The Fractal Analysis of Curing Processes of Epoxy Resins

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ABSTRACT: The possibility of applying the models of the irreversible aggregation and the fractal analysis for the description of curing kinetics of haloid-containing epoxy polymers was shown. There are two different modes of curing (homogeneous and nonhomogeneous), responding to conditions D = const and D = variant as a function of reaction time (D is the fractal dimension of microgels). The first condition corresponds to one dimension of the formed microgels, and the second one corresponds to the distribution of these dimensions. The mode of curing is determined by the level of fluctuations of density in the reaction medium. It was also shown that the fractal reactions at curing can be of the two following classes: reactions of fractal objects and reactions in fractal space. The basic difference of the two mentioned classes of reactions is the dependence of their rate on the fractal dimension of reaction products. The application of the methods of the fractal analysis and the theory of percolation allows us to find out that the first gelation point by crosslinking polymers is a structural transition, which is realized at filling by microgels of the whole reaction space. The physical nature of the autoacceleration (autostopping) effect in curing reactions is determined. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2558–2568, 2004

Key words: curing of polymers; modeling; hologenated epoxides; microgels; networks; fractal analysis

INTRODUCTION

The models of irreversible aggregation have come into use in physics recently. These models were developed for the description of such practically important processes as flocculation, coagulation, polymerization, etc. (see, for example ref. 1). Many examples of the successful applications of these models for the description of a number of the real processes have been obtained.[2–8] Therefore, the use of the same models for the description of the polymerization processes, in particular, curing of crosslinked polymers, is of an undoubted interest. It should be noted that the application of the percolation and some other models for the decision of this problem has not given the expected results.[9]

In the mentioned models of the irreversible aggregation, such general concepts for the physical processes as scaling and classes of the universality are widely used.[10] The sense of scaling (scale invariance) consists of abstracting from the details of the structure and allocation of simple universal features which are characteristic for a wide class of systems. Frequently used scaling parameters (indices) are the fractal dimensions. The hypothesis of the universality is closely connected to the hypothesis of scaling, the essence of which comprises the following: if the same limiting conditions (interaction of parts of system) are characteristic of the mechanism of formation of different systems, then these systems get to one class of the universality of the physical phenomena. Two most widespread classes of the universality (types of aggregates) during the irreversible aggregation are the systems formed by the particle–cluster[11] and cluster–cluster[12,13] mechanisms the distinction of which follows from their name. Earlier, the methods of the fractal analysis, the scaling approach, and the models of the irreversible aggregation were successfully applied for the description of various aspects of physics of polymers. Such aspects are the behavior of macromolecular coils in solutions,[14–17] the description of polymerization kinetics and its basic final parameters,[18–21] and the interrelation of polymer structures in a solution and in a condensed state.[22–24] It is especially necessary to note the successful attempts of application of the methods of the fractal analysis for the description of curing reaction.[25–27]

The purpose of the present article was to apply the above-mentioned models for the description of a specific type of polymerization—formation of crosslinked networks of epoxy polymers. It will be made by using as an example two series of haloid-containing epoxy polymers.[28]

EXPERIMENTAL

The kinetics of curing of haloid-containing oligomers on the basis of hexachlorobenzene was studied. This

oligomer (EPS-1) was cured by 4,4'-diaminodiphenyl-methane (DDM) at the stoichiometric ratio of DDM : EPS-1. Haloid-containing diepoxide with conditional designation EPS-1 have the following chemical constitution:
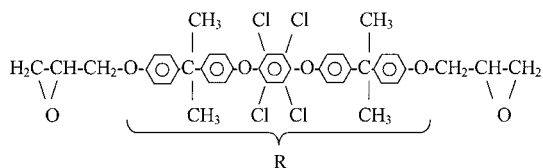
The curing kinetics of system EPS-1/DDM was studied by a method of inversed gas chromatography.[29] The basic parameter received from processing of the experimental data was the constant of reaction rate, k_r, determined for an interval of conversion degrees $\alpha = 0.1 \div 0.7$ of the kinetic curve degree of conversion time ($\alpha - t$). For the determination of k_r, the standard procedure was used: the dependences, α, on the reaction time, t, as $\lg[\alpha/(1 - \alpha)] = f(t)$, which appeared linear, were made. Then, the value k_r [see eq. (4)] was determined from a slope of these linear diagrams. Ketones (methyl ethyl ketone, 1,4-dioxsane, cyclohexanone) were chosen as the standard substance for the determination of retention time and argon as the gas carrier.

Besides, kinetics of curing of haloid-containing oligomer on a basis of diphenylolpropane and hexachloroethane was studied, having following chemical constitution:
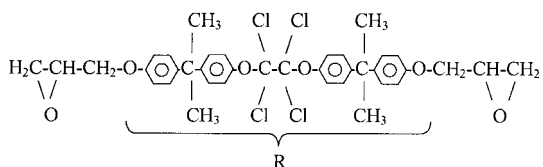

This oligomer (code designation 2DPP+HCE) also cured DDM at the stoichiometric ratio DDM : 2DPP+HCE.

The study of curing kinetics of system 2DPP+HCE/DDM was carried out by a method of IR spectroscopy by using a Perkin–Elmer spectrometer. To devoid the dependence on the thickness of a oligomer layer put on a substrate, a method of the internal standard was applied to measure the contents of epoxy groups; we accepted not only the optical density of an analytical band of 920 cm^{-1}, but also its ratio to the optical density of a standard, as which the IR band of skeletal vibrations for an aromatic ring 1510 cm^{-1} were used, as this concentration is constant during the process of curing. The optical densities of an analytical band and the bands of the standard were determined by a method of baseline.

