

The Physical Reasons for the Homogeneous and Nonhomogeneous Reactions of Haloid-Containing Epoxy Polymer Curing

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ABSTRACT: The homogeneous reaction of crosslinked polymer curing proceeded in the medium with small density fluctuations, and the nonhomogeneous one proceeded in the medium with large density fluctuations. A nonhomo-

geneous curing reaction was simulated as proceeding in a fractal space. In this case, its rate was sharply reduced in comparison with a similar reaction in a Euclidean space. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1202–1205, 2003

INTRODUCTION

In ref. 1, it was shown that the curing mode of various haloid-containing epoxy polymers could be of two types: homogeneous and nonhomogeneous. The first mode is characterized by the constant structure of clusters (microgels) formed in the curing process, described by the fractal dimension (D) in an interval (α) of the conversion degrees of the reaction of $\alpha \approx 0-0.7$. The monotonous increase of D is characteristic for the nonhomogeneous mode in the process of increasing reaction time in the same interval α . Such a difference is reflected in the form of the kinetic curves, where t is reaction time $\alpha(t)$. In ref. 1 it was shown that the cause of such a difference is a certain distribution of D values for nonhomogeneous reactions and the monodispersion of the mentioned values for homogeneous reactions. The authors of ref. 1 made the assumption that the physical basis of the presence of these two types of curing reactions is the level of density fluctuations in the reaction medium. If the reacting substances are distributed equipartitionally (if the fluctuations in density are small), at any point in the reaction medium, identical conditions for microgel formation with monodispersed D values will be formed. If the reacting substances are distributed nonuniformly (if the fluctuations in density are great), the different ratios of the curing agent to the oligomer at different points in the reaction medium will result in the formation of microgels with insufficient or extra degrees of curing, which finally will be expressed as different

microgel structures and a polydisperse distribution of D . The purpose of this study was to check this assumption with the scaling² and fractal³ approaches on samples of two haloid-containing epoxy polymers that showed homogeneous [diphenylolpropane (2DPP) + hexachloroethane (HCE)/4,4'-diaminodiphenylmethane (DDM)] and nonhomogeneous (EPS-1/DDM) modes of curing.

EXPERIMENTAL

The curing kinetics of a haloid-containing oligomer based on hexachlorobenzene were investigated. This oligomer (designated as EPS-1) was cured by DDM at a stoichiometric ratio of DDM to EPS-1.⁴

The curing kinetics the EPS-1/DDM system was studied by inverted gas chromatography.⁴ The basic parameter received from experimental data processing was the reaction rate constant k_r , determined for $\alpha = 0.1-0.7$ for the kinetic curve degree of conversion-time ($\alpha-t$). To determine k_r , the standard procedure was used: we calculated the dependence of α on t as $\log[\alpha/(1 - \alpha)] = f(t)$, which appeared to be constructed linearly. Then, k_r was determined from the slope of these linear diagrams. Ketones (methyl ethyl ketone, 1,4-dioxane, and cyclohexanone) were chosen as the standard substances for the determination of keeping time, and argon was chosen as the gas carrier.

Also, the curing kinetics of a haloid-containing oligomer based on 2DPP and HCE were studied. This oligomer (designated as 2DPP + HCE) was also cured by DDM at a stoichiometric ratio of DDM to 2DPP + HCE.

The curing kinetics of the 2DPP + HCE/DDM system was studied by IR spectroscopy with a PerkinElmer spectrometer. So the quantitative mea-

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surements would not depend on the thickness of the oligomer layer put on the substrate, we applied an internal standard. As a measure of the content of epoxy groups, we accepted not the optical density of analytical band 920 cm^{-1} but its ratio to the optical density of a standard, for which the IR band of skeletal vibrations for the aromatic ring at 1510 cm^{-1} was used, as this concentration was constant in the curing process. The optical densities of an analytical band and bands of the standard were determined by a method of a baseline.⁴

