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Abstract

Full Text

Physical Chemistry

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On the Evaluation of the Initiating Activity of Peroxides in Polymerization Reactions

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The kinetics of the process of radical polymerization, both in bulk and in emulsions, is determined to a considerable extent by the nature of the initiator used. The nature of the initiator determines the character of the primary free radicals formed, the rate of their formation, possible reactions of interaction with the components of the polymerization system and, thus, the overall rate of the polymerization process, the molecular weight of the polymers formed, and the structure of the macromolecules ([1,2]). In this connection, the method of evaluating the activity of an initiator is of great importance, especially since different authors, in evaluating initiator activity, proceed from its different properties. Some authors consider the measure of initiating activity to be the rate of initiation—the ratio of the polymerization rate to the number-average molecular weight of the polymers formed; others, the rate of polymerization initiated by a given initiator ([3]). This parameter is often judged from the thermal stability of the initiator under the conditions of the polymerization system. It seems to us that none of the indicated methods for evaluating initiating activity can be universal. It would be more correct to evaluate the initiating activity of an initiator in the polymerization process by the rate constant of interaction of the primary radicals formed upon decomposition of the initiator with monomer molecules, i.e., by the rate constant for the formation of growing polymer radicals. This rate constant is not equal to the rate constant of thermal decomposition of the initiator and makes it possible quantitatively to estimate the rate of formation of growing polymer chains for different monomers and initiators of different nature.

Fig. 1. $1/V_p$ in $l \cdot h \cdot mol^{-1}$, as a function of $V_{in}^{-1/2}$.
1—benzoyl peroxide; 2—caproyl peroxide; 3—lauryl peroxide.

Determination of the true value of this constant—K_{in}—is associated with a number of experimental difficulties. For its determination it is necessary to apply methods of nonstationary kinetics (the rotating sector). It is much easier to determine the ratio of the initiation constant to the square root of the termination constant (K_{term}). We believe that this ratio $K_{in}/K_{term}^{1/2}$ may also serve as a quantitative characteristic of the initiating activity of a peroxide for a given monomer under given temperature conditions.

The ratio $K_{in}/K_{term}^{1/2}$ can be determined from polymerization-rate data, the determination of which presents no difficulty, and the rate of—

the initiation rate V_{in} (the rate of formation of free radicals in the polymerization system), which can be determined either from the rate of unimolecular decomposition of the initiator under polymerization conditions, if the initiation efficiency is known, or from the magnitude of the induction periods of inhibited polymerization ([4]). These quantities are related by the equation:

$$V_p = \frac{K_p}{K_{term}^{1/2}}[M] \cdot V_{in}^{1/2}$$

(for steady-state conditions).

The determination of $K_{im}/K_{term}^{1/2}$ can be carried out on the basis of the following considerations for steady-state conditions of the polymerization process. Let us consider two types of radicals in the polymerization system—primary free radicals and secondary free radicals arising as a result of interaction of these primary radicals with monomer molecules. Let us denote the concentrations of these radicals in the system by n_1 and n_2, respectively, and by n the total concentration of all free radicals. Then the change in the concentration of the corresponding radicals in the polymerization system, assuming the steady-state condition and assuming that the rate of termination of growing polymer radicals does not depend on chain length, is expressed by the equations:

$$\frac{dn}{dt} = V_{in} - K_{term}n^2 = 0, \quad \text{whence}$$

$$n = \sqrt{\frac{V_{in}}{K_{term}}}; \tag{1}$$

$$\frac{dn_1}{dt} = V_{in} - K_{im}[M]\,n_1 - K_{term}n_1 \cdot n = 0, \quad \text{whence}$$

$$n_1 = \frac{V_{in}}{K_{im}[M] + \sqrt{V_{in}K_{term}}}; \tag{2}$$

$$\frac{dn_2}{dt} = K_{\text{im}}[M]\, n_1 + K_{\text{term}} n_2 \cdot n = 0, \quad \text{whence}$$

$$n_2 = \frac{K_{\text{im}}[M]\sqrt{V_{\text{in}}}}{K_{\text{im}}[M]\sqrt{K_{\text{term}}} + K_{\text{term}}\sqrt{V_{\text{in}}}}, \tag{3}$$

where $[M]$ is the monomer concentration, and K_{term} is the rate constant for the interaction of radicals with one another.

