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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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RADIATION POLYMERIZATION OF TETRAFLUOROETHYLENE IN THE SOLID STATE

(Presented by Academician S. S. Medvedev January 5, 1963)

The data available in the literature on the radiation polymerization of tetrafluoroethylene (TFE) are very few in number [1–3] and relate mainly to processes in the gas and liquid phases.

At the same time, the study of TFE polymerization in the solid state is of considerable interest (m.p. of the monomer, −131°). The present communication is devoted to this question.

It is known that a number of monomers, when irradiated in the solid state, polymerize at appreciable rates; moreover, some of them—styrene [5–7], 2,4-dimethylstyrene [6], acrylonitrile [4, 7–9], methacrylonitrile [10], formaldehyde [11, 12] —polymerize in the solid state substantially faster than in the liquid near the melting temperature of the monomer.

Fig. 1. Dependence of the initial rate of TFE polymerization (w_0) under γ-irradiation on temperature; dose rate (I) 180 rad/sec.
a—supercooled liquid

For our study we used TFE purified from stabilizer and impurities by distillation on a low-temperature column (30 theoretical plates) and dried by freezing out moisture. The purified monomer had m.p. −131°, b.p. −76°. The monomer was carefully freed of dissolved air in vacuum ($1 \cdot 10^{-3}$ mm Hg) and refrozen into glass ampoules for polymerization. Thermostatting of the samples at low temperatures on the γ-radiation source was carried out in a metal cryostat with an accuracy of ±0.5°; during irradiation with fast electrons, by blowing the ampoules with evaporating nitrogen, with an accuracy of ±2°.

Before irradiation the samples were frozen by immersion in liquid nitrogen and then held for 10 min at the temperature of the experiment.

The polymer yield was determined gravimetrically after rapid thawing of the irradiated samples (the thawing time from −134° was 10 sec, from −196° 60 sec). If the possibility of post-polymerization during thawing is allowed, then the amount of polymer formed in this way must be small and cannot introduce a

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Fig. 2. EPR spectra of TFE under irradiation with γ-rays and fast electrons

Figure 2: Fig. 2. EPR spectra of TFE under irradiation with γ-rays and fast electrons

substantial error into the experimental results. This is indicated by the following experimental facts: 1) the polymer yield in experiments at -143° is about 10 times higher than at -196°, although the thawing time in the second case is considerably longer; 2) the polymer yield at -196° ($I = 180$ rad/sec) proves to be the same for irradiation doses of 1.3 and 8 Mrad (in this case linear accumulation of radicals with dose continues in the system). Irradiation was carried out on a Co^{60} source with an activity of 60,000 g-eq radium [13] and on an electron accelerator with an electron energy of 1.5 MeV.

Electron paramagnetic resonance (EPR) spectra were recorded on RE-1301-type instruments in capillaries made of special LUCH-2 glass.

The absolute concentrations of radicals were calculated by comparing the signal areas of the sample under study and of a standard with a known concentration of paramagnetic particles (a single crystal of $CuCl_2 \cdot 2H_2O$).

The initial rate of polymerization of TFE in the solid state, w_0*, increases with increasing temperature, reaching a maximum near the melting of the monomer (Fig. 1). On transition to the liquid at the melting temperature, a sharp drop in the rate occurs (by more than an order of magnitude); subsequently, with increasing temperature the rate of polymerization of liquid TFE increases substantially with temperature.

Fig. 2. EPR spectra of TFE under irradiation with γ-rays and fast electrons:
a—at -196° after γ-irradiation; dose (D) 15 Mrad, $I = 550$ rad/sec, irradiation temperature -196°, polymer yield $\sim 1\%$;
b—at -185° during irradiation with fast electrons; $D = 65$ Mrad, $I = 0.85 \cdot 10^6$ rad/sec; polymer yield after irradiation with a dose of 75 Mrad $\sim 22\%$;
c—at 50° (for point 1 in Fig. 3).

The total activation energy of polymerization (E) in the solid phase in the temperature interval from -196° to -155° is 0.6 kcal/mole, and from -155° to -131°, $E = 1.6$ kcal/mole; for polymerization in the liquid, $E = 6$ kcal/mole, which is close to the value obtained in work ([3]).

