

# An e.s.r. study of the motion of peroxy radicals in isotactic and atactic polypropylenes

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E.s.r. spectra of peroxy radicals trapped in isotactic and atactic polypropylenes have been observed at various temperatures. The spectrum observed at 77 K was shown to be composed of one component by comparing it with that at 4 K. The spectra observed at higher temperatures comprised of two spectra arising from the rigid peroxy radicals and the mobile peroxy radicals. All of the observed spectra have been reconstructed by means of computer simulation and the changes in anisotropic  $g$ -values with temperature were estimated. The motion of the mobile fraction was shown to be rotation or rotatory vibration of the radicals around the chain axis both in the isotactic polypropylene and in the atactic polypropylene as well as in polyethylene and poly(tetrafluoroethylene) although the structures of the polymers are different, that is helical (polypropylene) or planar zigzag (polyethylene, poly(tetrafluoroethylene)).

(Keywords: e.s.r.; polypropylene; molecular motion; peroxy radical)

## INTRODUCTION

We have reported the e.s.r. spectra of peroxy radicals trapped in polyethylene in various states<sup>1-4</sup>. These studies have clarified the structure and the motion of peroxy radicals in polyethylene. The plane of C-O-O stands perpendicular to the  $c$ -axis of polyethylene and the motion of O-O· around the polyethylene chain is faster than that around the C-O bond. The faster motion of O-O· around the polymer chain than that around the C-O bond was also found in poly(tetrafluoroethylene)<sup>5,6</sup>. Moreover we can safely say that the hydrogen abstraction reaction of peroxy radicals is intermolecular rather than intramolecular in polyethylene<sup>3</sup>.

Although zigzag polymers such as polyethylene and poly(tetrafluoroethylene) have been extensively studied, the motion and structure of peroxy radicals trapped in helical chain polymers such as polypropylene have not been studied precisely. There have been many studies on the e.s.r. of peroxy radicals in isotactic polypropylene<sup>7-16</sup>. However, almost all of them have dealt with reaction of peroxy radicals. Only Suryanarayana and Kevan<sup>16</sup> tried to discuss peroxy radical motion and concluded C-O bond rotation with the O-O group, rather than the main chain rotation. Also many investigators studying the oxidation of polypropylene, employed the intramolecular hydrogen abstraction for the reaction mechanism of peroxy radicals<sup>17</sup> on the basis of an infra-red result that the intramolecularly hydrogen bonded hydroperoxides comprise more than the 90% of hydroperoxides in oxidated polypropylene. This intramolecular hydrogen abstraction may suggest C-O bond rotation. However, we doubt these conclusions because of our results on polypropylene and comparison with our conclusion in the case of polyethylene.

Here, we report on the e.s.r. spectra of peroxy radicals

trapped in polypropylene and compare their nature with that in polyethylene. The temperature dependent e.s.r. spectra of peroxy radicals for isotactic polypropylene and atactic polypropylene were observed and it was found that both spectra comprised of two components arising from rigid radicals and mobile radicals. All spectra were simulated and the motion of the peroxy radicals was discussed on the basis of the temperature dependence of  $g$ -values determined by simulation.

## EXPERIMENTAL

### Isotactic polypropylene

The sample used was Noblen MA-4 (Mitsubishi Petrochemical Co. Ltd.,  $M_v = 40 \times 10^4$ ). The sample was purified three times by dissolving in boiling toluene, precipitating by cooling and washing in acetone. After drying in a vacuum oven, the isotactic polypropylene was annealed at 405 K for 50 h *in vacuo*. This annealing assures us that the origin of any effects at temperatures below 405 K are not the macro movement of the polypropylene chain. The density of the sample was 0.919 ( $\chi_c = 81.7\%$ ). A powdered sample was sealed into an e.w.r. tube with a breakable seal under  $10^{-5}$  Torr and was irradiated with <sup>60</sup>Co  $\gamma$ -rays at room temperature. The total dosage was about 4.8 Mrad at a dose rate of 0.1 Mrad/hour. The irradiated sample was annealed at 313 K for 2 h. After it was verified that only the tertiary alkyl radicals of polypropylene ( $\sim\text{CH}_2-\dot{\text{C}}(\text{Me})-\text{CH}_2\sim$ ) were trapped by observing the 17-line e.s.r. spectrum<sup>18</sup>, the peroxy radical of the irradiated isotactic polypropylene was produced by breaking the seal in air at room temperature. 10 Torr of oxygen was sealed in the e.s.r. tube with this sample to suppress the reproduction of alkyl radicals by hydrogen abstraction of peroxy radicals at higher temperature.

