Macromolecules **1994,** *27,* 5141-5146

Modeling Diffusion during Thermoset Cure: An Approach Based on Dielectric Analysis

Yong Deng and George C. Martin*

Department of Chemical Engineering and Materials Science, Syracuse University, Syracuse, New York 13244

Received March 20, 1994; Revised Manuscript Received June 3, 1994[●]

ABSTRACT: To investigate the effect of diffusional limitations on the cure of thermosetting polymers, a modeling strategy has been developed for estimating the average diffusion coefficient of the molecular species in the curing systems. The modeling is based on the dielectric measurement of the mobility-related properties including the ionic conductivity and the dipole relaxation time. It was shown that the ionic conductivity is the dominant factor in the diffusion model valid in the pregel stage, while the dipole relaxation time may be utilized to evaluate the diffusivities in the postgel stage. This approach may find applications in the study of the diffusion-controlled cure kinetics and structure–property relationships in thermosetting polymer systems.

Introduction

During the curing of a thermosetting polymer, the molecular species cross-link to form an infusible network. In the early stages of cure, when the system consists mainly of monomers and oligomers, the reactions are kinetically controlled; i.e., the rate of reaction is a function only of the inherent reactivities and concentrations of the molecular species in the system. As the reaction proceeds, the viscosity of the system increases rapidly due to chain growth and cross-linking. Consequently, the rate of reaction becomes increasingly dependent not only on the reactivities but also on the diffusivities in the system as the molecular species collide and react. At high conversions, the rate of reaction is determined primarily by the mass transfer of the reactants. This phenomenon is known as diffusion control.

The diffusion-controlled regime is perhaps the most important part of the curing process. During this period, the chemical, mechanical, and electrical properties of the polymer attain their final values, and the glass transition temperature can increase by more than 100 °C as the resin approaches full cure. To accurately predict and control the properties of the final product and to completely characterize the processability of a thermosetting system, it is necessary to formulate a quantitative kinetic model that is valid over the entire range of cure. Moreover, in the presence of the diffusional limitations, the molecular species of unequal sizes possess unequal reactivities, which affects the evolution of the structure (or the structural properties) of the polymer. To accurately delineate the structure–property relationship, it is important to examine the effect of diffusion on the molecular size distribution, gelation, and network growth of the resin system.

The first step in comprehensively examining the diffusion-related phenomena in thermosetting systems is to characterize or model the cure-dependent molecular diffusion. During curing, the structure of a resin system undergoes dramatic changes—the small-molecule system is transformed to a network. And at high conversions, the reaction mixture is completely insoluble; spectroscopic techniques, such as FTIR or NMR, are ineffective, the reaction rate is very slow, and the rheological and viscoelastic properties are relatively insensitive to changes in chemical structure. In assessing material performance, dynamic dielectric analysis is useful over the entire range of cure. The properties that may be measured by this technique, such as the dielectric permittivity, dielectric loss factor, ionic conductivity, and dipole relaxation time, all reflect the mobility of the molecular species in the system. Therefore, dielectric analysis was adopted to characterize the molecular diffusion.

The objective of the current work was to study the diffusion-controlled kinetics and the diffusional limitations on the network formation during the curing of thermosetting polymers in order to develop a basis for describing the curing kinetics and the structural evolution of such systems. The present paper describes the diffusion modeling and then addresses the potential applications of the proposed modeling approach. The results on the cure-dependent diffusion and the diffusion-controlled kinetics are presented for a diepoxide–diamine resin system in a subsequent paper.[1]

Previous Work

Cure-dependent diffusion phenomena have been studied with an analysis based on the free-volume theory.[2,3] To estimate the overall diffusion coefficient during epoxy–amine cure, Huguenin and Klein[2] used an equation similar to the Doolittle equation:[4]

$$D = D_0 \exp\left\{b_D\left[1 - \frac{1}{f_g + \beta_f(T - T_g)}\right]\right\} \qquad (1)$$

where D is the diffusion coefficient, D_0 is a constant, b_D is a constant that includes the critical free volume required for diffusion, T is the temperature, T_g is the glass transition temperature, f_g is the fractional free volume at T_g, and β_f is the thermal expansion coefficient of the free volume. To determine the two adjustable constants, D_0 and b_D, the conversion data were fitted to a diffusion-controlled kinetic model which includes eq 1 as the diffusion model. The fractional free volume at the glass transition, f_g, was taken as 0.025, and the thermal expansion coefficient, β_f, was 4.8×10^{-4} K^{-1} for $T_g < T < T_g + 100$ K and 4.8×10^{-5} K^{-1} for $T < T_g$.[2] The kinetic data obtained from DSC (differential scanning calorimetry) were found to be better correlated by the diffusion-corrected model than by the intrinsic kinetic model. Rohr and Klein[3] used a dynamic percolation approach and assigned different diffusion coefficients for species of different molecular weights. Thus, the differences in reactivities among molecules of unequal sizes were included in the simulation method. Their results, along with those obtained for epoxy–amine linear polymerization,[5] showed that the difference between the model

---

[●] Abstract published in *Advance ACS Abstracts,* July 15, 1994.

