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V. I. TSVETKOVA, A. P. FIRSOV, and N. M. CHIRKOV

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Abstract

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ON THE POSSIBILITY OF DETERMINING THE CONSTANTS OF ELEMENTARY STEPS IN CATALYTIC POLYMERIZATION

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The determination of the constants of the elementary steps of initiation, propagation, and termination is closely connected with elucidating the mechanism of the polymerization process. A rigorous approach to the problem of regulating the molecular weights of polymers is impossible without knowledge of the constants of the elementary steps. With a certain modeling of the catalytic polymerization process under steady-state conditions, it is possible to find expressions that allow these constants to be calculated.

Let us adopt the following scheme of catalysis: 1) the total number of active centers (n_0) remains constant throughout the entire process; the initiation step consists in the addition of the first monomer molecule to an active center (n_i); 2) an active center bound to a growing polymer chain (n_p) does not participate in initiation until chain growth is complete, after which it is regenerated again into n_i; 3) addition of the second and subsequent units (chain propagation) occurs with identical constants; 4) termination of the growing chain may occur with participation of the monomer, impurities, catalyst components, and by separation of the growing polymer chain from the active center.

According to the above,

$$n_0 = n_p + n_i = \text{const}, \tag{1}$$

where n_0 is the total number of active centers; n_p is the number of active centers participating in the growth of polymer chains, and n_i is the number of active centers that do not have a single monomer molecule attached. Expressions for the rates of initiation (W_i), propagation (W_p), and termination (W) may be written as follows:

$$W_i = k_i n_i C_\text{M}, \tag{2}$$

$$W_p = k_p n_p C_\text{M}, \tag{3}$$

$$W \;\; = \sum_j k_j \;\; n_p C_j^a \;\; , \tag{4}$$

where k_i is the rate constant of initiation; k_p is the rate constant of chain propagation; k_j is the rate constant of chain termination; C_{M} is the monomer concentration; C_j is the concentration of the terminating agent.

Under steady-state conditions of the process, i.e., when

$$W_i = W \;\; , \tag{5}$$

and at sufficiently high chain lengths, the rate of monomer polymerization (W) is determined by expression (3).

From equation (5), using expressions (1), (2), and (4), we find:

$$n_p = \frac{k_i n_0 C_{\mathrm{M}}}{k_i C_{\mathrm{M}} + \sum_j k_j \;\; C_j^a}, \tag{6}$$

whence it is seen that n_p depends on the monomer concentration. Using this expression, for the polymerization rate we obtain

$$W_{\mathrm{p}} = k_p n_p C_{\mathrm{m}} = \frac{k_p k_i n_0 C_{\mathrm{m}}^2}{k_i C_{\mathrm{m}} + \sum_j k_{j\,\mathrm{br}} C_{j\,\mathrm{in}}^{\alpha}}, \tag{7}$$

or, separating out chain transfer to monomer, we transform this equation as follows:

$$W_{\mathrm{p}} = \frac{k_p k_i n_0 C_{\mathrm{m}}^2}{k_i C_{\mathrm{m}} + k_{\mathrm{br}}^{\mathrm{m}} C_{\mathrm{m}} + \sum_{j-1} k_{j\,\mathrm{br}} C_{j\,\mathrm{in}}^{\alpha}}. \tag{8}$$

As is seen, the polymerization rate in the general case depends in a complicated way on the monomer concentration. The temperature dependence of the reaction also has a complicated character.

In analyzing equation (8), two limiting cases may be distinguished:

1) $k_i C_{\mathrm{m}} + k_{\mathrm{br}}^{\mathrm{m}} C_{\mathrm{m}} \gg \sum_{j-1} k_{j\,\mathrm{br}} C_{j\,\mathrm{in}}^{\alpha}$. Expression (8) takes the form

$$W_{\mathrm{p}} = \frac{k_p k_i}{k_i + k_{\mathrm{br}}^{\mathrm{m}}} n_0 C_{\mathrm{m}}, \tag{8'}$$

i.e., the polymerization rate is first order with respect to the monomer.