The polymerization rate is determined from (4), taking into account only the growing polymer radicals,

$$V_{\text{p}} = -\frac{d[M]}{dt} = K_{\text{p}}[M]\, n_2, \tag{4}$$

where V_{p} is the polymerization rate and K_{p} is the chain-growth constant. Substituting the value of n_2 from (3) into (4), we obtain:

$$V = K_{\text{p}}[M]\, \frac{K_{\text{im}}[M]\sqrt{V_{\text{in}}}}{K_{\text{im}}[M]K_{\text{term}}^{1/2} + K_{\text{term}}V_{\text{in}}^{1/2}}.$$

Hence

$$\frac{1}{V} = \frac{K_{\text{term}}}{K_{\text{p}}K_{\text{im}}[M]^2} + \frac{K_{\text{term}}^{1/2}}{K_{\text{p}}[M]V_{\text{in}}^{1/2}}. \tag{5}$$

Equation (5) has the form $y = a + \dfrac{b}{\sqrt{V_{\text{in}}}}$. By plotting the dependence of $\dfrac{1}{V}$ as a function of $\dfrac{1}{\sqrt{V_{\text{in}}}}$, one can determine the intercept and the tangent of the angle of inclination of the straight line to the abscissa axis:

$$\frac{K_{\text{term}}}{K_{\text{p}}K_{\text{im}}[M]^2} \quad \text{and} \quad \frac{K_{\text{term}}^{1/2}}{K_{\text{p}}[M]}.$$

Their ratio can quantitatively characterize the initiating activity of the initiator, since we postulated at the outset that K_{br} does not depend on the length or nature of the radical,

$$\frac{b}{a} = \frac{K_{\text{im}}[M]}{K_{\text{br}}^{1/2}}.$$

Figure 1 gives examples of our calculation of the initial data for determining $K_{im}/K_{br}^{1/2}$ in the bulk polymerization of styrene initiated by several peroxide initiators (benzoyl, capronyl, and lauryl peroxides). In the calculations we used the rates of bulk polymerization of styrene, determined dilatometrically, in the presence of different initiator concentrations. The rate constants of monomolecular decomposition of the initiators were determined in ethylbenzene solution by extrapolation to zero peroxide concentration. The initiation efficiency for the indicated peroxides was taken as equal to 1 ([5]). The data obtained, together with the initiator decomposition rate constants, are summarized in Table 1.

Table 1

Initiating activity of various peroxides at $t = 73.5°C$

Initiator	K_{decomp}, min^{-1}	$K_{im}/K_{br}^{1/2}$
Benzoyl peroxide	$0.93 \cdot 10^{-3}$	$3.56 \cdot 10^{-2}$
Capronyl peroxide	$3.4 \cdot 10^{-3}$	$16.84 \cdot 10^{-2}$
Lauryl peroxide	$3.3 \cdot 10^{-3}$	$12.6 \cdot 10^{-2}$

Knowing K_{br}, it is easy to determine the true value of K_{im}. But even in this form, under identical conditions (temperature), the quantities obtained can be used to compare the initiating activity of peroxides. Comparison of the determined K_{im} (with allowance for K_{br}) with the rate constant for abstraction of hydrogen from a polymer molecule makes it possible to judge branching in the course of polymerization or chain-transfer reactions through the polymer.

Such a method for evaluating initiating activity may be useful in the choice of an initiator in copolymerization reactions and in graft-polymerization reactions.

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