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Abstract

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ON THE MECHANISM OF NUCLEATION OF THE POLYMER PHASE IN MONOMER CRYSTALS

The polymerization of crystalline monomers may be considered as the nucleation and growth of "nuclei" of a new polymer phase in monomer crystals (1). In the general case, the nucleus of the new phase that arises will be capable of further growth only if its size exceeds a certain critical value determined by the equality of the volume and surface free energies of its formation (a "supercritical" nucleus). At smaller sizes, the "gain" in volume free energy does not cover the "loss" of free energy associated with the emergence of stress at the phase boundary due to distortion of the crystal lattice of the initial substance, and the nucleus proves to be thermodynamically unstable. Polymerization in a crystal is, in the general case, inevitably associated with a redistribution of interatomic distances and, consequently, with the appearance of greater or lesser stresses. The growth of nuclei of the polymer phase includes the initiation and development of kinetic chains at the polymer–monomer interface. In this connection, one of the important questions in the kinetics of solid-phase polymerization is to clarify the relationship between the dimensions of a supercritical nucleus capable of further growth and those of an individual polymer chain growing from an active center of molecular dimensions.

The total change in free energy ΔG upon formation of a nucleus of the new phase is expressed by the equation

$$\Delta G = m\Delta G_0 + \sigma S, \tag{1}$$

where m is the number of molecules that have undergone transformation; ΔG_0 is the change in volume free energy in the reaction, referred to one molecule; σ is the work of formation of a unit surface of the new phase; S is the surface of the nucleus. Let us assume that the nucleus of the polymer phase has the form of a cylinder of radius r, formed by one macromolecule or by an aggregate of macromolecules packed closely and parallel to one another. Upon elongation of such a cylinder in the crystal, a stress arises whose total magnitude is proportional to the lateral surface of the cylinder. The larger the radius of the cylinder, i.e., the larger the number of chains growing in parallel, the smaller the magnitude of its specific lateral surface. However, upon elongation of a cylinder of a given radius, the specific lateral surface does not change. The total magnitude of the lateral surface is $s = 2\pi rl$, where l is the length of the cylinder.

Let us further assume that an extended polymer chain may be approximated by a cylinder of radius r_0. Then the number of chains packed in parallel in the cylindrical nucleus is given by the relation $x = \alpha r^2/r_0^2$, where α is the packing coefficient. Hence

$$r = x^{1/2} r_0/\alpha^{1/2}, \tag{2}$$

$$s = 2\pi rl = 2\pi l x^{1/2} r_0/\alpha^{1/2}. \tag{3}$$

Upon formation of a cylinder with lateral surface s, the amount polymerized is

$$m = xl/\lambda_0 \tag{4}$$

monomer molecules, where λ_0 is the elongation of the polymer chain upon addition of one unit. Substituting (2), (3), and (4) into (1), we obtain

$$\Delta G = xl\Delta G_0/\lambda_0 + 2\pi l x^{1/2} r_0 \sigma/a^{1/2}, \tag{5}$$

where $\Delta G_0 = \Delta H_0 - T\Delta S_0$ is the bulk free energy of polymerization. A critical nucleus capable of further growth arises when $\Delta G = 0$. From this condition we obtain the number of chains x^* in the critical nucleus

$$x^* = \frac{1}{a}\left(\frac{2\pi r_0 \sigma \lambda_0}{l\Delta G_0}\right)^2. \tag{6}$$

If $x^* > 1$, then the formation in the crystal of a single extended chain is thermodynamically unfavorable.

Let us take ΔG_0 to be of the order of $-5 \cdot 10^{-3}$ erg/molecule (-7 kcal/mole), $r_0\lambda_0 \simeq 1.5 \cdot 10^{-15}$ cm^2. The magnitude of σ is determined by the nature and state of the crystals of the polymerizing monomer, by the temperature, and, apparently, may vary within the limits from 10 to 10^3 erg/cm^2. If $\sigma \sim 10$, then $x^* \simeq 10^{-2}$, i.e., the growth of a single chain in the lattice encounters no thermodynamic difficulties. If, however, $\sigma \sim 10^3$, then $x^* \simeq 10^2$, i.e., the growing nucleus of the polymer phase must contain no fewer than 100 chains arranged in parallel.