Under curing of the mentioned epoxy oligomers by 4,4'-diaminodiphenylmethane, polymers with cross-linked structure are formed:
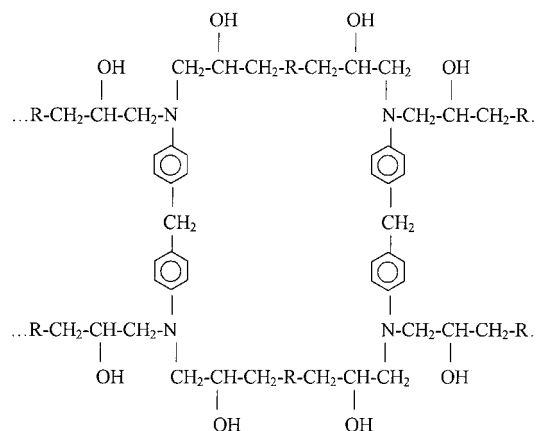
One can see that the hydroxyl groups (—OH) are formed, which according to the accepted models are a help to open the epoxy groups on the following scheme:
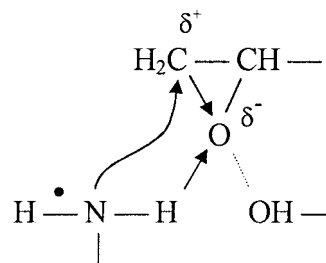

The following temperatures of curing T_{cur} were used: for system EPS-1/DDM, 383, 393, and 403 K; for system 2DPP+HCE/DDM, 295, 333, 353, 373, 393, and 513 K.

RESULTS AND DISCUSSION

In Figures 1 and 2, the kinetic curves $\alpha(t)$ for system 2DPP+HCE/DDM and EPS-1/DDM are given correspondingly. Two basic distinctions of curves $\alpha(t)$ for the pointed systems attract our attention. First, for the system 2DPP+HCE/DDM, the smooth decrease of a slope of curves $\alpha(t)$ is observed in the process of increasing t, whereas for system EPS-1/DDM, the linear dependence $\alpha(t)$ up to the large (about 0.8) values α is observed. Second, if the limiting degree of conversion of curing reaction for system 2DPP+HCE/DDM is the function of T_{cur} (the more T_{cur}, the more this degree), then for system EPS-1/DDM, such a dependence is not present, and at all used T_{cur}, the maximum values $\alpha \approx 1$ are observed.

Consider the reasons of the mentioned distinctions involving the representations of the models of the irreversible aggregation and of the fractal analysis. In

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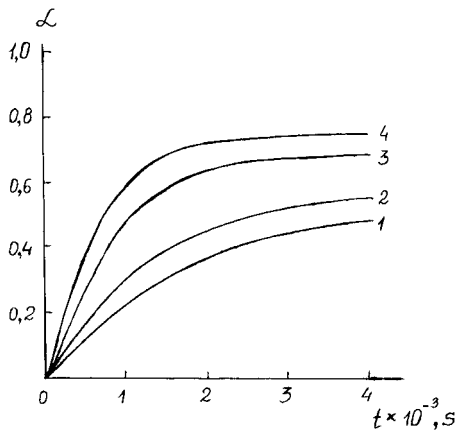
Figure 1 Kinetic curves $\alpha(t)$ for system 2DPP+HCE/DDM at curing temperatures: 353 (1), 373 (2), 393 (3), and 513 K (4).

terms of the fractal analysis, the kinetics of polymerization is described by a general relationship[18]:
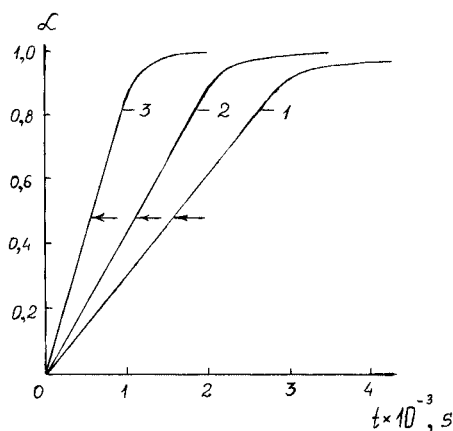
$$\alpha \sim t^{(3-D)/2} \qquad (1)$$

where D is a fractal dimension formed at the curing of a cluster, so-called microgel.[27,30]

The formal kinetics of curing within the framework of the traditional approaches are formulated in such a way:

$$\frac{d\alpha}{dt} = -k_r(1 - \alpha) \qquad (2)$$

Differentiating relationship (1) on t, we receive

$$\frac{d\alpha}{dt} \sim t^{(1-D)/2} \qquad (3)$$

Figure 2 Kinetic curves $\alpha(t)$ for system EPS-1/DDM at curing temperatures: 383 (1), 393 (2), and 403 K (3). The arrows points the first gelation point.

The combination of relationship (2) and (3) allows us to receive the equation connecting values of D and the kinetic parameters of the curing process

$$t^{(D-1)/2} = \frac{c_1}{k_r(1 - \alpha)} \qquad (4)$$

where c_1 is found constant from the boundary conditions.

