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Communications to the Editor

Structure of Peroxy Radicals of Isotactic Polypropylene

A number of studies[1,2] of the electron spin resonance (ESR) of peroxy radicals of isotactic polypropylene (it-PP) have been reported. However, there have been few studies of the structure of the peroxy radicals,[3] and there is little geometrical information about the internal rotation angle around the C–O bond, ϕ, and the bond angle $\angle$COO. Iwasaki et al.[4] and Hori et al.[5] concluded that the COO group lay in the plane perpendicular to the polymer main chain axis, as shown in Figure 1, the polymer chain having a planar zigzag conformation (like polyethylene) or a slightly distorted planar zigzag structure (like poly(tetrafluoroethylene)). However, it is hard to decide whether the orientation of the O–O bond is gauche ($\phi = 60°$) or skew ($\phi = -120°$) to the adjacent C–C bond, as shown in Figure 1. It is well-known that the chain structure of crystalline isotactic polypropylene is a 3_1 helix, and thus very different from a planar zigzag conformation, as shown in Figure 2. In this report we study the structure of stable peroxy radicals trapped in the crystalline regions of it-PP, affected by the helical conformation. In order to estimate the angles λ_1 and λ_3 between the principal directions of the **g** tensor and the polymer chain axis, the angular dependence of the ESR spectrum of the peroxy radicals with respect to the external magnetic field must be analyzed.

An isotactic polypropylene, Noblen MA-4 (product of Mitsubishi Petrochemical Co. Ltd., $M_v = 40 \times 10^4$), was heated and pressed into a film which was subsequently stretched at 393 K to obtain a stretch ratio of 6 (stretch ratio is defined to be the ratio of the film length after stretching to the original length). This elongated film was then cut into a narrow strip which was placed in a Spectrosil sample tube. The sample was prepared with the stretching direction perpendicular to the axis of the sample tube. The sample was evacuated to 10^{-5} torr and then irradiated at ambient temperature with ^{60}Co γ rays for a total dose of ca. 4.25 Mrd. After the irradiated sample was annealed at 318 K for 2 h, only the tertiary alkyl radicals of polypropylene ($\sim CH_2-\dot{C}(Me)-CH_2\sim$) were trapped. Oxygen molecules at a pressure of 200 torr were introduced into the sample tube, and peroxy radicals were produced by reaction of the alkyl radicals with oxygen at 263 K for 33 h. The ESR spectra of the peroxy radicals are composed of two spectra arising from the chemically identical peroxy radicals but having different mobilities.[1,6] In order to observe the ESR spectra of the rigid peroxy radicals trapped in crystalline regions, the sample was annealed at 313 K for 40 h.

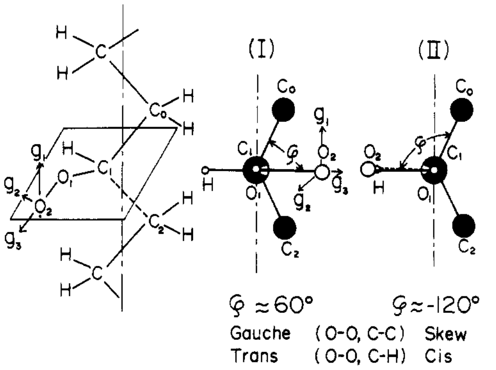

Figure 1. Schematic illustration of peroxy radicals of polyethylene and possible orientations of the O–O group to the adjacent C–C bond around the C–O bond, gauche (I) and skew (II).

The ESR spectrum of the rigid peroxy radicals showed a very marked angular dependence, as illustrated in Figure 3. With the external magnetic field along the stretching

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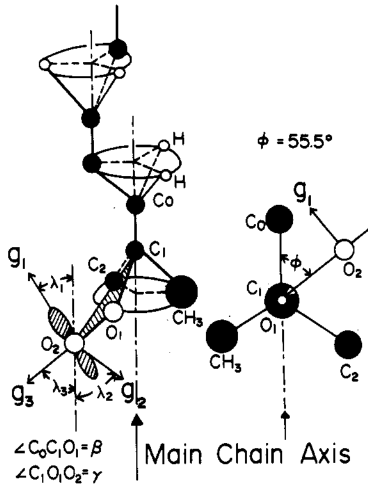

Figure 2. Schematic illustration of peroxy radical of isotactic polypropylene. λ_1, λ_2, and λ_3 are the angles between the principal directions of the **g** tensor and the polymer chain axis: g_1, perpendicular to the COO plane; g_3, direction of the O–O bond.

