ions. This transformation gives rise to a narrow phenolate-rich layer adjacent to the film/solution interface, the so-called penetration zone. From the moment the Novolak film is immersed in the base solution, the zone starts to build and it grows steadily until the time when the rate of transfer into solution of the highly ionized polymer chains at the back of the zone equals the rate of phenol deprotonation at the front. At that stage a stationary dissolution regime is established where the zone travels forward in the direction of the virgin matrix, without changing its thickness or its composition profile. Such a regime can be maintained only if the events at the front and at the back of the zone respond similarly to changes of conditions, such as changes in the concentration of base, in temperature, and also in the molecular weight of the resin. Willson's group has captured the behavior of the system at the back of the zone; we have concerned ourselves with the events at the front. Although these events are of a very different nature, we find that both are affected in similar ways by changes of resin molecular weight. Other examples of this complementarity could be cited, and the general conclusion is that only together do the two approaches provide a complete description of the dissolution process.

Introduction

Since Hanabata's classical work,[1] molecular weight has been recognized as an important factor in the formulation of high-resolution resists. Ouano[2] in 1984, and Turner et al.[3] in 1985 have shown that an increase in the molecular weight causes a sharp decrease in the dissolution rate of Novolak films, and recent work of Allen et al. at IBM[4] and of Willson and his group at the University of Texas, Austin,[5] has confirmed this. By now, the reciprocal relation between dissolution rate and molecular weight is part of the conventional wisdom of microlithography, but so far no explanation for the effect has been offered.

[†] Institute of Imaging Sciences.

[‡] Current address: International Specialty Products, Wayne, NJ 07470.

[§] Current address: Research Frontiers, Inc., Woodbury, NY 11797.

[||] Department of Chemistry.

S0024-9297(97)01546-5 CCC: $15.00

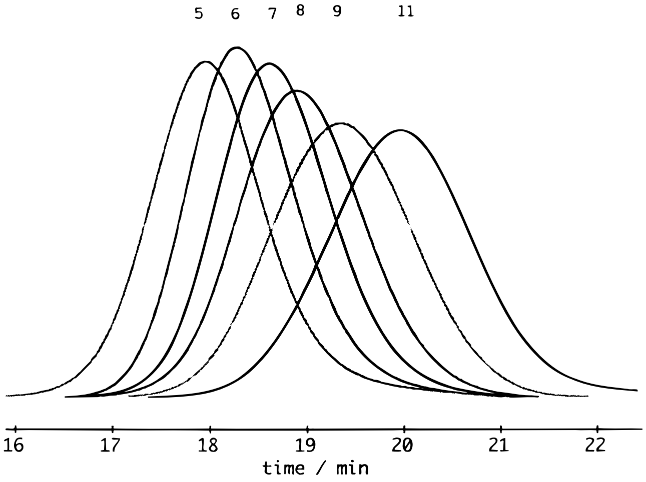

Figure 1. Chromatograms of Novolak fractions used in this study.

Table 1. Molecular Weight and Molecular Weight Dispersity of Novolak Fractions

no.	M_w	M_w/M_n	no.	M_w	M_w/M_n
3	1140	1.12	8	2810	1.06
4	1450	1.14	9	3170	1.05
5	1740	1.09	10	3420	1.06
6	2190	1.07	11	3670	1.07
7	2550	1.06			

We wondered how molecular weight might enter into a percolation model of dissolution. According to percolation theory,[6] the rate of diffusion of base depends only on the density of hydrophilic sites (OH groups), and the concentration of these sites does not change with the molecular weight of the resin. It seemed possible that molecular weight might affect the rate at which Novolak chains disentangle[7] during dissolution, and a remarkable paper by Peppas et al.[8] points the way here. However, chain entanglement sets in at chain lengths of 200 and more, and the Novolak resins of microlithography have chains of only 15−40 members. In this paper we have attempted an analysis of the dissolution process in terms of Eyring's transition state theory.[9]

We have limited our experiments to the molecular weight range between 1500 and 4000 where a fairly consistent behavior has generally been observed.[5] Below 1000 the effect of molecular weight on dissolution rate is less pronounced, and above 10 000 experimentation becomes rather difficult. We believe that the essence of the effect can be discerned in the range we chose.

