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Abstract

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INVESTIGATION BY THE E.P.R. METHOD OF THE PRIMARY RADICAL PRODUCTS OF RADIOLYSIS OF POLYVINYL ALCOHOL

(Presented by Academician A. N. Frumkin, 11 III 1963)

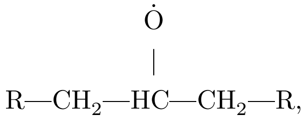
It is known that upon irradiation of solid polyvinyl alcohol (PVA) its destruction is observed predominantly ([1]), whereas in aqueous solutions structuring occurs ([2,3]). The destruction of PVA, which is a regular, linear polymer $(\text{—CH}_2\text{—CHOH—})_n$, is in contradiction with the rule according to which carbon-chain polymers are predominantly structured if each carbon atom is bonded to at least one hydrogen atom. It was therefore of interest to investigate by the e.p.r. method the nature of the primary radical products of its radiolysis under different conditions.

Of all the free radicals that may be formed under the action of radiation on PVA,

$$\text{R—CH}_2\text{—}\dot{\text{C}}\text{H—CH}_2\text{—R,} \tag{1}$$

$$\text{R—CHOH—}\dot{\text{C}}\text{H—CHOH—R,} \tag{2}$$

$$\text{R—CH}_2\text{—C}\dot{\text{O}}\text{H—CH}_2\text{—R,} \tag{3}$$



$$\overset{\dot{\text{O}}}{\underset{|}{}}\qquad \text{R—CH}_2\text{—HC—CH}_2\text{—R,} \tag{4}$$

$$\text{R—}\dot{\text{C}}\text{H}_2\text{,} \tag{5}$$

$$\cdot\text{CHOH—R,} \tag{6}$$

Fig. 1. E.p.r. spectra. a –irradiation temperature 20°, measurement temperature 20° and $-196°$, $I_d = 0.05$ ma; b –irradiation temperature 20°, measurement temperature $-196°$, $I_d = 0.3$ ma; c –measurement temperature 20°, $I_d = 0.05$ ma; d –irradiation temperature $-196°$, measurement temperature $-196°$

Figure 1: Fig. 1. E.p.r. spectra. a –irradiation temperature 20°, measurement temperature 20° and $-196°$, $I_d = 0.05$ ma; b –irradiation temperature 20°, measurement temperature $-196°$, $I_d = 0.3$ ma; c –measurement temperature 20°, $I_d = 0.05$ ma; d –irradiation temperature $-196°$, measurement temperature $-196°$

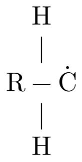
the occurrence of the first four indicates the possibility of cross-linking between the polymer chains and the formation of double bonds. Conversely, the preferential formation of radicals (5) and (6) is a consequence of rupture of the carbon chain of the polymer during irradiation and explains its destruction.

Fig. 1. E.p.r. spectra. **a** –irradiation temperature 20°, measurement temperature 20° and $-196°$, $I_d = 0.05$ ma; **b** –irradiation temperature 20°, measurement temperature $-196°$, $I_d = 0.3$ ma; **c** –measurement temperature 20°, $I_d = 0.05$ ma; **d** –irradiation temperature $-196°$, measurement temperature $-196°$.

Powdered PVA was placed in ampoules made of special glass that gives an insignificant e.p.r. signal upon irradiation (4), and was evacuated to $\sim 10^{-5}$ mm Hg (series 1).