In the polymerization of TFE in the solid state, "limiting" of the polymer yield is observed in the initial stages of the process, and the limiting conversion increases with rising temperature. At -196° ($I = 180$ rad/sec) the limiting yield is about 1% and is reached already at a dose of 1 Mrad, remaining essentially unchanged up to 8 Mrad; the radical concentration, however, continues to increase linearly with dose, reaching $2 \cdot 10^{18}$ radicals/g at 8 Mrad. In the case of irradiation of solid TFE with fast electrons at high intensities ($\sim 10^5$ rad/sec), conversions are reached that exceed, at least severalfold, the limiting values in experiments

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Fig. 3. Dependence of radical concentration on temperature at a constant sample-heating time

Figure 3: Fig. 3. Dependence of radical concentration on temperature at a constant sample-heating time

at low intensities ($\sim 10^2$ rad/sec, γ-rays).

The radiation-chemical yield of polymerization in the solid state for small extents of conversion (up to 1%) is 10^2 at $-196°$ and 10^3 molecules per 100 eV of absorbed energy near melting. The yield of radicals at $-196°$ for doses of 5-10 Mrad is ~ 0.4 per 100 eV.

The EPR spectra of TFE under irradiation with γ-rays and fast electrons are presented in Fig. 2a. The spectra were obtained in the absence of saturation. The spectrum obtained during irradiation with fast electrons does not change after the beam is switched off. When the temperature of the irradiated sample is raised in the range from -180 to $-140°$, an intense loss of radicals occurs (Fig. 3)**, and in samples for which the polymer yield is small ($\sim 1\%$) the radical concentration falls practically to zero, while in samples with a substantial polymer content (10-20%) it falls to a certain quantities and subsequently does not change over a wide temperature interval from -150 to $-80°$.

A further intense decrease in the radical concentration occurs in the region from -80 to $-50°$ C, above which the death of radicals slows down. In samples containing a considerable amount of polymer, the death of radicals in the temperature region from -180 to $-150°$ C is accompanied by a substantial change in the shape of the spectrum. It is transformed into a poorly resolved triplet with a splitting between the lines of about 40 gauss (see Fig. 2b). Upon further increase in temperature, the character of the spectrum changes essentially no further up to the disappearance of the radicals at temperatures close to 0°.

Fig. 3. Dependence of radical concentration on temperature at a constant sample-heating time (τ). 2 $-\gamma$-irradiation at $-196°$; $D = 13$ Mrad, $I = 550$ rad/sec, 1% polymer; $\tau = 5$ min; e.p.r. spectra after heating were recorded at $-196°$. 3 $-$irradiation with fast electrons at $-185°$; $D = 40$ Mrad, $I = 0.5 \cdot 10^5$ rad/sec, 13% polymer; $\tau = 10$ min; e.p.r. spectra were recorded at the heating temperature.

The described character of the death of radicals and the change in the form of

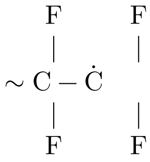
* w_0 was calculated from the polymer yield during the first 9 min of irradiation, which corresponds to conversions from 0.05 to 0.8%.

** Some difference in the course of the curves shown is apparently due to different sample heating times.

the e.p.r. spectrum makes it possible to suppose that the spectrum observed at low temperatures belongs to a radical arising in the monomer; in samples containing a considerable amount of polymer, the spectrum of a polymer radical is superimposed on this spectrum. The spectrum observed at temperatures of −150° and above belongs to the polymer radical. This is evidenced by the preservation of the spectral shape at temperatures exceeding the melting and boiling temperatures of the monomer.

The region of substantial death of these radicals found by us (−80 ÷ −50° C) corresponds to the first region of disinhibition of molecular motions in polytetrafluoroethylene (−65 ÷ −45°), found by Smith by the nuclear magnetic resonance method (^{14}).

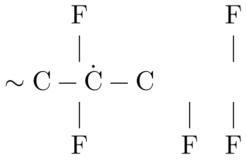
The polymer radical (Fig. 2b), apparently, has the structure



$$\sim \underset{F}{\overset{F}{C}} - \underset{F}{\overset{F}{\dot{C}}}$$

(I)

The formation of radicals of another structure, for example,



$$\sim \underset{F}{\overset{F}{C}} - \dot{C} - \underset{F\quad F}{\overset{F}{C}}$$

(II)

under the conditions of the experiment is unlikely. In addition, the EPR spectrum of radicals (II) has an entirely different, quadruplet, structure (15-18).

The occurrence of substantial concentrations of radicals (I) as a result of radiolysis of the polymer formed is also unlikely. It should therefore be assumed that radicals (I) were formed in the system as a result of growth of the polymer chain.

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