Now it is possible to calculate value D, using the reaction rate constant k_r for the studied systems given in ref.[28] as a function t or α. The calculation has shown the basic distinction of behavior D, which is characteristic of the microgels structure, for system 2DPP+HCE/DDM and EPS-1/DDM. For the first system, the value D does not depend on α at an initial part (approximately up to $\alpha \approx 0.7$) of curve $\alpha(t)$, but is the function of T_{cur}. So, in the interval $T_{cur} = 295 \div 513$ K, the value D changes within the limits of $1.22 \div 1.95$. Note that the values D calculated in this way correspond well to the values determined by a method of small-angle neutron scattering in ref.[26]. It means that the increase of curing temperature determines the formation of more compact microgels at smaller intervals t. For the system EPS-1/DDM, the similar (but weaker) dependence on T_{cur} is observed, but simultaneously there appears clearly expressed dependence D on t. So, in an interval of curing time $300 \div 3600$ s, the value D varies in such a way: at $T_{cur} = 383$ K, $D = 1.65 \div 2.24$, at $T_{cur} = 393$ K, $D = 1.60 \div 2.38$, and $T_{cur} = 403$ K, $D = 1.51 \div 2.42$. In Figure 3, the modeling calculations of a curve $\alpha(t)$ are given at $T_{cur} = 383$ K for different situations. So, curve 1 is an experimental curve $\alpha(t)$. The calculation according to
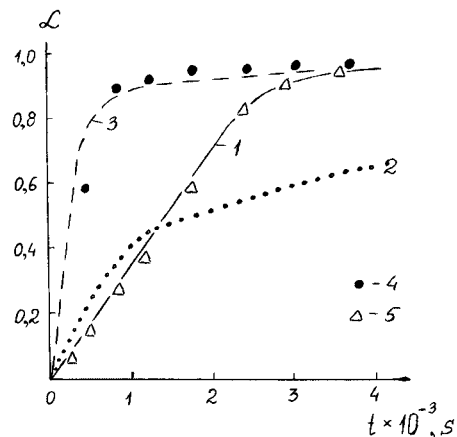
Figure 3 Comparison experimental (1, 4) and modeling (2, 3, 5) kinetic curves for system EPS-1/DDM. 1, experimental curve for $T_{cur} = 383$ K; 2, calculation on a relationship (1), under condition of $D = $ const $= 1.76$; 3, calculation on a relationship (1) under condition of $D = $ const $= 2.24$; 4, experimental data for $T_{cur} = 403$ K; 5, calculation on a relationship (1) with D, calculated in eq. (4).

relationship (1) under condition of D = const = 1.76 gives curve 2, which is not in agreement with the experimental curve, but is qualitatively very similar to curves $\alpha(t)$ for the system 2DPP+HCE/DDM (Fig. 1). The latter effect, proceeding from the condition of D = const = 2.24, gives curve 3, which again does not correspond to the experimental curve $\alpha(t)$, but is very similar to the curve $\alpha(t)$ for the same system at T_{cur} = 403 K (Fig. 2). This fact proves to be true by the comparison of curve 3 with experimental points 4 for the pointed experimental curve $\alpha(t)$. This comparison shows that the form of the curve $\alpha(t)$ at the initial parts of forming microgels in our case is characterized by its fractal dimension D. At last, the calculation by relationship (1), but with the variable value D, determined according to eq. (4), gives the excellent correspondence with the experiment (points 5). Modeling curves $\alpha(t)$ and their comparison with the appropriate experimental curve given in Figure 3 confirm the above assumption about the reason of the different form of the kinetic curves for systems 2DPP+HCE/DDM and EPS-1/DDM.

Consider the reasons of the different dependences $D(t)$ for the studied systems. As it was mentioned above, the common variation D for both systems as a function and t and T_{cur} makes D = 1.22 ÷ 2.42. This interval D corresponds to the aggregation mechanism of a cluster–cluster type.[10] It was shown[31] that dimension D of the cluster formed by the joining of two clusters with dimensions D_1 and D_2 ($D_1 \geq D_2$) in the case of the mentioned aggregation mechanism is determined in such a way

$$D = \frac{d(2D_1 - D_2)}{d + 2(D_1 - D_2)} \quad (5)$$

where d is the dimension of Euclidean space in which the process of clustering is considered. Obviously, in our case, d = 3.

From eq. (5), directly follows that the realization of condition D = const irrespective of t needs the realization of criterion:

$$D_1 = D_2 = D = \text{const} \quad (6)$$

For the realization of increase of D with increase t, it is required that at the previous stage of curing there should be clusters (microgels) in the system corresponding to the condition $D_1 \neq D_2$, or else the distribution of clusters' dimensions is required. So, the acceptation of the average dimension D = 1.64 at the previous stage needs an interval $D_1 ÷ D_2$ = 1.70 ÷ 1.58 (i.e., $\Delta D = D_1 - D_2$ = 0.12). The acceptation of average dimension D = 2.24 already needs an interval $D_1 ÷ D_2$ = 2.35 ÷ 2.12 (i.e., ΔD = 0.23) for the systems which are similar to EPS-1/DDM, in the process. Increasing t,

the average value of microgels' dimension D and the width of their distribution increase. Proceeding from these results, we have defined kinetics of curing which are similar to the observable system 2DPP+HCE/DDM (Fig. 1) and corresponding to the condition D = const as homogeneous, and similar to the observable for system EPS-1/DDM (Fig. 2) and corresponding to the condition D = variant as nonhomogeneous. One of the probable reasons determining the distinction of the mentioned types of curing kinetics is the different levels of fluctuation density in these systems.[32]

For the confirmation of this assumption, we have made an attempt to describe curves $\alpha(t)$, shown in Figures 1 and 2, in the frameworks of the scaling approaches for the reactions of low-molecular substance.[32] Consider the reaction in which particles P of a chemical substance diffuse in the medium containing the randomly located static nonsaturated traps T. By the contact of a particle P with a trap T, the particle disappears. Nonsaturation of a trap means that the reaction $P + T \rightarrow T$ can repeat itself an infinite number of times. It is usually considered that the concentration of particles and traps is large or the reaction occurs at intensive stirring, and the process can be considered the classical reaction of the first order. It also means the presence of large-scale fluctuations of density (heterogeneity) in reaction medium. Samples for studies by inverse gas chromatography were prepared by the dissolution of oligomer and a curing agent in acetone, putting a mixture of their solutions on a substrate and subsequent drying. Thus, the heterogeneity of a mixture existing in a solution was fixed during the evaporation of the solvent and was kept in a solid-state reaction of curing. In a sense, traps T in studied reactions are supposed to form microgels and particles are supposed to form molecules of oligomer. In this case, it is possible to consider that the concentration decrease of particles decreases with time as[32]

$$c(t) \approx \exp(-At) \quad (7)$$

where A is constant, and t is the reaction time.