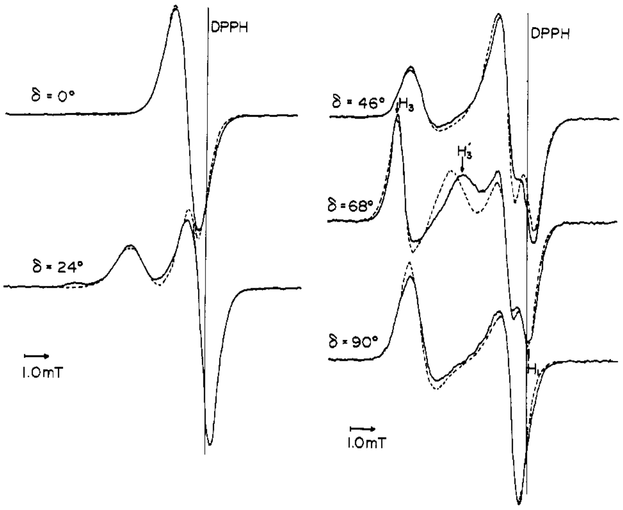

Figure 3. Angular dependences of the observed (solid) and calculated (dotted) ESR spectra of the peroxy radicals trapped in isotactic polypropylene upon rotation angle δ between the direction of elongation and that of the magnetic field. ESR spectra were observed at 77 K.

direction (δ = 0°), the intensity of the g_1 feature is enhanced. On the other hand, the ESR spectrum shows g_2 and g_3 features for the field perpendicular to the stretching direction (δ = 90°). (The directions of g_1, g_2, and g_3 are defined in Figure 2.) However, the g value corresponding to the characteristic resonance field, 2.0051 for δ = 0°, is different from g_1 = 2.0021 obtained previously from the ESR spectrum of an unoriented sample.[7] For the rotation angle δ = 68°, we could observe a new peak, H_3', as shown in Figure 3. These experimental facts suggest that the COO group does not lie in a plane perpendicular to the polymer chain axis, which is oriented along the stretching direction during elongation. Figure 4 shows the angular dependences of the characteristic resonance fields, H_1, H_3, and H_3', which are indicated in Figure 3. As expected, we can observe very strong dependences of the values of H_1 and H_3 on rotation angles, H_1 for δ = 39° giving a maximum value and H_3 for δ = 68° giving a minimum. The g values corresponding to the maximum and minimum resonance fields are in good agreement with the principal values of the peroxy radicals of it-PP, g_1 = 2.0021 and g_3 = 2.0353, respectively. From the experimental facts, the angles for the peroxy radicals can be estimated to be λ_1 = 39° and λ_3 = 68°. It is well-known that polymer main chains are partially oriented during the stretching of a polymer film. In order to estimate the angles exactly, we developed a computer simulation program to calculate the ESR spectrum of partially ordered peroxy radicals as a function of the orientation parameter, f, and rotation angle δ. The value of f corresponds to $\langle(3\cos^2\alpha - 1)\rangle/2$, where α is the angle between the stretching direction and the polymer chain. Details of this calculation will be given in a forthcoming paper. Using the values g_1 = 2.0021, g_2 = 2.0081, and g_3 = 2.0353 reported previously,[5,7] we generated computer-simulated spectra for different orientation parameters and angles λ_1 and λ_3. As expected, the simulated spectra have very strong dependences on the degree of order, f, and these angles. The profiles of the experimental spectra (solid lines) show good agreement with the spectra calculated (dotted lines) in Figure 3 for f = 0.968, λ_1 = 39°, and λ_3 = 68°. The calculated values of H_1, H_3, and H_3' are also indicated by crosses in Figure 4. The angular dependences of the experimental resonance fields show good agreement with those of the calculated fields for the same values of f, λ_1, and λ_3 estimated in Figure 3. By the computer simulation method mentioned above, we determined the values of λ_1 and λ_3 to be 39 ± 1° and 68 ± 1°, respectively. On the basis of estimated values of λ_1 and λ_3, one can then determine the structure of the peroxy radicals of it-PP. Figure 2 represents the orientation of the O–O group around the C–O bond with respect to the adjacent C_0–C_1 bond. The angle ϕ is the internal rotation angle. The angles of λ_1 and λ_3 can be obtained from the equations

