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Laser Light Scattering Studies of Epoxy Polymerization of 1,4-Butanediol Diglycidyl Ether with *cis*-1,2-Cyclohexanedicarboxylic Anhydride

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ABSTRACT: Epoxy polymers formed by curing 1,4-butanediol diglycidyl ether (DGEB) with *cis*-1,2-cyclohexanedicarboxylic anhydride (CH) in the presence of a catalyst, benzyldimethylamine (CA), at different temperatures (60, 70, 80, and 90 °C) and varying amounts of catalyst were studied by investigating the laser light scattering intensities near and past the gelation threshold of the polymer products in the reaction mixture. The degree of polymerization could be determined by chemical analysis. Structural changes of the branched epoxy polymer formed during the curing process were analyzed according to the Debye–Bueche theory of light scattering for inhomogeneous solids. The change in the correlation length (ξ) which characterizes the inhomogeneous domain and the mean-squared average dielectric constant fluctuation ($\overline{\eta^2}$) could be divided into three main stages which are responsible for the cross-linking polymerization reaction in the epoxy curing process.

Introduction

The copolymerization of epoxy resins and anhydrides with triamine as a catalyst produces a complex three-dimensional cross-linking network, which has a variety of desirable mechanical properties, such as impact resistance.[1,2] Many research efforts have been undertaken in order to understand the curing kinetics, mechanism, structure, and relationship between macroscopic properties and microstructure. An array of physical methods, such as light scattering envelope measurements,[3,4] fractal geometry analysis,[5,6] size-excluded chromatography,[7] and dynamic laser light scattering,[8] have been used to study the epoxy curing process. However, until now there remains a number of conflicting reaction kinetics and mechanisms which have been proposed by different research groups.[9] The complex nature of epoxy copolymerization processes and our limited knowledge on the molecular structure of the epoxy polymer products formed during the curing process are the main reasons which prevent us from achieving a deeper understanding of the epoxy polymerization reaction.[9] In this paper, we investigate the laser light scattering envelope of 1,4-butanediol diglycidyl ether (DGEB) cured with *cis*-1,2-cyclohexanedicarboxylc anhydride (CH) in the presence of different amounts of benzyldimethylamine (CA) at different temperatures (60, 70, 80, and 90 °C).

According to the Debye–Bueche theory,[10] the intensity of light scattered by an inhomogeneous medium is dependent upon the local refractive index difference in the inhomogeneous medium in terms of the mean-square average of local dielectric constant fluctuations $\overline{\eta^2}$, which could be related to structural changes during the copolymerization process. The changes can be divided into four main stages as the reaction progresses. We believe that one of the crossover points among the light scattering intensity variations could be defined as the gel point. Chemical analysis is also used to determine the extent of the copolymerization reaction. We propose a mechanism about the growth of the branched epoxy copolymer and also try to present a schematic picture of the formation of such types of three-dimensional networks.

Branching Kinetics

With triamine as a catalyst, reactions between epoxy resins or between anhydrides are suppressed.[11] The copolymerization of an epoxy resin (DGEB) and an anhydride (CH) is dominated by alternative linkage between DGEB and CH as shown graphically in Figure 1. It is not clear how triamine starts the reaction, i.e., we do not know whether triamine first reacts with the anhydride or the epoxy resin. If we examine mainly the branching process, we can ignore the initial mechanism. By assuming that (1) all catalyst molecules would start the polymerization reaction at the same time and have the same reactivity, (2) the reactivity is independent of polymer chain length, and (3) rings do not form, we could present a simplified model for the branching kinetics in the copolymerization process as follows.

