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THE TRANSITION NANOREACTOR-NANOPARTICLE IN EPOXY POLYMERS CURING PROCESS

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Abstract. It has been shown that for curing reaction in fractal space the reaction rate constant reduction is typical. Another typical feature of this reaction is the formation of a large number of microgels with smaller molecular weight in comparison with reaction in Euclidean space at the same conversion degree. The dimensional border between nanoreactor and nanoparticle for the curing reaction under consideration has been obtained.

Keywords: epoxy polymer, curing reaction, fractal space, nanoreactor, nanoparticle.

1. Introduction

In paper [1] it has been shown that the epoxy polymers curing can occur in both Euclidean three-dimensional space and the fractal one. In the last case the space dimension is equal to fractal dimension D of microgels, formed in the curing process. The main difference of kinetic curves named conversion degree-reaction duration (Q - t) in the last case is practically linear dependence $Q(t)$ almost up to gelation point and variation (increase) of D value on this part of curve $Q(t)$. The purpose of the present paper is further study of epoxy polymers curing in fractal space, in particular the reaction rate constant k_p and microgels self-diffusivity D_{sd} changing character on the example of haloid-containing oligomer on the basis of hexachlorobenzene curing [2].

2. Experimental

The kinetics of curing of haloid-containing oligomer on the basis of hexachlorobenzene (conditional designation EPS-1) was studied. This oligomer was cured by 4,4'-diaminodiphenylmethane (DDM) at stoichiometric ratio of DDM:EPS-1 [2].

The curing kinetics of system EPS-1/DDM was studied by the method of inverse gas chromatography

(IGC) [2]. The basic parameter received from processing of the experimental data was the conversion degree Q as a function of curing duration t , determined for an interval of kinetic curve $t \leq 3 \cdot 10^3$ s. Ketones (methyl ethyl ketone, 1,4-dioxane, cyclohexanone) were chosen as standard substances for the determination of retention time and argon was taken as a gas carrier.

The curing temperature of the system EPS-1/DDM was accepted equal to 393 K. The microgels fractal dimension D value varied within the limits of 1.61–2.38 [1].

3. Results and Discussion

As was shown in paper [1], the value of reaction rate constant k_p within the range $Q \approx 0$ –0.70 for curing reaction in Euclidean space is constant. The relation between k_p , Q and D has the following form [3]:

$$t^{(D-1)/2} = \frac{C_1}{k_p(1-Q)} \quad (1)$$

where C_1 is a constant.

For the system EPS-1/DDM the average value $k_p = 0.97 \cdot 10^{-3}$ mol·l/s was determined [2] by IGC method. From the equation (1) the value C_1 can be determined at the average values of the parameters included into it: $t = 1.5 \cdot 10^3$ s, $D = 1.99$ and $Q = 0.35$. In this case $C_1 = 0.0244$ mol·l/s. As the calculations showed, k_p reduction from $4.16 \cdot 10^3$ to $0.76 \cdot 10^{-3}$ mol·l/s was observed within the range $t = (0.5$ – $2.5) \cdot 10^3$ s. The range of the above indicated values D assumes that the microgels formation occurs according to the cluster-cluster mechanism, *i.e.* by the large microgel formation from the smaller ones [4]. In this case the microgels molecular weight MW value is determined according to the following scaling relationship [5]:

$$MW \sim Q^{2/(3-D)} \quad (2)$$

The microgel gyration radius R_g is connected with MW according to the following relationship [4]:

$$R_g \sim MW^{1/D} \sim Q^{2/D(3-D)}. \quad (3)$$

The obtained results allow to carry out the system EPS-1/DDM curing kinetics analysis within the frameworks of irreversible aggregation models [6]. In a general case the relationship between k_p and R_g can be presented as follows [6]:

$$k_p \sim R_g^{2\omega}. \quad (4)$$

Exponent ω is defined by the parameters describing clusters (microgels) motion in space and their structure. This intercommunication has the following form [6]:

$$2\omega = -\gamma + d - D_w \quad (5)$$

where γ characterizes the dependence of microgels self-diffusivity D_{sd} on their sizes ($D_{sd} \sim R_g^{-\gamma}$), d is dimension of the space, in which the curing reaction occurs, D_w is dimension of microgels random walk trajectory.

For the reactions in Euclidean space $d = 3$, $D_w = 2$ (Brownian motion of microgels), $\gamma = -1$ and then $\omega = 0$. This means, that in the given case the condition should be fulfilled:

$$k_p = \text{const} \quad (6)$$

The condition (6) is confirmed experimentally (k_p value is not changed at R_g increasing) [2]. For the curing reaction proceeding in fractal space the situation differs fully from the described above. This aspect attains special meaning within the frameworks of nanochemistry [7], therefore deserves consideration in more detail.

