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Abstract

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ON THE THEORY OF RADICAL POLYMERIZATION

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Until recently, all the available experimental data on the study of chain radical polymerization as a whole confirmed the general theory, the development of which was begun by P. Flory (1) on the basis of the concepts of the theory of chain reactions (2). In the simplest case the theory leads to the well-known expression

$$V = \frac{k_p}{k_0^{1/2}} V_{\text{in}}^{1/2}[\text{M}], \tag{1}$$

where V is the rate of polymerization, k_p and k_0 are the rate constants of chain growth and chain termination, V_{in} is the rate of initiation, and [M] is the monomer concentration. Thus it follows that the apparent activation energy of the polymerization process, within a narrow temperature interval, is, to a sufficiently good approximation, a constant quantity, which in the simplest case is equal to

$$E = E_p - \frac{1}{2}E_0 + \frac{1}{2}E_{\text{in}}, \tag{2}$$

where E_p, E_0, E_{in} are the activation energies of the elementary reactions.

However, recently N. S. Enikolopyan, in studying the low-temperature photopolymerization of methyl methacrylate, found that in the region of low temperatures (below 0°C) noticeable deviations from the Arrhenius law are observed, which were not explained within the framework of the usual theory (3). Later these results were confirmed by other authors as well (4,5). An explanation of the observed phenomenon was sought on the basis of concepts of collective interaction (3).

Figure 1 presents some new data obtained in the study of the theory of collective interaction; we believe that the role of coll- acetyl as a sensitizer. It follows from the figure that the value of E, from 12.5 kcal/mol at 30°C, decreases to 3.8 kcal/mol at −20° for the polymerization of styrene, and from 5.45 kcal/mol at 90° to 1.0 kcal/mol at −50° for the polymerization of methyl methacrylate.

Fig. 1

Figure 1: Fig. 1

Without calling into question the correctness of the general theoretical propositions of the theory of collective interaction, we believe that the role of collective processes is not of substantial importance in the polymerization in the liquid phase of such vinyl monomers as methyl methacrylate, styrene, etc., even at temperatures comparatively close to the melting temperatures.

The results obtained in the study of deep-phase polymerization of vinyl monomers proceeding at low rates (^{6}), and some other data, gave grounds to suppose that, with a decrease in temperature below 0°, at shallow degrees of conversion the rate constant of chain growth changes with temperature according to the Arrhenius law. The change in the activation energy of polymerization may be connected both with a change in the activation energy of chain termination and with the activation energy of the initiation process.

It was proposed that the change in the activation energy of the chain-termination reaction may be connected with diffusion control of this elemen-

of the elementary process in media with low viscosity. In addition, one could assume that in a number of cases, under photoinitiation, the apparent $\bar{E}_{\text{in}}$ is not only nonzero, but often is also a variable quantity.

The possibility of diffusion control of the chain-termination reaction in the polymerization of a number of vinyl compounds in media with the viscosity of the monomer was first demonstrated by S. Benson and A. North (^{7}). However, A. North (^{4}) believes that the change in the rate of chain termination with temperature cannot substantially distort the form of the straight-line dependence of $\lg V$ on $1/T$.

Fig. 1. Dependence of $\lg V_0$ on $1/T$ for the photopolymerization of methyl methacrylate (upper straight line) and styrene. Sensitizer—diacetyl. V is expressed as percent conversion in 1 hour.

Having confirmed the data of Benson and North on the possibility of diffusion control of chain termination at conversions close to zero, we assumed that the change in the viscosity of pure monomers (and also of solutions of polymers synthesized under the corresponding conditions) with temperature below 0°C cannot be strictly described by the equation

$$\eta = A e^{E_\eta / RT}.$$

Only in this case could one expect a noticeable curvature of the Arrhenius straight line.

Indeed, experiments showed that the activation energy of viscosity (of viscous flow) of such monomers as styrene and methyl methacrylate is a variable quantity (Fig. 2). Since the diffusion coefficient is inversely proportional to the

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

viscosity of the medium, the change in k_0 (at comparatively low temperatures) is determined by the change in viscosity. It may be assumed, with good approximation, that in the case considered the activation energies of viscosity and of chain termination are equal in absolute value.