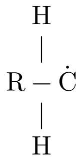
A portion of the evacuated samples was saturated for 3 hr with water vapor at room temperature (series 2). The samples were subjected to the action of Co^{60} radiation at a dose rate of $5 \cdot 10^{16}$ eV/g • sec. The spectra were recorded with an RÉ1301 radiospectrometer. In determining the number of radicals, a benzene solution of DPPH was used as the standard. The spectrum of polyvinyl alcohol irradiated at room temperature, recorded at $-196°$, is shown in Fig. 1a. The form of the spectrum did not change if the recordings were made at 20°, and represented a triplet with an intensity ratio of 1 : 6 : 1. The distance between the lines was 31 ± 1.5 oersted. The same charac-

the character of the spectrum was preserved if the recording was made directly during irradiation at 20° (6). Figure 2 shows the change in the height of the central line (curve *I*) and of the side lines (curve *II*) as a function of irradiation time at room temperature. It is seen that the dependence of the height on dose is different in the two cases. This shows that the PVA spectrum is a superposition of the spectra of two radicals. This conclusion is also reached by considering the saturation of different lines as a function of microwave (m.w.) power (Fig. 3). It is seen from the figure that the m.w. saturation of the central line differs from the m.w. saturation of the side lines, and for a correct estimate of the number of radicals the level of m.w. oscillation power should not exceed 0.05 mA in arbitrary units for the radicals associated with the side lines and 0.15 mA for the radicals corresponding to the central component of the spectrum at −196°. The saturation effect is more pronounced at low temperatures. Comparing PVA spectra recorded at the same temperature and at different levels of m.w. power, one can observe, at high powers, a broadening of individual components of the hyperfine structure caused by saturation (cf. Figs. 1*a* and 1*b*). A third proof of the composite character of the spectrum is the change in its shape upon heating. Before measurement at 20°, the irradiated PVA samples were warmed in a thermostat for 5 min at various temperatures from 20 to 70°. As a result, the intensity ratio gradually changed from 1 : 6 : 1 to 1 : 2 : 1, while the number of radicals decreased by a factor of 10. (The appearance of the spectrum of samples warmed at 70° is shown in Fig. 1*c*.) The same number of radicals arose upon irradiation of samples of series 2. The character of the spectrum in the latter case also corresponded to Fig. 1*b*, as was noted earlier (⁶). Of all the radicals listed above, a clear triplet with an intensity ratio of 1 : 2 : 1 at any measurement temperature is most probably associated with the radical



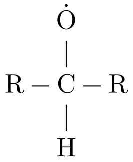
$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{R}-\dot{\mathrm{C}} \\ | \\ \mathrm{H} \end{array}$$

The spectrum in Fig. 1*a* may be regarded as a superposition of a triplet from



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{R}-\dot{\mathrm{C}} \\ | \\ \mathrm{H} \end{array}$$

(the dashed line) and a single line, which coincides in *g*-factor with the central component of the triplet and has a half-width of 18 ± 1.5 Oe. This line may be assigned to the radical

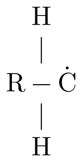


$$\begin{array}{c} \dot{\mathrm{O}} \\ | \\ \mathrm{R}-\mathrm{C}-\mathrm{R} \\ | \\ \mathrm{H} \end{array}$$

(⁷-¹⁰). The total intensity ratio 1 : 6 : 1 corresponds to equal amounts of the radicals

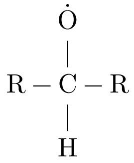
Fig. 2. Dependence of the height of individual components of the PVA spectrum on irradiation time

Figure 2: Fig. 2. Dependence of the height of individual components of the PVA spectrum on irradiation time



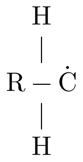
$$\begin{array}{ccc} & & \mathrm{H} \\ & & | \\ \mathrm{R} & - & \dot{\mathrm{C}} \\ & & | \\ & & \mathrm{H} \end{array}$$

and



$$\begin{array}{ccccc} & & \dot{\mathrm{O}} & & \\ & & | & & \\ \mathrm{R} & - & \mathrm{C} & - & \mathrm{R} \\ & & | & & \\ & & \mathrm{H} & & \end{array}$$

in the samples. From a comparison of the spectra of the radical



$$\begin{array}{ccc} & & \mathrm{H} \\ & & | \\ \mathrm{R} & - & \dot{\mathrm{C}} \\ & & | \\ & & \mathrm{H} \end{array}$$

(the dashed line in Fig. 1*a* and Fig. 1*b*) it is seen that the width of an individual hfs component is greater in the case when the sample contains