Thus, depending on the heat effect and entropy of polymerization, and depending on the temperature and properties of the crystal lattice, the supercritical nuclei in monomer crystals may be either individual chains or bundles of chains. The latter type of nucleation should be favored by low heats of polymerization, a high value of the energy of the monomer crystal lattice, and the absence of coherence, i.e., structural correspondence between the monomer and polymer phases. Apparently, it was precisely this type of nucleation and development of the polymer phase that was observed in an electron-microscopic study of the polymerization of single crystals of certain monomers (^{2}). For the formation of a bundle of growing chains it is necessary that several active centers be concentrated in some region of the monomer crystal. Dislocations, interfaces between neighboring crystallites, and other defects may serve as such regions.

These considerations make it possible to explain the S-shaped form of kinetic curves observed in the polymerization of a number of crystalline monomers (^{3}). The S-shape is associated with slow nucleation of supercritical domains of the polymer phase. The emergence of these domains and the appearance of a polymer–monomer interface lead to an increase in the rate of transformation, i.e., to autocatalysis (^{4}). The same occurs in most solid-phase reactions of low-molecular substances.

Considerations concerning the possible thermodynamic instability of an individual chain in a monomer crystal also make it possible to put forward a hypothesis about one of the reasons for the limitation of conversion of crystalline monomers, which in a number of cases is observed during their radiation polymerization.

There are grounds to suppose (^{5}) that, under the action of high-energy radiation on certain crystalline monomers, "hot" regions arise in them, in which polymer chains are formed. Under continuous irradiation a stationary concentration of these regions is rapidly established. If, under the reaction conditions, $x^* > 1$ (see above), then an individual polymer chain that has grown in a "hot" region will prove thermodynamically unstable. Then repeated action of radiation on this chain may lead to its rapid chain degradation down to monomer. The degradation will occur provided that, during the time elapsed from the formation of the metastable macromolecule to the repeated action of radiation, annealing of the stress arising as a result of its growth and the "cooling" of the hot region has not had time to take place.

For simplicity of calculation, let us assume that in each "hot" region an average of $\bar{v}$ monomer molecules can polymerize. Let n^* and n be, respectively, the numbers of unstable and annealed chains at any time t, and let N_0 be the number of monomer molecules per unit volume. Then the degree of conversion q is given by

$$q = \bar{v}(n^* + n)/N_0. \tag{7}$$

The rate of accumulation of unstable chains in the general case is equal to

$$dn^*/dt = \alpha I(n_0 - n - n^*) - \beta I n^* - \gamma n^*, \tag{8}$$

where α, β, and γ are, respectively, the probabilities of formation, chain rupture, and annealing of an unstable chain; n_0 is the maximum number of chains that can be formed under the given conditions per unit volume of the crystal (the number of "blanks," in the terminology of Barkalov et al. (5))* . The rate of accumulation of stable macromolecules as a result of annealing of unstable ones is

$$dn/dt = \gamma n^*. \tag{9}$$

Solving the system of differential equations (8) and (9) and substituting the solutions into (7), we obtain

$$\begin{aligned} q = \frac{n_0\bar{v}}{N_0}\Bigg\{1 - \frac{\exp[-\frac{1}{2}(\alpha I + \beta I + \gamma)]}{2\sqrt{(\alpha I + \beta I + \gamma)^2 - 4\alpha\gamma I}}\,[(\alpha I - \beta I - \gamma + \\ + \sqrt{(\alpha I + \beta I + \gamma)^2 - 4\alpha\gamma I})\exp\sqrt{(\alpha I + \beta I + \gamma)^2 - 4\alpha\gamma I} - \\ -(\alpha I - \beta I - \gamma - \sqrt{(\alpha I + \beta I + \gamma)^2 - 4\alpha\gamma I}) \times \exp[-\sqrt{(\alpha I + \beta I + \gamma)^2 - 4\alpha\gamma I}]]\Bigg\}. \end{aligned} \tag{10}$$