### Atactic polypropylene

The atactic polypropylene used in this study was kindly presented by Mitsubishi Petrochemical Co. Ltd. The sample was purified three times by dissolving in boiling toluene, precipitating by dropping the solution into methanol and washing in acetone. The polypropylene molecular weights, after drying in a vacuum oven, were  $\bar{M}_w = 2.66 \times 10^4$  and  $\bar{M}_n = 5.2 \times 10^3$ . Its crystallinity was estimated to be about 0% from a d.s.c. measurement. A powdered sample was sealed into an e.s.r. tube with a breakable seal under vacuum conditions and was irradiated with  $^{60}\text{Co}$   $\gamma$ -rays at liquid nitrogen temperature. The irradiated sample was annealed at 273 K. After the 17-line e.s.r. spectrum was observed, 10 Torr of oxygen was introduced into the sample tube at 273 K and then the tube was sealed off.

### E.s.r. measurement

The e.s.r. measurements were made using a JEOL ME-3X spectrometer with a JES-SCXA microwave unit (X-band) or with a JES-SK unit (K-band), with 100 KHz modulation. DPPH was used as a standard for  $g$ -values, and the  $g$ -value of DPPH was taken as 2.0036. Magnetic field sweep was calibrated with known splitting constants of  $\text{Mn}^{2+}$ . The signals were recorded by a MELCOM 70/25 minicomputer. The spectra were observed at 4 K and 77 K and at various temperatures ranging from 146 to 284 K.

## SIMULATION AND EXPERIMENTAL RESULTS

### Simulation method

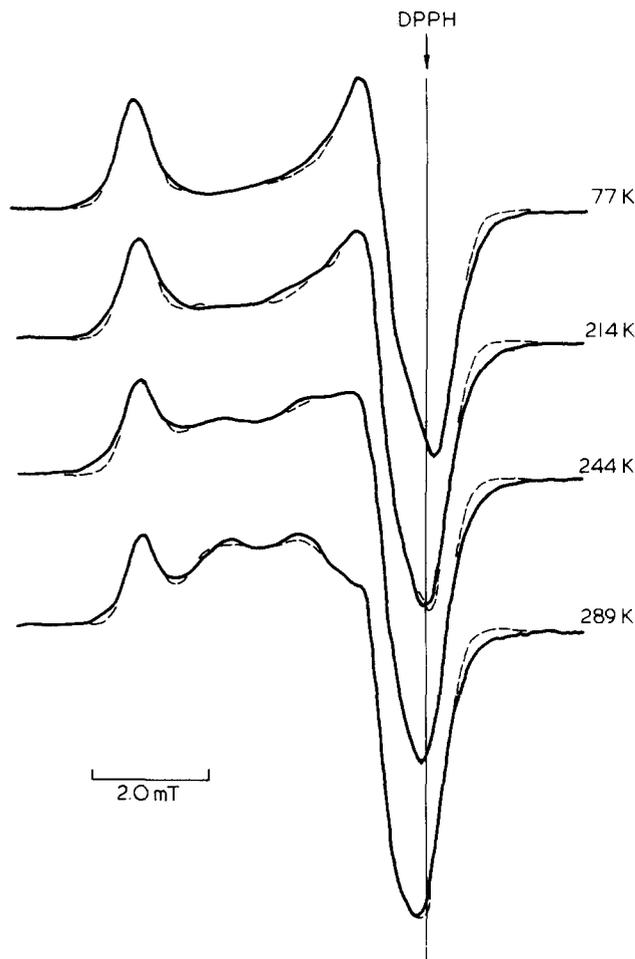
The method of simulation was essentially the same as that described in previous articles<sup>1,2</sup>. We assumed that there were two groups of peroxy radicals. One of them is rigid (A radical) and the other is more mobile (B radical). Parameters used were  $g_1 < g_2 < g_3$ ,  $\Delta H_1$ ,  $\Delta H_2$  for A radical and  $g_1' < g_2' < g_3'$ ,  $\Delta H_1'$ ,  $\Delta H_2'$  for B radical, and ratio of concentrations,  $[\text{B}]/[\text{A}]$ . Several line shape functions were tested by considering three points of view; i.e., fitting of both spectra for low and high temperature ranges, applicabilities for both cases using X-band and K-band frequencies, and computing time. The Gaussian function was determined to be useful. The following remarks were obtained.