At a fixed molar ratio of epoxy resin to anhydride and temperature T, the rate of change of the number of polymer molecules having 0, 1, 2, ..., $(n - 1)$ branching points, $\mathrm{d}N_1/\mathrm{d}t$, $\mathrm{d}N_2/\mathrm{d}t$, $\mathrm{d}N_3/\mathrm{d}t$, ..., $\mathrm{d}N_n/\mathrm{d}t$, can be expressed as follows:

$$\mathrm{d}N_1/\mathrm{d}t = -\bar{f}N_1 \sum_{i=1}^{\infty}(1 + i)N_i \tag{1-1}$$

$$\mathrm{d}N_2/\mathrm{d}t = \bar{f}N_1N_1 - \bar{f}N_2 \sum_{i=1}^{\infty}(2 + i)N_i \tag{1-2}$$

$$\mathrm{d}N_n/\mathrm{d}t = \tfrac{1}{2}\bar{f} \sum_{i+j=n} (i + j)N_iN_j - \bar{f}N_n \sum_{i=1}^{\infty}(n + i)N_i \tag{1-3}$$

where $\bar{f}$ is the average probability for one active site on one molecule capable of reacting with another molecule and is a function of catalyst concentration and extent of conversion. A polymer molecule with $(n - 1)$ branching points has n active sites. The probability for a polymer with i active site (i.e., $(i - 1)$ branching points) to react with another polymer molecule with j active site should be $(i + j)\bar{f}$. In the formulation, we have not considered the reaction of polymers with monomers because N_n does not change if the polymer reacts with a monomer. Equations 1-1, 1-2, and 1-3 suggest that $\mathrm{d}N_n(t)/\mathrm{d}t$ can be divided into two parts. N_n increases with time when one polymer having $(i - 1)$ branching points reacts with another polymer

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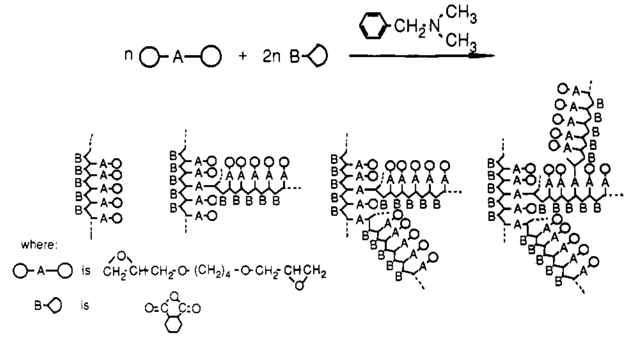

Figure 1. Schematic representation of copolymerization of an epoxy resin (DGEB) and an anhydride (CH). The reaction is dominated by alternating linkages between DGEB and CH.

having $(j - 1)$ branching points where $(i + j) = n$, but N_n also decreases with time when a polymer molecule having $(n - 1)$ branching points reacts with any other polymer. We have formulated the basic idea on branching kinetics. The results of our light scattering studies will be used to compare with the generalized kinetic equation, which was identified by Stell to be a form of the Smoluchowski equation, in a later article.

Experimental Methods

Materials. 1,4-Butanediol diglycidyl ether (DGEB, M_w = 202.3) and *cis*-1,2-cyclohexanedicarboxylic anhydride (CH, M_w = 154.2) were purchased from Aldrich Chemical Co. and used without further purification. The same experimental results were obtained after both components were purified by vacuum (≈0.01 mmHg) distillation. The catalyst (CA), benzyldimethylamine (M_w = 135.2), courtesy of Gary L. Hagnauer, Polymer Research Division, Army Materials Technology Laboratory, Watertown, MA, was vacuum distilled before use.

Preparation of Solutions. The procedure for preparing the reaction mixture has been described in detail elsewhere.[3] Well-mixed reaction mixtures containing different molar ratios of epoxy (DGEB):curing agent (CH):catalyst (CA) were centrifuged at 17000*g* and 35 °C for approximately 1 h. A middle portion of the centrifuged solution was then transferred to a dust-free light-scattering cell by using a dust-free pipet. The scattering cell was immediately capped with Teflon tape.

