3862 *Macromolecules* 1993, *26*, 3862–3869

A Percolation View of Novolak Dissolution. 2. The Statistics of a Three-Dimensional Cubic Percolation Field and a Generalized Scaling Law

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Received February 9, 1993; Revised Manuscript Received April 23, 1993

ABSTRACT: A three-dimensional cubic percolation field is proposed as a model for the behavior of amphiphilic resins in aqueous bases. From the statistics of this model it is found that the percolation parameter is linearly related to the degree of occupation of the field. This result is used in the experimental validation of the percolation model on seven different groups of phenolic (amphiphilic) resins. The consistent similarly in the behavior of different amphiphilic resins makes it possible to formulate a generalized dimensionless scaling law $\log(R,R_1) = 2\log[(p - p_c)/(1 - p_c)]$ where R_1 is the rate of dissolution of a reference resin, usually the resin with the highest dissolution rate in a given group. This scaling law accommodates all the experimental results of this study, and it is invariant with temperature.

Introduction

The dissolution of phenolic resins in aqueous base is of interest in connection with a whole class of photoresists that are presently the most important imaging materials of the semiconductor device industry.[2] The imaging function of these resists is based on the inhibition of the dissolution of novolak or other phenolic resins in aqueous alkali, brought about by the presence of various photoreactive addenda, in particular of naphthodiazoquinone derivatives. On exposure to light, diazoquinones are converted to indenecarboxylic acids and lose their inhibiting power. Thus, irradiated and unirradiated areas of the film can be distinguished by a large difference in dissolution rate.

While the photochemistry of diazoquinones has been known since 1944,[3] the nature of the inhibition effect has remained unexplained for a long time, mainly because the molecular mechanism of the dissolution process itself was not understood. In a recent paper[1,5] a percolation approach to the problem of novolak dissolution was proposed and demonstrated on a single series of resins. While the model was successful in describing the behavior of this system, our approach to the model had been rather intuitive, and it was by no means clear whether the concept could be extended to other structures. In this paper some of the premises of the model are investigated more carefully, and its validity is tested on a wider range of phenolic resins and on one group of amphiphilic resins which do not contain phenolic units. The effect of temperature on the percolation parameter is considered, and a generalized scaling law of resin dissolution is presented.

The main features of the percolation model are briefly reviewed. The key to an understanding of the behavior of phenolic resins is the realization that they are amphiphilic systems which contain hydrophilic as well as hydrophobic components. The hydrophilic moieties of novolak and of other phenolic resins are the hydroxyl groups of the phenols or, in the stationary phase of the dissolution process, the phenolate/counterion pairs which arise in the deprotonation reaction preceding dissolution[4]

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

When a resist film is submerged in an aqueous solution of base, the ions of the base penetrate into the solid matrix where they are attracted by the hydrophilic sites and repelled by the hydrophobic regions of the medium. As a result, base travels through the matrix by hopping from one hydrophilic site to the next, in a process which has been termed percolative diffusion.[6,7] The rate of dissolution is expected to follow a scaling law of the form,[1,7]

$$R = \text{constant} \times (p - p_c)^2 \qquad (1)$$

where R is the rate of dissolution, e.g., in microns per minute, p is a percolation parameter which characterizes the state of the percolation field, and p_c is a critical percolation threshold below which dissolution no longer occurs. In a bond percolation field the parameter p is defined as the fraction of open bonds formed between adjacent sites.

In applying percolation theory to the dissolution of novolak, we view the resin as a hydrophobic continuum in which hydrophilic sites are embedded. Because the hydrophilic sites (the OH groups) are attached to a polymer, their relative positions are circumscribed by the configurations of the polymer backbone. The hydrophilic sites are thus confined each to a limited available volume and constitute what Ziman[8] has called a topologically disordered system. Such a system can be described by an ensemble of adjoining cells, where the sites themselves may be located anywhere within the cells, as is indicated schematically in Figure 1.

The Pair Distribution Function

Following Ziman[8] the state of a topologically disordered system is described in a general way by a pair distribution function,

$$g(1,2) = g(r) \qquad (2)$$

where r is the (scalar) separation between any two sites in the ensemble. It is assumed that in a homogeneously

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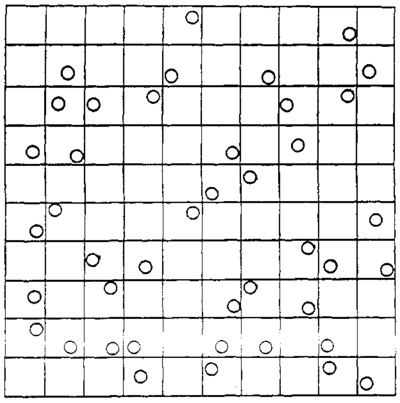


Figure 1. Topologically disordered two-dimensional percolation field with a degree of occupation of $x = 0.42$.