Experimental Section

Fractionation of Novolak. A commercial Novolak sample supplied to us by Hoechst Celanese Corp. was fractionated in supercritical CO_2 into several fairly narrow molecular weight fractions. The method has been developed by Krukonis and his associates[10,11] at Phasex Corp. in Lowell, MA.

Chromatography of the Fractions. The molecular weights of six fractions were determined by gel-permeation chromatography in a column (Jordi Gel DVB, 500 A, 250 mm × 10 mm), with a Waters 510 pump and a 410 differential refractometer. The eluent was THF flowing at 1 mL/min. The column was calibrated with polystyrene standards of molecular weight from 600 to 49 000. Figure 1 shows the chromatograms of the fractions; Table 1 lists their molecular weight and molecular weight dispersity.

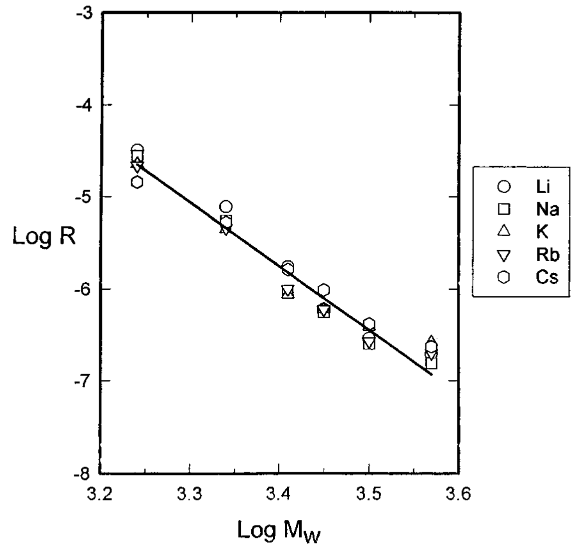

Figure 2. Rate of dissolution in 0.20 N solutions of the alkali metal bases plotted as a function of the logarithm of weight average molecular weight of Novolak fractions.

Dissolution Rate Measurement. The resin samples were coated onto 2 in. silicon wafers, from a coating solution of 26% Novolak in isoamyl acetate. A spinner was used at 3000 rpm, and the dried films were about 1 μm thick. The dissolution rate was measured with a single channel laser interferometer described earlier.[12] The concentration of the developer solution was determined daily by titration with a standard HCl solution, and the sample block and the developer solution were carefully thermostated to ±0.1 deg. The recorder trace of the interferometer was evaluated by the method of Rodrigues et al.,[13] and the rate in the stationary regime of the dissolution process was taken for analysis.

We measured the dissolution rate of the fractions in 0.20 N solutions of the alkali metal bases LiOH, NaOH, KOH, RbOH, and CsOH. The direct results of these measurements are plotted against log M_w in Figure 2.

Eyring Analysis of Base Diffusion in Novolak Films

Eyring developed a transition state theory of diffusion[9] that leads to a rate equation of the form shown below.

$$D = e\frac{kT}{h}\lambda^2 e^{\Delta S^{\ddagger}/R}\, e^{-E/RT} \tag{1}$$

Here e, k, h, and R are universal constants and λ is the diffusion length of the transport process (in the case of percolative diffusion it is the average jump distance between sites). E is the experimental (Arrhenius) activation energy, and $\Delta S^{\ddagger}$ is the activation entropy of diffusion. The diffusion coefficient D is linked to the dissolution rate, **R**, by the expression

$$D = \mathbf{R}\delta \tag{2}$$

where δ is the thickness of the penetration zone (see next section). It was assumed throughout that $\delta = 100$ Å.