However, if the concentration of the randomly located traps is small, the space exists as areas, practically free from traps. The particles getting into these areas can reach the traps only during rather a long period of time and, hence, the decrease of their number in the course of reaction will be slower. The formal analysis of this problem shows that the concentration of particles falls down under the law[32]

$$c(t) \approx \exp(-Bt^{d/(d+2)}) \quad (8)$$

being dependent on the dimension of space d (B is constant).
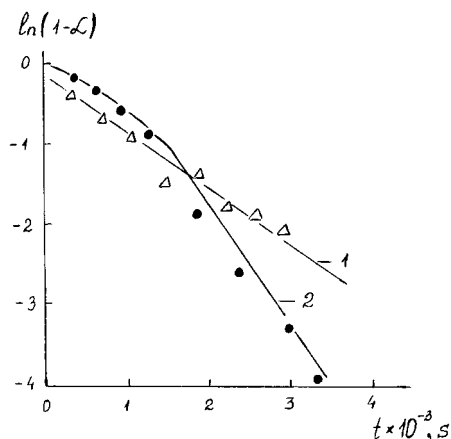
Figure 4 Dependences $(1 - \alpha)$ on reaction time t in logarithmic coordinates corresponding to eq. (7) for systems 2DPP+HCE/DDM (1) and EPS-1/DDM (2).

If the traps can move, their mobility averages the influence of spatial heterogeneity, so the assumptions resulting in (7) will be carried out better. In this case, the concentration of the particles drops under the combined law:[32]

$$c(t) \sim \exp(-At)\exp(-Bt^{d/(d+2)}) \qquad (9)$$

In Figure 4, the dependencies $\ln(1 - \alpha)$ on t, corresponding to eq. (7), for systems 2DPP+HCE/DDM and EPS-1/DDM cured at $T_{cur} = 393$ K, are given. As it follows from the given graphs, the kinetics of curing of the system 2DPP+HCE/DDM is well described by the linear dependence on coordinates of Figure 4, whereas dependence $[\ln(1 - \alpha)](t)$ for system EPS-1/DDM deviates from linearity. It means that the homogeneous reaction of curing of system 2DPP+HCE/DDM, described by eq. (7) under the above-mentioned conditions, is a classical reaction of the first order proceeding in reaction medium with the small fluctuations of density.

The attempts to linearize the dependence $(1 - \alpha)$ on t for system EPS-1/DDM with the use of eqs. (8) and (9) were not successful. It means that the pointed nonhomogeneous reaction proceeds in the reaction medium with large fluctuations of density, but is not described by eqs. (8) and (9) for low-molecular substances. Thus, the assumption about the connection of curing reaction type with a level of fluctuations of density of reaction medium is confirmed.

For the theoretical description of nonhomogeneous reaction of curing, the following assumption was made. Equation (8) describes kinetics of low-molecular substances reaction at large fluctuations of density in Euclidean space with dimension d (equal to 3 in the considered case). If we assume that the formation of fractal clusters (microgels) with dimension D defines a

course of curing reaction in a fractal space with dimension D, dimension d in eq. (8) should be replaced by D. The dependence $\ln(1 - \alpha)$ on $t^{D/(D+2)}$, corresponding to eq. (8) with the mentioned replacement, is given in Figure 5. In such a treatment, the scaling relationship (8) gives the linear correlation and this circumstance points out that the nonhomogeneous curing reaction of system EPS-1/DDM proceeds at the conditions of large fluctuations of density in fractal space with dimension D.

Hence, the fractal reactions of polymerization can be divided, as a minimum, into two classes: reactions of fractal objects (homogeneous), whose kinetics are described similarly to the curves shown in Figure 1, and reactions in a fractal space (nonhomogeneous), whose kinetics are described similarly to the curves shown in Figure 2. The reactions of the second class correspond to the formation of structures on fractal lattices.[33] The basic distinction of the pointed classes of reactions is the dependence of their rate on fractal dimension D of products forming during the reaction (macromolecular coils, microgels). The first class of reactions is well described by eq. (1). The example of such description is given in Figure 6 for the system 2DPP+HCE/DDM, cured at 393 K, under the following conditions: D = const = 1.78 and constant equal 8.06×10^{-3}. As can be seen, the rather good correspondence of an experimental and theoretical curve up to t = 2400 s is received where there is a change of a class of universality of the system owing to the gelation and the appropriate change of value D from 1.78 up to ~ 2.5.[34,35] Relationship (1) is deduced on the basis of the theoretical conclusions of article,[36] where it is supposed that the less D is, the less compact is the structure of a fractal cluster and there more are tree sites on the cluster surface which are accessible to reaction. In Figure 7, three modeling curves $\alpha(t)$, appropriate to
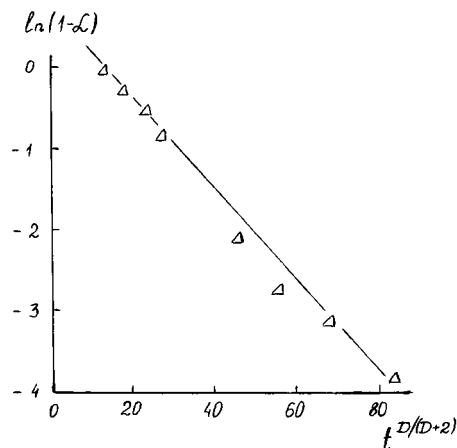
Figure 5 Dependence $(1 - \alpha)$ on parameter $t^{D/(D+2)}$ in logarithmic coordinates corresponding to eq. (8) for the system EPS-1/DDM.
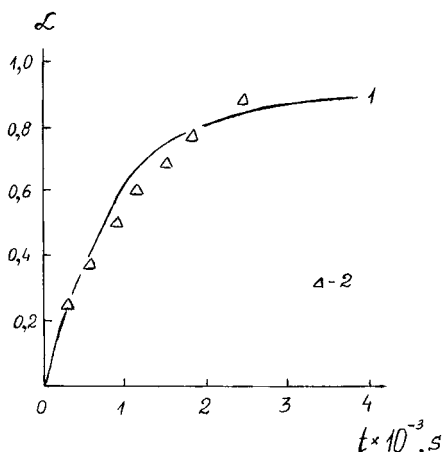
Figure 6 Comparison experimental (1) and calculated on a relationship (2) kinetic curves $\alpha(t)$ for system 2DPP+HCE/DDM.