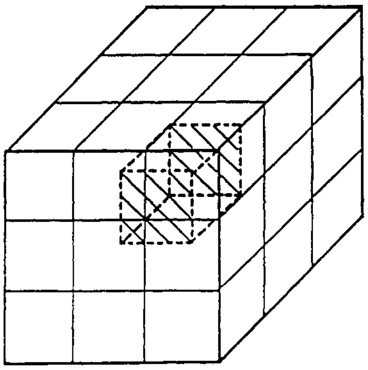


Figure 2. Three-dimensional cubic percolation field of 3 × 3 × 3 cubic cells. The reference site occupies the cell at the center of the system.

disordered system[8] the statistics of a representative volume element correctly reflect the behavior of the whole. In that case the pair distribution function can be derived by considering the immediate surroundings of a single site in the ensemble.

We have argued earlier[1,5] that a solid film of an amphiphilic resin may be regarded as a three-dimensional disordered cubic system. We now propose as a significant model of the characteristic volume element a cube of 27 (3 × 3 × 3) cubic cells, where the center of the cube is occupied by the reference site, and where all the other 26 cells are also occupied by hydrophilic sites (see Figure 2). To derive the pair distribution function (the distribution of intersite distances between site pairs) in such a system, we shall assume for the time being that all sites are located exactly at the center of their cells. In considering the distances from the reference site to all the 26 other sites, it is found that only three values of intersite distance (bond length) occur in the system. Measured in units of cell length, they are

$$r_1 = 1.000, \quad r_2 = 1.414, \quad r_3 = 1.732$$

Of the 26 bonds emanating from the central site, 6 bonds are of length r_1, 12 bonds are of length r_2, and 8 bonds are of length r_3. The relative frequencies of occurrence of these bond lengths in the ensemble are

$$g_1 = 6/26 = 0.231, \quad g_2 = 12/26 = 0.461, \quad g_3 = 8/26 = 0.308$$

In the system where all sites are at the center of the cells, the three delta functions, $g_1(r_1)$, $g_2(r_2)$, and $g_3(r_3)$ constitute the pair distribution function of the system. This is represented in Figure 3 by three bold vertical lines.

The cubic model can be made more realistic by allowing the sites to assume other positions within the cells, as was indicated in Figure 1. To describe the system in this new state, we have assumed that the distribution of positions within the cell can be represented by a scaled Gaussian of the form

$$\varphi_i = g_i \exp(-s^2/2\sigma^2) \tag{3}$$

The width of the distribution was chosen so as to locate 90% of the sites inside the cells, allowing only a modest overspill probability. This condition corresponds to a value of $\sigma = 2$. By applying the scaled Gaussians to the delta functions $g_i(r_i)$, the distribution around the delta functions is broadened as shown in Figure 3. The pair distribution function of the system is the sum of the three Gaussians and is indicated in Figure 3 by the solid curve.

$$g(r) = \sum_i g_i \exp[-8(r - r_i)^2] \tag{4}$$

With the pair distribution function known, the fraction of open bonds can be estimated. A bond is considered open if transfer of diffusant is possible between the two participating sites. Whether a bond is open or closed is decided by the intersite separation or, more accurately, by the energy barrier separating the two sites.[1] Clearly, there must exist a critical intersite distance (or energy) beyond which transfer will no longer be possible. Let us assume, e.g., that this distance is $r_c = 1.3$ units and that only bonds shorter than 1.3 units of length are open, as indicated in Figure 4. This condition means, approximately, that in the cubic percolation field transfer of diffusant is only possible between cells which share a side, while cells which share only an edge or a corner are excluded. In that case the shaded area under the distribution curve in Figure 4 represents open bonds, and the fraction of open bonds (which is the percolation parameter p) is given by the ratio

$$p = \int_0^{r_c} g(r)\,dr \Big/ \int_0^{\infty} g(r)\,dr \tag{5}$$

It will be noted that the value of p changes when, for one reason or another, the critical site separation r_c is altered.

We come now to the practically important question: How does p change when the composition of the system is changed? Under system composition we understand here the density of hydrophilic sites and we measure it as the fraction (x) of occupied cells in the percolation field. For the system described by the pair distribution function of Figure 3 the degree of occupation is $x = 1$. To change the composition of this system, one has to remove one or more sites from the core cube.

Let us at first assume that a single site is removed. At the location of the vacancy, a site outside the core cube will become one of the 26 nearest neighbors of the reference site. We shall assign a default value of $r_d = 3.0$ units to the distance from the reference site to any site outside the core cube. To deal with the configurational statistics of the system, we note that the vacancy created by the random removal of a single site can be located in any of the 26 cells of the cube. There are, therefore, 26 distinguishable site configurations to be considered. We have to determine first how often the individual bond lengths r_1, r_2, r_3, and r_d occur in each of the 26 configurations. The overall frequency of occurrence of a particular bond length in the ensemble is the sum of these 26 counts.