The curing temperature of both systems was identical and equal to 393 K. In this case, the calculated value of D was equal to 1.78 for 2DPP + HCE/DDM and varied from 1.61 to 2.38 for EPS-1/DDM.³

RESULTS AND DISCUSSION

Let us consider the reaction in which particles of a chemical substance diffuse in a medium containing randomly located statistical nonsaturated traps. At contact of a particle (P) with a trap (T), the particle disappears. The nonsaturation of a trap means that the reaction $P + T \rightarrow T$ can repeat itself an infinite number of times. Usually, if the concentration of particles and traps is considered large or the reaction occurs with intensive stirring, the process can be considered a classical reaction of the first order. The samples for inverted gas chromatography were prepared by the dissolution of the oligomer and a curing agent in acetone, with the mixture of their solutions placed on a substrate and subsequently dried. Thus, the heterogeneity of the mixture existing in solution was fixed during the evaporation of the solvent and was kept in a solid-state curing reaction. In this case, it was possible to consider that the law of the concentration decrease of particles with time would look like²

$$c(t) \approx \exp(-At) \quad (1)$$

where A is a constant and t is the duration of the reaction.

However, if the concentration of the randomly located traps is small, by necessity there exist areas of space practically free from traps. The particles getting into these areas can reach the traps only during rather long times, and hence, the decrease in their number over the course of reaction will be slower. The formal analysis of this problem shows that the concentration of particles falls down under the law²

$$c(t) \approx \exp[-Bt^{d/(d+2)}] \quad (2)$$

which is dependent on the dimension of space d (where B is constant). It also indicates the presence of

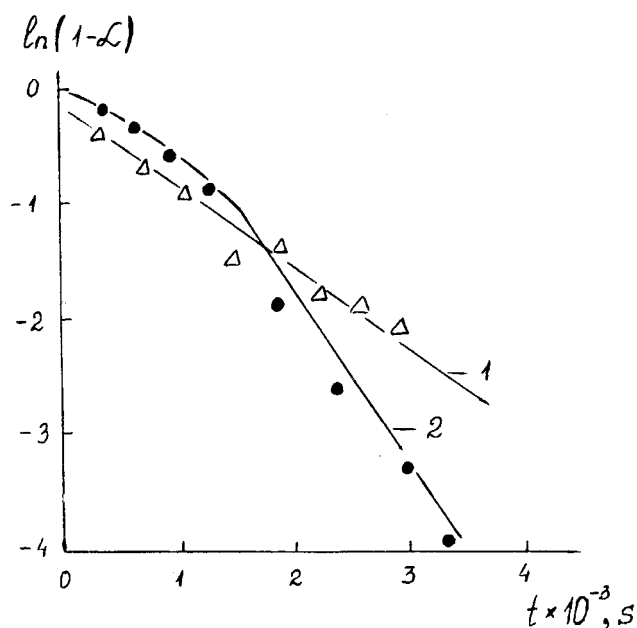


Figure 1 Dependence of $(1 - \alpha)$ on t in logarithmic coordinates corresponding to eq. (1) for the (1) 2DPP + HCE/DDM and (2) EPS-1/DDM systems.

large-scale fluctuations of density (heterogeneity) in the reaction medium.

If the traps can move, their mobility averages the influence of spatial heterogeneity, so the assumption resulting from eq. 1 will be carried out better. In this case, the concentration of particles falls down under the combined law.²

$$c(t) \approx \exp(-At) \exp[-Bt^{d/(d+2)}] \quad (3)$$

An attempt to describe the kinetic curves $[\alpha(t)]$ for the 2DPP + HCE/DDM and EPS-1/DDM systems within the framework of eq. (1)–(3) was undertaken. In this case, we supposed that

$$c(t) = 1 - \alpha \quad (4)$$

In Figure 1, the dependence of $\ln(1 - \alpha)$ on t , corresponding to eq. (1), for the 2DPP + HCE/DDM and EPS-1/DDM systems are given. As follows from the given plots, the curing kinetics of the 2DPP + HCE/DDM system were well described by the linear dependence in the coordinates of Figure 1, whereas the dependence of $[\ln(1 - \alpha)](t)$ for the EPS-1/DDM system failed to linearize. This means that the homogeneous curing reaction of the 2DPP + HCE/DDM system, described by eq. (1) under the previously mentioned conditions, was a classical reaction of the first order proceeding in a reaction medium with small density fluctuations.

