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Abstract

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ON AUTOCATALYSIS IN POLYMERIZATION REACTIONS

The acceleration of polymerization upon accumulation of polymer in the system is usually associated with a decrease in the rate constant for termination of kinetic chains, caused by the hindrance of diffusion of polymeric active centers as the viscosity of the medium increases (gel effect). This approach is valid for systems characterized by quadratic termination (recombination or disproportionation of radicals). At the same time, there apparently also exist other possibilities for autocatalytic acceleration, connected, for example, with an increase in the rate constant for chain growth if the active center comes into contact with an already completed macromolecule or with an aggregate of macromolecules. Thus, for example, if the destruction of the crystal lattice is necessary for chain growth in a solid monomer, then, naturally, this process will occur more easily at the monomer–polymer interface, when the growing chain has the possibility of "adjusting itself" to an already completed macromolecule or aggregate ("matrix"). Association of the growing active center with the matrix may lead to a decrease in the free energy of activation of the process. In polymerization leading to the formation of chains with a system of conjugated double bonds, specific interactions between aggregates of macromolecules and active centers adsorbed on them probably play an important role in bringing about autocatalysis (^1).

Of greatest interest from the standpoint of studying autocatalytic polymerization are systems for which the termination reaction is not associated with collisions of two macroradicals, since in the latter case the matrix effect is difficult to separate from the gel effect.

The simplest kinetic scheme of autocatalytic polymerization of this type may be represented as follows.

Initiation

$$\mathrm{I}_0 + \mathrm{M} \xrightarrow{k_{\mathrm{in}}} \mathrm{A}, \qquad \mathrm{I}_0 + \mathrm{M} + \mathrm{P} \xrightarrow{k'_{\mathrm{in}}} \mathrm{A}' + \mathrm{P},$$

Chain growth

Fig. 1. Kinetic curves constructed according to equation (2)

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$$\mathrm{A}_n + \mathrm{M} \xrightarrow{k_p} \mathrm{A}_{n+1}, \qquad \mathrm{A}'_n + \mathrm{M} \xrightarrow{k'_p} \mathrm{A}'_{n+1},$$

Chain termination

$$\mathrm{A}_n + \mathrm{M} \xrightarrow{k_o} \mathrm{P}_{n+1}, \qquad \mathrm{A}'_n + \mathrm{M} \xrightarrow{k'_o} \mathrm{P}_{n+1},$$

where I_0 is the initiator, M the monomer, P a unit of a previously formed polymer chain, A an active center arising in the environment of monomer molecules, and A′ an active center arising in contact with the polymer chain (below these same symbols will be used to denote the concentrations of the reacting species); k_{in} and k'_{in}, k_p and k'_p, k_o and k'_o are, respectively, the rate constants of initiation, growth, and termination of chains characteristic of active centers A and A′. For generality it may be assumed that active centers A and A′ are capable of transforming into one another. Taking the quasi-stationary condition with respect to the concentrations of A and A′, and assuming that in the quasi-stationary state the rates of mutual transformation of the active centers are equal, it is easy to obtain an expression for the rate

polymerization in the form:

$$-\frac{dM}{dt} = (\alpha + \beta M_0) I_0 M - \beta I_0 M^2, \tag{1}$$

where

$$\alpha = \frac{k_{\text{in}} k_p}{k_o}, \qquad \beta = \frac{k'_{\text{in}} k'_p}{k'_o}.$$

If

$$\delta = \frac{\beta M_0}{\alpha} > 1,$$

then the process proceeds autocatalytically.

The quantity δ shows by how many times the specific rate of matrix polymerization exceeds the rate of formation of polymer chains in the medium of monomer molecules. In the special case, if $k_{\text{in}} = k'_{\text{in}} M_0$ and $k_o = k'_o$, the quantity δ represents the ratio of the chain-growth rate constants in the presence and in the absence of the matrix.

Fig. 1. Kinetic curves constructed according to equation (2)

Integrating equation (1), we obtain

$$Q = \frac{M_0 - M}{M_0} = \frac{e^{\alpha(1+\delta)I_0 t} - 1}{e^{\alpha(1+\delta)I_0 t} + \delta}, \tag{2}$$

where Q is the degree of conversion. In form, equation (2) is completely analogous to the expression obtained by N. S. Enikolopyan, which describes the accumulation of an intermediate product in chain reactions with degenerate branchings (^{2}).

Figure 1 presents kinetic curves constructed according to equation (2) for different values of αI_0 and δ. The constants α and β can be found from the corresponding experimental curves by means of simple calculations. It can be shown that

$$\ln\delta = \frac{4\delta t_m \tan x}{1+\delta}, \qquad \alpha = \frac{4\delta \tan x}{(1+\delta)^2 I_0} \quad \text{and} \quad \beta = \frac{\alpha\delta}{M_0},$$

where t_m is the abscissa of the inflection point on the kinetic curve, and x is the angle of inclination of the tangent to the inflection point. If $\delta \gg 1$, then $\ln\delta \simeq 4t_m \tan x$,

$$\alpha \simeq \frac{4\tan x}{\delta I_0}.$$

In this case t_m is the half-conversion time.

It can further be shown that the number-average degree of polymerization ($\overline{P}$) of the chains formed at time t is equal to:

$$\overline{P} = \frac{e^{\alpha I_0(1+\delta)t} + \delta}{(1+\delta)e^{\alpha I_0(1+\delta)t}} \frac{k_p}{k_o} + \frac{\delta\left(e^{\alpha I_0(1+\delta)t} - 1\right)}{(1+\delta)e^{\alpha I_0(1+\delta)t}} \frac{k_p'}{k_o'}. \tag{3}$$

Important consequences follow from equation (3): 1) the molecular weight of the polymer being formed increases with time if

$$\frac{k_p'}{k_o'} > \frac{k_p}{k_o};$$

2) at a fixed polymerization time, the molecular weight of the polymer formed is the higher, the higher the concentration of initiator (or the irradiation intensity in radiation polymerization). This latter unusual circumstance may serve as a distinguishing feature of autocatalytic polymerization characterized by linear chain termination.

