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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

Full Text

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ON THE MECHANISM OF THE RADIATION POLYMERIZATION OF ETHYLENE

(Presented by Academician S. S. Medvedev, December 20, 1963)

The radiation polymerization of ethylene at temperatures below the melting point of the polymer is characterized by the fact that the reaction rate increases at the beginning of the process, reaches a maximum, and then decreases ([1]); the observed effect is not associated with a change in the composition of the gas phase, but is determined by the accumulation of solid polymer ([1]). In the present work, the kinetics of the radiation polymerization of ethylene was studied with the aid of a specially designed dilatometer, in which the reaction rate was measured at strictly constant pressure*. Ethylene was used whose composition

Fig. 1. Dependence of the polymer yield on time at various pressures; 25°, $I = 9$ rad/sec. The numbers on the curves are the ethylene pressure (in atm)

Fig. 2. Dependence of the polymer yield on time at various temperatures; 250 atm, $I = 9$ rad/sec. The numbers on the curves are the temperature (°C)

is given in ([1]). The polymerization was carried out on a γ-radiation source ([2]) K-60000 at 100-250 atm, 25-55°, and a dose rate (I) of 9 rad/sec. The kinetic curves (Figs. 1, 2) are characterized by a maximum in the rate ($W_{\max}$) (Fig. 3). With increasing temperature at constant pressure, the value of $W_{\max}$ decreases and the maximum shifts into the region of lower degrees of conversion (Fig. 2). Experiments involving replacement of the ethylene during the process showed that the slowing of polymerization is not associated with the accumulation of inhibiting products in the gas phase. Polymerization ceases no later than 3-10 min after the radiation source is switched off. Thus, the initial acceleration of the reaction cannot be explained by the presence of long-lived radicals.

The radiation polymerization of ethylene may proceed in the gas phase and in the solid polymer, owing to the ethylene dissolved in it. It was shown earlier

Fig. 3. Dependence of the polymerization rate on the polymer yield; 25°, $I = 9$ rad/sec. The numbers on the curves are the ethylene pressure (in atm)

Figure 3: Fig. 3. Dependence of the polymerization rate on the polymer yield; 25°, $I = 9$ rad/sec. The numbers on the curves are the ethylene pressure (in atm)

(3) that the reaction of ethylene addition to radicals contained in the solid polymer, at a specific surface area of the latter of 10-20 m^2/g, proceeds uniformly throughout the entire volume of the polymer. Then the polymerization rate per unit volume of the reaction vessel (W) can be represented by the equation

$$W = W_g(1 - \Pi) + W_p\Pi, \tag{1}$$

where W_g, W_p are the rates of polymer formation per unit volume of the gas phase and per unit volume of polymer, respectively, and Π is the amount of polymer per unit volume of the reaction vessel.

* The design of the dilatometer will be described in a special article.

Radicals in solid polyethylene are formed as a result of the transition of radicals from the gas phase and irradiation of the polymer. Studies of the e.p.r. spectra of irradiated polyethylene (4) showed that the alkyl radicals formed, of the type $-CH_2-\dot{C}H-CH_2-$, at room temperature either perish as a result of quadratic termination or are converted into allyl radicals of the type $-CH_2-CH-\dot{C}H = CH - CH_2-$ through interaction with trans-vinylene double bonds that arise during irradiation of polyethylene (5). The radiation yield of double bonds does not depend on the irradiation temperature (5), and their concentration does not change upon heating of previously irradiated samples (6). Thus, in solid polyethylene, addition of alkyl radicals to trans-vinylene bonds practically does not occur.

Fig. 3. Dependence of the polymerization rate on the polymer yield; 25°, $I = 9$ rad/sec. The numbers on the curves are the ethylene pressure (in atm)

The study we carried out of the e.p.r. spectra of radiation polyethylene,* irradiated in vacuum (10^{-5}—10^{-6} mm Hg) at −196°, showed that in such polyethylene the lifetime of alkyl radicals at room temperature coincides, in order of magnitude, with the period of the dark reaction. The radicals stable at room temperature have a seven-component e.p.r. spectrum characteristic of allyl radicals.

On the basis of these studies, the following kinetic scheme of polymerization may be adopted:

Figure 4

Figure 4: Figure 4

Gas phase

$$M \xrightarrow{h\nu} R_0 \quad \text{(initiation)}$$

$$R_0 + iM \xrightarrow{h\nu} R \quad \text{(growth)}$$

$$\left.\begin{array}{r} R \xrightarrow[\text{crystallization}]{} R_{\parallel} \\ R + R \to P \xrightarrow[\text{crystallization}]{} \end{array}\right\} \text{termination}$$