0024-9297/94/2227-5141$04.50/0

using an average diffusion coefficient and that using molecular weight dependent diffusion coefficients is not significant in the prediction of the rate of reaction. The *effect of diffusional limitations on the network formation* process was also studied.

Another model for cure-dependent diffusion has been proposed by Havlíček and Dušek.[6,7] The Adam–Gibbs theory of cooperative rearrangement[8] was employed to estimate the diffusion coefficient:

$$D = D_0 \exp\left[-\frac{m}{T\ln\left(\frac{T}{T_g - 50}\right)}\right] \qquad (2)$$

where m is inversely proportional to the discontinuity in the isobaric heat capacity, ΔC_p, at the glass transition and is regarded as a material quantity or a constant. For the epoxy–amine resin studied, m was chosen as 10^3 K, which is typical of polymers. ΔC_p was assumed to be independent of conversion in order to derive this diffusion model. But, since ΔC_p may change slightly during cure and the diffusion coefficient is an exponential function of m and thus an exponential function of ΔC_p, the errors in the prediction may be significant.

There are few reports on the direct measurement of the diffusion during cure. Using the pulsed-gradient spin–echo NMR method, Yu and von Meerwall[9] have recently measured the diffusivity in two epoxy–amine systems that contain probe molecules. The molecular weight distribution was assumed to be characterized by the Schulz–Zimm distribution and the diffusion coefficient of a single chain was assumed to be inversely proportional to its molecular weight. The echo attenuation data were then fitted to the diffusion model to find the average diffusion coefficient of the polymer. Their results indicate that the polymer diffusion coefficient becomes distinguishable from the probe diffusion coefficient only when a conversion of about 30% is reached. To accurately determine the diffusivity in the postgel stage, it is necessary to know the echo contribution of the gel.

Analyzing Diffusion in the Pregel Stage

Typically, a thermosetting system consists of not only molecular species but also ionic species. The ionic species may result from the impurities in the resin or may be generated by the cure itself. In epoxies, the ions are due to chloride derivtives formed during the synthesis of the starting materials. In commercial DGEBA (diglycidyl ether of Bisphenol A) resins, the ion concentrations are typically tens of ppm.[10] Thus, besides the molecular diffusion process, there exists the diffusion process of ionic species in the cure system.

The starting point of most studies on ionic conductivity is the assumption that, if the cure itself does not generate ions, the ions are primarily due to impurities and the ion concentration does not change appreciably during cure. This has been considered as a good approximation for resins such as epoxies.[11-13] The ionic conductivity has been utilized as a probe or cure monitoring parameter in many cases[12,14-18] and has been shown experimentally to be, generally, inversely proportional to the viscosity of the cure system in the pregel stage.[14]

Diffusion is a direct result of the Brownian motion of particles (molecular or ionic species) in the system, which is a purely thermal effect. The diffusion processes tend to have all the species uniformly distributed in the system. In the presence of an electric field, there exists another transport process, conduction or migration of charged particles,[19,20] which tends to cause the ionic species to move in the direction of the field. Therefore, the well-known Einstein relationship exists between the mobility of ions and the ionic diffusion coefficient:[19,21,22]

$$\mu_i = \frac{q_i}{k_B T} D_i \qquad (3)$$

where μ_i is the mobility of ions, D_i is the diffusion coefficient of ions, q_i is the charge carried by each ion, and k_B is Boltzmann's constant. If only one type of ion is considered, the ionic conductivity may be expressed as

$$\sigma = q_i N_i \mu_i \qquad (4)$$

where σ is the ionic conductivity and N_i is the number of ions per unit volume. Thus, for isothermal cure without generation of ions, the ionic conductivity is proportional to the diffusion coefficient of ions.

Evidently, eqs 3 and 4 correlate the diffusion coefficient of ions with the mobility of ions. There are, however, certain limitations to this correlation since diffusion and conduction are different transport processes.[19] One limitation arises because diffusivity and conductivity may exhibit different ion-concentration dependences. Another limitation is due to the fact that only free ions are involved in conduction while ion pairs, if they exist, also contribute to the diffusion of ions. The first limitation has little effect on the correlation between the diffusivity and the mobility if the ion concentration is very low.[19] In the case where there are a substantial number of ion pairs compared to the amount of free ions, the second limitation is negligible only if the ion concentration holds constant and the diffusion coefficient, D_i, is restricted to that of free ions only.