Methods of Measurement. A fully computerized light scattering spectrometer, which is capable of operating at high temperatures, was used for measurements of the angular distribution of absolute scattered intensity at different time intervals, varying from 15 min to 1 h, depending upon the total reaction time. The scattering angular range covered was from 15° to 140°. Each scan of 20 scattering angles took approximately 3 min. The light-scattering measurements during the copolymerization reaction were carried out in situ. The "solvent" scattering intensity was taken as the scattered intensity of the reaction mixture with the same molar ratio of epoxy resin and anhydride as in the copolymerization reaction, but without triamine as the catalyst.

Results and Discussion

Chemical Analysis. A standard chemical analysis procedure was used to monitor the conversion of anhydride.[12] Figure 2 shows how the anhydride conversion changes with reaction time at two different temperatures, 60 and 80 °C. Solid lines in the figure denote the least-squares fitting of the zeroth-order kinetics and dot lines for the first-order kinetics. The data we obtained covered only the anhydride conversion range from 0% to about 50% when the reaction mixture became a very viscous gellike medium. From the limited conversion with only half of the anhydride being reacted, it is difficult for us to determine the reaction order within the precision of our data as the rate of conversion for both the zeroth-order and the first-order reactions behaves in a similar way over the 0–50% conversion range. Thus, the reaction order, which has been a challenge for many research groups,[9] remains an open question. Here, we only suggest that our limited experimental data seem to fit the zeroth-order reaction kinetics better because the error for the zeroth-order fitting is about half of that fitted by the first-order kinetics. Based on the zeroth-order kinetics, we calculated the zeroth-order reaction constant (k_0) at four temperatures, 60, 70, 80, and 90 °C. The results are listed in Table I. The logarithm of k_0 depends linearly on the reciprocal temperature $(1/T)$. By using the well-known formula, $k_0 = Ae^{-(E/kT)}$, the activation energy, E = 12.5 ± 0.5 (kcal/mol), is obtained. We also repeated the experiments at fixed temperatures and varying catalyst concentrations. The results are also listed in Table I. The zeroth-order rate seems to persist over a wide range of catalyst concentrations for the reaction at 80 °C. In this way, we obtained k_0 at four different ratios of catalyst to epoxy resin concentrations (0.1%, 0.3%, 0.6%, and 1.0%) at 80 °C. The zeroth-order reaction rate is proportional to the catalyst concentration. Mathematically the equation takes on the form[13]

$$\frac{R_x - A}{R_y - A} = B\frac{C_x}{C_y} \tag{2}$$

where R_x and R_y represent the rates at catalyst concentrations C_x and C_y, respectively, A is the intercept at zero catalyst concentration, and B is a constant. Physically, A may be taken as the rate of the uncatalyzed reaction and B as an efficiency factor representing the portion of the triamine which is catalytically effective. For our epoxy–

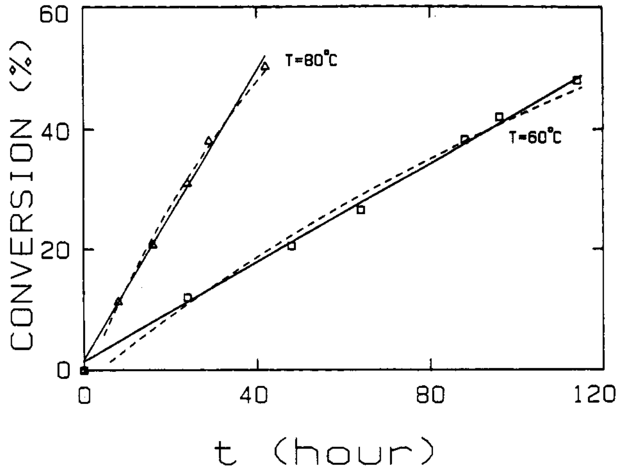

Figure 2. Anhydride (CH) conversion (([CH]$_0$ – [CH]$_t$)/[CH]$_0$, %) versus reaction time t at two different temperatures, 60 and 80 °C. The molar ratio of DGEB:CH:CA = 1:2:0.001. Solid line for zeroth-order fitting. Dot line for second-order fitting.

