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Abstract

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ON THE KINETICS OF SOLID-PHASE POLYMERIZATION

Extensive experimental material on the polymerization of solid monomers, obtained in recent years, demonstrates an abundance of various, sometimes even opposite, kinetic characteristics of processes grouped without any detail under the name of solid-phase polymerization ([1–3]). Below we consider the kinetic regularities of catalytic and radiation postpolymerization in the solid phase.

In the solid phase the rate of chain growth is determined not only by the reactivity of the monomer in the usual sense of the word, but also to a large extent by the mutual spatial orientation of the monomer units. Let us consider here the following variant. Let propagation of the polymer chain in a crystalline monomer occur only in one of the crystallographic directions, from the site of chain initiation to a defect in the crystal lattice. One or several preferential directions of propagation of the polymer chain in the crystal are connected with the fact that the rigid fixation of monomer molecules forbids, for purely geometric reasons, polymerization in other directions. In this case, in contrast to the liquid phase, at each elementary stage there is no competition between chain propagation and termination; when the growing polymer radical reaches a lattice defect, chain growth ceases. In such a case the chain length is, as it were, predetermined by the properties of the monomer crystal, and a natural consequence of this is the absence of an activation energy for radiation solid-phase polymerization ([4]).

Based on these premises, the kinetic scheme of solid-phase polymerization must also take into account limitations associated with the presence of a preferential direction of propagation of the polymer chain.

Initiation. The formation of active centers leading to postpolymerization may occur in a primary or in a secondary reaction.

1. Under the action of irradiation, active centers A are formed in the crystal; they decay by a monomolecular mechanism, which leads to the following equation for their accumulation:

$$[A] = \frac{GI}{k_1}\left(1 - e^{-k_1 t}\right), \tag{1}$$

where G is the radiation-chemical yield of A; k_1 is the constant of monomolecular death of active centers; I is the radiation intensity. When active centers are formed in the primary reaction, the value of $[A]$ (at constant dose D) either increases with intensity ($[A] = GI/k_1$ as $I \to 0$), or does not depend on it ($[A] = GD$ as $I \to \infty$).

2. Active centers are formed in a secondary reaction:

$$\mathrm{M} \xrightarrow{G} \mathrm{B} \begin{array}{l} \xrightarrow{k_1} \text{death} \\ \xrightarrow{k_2} \mathrm{A}. \end{array}$$

With such a mechanism, the following expressions are obtained for the accumulation of A with time:

$$[\mathrm{A}] = GI\left[t - \frac{1}{k_2}\left(1 - e^{-k_2 t}\right)\right], \tag{2}$$

if loss of the intermediate product B is absent;

$$[\mathrm{A}] = \frac{GIk_2}{k_1 + k_2}\left\{t - \frac{1}{k_1 + k_2}\left[1 - e^{-(k_1 + k_2)t}\right]\right\} \tag{3}$$

for monomolecular loss of B, and

$$[\mathrm{A}] = \frac{k_2}{2k_1}\left(\sqrt{k_2^2 + 4k_1 GI} - k_2\right)t \tag{4}$$

for bimolecular loss of B (for the stationary case). In the course of radiation initiation in the crystal, in addition to those already present, new defects may also be formed, for example, through the formation of radiolysis products. In this case the probability of encountering a defect during propagation of the polymer chain in the crystal has the following form:

$$\alpha = \alpha_0 + gIt, \tag{5}$$

where α_0 is the probability of encountering a defect in an unirradiated crystal; α is the probability of encountering a defect in an irradiated crystal; g is the ratio of the radiation yield of defects to the monomer concentration. Expression (5) applies both to "annealable" and to "non-annealable" defects.