According to the Stokes–Einstein equation, the diffusion coefficient of a particle is inversely proportional to its size:

$$D_p = \frac{k_B T}{\zeta} = \frac{k_B T}{6\pi\eta R} \qquad (5)$$

where D_p is the diffusion coefficient of the particle, ζ is the fraction coefficient, η is the viscosity, and R is the radius of the particle. The second equality holds if one considers that the diffusing particle behaves as a sphere moving slowly in a homogeneous continuum. Because the Stokes law is based on the theory of macroscopic hydrodynamics, the diffusing particle is usually assumed to be many times larger than the other particles in the system. However, the Stokes–Einstein equation has been found to successfully correlate experimental data in many cases beyond the scope just described.[23,24] Using a thermodynamic approach, Schiller has recently proposed a new derivation of the Stokes–Einstein equation without any recourse to microscopic concepts.[25] Consequently, during thermoset cure, the diffusion coefficient of ions and the diffusion coefficient of monomer may be correlated to the viscosity of the system using the Stokes–Einstein equation. Equation 5, together with eqs 3 and 4, is an explanation to the observation that the ionic conductivity is inversely proportional to the viscosity. More importantly, eq 5 establishes a direct relationship between the size of a particle and its diffusion coefficient. Therefore, the diffusion coefficient of ions and the diffusion coefficient of monomer may be correlated through their sizes. During an isothermal cure, the ratio of the sizes of ions and *monomer can be treated as a constant.* Then, the diffusion coefficient of monomer is proportional to the ionic conductivity:

$$D_m = K_2 D_i = \frac{K_2}{K_1}\sigma \qquad (6)$$

where D_m is the diffusion coefficient of monomer, $K_1 = q_i^2N_i/k_BT$, and K_2 is the ratio of the size of ions to that of monomer.

In an actual cure system, there exist at least one type of anionic and one type of cationic ions. It can be easily shown that eq 6 may also be found for systems with many types of ions.

Now, it remains to correlate the monomer diffusion to the overall diffusion. For a thermoset polymerizing by a stepwise mechanism, the system is composed of monomers, oligomers, and a small amount of polymers in the pregel stage. At conversions much lower than the gel conversion, there are virtually no chains with molecular weights exceeding the entanglement molecular weight M_e (usually 100 monomer units or more) in the system. Reptation of the chains cannot occur and the diffusion of the molecular species may be characterized as Rouse diffusion so that the effect of coupling between molecules is negligible. Then, the diffusion coefficient of any chain, including branched, is inversely proportional to its molecular weight.[26,27] Even at conversions close to the gel point, there are few polymer chains longer than the entanglement threshold due to the stepwise reaction mechanism. Moreover, the many chain branches existing near the gel conversion have the effect of suppressing entanglements. Therefore, before gelation, the molecular species in the cure system are essentially not entangled and the diffusion can simply be approximated as Rouse diffusion so that the diffusion coefficient of a single chain is inversely proportional to its molecular weight.

The diffusion coefficient of a particle is by definition[28]

$$D_p = \langle \delta^2 \rangle / 6t \tag{7}$$

where $\langle \delta^2 \rangle$ is the mean square displacement that the molecule as a whole undergoes over a time period t. By evaluating the total mean square displacement of all the monomer units in the system during the same time period, the overall diffusion coefficient, or the average diffusion coefficient of monomer unit, can be found as

$$D = D_m \bar{x}_n^{-1} \tag{8}$$

where $\bar{x}_n$ is the number-average degree of polymerization. Consequently, before gelation, the overall diffusion coefficient can be estimated using the following diffusion model by substituting eq 6 into eq 8:

$$D = \frac{K_2}{K_1} \sigma \bar{x}_n^{-1} \tag{9}$$

In this diffusion model, there are four factors that affect the overall diffusion coefficient. The first factor, K_1, is related to the number of ions and the number of charges carried by each ion. If the cure does not generate ions, K_1 may be considered as a constant for isothermal cure. The second factor, K_2, correlates the diffusion of ions to the diffusion of monomer. By using the Stokes–Einstein equation as an approximation, K_2 may also be considered as a constant for isothermal cure. The third factor, $\bar{x}_n^{-1}$, correlates the overall diffusion coefficient to the diffusion coefficient of monomer. The fourth factor is the ionic conductivity. For the stoichiometrically balanced DGEBA–DDM (4,4′-diaminodiphenylmethane) resin, the ionic conductivity was measured experimentally and is shown in Figure 1 for three curing temperatures. The arrows in the figure indicate the gel times, at which the epoxide conversion attains the 58% gel conversion predicted by the recursive approach (assuming equal reactivity of the hydrogen atoms in the diamine).[29,30] Detailed information about this resin system, including the experimental procedure, may be found in a subsequent paper.[1] As shown in Figure 1, the ionic conductivity decreases approximately 3 orders of magnitude from the onset of the cure to the gel point. During the same period, $\bar{x}_n^{-1}$ ($=1 - 4\alpha/3$, where α is the conversion) decreases only about 4 times if no cycle formation in the pregel stage is assumed. Therefore, the ionic conductivity is the dominating factor in the diffusion model, while the other three factors are relatively unimportant. Any error in the prediction of the overall diffusion coefficient will be primarily due to the determination of the ionic conductivity, and approximations for the other three factors, such as the choices made in the present work, are permissible.