Fig. 2. Dependence of the height of individual components of the PVA spectrum on irradiation time.

two radicals. This means that the radicals $\mathrm{R}-\dot{\mathrm{C}}\mathrm{H}_2$ and $\mathrm{R}-\dot{\mathrm{C}}\mathrm{H}-\mathrm{R}$ are so close to one another that their interaction leads to broadening of the individual components of the spectrum. The formation of the radical $\mathrm{R}-\dot{\mathrm{C}}\mathrm{H}_2$ under irradiation indicates rupture of the carbon chain. In this case, however, the radical $\dot{\mathrm{C}}\mathrm{H}(\mathrm{OH})-\mathrm{R}$ should simultaneously appear, which is not observed in the spectrum of polyvinyl alcohol irradiated at room temperature.

Irradiation and recording of spectra at −196° without intermediate heating made it possible to clarify this question. The form of the spectrum in this case is shown in Fig. 1e, in which the radical $\mathrm{R}-\dot{\mathrm{C}}\mathrm{H}_2$ is indicated by a dashed line. The difference, marked by a dash-dotted line, between the total spectrum and the spectrum of the radical $\mathrm{R}-\dot{\mathrm{C}}\mathrm{H}_2$ is a broadened doublet with a spacing between components of 28 ± 1.5 oersted. Of the six possible radicals, such a spectrum can with greatest probability be assigned to the radical $\dot{\mathrm{C}}\mathrm{H}(\mathrm{OH})-\mathrm{R}$. Comparison of the areas corresponding to both radicals shows that they are present in the samples in equal amounts. No other radicals are formed in appreciable amounts. This leads to the conclusion that the primary event under radiation action on PVA is rupture of the polymer chain at a C–C bond. The radiation-chemical yield of radicals is equal to $5 = 0.5$ rad/100 eV, i.e., in other words, PVA is characterized by 2–3 chain ruptures per 100 eV absorbed. This comparatively

Fig. 3

Figure 3: Fig. 3

small number of chain ruptures is explained by the fact that the radicals are formed in pairs, close to one another, and readily recombine. If after irradiation at −196° the PVA was heated to room temperature and then the measurement was again carried out at −196°, then $\sim 80\%$ of the radicals remained, but the spectrum irreversibly changed into that shown in Fig. 1a in the case of samples of series 1 and disappeared completely in samples of series 2. This means that the radicals $R-\dot{C}H_2$ are stable,

Fig. 3. Saturation of the lines of the PVA spectrum as a function of microwave power. I_d is the detector current of microwave oscillations in milliamperes, proportional to the microwave power stored in the resonator. h/h_{DPPH} is the ratio of the height of the side lines at −196° (**I**), of the central line at −196° (**II**), and of the central line at −20° (**III**) to the height of the DPPH line.

and the radicals $\underset{OH}{\overset{H}{\dot{C}}}-R$, upon heating to room temperature, were irreversibly transformed into the radicals $H-\underset{\dot{O}}{\overset{H}{C}}-R$. Such a transformation explains the close arrangement of the radicals $R-\underset{H}{\overset{H}{\dot{C}}}$ and $H-\underset{\dot{O}}{\overset{H}{C}}-R$ mentioned above, as well as the observation made in work ⁽¹¹⁾ that deuterium substitution in the OH groups in PVA does not substantially change the form of the spectrum. The complete disappearance of radicals upon heating to room temperature of the samples of series 2 irradiated at −196° shows that, in the presence of sorbed pairs of water, the polymer chains are sufficiently mobile and cross-linking of radicals with formation of an ether bond is possible.

Thus, the results obtained show that primary free radicals are formed upon irradiation of solid PVA only as a result of rupture of the carbon chain of the polymer, as is also consistent with degradation. In aqueous solutions, polyvinyl alcohol, upon irradiation, is subjected mainly to the action of the products of water radiolysis, H and OH, which should lead to the formation of radicals (1)-(4), responsible for cross-linking.

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