Table I
Temperature and Catalyst Concentration Dependence of the Zeroth-Order Reaction Constant k_0

Temperature Dependence
(Molar Ratio of DGEB:CH:CA = 1:2:0.001)

temp, °C	k_0, mol mL^{-1} h^{-1}	temp, °C	k_0, mol mL^{-1} h^{-1}
60	1.88×10^{-5}	80	5.72×10^{-5}
70	3.51×10^{-5}	90	9.02×10^{-5}

Catalyst Concentration Dependence
(Temp = 80 °C, Molar Ratio of DGEB:CH:CA = 1:2:X)

catal concn X	k_0, mol mL^{-1} h^{-1}	catal concn X	k_0, mol mL^{-1} h^{-1}
0.1	5.72×10^{-5}	0.6	3.19×10^{-4}
0.3	1.47×10^{-4}	1.0	5.04×10^{-4}

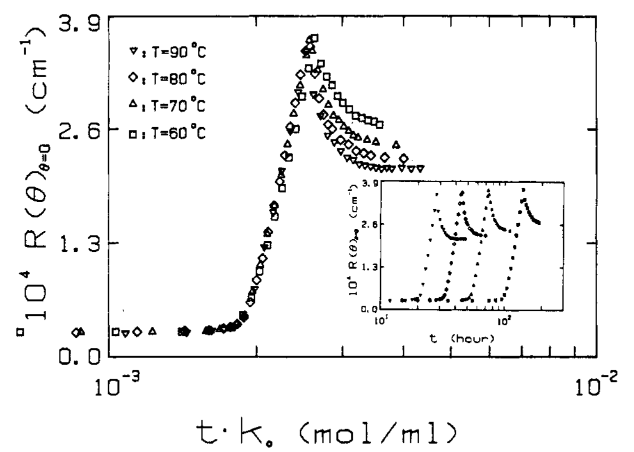

Figure 3. $R_{vv}(\theta)_{\theta=0}$ versus scaled reaction time, k_0t (in units of mol/mL), at four different reaction temperatures, 60, 70, 80, and 90 °C. The molar ratio of DGEB:CH:CA = 1:2:0.001. Inset: Unscaled $R_{vv}(\theta)_{\theta=0}$ versus reaction time t (in units of hours).

anhydride system at 80 °C, we find that $A = 5.18 \times 10^{-6}$ (mol mL^{-1} h^{-1}) and $B = 99.4\%$, i.e., doubling the catalyst concentration increases the reaction rate by a factor of 1.99, which takes into account a small amount of impurities ($\approx 0.5\%$) in the triamine molecules. The B value suggests that the catalyst we used was very pure after vacuum distillation. The plot of k_0 versus the catalyst concentration also shows a straight line.

Laser Light Scattering. Debye and Bueche[10] proposed that the intensity of scattered light (i) of an inhomogenous solid follows the expression

$$i \propto 4\pi\overline{\eta^2}V\int_0^\infty r^2\gamma(r)\frac{\sin(Kr)}{Kr}\,dr \qquad (3)$$

where V is the scattering volume, $K = (4\pi/\lambda)\sin(\theta/2)$, with θ and λ being the scattering angle and the wavelength of light in the scattering medium, respectively, $\overline{\eta^2}$ is the mean-square average local dielectric constant fluctuations, and $\gamma(r)$ is a correlation function defined by

$$\gamma(r) = \langle\eta_1\eta_2\rangle/\overline{\eta^2} \qquad (4)$$

where η_1 and η_2 are the local dielectric constant fluctuations in volume elements 1 and 2, respectively. For all pairs of volume elements separated by a scalar distance r inside the scattering volume, $\langle\eta_1\eta_2\rangle$ is the average value of $\eta_1\eta_2$. If we take the correlation to be random

$$\gamma(r) = e^{-r/\xi} \qquad (5)$$

where ξ is the correlation length defining the local inhomogeneities. The Rayleigh ratio for unit scattering volume has the form

$$R_{vv}(K) = \frac{8\pi^3\overline{\eta^2}\xi^3}{\lambda_0^4(1+K^2\xi^2)^2} \qquad (6)$$

where λ_0 is the wavelength of light in vacuum. We could calculate ξ and $\overline{\eta^2}$ from the Rayleigh ratio by plotting $(R_{vv}(K))^{-1/2}$ versus K^2.