Attempts to linearize the dependence of $(1 - \alpha)$ on t for the EPS-1/DDM system with eq. (2) and (3) did

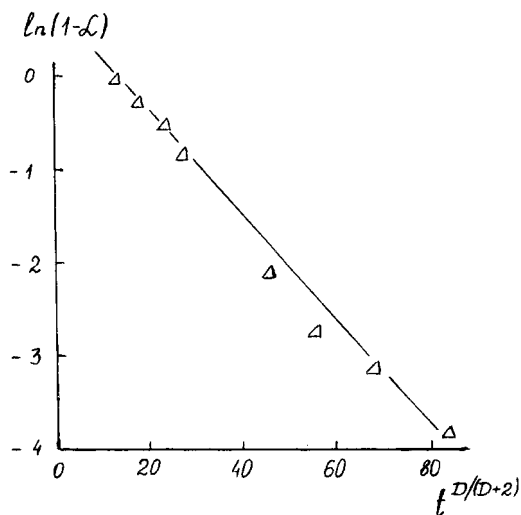


Figure 2 Dependence of $(1 - \alpha)$ on parameter $t^{D/(D+2)}$ in logarithmic coordinates corresponding to eq. (2) for the EPS-1/DDM system.

not result in success. So, the following assumption was made. Equation (2) describes kinetics of low-molecular substance reactions with large density fluctuations in a Euclidean space with dimension d (3 in the considered case). If we assumed that the formation of fractal clusters (microgels) with dimension D defined the course of the curing reaction in a fractal space with dimension D , the dimension d in eq. (2) would be replaced by D . The dependence of $\ln(1 - \alpha)$ on $t^{D/(D+2)}$, corresponding to eq. (2) with the mentioned replacement, is given in Figure 2. In such a treatment, the scaling relationship (8) gave the linear correlation, and this circumstance pointed out that the nonhomogeneous curing reaction of the EPS-1/DDM system proceeded with large density fluctuations in a fractal space with dimension D . This basically distinguishes the mentioned reaction from the reactions of fractal objects in Euclidean spaces, and the principle itself is similar to the formation of structures on fractal lattices.⁶

With the determined values of factors A and B from the slopes of the corresponding linear plots of Figures 1 and 2, it was possible to theoretically describe the kinetic curves $[\alpha(t)]$ by means of eq. (1) and (2) for the 2DPP + HCE/DDM and EPS-1/DDM systems accordingly. The comparison of the values calculated by this method and the experimentally received curves for both examined systems is given in Figure 3. As follows from the plots shown in Figure 3, there was good correspondence between the theory and experiment.

With regard to the construction of the theoretical curve $\alpha(t)$ for the EPS-1/DDM system, it is necessary to make an important remark. As follows from eq. (2), at $t = 0$ $c(t) = 1$ or $(1 - \alpha) = 1$, that is at $t = 0$, $\alpha = 0$, which is obvious. However, it follows from the plot of

Figure 2 that the straight line $[\ln(1 - \alpha)](t^{D/(D+2)})$ is extrapolated to $\ln(1 - \alpha) = 0$ (or $\alpha = 0$) at the finite value of $t^{D/(D+2)}$ equal to about 12. It means that the nonhomogeneous curing reaction of the EPS-1/DDM system had a period of induction (t_{in}) estimated at approximately 150 s. The physical basis of such an effect was clear. In the beginning of the curing reaction (at $t = 0$), there were no fractal clusters (microgels), in the reaction mixture, and it was possible to consider the available molecules of oligomer and curing agent either as the points or as the short rods (one-dimensional objects). The formation of microgels, creating the fractal reaction space, needed a certain time, which was the period of the theoretical curve $\alpha(t)$. So, it was necessary to use not the actual time of reaction t but the difference $t - t_{in}$.