A description of the counting procedure which leads to the pair distribution function in systems with more than one vacancy is given in the Appendix. Table I lists the pair distribution functions in the form of the delta functions of the four site separations that occur in the cubic percolation field. The functions are listed for systems

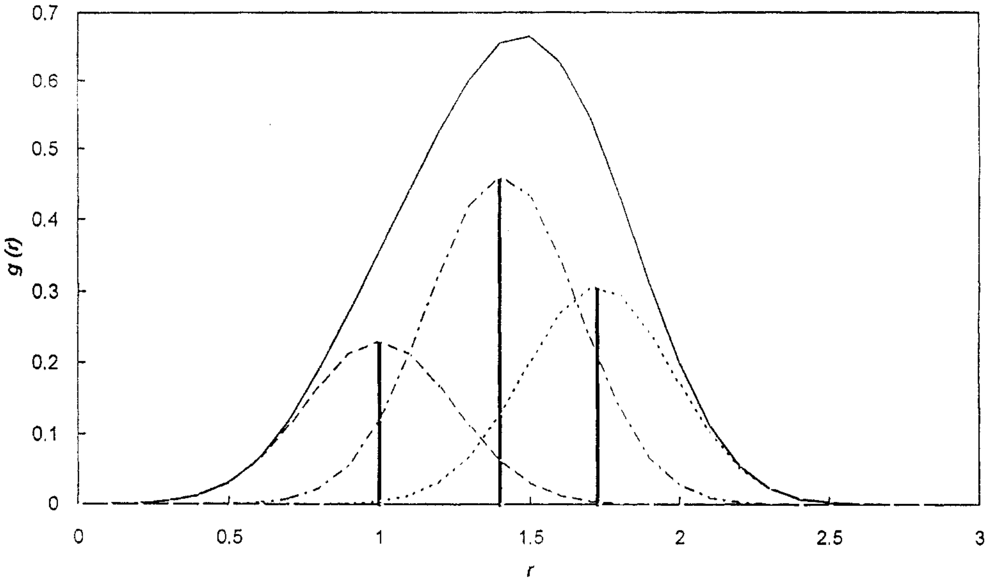


Figure 3. Constructing the Gaussian pair distribution function of a fully occupied cubic percolation field of 27 cells. The pair distribution function of a system where all sites are located at the center of their cells consists of three delta functions which are indicated by the bold vertical lines at the positions $r = 1.000$, $r = 1.414$, and $r = 1.732$ units. The pair distribution functions for a system where the sites are allowed to occupy any position within the cell is represented by the sum of the three scaled Gaussians.

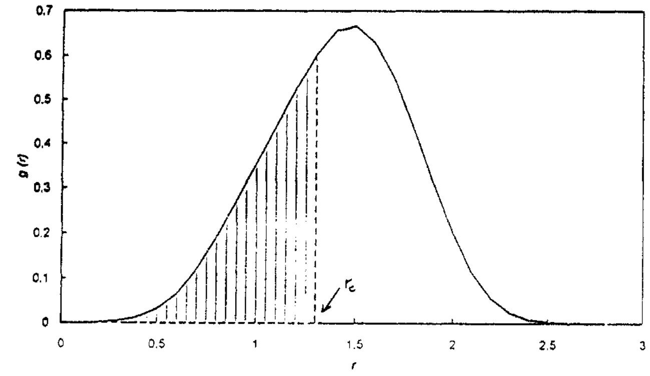


Figure 4. Determining the percolation parameter as the fraction of open bonds in the field. If the critical distance beyond which transfer between sites is not possible is as indicated in the figure, the shaded area under the distribution curve represents the open bonds.

Table I. Pair Distribution Function of a Three-Dimensional Cubic Percolation Field for Different Degrees of Occupation[a]

	26/26, $x = 1.00$	20/26, $x = 0.77$	13/26, $x = 0.50$	6/26, $x = 0.23$
g_1	0.231	0.178	0.115	0.053
g_2	0.462	0.355	0.231	0.107
g_3	0.307	0.236	0.154	0.071
g_d	0	0.231	0.500	0.769

[a] x = fraction of cells occupied.

with the degrees of occupation $x = 1.00$, $x = 0.77$, $x = 0.50$, and $x = 0.23$. The corresponding Gaussian pair distribution functions are presented in Figure 5.

The most important result of this investigation is the finding that the percolation parameter p (i.e., the fraction of open bonds derived from the pair distribution function) is a linear function of the degree of occupation x, irrespective of the value of the critical bond length or the critical intersite energy barrier. This linear relation was used intuitively in an earlier paper;[1] it constitutes here the basis of the extensive experimental tests of percolative dissolution to be described in a later section.

Linking the Percolation Parameter with Resin Composition

Following the results of the preceding section, the percolation parameter is a linear function of the degree of occupation x of the percolation field.

$$p = ax + b \tag{6}$$

In transferring from a theoretical percolation field to an actual resin, we have no a priori information on the size or number of the percolation cells. The percolation parameter in a resin is therefore defined only with reference to a group of resins of similar type which, however, differ in the concentration of hydrophilic sites. We adopt a normalization convention whereby the resin with the highest concentration of hydrophilic sites is chosen as the reference system. The fraction of occupied cells (active hydrophilic sites) of the reference resin and its percolation parameter are assigned values of unity, $x = 1$ and $p = 1$. This eliminates the constant b from eq 6

$$a + b = 1 \tag{7}$$

The constant a is obtained from the identity

$$p_c = ax_c + (1 - a)$$

or

$$a = \frac{1 - p_c}{1 - x_c} \tag{8}$$

Here x_c is the composition corresponding to the percolation threshold p_c. It is found by inspection from a plot of log R as a function of x. Such a plot is shown in Figure 6 for the resins of group II. It can be seen that the curve approaches x_c asymptotically as log R goes to $-\infty$.

