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DETERMINATION OF THE EFFECTIVENESS OF WEAK INHIBITORS IN VISCOUS MEDIA

Many studies have been devoted to the investigation of the processes of inhibition of chain radical polymerization ([1,2]). A number of possible reaction schemes for the interaction of polymer radicals with inhibitors have been proposed. Thus, in polymerization in the presence of an inhibitor that reacts with polymer radicals to form inert products, the following simple kinetic scheme is applicable:

$$\begin{array}{ll} \text{(a) Initiator} \rightarrow 2R^{\cdot}_{\text{pair}} & v_{\text{in}} \\ \text{(b) } R^{\cdot}_{\text{pair}} + M \rightarrow R^{\cdot}_1 & \\ \text{(c) } R^{\cdot}_n + M \rightarrow R^{\cdot}_{n+1} & k_p \\ \text{(d) } R^{\cdot}_n + Z \rightarrow \text{inert product} & k_z \\ \text{(e) } R^{\cdot}_n + R^{\cdot}_m \rightarrow P_{n+m} \text{ or } P_n + P_m, & k_0, \end{array} \qquad \text{(I)}$$

where v_{in} is the rate of initiation; k_p, k_z, k_0 are the rate constants of the corresponding processes.

If the rate of consumption of inhibitor and monomer can be determined with sufficient accuracy, it is easy to find the ratio k_z/k_p. Further, knowing the value of k_p, one can obtain the value of k_z.

A whole series of kinetic schemes has been proposed that take into account the possibility of copolymerization of the inhibitor with the monomer, chain termination through interaction of macroradicals of the type Z'_n, Z'_m, R'_n, and so forth. For example, Cais ([3,4]) considered one such scheme and showed that it is applicable to the polymerization of methyl methacrylate in the presence of a number of weak inhibitors.

However, the known methods do not allow the effectiveness of extremely weak inhibitors, such as nitrobenzene, diphenylamine, and others, to be determined with sufficient accuracy; for example, these exhibit extremely weak activity in the polymerization of methyl methacrylate ([3,4]) and other vinyl monomers.

When inhibition reactions by weak inhibitors are studied in viscous media, it becomes possible to simplify the kinetic schemes considerably and, in a number of cases, to determine the constant k_z directly. This possibility is associated with the fact that, in a medium of sufficiently high viscosity, some of the elementary reactions become diffusion-controlled.

As an example, let us consider scheme (I).

If, during polymerization in the presence of an extremely ineffective inhibitor in a low-viscosity medium, the rates of processes (d) and (e) may be quite comparable, then in a medium of high viscosity it is easy to choose conditions such that $v_{oRZ} \gg v_{oRK}$. When this condition is fulfilled, using the method of photochemical aftereffect, it is easy to determine k_z.

Let the system contain a weak inhibitor. Then, upon cessation of irradiation, the radicals disappear according to the law

$$\frac{d[R\cdot]}{dt} = -k_z[R\cdot][Z]. \tag{1}$$

Integration of this expression over the limits from $[\mathrm{R}\cdot]_{\mathrm{st}}$ to $[\mathrm{R}\cdot]$ and from 0 to t gives:

$$\ln\frac{[\mathrm{R}\cdot]}{[\mathrm{R}\cdot]_{\mathrm{st}}} = -k_z[Z]t$$

or

$$\ln\frac{v_{\mathrm{st}}}{v_{\mathrm{cur}}} = k_z[Z]t, \tag{2}$$

where v_{st} is the stationary rate of polymerization at the moment when the light source is switched off, and v_{cur} is the reaction rate at time t.

It follows from equation (2) that, by constructing the dependence $\ln v_{\mathrm{st}}/v_{\mathrm{cur}}$ on t, it is easy to determine $k_z[Z]$. Then k_z can be calculated, since the concentration of the weak inhibitor $[Z]$, to a sufficiently good approximation, does not change during the experiment. The latter follows from the well-known expression

$$\frac{\Delta M}{[M]_0} = 1 - \left(\frac{[Z]}{[Z]_0}\right)^{k_p/k_z},$$

where $\Delta M = [M]_0 - [M]$; $[M]_0$, $[M]$, and $[Z]_0$, $[Z]$ are the initial and current concentrations of monomer and inhibitor, respectively.