We have determined the activation energy of dissolution for the six molecular weight fractions of our Novolak sample by measuring their dissolution rate in 0.20 N solutions of the alkali metal bases at temperatures beween 10 and 30 °C, and plotting log **R** as a function of 1/T. The values of E were derived from the slope of these plots. From the activation energies and

Table 2. Kinetic Characteristics of Novolak Dissolution in 0.26 N KOH

no.	M_w	10^6R, cm/s	E, kcal/mol	$-\Delta S^{\ddagger}$, eu	kcal/mol $\Delta H^{\ddagger}$	kcal/mol $-T\Delta S^{\ddagger}$	kcal/mol $\Delta F^{\ddagger}$
5	1740	22.9	7.45	17.4	6.86	5.07	11.9
6	2190	4.49	6.30	24.4	5.71	7.15	12.9
7	2550	1.50	5.39	30.8	4.80	9.02	13.8
8	2810	1.30	4.78	33.7	4.19	9.80	14.0
9	3170	0.39	4.17	36.5	3.58	10.69	14.3
11	3670	0.20	3.48	42.0	2.89	12.30	15.2

from the values of the dissolution rate (diffusion coefficient of base) below the glass transition temperature of the penetration zone,[14] the activation entropies were calculated using eq 1. These and other kinetic data for dissolution of the Novolak films in 0.26 N KOH are listed in Table 2.

The kinetic characteristics of the six Novolak fractions in Table 2 have very unusual features. In most systems, when the value of the activation energy decreases, the reaction rate increases. Here it is the opposite: for resins of higher molecular weight the activation energy becomes smaller (less positive), yet the dissolution rate decreases too. The formal reason for this behavior can be seen when we combine the activation enthalpy $\Delta H^{\ddagger}$,

$$\Delta H^{\ddagger} = E - RT \tag{3}$$

and the activation entropy to form the activation free energy of percolative diffusion, $\Delta F^{\ddagger}$. (See Table 2.) The (Gibbs) free energy of activation

$$\Delta F^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \tag{4}$$

directly determines the diffusivity of base and, by implication, the dissolution rate, **R**.

$$\mathbf{R} = \frac{kT}{h}\frac{\lambda^2}{\delta}\mathrm{e}^{-\Delta F\ddagger/RT} \tag{5}$$

It can be seen that the changes in the activation enthalpy and in the activation entropy brought about by changes of molecular weight are larger than the changes in the activation free energy. The reason for this is that the enthalpy change, $\Delta H^{\ddagger}$, and the entropy term, $-T\Delta S^{\ddagger}$, move in opposite directions (see Figure 3) and partly compensate each other. In forming $\Delta F^{\ddagger}$, the entropy term overwhelms the enthalpy term, and the free energy of activation increases, thereby lowering the dissolution rate. The task of understanding the effect of resin molecular weight on the dissolution rate is thus "reduced" to an interpretation of the effect of molecular weight on the activation entropy and on the activation energy of the dissolution process.

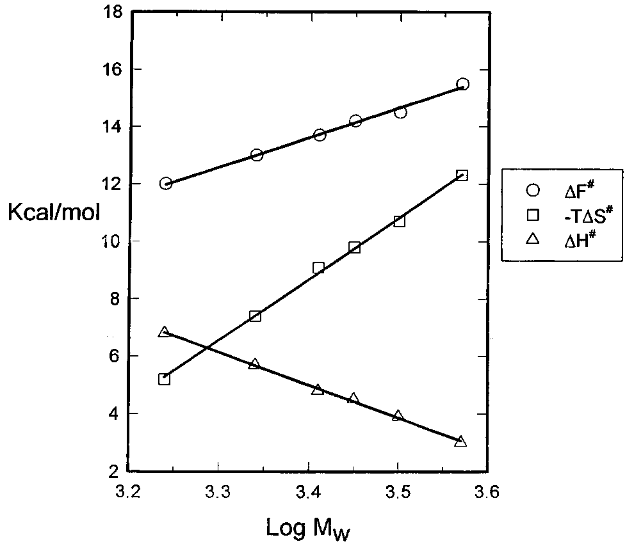

Figure 3. Kinetic characteristics of the dissolution of six Novolak fractions in 0.26 N KOH plotted against log M_w.

