The Anisotropy of the ESR Spectrum of Irradiated Poly(β-propiolactone)

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Many works have reported on the electron spin resonance (ESR) of irradiated polymes. Most of these studies, however, have been made with unoriented specimens. They have usually been amorphous polymers, or, even when they have been highly-crystalline, the crystallites are oriented randomly in the specimens. Recently, however, a few studies[1-6] have appeared using some oriented polymers as the samples. Analysis of the anisotropy in the ESR spectra obtained from such oriented specimens would inform us of the structure as well as of orientation of the free radicals in the specimens, as is evident from studies of single crystals of low-molecular-weight compounds. Using stretched polyethylene, Kiselev et al.[1] and Libby and Ormerod[2] have made definite the previous identification of the alkyl-type radical while Ohnishi et al.[3] have given a conclusive choice on the identification of the allyl-type radical. Kashiwagi[4] has discussed molecular orientation in polyethylene on the basis of the doublet splitting in the double-quintet spectrum of the alkyl-type radical.

In the present paper we have measured the angular variation of the ESR spectrum of irradiated poly(β-propiolactone). The polymer was obtained by radiation-induced solid-state polymerization of a single crystal of the

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[1] A. G. Kiselev, M. A. Mokul'sky and Yu. S. Lazurkin, *Vysokomolekularnye Soedineniya*, **2**, 1678 (1960).

[2] D. Libby and M. G. Ormerod, *J. Phys. Chem. Solids*, **18**, 316 (1961).

[3] S. Ohnishi, S. Sugimoto and I. Nitta, *J. Chem. Phys.*, **37**, 1283 (1962).

[4] M. Kashiwagi, ibid., **36**, 575 (1962).

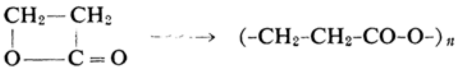
[5] H. Fischer and K.-H. Hellwege, *J. Polymer Sci.*, **56**, 33 (1962).

[6] D. W. Ovenall, *J. Chem. Phys.*, **38**, 2448 (1963).

monomer at low temperatures. The sample thus obtained was known to be a highly-oriented crystalline polymer.⁷⁾ From an analysis of the anisotropy of the spectra, we have made a definite identification of the radical produced, and we have also discussed molecular orientation in the specimen through the α-proton hyperfine-coupling tensor.

Experimental

Material. — The monomer (Celanese Co. Ltd.) was distilled twice in a nitrogen stream. The single crystal was obtained as a thin plate ($\sim 2.5\times 1.5\times 0.2$ mm^3) by keeping the monomer at -35°C. The polymer was obtained by irradiating the single crystal of the monomer with γ-rays from a cobalt-60 source at -78°C to a dose of 2 Mrad. After



polymerization, the unreacted monomer was removed by washing it several times with methanol, and then the polymer was dried in a vacuum at 50°C. The polymer sample thus obtained had a shape quite similar to the thin plate of the monomer crystal, although the polymerization yield never exceeded 15%. A sketch of the sample and the orthogonal coordinate system xyz used in the present investigation are shown in Fig. 1. X-Ray photographs taken perpendicular to the xy and yz planes showed a fiber structure, while the photograph perpendicular to the xz plane gave only a halo. Okamura et al.⁷⁾ suggested that the molecular conformation is a planar zigzag chain pointed in the z direction.

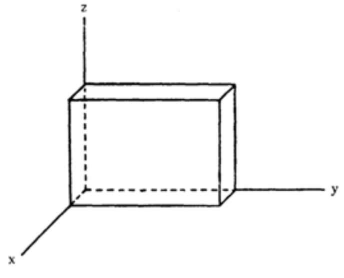


Fig. 1. A sketch of the polymer sample and the xyz coordinate system.

ESR Measurement. — The polymer was irradiated in a vacuum at -196°C with an electron beam from a Van de Graaff accelerator to a dose of 30 Mrad. The ESR spectra of the radical produced were measured at -196°C with a Varian Model V4500 spectrometer (operating frequency: 9160 Mc.). The angular variation of the spectra was measured at 15° intervals in the three planes. Hyperfine splitting values were estimated on the derivative tracing, based on the splitting value of Mn^{2+} resonance.

Results and Discussion

Angular Dependence of the Spectrum. — The spectrum showed anisotropy in the yz and zx planes, while in the xy plane it was nearly the same at all angular positions. The change of the spectrum in the zx plane is shown in Fig. 2. The main four-line spectrum at an angle $\phi=0°$ changes to a six-line one at $\phi=90°$. Here ϕ is the rotation angle measured from the z axis. The feature of the spectral change suggests that this is a double-triplet spectrum and that the doublet splitting changes with the angle, while the triplet remains almost unchanged. The free radical showing this spectrum, therefore, should have an α proton and two β protons. The angular variation of the spectrum in the yz plane is similar to that in the zx plane. At a magnetic field parallel to the z axis, the spectrum is the same one as that observed at $\phi=0°$ in Fig. 2, and, as the field direction changes, it is gradually converted to the six-line spectrum. The spectrum in the xy plane does not change appreciably with the angle, and it is a six-line spectrum similar to the one shown in Fig. 2(4) at all field orientations.