- (1)  $g_1$  and  $g_3$  determined by simulation are very good and their uncertainty is estimated to be  $\pm 0.0001$ .
- (2) The uncertainty of  $g_2$  is  $\pm 0.0002$ .
- (3)  $g_1'$ ,  $g_2'$  and  $g_3'$  are not so good and their uncertainties are estimated to be about  $\pm 0.0004$ ,  $\pm 0.0006$  and  $\pm 0.0010$  respectively.
- (4) The absolute value of the concentration ratio,  $[\text{B}]/[\text{A}]$ , is doubtful but its relative value can be reliable.

### Isotactic polypropylene

E.s.r. spectra of peroxy radicals in isotactic polypropylene observed at 4 K and at 77 K were identical. This result indicates that the peroxy radicals even at 77 K do not make any motion which affects the e.s.r. spectrum.

The temperature dependent spectra of the peroxy radicals trapped in isotactic polypropylene were observed and some of these spectra are shown in Figure 1 with simulated spectra. These spectra were changing reversibly with the observing temperature, except for the sample stored for a long time at a higher temperature. At a higher



**Figure 1** Examples of temperature dependent e.s.r. spectra of the peroxy radicals trapped in isotactic polypropylene with simulated spectra. (—) observed spectra, (---) simulated spectra

temperature, the decay of the B-radical (mobile fraction) was observed and this decay reaction will be reported elsewhere<sup>19</sup>.

The temperature dependence of the obtained  $g$ -values and the concentration ratio,  $[\text{B}]/[\text{A}]$ , were plotted in Figures 2 and 3 respectively. In Figure 3, the value of  $[\text{B}]/[\text{A}]$  at 77 K is not zero, although the spectrum of 77 K should be composed of one component. This contradiction may arise from the use of Gaussian line shape function because the spectrum was well simulated by one component when we used a Gaussian-Lorentzian product function as the line shape function. Then B radical at 77 K apparently simulates the spectrum at 77 K (broken line in Figure 3). Below this broken line should be thought of as simulating the rigid fraction and above this line may be thought of as the true mobile fraction.

For polyethylene, we reported that  $g_1$  and  $g_1'$  have the same value at all temperatures<sup>1-3</sup>. But it has been shown that the values of  $g_1$  and  $g_1'$  are different at higher temperature for polypropylene as seen in Figure 2. This difference between  $g_1$  and  $g_1'$  was obtained not only by simulation of the X-band e.s.r. spectra, but also we clearly observed both peaks arising from  $g_1$  and  $g_1'$  by means of a K-band e.s.r. spectrometer.

### Atactic polypropylene

The temperature dependent spectra of the peroxy radicals trapped in atactic polypropylene were observed

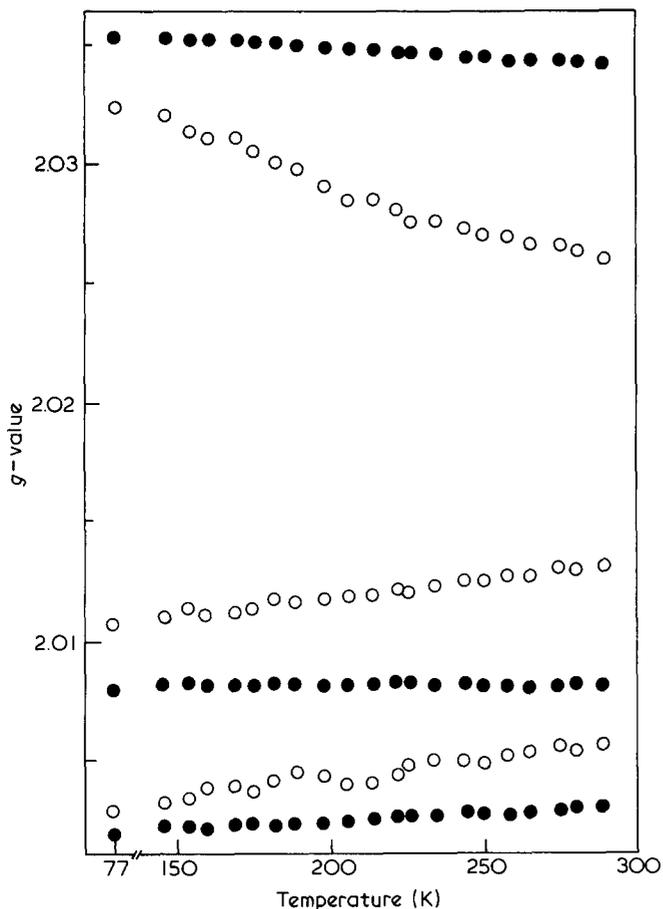


Figure 2 Change in  $g$ -values of the peroxy radicals trapped in isotactic polypropylene with temperature. ●, A-radical; ○, B-radical