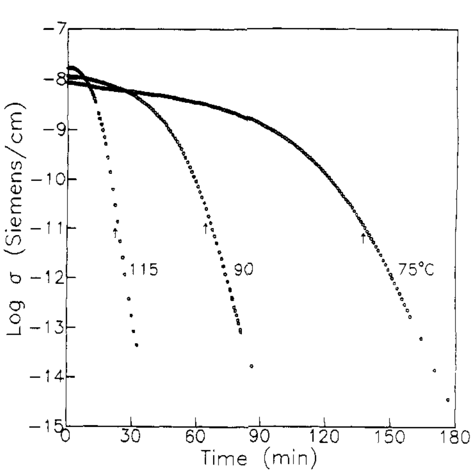

Figure 1. Ionic conductivity measured during the curing of the DGEBA–DDM resin at 75, 90, and 115 °C. The arrows indicate gel times.

The ionic conductivity may be obtained from the dielectric analysis, and the number-average degree of polymerization may be either calculated or measured experimentally. Since the ratio K_2/K_1 is a constant for isothermal cure without generation of ions but its value is unknown, the overall diffusion coefficient obtained using eq 9 is, in fact, a relative or normalized diffusion coefficient, e.g., normalized with respect to the value at 0% conversion.

Analyzing Diffusion in the Postgel Stage

Since a scaling relationship between the diffusion of the gel and the diffusion of free chains is not known to exist, a model similar to the proposed diffusion model, eq 9, cannot be obtained to determine the postgel diffusion coefficient.

However, the postgel diffusion can be analyzed by utilizing the dipole relaxation time since the mobility of the dipoles offers another indication of the mobility of polymer chains. The ionic conductivity is directly related to the mobility of the ionic species, while the dipole relaxation time is a direct indicator of the mobility of the molecular species.

The free-volume theory of Cohen and Turnbull[31] has been used successfully to model the mobility-related properties of thermosetting polymers. The underlying concept for the modeling is that the molecules or chain segments reside in cages bound by their neighbors for most of the time and their ability to rearrange their positions is dependent on the existence of sufficient free space (volume) to accommodate the motion. When there is a large amount of free volume, the chains may move without much difficulty. As the free volume decreases, there is less and less room for the chains to move and they tend to collide more frequently with their neighbors. The mobility of the chain segments is, therefore, reduced.

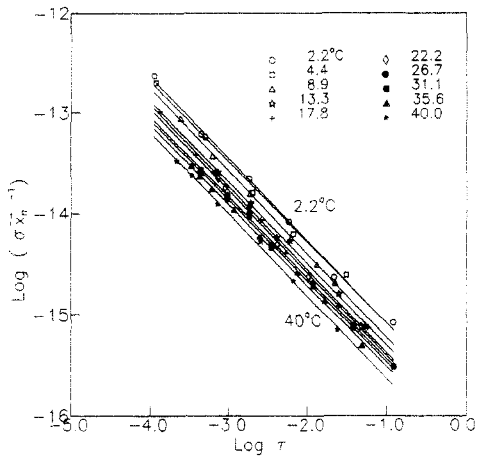

Figure 2. Plot of log (σx_n^{-1}) against log τ for the DGEBA–DDM resin. Lines are the best linear fits.

The model that describes the free-volume dependence of diffusivity is similar to eq 1 and given by[31,32]

$$D = D_0 \exp\left(-b_D \frac{\nu^*}{\nu_f}\right) \tag{10}$$

where ν_f is the average free volume and ν^* is the average close-packed-sphere volume or the critical free volume which is needed for a segmental jump to take place.

For the dipole relaxation time, the free-volume model may be written as[33]

$$\tau = \tau_0 \exp\left(b_\tau \frac{\nu}{\nu_f}\right) \tag{11}$$

where τ is the dipole relaxation time, τ_0 is a constant, b_τ is a constant that includes the critical free volume for dipole relaxation and ν ($=\nu^* + \nu_f$) is the average volume per chain segment. Studies[34,35] have shown that the dipole relaxation time of thermosets exhibits free-volume dependence or obeys the WLF (Williams–Landel–Ferry) equation, which is equivalent to the free-volume model.