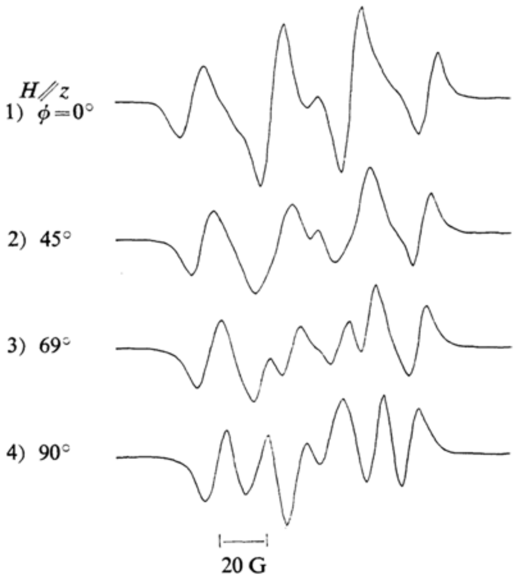


Fig. 2. Angular variation in the zx plane of the ESR spectrum of the irradiated polymer.

The doublet splitting of the α proton, A_α, was read from the separation between the first and the second peaks of the derivative curve; it is plotted against the rotation angle in Fig. 3. The curves in the yz and zx planes approximately obey the $(3\cos^2\phi-1)$ rule, as expected for the dipolar interaction. The triplet splitting value of the β proton, A_β,

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7) S. Okamura, K. Hayashi and Y. Kitanishi, *J. Polymer Sci.*, **58**, 925 (1962).

was estimated by using the relation:

$$A_\beta = (\Delta H_{overall} - A_\alpha)/2 \qquad (1)$$

Here $\Delta H_{overall}$ means the distance between the outermost peaks.

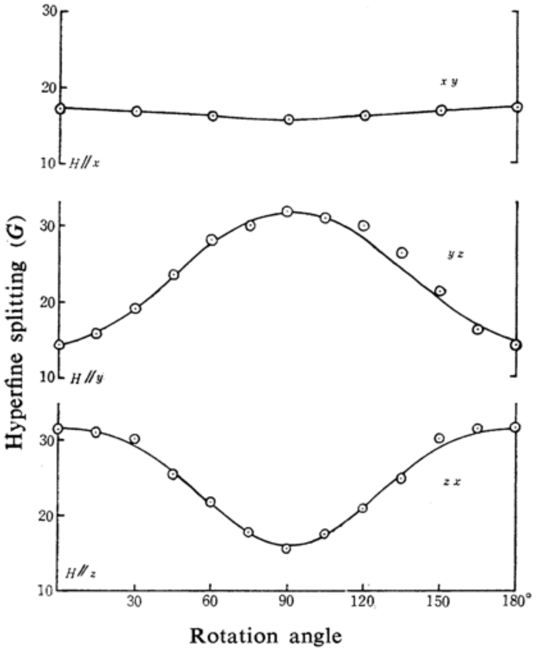

Fig. 3. Angular dependence of the hyperfine splitting of the α proton in the three basic planes.

The triplet splitting was almost isotropic, changing, for example in the yz plane, from 31.2 to 32.5 gauss.

These results indicate that the radical showing the spectrum can be attributed to $-CH_2-\dot{C}H-CO-O-$ or $-CH_2-\dot{C}H-O-CO-$, and also that the orientation of the radical is almost at random in the xy plane, although in the other planes the radicals are highly oriented. Of the two radical species proposed, the former one seems to be more probable because of the resonance stabilization.

Hyperfine-Coupling Tensor.—From the above data, the hyperfine-coupling tensor can be obtained. The spin Hamiltonian for the hf interaction with one proton may be written as[8]

$$\mathscr{H} = \beta\vec{S}\tilde{g}\vec{H} + \vec{S}\tilde{T}\vec{I} - g_N\beta_N\vec{I}\vec{H} \qquad (2)$$

where β is the Bohr magneton, β_N the nuclear magneton, g_N the nuclear g-factor, $\tilde{g}$ the g-tensor, $\tilde{T}$ the hf-coupling tensor, $\vec{H}$ the external field, and $\vec{S}$ and $\vec{I}$ the electron spin and nuclear spin operators respectively. Since the electron g-factor showed only a slight anisotropy and since its value was nearly the free-spin value, the g-tensor is taken to be isotropic for the present radical. Moreover, the strong-field approximation is assumed to be as usual; i.e., $\vec{S}$ is replaced by $M_S\vec{Z}$, where $\vec{Z} = \vec{H}/|H|$. Then the spin Hamiltonian becomes:

$$\mathscr{H} = \beta g M_S H + M_S\vec{Z}\tilde{T}\vec{I} - g_N\beta_N\vec{I}\vec{H} \qquad (3)$$

