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Investigation of E.P.R. Spectra of Certain Polymers Irradiated at 77°K

To clarify certain questions connected with the structure and chemical behavior of organic radicals in the solid phase, and to study the mechanism of chemical transformations arising in solid organic bodies under the action of penetrating radiation, an investigation was undertaken, by the method of electron paramagnetic resonance (E.P.R.), of the free radicals formed upon irradiation of a number of polymers and materials based on them at 77°K. The literature contains indications that experiments of this kind have been carried out in a number of laboratories ([1], [2]); however, no fairly complete systematic studies comparing the E.P.R. spectra of different irradiated substances with one another have been published.

We investigated polyethylene, polyvinyl chloride, Teflon (polytetrafluoroethylene), polydimethylsiloxane, polyisobutylene, polymethyl methacrylate, polystyrene, polybutyl methacrylate, and natural rubber. After irradiation at 77°K in a nuclear reactor ([3]) (the irradiation time was about 1.5 hours, dose 40 Mrad*) the cylindrical specimens ($d = 5$ mm, $l = 15$ mm) were transferred without thawing into a special Dewar vessel placed in the cylindrical resonator (type H_{011}, $Q \approx 5000$) of a spectrometer with high-frequency magnetic modulation. The E.P.R. signal was recorded in the form of the first derivative. The line widths given below were measured between the extreme points of the first derivative with the aid of a nuclear probe.

In all the substances studied, when the specimens were stored at 77°K without thawing, a very intense E.P.R. signal was observed, with a g-factor close to 2.0036. Under the irradiation conditions indicated above, the total concentrations of radicals ranged from $\sim 10^{17}$ cm^{-3} (for polystyrene) to $\sim 10^{20}$ cm^{-3} (for polyethylene). At a klystron power of $\sim$ 50–100 mW, saturation of the E.P.R. signal was observed in most cases. Upon thawing the specimen to room temperature, a change in the signal was observed in all cases. In some specimens the signal disappeared completely upon thawing (polyisobutylene, polydimethylsiloxane, natural rubber); in the case of polyethylene, Teflon, polyvinyl chloride, polymethyl methacrylate, and polybutyl methacrylate, the character of the signal and its hyperfine structure changed sharply. Upon repeated freez-

Fig. 1. E.p.r. spectra of irradiated polyethylene (77° K) (a), polyethylene (300° K) (b), and polyvinyl chloride (77° K) (c)

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ing of polymethyl methacrylate and polyethylene specimens, the signal remains the same as at room temperature, whereas in Teflon, upon repeated freezing and thawing, quite reproducible reversible changes of the spectrum occur (see below).

Comparison of all the data obtained shows that the character of the spectra obtained in the study of unthawed specimens can be explained quite satisfactorily if it is assumed that the predominant primary chemical act upon irradiation is the rupture of one of the C–H bonds in the main chain or, if such bonds are absent (as

* For polyethylene.

for example, in polysiloxane), rupture of a C–H bond in the side chain. We found no direct indications that rupture of the main chain is the primary irreversible chemical consequence of irradiation.

From the standpoint of comparison with the results obtained upon irradiation of frozen unbranched saturated hydrocarbons and cyclohexane ([4]), the study of irradiated polyethylene is of greatest interest. The e.p.r. spectrum of polyethylene, recorded at 77°K (Fig. 1a), consists of six components with a splitting between them of 26 ± 3 oersted. The spectrum of cyclohexane irradiated at 77°K also consists of six components. The spectrum of cetane, recorded under the same conditions, also has an even number of components. The even character of the spectrum in all these cases can be associated with the formation of the radical:

$$\sim CH_2 - \dot{C}H - CH_2 \sim . \tag{1}$$

Fig. 1. E.p.r. spectra of irradiated polyethylene (77°K) (a), polyethylene (300°K) (b), and polyvinyl chloride (77°K) (c)

Primary rupture of a C–C bond or secondary rupture of the chain in (1), with formation of $\sim CH = CH_2$, would lead to the appearance of the radical:

$$\sim CH_2 - \dot{C}H_2, \tag{2}$$

in whose spectrum an odd number of components should be observed, as is in fact the case when, in the primary act, a C–H bond in the methyl group of a saturated hydrocarbon is broken ([4]).