Combining eqs 10 and 11 yields

$$D\tau^n = K_3 \tag{12}$$

where n ($=b_D/b_\tau$) is a constant independent of conversion and temperature and K_3 is a constant. This equation indicates that the relationship between the diffusion coefficient and the dipole relaxation time may be written as a power law. With the power-law index known, the diffusion coefficient in the postgelation stage may be obtained by measuring the dipole relaxation time during cure.

Since the diffusion coefficient in the pregel stage may be estimated using the diffusion model, eq 9, the power-law index may be easily determined by measuring the dipole relaxation times of the pregel samples. The following is an equivalent form of eq 12:

$$\log D = -n \log \tau + \log K_3 \tag{13}$$

Substitution of eq 9 yields

$$\log(\sigma \bar{x}_n^{-1}) = -n \log \tau + \log K_3' \tag{14}$$

where K_3' ($=K_1K_3/K_2$) depends only on the temperature. This equation indicates that, on the double-log plot of ($\sigma \bar{x}_n^{-1}$) against τ, the data points of various temperatures should constitute straight lines with an equal slope ($-n$) but different intercepts, i.e., a series of parallel straight lines. Determination of the slope yields the value of n. In Figure 2, such a plot is shown for the stoichiometrically balanced DGEBA–DDM resin (the experimental and data reduction procedures are given elsewhere[1]). The measurement temperatures were between 2.2 and 40 °C, and the epoxide conversions of the samples were between 0 and 48%. The data collected at each temperature exhibit linear dependence between log ($\sigma \bar{x}_n^{-1}$) and log τ. The best linear fits at all the temperatures form parallel lines with an average slope of −0.81. Hence, for this resin system, $n = 0.81$.

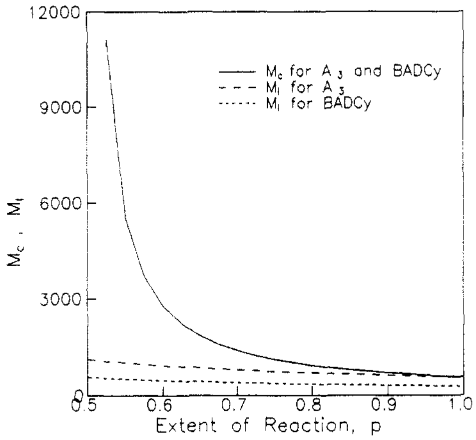

Figure 3. Calculated molecular weight between cross-links and molecular weight of the longest chain in the sol for A_3 homopolymerization ($M_A = 278$) and BADCy polymerization.

Thus, the overall diffusion coefficient may be determined using eq 9 in the pregel stage and eq 12 in the postgel stage. Note that, in principle, eq 12 is also useful for estimating the pregel diffusion but, under commercial curing conditions, it is difficult to measure the pregel dipole relaxation as the dipole contribution to the loss factor is overshadowed by the ionic contribution.

Before the solubles are completely incorporated into the network, the sol, which is soluble, and the gel, which is insoluble, coexist in the postgel system; the overall diffusion is composed of a sol contribution and a gel contribution.

The average molecular weight of the sol has been shown to decrease as the conversion increases;[36,37] i.e., longer chains exhibit higher tendencies to become incorporated into the gel. Thus, the sol consists mainly of monomer and short chains. According to de Gennes,[38] the diffusion of free chains in the presence of a network depends not only on the molecular weight of the chains but also on the molecular weight between cross-links. If the free chains are shorter than the arms between cross-links, the diffusion coefficient of a free chain is also inversely proportional to its molecular weight.

Because the case studied by de Gennes[38] involves only linear chains and chain segments in a network while the case discussed in this work involves branched chains and chain segments, the following two molecular weights are compared.

The number-average molecular weight between cross-links, M_c, and the number-average molecular weight of the longest chain in the sol (the molecular weight of the longest chain in a molecule excluding the weight of the branches), M_l, may be easily determined using the recursive approach.[37] These average molecular weights are illustrated in Figure 3 for two resin systems: a dicyanate ester resin (Bisphenol A dicyanate or BADCy) and an A_3-homopolymerization system with the molecular weight of the A unit being 278, the same molecular weight of the BADCy monomer. Detailed evaluation of M_c and M_l is given in the Appendix. The gel conversion is 50% for both systems according to the recursive approach. As shown in Figure 3, the molecular weight of the longest chain in the sol is small and decreases slowly with increasing conversion, while the molecular weight between cross-links is very large immediately after gelation ($M_c = \infty$ at the gel point) and, at high conversions, approaches a value of $2M_l$ for BADCy polymerization and M_l for A_3 homopolymerization. The difference between the values of M_l for the two systems is due to the fact that the BADCy polymerization is not an A_3 homopolymerization since the cyanate molecules first form A_3-like trimers and, then, the trimers polymerize.[37] Although the recursive approach does not predict material properties very accurately, this example shows that the network is quite "loose" compared to the chains in the sol and M_c remains larger than M_l even at very high conversions.