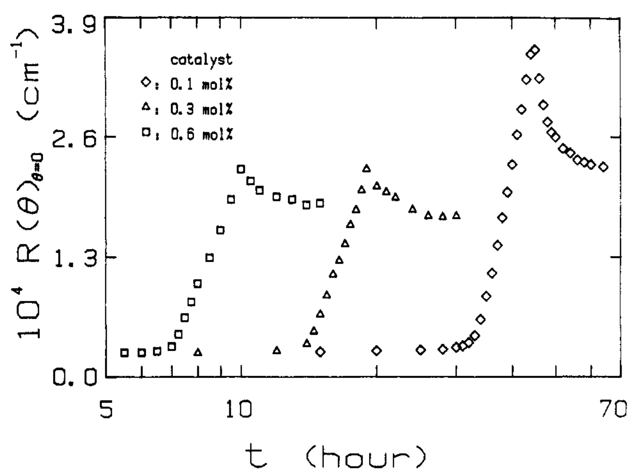

Figure 4. $R_{vv}(\theta)_{\theta=0}$ versus reaction time t (in units of hours) at three different catalyst concentrations (0.1%, 0.3%, and 0.6%) but the same molar ratio of DGEB:CH = 1:2 and 80 °C.

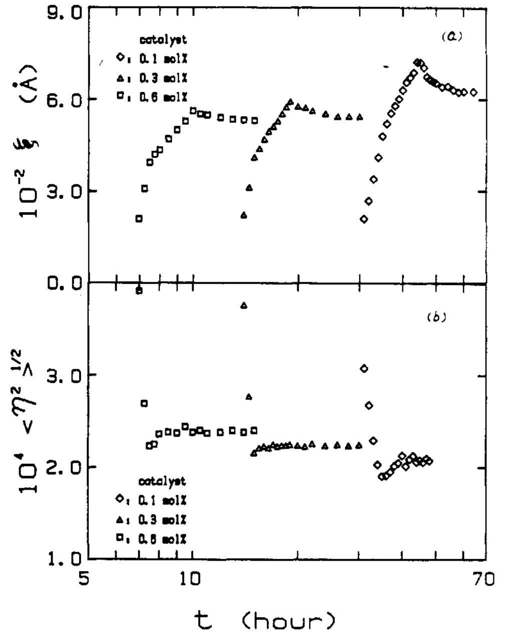

Figure 5. (a) Correlation length (ξ) of local optical inhomogeneities versus reaction time t at three different catalyst concentrations (0.1%, 0.3%, and 0.6%) but the same molar ratio of DGEB:CH = 1:2 and 80 °C. (b) Mean-square average local dielectric constant fluctuations ($\overline{\eta^2}$) versus reaction time t at three different catalyst concentrations (0.1%, 0.3%, and 0.6%) but the same molar ratio of DGEB:CH = 1:2 and 80 °C.