The data of all our experiments are well represented using a percolation threshold of $p_c = 0.20$. This is a reasonable value; it lies midway between the theoretical predictions[7] of the bond percolation threshold for various cubic systems: $p_c = 0.12$ applies for face-centered, $p_c = 0.18$ for body-centered, and $p_c = 0.25$ for simple cubic systems. With a and b known the relation between the percolation parameter, p, and the fraction of occupied hydrophilic sites, x, is established.

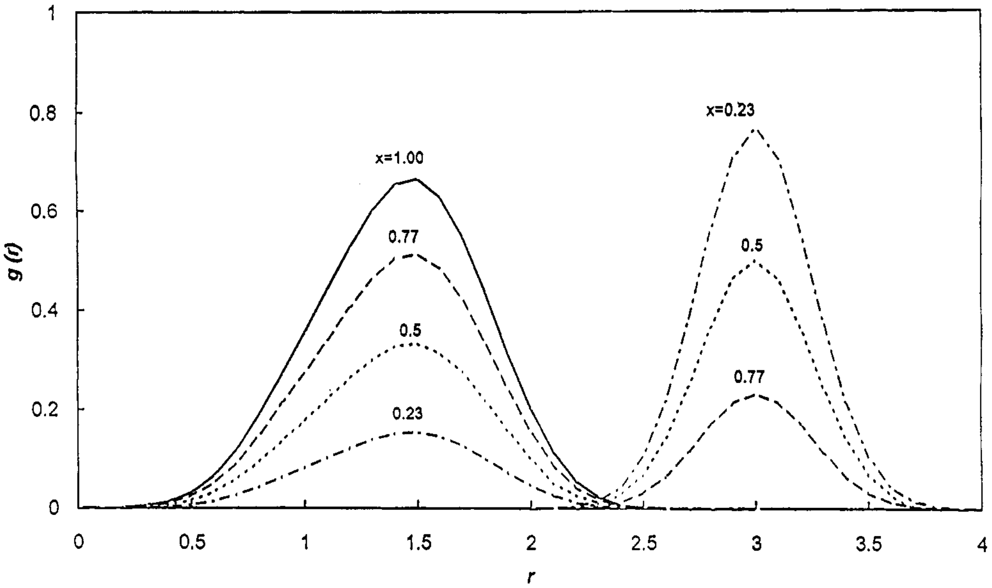
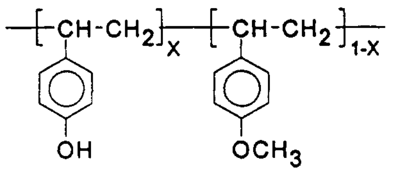


Figure 5. Pair distribution functions $g(r)$ for a cubic percolation system at different degrees of occupation of the cells. The distance from the reference site to sites outside the core cube has been set at the default value of 3 units of length.

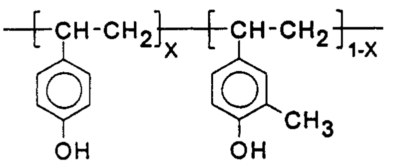
Testing the Scaling Law of Equation 1

In an earlier paper,[1] the scaling law of eq 1 was tested on a series of partially methylated poly(4-hydroxystyrene) resins. This study investigates the validity of the percolation approach on a wider range of amphiphilic polymers. We report here on the following systems.

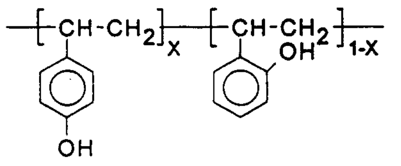
I. Partially methylated poly(4-hydroxystyrene) resins:[1,5]



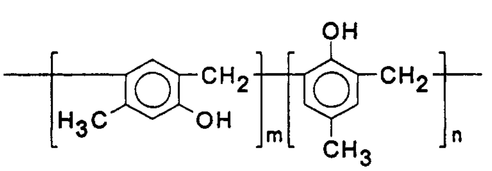
II. Copolymers of 4-hydroxystyrene and 3-methyl-4-hydroxystyrene:[9]



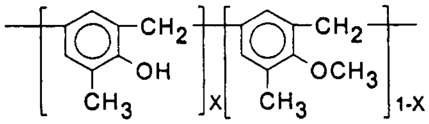
III. Copolymers of 4-hydroxystyrene and 2-hydroxystyrene:[10]



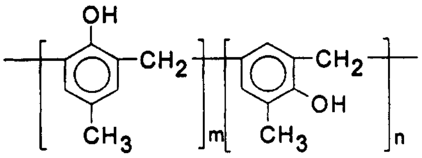
IV. Novolak resins made from mixtures of *m*-cresol and *p*-cresol:[11]



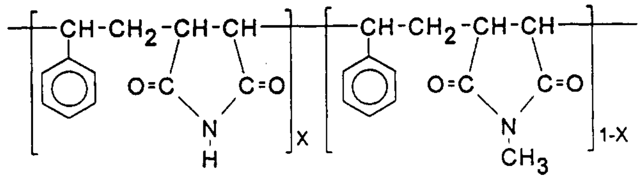
V. Partially methylated *o*-cresol novolak resins:



VI. Partially methylated novolak resins made from equimolar quantities of *o*-cresol and *p*-cresol.



VII. Partially methylated alternant copolymers of styrene and maleimide:



Except for the resins of group IV, where we used the data of Hanabata et al.,[11] several members of each group were prepared, characterized, coated onto silicon wafers, and prebaked in a unified manner. Their rates of dissolution in aqueous KOH were determined by laser interferometry.