Chain growth. Active centers usually begin to carry out post-polymerization effectively at a higher temperature than that at which they were formed. Chain growth ceases when a growing polymer radical enters a lattice defect.

$$\mathrm{A} \xrightarrow{k_i} \mathrm{R}; \qquad \mathrm{R} + \mathrm{M} \xrightarrow{k_p} \mathrm{R}; \qquad \mathrm{R} + \mathrm{M} \xrightarrow{k_p} \mathrm{R}_\alpha \text{ termination.}$$

The growth of a polymer chain in a crystal may cause more or less severe breaking of the crystal lattice and the formation of additional defects beyond those already present in the crystal. When $\Delta M = \Pi$ monomer molecules are polymerized in 1 cm^3, then for each monomer molecule converted into polymer an average of σ new defects is formed. If 1 cm^3 of a monomer crystal contains N monomer molecules, then the probability of encountering a defect will be equal to $\beta\Pi = \sigma\Pi/N$. The process of post-polymerization in this case will be described by the following system of equations:

$$\frac{d[\mathrm{R}]}{dt} = k_i[\mathrm{A}]_0 e^{-k_i t} - k_p(\alpha + \beta[\Pi])[\mathrm{R}], \tag{6}$$

$$\frac{d[\Pi]}{dt} = k_p[\mathrm{R}], \tag{7}$$

where $[\mathrm{A}]_0$ is the initial concentration of active centers; $\alpha+\beta[\Pi]$ is the probability of encountering a defect in the lattice. Let us consider the solution of this system for three limiting cases.

1. Rapid initiation and slow chain growth. Then equation (6) can be written as $d[\mathrm{R}]/dt = -k_p(\alpha+\beta[\Pi])[\mathrm{R}]$. The solution of such a system of equations gives the following expression for the polymer yield [$\Pi = \Delta M$]:

$$[\Pi] = \frac{\gamma - \alpha}{\beta} \frac{1 - e^{-k_p \gamma t}}{1 + \dfrac{\gamma - \alpha}{\gamma + \alpha} e^{-k_p \gamma t}}, \tag{8}$$

where $\gamma = (\alpha^2 + 2[\mathrm{R}_0]\beta)^{1/2}$, and $[\mathrm{R}_0] = [\mathrm{A}]_0$. The limiting polymer yield as $t \to \infty$ will be equal to

$$[\Pi]_\infty = \frac{\gamma - \alpha}{\beta}. \tag{9}$$

This makes it possible, from kinetic data, to distinguish polymers that strongly and weakly break the crystal lattice during their growth, since for

$$\beta \gg \frac{\alpha^2}{2[R]_0} \quad [\Pi]_\infty \simeq \left(\frac{2[R_0]}{\beta}\right)^{1/2}, \quad \text{whereas for} \quad \beta \ll \frac{\alpha^2}{2[R_0]} \quad [\Pi]_\infty \simeq \frac{[R]_0}{\alpha}.$$

The number-average $\overline{M}_n$ and weight-average $\overline{M}_w$ molecular weights in the initial stage of the process are equal to $\overline{M}_n = \overline{M}_w = \dfrac{[\Pi]}{[R]_0}$, but in the final stage $\overline{M}_w$ grows faster than $\overline{M}_n$, and as $t \to \infty$ and $\beta \gg \dfrac{\alpha^2}{2[R]_0}$,

$$\overline{M}_n = \sqrt{\frac{2}{[R]_0\beta}}, \qquad \overline{M}_w = 2\ln 2\sqrt{\frac{2}{[R]_0\beta}},$$

whereas for $\beta \ll \dfrac{\alpha^2}{2[R]_0}$,

$$\overline{M}_n \to \frac{1}{\alpha} \quad \text{and} \quad \overline{M}_w \to \frac{2}{\alpha}.$$

2. Slow initiation and rapid chain growth. Then, applying the stationarity condition $d[R]/dt = 0$, we obtain the following expression:

$$[\Pi] = \frac{\left[\alpha^2 + 2[R]_0 \cdot \beta(1 - e^{-k_i t})\right]^{1/2} - \alpha}{\beta}. \tag{10}$$

The limiting polymer yield, as in case 1, is expressed by equation (9). As in the first case, from the dependence of the limiting polymer yield on $[R]_0$ one can distinguish polymers that strongly and weakly break the crystal lattice. Note that $(d[\Pi]/dt)_0 = k_i[R]_0/\alpha$, and if k_i does not depend on temperature, as, for example, in radiation ([4]) or mechanochemical ([5]) polymerization, then the effective activation energy is also equal to zero. The change in $\overline{M}_n$ with time in this case is given by the expression:

$$\frac{1}{\overline{M}_n} = \frac{\beta[R]_0(1 - e^{-k_i t})}{\left[\alpha^2 + 2[R]_0\beta(1 - e^{-k_i t})\right]^{1/2} - \alpha} = \alpha + \frac{\beta}{2}[\Pi]. \tag{11}$$

The decrease in molecular weight during polymerization obtained in ([6]) and ([7]) is described by equation (11) (Fig. 1). Thus, the values of α and β can be simply determined from these experimental dependences.