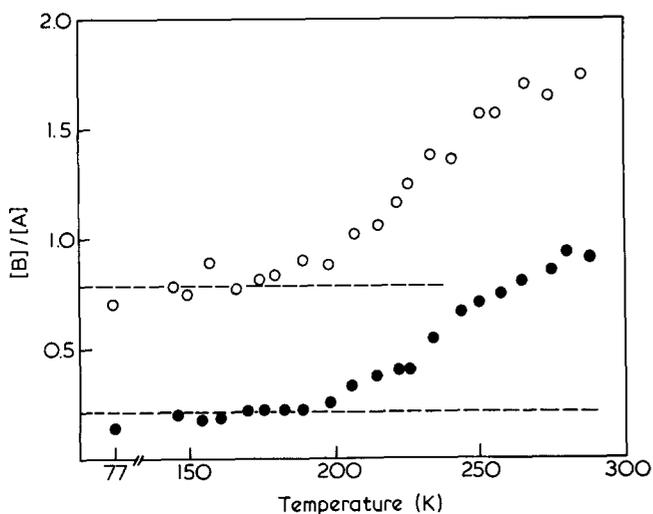


Figure 3 Change in the ratio,  $[B]/[A]$ , with temperature. ●, peroxy radical trapped in isotactic polypropylene; ○, in atactic polypropylene. For explanation of broken lines see text

and examples of these spectra are shown in Figure 4 with simulated spectra. One of the differences between the isotactic and atactic polypropylenes shown in Figures 1 and 4 is that there is one broad peak for the B-radical in the spectra for atactic polypropylene observed at the higher temperature, but two peaks for isotactic polypropylene.

The temperature dependence of  $g$ -values determined by

simulation and the concentration ratio,  $[B]/[A]$ , were plotted in Figures 5 and 3 respectively. In Figure 3, a broken line represents a boundary between the true and imaginary parts of the mobile fraction as mentioned for isotactic polypropylene. The higher value of this line than that for isotactic polypropylene is a reflection of the fact that the spectrum for atactic polypropylene at 77 K was poorly simulated by one component. The difference of  $g_1$  and  $g_1'$  values is also shown as being similar to that for isotactic polypropylene.

### DISCUSSION

We have concluded that the peroxy radicals trapped in isotactic polypropylene at 77 K exist in a rigid state based on the fact that the e.s.r. spectrum observed at 77 K was similar to that at 4 K. The spectrum at 77 K was not well simulated by a one component assumption with a Gaussian line-shape function but was well simulated with the Gaussian-Lorentzian product line-shape function. These results suggest to us that the peroxy radicals are trapped in the various sites with differing configurations, and that the  $g$ -values have a broad distribution whose function is dependent on the conditions surrounding the trapping sites. The e.s.r. spectrum of the peroxy radicals trapped in isotactic polypropylene at 77 K differs from that for atactic polypropylene at 77 K, and this fact may support the hypothesis that the distribution function of  $g$ -values of the peroxy radicals in the rigid state depends on the