2) $k_i C_{\mathrm{m}} + k_{\mathrm{br}}^{\mathrm{m}} C_{\mathrm{m}} \ll \sum_{j-1} k_{j\,\mathrm{br}} C_{j\,\mathrm{in}}^{\alpha}$. Expression (8) takes the form:

$$W_{\mathrm{p}} = \frac{k_p k_i}{\sum_{j-1} k_{j\,\mathrm{br}} C_{j\,\mathrm{in}}^{\alpha}}\, n_0 C_{\mathrm{m}}^2, \tag{8”}$$

i.e., the polymerization rate is second order with respect to the monomer and, according to equation (6), $n_p \ll n_0$.

Thus, with an increase in monomer concentration, the reaction order changes from second to first. This conclusion is evidently valid only if n_0 does not depend on the monomer concentration.

For the further exposition it is convenient to represent expression (8) in the form

$$\frac{C_{\mathrm{m}}}{W_{\mathrm{p}}} = \frac{1}{k_p n_0} + \frac{k_{\mathrm{br}}^{\mathrm{m}}}{k_p k_i n_0} + \frac{\sum_{j-1} k_{j\,\mathrm{br}} C_{j\,\mathrm{in}}^{\alpha}}{k_p k_i n_0} \frac{1}{C_{\mathrm{m}}}. \tag{9}$$

As is known, the degree of polymerization ν is determined by the equation:

$$\nu = \frac{W_{\mathrm{p}}}{W_{\mathrm{br}}} = \frac{k_p n_p C_{\mathrm{m}}}{k_{\mathrm{br}}^{\mathrm{m}} n_p C_{\mathrm{m}} + \sum_{j-1} k_{j\,\mathrm{br}} C_{j\,\mathrm{in}}^{\alpha}} = \frac{k_p C_{\mathrm{m}}}{k_{\mathrm{br}}^{\mathrm{m}} C_{\mathrm{m}} + \sum_{j-1} k_j C_{j\,\mathrm{in}}^{\alpha}}$$

or

$$\frac{1}{\nu} = \frac{k_{\mathrm{br}}^{\mathrm{m}}}{k_p} + \frac{\sum_{j-1} k_{j\,\mathrm{br}} C_{j\,\mathrm{in}}^{\alpha}}{k_p} \frac{1}{C_{\mathrm{m}}}. \tag{10}$$

It follows from this that, at low monomer concentrations, the degree of polymerization should increase proportionally to C_{m}, whereas in the region of high concentrations one should expect ν to be independent of C_{m}.

In studying the polymerization of ethylene and propylene on complex catalysts, including titanium trichloride and various organometallic compounds, we observed the described character of the dependences of W_{p} and ν on C_{m}.

With a linear dependence of $C_{\mathrm{m}}/W_{\mathrm{p}}$ and $1/v$ on $1/C_{\mathrm{m}}$, which follows from equations (9) and (10), by combining these equations one can determine the constants of the individual elementary steps. Thus, from the dependence of the degree of polymerization on the concentration of monomer and of other chain-termination agents, one can determine the ratio of the corresponding termination constants to the propagation constant: in a graphical representation of the dependence of $1/v$ on $1/C_{\mathrm{m}}$, the ordinate intercept is $k_{\mathrm{term}}^{\mathrm{m}}/k_{\mathrm{p}}$, while the slope gives the value $\sum_{j-1} k_{j\,\mathrm{term}} C_{j\,\mathrm{in}}^{\alpha}/k_{\mathrm{p}}$.

Studying the dependence of $C_{\mathrm{m}}/W_{\mathrm{p}}$ and $1/v$ on C_{m}, one can determine $k_i n_0$, $k_{\mathrm{p}} n_0$, $k_{\mathrm{term}}^{\mathrm{m}} n_0$, and $\sum_{j-1} k_{j\,\mathrm{term}} n_0 C_{j\,\mathrm{in}}^{\alpha}$, i.e., the values of the constants referred to one and the same number of active centers.

It should be noted that the character of the dependences of W_{p} and v on C_{m} is preserved if the monomer is a chain-transfer agent rather than a termination agent. In this case, the second term in the denominator is omitted in equation (8), and equation (9) changes accordingly.

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