Thus, the diffusion coefficient of a free chain may be considered being inversely proportional to its molecular weight; the diffusion model, eq 9, is also valid for the sol diffusion in the postgel stage.

Now, consider the overall diffusion which involves the diffusion of both the sol and the gel. Let D_s be the average diffusion coefficient of the sol and D_g the average diffusion coefficient of the gel. By evaluating the total mean square displacement of all the monomer units over a time period t using eq 7, the following relationship may be easily obtained:

$$D = w_s D_s + w_g D_g \tag{15}$$

where w_s is the weight fraction of solubles and w_g is the weight fraction of the network.

The diffusivity of the gel may also be estimated based on experimental data for the diffusion of star molecules. Bartels et al.[40] have measured the diffusion coefficient of three-arm star hydrogenated polybutadienes using small-angle neutron scattering and correlated the diffusion coefficient of star polymers to that of linear chains with the same molecular weight. The ratio of the two diffusion coefficients was found to range from 10^{-2} to 10^{-5} depending on the ratio of the molecular weight of the star polymer and the entanglement molecular weight. Thus, in a percolation approach, Rohr and Klein[3] used 10^{-2} as the ratio of the diffusion coefficient of the chain segment between cross-links to the diffusion coefficient of the linear chain, the length of which is the same as that of the chain segment. Since the average length of the chain segments between cross-links is longer than or equal to the average length of the chains in the sol, the ratio of the gel diffusion coefficient to the sol diffusion coefficient is expected to be even smaller than the above-mentioned ratio (10^{-2}–10^{-5}). Then, based on eq 15, during the period when the sol fraction w_s is not much smaller than the gel fraction w_g, the overall diffusion will be dominated by the sol diffusion. In other words, the overall diffusion is approximately equal to the sol diffusion coefficient and the gel diffusion coefficient is negligible during this period of time. Any attempt to determine the gel diffusion by partitioning the overall diffusion using eq 15 would most likely lead to significant errors. Instead of partitioning, the overall diffusion may be estimated using the sol diffusion. At very high conversions, the gel contribution to the overall diffusion becomes important when the sol fraction is close to zero. Hence, for the period of cure when the sol fraction is not much smaller than the gel fraction, the overall diffusion coefficient is approximately equal to the contribution of the sol diffusion determined using the diffusion model, eq 9.

Potential Applications of the Modeling Strategy

Diffusion-Controlled Cure Kinetics. The Rabinowitch model[41] for small-molecule reactions has been employed in the studies of the diffusion-controlled kinetics of thermosetting resins:[2,3,5,6]

$$\frac{1}{k(T,\alpha)} = \frac{1}{k_c(T)} + \frac{1}{k_{d0}(T)\, D(T,\alpha)} \tag{16}$$

where k is the apparent rate constant, k_c is the intrinsic rate constant, D is the diffusion coefficient, and k_{d0} is a constant related to local conditions for creation of the chemical bond. A kinetic model that includes the diffusional limitations may be constructed by inserting eqs 9 and 12 into the Rabinowitch model. The constant k_{d0} combines with the unknown constants (K_2/K_1 and K_3) in eqs 9 and 12 to form a new constant. Since the intrinsic rate constant may be determined in the kinetic-controlled regime, the new constant is the only adjustable parameter in the diffusion-controlled kinetic model; i.e., using the normalized diffusion coefficient obtained from the proposed approach does not introduce additional adjustable parameters into the diffusion-controlled kinetic model. Note that the Rabinowitch model is derived from the general theory based on the formation of activated complex, and the effects of diffusion control, excluded volume, and cycle formation may be taken into account through generalized Smoluchowski coagulation equations.[42,43]

Network Buildup. It is known that the sol fraction decreases more rapidly than that predicted by the recursive approach and the sol disappears prior to full cure.[44] While this phenomenon may be related to cycle formation in the solubles, the diffusional effect may also play an important role. The prediction of the recursive approach is based on the equal-reactivity assumption but, under diffusional limitations, the reactivity of a functional group depends on the mobility of the molecule to which it is attached; for example, a functional group in a gel can be significantly less reactive than that of the same type in the sol. To account for the diffusional effect in the network buildup process, the reactivities of the sol and the gel may be separately evaluated using the Rabinowitch model based on their estimated diffusivities. The structural parameters of the network may then be determined by considering the unequal reactivities in order to study the structure–property relationship.