Equation (2) was obtained under the assumption that the monomer concentration remains constant during the post-effect and that macroradicals identical in kinetic respect are present in the system.

In the case of a noticeable change in $[M]$, the corresponding corrections must be introduced into the values of v_{cur}.

Moreover, because of the presence of a distribution of macroradicals by molecular weight, in a real system there must always be radicals of small size, capable of disappearing as a result of bimolecular interaction. Therefore equation (2) should not hold at the initial stage of the post-effect, and, for determining k_z, it is necessary to integrate equation (1) over the limits from $[\text{R}\cdot]_1$ to $[\text{R}\cdot]$ and from t_1 to t, and to carry out the calculations at the final stage of the post-effect, when only macroradicals are present in the system, whose termination by mutual interaction is hindered in comparison with termination on the inhibitor.

Thus, k_z can be calculated from the expression

$$\ln(v_1/v_{\text{cur}}) = k_z[Z](t - t_1), \tag{3}$$

where v_1 is the reaction rate corresponding to time t_1, at which equation (3) becomes applicable.

In order to select practically the conditions under which equation (3) is obeyed, i.e., when $v_{\text{oRZ}} \gg v_{\text{oR}\cdot\text{R}\cdot}$, it is necessary to study the post-effect in the presence and in the absence of a weak inhibitor.* If it turns out that, during polymerization with an inhibitor, ΔM_{post} is much smaller than the corresponding value in the absence of inhibitor, then the above condition is well satisfied.

Experiments showed that, when carrying out polymerization in highly viscous solutions, it is easy to select conditions under which equation (3) is well obeyed.

Fig. 1. Dependence of $\lg v_1/v_{\text{cur}}$ on t for the post-illumination polymerization of methyl methacrylate in the presence of nitrobenzene in a viscous solution of polymethyl methacrylate (temperature 40°, inhibitor concentration 0.1%, t_1 taken as 0)

Figure 1 shows the dependence of $\lg v_1/v_{\text{cur}}$ on t for the final stage of the post-effect in the photopolymerization ($\lambda = 436$ mμ) of methyl methacrylate

* Of course, the process of termination on the inhibitor must proceed in the kinetic region. The latter can be established by studying the process in media of different viscosity.

in a polymer solution in the presence of nitrobenzene. It is seen that experiment agrees with theory. The value of k_z, calculated from the slope of the straight line, is equal to $2.5 \cdot 10^{-2}$ mole/l • sec.

The validity of expression (3) for the system under consideration may serve as evidence that, when methyl methacrylate polymerization is inhibited by nitrobenzene, sufficiently inert products are formed ([1,5]), which, if they do react with the monomer, do so extremely slowly.

Consideration of more complex kinetic schemes shows that they too can be somewhat simplified. Thus, the scheme proposed by Kice, when realized in a medium of sufficiently high viscosity, apart from reactions (a–) of scheme (I), should take into account only one process

$$Z_n + M \rightarrow R_{n+1} k_{zp}.$$

Thus, the proposed method makes it possible to directly evaluate the inhibiting capacity of a large class of compounds in chain radical polymerization processes, which is in principle inaccessible to other methods.

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REFERENCES

[1] K. Bemford et al., *Kinetics of Radical Polymerization of Vinyl Compounds*, IL, 1961. [2] Kh. S. Bagdasar' yan, *Theory of Radical Polymerization*, Publishing House of the Academy of Sciences of the USSR, 1959. [3] J. L. Kice, *J. Am. Chem. Soc.*, **76**, 6274 (1954). [4] J. L. Kice, *J. Polymer Sci.*, **19**, 123 (1956). [5] C. C. Price, *Mechanisms of Reactions at Carbon–Carbon Double Bonds*, Interscience, N. Y., 1946.

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