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Al. Al. Berlin, I. M. Barkalov,

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Abstract

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Al. Al. Berlin, I. M. Barkalov,
Corresponding Member of the Academy of Sciences of the USSR V. I. Goldanskii,
N. S. Enikolopyan

KINETIC FEATURES OF ANISOTROPIC POLYMERIZATION IN THE SOLID PHASE

In most works that have appeared in recent years, the concept of isotropic growth of a polymer chain—quite valid only for the liquid phase—is carried over to the solid-phase process. However, owing to the rigid spatial orientation of monomer units in the crystal lattice, the mutual arrangement of reactive groups and the distances between them must in general be different in different directions. Thus, the rate of polymerization will differ depending on the direction in which the polymer chain propagates. Such anisotropy of solid-phase polymerization should naturally affect the kinetics of the process.

In the present article the kinetic features of solid-phase polymerization are considered with allowance for anisotropic growth of the polymer chain. Here, as in the one-dimensional case ([1]), we shall consider a postpolymerization process, i.e., a process in which the formation of active centers and the growth of the chain are separated in time. It is of interest to consider the following three cases.

1st case. The growth of the polymer chain proceeds from an active center to a defect in the crystal lattice. We shall regard the defects as non-annihilating, i.e., they are only traps for growing polymer radicals; however, the total concentration of free and occupied traps remains constant during the process. We shall also assume that in the crystal lattice of the monomer there are two directions of propagation of the polymer chain, differing from one another by different polymer-chain growth constants k_1 and k_2. In this case active centers identical in nature will differ in their activity depending on their position in the crystal lattice. Let us denote active centers for which polymerization is possible in both directions by R_{12}; those for which polymerization is possible only in the first direction, while in the second direction there is a defect, by R_{10}; those for which polymerization is possible only in the second direction, while in the first direction there is a defect, by R_{20}; and those for which polymerization is altogether impossible, i.e., defects are located in both the first and the second directions, by R_{00}.

The postpolymerization process will be described by the following system of equations:

$$\frac{dR_{12}}{dt} = -\alpha(2-\alpha)(k_1+k_2)R_{12} + k_1(1-\alpha)^2R_{10} + k_2(1-\alpha)^2R_{20},$$

$$\frac{dR_{10}}{dt} = \alpha(1-\alpha)(k_1+k_2)R_{12} - k_1(1-\alpha+\alpha^2)R_{10} + k_2\alpha(1-\alpha)R_{20},$$

$$\frac{dR_{20}}{dt} = \alpha(1-\alpha)(k_1+k_2)R_{12} + k_1\alpha(1-\alpha)R_{10} - k_2(1-\alpha+\alpha^2)R_{20}, \tag{1}$$

$$\frac{d\Pi}{dt} = (k_1+k_2)R_{12} + k_1R_{10} + k_2R_{20},$$

$$\alpha = \varphi(\Pi),$$

where α is the probability of encountering a defect. If the initial distribution of active centers is random, then we have the following initial conditions

$$\begin{aligned} R_{12}^0 &= (1-\alpha)^2R^0, \\ R_{10}^0 &= \alpha(1-\alpha)R^0, \\ R_{20}^0 &= \alpha(1-\alpha)R^0, \qquad \text{at } t=0, \\ R_{00}^0 &= \alpha^2R^0, \\ \alpha &= \alpha_0, \end{aligned}$$

where R^0 is the initial concentration of radicals in the volume.

A complete solution of this system is complicated; however, under the conditions $k_1 \gg k_2$ and $\alpha = \text{const}$, the system can be substantially simplified and reduced to two equations

$$\begin{aligned} \frac{dR_1}{dt} &= -k_1\alpha R_1 + k_2R_2 - k_1\delta R_1, \\ \frac{dR_2}{dt} &= k_1\alpha R_1 - k_2R_2, \end{aligned} \tag{2}$$

where δ is the probability of complete destruction of an active center (chemical interaction with an impurity; encounter with a crack or the edge of a crystal; encounter of two defects in both directions—the probability of the latter event is α^2), $R_1 = R_{12} + R_{10}$ and $R_2 = R_{20}$. Solving this system, we obtain the expression for

$$R_1 \simeq R_0\left(e^{-k_1\alpha t} + \frac{k_2}{k_1\alpha}e^{-[k_2\delta/\alpha]t}\right) \qquad \text{for } k_2 \ll k_1\alpha. \tag{3}$$

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

Taking into account the simplifications made above, one may assume that $d\Pi/dt = k_1 R_1$. Substituting into this expression the value of R_1 from (3), we obtain the equation for the kinetic curve

$$\Pi \simeq \frac{R_0}{\alpha}\left(1 - e^{-k_1 \alpha t}\right) + \frac{R_0}{\delta}\left(1 - e^{-[k_2 \delta/\alpha]t}\right). \tag{4}$$

It is easy to see that on the kinetic curve specified by equation (4) there must be two rectilinear portions with substantially different slopes, $k_1 R_0 \gg k_2 R_0/\alpha$. Such distinctive kinetics is apparently observed in the case of post-polymerization of acrylamide. The kinetic curve of the post-polymerization of this monomer, obtained in (2), and the theoretical curve described by equation (4), are shown in Fig. 1.