$R_{vv}(K)_{K=0}$ at a fixed catalyst concentration (0.1%) changes with reaction time at four different temperatures. In order to find the temperature effect, we rescaled the reaction time at each temperature by multiplying it with the corresponding k_0 value. The results are shown in Figure 3. We note that the temperature has little effect on $R_{vv}(K)_{K=0}$ before $R_{vv}(K)_{K=0}$ reaches its maximum value. After having passed the maximum, $R_{vv}(K)_{K=0}$ tends to behave differently at different temperatures. The higher the reaction temperature, the smaller the value of $R_{vv}(K)_{K=0}$ becomes. The phenomenon is reasonable because the system becomes more uniform and scatters less light at higher reaction temperatures. A similar phenomenon was observed when we changed the catalyst concentration, i.e., the higher the catalyst concentration, the more uniform the reaction mixture becomes and the less the scattered intensity. Figure 4 shows the effect of catalyst concentration on the magnitude of scattered intensity. We note that $R_{vv}(K)_{K=0}$ behaves almost in the same way for catalyst concentrations of 0.3% and 0.6% except that the reaction rate has been changed. The optical behavior tells us that the polymerization reaction produced essentially the same degree of local dielectric constant fluctuations as long as the catalyst concentration is greater than a threshold value (say $\approx 0.3\%$). Figures 5 and 6 show how ξ and $\overline{\eta^2}$ change with respect to temperature and catalyst concentration. From the figures, we can make the following observations:

(1) The higher the temperature, the smaller the $\overline{\eta^2}$ value

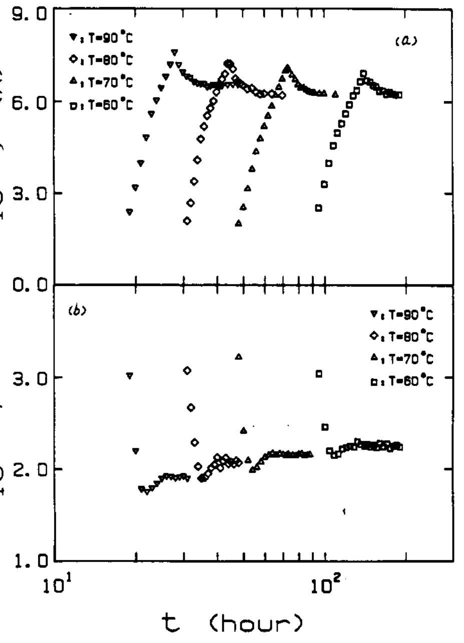

Figure 6. (a) Correlation length (ξ) of local optical inhomogeneities versus reaction time t at four different reaction temperatures, 60, 70, 80, and 90 °C. The molar ratio of DGEB:CH:CA is 1:2:0.001. (b) Mean-square average local dielectric constant fluctuations ($\overline{\eta^2}$) versus reaction time t at four different reaction temperatures, 60, 70, 80, and 90 °C. The molar ratio of DGEB:CH:CA is 1:2:0.001.

and the larger the extension of local inhomogeneities, in terms of ξ.

(2) The lower the catalyst concentration, the smaller the $\overline{\eta^2}$ values and the larger the extension of local optical inhomogeneities. This observation suggests that at lower catalyst concentrations each polymer molecule has more chance to grow bigger before it reacts with other polymer molecules.

(3) There are two different rates associated with the characteristic length increases with time. After having reached its maximum value (around 70 nm), the correlation length ξ gradually decreases to a constant value at around 60 nm. The changes in the $\overline{\eta^2}$ values also show three main steps: a sharp drop, a gradual increase, and then a steady state. Each crossover point on the $\overline{\eta^2}$ values corresponds to a change of behavior on the average characteristic length of local inhomogeneities.

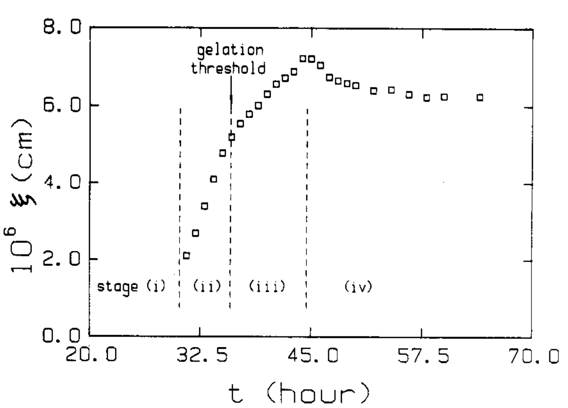

Figure 7. Correlation length (ξ) of local optical inhomogeneities versus reaction time t at 80 °C. Catalyst concentration is 0.1% and the molar ratio of DGEB:CH = 1:2.