Figure 2

Figure 2: Figure 2

All the relations given above have been obtained under the assumption that the reaction proceeds homogeneously. However, under certain assumptions they may also be extended to heterogeneous processes, when the reaction is accelerated at the boundary of the monomer and polymer phases. It is not difficult to show that equation (2) is suitable for describing heterogeneous autocatalytic polymerization provided that the number of particles constituting the polymer phase (N) increases in proportion to the degree of conversion (Q). As applied to the description of heterogeneous radiation polymerization of crystalline monomers, in order for equation (2) to hold, instead of the condition $N \sim Q$ it is sufficient to assume that the rate of formation of active centers A' on the popr-

surface of the polymer—monomer interface is proportional to the number of quanta absorbed per unit time in the volume of the polymer. This is possible if there exists some mechanism for the transfer of excitation energy in the system of polymer chains.

The applicability of equation (2) for describing the polymerization of crystalline monomers can be illustrated by certain experimental data available in the literature. Adler, Ballantine, and Baysal (^3) have unambiguously shown that the polymerization of crystalline acrylamide occurs mainly at the monomer—polymer interface; analogous observations were made by us jointly with V. P. Zubov and I. M. Papisov for the case of polymerization of crystalline methyl methacrylate (^4). Figure 2 presents two typical kinetic curves for the radiation polymerization of acrylamide, obtained at a temperature of 27° and at different irradiation intensities (0.650 Mrad/hour and 0.410 Mrad/hour) (^5), and showing that the polymerization proceeds with clearly pronounced self-acceleration. From these curves the values $\gamma = \alpha I_0(1+\delta)$ and δ were calculated. For curve 1: $\gamma_1 = 2.3$ hour^{-1}, $\delta_1 = 7.6 \cdot 10^2$; for curve 2: $\gamma_2 = 1.55$ hour^{-1}, $\delta_2 = 6.3 \cdot 10^2$. The constants γ and δ do not depend on I_0. Therefore, as was to be expected, within the limits of error $\delta_1 = \delta_2$, and

$$\frac{\gamma_1}{\gamma_2} = \frac{I_{01}}{I_{02}} = 1.5.$$

Fig. 2. Kinetics of radiation polymerization of crystalline acrylamide (^5). Temperature 27°.
1 $-I_0 = 0.650$ Mrad/hour, 2 $-I_0 = 0.410$ Mrad/hour.

The latter value is in satisfactory agreement with the actual ratio of the intensities in the experiment, equal to 1.6. Thus, at 27° the rate of "matrix" polymerization of crystalline acrylamide (at the monomer—polymer interface) is more than 2.5 orders of magnitude higher than the rate of polymerization

Figure 3

Figure 3: Figure 3

in the medium of the crystalline monomer. The kinetic curves plotted according to equation (2), using the calculated values of γ and δ (Fig. 2, dashed line), practically coincide with the experimental ones. The kinetics of radiation polymerization of N-vinylsuccinimide, according to the data of Hardy et al. (^6), likewise has a clearly pronounced autocatalytic character. Figure 3 presents one of the kinetic curves. From it the constants γ and δ were calculated, respectively equal to 0.45 hour^{-1} and $8 \cdot 10^2$.

Fig. 3. Kinetics of radiation polymerization of crystalline N-vinylsuccinimide (^6). $t = 20°$, $I_0 = 16\,800$ r/hour.

The acceleration of polymerization at the polymer—monomer boundary is connected with the fact that the mobility of molecules here is always higher than in the bulk. At the same time, this mobility is combined with a certain ordering in the boundary layer. In other words, at the interface conditions arise that are somewhat similar to those realized during phase transitions, which ensure rapid explosive polymerization of frozen monomers (^4). The possibility of aggregation of newly forming chains with already formed ones probably creates additional advantages for the chain-growth reaction to occur. The relative role of these factors is all the greater

higher the greater are the obstacles to the "sprouting" of the polymer chain in the medium of molecules of the crystalline monomer, associated with the necessity of molecular rearrangements, i.e., the less favorable the orientation of the molecules in the crystal is for polymerization. This means that the parameter δ, which determines the ratio of the specific rates of polymerization in contact with already formed macromolecules and in the bulk of the crystalline monomer, can serve as a certain characteristic of the structural correspondence between the monomer lattice and the polymer chain. If such a correspondence exists, then the rates of chain growth in the bulk of the monomer and at the interface may turn out to be commensurable. Then the value of δ approaches 1, and the autocatalytic character of the polymerization is leveled out (Fig. 1a). Indeed, in the case of monomers for which it is known, or may be assumed, that the lattice parameters are close to the chain parameters (trioxane, β-propiolactone, cetyl methacrylate, etc.), the polymerization rate is high from the very beginning and decreases with increasing depth of conversion (Fig. 4) [6]. Conversely, if polymerization requires a substantial rearrangement of the lattice, then the reaction rate at the interface is much higher than in the bulk of the crystals and $\delta \gg 1$.

Fig. 4. Kinetics of radiation polymerization of crystalline cetyl methacrylate [6]

In conclusion, the authors express their gratitude to N. S. Enikolopyan for discussion of the work.

Fig. 4. Kinetics of radiation polymerization of crystalline cetyl methacrylate

Figure 4: Fig. 4. Kinetics of radiation polymerization of crystalline cetyl methacrylate

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CITED LITERATURE

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