The values of the percolation parameter of the resins were determined via the correlation constant a as described in the preceding section. For the resins of group I eq 6 takes the form

$$p = 2.86x - 1.86$$

For the systems of group II the equation is

$$p = 0.72x + 0.28$$

The values of the critical compositions x_c and of the correlation constant a for the resin groups I–VII are listed in Table II.

The scaling law of eq 1 was tested by plotting the experimentally determined dissolution rate logarithmically

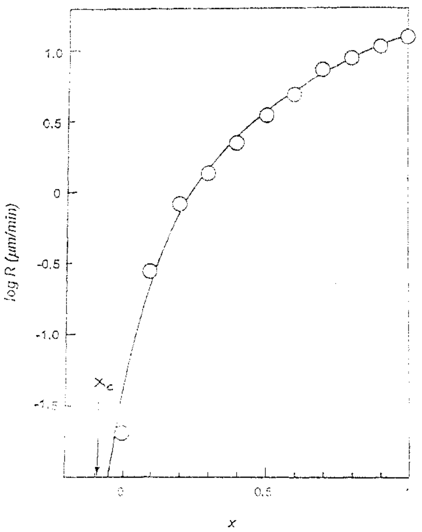


Figure 6. Plot of log R as a function of composition x for the resins of group II. The critical composition is $x_c = -0.095$. Because all members of this series are soluble, the percolation threshold corresponds to a notional critical composition with a negative value of x, i.e., to a composition where the concentration of free, unhindered OH groups is even smaller than in pure poly(3-methyl-4-hydroxystyrene).

Table II. Dissolution Rate of Reference Resin, Critical Composition, and Correlation Constant *a*

resin group	log R_1 (µm/min)	x_c	a
I	1.881	0.72	2.86
II	1.100	0.095	0.72
III	1.203	0.35	1.24
IV	1.890	0.33	1.19
V	1.331	0.77	3.50
VI	1.030	0.79	3.81
VII	0.830	0.56	1.80

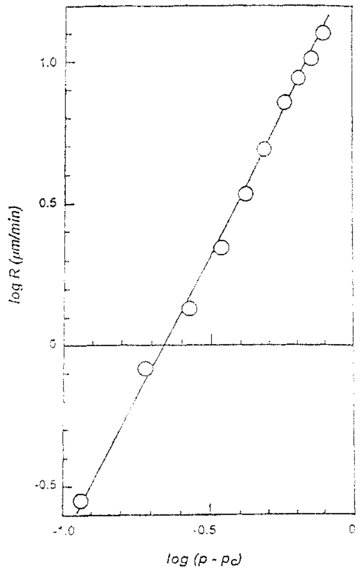


Figure 7. Testing the scaling law of eq 1 by plotting log R against log($p - p_c$).

against the difference ($p - p_c$).

$$\log R = \text{constant} + 2\log(p - p_c) \qquad (9)$$

Figure 7 shows that for the resins of group II a linear plot is obtained with a slope of 2, as demanded by percolation theory.[7]

The same procedure was applied to all the resins of this study, and in every case it resulted in a linear plot with a slope of 2. The data are presented in Figure 8. It will be noted that the resins of group VII do not contain hydroxyl groups. The percolation approach is thus not limited to phenolic resins but is valid generally for the description of the behavior of amphiphilic solids.

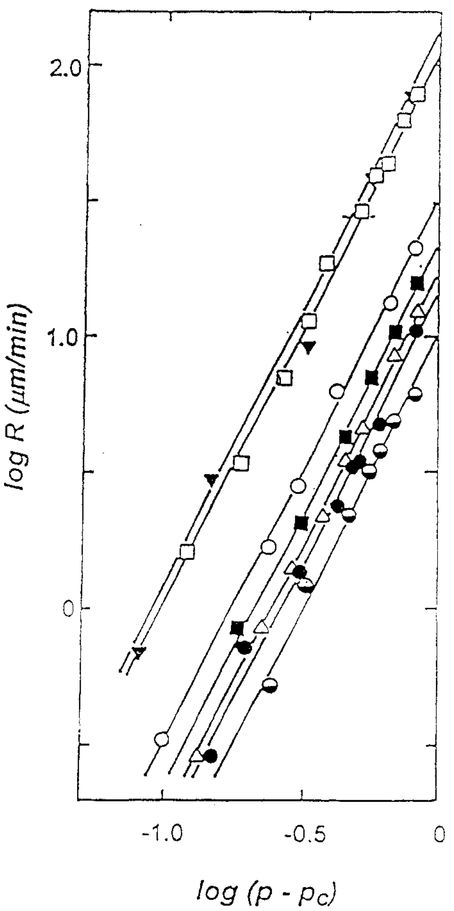


Figure 8. Cumulative plot of log R against log($p - p_c$) for all the resins of this study. (□) group I, (△) group II, (■) group III, (▼) group IV, (○) group V, (●) group VI, (◒) group VII.

