# Physical Chemistry

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1962

SovietRxiv

## Abstract

## Full Text

*Physical Chemistry*

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# PLASTICIZATION OF POLYETHYLENE UNDER LOW-TEMPERATURE RADIOLYSIS

*(Presented by Academician V. N. Kondrat' ev, July 19, 1962)*

In many organic substances irradiated at low temperature with fast electrons or gamma rays, upon subsequent heating luminescence is observed ([1,2]), associated with recombination of active centers formed and stabilized in these substances during their irradiation. As was noted ([2,3]), the intensity of such emission increases sharply (passes through maxima) in those temperature intervals where the mobility of the molecules of the substance is unfrozen; in particular, flashes of emission are observed during the devitrification of irradiated amorphous compounds. Therefore the glow curve makes it possible to obtain information on those changes that occur in the substance under study as the temperature rises. Using this method, we found that if the irradiation dose is increased, the positions of the maxima on the glow curves of some organic compounds shift monotonically toward lower temperatures.

Below are the results of an investigation of this phenomenon in high-pressure polyethylene. Disks of polyethylene 10 mm in diameter and 2 mm thick were irradiated at a temperature of 77°K with fast electrons in the dose range 1—70 Mrad. They were then heated at a prescribed constant rate, and their emission was recorded with an FEU-19 photomultiplier.

As is known ([2]), the glow curve of high-pressure polyethylene irradiated with small doses has two maxima: at 153°K and at about 233°K, the latter maximum corresponding to the transition of polyethylene into the rubbery-elastic state; the position of the maximum thus characterizes the glass-transition temperature of the polymer.

With an increase in the irradiation dose we observed that this maximum shifts toward lower temperatures. Figure 1 shows glow curves of polyethylene samples in the interval 170—270°K and at a heating rate of 20° per minute, irradiated at doses of 1, 20, and 40 Mrad. In all curves of Fig. 1, for ease of comparison, the intensity at the maximum is taken as unity. Figure 2 shows the dependence of the temperature $T_m$, corresponding to the emission maximum, on the dose with which the sample was irradiated. As is seen from the figures, the transition temperature of polyethylene into the rubbery-elastic state decreases in the irradiated samples, and at a dose of 70 Mrad this decrease amounts to almost 40°. The shift of the temperature region of glass transition of irradiated polyethylene

Fig. 1. Glow curves of polyethylene samples irradiated at 77°K with fast electrons: 1—irradiation dose 1 Mrad, 2—20 Mrad, 3—40 Mrad, 4—1 Mrad; the sample had previously been irradiated with a dose of 20 Mrad and heated to 300°K.

Figure 1: Fig. 1. Glow curves of polyethylene samples irradiated at 77°K with fast electrons: 1—irradiation dose 1 Mrad, 2—20 Mrad, 3—40 Mrad, 4—1 Mrad; the sample had previously been irradiated with a dose of 20 Mrad and heated to 300°K.

is temporary in character and disappears already after the first heating of the sample to room temperature. Indeed, if a sample irradiated at a temperature of 77°K with a dose of 20 Mrad is heated to 300°K, immediately thereafter cooled to 77°K, irradiated again with a dose of 1 Mrad, and again heated to 300°K, then the glow curves obtained during the first and second heatings are represented, respectively, by curves 2 and 4 of Fig. 1. As can be seen, curve 4 is more similar to curve 1

and differs from it only by a slight shift toward the higher-temperature side*. However, with an increase in the dose of repeated irradiation of such a sample at 77°K, its glow curve again changes shape, and the position of the maximum on the curve will again shift toward lower temperatures.

The shift of the transition region into the rubbery-elastic state, observed in polyethylene samples subjected to low-temperature radiolysis, is apparently associated with plasticization of the polymer by low-molecular radiolysis products, chiefly molecular hydrogen and light hydrocarbons. The accumulation of these products in appreciable amounts in the volume of the irradiated sample may be associated with the slowing of their diffusion at low temperatures. An effect of this kind was found in our institute by G. K. Vasil' ev, V. E. Skurat, and V. L. Tal' roze, who showed that in polyethylene irradiated at the temperature of liquid nitrogen a considerable amount of gaseous products, mainly molecular hydrogen, is retained; their release upon heating the sample occurs up to room temperature. Apparently, the disappearance of the effect we observed in samples heated after radiolysis to room temperature is associated with the removal of gases from the polymer. Owing to the finite rate of diffusion of radiolysis products to the sample surface, one may expect that, under rapid heating, the amount of such plasticizing products retained in the sample volume by the time of its vitrification will be greater than under slow heating.

**Fig. 1.** Glow curves of polyethylene samples irradiated at 77°K with fast electrons: **1**—irradiation dose, 1 Mrad; **2**—20 Mrad; **3**—40 Mrad; **4**—1 Mrad, the sample had previously been irradiated with a dose of 20 Mrad and heated to 300°K.

To verify this, we investigated how the position of the maxima on the glow curves of polyethylene samples irradiated at two dose values, 0.5 and 4 Mrad, changes

Fig. 2. Dependence of $T_m$ in polyethylene samples on irradiation dose.

Figure 2: Fig. 2. Dependence of $T_m$ in polyethylene samples on irradiation dose.

as a function of the heating rate. In these cases thin polyethylene samples cut from a tape 60 $\mu$ thick were used. It was found that samples irradiated with a dose of 4 Mrad devitrify at a temperature 4–6° lower than samples irradiated with a dose of 0.5 Mrad, if they are heated at a rate of 40–50° per minute. However, at a heating rate of 5° per minute, all these polyethylene samples, within the accuracy of measurement, devitrify in one and the same temperature interval.

**Fig. 2.** Dependence of $T_m$ in polyethylene samples on irradiation dose.

These results indicate that, at a low heating rate, the radiolysis products are for the most part removed from the volume of the thin sample during its heating up to the glass-transition temperature.

On the basis of the data obtained, it may be concluded that, in low-temperature radiolysis of polyethylene, alongside the process of radiation

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* In work (3) it was shown that such a shift of $T_m$ toward higher temperatures is associated with crosslinking of polyethylene as a result of the first irradiation (dose 20 Mrad).

crosslinking is accompanied by its plasticization by gaseous products. And if crosslinking leads to an increase in the polymer' s $T_g$, then plasticization, on the contrary, facilitates the mobility of segments of the polymer chain and thereby lowers the temperature at which the irradiated polyethylene specimen passes into the rubbery-elastic state. It is quite possible that this effect also plays a role in other phenomena associated with the unfreezing of molecular mobility in irradiated substances.

The authors express their gratitude to M. V. Alfimov and D. N. Sapozhnikov for their assistance in the work.

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Received
16 VII 1962

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