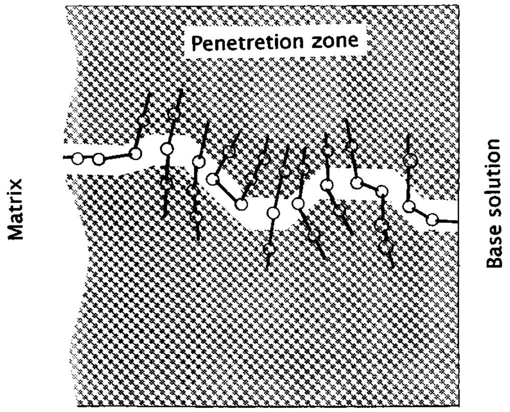

Figure 4. Percolation channel of the penetration zone of a Novolak film. The phenolate ions are shown as members of polymer chains. Only the parts of the chains adjoining the channel are indicated.

Penetration Zone

In trying to interpret the kinetic characteristics of the dissolution process it must be remembered that the kinetics of Novolak dissolution are controlled by events occurring inside and at the edge of the penetration zone (Figure 4). This zone is a thin layer of resin-bound phenolate ions, formed by the intrusion of base into the resin matrix.[15] Arcus,[16] who discovered the penetration zone, showed in an elegant laser interference experiment that the resin-bound phenolate ions form a continuously connected phase. Every phenolate ion is associated with its countercation and with one molecule of water, which is the product of the deprotonation reaction

$$\mathrm{POH} + \mathrm{OH}^- = \mathrm{PO}^- + \mathrm{H_2O}$$

Because base reacts with phenol, free base can exist only in the penetration zone; in fact, *every phenolate site contains also one ion pair of base.* The five particles, namely the resin-bound phenolate ion, its countercation (e.g., K^+), water, and an ion pair of base (K^+, OH^-), make up every percolation site of the zone. The ions of the site are held together by electrostatic forces and are firmly embedded in an ensemble of similar units. The strong interactions between the ions make the penetration zone a solid polyelectrolyte of exceptional ionic strength.[3] (As a result, the glass transition temperature of the zone is usually above 30 °C.) Because of this, the ions in the zone are correlated: when an ion leaves its originl location, it must be immediately replaced by a similar one. No vacancy is allowed to arise anywhere in the channel, neither can an ion site be doubly occupied.

Energy Transport in an Ensemble of Chains

In a resin film made up of chains, thermal excitation propagates faster along the chains than between them,

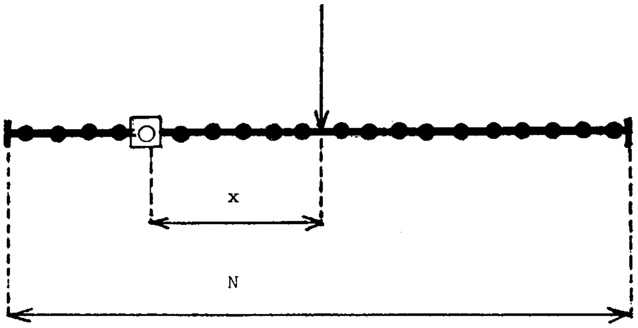

Figure 5. Situation on a polymer chain of N members where an energy fluctuation enters at point x. The position of the target site is indicated by a square.

since the members of the chain are vibrationally coupled. As a result, the critical fluctuation, which is the activating energy, will come to a percolation site almost exclusively via the chain of which it is a member. What is the chance that this energy fluctuation will reach a particular site in the chain? On entering the chain the critical fluctuation will execute a one-dimensional random walk along the chain. On that walk it may encounter a particular site (the target site) or not. The probability of reaching the target site depends on the number of steps from the entry point to the target site. We wish to find the mean expectation value of this number.

