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Abstract

Full Text

PHYSICAL CHEMISTRY

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RADIOTHERMOLUMINESCENCE OF ORGANIC COMPOUNDS

(Presented by Academician V. N. Kondrat' ev on 28 IV 1960)

It is known (1) that many substances irradiated at low temperature with γ-rays or fast electrons luminesce upon subsequent warming. In the present work this glow, radiothermoluminescence, was studied for several organic compounds.

The substance under investigation was irradiated in a nitrogen atmosphere with fast electrons of energy 1.5 MeV at a dose rate of $5 \cdot 10^5$ rad/sec. The temperature during irradiation was maintained at about 100° K. Usually the samples used were in the form of thin films or sections, weighing from 1 mg to 100 mg; liquids were frozen in silvered brass capsules, the layer thickness always being considerably less than the electron range. The irradiated samples were stored in liquid nitrogen, and then, when they were heated at a constant rate of 15 deg/min, the glow curve was recorded (the intensity of the glow as a function of temperature). The electrophotometer used for this purpose consisted of an FEU-19 photomultiplier, a direct-current amplifier, and an EPP-09 electronic self-recording potentiometer. The integral luminous flux, determined by the spectral sensitivity of the FEU-19, was recorded; the spectral composition of the radiation was not studied. The temperature of the sample was measured with a fine copper-constantan thermocouple.

Fig. 1. Glow curves of polyethylene:
1 —high-pressure polyethylene, 2 —low-pressure polyethylene; irradiation dose 10^6 rad.

Glow curves are characterized by the presence of one or several maxima at definite temperature values. Thus, in samples of high-pressure polyethylene we observed two thermoluminescence flashes, the temperature values at the maxima being $T_{M_1} = -120°\text{C}$ and $T_{M_2} = -40°\text{C}$ (see Fig. 1, 1). Figure 1 also shows the glow curve for one of the samples of low-pressure polyethylene (curve 2), on

Figure 2

Figure 2: Figure 2

which there is a maximum at −119°C and a weak, poorly resolved maximum at −59°C. Polyethylene samples from ten batches were used in the work, and similar results were obtained for different batches. For example, in samples of high-pressure polyethylene the position of T_{M_1} varied within the limits −124 to −116°C, and T_{M_2} from −43 to −31°C. It should be noted that, when working with samples from the same batch, the reproducibility of the results did not go beyond one or two degrees.

As is known, low-pressure polyethylene differs from high-pressure polyethylene by the low degree of branching of the molecule (^{2}), which leads to certain differences in their physical properties. Study of the temperature dependence of the elastic modulus and of mechanical and dielectric losses in the interval −150 to 0°C showed that, in high-pressure polyethylene,

there are two distinct structural transitions in this region $^{(3-6)}$. One, at $-125 \div -105$°C, was found for many polymers and is apparently associated with the appearance of collective vibrations of segments of the main chain and side chains $^{(7,8)}$. The second transition, at $-70 \div -20$°C, is characteristic only of branched polyethylene $^{(6)}$. Usually the temperature of this transition is called the glass-transition temperature of polyethylene. A different picture is observed in the case of low-pressure polyethylene and polymethylene. The mechanical and dielectric losses also have a maximum in these compounds at $-115 \div -105$°C; however, the maximum at $-70 \div -20$°C is absent or very weakly expressed $^{(4,9)}$, which is connected with the small number of side groups in the molecules of these polymers. Thus, in polyethylene there is a certain analogy between the maxima on the glow curves and on the curves of mechanical and dielectric losses.

In the present work it was also established that the position of the maxima on the glow curves, in particular the position of T_{M_2}, changes depending on the dose of preliminary irradiation (degree of crosslinking of the polymer), on the thermal prehistory of the specimen, and with changes in the heating rate, and the shift of T_{M_2} corresponds to the shift, under these conditions, of the glass-transition temperature of the polymer. Comparing all these facts, one may conclude that the flashes of thermoluminescence of polyethylene are associated with the defreezing of hindered molecular motion in this polymer.

Fig. 2. Glow curve at a dose of 10^6 rad (1) and thermomechanical curve (2), obtained for one and the same specimen of polyisobutylene

Table 1

Substance studied	T_M, °C	T_{MD}, °C	Substance studied	T_M, °C	T_P, °C	T_{MD}, °C
High-pressure polyethylene	−124, −116^1 −43, −31	−120$^{(4)}$, −108$^{(6)}$; −45$^{(11)}$; −128$^{(11)}$	Polyisobutylene	−45	−52^3	
Low-pressure polyethylene	−119 −59		Teflon	−125 +22		−96$^{(14)}$; −105$^{(15)2}$ +20$^{(14)}$; +23$^{(15)}$; +21$^{(16)}$
Paraffin $\sim n$-$C_{28}H_{58}$	−121 −50^1 +50÷ +55	Melt +60	Natural rubber	−137 −58	−57^2	−61$^{(17)}$
Plasticized paraffin (1% CCl_4)	−134 −71		Rubber SKI	−126 −58 +63	−56^3 +80^3	
Octadecane n-$C_{18}H_{38}$	−111 +20	+24$^{(12)}$; m.p. +28	Rubber SKB	−49 +60	−46^2 +50÷ +70	
Nonane n-C_9H_{20}	−112 −57 −54		Cyclohexane	−148 −115 −87 −72		−120 ÷ −90$^{(18)}$; −87.1$^{(19)4}$; −50$^{(18)5}$
Polydimethylsiloxane	−119					

[1] On the basis of nuclear magnetic resonance spectra it is assumed $^{(12)}$ that rotation of methyl groups begins to appear in n-$C_{28}H_{58}$ at −45°C and in n-$C_{32}H_{66}$ at −40°C; ^{2} transition to a rubbery-elastic state; ^{3} transition to a viscous-fluid state; ^{4} change in the crystal lattice; ^{5} onset of self-diffusion.

Preliminary measurements were also carried out of the radiothermoluminescence of several rubber specimens and of certain linear and cyclic hydrocarbons at an irradiation dose of 10^6 rad. The temperature values at which maxima were observed on the glow curves are given in the column T_M of Table 1. For certain specimens of rubber and polyisobutylene,

which were used in the work, thermomechanical curves were recorded under a load of 0.7 kg/cm^2 and a heating rate of 1 deg/min. The results of these measurements are given in Table 1 in the column T_p. Finally, the column T_m contains literature data on structural transitions obtained from the temperature dependence of Young' s modulus, dielectric or mechanical losses, heat capacity, specific volume, by stretching films, and by the method of nuclear magnetic resonance. Attention is drawn to the close agreement of the maxima on the glow curves with the points of structural transitions in these compounds, determined by other methods.

On the basis of the results presented, it may be concluded that, for many irradiated organic compounds, the shape of the glow curve makes it possible to detect the onset of molecular motion and changes in the crystal lattice. Therefore radiothermoluminescence can become a very sensitive method for studying structural changes in a substance. Along with good accuracy and simplicity, this method also has the advantage that it makes it possible to work with a small amount of the compound under study (in some cases down to 10^{-4} g).

In the future, for a number of compounds it is proposed to investigate the dependence of the shape of the glow curve on the irradiation dose, as well as the spectral composition of the radiation.

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