eq. (1) with an identical constant for $D = 1.5$, 1.8, and 2.1, are shown. As it follows from the given curves, the increase in D really sharply reduces the rate of reaction and decreases α at the comparable values of t.

As to reactions in fractal spaces, here the situation is quite the opposite. As it is known,[37] to consider a trajectory of diffusive movement of oligomer and curing agent molecules as a trajectory of random walks, the number of sites $\langle S \rangle$, visited by means of such walks, is proportional to

$$\langle S \rangle \sim t^{d_s/2} \tag{10}$$

where d_s is a spectral dimension of space describing its connectivity.[38]

For Euclidean space, $d_s = 3$;[39] for cured microgels, $d_s = 1.33$.[38] From relationship (10), it follows that the value $\langle S \rangle$, which can be treated as a number of contacts
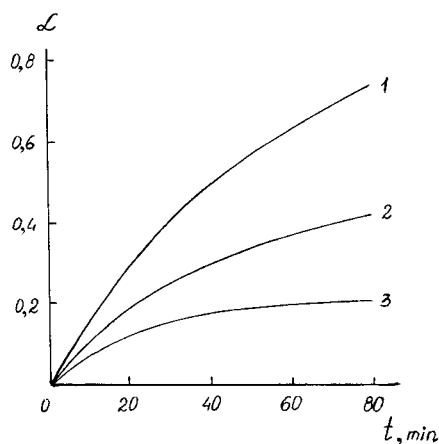
of reacting molecules, is proportional to $t^{1.5}$ in Euclidean and $t^{0.655}$ in fractal spaces. At identical t, the greater number of the pointed contacts in Euclidean space determines the faster curing reaction in comparison with a fractal space.[21]
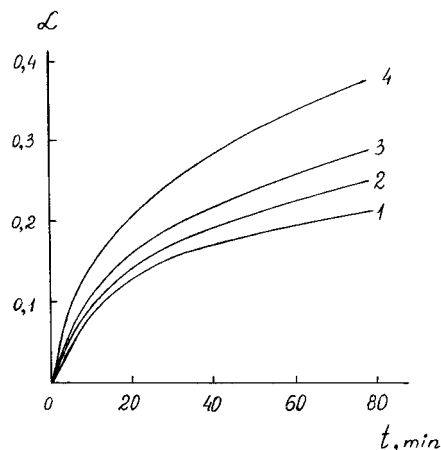
In this connection, we shall note an interesting detail. As shown in ref. [27] for an ideal phantom network, the relationship is correct:

$$\frac{D}{D+2} = \frac{d_s}{2} \tag{11}$$

It is easy to see the obvious analogy between the parameters of eq. (8) (at replacement d on D) and relationship (1).

In Figure 8, the curves $\alpha(t)$, calculated according to eq. (8) under the condition $B = $ const for $D = 1.5$, 1.8, and 2.1 and also for $d = 3$, are given. It is easy to see that in accordance with the above-stated treatment the rate of reaction increases in the process of an increase in D and reaches the greatest value in Euclidean space at $d = 3$. It should be noted that in reactions of fractal objects according to relationship (1) at $D = d = 3$ α = const, and in view of a boundary condition $\alpha = 0$ at $t = 0$, it means that such reactions for three-dimensional Euclidean objects do not proceed at all.

Further, we shall consider the conditions of formation of microgels in curing reactions of haloid-containing epoxy polymers. The first theory of crosslinking of polymers and gelation, developed by Carothers and Flory, considers a gelation point as a formation of an infinite network of chemical links.[30] As this theory does not always correspond to the experimental data, the concept of the gelation period was suggested. According to the pointed concept, there are two gelation points. The first of them corresponds to the moment of appearance of branched crosslinked clusters (micro-

Figure 7 Modeling curves $\alpha(t)$ for reactions of fractal objects calculated on a relationship (1) at $D = 1.5$ (1) and 1.8 (2), and 2.1 (3).