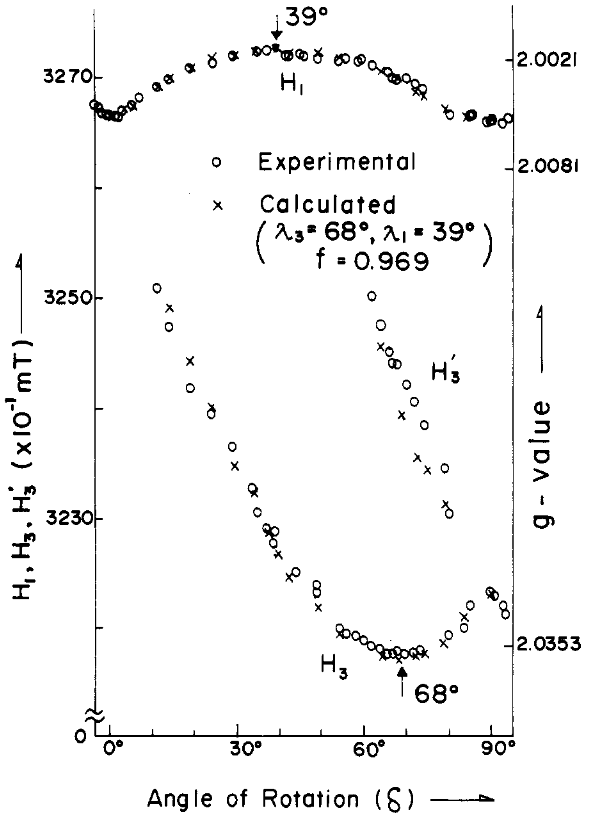

Figure 4. Angular dependences of the characteristic resonance field of the peroxy radicals trapped in isotactic polypropylene upon rotation angles (δ). The open circles are observed values at 77 K. The crosses are calculated values for f = 0.969, λ_1 = 39°, and λ_3 = 68°.

$$\cos\lambda_1 = \sin\beta\sin\phi \qquad (1)$$

$$\cos\lambda_3 = -\cos\beta\cos\gamma + \sin\beta\sin\gamma\cos\phi \qquad (2)$$

where β and γ mean the bond angles $\angle C_0C_1O_1$ and $\angle C_1O_1O_2$, respectively. From eq 1 and 2, we obtain

$$\cos \gamma = -\cos \lambda_3 \cos \beta - [(1 - \cos^2 \lambda_1 - \cos^2 \beta) \times (1 - \cos^2 \lambda_3 - \cos^2 \lambda_1)]^{1/2}/(1 - \cos^2 \lambda_1) \quad (3)$$

$\gamma = 111^{+2°}_{-1°}$ and $\phi = 55.5 \pm 1.5°$ can be obtained from eq 1 and 3. When the angle $\beta = 109°28'$ (tetrahedral angle) and the observed angles $\lambda_1 = 39 \pm 1°$ and $\lambda_3 = 68 \pm 1°$, the value of ϕ, 55.5°, is close to 60°, corresponding to the gauche conformation, as represented in Figure 1-(I). The deviation of 4.5° from the gauche conformation may be caused by the fact that the 3_1-helical structure deviates very much from a planar zigzag conformation. The fact that one could get this resonable radical structure in it-PP closely similar to a gauche conformation suggests also that the orientation of the O–O bond of a peroxy radical in the case of PE and PTFE is not skew ($\phi = -120°$) to the adjacent C–C bond, but gauche ($\phi = 60°$), as shown in Figure 1-(II).

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