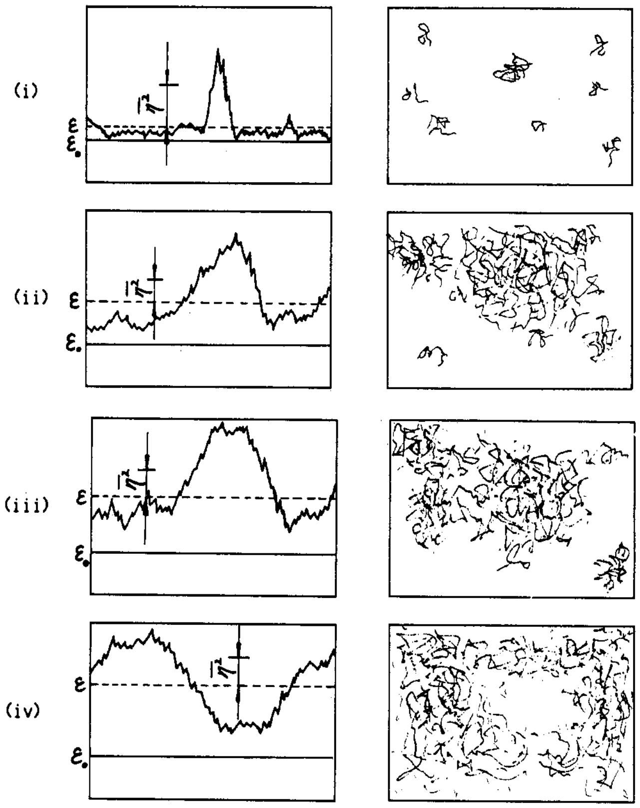

Figure 8. Four proposed reaction stages are shown schematically: (i) first stage; (ii) second stage; (iii) third stage; (iv) fourth stage. $\overline{\eta^2}$ is the mean-square average dielectric constant fluctuation. ξ is the correlation length defining the extension of local optical inhomogeneities. ε is the average dielectric constant.

By combining this observation with the knowledge we gained based on previous studies of the same system,[5,6,8] we propose that the reaction process can be divided into four main regions. This is shown in Figure 7. (i) In the very beginning, the size of inhomogeneities is too small to be observed by laser light scattering. Most of the initial polymer products are linear or slightly branched polymer molecules. This stage is shown schematically in Figure 8i. The growth of the polymer chains in this first stage is accompanied mainly by the reaction of the epoxy monomers with the curing agent. There is a gradual increase in the size of inhomogeneities through the growth of polymer molecules with some cross-linking. At the same time, the optical density difference between the polymer chains and the reaction mixture becomes larger as the polymer size becomes larger. The $\overline{\eta^2}$ value must gradually increase to its maximum value until cross-linking dominates the copolymerization reaction. In the above discussion, we have assumed that polymers are formed only at the catalytic centers and, therefore, there is no increase in polymer number concentration. With increasing extent of conversion, the concentration of lower molecular weight polymers whose refractive index increment has reached a plateau value becomes higher and higher. Then the system enters the second stage. (ii) In the second stage, the polymer molecules have more chance to react with each other to form larger and more highly branched polymer molecules. Figure 8ii shows schematically the changes related to the second reaction stage. It is easy to understand that the characteristic size of the inhomogeneities increases very fast because the polymer chains almost double themselves in size by covalent bonding among the polymer chains. We also notice that the values of $\overline{\eta^2}$ decrease by a factor of about 2. How do we interpret this observation? Let us look at the definition of $\overline{\eta^2}$. η is a local variation of the dielectric constant superimposed on the average dielectric constant ε. In the second stage when the polymer molecules have overlapped to form local polymer