If, under the conditions of the reaction, for example at low temperatures, the probability of annealing is negligibly small ($\gamma = 0$), equation (10) is simplified:

$$q = \frac{\alpha n_0\bar{v}}{N_0(\alpha+\beta)}\{1 - \exp[-(\alpha+\beta)It]\}. \tag{11}$$

With time, a stationary concentration of metastable chains is established in the irradiated crystals, determined by the relation

$$q_\infty = (n_0\bar{v}/N_0)[\alpha/(\alpha+\beta)]. \tag{12}$$

In principle, the quantity $n_0\bar{v}/N_0$ may vary within the limits from 0 to 1 and depend on temperature in a complex manner.

The quantity β may also depend on temperature. The temperature dependences of $n_0\bar{v}/N_0$ and β determine the temperature behavior of the limiting conversion. The initial rate of conversion can be found from the equation

$$\left(\frac{dq}{dt}\right)_{t=0} = \frac{n_0\bar{v}}{N_0}\alpha I; \tag{13}$$

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

it is easy to see that the initial rate of conversion depends on temperature only if $n_0\bar{v}/N_0$ is a function of temperature. For example, if $n_0\bar{v}/N_0$ increases with increasing temperature, then the plots of the depend— depth of conversion on time will have the form shown in Fig. 1a. If, however, the temperature dependence of the limits is associated with a change in β, while $n_0\bar{\nu}/N_0$ does not depend on temperature, then the apparent activation energy of polymerization is zero (Fig. 1b).

In a phase transformation, melting, or dissolution of crystals containing metastable macromolecules, stress annealing occurs and the stable polymer is separated out.

As confirmation of the proposed hypothesis, one may cite the data of [6], where the kinetics of polymerization of crystalline hexamethylcyclotrisiloxane was studied. After irradiating the monomer at low temperature with fast electrons and reaching the limiting conversion, the authors raised the temperature and again irradiated the partially polymerized monomer. It turned out that the depth of conversion then decreased. The result obtained can evidently be explained by chain degradation of a certain number of unstable macromolecules from among those stored in the first "round" of irradiation, and by the establishment of a new stationary concentration n^*.

Fig. 1. *a*—dependence of q on dose for different numbers of embryos $n_0\bar{\nu}/N_0$ (at $\beta = 0$). 1—$n_0\bar{\nu}/N_0 = 0.1$; 2—0.25; 3—0.5; 4—1. *b*—dependence of q on dose for different depolymerization rates β (at $n_0\bar{\nu}/N_0 = 0.5$); $\beta_1 > \beta_2 > \beta_3 > \beta_4$.

Fig. 2. Dependence of q on dose for different annealing rates of unstable molecules γ (at $\beta = \text{const}$ and $n_0\bar{\nu}/N_0 = 0.5$). $\gamma_5 > \gamma_4 > \gamma_3 > \gamma_2$; $\gamma_1 = 0$.

In the general case, when the probability of annealing cannot be neglected, the process is described by equation (10), which for increasing values of γ gives the family of curves shown in Fig. 2. For $\gamma > 0$, $q_\infty = n_0\bar{\nu}/N_0$.

Within the framework of the hypothesis, data on the decrease of molecular weight with depth of conversion (dose), which is often observed experimentally, may find an explanation. One of the possible causes is associated with the

* Here, for simplicity of calculation, we assume that the rates of formation and rupture of unstable polymer chains are proportional to the radiation intensity to the first power, although in the general case a more complex dependence is also possible.

appearance, during irradiation and as polymer is formed, of defects in the crystal lattice, leading to a decrease of $\bar{\nu}$ (damage to the "embryos"). The second is annealing not of the whole macromolecule as a unit, but of its individual parts. Then only the unannealed segments of macromolecules will undergo chain degradation. This will lead to a gradual accumulation of shortened stable macromolecules.

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