Solid polymer

$$\left. R \xrightarrow[\text{crystallization}]{} R_{\mathrm{P}} \quad \right\} \text{initiation}$$

$$P \xrightarrow{h\nu} R_{\mathrm{P0}}$$

$$R_{\mathrm{P0}} + iM \xrightarrow{K_p} R_{\mathrm{P}} \quad \text{(growth)}$$

$$P \xrightarrow{h\nu} D$$

$$\left.\begin{array}{l} R_{\mathrm{P}} + R_{\mathrm{P}} \xrightarrow{K_{\mathrm{ob}}} P \\ R_{\mathrm{P}} + D \to R_a \\ R_{\mathrm{P}} + R_a \to D \end{array}\right\} \text{termination}$$

Here: M is ethylene, R_0 are primary radicals, R are polymer radicals in the gas phase, P is polymer, R_{P0} are primary radicals in the solid polymer of the type $-\mathrm{CH_2} - \dot{\mathrm{C}}\mathrm{H} - \mathrm{CH_2}-$, R_{P}, R_a are polymeric alkyl and allyl radicals in the solid phase, and D are trans-vinylene bonds in the polymer.

Cocrystallization of radicals with polymer molecules occurs at high rate. Therefore the concentration of radicals in the gas phase is extremely small, and the interaction of these radicals with radicals in the polymer may be neglected. The scheme also lacks the transfer reaction through

* We express our gratitude to A. K. Piskunov and V. L. Muromtsev for assistance in measuring the e.p.r. spectra.

monomer, which is unlikely under our conditions. In the temperature interval studied, allyl radicals do not interact with ethylene molecules, and the formation of such radicals may be regarded as a chain-termination reaction. The short lifetime of alkyl radicals in the polymer also gives grounds for assuming that, in the course of polymerization, a stationary concentration of growing chains is established in the polymer.

It follows from the above scheme of the process that, along with an increase in W as a result of polymer accumulation, there is a decrease in W owing to an increase in the concentration of double bonds. The total change in the polymerization rate depends to a considerable extent on the probability of transfer of radicals between individual regions of the solid polymer, i.e., on the dispersity of the polymer. We considered two models of polymerization: 1) the entire polymer is a homogeneous system; 2) the polymer is a set of noninteracting homogeneous regions formed at different times.

Fig. 4. Dependence of $\ln\dfrac{\Pi}{t}$ on $I^{1/2}$; 100 atm; 12 h; 25°. Π is expressed in g/l, t in hours. *a*—experimental data, *b*—data from work (^{1})

In the initial stage the polymer is formed as a highly disperse charged aerosol (^{7}), i.e., the second model is realized. With increasing conversion depth the dispersity of the polymer decreases sharply (^{3}) and the "weight" of the first model increases. Mathematical analysis shows that the first model is characterized by a maximum rate, but the time required to reach the maximum is considerably less than that observed experimentally. According to the second model, the polymerization rate should increase continuously with the accumulation of solid polymer. In accordance with the adopted kinetic scheme, the polymerization rate will decrease as the dispersity of the polymer decreases. Thus, the experimental kinetic curve lies between the kinetic curves of the first and second models. It is evident that in the initial stage, when the concentration D is small, the curves of both models coincide and the polymerization rate is determined by the equation

$$W = W_0 + \frac{W_{\text{in}}^{1/2} K_p}{K_{\text{ob}}^{1/2}} C_p \Pi \ldots, \tag{2}$$

where W_0 is the initial polymerization rate, W_{in} is the rate of formation of radicals in the polymer under the action of radiation, and C_p is the concentration of ethylene dissolved in the polymer*. As is seen from Fig. 3, this equation is well obeyed for the initial stage of polymerization at 25°. At $I = 9$ rad/sec ($5.4 \cdot 10^{14}$ eV/g polymer · sec) and a polymer density of 950 g/l, taking the radiation yield of radicals in the polymer (^{4}) per 100 eV to be equal to three, we obtain $W_{\text{in}} = 2.6 \cdot 10^{-8}$ mol/l · sec. From the slope of the straight line (Fig. 3) for 25° and 193 atm,

$$K = \frac{W_{\text{in}}^{1/2} K_p C_p}{K_{\text{ob}}^{1/2}} = 3.6 \cdot 10^{-5}\ \text{sec}^{-1}.$$

Under these conditions, according to the data of work (^{3}), $C_p = 4.0 \cdot 10^{-2}$ g/g polymer. Thus, $K_p/K_{\text{ob}}^{1/2} = 5.6\ \text{l}^{1/2} \cdot \text{sec}^{-1/2} \cdot \text{mol}^{-1/2}$. The results of calculations for the other pressures studied are close to this value.