The calculation of the theoretical curve $\alpha(t)$ under the reaction condition proceeding in Euclidean space [the use in eq. (2) of $d = 3$ instead of D] gave a faster curing reaction. The curve $\alpha(t)$ for this case is shown in Figure 3 with the broken line. It is easy to see the reasons of the various courses of the $\alpha(t)$ curves in Euclidean and fractal spaces in frameworks of the fractal analysis. When the trajectory of the diffusive movement of oligomer and curing agent molecules as a trajectory of random walks is considered, the number of sites $\langle S \rangle$ visited by such walks is proportional to⁷

$$\langle S \rangle \approx t^{d_s/2} \quad (5)$$

where d_s is the spectral dimension of space describing its connectivity.⁸

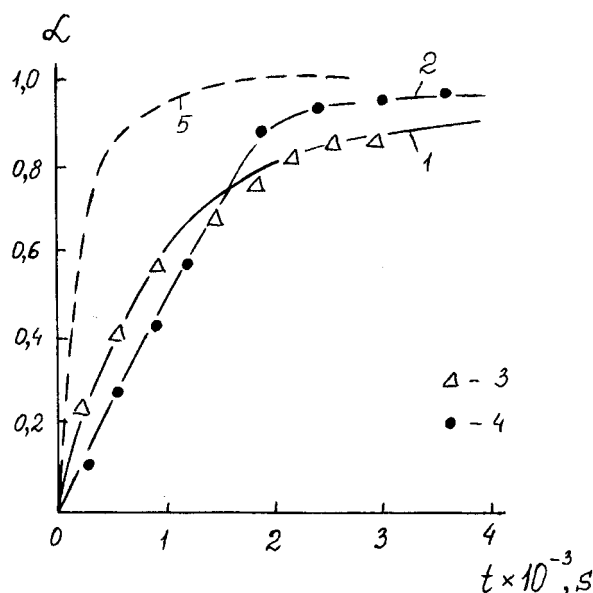


Figure 3 (1 and 2) Experimental and (3, 4, and 5) theoretical kinetic curves $[\alpha(t)]$ for the (1 and 3) 2DPP + HCE/DDM and (2, 4, and 5) EPS-1/DDM systems. Curve 5 corresponds to the curing reaction of the EPS-1/DDM system in a Euclidean space.

For a Euclidean space, $d_s = 3$,⁹ and for cured microgels, $d_s = 1.33$.⁸ It follows from eq. (5) that the value $\langle S \rangle$, which can be treated as the number of contacts of reacting molecules, is proportional to $t^{1.5}$ in a Euclidean space and to $t^{0.655}$ in a fractal space. At the equal t the greater number of pointed contacts in a Euclidean space determines a faster curing reaction in comparison to a fractal space.¹⁰

Here we note an interesting detail. As shown in ref. 11, for an ideal phantom network, the following relationship is correct:

$$\frac{D}{D+2} = \frac{d_s}{2} \quad (6)$$

It is easy to see the obvious analogy between the parameters of eq. (2) (with the replacement of d with D) and eq. (6).

CONCLUSIONS

Thus, the results of this study show that the homogeneous reaction of crosslinked polymer curing proceeded in the medium with small density fluctuations

and the nonhomogeneous one proceeded in the medium with large density fluctuations. The nonhomogeneous curing reaction could be simulated in terms of the scaling eq. (2) as proceeding in a fractal space. In this case, its rate was sharply reduced in comparison with a similar reaction in a Euclidean space.

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