As is known [7], in nanochemistry there are two fundamental notions – nanoparticle and nanoreactor: the first characterizes dimensional parameter while the second defines nanoobject function. Thus, iron cluster loses almost fully its specific properties (ionization energy, magnetism) and approaches metallic iron with a number of atoms in cluster $n = 15$. At $n > 15$ it remains a nanoobject in dimensional sense, but loses “nanoreactor” qualities, for which properties become a size function. In Fig. 1 the dependence of curing rate constant k_p on microgels diameter $2R_g$, which has a very specific form, is adduced. Within the range of microgels (although the term “nanogel” is more precise) diameters less than 10 nm, the value k_p is a clearly expressed rapidly decreasing function of diameter $2R_g$ and at $2R_g \geq 100$ nm the indicated dependence is practically absent. Let us note that the size 100 nm is assumed as an upper limit (although conditionally enough) for nanoworld objects [7]. Hence, the data in Fig. 1 clearly demonstrate that microgel at $2R_g < 100$ nm is a nanoreactor in which reaction (curing) rate is a strong function of its size, and at $2R_g \geq 100$ nm microgel loses this function and as a matter of fact becomes chemically inert particle. Let

us note that the indicated transition nanoreactor–nanoparticle is possible only in the fractal space. In Euclidean space these notions do not differ ($k_p = \text{const}$).

In Fig. 2 the dependence $k_p(R_g)$ for the system EPS-1/DDM in log-log coordinates is shown, which is well approximated by a straight line. From the slope of this straight line the value $2\omega = -0.58$ can be determined. As was noted above, the dimension of the space, in which curing reaction occurs, is equal to D and the value D_w can be determined according to the Aarony-Stauffer rule [8]:

$$D_w = D + 1 \quad (7)$$

Hence, the equation (5) for the considered case can be rewritten as follows (for any D value):

$$2\omega = -\gamma - 1 \quad (8)$$

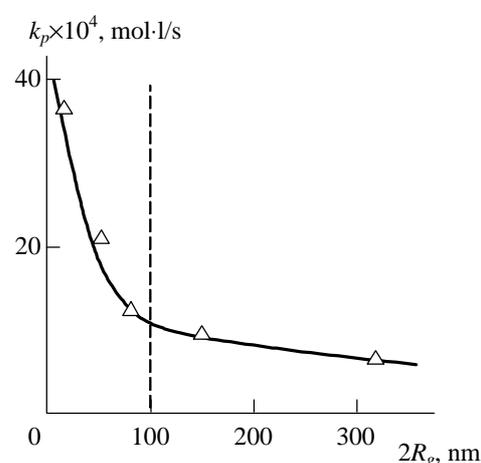


Fig. 1. The dependence of reaction rate constant k_p on microgels diameter $2R_g$ for system EPS-1/DDM.

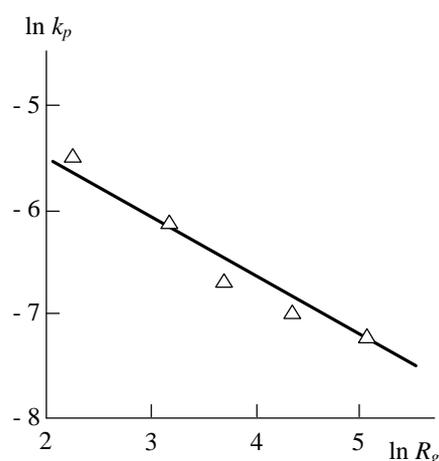


Fig. 2. The dependence of reaction rate constant k_p on microgels gyration radius R_g in log-log coordinates for system EPS-1/DDM.

Then according to the equation (8) $\gamma = -0.42$ can be obtained. This means that the self-diffusivity value D_{sd} decreases with R_g increasing much slower ($D_{sd} \sim R_g^{-0.42}$) in comparison with the reaction in Euclidean space ($D_{sd} \sim R_g^{-1}$). The indicated difference is demonstrated in Fig. 3.

The microgels molecular weight MW depends on curing duration t as follows [6]:

$$MW \sim t^{D/(D-2\omega)} \quad (9)$$

As was noted above, in Euclidean space $2\omega = 0$ and the exponent in the relationship (9) is equal to one, which assumes $MW \sim t$. For the reaction in fractal space $2\omega < 0$ and the exponent in the relationship (9) is less than one. This means that in fractal space the value MW grows slower than in Euclidean one. This relation for the system EPS-1/DDM is shown in Fig. 4. As Q value in the second case is larger this means that the reaction in fractal space gives a larger number of small clusters (microgels).

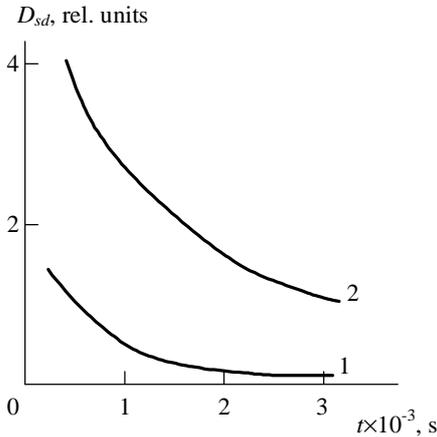


Fig. 3. The dependences of microgels self-diffusivity D_{sd} on curing reaction duration t in Euclidean (1) and fractal (2) spaces for system EPS-1/DDM.

