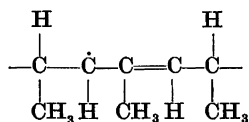


Electron Spin Resonance Study of Oriented Polypropylene

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Oriented polypropylene film was irradiated with gamma rays from a ^{60}Co source and the trapped free radicals were studied by electron spin resonance spectroscopy. After irradiation at about 20°C , spectra with marked anisotropy were observed and assigned to the free radical

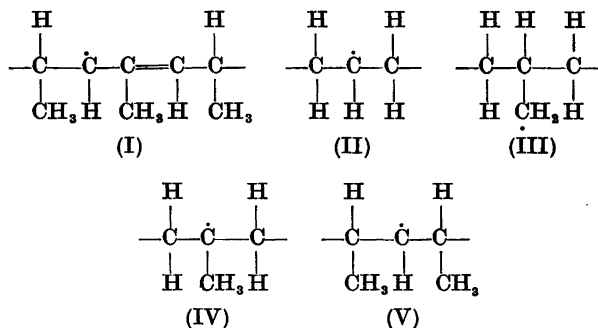


in agreement with earlier published work. The temperature dependence of the spectral shape was determined by obtaining spectra in the range from -196°C to 12°C and the results give additional support to the previous assignment. It was found that the rotation of the central methyl group, adjacent to the double bond, is frozen and the two alpha hydrogens are not equivalent with respect to hyperfine interaction with the odd electron at temperatures less than about -130°C . The ESR spectra of polypropylene samples irradiated at low temperatures (-180°C) also contain spectral components for which new assignments are proposed.

1. INTRODUCTION

Since the first report of Tsvetkov *et al.*¹ several investigations of the electron spin resonance (ESR) of irradiated polypropylene have been made. Ohnishi *et al.*² and Fischer and Hellwege³ observed similar ESR spectra at room temperature. The former authors considered the spectrum to be the sum of sextet, septet, and octet components, while the latter, examining oriented polymer samples, assigned the spectrum to the free radical (I). The ESR spectra have been studied also at -196°C with the polymer irradiated at the same temperature. Although the spectra reported by different authors are similar, the interpretations are not in agreement. Libby *et al.* considered the ESR spectrum to be a sextet due to the free radical (II)⁴. On the other hand, Loy concluded, using a deuterium substituted polymer, that the spectrum consists of a quartet,

due to the free radical (III), and a trace of nonet due to the free radical (IV).⁵ Forrestal and Hodgson considered the spectrum to be the sum of a quartet, due to the free radicals (III) and (V), and an octet due to (IV).⁶ The effect on the spectrum of warming the polymer irradiated at -196°C have been studied by several authors.^{3,5,6}



Lack of agreement in the interpretations may be partly caused by differences in the samples used by the various investigators. The tacticity of the polymer affects the nature and the behaviour of the free radicals trapped in the polymer.^{3,5} To some extent the disagreement is centered around the less well resolved hyperfine structure of the ESR spectra of irradiated polypropylene. To overcome this difficulty, it is useful to study the anisotropic spectra of the oriented polymer, as Fischer and Hellwege have done.³ The conformation of the polypropylene molecular chain is not simple, having a spiral form. Thus the interpretation of the anisotropic spectra of polypropylene is more complex than that of polymers having the plane zig-zag conformation.

The present investigation of oriented polypropylene is divided into two parts. In the first part, the dependence of the spectral line shape on the measuring temperature is studied for the anisotropic spectra of the samples irradiated at room temperature (about 20°C). The interpretation of the observed dependence is not in contradiction to the assignment made by Fischer and Hellwege, *i.e.* attributing the spectrum to the free radical (I). It is found that the asymmetric nature of the free radical at low temperature should be taken into account. In the second part, the changes of the spectral line shape are studied while warming polymer samples irradiated at low temperature. Examining the anisotropy of the spectra, a new assignment is proposed, assuming that the spectra are the sum of the components due to the free radical (I) and the quartet spectrum (III and V), respectively.

2. EXPERIMENTAL

Profax isotactic polypropylene (a sample of high crystallinity from Hercules Powder Co.) was used after purification. It was compressed at 175°C to a 1 mm thick sheet, and stretched uniaxially at 140°C with about 600 % elongation. The X-ray diffraction pattern of the stretched polymer indicated that the molecular chains were well oriented and crystallized in good lattice order.