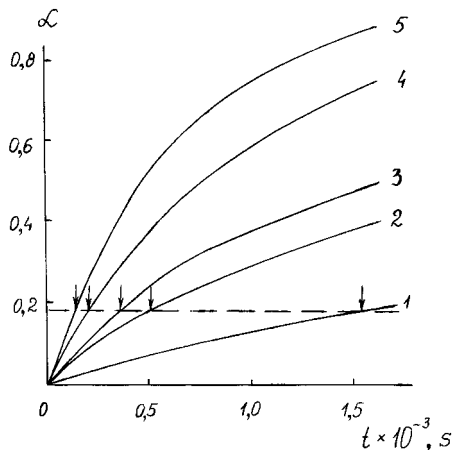

Figure 8 Modeling curves $\alpha(t)$ for reactions of fractal space, calculated on relationship (1) at $D = 1.5$ (1), 1.8 (2), 2.1 (3) and $d = 3$ (4).
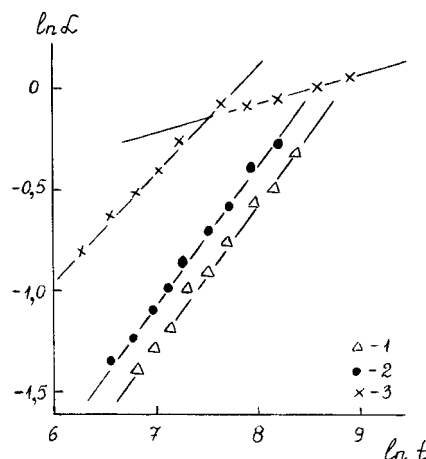
gels) particles, characterized by infusibility and indissolubility in the reaction medium. The second point of gelation responds to a considerably later stage of reaction—crosslinking the very microgel particles and transformation of fluid system with crosslinked clusters into elastic polymer.[40] This reaction is determined by the total area of microgel particles and is described as a particle reaction of the first order by the Avrami–Erofeev equation. The theoretical conditions of achievement of the first gelation point with the inclusion of methods of fractal analysis and theory percolation will be considered below.[39,41]

In Figure 9, the kinetic curves $\alpha(t)$ for system 2DPP+HCE/DDM at five temperatures of curing are given. As it follows from relationship (1), if we put the dependence $\alpha(t)$ on the graph in double-logarithmic coordinates, in the case of their linearity from a slope of these diagrams, it is possible to estimate values of D. In Figure 10, such dependences for system 2DPP+HCE/DDM are given at three temperatures of curing. As it follows from these graphs, the increase of T_{cur} is accompanied by the decrease of a slope of the linear graphs $\alpha(t)$ in double-logarithmic coordinates or an increase of D. In the interval $T_{\mathrm{cur}} = 295 \div 513$ K, the increase D from 1.22 up to 1.95 is observed, as was mentioned above. For the highest $T_{\mathrm{cur}} = 513$ K, the discrete change of a slope of the graph corresponding to the increase of D from 1.95 up to ~ 2.68 is observed. Such a transition in terms of the fractal analysis corresponds to the second gelation point,[34,35] (i.e., a formation of a network which is spreading over all the sample). From Figure 10, it also follows that the second gelation point for $T_{\mathrm{cur}} = 353$ and 373 K in scale t of Figure 9 is not reached.

In Table I the experimental values of gelation time t_1^e for the first gelation point, determined by a method of IR spectroscopy, are given. These values in Figure 9

Figure 10 Dependences of a degree of conversion α on time of reaction t in double logarithmic coordinates corresponding to a relationship (1) for system 2DPP+HCE/DDM at $T_{\mathrm{cur}} = 353$ (1), 373 (2), and 513 K (3).

are marked by vertical arrows. It is interesting to note that the mentioned gelation point for all T_{cur} is reached approximately at an identical value of α, equal to ~ 0.19. To explain this observation, we use the percolation theory[41] and the model irreversible aggregation,[42] appropriate to the simultaneous growth of many clusters, that will correspond to the real situation at curing of epoxy polymers. According to the model,[42] the growth of such clusters stops in the case of their contact. Therefore, we can consider the first gelation point, characterized by time t_1^e, as a point in which the contact of many spherical microgels is realized. According to the percolation theory,[41] the volume fraction of such spheres f can be determined from the relationship:

$$fx_c \approx 0.15 \qquad (12)$$

where x_c is a percolation threshold.

If we assume that the time t_1^e corresponds to a threshold of percolation of spherical microgels densely filling the reactionary space, then $x_c = 0.19$ and $f = 0.79$. Such value f really corresponds to dense

Figure 9 Kinetic curves $\alpha(t)$ for system 2DPP+HCE/DDM at $T_{\mathrm{cur}} = 333$ (1), 353 (2), 373 (3), 393 (4), and 513 K (5). The arrows points the first gelation point.

TABLE I
The Dependence of Time of Achievement of the First Gelation Point t_1^e from Curing Temperature T_{cur} for System 2DPP+HCE/DDM

T_{cur} (K)	$t_1^e \times 10^{-3}$ (s)
295	5.04
333	1.44
353	0.36
373	0.30
393	0.18
513	0.12

packing of spheres of about an equal diameter.[43] This implies that the first gelation point is characterized by the termination of microgels densely filling the reactionary space, at their contact.

From relationship (1), it is possible to write down

$$t_1^T \sim \left(\frac{\alpha_1}{\eta_0}\right)^{2/(3-D)} \tag{13}$$
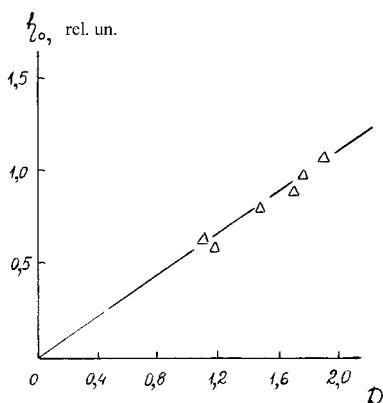
where t_1^T is a theoretical value of time of the first gelation point achievement, α_1 is value α, corresponding to t_1^e and equal to ~ 0.19, η_0 is viscosity of reaction medium, which enters into complex proportionality factor of relationship (1), representing the product: $K_1\eta_0 c_0$, where K_1 is a constant, and c_0 is initial concentration of reagents.