A Generalized Scaling Law

Because of the consistent similarity of the behavior of different groups of resins, it is possible to generalize the scaling law of eq 1 and present it in dimensionless form. That is achieved by expressing the rate of dissolution in terms of the dissolution rate of the reference resin, for which we have postulated $x = 1$ and $p = 1$. If R_1 signifies the dissolution rate of the reference resin under the conditions of the experiment, the scaling law for that resin takes the form

$$\log R_1 = \text{constant} + 2\log(1 - p_c) \qquad (10)$$

The ratio of the rate of dissolution of any resin (percolation parameter p) to that of the reference resin (percolation parameter 1) is then given by the expression

$$\log\frac{R}{R_1} = 2\log\frac{p - p_c}{1 - p_c} \qquad (11)$$

For a percolation threshold of 0.20 eq 11 takes the form

$$\log(R/R_1) = 0.194 + 2\log(p - 0.20) \qquad (12)$$

and that function is plotted as a solid line in the diagram of Figure 9. To illustrate the validity of the generalized scaling law of eq 11, we have entered in Figure 10 all the experimental points of this study. It can be seen that, within experimental error, they are well accommodated by the mastercurve.

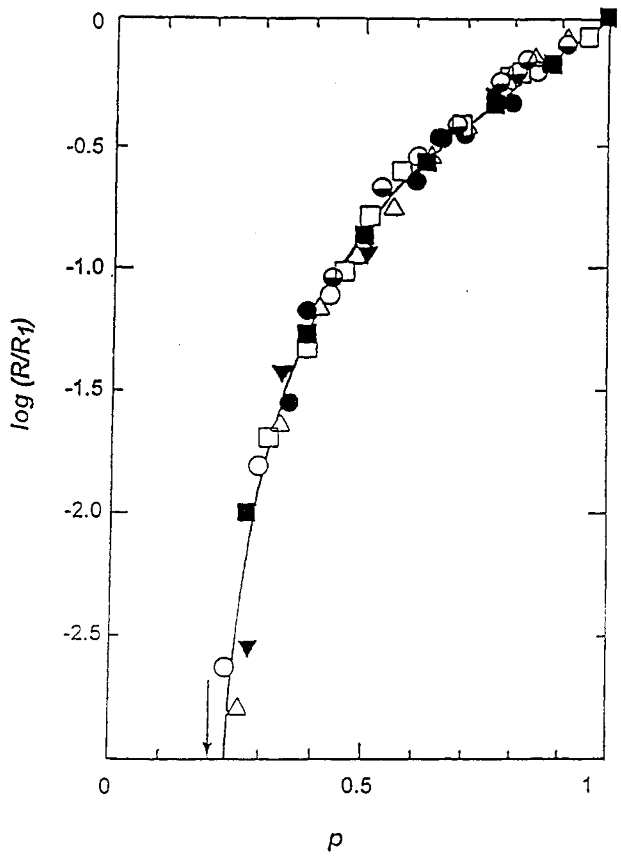


Figure 9. Generalized dimensionless scaling law, eq 14. (□) group I, (△) group II, (■) group III, (▼) group IV (○) group V, (●) group VI, (◒) group VII.

The mastercurve in Figure 9 allows a chemical engineering approach to the prediction of dissolution rates and to the selection of a resin with a desired dissolution rate. For that, one needs the dissolution rate of the reference resin and the correlation constant which converts p into x. The dissolution rates of the reference resins are usually available without difficulty (for the groups of resins of this study they are listed in Table II). To obtain the correlation constant, one needs the composition and the dissolution rate of only one other resin of the group.

The Effect of Temperature on the Percolation Field

Temperature affects the percolation field because it changes the probability of crossing over a given energy barrier and hence changes the percolation parameter p. The temperature dependence of the dissolution rate can be described by an Arrhenius equation;[1] the temperature coefficient of p is obtained by differentiating eq 11 with respect to temperature.

$$\frac{\mathrm{d}\log(R/R_1)}{\mathrm{d}T} = 2\log e\,\frac{1-p_c}{p-p_c}\frac{\mathrm{d}p}{\mathrm{d}T} \qquad (13)$$

Combining this with the derivative of the Arrhenius equation (eq 13)

$$\frac{\mathrm{d}\log(R/R_1)}{\mathrm{d}T} = \log e\,\frac{E-E_1}{RT^2} \qquad (14)$$

the temperature coefficient of the percolation parameter is obtained in the form

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{1}{2}\frac{E-E_1}{RT^2}\frac{p-p_c}{1-p_c} \qquad (15)$$

$E - E_1$ is the difference in activation energy between a given resin and the reference resin. Since this difference tends to zero for $p = 1$, $\mathrm{d}p/\mathrm{d}T = 0$ at $x = 1$ and $p = 1$, in agreement with the normalization condition. It is also zero at the percolation threshold $p = p_c$. While the percolation threshold is assumed to be independent of temperature, the critical composition x_c is not. As a result, changes in temperature will affect the correlation constant which links p and x. The temperature coefficient of a can be expressed in the form

$$\frac{\mathrm{d}a}{\mathrm{d}T} = \frac{1-p_c}{(1-x_c)^2}\frac{\mathrm{d}x_c}{\mathrm{d}T} \qquad (16)$$

The temperature coefficient of x_c can be found from experiment; it is typically on the order of 0.01–0.03.