The samples were placed in quartz-glass tubes and evacuated to a vacuum better than 10^{-4} mm Hg. Then the tubes were sealed and irradiated with gamma rays from a ^{60}Co source, at a dose rate of 0.3 Mrad/h.

The ESR spectra were recorded with an X-band reflection type spectrometer (JES-3B), using 100 kc modulation. The angle θ between the stretching direction of the sample and the applied magnetic field was changed by rotation of the sample tube inserted in the rectangular TE_{102} sample cavity. The accuracy of the measured orientation angle θ was better than $\pm 5^\circ$.

3. RESULTS AND DISCUSSION

3.1. Spectra of polypropylene irradiated at room temperature. Stretched polypropylene irradiated at about 20°C with a dose of about 10 Mrad gave, at 12°C , anisotropic spectra which were the same as those observed previously.³ An example of the recorded spectra is shown in Fig. 1 (a). Better resolution of the hyperfine components was obtained for $\theta = 0^\circ$ than with other orienta-

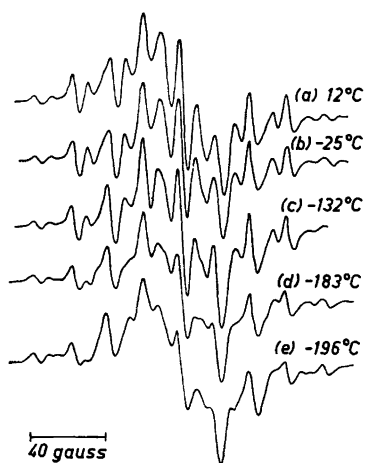


Fig. 1. The ESR spectra of stretched polypropylene observed at different temperatures for $\theta = 0^\circ$. Irradiation at room temperature with the dose of 8.9 Mrad.

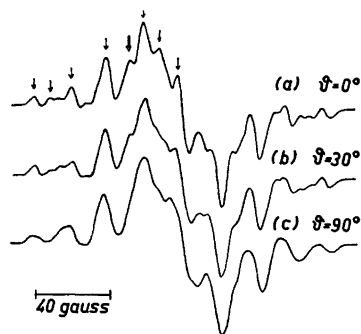


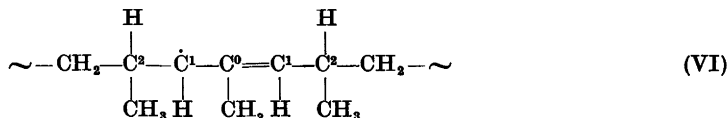
Fig. 2. The dependence of the ESR spectra of stretched polypropylene at -196°C . on the sample orientation θ . Irradiation at room temperature with the dose of 8.9 Mrad.

tions. The same sample was examined at different temperatures ranging from 12°C down to -196°C . The temperature dependence of the spectral line shape for $\theta = 0^\circ$ is illustrated in Fig. 1. Above -130°C the spectrum remained unchanged. Below this temperature, it became less well resolved with decreasing temperature. The dependence of the spectra on θ at -196°C is illustrated in Fig. 2. For larger values of θ , the spectrum looked like a nonet, which is similar to the spectrum of unoriented polypropylene.

The anisotropic spectra of stretched polypropylene observed at room temperature were interpreted by using the relation (1)³ between the position of the hyperfine components and the orientation θ .

$$H = H_0 - [A_1 + B_1 (3 \cos^2 \theta - 1)] \sum I_{H1} - A_0 \sum I_{H0} - A_2 \sum I_{H2} \quad (1)$$

H_0 is the center position of the spectra, A_i isotropic hyperfine coupling constant, B_i anisotropic hyperfine coupling constant and I_{H_i} total spin quantum number of protons attached to the i th carbon atoms. Subscript i defines the carbon atoms in the free radical (I), as shown in (VI).



Accordingly, I_{H0} has four possible values, $3/2$, $1/2$, $-1/2$ and $-3/2$, and I_{H1} I_{H2} have three values, 1 , 0 and -1 . It was found that

$$4(|A_1| + |2B_1|) \approx 2|A_0| \approx |A_2|$$

It was assumed implicitly that the free radical chains, $\text{C}^2\text{---C}^1\text{---C}^0\text{---C}^1\text{---C}^2$ are substantially parallel to the stretching direction of the sample. This is, however, a necessary approximation in the interpretation of the anisotropic spectrum of polypropylene, of which the molecular chain conformation is a 3_1 type spiral⁷ and, accordingly, each $\text{C}^2\text{---C}^1\text{---C}^0\text{---C}^1\text{---C}^2$ chain forms a helix with its axis in the stretching direction.