From relationship (13), it follows that the value t_1^T is defined by two parameters: η_0 and D. Therefore, it is possible to assume that the pointed parameters are connected by the certain correlation. Such correlation is given in Figure 11, and a very strong increase η_0 follows in the process of increasing D, analytically expressed as:
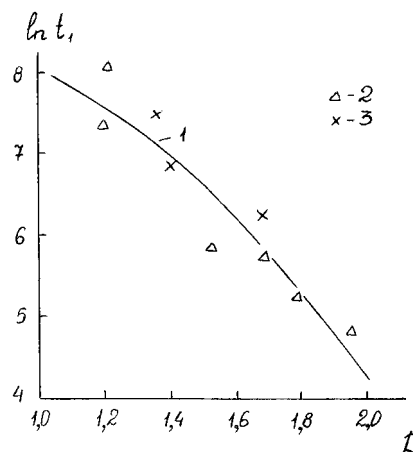
$$\eta_0^{1/8} = 0.585D \tag{14}$$

Note that the extrapolation of dependence $\eta_0^{1/8}(D)$ to $\eta_0 = 0$ gives $D = 0$ [i.e., the zero viscosity is reached in a limit of low-molecular substances (points or zero-dimensional objects)].

The combination of relationships (13) and (14) allows us to estimate the value t_1^T. The comparison of experimental and theoretical dependences of gelation time for its first point from fractal dimension of microgels D for system 2DPP+HCE/DDM is given in Figure 12. As it follows from this comparison, the good correspondence to the theory and experiment is
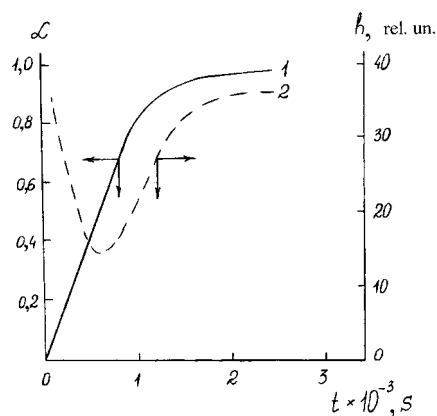

Figure 12 Comparison experimental (1) and theoretical (2, 3) dependences of gelation time t_1 on fractal dimension of microgels D in logarithmic coordinates systems 2DPP+HCE/DDM (2) and EPS-1/DDM (3).

received (the use of logarithmic scale for t_1 was done out of the reasons of convenience).

In Figure 2, the kinetic curves $\alpha(t)$ at three values T_{cur} for system EPS-1/DDM are shown; in Figure 13 is shown the comparison of dependences of peak height of inverted gas chromatography $h(t)$ and curve $\alpha(t)$ for $T_{cur} = 403$ K. The minimum of dependence $h(t)$ corresponds to time t_1^e on a scale t. In Figure 2, these values are marked by arrows. Again value t_1^e is reached under condition $\alpha_1 = $ const, but the absolute values, in this case, are equal to ~ 0.47. If we use eq. (12) for estimating the value f, then for system EPS-1/DDM, we shall receive $f \approx 0.32$. Such value f will well correspond to a volume fraction of spheres for chain structures consisting of overlapping spherical microgels.[43] Thus, in homogeneous and nonhomogeneous reactions of curing, the different types of percolation structures of microgels are formed, subsequently, at the

Figure 11 A correlation between viscosity of reaction medium η_0 and fractal dimension of microgels D for system 2DPP+HCE/DDM.

Figure 13 Kinetic curve $\alpha(t)$ (1) and dependence of height h of inverted gas chromatography on reaction time t (1) for system EPS-1/DDM, curing at $T_{cur} = 403$ K.

transition of epoxy polymers in the condensed state forming globules.[30] Again, such a distinction should be connected to the different levels of fluctuation of density in reaction medium.[32]

As a conclusion of the present article, we shall consider the fractal treatment of the crosslinking polymers. There are two modified variants of eq. (2), which take into account the course of curing reactions with autoacceleration or slowing-down[44]

$$\frac{d\alpha}{dt} = k_r(1 - \alpha)(1 + c\alpha) \qquad (15)$$

$$\frac{d\alpha}{dt} = k_r(1 - \alpha)(1 - \xi\alpha) \qquad (16)$$

where c and ξ are characteristics of effects of autoacceleration and autostopping, accordingly.

By using the same procedure, as well as at the deduction of eq. (4), we receive

$$t^{(D-1)/2} = \frac{c_r}{k_r(1 - \alpha)(1 + c\alpha)} \qquad (17)$$

$$t^{(D-1)/2} = \frac{c_r}{k_r(1 - \alpha)(1 - \xi\alpha)} \qquad (18)$$

where c_2 is a constant.

