Reports of the Academy of Sciences of the USSR

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1965

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1965. Volume 163, No. 6

PHYSICAL CHEMISTRY

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ON THE PECULIARITIES OF LOW-TEMPERATURE PHOTOPOLYMERIZATION OF STYRENE

(Presented by Academician S. S. Medvedev, 12 II 1965)

In work ([1]), general propositions were put forward that make it possible to explain the peculiarities of low-temperature photo- and initiated polymerization of certain vinyl monomers. It was shown that these propositions agree well with data on sensitized photopolymerization of methyl methacrylate and styrene.

In the present work it is shown that anomalies in the photopolymerization of styrene can be observed during polymerization in the absence of a sensitizer. Using the inhibition method, it was also established that the deviations from the Arrhenius law described for photopolymerization in the presence of diacetyl are associated mainly with a change in the apparent activation energy of the initiation energy.

Figure 1 gives the dependence of $\lg V$ on $1/T$, obtained in studying the photopolymerization of styrene. Curve 3 was constructed on the basis of measurements of the initial rates of photopolymerization of styrene under the action of ultraviolet light with $\lambda = 365$ mμ. Curve 1 was constructed for the previously considered case of polymerization of styrene in the presence of diacetyl as sensitizer ([1]), and curve 2 was drawn on the basis of rate data for sensitized polymerization at a degree of monomer conversion into polymer of 5%. Examination of the figure shows that there are certain differences between the course of curves 1, 2, and 3. It is seen that the character of the deviation from the Arrhenius law depends on the conversion even at low degrees of conversion. This agrees well with the propositions stated earlier and shows that the determined values of kinetic parameters may depend substantially on the method of investigation used.

Fig. 1. Dependence of $\lg V$ (%/h) on $1/T$ for photopolymerization of styrene

Fig. 2

Figure 2: Fig. 2

Fig. 2. Dependence of $\lg V_{\text{in}}$ on $1/T$ for photopolymerization of styrene in the presence of diacetyl (V_{in} in mol/l · h)

Thus, when the usual rotating-sector method is used to determine the ratio k_p/k_o, polymerization is carried out in practice in a solution containing polymer, whereas the modified rotating-sector method ([2]) and the method of adiabatic dilatometry ([3]) involve determination of the indicated ratio at a conversion practically equal to zero. The same applies

and for other cases. The change in the rate of initiation with temperature was judged on the basis of experiments to determine $\dot{V}_{\text{in}}$ by the inhibition method. Quinone was used as the inhibitor, its concentration being chosen in such a way that the rate of initiation could be judged with a sufficient degree of accuracy. The corresponding results for sensitized photopolymerization are presented in Fig. 2. It follows from the figure that the activation energy, from a value of 6–8 kcal/mole at 40°, changes to −(6–8) kcal/mole at −20°. The results obtained are confirmed by experiments measuring the molecular weight of polymers synthesized at various temperatures.

Fig. 3. Dependence of $\lg \tau$ on $1/T$ for solutions of polystyrene in monomer, synthesized at 40°

A study of the viscosity of solutions of polymers synthesized over a wide temperature range shows that the activation energy of viscous flow changes substantially on going from positive temperatures to negative ones. Moreover, the value of E_η depends on the concentration of the polymer. In Fig. 3, by way of example, the dependences of $\lg \tau$ (τ is the efflux time) on $1/T$ are given for polymer solutions of various concentrations, synthesized at 40°.

The observed regularities agree with the literature data. For example, Tager and Dreval' ([4]) showed that a change in the concentration of polystyrene in solution leads to a rapid change in E_η.

The calculation carried out from the equation

$$E = E_p - \frac{1}{2}E_o + \frac{1}{2}E_{\text{in}}$$

on the basis of data on the change of E_{in} and E_o with temperature is in good agreement with the experimental results. The data presented, as well as experiments on measuring the lifetime of free radicals by the method of adiabatic dilatometry, give grounds to suppose that, within the limits of experimental error, the value of E_p changes with temperature according to the Arrhenius law.

Fig. 4. Dependence of $\lg V_0$ on $1/T$ for the polymerization of methyl methacrylate in the presence of dimethacrylate triethylene glycol (0.1%), initiated by dicyclohexyl peroxydicarbonate

Yet another example confirming the stated proposition that deviations from the Arrhenius law in the polymerization of vinyl monomers are mainly connected with changes in E_o and E_{in} is the polymerization of methyl methacrylate in the presence of cross-linking agents. In Fig. 4 the dependence of $\lg V_0$ on $1/T$ is shown for the polymerization of methyl methacrylate in the presence of dimethacrylate triethylene glycol, initiated by dicyclohexyl peroxydicarbonate. It follows from the figure that the value of E at a temperature of 20° is 14 kcal/mole, whereas at a temperature of 60° $E = 19.5$ kcal/mole. In this

In this case, the effect of an increase in the activation energy of polymerization with temperature is associated with a significant increase in E_0 in the low-temperature region. The latter is due to a sharp increase in the viscosity of the medium with decreasing temperature, not only because of the purely temperature dependence of the viscosity, but also because of the increase in the molecular weight of the polymer with decreasing temperature*.

In general, various apparent deviations from the Arrhenius law are possible, associated with a decrease in the rates of initiation and chain termination as the viscosity of the medium increases. These effects are oppositely directed, and the observed deviations from the usual regularities are determined by the resultant of their superposition**.

The authors express their gratitude to Acad. S. S. Medvedev, Acad. of the Academy of Sciences of the Kazakh SSR S. R. Rafikov, and Prof. N. S. Enikolopyan for valuable discussion and advice.

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Received
10 II 1965

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* The initial rate of polymerization was determined by the dilatometric method on the basis of studying the reaction at conversions of 0-5%.

** Naturally, in photopolymerization it is necessary to take into account the possible change in the absorption coefficient with temperature. The latter, as already indicated, may lead to a change in the apparent value of E_{in} with temperature.

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

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