According to these results, each hyperfine component in the spectrum at room temperature for $\vartheta = 0^\circ$ is designated with a set of the three numbers, (I_{H0} , I_{H1} , I_{H2}). The outmost component is designated by $(3/2, 1, 1)$ and the second outmost by $(3/2, 0, 1)$. The third outmost component is the superposition of two subcomponents, $(1/2, 1, 1)$ and $(3/2, -1, 1)$. The changes in the spectral line shape observed after lowering the temperature are, in general, caused by a gradual freezing of molecular motions in the free radical, so that the protons attached to C^i become non equivalent. This leads to the result that only the hyperfine components with $I_{H0} = \pm 1/2$ and/or I_{H1} , $I_{H2} = 0$ are broadened and divided.

It is seen in Fig. 1, that the second outmost component is divided into two subcomponents at low temperature owing to $I_{H1} = 0$. It is assumed that the two H^1 protons became unequivalent at low temperature. The broadening of the third outmost component was necessarily caused by the broadening of the subcomponent $(1/2, 1, 1)$ probably because of the freezing of methyl group rotation. It is reasonable that the outmost component remained unchanged.

Woodward *et al.*⁸ studied polypropylene using nuclear magnetic resonance spectroscopy and observed an increase of the second moment below -140°C due to the freezing of methyl group rotation. The hyperfine structures due to H^0 protons in the ESR spectra are expected to change in the same temperature range, because the same frequency of the rotation (higher than about 10 Mc/sec) should result in both narrowing of the nuclear magnetic resonance spectra and equalization of all H^0 protons in the ESR spectra. In fact, this was proved to be the case with the broadening of the third outmost component which occurred upon cooling the sample below -130°C .

The conformation of the molecular chain of the free radical (I) trapped in a crystalline region is considered to be as shown in Fig. 3, which is based on

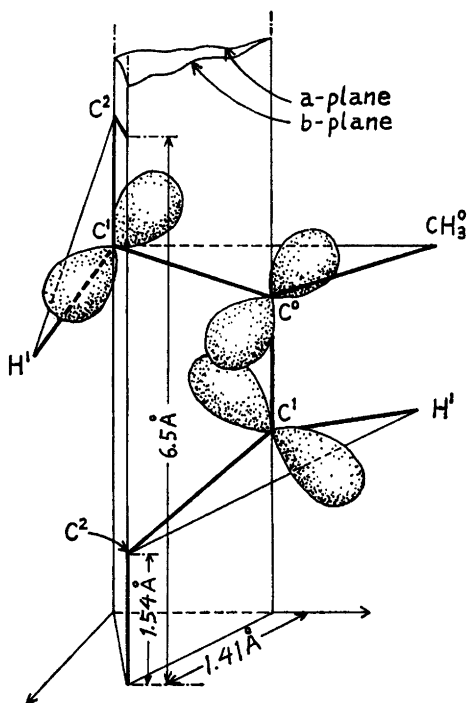


Fig. 3. The conformation of the free radical (I) in crystalline regions of polypropylene.

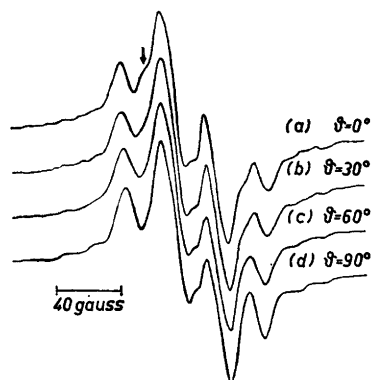


Fig. 4. The ESR spectra of stretched polypropylene recorded at about -180°C for different values of θ . Irradiation at about -180°C with the dose of 1.5 Mrad.

the assumption that the original main chain conformation⁷ is not changed by abstraction of the three hydrogen atoms and that the free radical is contained in ordinary sp^2 and π electron configurations. Three adjacent π -orbitals cannot lie in the same plane, as in a usual conjugated double bond system. The π -orbital of C^0 carbon atom has presumably an a -plane or a b -plane as its nodal plane. The two C^1 carbon atoms are, accordingly, non equivalent with respect to the central π -orbital. It is probable that, at low temperature the two H^1 protons become non equivalent and have different values of A_1 and B_1 . At high temperature, thermal motions of the molecular chain equalize, more or less, the two H^1 protons. This is a possible interpretation of the splitting of the second outmost component at low temperature. It seems reasonable to assume the free radical (I) is stable at room temperature only in the crystalline regions of the polymer.⁶