When the polyethylene sample irradiated at 77°K is thawed to room temperature, as was already indicated above, a sharp change in the spectrum occurs (Fig. 1b). It now consists of an odd number of components with approximately half the splitting (14 ± 1 oersted). On storing the sample at room temperature, the intensity of the spectrum gradually decreases, and it disappears almost completely within one hour. The change in the spectrum upon thawing indicates that, when the temperature is raised, the free radical (1) undergoes some substantial transformations. The simplest explanation of these spectral changes might be the assumption that the following reaction proceeds at room temperature:

$$\sim CH_2 - \dot{C}H - CH_2 - CH_2 - CH_2 \sim \rightarrow \sim CH_2 - CH = CH_2 + \dot{C}H_2 - CH_2 \sim .$$

Against such an explanation as the only one, however, several objections may be raised. Among the most obvious are the excessively large value of the energy for rupture of C–C bonds in alkyl radicals (27 kcal/mol ([5])) and the unclear decrease in the hyperfine splitting from 26 to 14 oersted. In view of this, we attempted to formulate another possible explanation of the data obtained. According to this hypothesis, the initially formed radical (1), upon thawing, interacts with a neighboring polyethylene molecule, forming a hydrogen bridge between two adjacent chains:

$$\begin{array}{ll} \sim CH_2 - CH_2 - CH_2 \sim & \sim CH_2 - \overset{*}{\dot{C}}H - CH_2 \sim \\ & \Big| \\ & H \\ & \Big| \\ \sim CH_2 - \dot{C}H - CH_2 \sim & \sim CH_2 - \overset{*}{\dot{C}}H - CH_2 \sim \end{array} \qquad (3)$$

Here the decrease in the hyperfine splitting by approximately a factor of two can be understood if it is assumed that the spin density of the unpaired

the electron is distributed approximately uniformly among the C atoms marked with an asterisk, while at the bridging hydrogen it is close to zero. In this case an even number of protons will take part in the splitting and the number of components will be odd, which is also observed experimentally. System (3) is not stable, and within an hour at room temperature direct "cross-linking" of two neighboring molecules occurs through removal of the comparatively weakly bound bridging hydrogen atom. The proposed hypothesis, of course, requires direct experimental confirmation.

Let us now compare the results obtained by us in the study of polyethylene with the data for polyvinyl chloride. As is seen from the spectrum (Fig. 1c), in

this case two lines are observed with approximately identical g-factor, without any hyperfine structure, with widths equal respectively to 79 ± 2 and 44 ± 2 oersteds. Let us consider possible pathways for formation of a free radical with preservation of the main chain. Two of them correspond to rupture of a C–H bond:

$$\sim \mathrm{CHCl} - \dot{\mathrm{C}}\mathrm{H} - \mathrm{CHCl} \sim \tag{4}$$

and

$$\sim \mathrm{CH_2} - \dot{\mathrm{C}}\mathrm{Cl} - \mathrm{CH_2} \sim . \tag{5}$$

In both of these radicals the free valence is located in the immediate vicinity of Cl atoms. Upon interaction of the free spin with H and Cl nuclei ($I = 3/2$), a very large number of unresolved components of the hyperfine structure may arise, giving rise to the large width of the observed e.p.r. lines. Formation of a stable radical by rupture of a C–Cl bond,

$$\sim \mathrm{CH_2} - \dot{\mathrm{C}}\mathrm{H} - \mathrm{CH_2} \sim \tag{6}$$

is, apparently, unlikely, since Cl atoms are much more difficult to move to a considerable distance than H atoms. In addition, if radical (6), which in its structure is very close to the polyethylene radical (1), were present in the system under study in appreciable concentrations, then the corresponding hyperfine structure should have appeared in the resultant spectrum, superimposed on the lines of the other two radicals. In the present case, however, the observed spectrum does not exclude the possibility of formation of radicals through rupture of a C –C bond in the main chain.

The results obtained in the study of Teflon are of considerable interest. First of all it should be noted that, whereas upon irradiation at room temperature Teflon, as a result of destruction [(6)], sharply changes its mechanical properties already at doses below 1 Mrad, becoming a rigid, extremely brittle material, upon irradiation at 77°K and subsequent thawing such changes do not occur even at doses of $\sim$ 40 Mrad. Consideration of the e.p.r. spectrum leads to the following conclusions. The initial spectrum, measured at 77°K (Fig. 2a), is a superposition of an asymmetric line (α) of width about 50 oersteds on another very broad line. Upon thawing to room temperature in vacuum or in an atmosphere of nitrogen (Fig. 2b), line α changes into a narrower asymmetric line α', the broad line disappears, and in addition a complex spectrum is observed which, as shown in the figure, is a superposition of two quintuplets with an intensity ratio $1 : 4 : 6 : 4 : 1$. The appearance of this spectrum is apparently due to formation of the radical

$$\sim \mathrm{CF_2} - \dot{\mathrm{C}}\mathrm{F} - \mathrm{CF_2} \sim . \tag{7}$$

Fig. 2. EPR spectra of irradiated Teflon at 77°K. *a*—before thawing the sample at 77°K; *b*—sample thawed in vacuum (300°K); *v*—sample *b* frozen in vacuum (77°K); *g*—sample thawed in air (300°K).