Fig. 2. Dependence of $\lg \eta$ on $1/T$ for methyl methacrylate (1) and styrene (2)

Fig. 3. Dependence of $\lg V_{\text{in}}$ on $1/T$ for the photopolymerization of styrene in the presence of diacetyl (V_{in} in mol/l • sec)

On the basis of the data in Fig. 2, it follows that for styrene E_η in the temperature interval studied changes from -2.0 to -3.4 kcal/mol. Hence, on passing to low temperatures, E_0 should increase by 1.4 kcal/mol. For solutions of polymers corresponding to 0.5% conversion, ΔE_η is equal to 3.2 kcal/mol. Calculation of the initiation rate in the photopolymerization of styrene from data on measurements of the reaction rates and degree of polymerization at various temperatures ($V_{\text{in rec}} = 2V/P$) shows that the value of E_{in} changes from 8.0 to -8.0 kcal/mol in the temperature interval from 30 to -20° (Fig. 3). The observed-

this phenomenon is associated not only with the change in the absorption coefficient with temperature, but also with a change in the efficiency of initiation as a result of an increase in the viscosity of the medium with decreasing temperature. It should be noted that the character of the change in E_{in} with temperature may depend not only on the nature of the sensitizer, but also on the spectral region used.

Thus, knowing the activation energy in one temperature region (for example, at 30°), one can calculate the corresponding value in another. Using equation (2), it is easy to show that if E_{30° is equal to 12.5 kcal/mole, then E_{-20° should be 3.8 ± 1 kcal/mole. The latter value agrees with experiment (Fig. 1).

In the photopolymerization of methyl methacrylate, deviations from the Arrhenius law are less pronounced (Fig. 1) and are due to a considerable extent to the change in the activation energy of chain termination. Calculation of the ratio $k_p/k_0^{1/2}$ from measurements of the degree of polymerization shows that $E_p - \frac{1}{2}E_0$ changes from a value of 3.5 kcal/mole at 30° to 1.0 kcal/mole at -50°. These values are in reasonable agreement with the changes in viscosity and explain the fact that the molecular weights of the polymers increase with decreasing temperature (in the temperature range -30°—-50°). It should be noted that here there is a certain analogy with the phenomenon of autoacceleration observed in bulk polymerization of methyl methacrylate $^{(8-10)}$.

The results obtained make it possible to explain the existing discrepancies in the data of various authors (8–10) and show that in a number of cases it is necessary to take into account possible changes in the apparent activation energy of the initiation reaction, as well as in the activation energy of chain termination, which may be observed when this process proceeds in the diffusion region.

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REFERENCES CITED

1. P. J. Flory, *J. Am. Chem.*, **59**, 241 (1937).
2. N. N. Semenov, *Chain Reactions*, L., 1934.
3. N. N. Semenov, *Chemistry and Technology of Polymers*, No. 7–8, 196 (1960).
4. A. M. Nort, *Vysokomolek. soed.*, **3**, 1874 (1961).
5. G. P. Gladyshev, S. R. Rafikov, *Vysokomolek. soed.*, **5**, No. 5, 700 (1963).
6. N. F. Khasanova, N. V. Churbakova, G. P. Gladyshev, *Synthesis and Study of High-Molecular Compounds*, Proceedings of the Institute of Chemical Sciences, Academy of Sciences of the Kazakh SSR, Alma-Ata, 1964, p. 30.
7. S. W. Benson, A. M. North, *J. Am. Chem. Soc.*, **81**, 1339 (1959).
8. Kh. S. Bagdasaryan, *Theory of Radical Polymerization*, Publishing House of the Academy of Sciences of the USSR, 1959.
9. K. Bemford et al., *Kinetics of Radical Polymerization of Vinyl Compounds*, IL, 1961.
10. G. P. Gladyshev, *Polymerization of Vinyl Monomers*, Alma-Ata, 1964.

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