While the percolation parameter p_c, x_c, and the correlation constant a change with temperature, the dimensionless scaling law is completely temperature independent. We have shown in Figure 10 how the percolation parameter for resins of a given composition x changes with a temperature increase of 10° and how this affects the dissolution rate while respecting the unique and temperature invariant relation between log R and p of the dimensionless scaling law.

Experimental Part

Materials. The resins of group I were prepared by partially methylating with dimethyl sulfate a single batch of poly(4-hydroxystyrene), MW 22 000, obtained from Polysciences. Details of the preparative and analytical procedures are given in ref 5.

The resins of groups II and III were obtained from the laboratory of Hoechst AG in Frankfurt, Germany. The syntheses of the polymers have been described in refs 9 and 10.

The data on the resins of group IV were taken directly from the work of Hanabata et al.[11]

The resins of group V were prepared by condensing 212.7 g of *o*-cresol with 143.7 g of a 37% formaldehyde solution in water. Toluensulfonic acid (10 g of a 30% solution) was added as catalyst. The mixture was heated to 100 °C for 3 h. The polymer was washed with water and then heated in a vacuum (2 mmHg) to 180–185 °C. The crude product was dissolved in acetone and reprecipitated twice into water. The *o*-cresol novolak (188 g) was dried in a vacuum oven [90 °C (2 mmHg)] overnight. The methylation of this resin was carried out by the method described below for the resins of group VI.

The resins of group VI were prepared by the condensation of an equimolar mixture of *p*-cresol and *o*-cresol with formaldehyde. A quantity of 101.8 g of *p*-cresol and 101.8 g of *o*-cresol was dissolved in 137.3 g of a 37% solution of formaldehyde in water. Toluenesulfonic acid, 20.6 of a 30% aqueous solution, was added as catalyst. The mixture was heated for 2 h to 120 °C, whereupon the aqueous layer was discarded and the rest washed with water. The last traces of water were then removed by heating to 180–190 °C under vacuum (2 mmHg). The crude product of the reaction was dissolved in acetone and twice reprecipitated into water. The resultant *o*-cresol-*co*-*p*-cresol novolak (172 g) was dried overnight in a vacuum oven (2 mmHg) at 90 °C.

The partial methylation of this resin was carried out by dissolving 8.0 g of the material in 150 mL of 7% aqueous NaOH. Varying quantities of dimethyl sulfate (from 0.2 to 2 mL) were added, and the mixture was refluxed for 1 h. The product was precipitated into acidic water (50 mL of HCl in 1000 mL of H_2O) and purified by dissolution in acetone and reprecipitation into water. The final product was dried overnight in a vacuum oven at 90 °C (2 mmHg). The resins were characterized by NMR, and the degree of methylation was derived from the integrated OH peaks.[5]

Film Casting. Solutions of the resins in isoamyl acetate (25–28% solids) or, in the case of group VII, in cyclohexanone were spin coated onto silicon wafers at about 2000 rpm. The wafers carrying the films were prebaked in a convection oven at 90 °C for 1 h and subsequently stored in a dessicator.

Dissolution Rate Measurements. The thickness of the resin films was monitored by laser interferometry as described in ref 5. The rate values used in the calculations, and quoted in the tables and figures, are the constant rate values which establish themselves after an early induction period. The base strength of the KOH developer solution was 0.2 N and it was determined separately for every run by titration with a standard solution of HCl. The temperature was controlled within 0.5 °C by a thermostated water circulator. From the reflection interference signals the rate of dissolution was determined by the method of Rodriguez et al.[13]

Acknowledgment. T.-F.Y and A.R. are grateful to the Office of Naval Research and to the National Science Foundation for financial support of this work.

Appendix

The method of counting of appearances of individual intersite separations in an ensemble of sites is demonstrated on the 27 cell cubic field of Figure 2. If all cells are fully occupied, the intersite distance $r_1 = 1.00$ occurs 6 times in the system, the intersite distance $r_2 = 1.41$ occurs 12 times, and the intersite distance $r_3 = 1.73$ occurs 8 times. We have seen in the main text of the paper how the delta functions of the pair distribution follow directly from these values.

If a single site is removed from the system, the corresponding vacancy can appear in any of three types of cells c_1, c_2, and c_3, corresponding to the intersite distances r_1, r_2, and r_3. A single vacancy can be assigned to one of the three types of cells in three ways, and these are represented in the following character table:

j	1	2	3
c_1	1	0	0
c_2	0	1	0
c_3	0	0	1
site configurations h_j	6	12	8

total: $\sum_j h_j = 26$

In the cells of group c_1 the vacancy can appear at 6 different locations; it can appear at 12 different locations in the cells c_2 and at 8 different locations in cells c_3. This makes a total of 26 distinguishable configurations. The number of times the intersite distance r_1 appears in any of the 6 configurations of c_2 is 5. In all the other configurations r_1 appears 6 times. The total number of appearances of r_1 (and of r_2 and r_3) in all the 26 configurations is given below.