For the allylic type free radical in irradiated polyethylene, Ohnishi *et al.* observed a temperature dependence of the hyperfine interaction due to H^2 protons⁹ (four protons for polyethylene). In the present investigation, however, all hyperfine components with $I_{\text{H}^2} = 0$ were superimposed on $I_{\text{H}^2} = \pm 1$

components, which makes it impossible to observe the temperature dependence of the hyperfine interaction due to H^2 protons.

3.2. *Spectra of polypropylene irradiated at low temperature.* Stretched polypropylene irradiated at about -180°C (liquid air temperature) with the dose of 1.5 Mrad gave, at the same temperature, the ESR spectra shown in Fig. 4. Although the spectra are similar to those reported previously,^{1,4-6} they showed a slight anisotropy in the present investigation. After warming the sample to 20°C the spectral line shape changed gradually from the original quartet to the anisotropic spectra of the free radical (I). The intensity of the spectra decreased simultaneously as illustrated for $\vartheta = 0^\circ$ in Fig. 5. The spectra in Fig. 6 are those recorded after warming the samples to 20°C for 6 min, and they show a remarkable anisotropy.

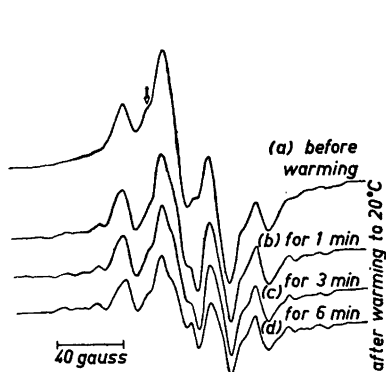


Fig. 5. Changes in the ESR spectra of stretched polymer while warming the sample to 20°C for different periods. Irradiation at about -180°C with the dose of 1.5 Mrad. Measurement at about -180°C for $\vartheta = 0^\circ$.

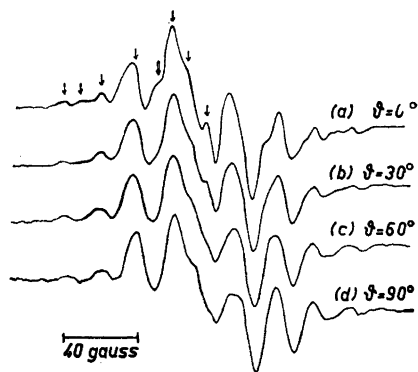


Fig. 6. The ESR spectra of stretched polypropylene observed at about -180°C for different values of ϑ , after warming the sample to 20°C for 6 min. Irradiation at about -180°C with the dose of 1.5 Mrad.

The hyperfine components of the spectra in Figs. 6 and 2 agree well with each other, especially for $\vartheta = 0^\circ$ as shown by black arrows. The spectra in Fig. 6 are considered to be the sum of the anisotropic spectrum of the free radical (I) and the quartet spectrum which is predominant immediately after the irradiation. Moreover, the anisotropic components shown by white arrows in Figs. 2, 4, 5, and 6 suggest that the original ESR spectra of the sample irradiated at low temperature also consist partly of the spectrum of the free radical (I).

Fischer and Hellwege observed an isotropic octet spectrum in the course of warming a sample irradiated at -196°C and assigned it to the free radical (IV).³ Loy reported that an irradiated sample, due to the free radical (IV), gave a nonet spectrum which was distorted by the quartet still remaining after warming to room temperature.⁵ In the present investigation, neither the isotropic octet spectra nor the isotropic nonet spectra were observed.

At this stage of the investigations, the present authors consider it likely that the ESR spectrum of oriented polypropylene irradiated at low temperature is the sum of the quartet spectrum previously reported by other investigators,⁵ *e.g.* due to the free radicals (III) and/or (V), and an anisotropic spectrum due to the free radical (I). At a later period of radical disappearance during warming of irradiated polypropylene, there is even more evidence that the ESR spectra are sums of the two spectra mentioned above. This seems to be the most probable interpretation, but there are also other possibilities.

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