We shall assume in a first approximation that we are dealing with linear chains. If the length of the polymer chain is N and the distance from the entry point to the target is x (see Figure 5), it can be shown (see the Appendix) that the expectation number of steps to the target is

$$n(x) = -x^2 + 2xN \tag{6}$$

We assume that the target site can be anywhere on the chain and that energy can reach the target site from both parts of the chain. In that case a fair approximation to the statistical mean can be obtained by letting x in eq 6 vary from 1 to N, adding the step numbers and dividing the sum by the chain length. The mean step number $\langle n(x)\rangle$ is found in this way.

$$\langle n(x)\rangle = (2/3)N^2 + (1/2)N - 1/6 \tag{7}$$

The probability that a critical fluctuation will enter a chain in unit time is proportional to chain length. The probability that the fluctuation, once it has entered the chain will reach a target site on that chain is inversely proportional to $\langle n(x)\rangle$. As a result, the probability P_i that an activating energy quantum will appear in unit time at a particular site, i, of a chain of N members is

$$P_i = (\text{const})[N/(0.67N^2 + 0.5N - 0.17)] = (\text{const})(1/N) \tag{8}$$

The constant in eq 8 depends on the density of critical fluctuation in the ensemble (i.e., on temperature), and it depends on the lifetime of the critical fluctuations within the chain, but it does not depend on chain length.

Activation Entropy

The activation entropy is part of the frequency factor of the Arrhenius–Eyring equation (1). It is thus linked to the encounter frequency of the "reactants" of the rate-determining step. The rate-determining step of Novolak dissolution is the deprotonation of a phenol group at the interface of the penetration zone with the virgin matrix.[17,18]

This requires the appearance of an extra ion pair of base near a phenol group located just in front of the penetration zone. The activation entropy, $\Delta S^{\ddagger}$, is linked to the probability of this event. The question arises: how is base transported from the developer solution to the front of the zone?

The emergence of a base pair in front of the zone is made possible by the arrival of a new base pair at the back of the zone, which has been injected there from the developer solution. The base pair at the front of the zone is connected to the freshly arrived base pair at the back by a series of ionic percolation sites that form a channel of open percolation bonds. (See Figure 4). Because the ions are correlated, *all base pairs in the channel have to move in synchronism* to convey an extra ion pair of base to the front of the zone.

Within the zone, the movement of base from one site to the next requires an appropriate activation energy. For the base ions in a channel to move in unison, every channel site must receive an activating energy quantum simultaneously with all the others. To ensure that *all* sites receive a quantum at the same time, the quanta have to be associated with individual sites in the channel on a one-to-one basis. Equation 8 makes it possible to express the condition of simultaneity for the activation of all sites of a percolation channel. If the number of sites contained in the channel is designated by γ, and if it is assumed that all resin chains of the film have N members, the probability that activation quanta will be associated *simultaneously with every one of the channel sites* is

$$\mathbf{P} = P_1P_2P_3...P_\gamma = (\text{const})(1/N)^\gamma \tag{9}$$

That is the probability that an ion pair of base will emerge at the front of the penetration zone of a system composed of polymer chains of length N. It is also the encounter probability of the reactants. The activation entropy is linked to that compound probability.

$$\Delta S^{\ddagger} = R \ln \mathbf{P} = -R\gamma \ln N + \text{const} \tag{10}$$

The constant in eq 10 has to be found from experiment; therefore only the change in the activation entropy can be so determined.

$$\Delta S^{\ddagger}{}_2 - \Delta S^{\ddagger}{}_1 = -R\gamma \ln(N_2/N_1) \tag{11}$$

Equation 11 describes the relation between the activation entropy of Novolak dissolution and the chain length (molecular weight) of the resin. Figure 6 shows a plot of $\Delta S^{\ddagger}$ against log M for the bases of the five alkali ions. All the plots are linear, as predicted by eq 10. The differences in the positions of the lines are caused by differences in the size (i.e., free volume requirements) of the cations. This aspect is addressed in more detail in an earlier communication.[18]