$$\begin{aligned}
n_1 &= 6 \times 5 + 12 \times 6 + 8 \times 6 &&= 150\\
n_2 &= 6 \times 12 + 12 \times 11 + 8 \times 12 &&= 300\\
n_3 &= 6 \times 8 + 12 \times 8 + 8 \times 7 &&= 200\\
n_d(r_d) &= 6 \times 1 + 12 \times 1 + 8 \times 1 &&= \underline{\ 26\ }
\end{aligned}$$

total number of bond configurations = 26 × 26 = 676

From this, the relative frequencies of occurrence of individual bond lengths (which are the delta functions g_i of the pair distribution) follow as the ratios given below.

$$\begin{aligned}
g_1 &= 150/675 = 0.222\\
g_2 &= 300/675 = 0.444\\
g_3 &= 200/675 = 0.296\\
g_d &= \ \ 26/675 = \underline{0.038}\\
& \qquad\qquad\quad 1.000
\end{aligned}$$

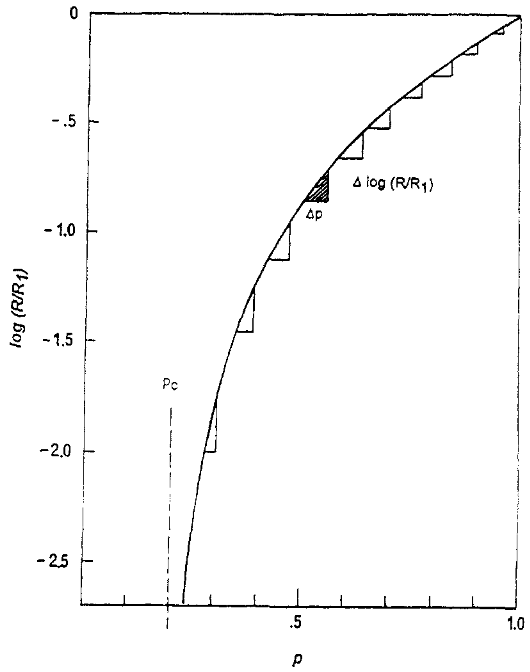


Figure 10. Effect of a 10° increase in temperature on the percolation parameter p and on the dissolution rate R for the resins of group II, as incorporated into a plot of the scaling law $\log(R/R_1) = f(p)$ of eq 11.

Having derived the (static) pair distribution function for a system with a single vacancy, we apply the same procedure now to a system with 2 vacancies ($x = 24/26 = 0.923$). Here the number of combinations (3 cells × 2 vacancies) = 6, and the character table takes the following form.

j	1	2	3	4	5	6
c_1	2	1	0	0	0	1
c_2	0	1	2	1	0	0
c_3	0	0	0	1	2	1
h_j	(6 × 5)/2 15	6 × 12 72	(12 × 11)/2 66	12 × 9 96	(8 × 7)/2 28	6 × 8 48

total: $\sum_j h_j = 325$

The number of appearances n_1, n_2, etc., of the individual site separations in each of the j combinations are listed below.

n_1	15 × 4	72 × 5	66 × 6	96 × 6	28 × 6	48 × 5	1800
n_2	180	92	660	1056	336	576	3600
n_3	120	576	528	672	168	336	400
n_d	30	144	132	192	56	96	650

total number of bond configurations 325 × 26 = 8450

The delta function components of the pair distribution are again given as the ratios

$$\begin{aligned}
g_1 &= 1800/8450 = 0.213\\
g_2 &= 3600/8450 = 0.426\\
g_3 &= 2400/8450 = 0.284\\
g_d &= \ \ 650/8450 = \underline{0.077}\\
& \qquad\qquad\quad\ \ 1.000
\end{aligned}$$

As more vacancies are created in the field, the number of site configuration increases rapidly. For example, the number of configurations for a system with 6 vacancies is almost a quarter of a million (320 320). To deal with these numbers, combinatorial recursion formulas have to be developed. These are now presented.

The number of ways in which v vacancies can be assigned to c types of cells is

$$j = cv \tag{A1}$$

and that number determines the form (number of columns) of the character table. The number of site configurations in any of the j columns of the character table is given by the expression

$$h_j = \sum_i \frac{c_i!}{(c_i - v_{ij})!v_{ij}!} \tag{A2}$$

where c_i is the number of cells of type i and v_{ij} is the number of vacancies appearing in row i of column j. The total number of site configurations in the ensemble of cells is

$$\sum_j h_j = \frac{c!}{(c - v)!v!} \tag{A3}$$

and the number of appearances of an individual intersite distance r_i in any of the j configurations is n_{ij}

$$n_{ij} = \frac{c_i!}{(c_i - v_{ij})!v_{ij}!}(c_i - v_{ij}) \tag{A4}$$

The total number of appearances of an intersite distance r_i in the whole ensemble of configurations is the delta function g_i of that intersite distance r_i.

$$g_i = \frac{\sum_j n_{ij}}{\sum_j h_j} \frac{1}{c} \tag{A5}$$

The pair distribution function, in terms of the delta functions of the four site separations in the cubic percolation field, are listed in Table I for the fully occupied system and for systems with 6, 13, and 20 vacancies, corresponding to degrees of occupation of $x = 1.00$, $x = 0.77$, $x = 0.50$, and $x = 0.23$.

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