From the eigen value of the Hamiltonian, the doublet splitting of the α proton is given as:

$$\begin{aligned} A_\alpha = {} & [l^2(1/2A - \nu_H)^2 + m^2(1/2B - \nu_H)^2 \\ & + n^2(1/2C - \nu_H)^2]^{1/2} \\ & + [l^2(1/2A + \nu_H)^2 + m^2(1/2B + \nu_H)^2 \\ & + n^2(1/2C + \nu_H)^2]^{1/2} \end{aligned} \qquad (4)$$

Here ν_H is the nuclear resonance frequency, A, B and C are the principal values of the hf coupling tensor, and l, m, and n are the direction cosines of the field direction with respect to the three principal axes, a, b and c. When evaluating the tensor component from the experimental data, the further assumption was made that the nucleus is also aligned along the field direction.[9] In this case the doublet splitting can be given by a simple formula:

$$\begin{aligned} A_\alpha = \vec{Z}\tilde{T}\vec{Z} = {} & l^2T_{xx} + m^2T_{yy} + n^2T_{zz} \\ & + 2(lmT_{xy} + lnT_{xz} + mnT_{yz}) \end{aligned} \qquad (5)$$

Making use of Eq. 5, the tensor components were evaluated and the principal values, as well as the principal directions were calculated (cf. Table I).

As for the hf coupling tensor of the β-proton, only the isotropic component was evaluated as the average of the diagonal components. Its value was found to be 31.9 gauss.

The Orientation of the Free Radical. — The anisotropic hf couping of the α proton in organic radicals has been extensively studied, and the principal axes as well as the principal values of the tensor have been determined for many radicals.[10] For the HOOCCHCOOH radical in malonic acid, for example, the principal values, A, B and C, are reported to be -61, -29 and -91 Mc./sec, with the principal axes parallel to the unpaired π-axis,

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[8] B. Bleaney and K. W. H. Stevens, *Reports on Progress in Physics*, **16**, 108 (1953).

[9] D. K. Ghosh and D. H. Whiffen, *Mol. Phys.*, **2**, 285 (1959).

[10] D. H. Whiffen, "Free Radicals in Biological Systems," Ed. by M. S. Blois, Jr., et al., Academic Press, New York and London (1961), pp. 227—238.

TABLE I. HYPERFINE COUPLING TENSOR OF THE α PROTON

Tensor			Principal value	Principal axis		
				l	*m*	*n*
−16.3 (−45.6)	− 0.18 (− 0.52)	− 2.52 (− 7.06)	−15.9 (−44.5)	0.983,	0.092,	−0.160
− 0.18 (− 0.52)	−15.1 (−42.2)	− 0.65 (− 1.83)	−15.0 (−42.1)	−0.097,	0.995,	−0.026
− 2.52 (− 7.06)	− 0.65 (− 1.83)	−31.7 (−88.8)	−32.1 (−90.0)	0.160,	0.039,	0.986

Isotropic component: −21.0 (−58.9)

Values are shown in gauss. Those given in parentheses are in Mc./sec.

to the C–H$_\alpha$ bond, and to the direction perpendicular to both a and b axes respectively.[11] Comparing the values with those obtained for the present radical, the value C, −91 Mc., agrees fairly well with one of the observed values, −90.0 Mc. whose axis is almost parallel to the z axis (l=0.160, m=0.039, n=0.986). This suggests that the carbon zigzag chain of the polymer points in the z direction. On the other hand, the other principal values, −44.5 and −42.1 Mc., deviate from the reported values, −61 and −29 Mc., for malonic acid and take some averaged. values. This is a consequence of the almost axially-random orientation of the radical- or zigzag-plane. We may formally evaluate the degree of orientation of the radical in the xy plane from the observed principal values. Suppose that the magnetic field is set along the a axis and that θ measures the angle of the deviation of the π-axis of a radical from the field direction. Making use of Eq. 4 and putting $A_\alpha = -44.5$ Mc., $n=0$ and $\nu_H = 13.9$ Mc. into the equation, $\langle l^2 = \cos^2\theta\rangle = 0.337$ was obtained. If we use the following relationship[12] to define the degree of orientation, f becomes 0.02 for the present case.

$$f = (3\langle\cos^2\theta\rangle - 1)/2 \qquad (6)$$

Conclusion

Some conclusions can be drawn from the present ESR study. The produced radical in irradiated poly(β-propiolactone) can be assigned to $-CH_2-\dot{C}H-CO-O-$. The zigzag chain of the radical almost points in the z direction of the sample. In the x and y directions, however, the orientation of the C–H$_\alpha$ and the unpaired π-axis (i.e., the zigzag plane) is almost at random. These resuts are consistent with the reported X-ray result.[7] However, some slight orientation of the zigzag plane is evident from the present study; the principal values, A and B, are not the same but are slightly different. The average orientation of the π-axis, although almost random, is nearly parallel to the x axis (l=0.983, m=0.092, n=−0.160).

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[11] H. M. McConnell, C. Heller, T. Cole and R. W. Fessenden, *J. Am. Chem. Soc.*, **82**, 766 (1960).

[12] P. H. Hermans and P. Platzek, *Kolloid Z.*, **88**, 68 (1939).