Figure 2: Fig. 2. EPR spectra of irradiated Teflon at 77°K. *a*—before thawing the sample at 77°K; *b*—sample thawed in vacuum (300°K); *v*—sample *b* frozen in vacuum (77°K); *g*—sample thawed in air (300°K).

Upon repeated freezing, line α is restored (Fig. 2c), while the broad line is not observed. Upon repeated thawing and freezing without access of oxygen, spectra 2b and 2c reversibly transform into one another. In the presence of oxygen at room temperature the complex spectrum of radical (7) gradually weakens, while the intensity of line α' ra—

···increases (Fig. 2d), and, correspondingly, the intensity of line *a* increases upon freezing. The presence of an asymmetric line upon irradiation of Teflon had also been observed earlier ([2]); however, other features of the spectrum, as far as we know, had not been noted. It seems to us that the observed picture can be explained as follows. Upon irradiation at 77°K in Teflon, radicals of type (7) and F atoms are formed, which account for the appearance of the broad, diffuse line in spectrum 2a. Because Teflon contains a small amount of oxygen in dissolved form, a certain amount of peroxide-type radicals is formed from radical (7), and these account for the appearance of line *a*. Upon thawing, the fluorine atoms either recombine or break C—C bonds, leading to partial destruction of (7), while the spectrum of radicals (7) appears more distinctly. In the presence of oxygen, it diffuses to radicals (7) and converts them into peroxide radicals, which are very stable. As a result, the intensity of line *a* increases. The change in the shape of lines *a* upon freezing can be explained if it is assumed that at 77°K the peroxide group C—O—O is frozen, whereas at room temperature free rotation about the C—O bond takes place. Calculations carried out under this assumption showed that the COO angle in a peroxide radical of the type considered is $75 \pm 15°$.

Fig. 2. EPR spectra of irradiated Teflon at 77°K. *a*—before thawing the sample at 77°K; *b*—sample thawed in vacuum (300°K); *v*—sample *b* frozen in vacuum (77°K); *g*—sample thawed in air (300°K).

In the proposed scheme there is no explanation of the causes that bring about the disappearance of the spectrum of radical (7) upon freezing. From the reversibility of this phenomenon it is clear, however, that the radical itself does not disappear.

Thus, by irradiating Teflon at low temperatures one can obtain a material entirely satisfactory in its mechanical properties, containing a large ($\sim$ 0.1%) amount of free radicals, fluoroalkyl or peroxide.

It is very interesting to note, in addition, that absorption lines of type *a* are observed when other organic compounds are irradiated in the presence of air

([7]). Lines of this type were also observed by us in finely dispersed polyethylene irradiated in the presence of air. It appears very probable that the appearance, as a result of irradiation, of lines of this kind may serve as a direct indication of the formation of peroxide radicals.

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CITED LITERATURE

1. E. E. Schneider, *Disc. Farad. Soc.*, **19**, 158 (1955); J. Uebersfeld, *C. R.*, **239**, 240 (1954).

2. W. B. Ard, H. Shields, W. Gordy, *J. Chem. Phys.*, **23**, 1727 (1955).

3. *Collection: The Use of Atomic Energy and the Theory of Reactors. Reports of the Soviet Delegation at the Geneva Conference*, Publishing House of the Academy of Sciences of the USSR, 1955, p. 91.

4. N. Ya. Chernyak, N. N. Bubnov et al., *Dokl. Akad. Nauk SSSR*, **120**, 346 (1958).

5. V. V. Voevodskii, *Proceedings of the Kiev Conference on Problems of the Mechanism of Organic Reactions*, Kiev, 1953, p. 58.

6. J. W. Ryan, *Mod. Plast.*, **31**, 51 (1953).

7. G. McCormick, W. Gordy, *Bull. Am. Phys. Soc.*, **1**, 200 (1956); H. N. Rexroad, W. Gordy, *Bull. Am. Phys. Soc.*, **1**, 200 (1956).

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