The constant γ in eqs 10 and 11 represents the average number of sites in a percolation channel of the zone. For the base KOH, the slope of the plot in Figure 6 has a value of 28.6. The gas constant R is 2.0 cal/deg. That makes γ equal to 14.3. If γ is multiplied by

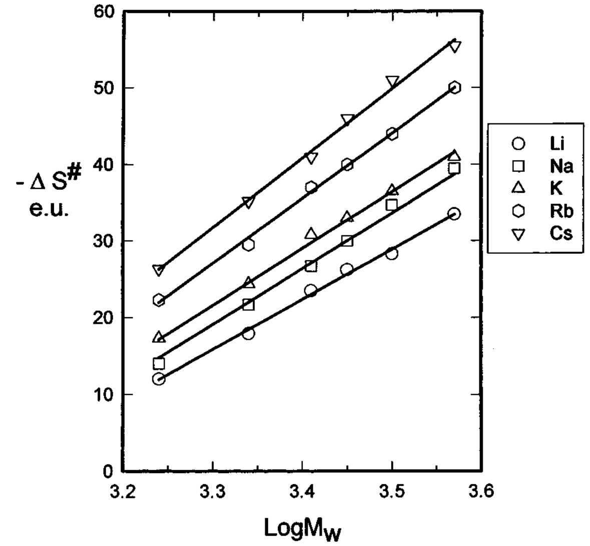

Figure 6. Activation entropy of dissolution of six Novolak fractions in 0.2 N solutions of the alkali metal bases, plotted against log M_w.

Table 3. Slopes β, γ, and α of the Correlation between Activation Entropy, Activation Energy, Logarithm of Dissolution Rate, and Molecular Weight

	β	γ	α	r_i^3 (Å^3)[a]
Li	6.2	12.5	6.3	0.22
Na	7.6	13.6	6.0	0.86
K	8.7	14.3	5.9	2.35
Rb	9.6	15.8	6.3	3.24
Cs	11.5	17.8	6.3	4.83

[a] Ionic radii are taken from: Pauling. *General Chemistry*, 3rd ed.; Freeman and Co.: San Francisco, 1970.

the jump distance λ, the average channel length is obtained.

$$\gamma\lambda = 14.3 \times 6 = 86\ \text{Å}$$

This value corresponds quite well with the estimated thickness $\delta = 100$ Å of the penetration zone. We believe that this supports the validity of the percolation channel concept. The slope of the $\Delta S^{\ddagger}$ vs log M plot increases somewhat with the size of the cation of the developer base (see Table 3), and the penetration zone may indeed vary in thickness for different bases, depending on the relative rate of the events at the front and at the back of the zone.

Activation Energy

The rate-determining event in Novolak dissolution involves not only the hydroxyl ion, which abstracts a proton from an OH group just in front of the penetration zone, but also the base cation, which has to transfer to the freshly formed phenolate ion in order to complete the transaction. It is the movement of the cation that ultimately controls the kinetics of the process, and the activation energy, E, characterizes the crossing frequency of the cations.

In base diffusion the activation energy is identified with the energy barrier separating two equilibrium positions of the cation, i.e., two phenolate sites at the front of the penetration zone. This barrier is clearly independent of resin molecular weight, and it seems therefore strange that the activation energy of dissolution whould be affected by the length of the polymer chain. However, if we remember how the activation energy is obtained, this observation is less surprising. What we actually measure in our experiments is the effect of temperature on the dissolution rate, and from the temperature coefficient of that rate the Arrhenius activation energy is inferred by a standard formula which implies a completely random system. This assumption does not strictly apply for an ensemble of chains.