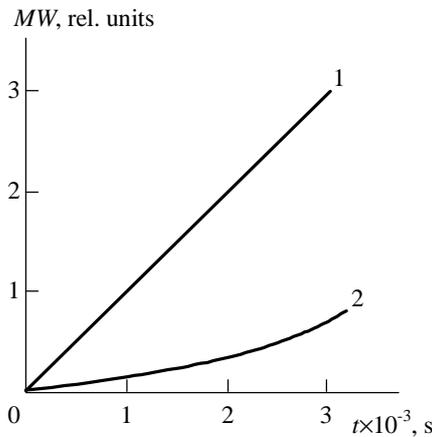


Fig. 4. The dependences of molecular weight MW of microgels on curing reaction duration t in Euclidean (1) and fractal (2) spaces for system EPS-1/DDM.

k_p change indicated above can be obtained immediately from the Smoluchowski formula, which has the following form [6]:

$$k_p = 8\pi D_{sd} R_g \quad (10)$$

For the reaction in Euclidean space $D_{sd} \sim$ and $k_p = \text{const}$, for the reaction in fractal space for the EPS-1/DDM system $D_{sd} \sim$ and $k_p \sim$, *i.e.*, it is that k_p is reduced as supposed at curing reaction proceeding (the increase of R_g or MW).

Let us note in conclusion the strong dependence of k_p on the microgels structure, characterized by the fractal dimension D (Fig. 5).

As follows from Fig. 5, k_p sharp decay is observed for D increase at $D < 2$ and the attainment of the values k_p on asymptotic branch at $D > 2$. As it is known [6], within the frameworks of irreversible aggregation models the relationship is true:

$$k_p \sim D_{sd} R_g^{d-2} \quad (11)$$

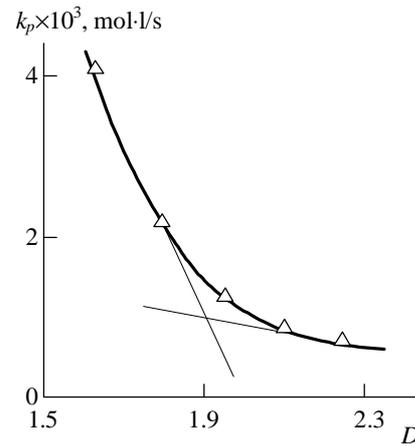


Fig. 5. The dependence of reaction rate constant k_p on microgels fractal dimension D for system EPS-1/DDM.

If for Euclidean space, for example, with $d = 3$, the exponent in the relationship (11) is constant and equal to one, then for fractal space with variable value D the situation will be essentially different. For $D < 2$ the exponent in the relationship (11) is less than zero and R_g growth results in k_p reduction under other equal conditions. At $D = 2$ k_p depends on R_g . And finally, at $D > 2$ k_p value should increase at R_g rising. This is expressed by the sharp decay of k_p at $D < 2$, since both D_{sd} and reduce this parameter at microgels MW increasing. At $D > 2$ D_{sd} reduction is compensated to a certain extent by growth and k_p decay at MW increasing is decelerated. It is easy to see that at $D = 2.48$ for EPS-1/DDM system the condition $k_p = \text{const}$ is fulfilled. Analytically the correlation $k_p(D)$ can be presented as follows

$$\lg k_p = -1.56 - 1.26(D-1) \quad (12)$$

4. Conclusions

The results presented in this paper have shown that for curing reaction proceeding in fractal space the reaction rate constant reduction is typical. Formation of a large number of microgels with smaller molecular weight in comparison with reaction in Euclidean space at the same conversion degree is also typical of such reaction. The dimensional border between nanoreactor and nanoparticle for the considered curing reaction has been obtained.

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ПЕРЕХІД НАНОРЕАКТОР-НАНОЧАСТИНКА В ПРОЦЕСІ СТРУКТУРУВАННЯ ЕПОКСИДНИХ ПОЛІМЕРІВ

***Анотація.** Показано, що для реакцій структурування у фрактальному просторі типовим є зниження константи швидкості реакції. Іншою типовою особливістю цієї реакції, порівняно з реакцією в Евклідовому просторі, є утворення великої кількості мікрогелю з невеликою молекулярною масою за однакового ступеня перетворення. Для розглянутої реакції структурування одержано межю переходу у просторовий стан між нанореактором і наночастишкою.*

***Ключові слова:** епоксидний полімер, реакція затвердження, фрактальний простір, нанореактор, наночастинка.*