Gelation. If the diffusional limitations affect the cure in the pregel stage, gelation will be delayed to a higher conversion compared to the predicted gel conversion of the recursive approach. The diffusional limitations induce unequal reactivities among chains of unequal lengths and promote cycle formations. To account for the diffusional effect, molecular species in the entire curing system may be partitioned into two groups—one with long chains and one with short chains—and those in the same group are assumed to have the same diffusivity and reactivity at any time during cure. The diffusivities of the two groups are determined based on their average chain lengths. Modeling of the curing process will then provide information on the effect of the diffusional limitations on the delay of gelation.

Summary

The diffusion of the polymer chains in a thermosetting system was treated as a process parallel to the diffusion of the ionic species. Based on this consideration, a diffusion model, eq 9, was developed for estimating the overall diffusion in the pregel stage and the sol diffusion in the postgel stage. The polymer diffusion coefficient was written as a function of four factors dominated by the ionic conductivity. The overall diffusivity in the postgel stage may be determined by utilizing the free-volume relationship between the diffusion coefficient and the dipole relaxation time or by using the contribution of the sol diffusion alone as an approximation. Potential applications of the modeling strategy include the study of the diffusion-controlled cure kinetics and the structure–property relationships of thermosetting systems.

Appendix

By following the method suggested in ref 37, the number-average molecular weight between cross-links and the number-average molecular weight of the longest chain may be evaluated for A_3 homopolymerization and the polymerization of dicyanate assuming that the cyclotrimerization is the sole reaction pathway.

Let C_A^{out} be the mass of the chain looking out from a randomly chosen A unit toward a cross-link. Then its expected weight is

$$E(C_A^{out}) = E(C_A^{in}) \qquad \text{(A1)}$$

and

$$E(C_A^{in}) = M_A(1 - C) + [2M_A + E(C_A^{out})]C \qquad \text{(A2)}$$

where M_A is the molecular weight of an A unit and C is the probability that an A_3 molecule is not a cross-link but rather a reacted monomer that is part of a chain connecting two cross-links. C may be written as

$$C = \frac{\binom{2}{1}[1 - P(F_A^{out})]P(F_A^{out})}{\sum_{i=1}^{2}\binom{2}{i}[1 - P(F_A^{out})]^i P(F_A^{out})^{2-i}} \qquad \text{(A3)}$$

where $P(F_A^{out})$ is the probability of a finite chain as discussed in ref 30. $E(C_A^{out})$ may be obtained by solving eqs A1 and A2 simultaneously. Then, the number-average molecular weight between cross-links, M_c, is

$$M_c = M_A + E(C_A^{out}) = \frac{2M_A}{1 - C} \qquad \text{(A4)}$$

The above is also valid for the polymerization of dicyanate if each dicyanate unit, rather than each cyanate unit, is considered as an A unit.

To calculate the number-average molecular weight of the longest chain, randomly pick an A unit that is part of the longest chain of a molecule. Let L_A^{in} be the mass of the longest chain looking into the randomly chosen A. Because the branches of the molecule are not considered part of the longest chain, the expected weight is

$$E(L_A^{in}) = 2M_A + E(L_A^{out}) \qquad \text{(A5)}$$

and

$$E(L_A^{out}) = pE(L_A^{in}) + (1 - p)\cdot 0 \qquad \text{(A6)}$$

where p is the extent of reaction. $E(L_A^{in})$ may be solved using eqs A5 and A6.

Randomly pick a longest-chain end A. The expected weight or the number-average molecular weight of the longest chain, M_l, is then

$$M_l = E(L_A^{in}) = \frac{2M_A}{1 - p} \qquad \text{(A7)}$$

This equation also holds for the solubles in the postgel stage as long as the extent of reaction, p, is replaced by the extent of reaction of the sol, p_s. The above is also valid for the polymerization of dicyanate if each cyanate unit is considered as an A unit.