3. Growth of the polymer chain in the monomer crystal is not accompanied by fracture of the latter, $\beta = 0$. Then equation (6) will have the form:

$$\frac{d[R]}{dt} = k_i[A]_0 e^{-k_i t} - k_p\alpha[R]. \tag{12}$$

Solving (12), and then integrating (7), leads to the following expression for the change of [Π] with time:

$$[\Pi] = \frac{k_p k_i [A]_0}{k_p\alpha - k_i}\left[\frac{1}{k_i}(1 - e^{-k_i t}) - \frac{1}{k_p\alpha}(1 - e^{-k_p\alpha t})\right]. \tag{13}$$

The limiting yield as $t \to \infty$, $[\Pi]_\infty = [A]_0/\alpha$, depends only on the ratio $[A]_0/\alpha$. The change in the molecular weight of the polymer is described by the following equation:

$$\overline{M}_n = \frac{k_p k_i}{k_p\alpha - k_i}\left[\frac{1}{k_i} - \frac{1}{k_p\alpha}\frac{(1 - e^{-k_p\alpha t})}{(1 - e^{-k_i t})}\right]. \tag{14}$$

4. In all the preceding cases it was assumed that α is the probability of encountering a non-annealable defect. However, under irradiation defects may also form that are annealed at elevated temperature. The possibility of such annealing greatly complicates the picture of post-polymeriza-

Let us consider this influence for the example of case (1), assuming that $\beta = 0$; then:

$$\frac{d[\mathrm{R}]}{dt} = -k_p\delta[\mathrm{R}] + k_{\mathrm{ot}}[\mathrm{R}_\delta] - k_p\alpha[\mathrm{R}],$$

$$\frac{d[\mathrm{R}_\delta]}{dt} = k_p\delta[\mathrm{R}] - k_{\mathrm{ot}}[\mathrm{R}_\delta], \tag{15}$$

where $\delta = \delta_0 e^{-k_{\mathrm{ot}} t}$ is the probability of encountering an annealable defect; $[\mathrm{R}_\delta]$ is the concentration of active centers temporarily captured by annealable defects; k_{ot} is the annealing-rate constant.

Fig. 1. Change in the molecular weight of the polymer during polymerization; the straight lines are calculated from equation (11). The points are experimental data obtained in ([7]) at different temperatures (1—20°, 2—40°, 3—50°). The reduced viscosity number serves as the characteristic of the polymer molecular weight; its reciprocal is plotted along the ordinate axis.

Neglecting the term $k_p\alpha[\mathrm{R}]$ and solving this system under the condition $d[\mathrm{R}]/dt = 0$, we obtain:

$$[\mathrm{P}] = k_p[\mathrm{R}]_0 t - \frac{k_p[\mathrm{R}]_0}{k_{\mathrm{ot}}}\ln\frac{k_{\mathrm{ot}} + k_p\delta_0}{k_{\mathrm{ot}} + k_p\delta_0 e^{-k_{\mathrm{ot}} t}}. \tag{16}$$

It is clear that in this case the kinetic curve will have a more or less pronounced induction period, since

$$\left(\frac{d[\mathrm{P}]}{dt}\right)_0 = \frac{k_{\mathrm{ot}}}{\delta_0}[\mathrm{R}]_0, \quad \text{and} \quad \left(\frac{d[\mathrm{P}]}{dt}\right)_\infty = k_p[\mathrm{R}]_0.$$

Since in the process of post-polymerization the formation of active centers and defects is separated in time from chain growth, it is natural that a combination of the cases of initiation and chain growth considered above may give a variety of kinetic regularities of the process. In conclusion, we note that all this consideration has been carried out for the case of propagation of the polymer chain in only one possible direction in the crystal. However, the form of the basic equations will not undergo substantial changes under the assumption of isotropic growth of the polymer chain. In a subsequent communication, the kinetic regularities of post-polymerization in the presence of two or several preferred directions of propagation of the polymer chain will be considered.

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Note: Figure translations are in progress. See original paper for figures.