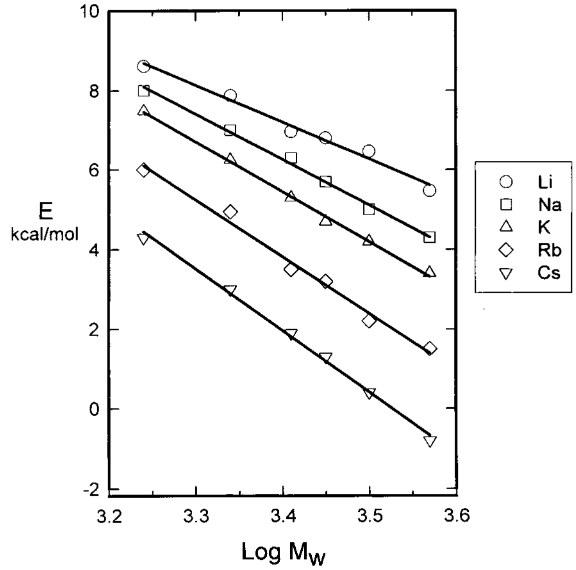

Figure 7. Activation energy of dissolution of six Novolak fractions in 0.2 N solutions of the alkali metal bases, plotted against log M_w.

We can use eq 8 to interpret the molecular weight dependence of the activation energy. From the experimental results in Figure 7 we find that the activation energy decreases linearly with the increasing logarithm of molecular weight. The slope of the correlation line is $-\beta RT$.

$$E = \text{const} \ln N = -\beta RT \ln N \qquad (12)$$

As a result, the crossing frequency of the cation can be expressed in the form below.

$$\text{crossing frequency} = \exp(-E/RT) = (1/N)^{\beta} \qquad (13)$$

We know from the earlier discussion that the fraction $(1/N)$ is related to the probability that an energy quantum arrives at a particular site belonging to an N-membered chain. We interpret, therefore, the slope of the linear dependence of eq 12 to mean that β energy quanta will appear simultaneously at β sites surrounding the base cation. It is these quanta that, together, convey the activation energy to the base cation waiting to cross the energy barrier. We have indicated the situation schematically in Figure 8. It will be noted that from the change in the slope of the correlation lines in Figure 7 it follows that the value of β increases with the size of the base cation. (See Table 3.) This agrees with the view that the energy required for the transfer of the cation is supplied by the simultaneous coming together of several (β) smaller vibrational quanta within a nest of sites surrounding that ion.

Summary

The effect of molecular weight on the dissolution rate of Novolak can be understood if the problem is approached from the point of view of Eyring's transition

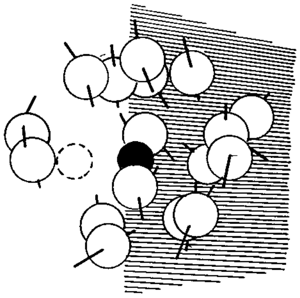

Figure 8. Nest of excitation sites surrounding a base cation at the egde of the penetration zone.

state theory. Transition state theory characterizes the kinetics of percolative dissolution by an activation entropy and an activation energy. Both are found to depend on resin molecular weight.

The activation entropy characterizes the encounter complex of the system, comprising a free ion pair of base and a phenol group. The formation of this transition state requires the transport of an ion pair of base from the back of the penetration zone (developer solution) to the front. The conveyance of base across the penetration zone involves the simultaneous activation of all, γ, sites of a percolation channel. The probability that a thermal energy quantum appears on a particular site that is part of a chain of N members is inversely proportional to chain length. The necessity of the simultaneous activation of a number of such sites is the reason for the observed steep dependence of **R** on molecular weight.

The activation energy characterizes the crossing frequency of the base cation over the energy barrier separating the two phenolate sites of the transition state. The slope of the linear dependence of the experimentally determined activation energy on chain length is interpreted to mean that the activation energy required for barrier crossing is transmitted to the base cation by the simultaneous activation of a number of the surrounding sites.

Acknowledgment. We thank the Semiconductor Research Corp., the National Science Foundation, the Eastman Kodak Co., Imation, and the Xerox Corp. for financial support of this work. J.G. in particular thanks ONR and NSF for support. We are grateful to Phasex Corp. for allowing one of us to participate. We have enjoyed and benefited from discussions with Grant Willson (University of Texas, Austin), Ralph Dammel (Clariant), and Herbert Morawetz and Peter Riseborough (Polytechnic University).