2nd case. Equation (4) is valid only in the case when the prepared active centers pass into growing polymer centers very rapidly. If this transition occurs slowly (the initiation rate is small), then system (2) takes the form

$$\begin{aligned} \frac{dR_1}{dt} &= k_{iA}0e^{-k_it} - k_1 \alpha R_1 + k_2 R_2, \\ \frac{dR_2}{dt} &= k_1 \alpha R_1 - k_2 R_2, \end{aligned} \tag{5}$$

where k_i is the initiation constant, and A_0 is the initial concentration. The solution of this system gives the following expression for the kinetic curve

$$\Pi = \frac{k_2 A_0}{\alpha} t + \frac{k_i - k_2}{k_i \alpha} A_0 \left(1 - e^{-k_it}\right). \tag{6}$$

The form of this curve differs depending on the sign of the difference $k_i - k_2$. For $k_i - k_2 > 0$ the curve is similar to the kinetic curve obtained in the first case; for $k_i - k_2 = 0$ the curve degenerates into a straight line and, finally,

when $k_i - k_2 < 0$ the kinetic curve has a quasi-induction period. In Fig. 2 all three types of kinetic curves (equation (6)) are presented; in the same figure are also given experimental points for the solid-phase polymerization of benzamidostyrene and acetamidostyrene, which are analogous to the theoretical curves.

In the preceding cases we considered nonannealable defects; however, in the process of formation of active centers in a crystalline monomer,

Fig. 1. Kinetic curve of postpolymerization of acrylamide: experimental points from (2), the solid curve was calculated from equation (4)

Fig. 2. Kinetic curves of polymerization. 1—acetamidostyrene at 120.7° (1*a*) and at 100° (1*b*), experimental points taken from (^{3}), solid curves calculated from equation (6) ($k_i - k_2 < 0$ (a) and $k_i - k_2 = 0$ (b)); 2—benzamidostyrene at 106.0°, experimental points taken from (^{3}), the solid curve calculated from equation (6) ($k_i - k_2 > 0$)

annealable defects may also arise (their number decreases more or less rapidly with time).

3rd case. If it is assumed that the defects are annealed by a monomolecular mechanism, then the process of postpolymerization will be described by the system of equations

$$\frac{dR_1}{dt} = -k_i\alpha R_1 - k_i\delta_0 e^{-k_{\text{ot}}t}R_1 + k_2R_2 + k_{\text{ot}}R_\delta,$$

$$\frac{dR_2}{dt} = k_i\alpha R_1 - k_2R_2, \tag{7}$$

$$\frac{dR_\delta}{dt} = k_i\delta_0 e^{-k_{\text{ot}}t}R_1 - k_{\text{ot}}R_\delta,$$

where δ_0 is the initial concentration of annealable defects, k_{ot} is the annealing-rate constant, and R_δ is an active center captured by an annealable defect. We shall also assume that at the beginning of postpolymerization all the active centers present are captured by annealable defects, i.e. $R_\delta = R_0$. The solution of system (7) under the condition $dR_1/dt = 0$ and $k_{\text{ot}} \gg k_2$ leads to the following expression for the change of R_δ with time:

$$R_\delta \simeq \left[(\alpha+\delta_0)R_0 + k_2\delta_0R_0t\right]e^{-k_{\text{ot}}t}\left(\alpha+\delta_0e^{-k_{\text{ot}}t}\right)^{-1} \tag{8}$$

and, for the change in R_1 with time,

$$R_1 \simeq \frac{k}{k_1}\left[(\alpha+\delta_0)R_0 + k_2\delta_0R_0t\right](\alpha+\delta_0e^{-k\ t})^{-2}e^{-k\ t} + \frac{k_2R_0}{k_1}(\alpha+\delta_0e^{-k\ t})^{-1}. \tag{9}$$

Continuing to take $d\Pi/dt = k_1R_1$, substituting equation (9) into this expression and integrating, we obtain the dependence of the polymer yield on time

$$\Pi \simeq \frac{k_2R_0t + R_0(1-e^{-k\ t})}{\alpha+\delta_0e^{-k\ t}}. \tag{10}$$

Depending on the ratio of the constants, the shape of such a kinetic curve has a more or less pronounced S-shape. Figure 3 shows the change with time of the

Fig. 3. Theoretical curves of change with time: 1—the concentration of active centers $[R_1]$, and 2—the polymer yield, calculated from equations (9) and (10).

Figure 2: Fig. 3. Theoretical curves of change with time: 1—the concentration of active centers $[R_1]$, and 2—the polymer yield, calculated from equations (9) and (10).

polymer yield and the concentration R_1. These dependences are very similar to those for autocatalytic processes. Recently, V. A. Kargin and V. A. Kabanov[4], in considering the mechanism of solid-phase polymerization, obtained similar kinetic dependences, proceeding from somewhat different assumptions. The mechanism described by them is apparently valid for the case in which substantial breaking of the monomer crystal by the polymer molecule is observed; however, it is not applicable to monomers whose lattice does not undergo substantial breaking in the course of polymerization, for example, trioxane. Therefore, the experimental observation of S-shaped curves in the polymerization of such monomers as trioxane, and correlation with the kinetics of defect annealing during post-polymerization, would confirm the particular case considered here, connected with defect annealing. As for the basic proposition concerning the anisotropic growth of the polymer chain, it apparently admits of no doubt, since its validity has been confirmed not only by structural studies[5], but also by observations of the process directly under the microscope[3].

Fig. 3. Theoretical curves of change with time: 1—the concentration of active centers $[R_1]$, and 2—the polymer yield, calculated from equations (9) and (10).

It should be noted that the kinetic regularities will not undergo substantial changes if k_2 is taken to be the rate constant of any elementary step (chain growth, chain transfer, copolymerization, defect migration, etc.).

Institute of Chemical Physics
Academy of Sciences of the USSR

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