References and Notes

(1) Deng, Y.; Martin, G. C. *Macromolecules*, following paper in this issue.
(2) Huguenin, F. G. A. E.; Klein, M. T. *Ind. Eng. Chem. Prod. Res. Dev.* **1985**, *24*, 166.
(3) Rohr, D. F.; Klein, M. T. *Ind. Eng. Chem. Res.* **1990**, *29*, 1210.
(4) Doolittle, A. K. *J. Appl. Phys.* **1951**, *22*, 1471.
(5) Rohr, D. F.; Klein, M. T. *Ind. Eng. Chem. Res.* **1988**, *27*, 1361.
(6) Havlíček, I.; Dušek, K. In *Crosslinked Epoxies*; Sedláček, B., Kahovec, J., Eds.; Walter de Gruyter: Berlin, 1987.
(7) Dušek, K.; Havlíček, I. *Prog. Org. Coat.* **1993**, *22*, 145.
(8) Adam, G.; Gibbs, J. H. *J. Chem. Phys.* **1969**, *43*, 139.
(9) von Meerwall, E.; Palunas, P. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1439.
(10) Wright, W. W. *Br. Polym. J.* **1983**, *15*, 224.
(11) Senturia, S. D.; Sheppard, N. F., Jr. *Adv. Polym. Sci.* **1986**, *80*, 1.
(12) Sheppard, N. F., Jr. Ph.D. Dissertation, Massachusetts Institute of Technology, 1986.
(13) Fava, R. A.; Horsfield, A. E. *Br. J. Appl. Phys. (J. Phys. D), Ser. 2* **1968**, *1*, 117.
(14) Day, D. R. *Polym. Eng. Sci.* **1986**, *26*, 362.
(15) Kranbuehl, D.; Delos, S.; Hoff, M.; Weller, L.; Haverty, P.; Seeley, J. In *Cross-Linked Polymers*; Dickie, R. A., Labana, S. S., Bauer, R. S., Eds.; American Chemical Society: Washington, DC, 1988.
(16) Kranbuehl, D.; Delos, S.; Yi, E.; Mayer, J.; Jarvie, T. *Polym. Eng. Sci.* **1986**, *26*, 338.
(17) Bidstrup, W. W.; Senturia, S. D. *Polym. Eng. Sci.* **1989**, *29*, 290.
(18) Simpson, J. O.; Bidstrup, S. A. *Polym. Mater. Sci. Eng.* **1991**, *65*, 359.
(19) Bockris, J. O'M.; Reddy, A. K. N. *Modern Electrochemistry*; Plenum: New York, 1970.
(20) Newman, J. S. *Electrochemical Systems*; Prentice-Hall: Englewood Cliffs, NJ, 1973.
(21) Levich, V. G. *Physicochemical Hydrodynamics*; Prentice-Hall: Englewood Cliffs, NJ, 1962.
(22) Weston, R., Jr.; Schwarz, H. A. *Chemical Kinetics*; Prentice-Hall: Englewood Cliffs, NJ, 1972.
(23) Tyrrell, H. J. V.; Harris, K. R. *Diffusion in Liquids*; Butterworths: London, 1984.
(24) Atkins, P. W. *Physical Chemistry*; Oxford University Press: Oxford, 1978.
(25) Schiller, R. *Radiat. Phys. Chem.* **1991**, *37*, 549.
(26) Rouse, P. E. *J. Chem. Phys.* **1953**, *21*, 1272.
(27) Klein, J. *Contemp. Phys.* **1979**, *20*, 611.
(28) Bueche, F. *Physical Properties of Polymers*; Interscience: New York, 1962.
(29) Macosko, C. W.; Miller, D. R. *Macromolecules* **1976**, *9*, 199.
(30) Miller, D. R.; Macosko, C. W. *Macromolecules* **1976**, *9*, 206.
(31) Cohen, M. H.; Turnbull, D. *J. Chem. Phys.* **1959**, *31*, 1164.
(32) Kumins, C. A.; Kwei, T. K. In *Diffusion in Polymers*; Crank, J., Park, G. S., Eds.; Academic Press: New York, 1968.
(33) Hill, N. E.; Vaughan, W. E.; Price, A. H.; Davies, M. *Dielectric Properties and Molecular Behavior*; Van Nostrand Reinhold: London, 1969.
(34) Sanford, W. M.; McCullough, R. L. *J. Polym. Sci., Polym. Phys. Ed.* **1990**, *28*, 973.
(35) Shito, M. *J. Polym. Sci., Part C* **1968**, *23*, 569.
(36) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(37) Miller, D. R.; Valles, E. M.; Macosko, C. W. *Polym. Eng. Sci.* **1979**, *19*, 272.
(38) de Gennes, P.-G. *Macromolecules* **1986**, *19*, 1245.
(39) Owusu, A. O. Ph.D. Dissertation, Syracuse University, 1992.
(40) Bartels, C. R.; Crist, B.; Fetters, L. J.; Graessley, W. W. *Macromolecules* **1986**, *19*, 785.
(41) Rabinowitch, E. *Trans. Faraday Soc.* **1937**, *33*, 1245.
(42) Smoluchowski, M. *Z. Phys. Chem.* **1918**, *92*, 129.
(43) Family, F.; Landau, D. P., Eds. *Kinetics of Aggregation and Gelation*; North-Holland: Amsterdam, 1984.
(44) For example: Heise, M. S. Ph.D. Dissertation, Syracuse University, 1989.