At low pressures (about 100 atm) one may, as a first approximation, neglect the value W_0 (Fig. 3). Then, at small doses,

$$K = \ln \Pi / t \tag{3}$$

(t is the polymerization time) and, according to (2), $\ln \Pi / t = a\sqrt{I}$, where a is a constant—

quantity. The experimental results confirm this dependence (Fig. 4). At large doses, $\ln P < Kt$ owing to the influence of double bonds. The slope of the straight line in Fig. 4 gives the value $a = (K/\sqrt{I})_{100\ \mathrm{atm}} = 1.25 \cdot 10^{-5}\ \mathrm{rad}^{-1/2} \cdot \mathrm{sec}^{-1/2}$. At 110 atm, 9 rad/sec, and 25°, $K = 3.1 \cdot 10^{-4}\ \mathrm{sec}^{-1}$ (Fig. 3) and $a = 1.03 \cdot 10^{-5}\ \mathrm{rad}^{-1/2} \cdot \mathrm{sec}^{-1/2}$. Taking into account the approximate character of equation (3), the agreement between the values of a calculated from the data of Figs. 3 and 4 may be regarded as satisfactory.

With increasing temperature the probability of formation of an allyl radical increases, and the kinetic curve already in its initial stages deviates from equation (2). We therefore were unable to determine $K_p/K_{\mathrm{ob}}^{1/2}$ at temperatures above room temperature; however, comparison of the initial portions of the curves in Fig. 2 shows that, for heterogeneous polymerization of ethylene, $E_p - \frac{1}{2}E_{\mathrm{ob}} \simeq 0$*.

The value obtained for $K_p/K_{\mathrm{ob}}^{1/2}$ is considerably higher than those given in the literature (see Table 1). For homogeneous polymerization of ethylene at high

Table 1

Temp., °C	Total pressure, atm	C_{ethylene}, mole/l	Phase state of the system	Initiator	Medium	$K_p/K_{\mathrm{ob}}^{1/2}$	Literature source, reference
0	40	12.5 (liquid ethylene)	Heterogeneous	Azoisobutyric acid ester. Photoinitiation	—	$5.2 \cdot 10^{-4}$	(10)
70	500	—	Same	Dinitrile of azoisobutyric acid	Benzene, 0.14 mole/l	$1.7 \cdot 10^{-2}$	(11)
83		6.1	Homogeneous	Photoinitiation, azoisopropane	Benzene, 71.9 wt. %	$1.5 \cdot 10^{-2}$	(12)
129	750—2500	10.4	Same	tert-Butyl peroxide	Propane	0.22—0.73	(13)

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* In the pressure interval studied, as a first approximation one may neglect the effect of pressure on K_p and K_{ob}.

temperatures this is explained by the fact that K_{ob} in a liquid is usually several orders of magnitude higher than in a solid polymer ([8,9]).

The values of $K_p/K_{\text{ob}}^{1/2}$ obtained in work on heterogeneous polymerization are not entirely reliable, since the mechanism of polymerization in these studies was either not investigated at all or was insufficiently physically substantiated. In particular, data are completely lacking on the relation between the reaction at the surface and in the bulk of the polymer. In addition, in calculating $K_p/K_{\text{ob}}^{1/2}$ in all the works the concentration of ethylene in the gas or liquid phases is used, and not its concentration in the polymer. This may lead to greatly lowered values of $K_p/K_{\text{ob}}^{1/2}$.

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CITED LITERATURE

1. S. S. Medvedev, A. D. Abkin et al., *Vysokomolek. soed.*, **2**, 904 (1960).
2. A. Kh. Breger, V. B. Osipov, V. A. Gol' din, *Atomnaya energiya*, **8**, 441 (1960).
3. G. N. Gerasimov, A. D. Abkin, P. M. Khomikovskii, *Vysokomolek. soed.*, **5**, 479 (1963).
4. A. T. Koritskii, Yu. N. Molin et al., *Vysokomolek. soed.*, **1**, 1182 (1959).
5. E. I. Lawton, R. S. Powell, I. S. Balwit, *J. Polym. Sci.*, **32**, 257 (1958).
6. N. A. Slovokhotova, A. T. Koritskii et al., *Vysokomolek. soed.*, **5**, 568 (1963).
7. V. S. Bogdanov, Izd. AN SSSR, OKhN, 1961, No. 8, 1520.
8. K. Bemford, U. Barbi et al., *Kinetics of Radical Polymerization of Vinyl Compounds*, IL, 1961.
9. A. Charlesby, D. Libby, M. G. Ormerod, *Proc. Roy. Soc.*, **A262**, 207 (1962).
10. W. M. Padgett, E. Perri, *J. Polym. Sci.*, **37**, 543 (1959).
11. B. L. Erussalimsky, S. G. Lyubetzky et al., *Polymers* (London), **3**, 639 (1962).

12. Z. Laita, Z. Machaček, *J. Polym. Sci.*, **38**, 459 (1959).

13. K. O. Symcox, P. Ehrlich, *J. Am. Chem. Soc.*, **84**, 531 (1962).

* In the temperature interval studied, C_p at constant pressure changes within 5% (^{3}).

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

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