Appendix

The derivation of eq 6 is an exercise in basic probability. We assume the following model of a random walk: A polymer chain consists of N monomer units, numbered 1 to N. If an energy quantum enters the chain at monomer x at time t, it will be at position $x + 1$ or $x - 1$ at time $t + 1$, each with the probability 1/2. The target site is at position $x = 1$. Let $T(x)$ be the number of steps, starting at x, needed for the excitation to reach the target site, and let $n(x)$ be the expectation value of the random quantity $T(x)$.

$$N(x) = \langle T(x) \rangle$$

Equation 6 is derived by finding a difference equation for $n(x)$ and solving it. The difference equation is obtained by considering the first step of the random walk. If the excitation starts at one of the interior monomers, $x + 2$ ... $N - 1$, then it moves first to one of the neigboring monomers, and after that continues until it hits the target. If it moves to the left, then $T(x) = T(x - 1) + 1$. Otherwise, $T(x) = T(x + 1) + 1$. Taking expected values leads to

$$N(x) = 1/2\{n(x + 1) + n(x - 1)\} + 1$$

If $x = 1$, if the excitation moves to the left, it is absorbed. Therefore

$$N(1) = (1/2)n(2) + 1$$

If $x = N$, then the excitation must move to the left:

$$n(N) = n(N - 1) + 1$$

A few minutes of algebra show that eq 6 satisfies each of these requirements.

References and Notes

(1) Hanabata, M.; Oi, F.; Furuta, A. *Proc. SPIE* **1991**, *1466*, 132.
(2) Ouano, A. C. In *Polymers in Electronics*; Davidson, T., Ed.; ACS Symposium Series No 242; American Chemical Society: Washington, DC, 1984.
(3) Turner, S. R.; Arcus, R. A.; Houle, C. H.; Schleigh, W. R. *Proc. SPE* (Technical Conference on Photopolymers, Ellenville, New York) **1985**, 34−47.
(4) Allen, R. D.; Chen, K. J. R.; Gallagher-Wetmore, P. M. *Proc. SPIE* **1995**, *2438*, 250.
(5) Tsiartas, P. C.; Simpson, L. S.; Qin, A.; Willson, C. G.; Allen, R. D.; Krukonis, V. J.; Gallagher-Wetmore, P. M. *Proc. SPIE* **1995**, *2438*, 261.
(6) Stauffer, D. *Introduction to Percolation Theory*; Taylor & Francis: London, 1985.
(7) De Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, and London, 1979.
(8) Peppas, N. A.; Wu, J. C.; von Meerwall, E. D. *Macromolecules* **1994**, *27*, 5626.
(9) Glasstone, S.; Laidler, K. J.; Eyring, H. *The Theory of Rate Processes*; McGraw-Hill Book Co. Inc.: New York and London, 1941; Chapter 10.
(10) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction: Principles and Practice*, 2nd ed.; Butterworth-Heinemann: Boston 1994.
(11) Gallagher-Wetmore, P. M. *Proc. Int. Symp. Supercrit. Fluids*, **1994**, *3*, 253ff.
(12) Yeh, T. F.; Shih, H. Y.; Reiser, A. *Macromolecules* **1992**, *25*, 5345.
(13) Rodriguez, F.; Krasicky, P. D.; Groele, R. J. *Solid State Technol.* **1985**, *28* (5), 125.
(14) Yeh, T. F.; Reiser, A.; Dammel, R. R.; Pawlowski, G.; Roeschert, H. *Macromolecules* **1993**, *26*, 6, 3862.
(15) Reiser, A.; Shih, H. Y.; Yeh, T. F.; Huang, J. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2428−2440.
(16) Arcus, R. A. *Proc. SPIE* **1986**, *631*, 124.
(17) Kim, M. S.; Reiser, A. *Macromolecules* **1997**, *30*, 3860.
(18) Shih, H. Y.; Reiser, A. *Macromolecules* **1997**, *30*, 4353.

MA971546H