From the comparison of eqs. (4), (17), and (18), it is easy to see that in the case of D = const (homogeneous reaction of curing), the members in the numerator of eqs. (17) and (18) [$(1 + c\alpha)$ and $(1 - \xi\alpha)$, accordingly] are equal to 1. In the case of $D = D(t)$ (nonhomogeneous reaction of curing), two ways of the description of kinetic curves $\alpha(t)$ (see Figs. 1 and 2) are possible. The first way provides the application of function $D(t)$, determined by some independent way, and then $c = 0$
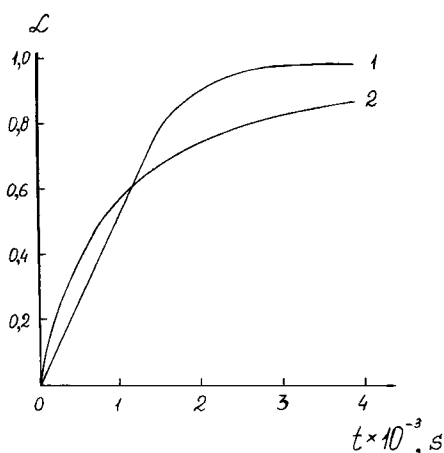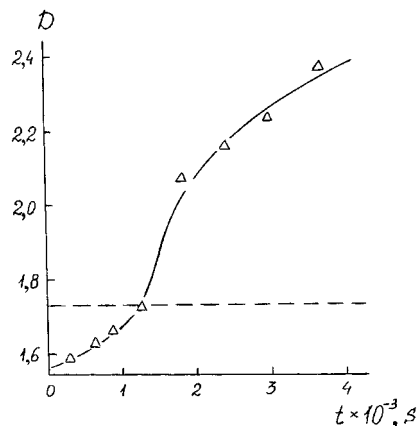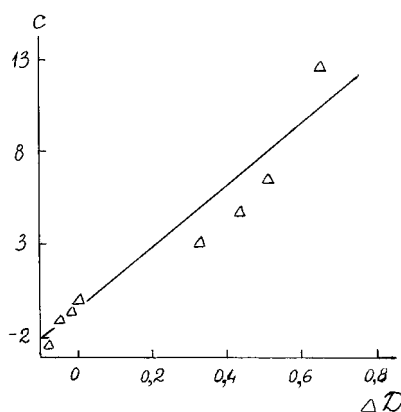

Figure 15 Dependence of the fractal dimension of microgels D on the reaction time t for system EPS-1/DDM. Broken line shows the condition D = const for system 2DPP+HCE/DDM.

and $\xi = 0$. The second way assumes D = const, and the value D can be arbitrary chosen from the interval $D(t)$ for the concrete curing reaction. The comparison given in Figure 14 of kinetic curves for system 2DPP+HCE/DDM and EPS-1/DDM shows that at $t < 1200$ s; the curing reaction for the first system proceeds faster than for the second system, and for $t > 1200$ s, the opposite occurs. It means that at curing of system EPS-1/DDM at $t < 1200$ s, the effect of autostopping is observed, and at $t > 1200$ s, effect of autoacceleration is observed. Having calculated a value of D at $t = 1200$ s, on known values k_r and α from eq. (4), and believing it to be a constant, it is possible to estimate parameters c and ξ in eqs. (17) and (18) accordingly. Actually speaking, at such an approach, the use of the two mentioned equations is no longer required: if in eq. (17), $c < 0$, it means the presence of autostopping effect, and if $c > 0$, it means the presence of autoacceleration. In Figure 15, the dependence $D(t)$ for system EPS-1/DDM calculated from eq. (4) is given, and the broken line shows a constant value D for the system 2DPP+HCE/DDM. The data show that when $t = 1200$ s, the value D for both of the systems is equal; when $t < 1200$ s, the value D for the system EPS-1/DDM is lower than the corresponding value for the system 2DPP+HCE/DDM, and when $t > 1200$ s, the opposite occurs. The comparison of the graphs in Figures 1 and 2 enables us to make the next two conclusions. First, the effect of autoacceleration (autostopping) can be realized only in reactions of nonhomogeneous curing. In reactions of homogeneous curing (D = const), $c = 0$ and $\xi = 0$. The value c (or ξ) is defined by the relation of the values D in homogeneous (D_{hom}) and nonhomogeneous (D_{non}) reactions of curing. In the case when $D_{hom} > D_{non}$, $c < 0$, the effect of autostopping is observed; in the case where $D_{non} > D_{hom}$, $c > 0$,

Figure 14 Kinetic curves $\alpha(t)$ of the process of curing for systems EPS-1/DDM (1) and 2DPP+HCE/DDM (2).

Figure 16 Correlation between the characteristic of autoacceleration (auto-stopping) c (or ξ) and difference ΔD for system EPS-1/DDM.

the effect of autoacceleration is seen. Thus, in the suggested treatment both the absolute value and the sign c are defined by the given difference $D_{hom} - D_{non} = \Delta D$. In Figure 16, the correlation c (ΔD) for the system EPS-1/DDM is given, where the value c is calculated from eq. (17) on the condition $D = $ const $= 1.75$. As it was supposed, the negative values ΔD correspond to the negative magnitudes c (autostopping) and the positive values D correspond to the positive magnitudes c (autoacceleration). The correlation of absolute values ΔD and c is well approximated by a linear dependence (Fig. 16).

CONCLUSION

Thus, the results of the present article have shown the possibility of application of the models of the irreversible aggregation and the fractal analysis to the description of curing kinetics of haloid-containing epoxy polymers. There are two different modes of curing (homogeneous and nonhomogeneous), responding to conditions $D = $ const and $D = $ variant as a function of reaction time t. The first condition corresponds to the one dimension of formed microgels, and the second one corresponds to the distribution of these dimensions. The mode of curing is determined by a level of fluctuations of density in reaction medium. Besides, it was shown that the fractal reactions at curing of crosslinked polymers can be of two classes: reactions of fractal objects and reactions in fractal space. The basic difference of the two mentioned classes of reactions is the dependence of their rate on the fractal dimension of reaction products.

The application of the methods of the fractal analysis and percolation theory allows us to find out that the first gelation point of crosslinked polymers is a structural transition, which is realized at filling by microgels of reaction space. The gelation time in the

mentioned point is defined by fractal dimension D of microgels. Between values D and the viscosity of reaction medium η_0, there is a correlation: the increase of D causes a strong increase in η_0.

The physical nature of autoacceleration (autoslowing down) effect in curing reactions was determined. This effect is realized only for nonhomogeneous reactions of curing and its sign and intensity are defined by the relation of the values D when $D = $ const and $D = D(t)$. Otherwise, the mentioned factors are defined by the character of changing of the microgels structure in the process of curing together as the function of time.

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