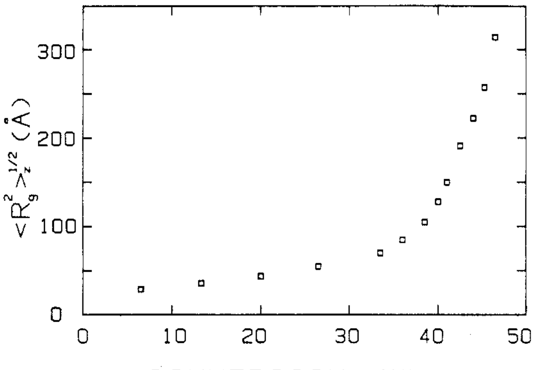

Figure 9. Radius of gyration of polymer chains from the reaction mixture in MEK versus CH conversion (%).

networks, the amount of polymer per unit volume is increasing, but the crosslinked polymer networks tend to shrink in size. So, the relative values of $\overline{\eta^2}$ decrease. As the polymer molecules become bigger and bigger, all polymer molecules inside the network will tend to become more connected with one other. Then the gel state has fewer and fewer loose polymer molecules not connected with the network. (iii) The third stage is shown schematically in Figure 8iii. In this stage, most of the polymer chains cannot move freely and the viscosity of the system becomes higher; i.e., the polymer chains are localized. Direct reaction between polymer chains becomes more difficult, but the monomers (and small polymer chains) are still moving around to react with the localized larger polymer chains. The extent of local optical inhomogeneities increases at a lower rate. At the same time, the localized polymerization reaction densifies the branched polymer chains, thus increasing the contrast of the polymer domain to the average background of the system. However, this increase is limited, as shown by a small increase in the $\overline{\eta^2}$ value during the third stage. We suggest that the crossover point for the average size of local optical inhomogeneities from one rate to another, or the lowest value of $\overline{\eta^2}$, could be considered as the gel point, which we marked in Figure 7. In the experiment, we tested the supposition by withdrawing the reaction mixture from the reaction vessel near the crossover point and by dissolving the polymer product in methyl ethyl ketone (MEK). We found that the reaction mixture contained a small amount of insoluble polymer particles just around the crossover point. In the third stage, the viscosity of the system increased tremendously. The state of the system changes from a viscous medium to a gellike soft solid. (iv) In the final stage, the unreacted monomers still move inside the system to react with the cross-linked polymer chains. Experimentally we observed that the size of local optical inhomogeneities reduced to a constant value and $\overline{\eta^2}$ values remained unchanged. This observation suggests that light scattering observes different sources of local optical inhomogeneities. Perhaps the denser part of the polymer network becomes the background and light scattering is produced by the "holes" in the denser polymer network. So the "hole" sizes decrease as the polymer network begins to be filled out. Finally, the reaction stops when all the monomers have been used up. Figure 8iv shows a schematic representation of the fourth stage.

In order to check the size of local optical inhomogeneities, we determined the radius of gyration of the polymer chains from the reaction mixture in MEK. The results are shown in Figure 9. They are reasonably close to the values we obtained for the size of inhomogeneities. It should be noted that both methods measure similar though not identical physical properties of the extension of local density fluctuations.

Conclusions

The Debye–Bueche theory for inhomogeneous solids has been applied to studies of the formation of polymer networks in an epoxy polymerization reaction. As an on-line technique, laser light scattering has a unique advantage, capable of monitoring the local optical inhomogeneities during the curing process. Based on our experimental data, four main reaction stages are proposed. By combining our results with other measurements of the mechanical properties of the system, we could establish a relationship between the microstructure and macroscopic properties of the cured epoxy resins. Finally, light scattering could also be used to estimate the gel point in optically clear epoxy resins.

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Registry No. (DGEB)(CH) (copolymer), 113810-65-4.

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