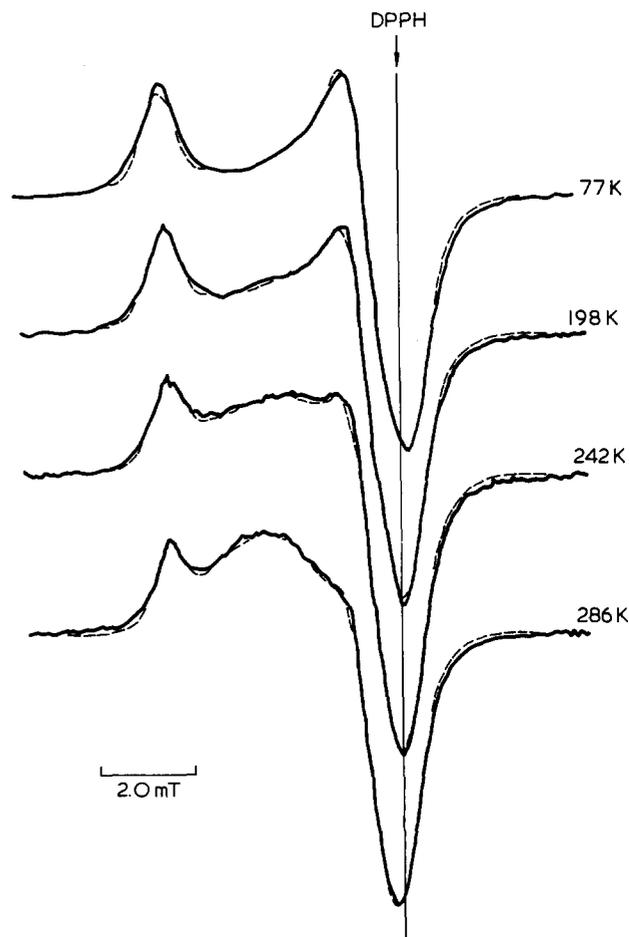
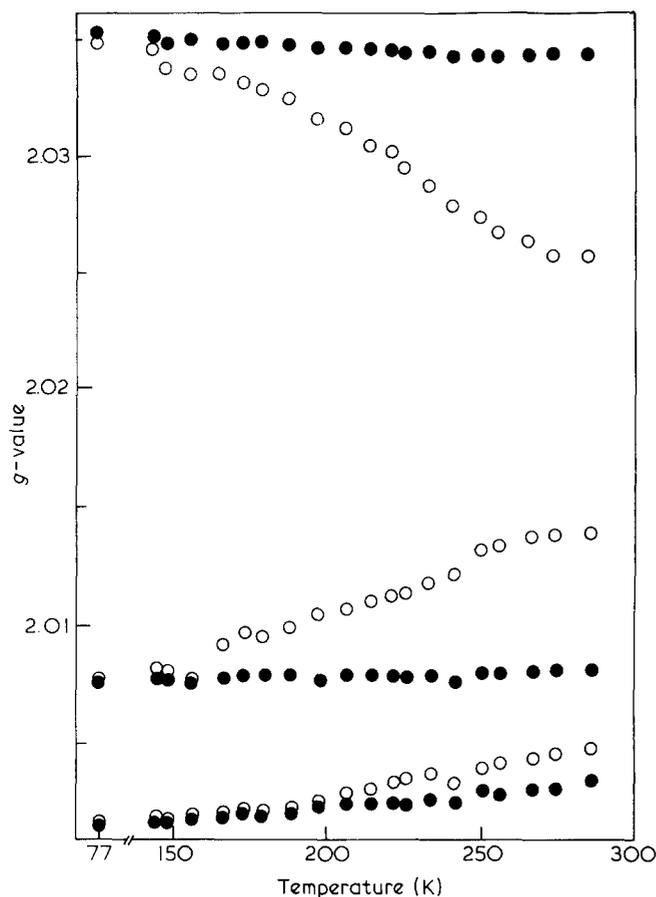


Figure 4 Examples of temperature dependent e.s.r. spectra of the peroxy radicals trapped in atactic polypropylene with simulated spectra. (—) observed spectra, (---) simulated spectra



**Figure 5** Change in  $g$ -values of the peroxy radicals trapped in atactic polypropylene with temperature. ●, A-radical, ○, B-radical

material and on the histories of the samples. We will now consider this line-shape problem of the e.s.r. spectra of peroxy radicals for a number of materials.

In both of isotactic and atactic polypropylenes, we found that the peroxy radicals are divided into two groups, rigid peroxy radicals (A-radical) and mobile peroxy radicals (B-radical), and that the ratio,  $[B]/[A]$ , increases with increase in the observing temperature (see *Figure 3*). These two facts have also been observed with polyethylene<sup>1,2</sup>. These facts can be explained by assuming that the mobility of various trapping sites has a wide distribution and the mobility and the distribution are dependent on the temperature. Naturally, this assumption does not explain there being only two groups of radicals. The mobile fraction may not have a single mobility value but may have a distribution of values, and a one group assumption for the mobile fraction can be employed as a first step approximation. However, we think that the result of having two groups, the rigid and mobile fractions, is a reflection of the actual distribution of mobility of the peroxy radicals. In short, there may be two motional modes, one expresses the rigid state and the other the mobile state. The rigid state mode or less mobile state mode then has a narrow distribution and the mobile state has a broad distribution.

Firstly, we will consider the motion of the rigid state mode. We have observed the temperature dependence of  $g$ -values for the A-radical, (rigid state radical). As can be seen in *Figure 2*,  $g_3$  (maximum  $g$ ) decreased and  $g_1$  (minimum  $g$ ) increased slightly with increasing temperature. These are similar to the results reported by Suryanarayana and Kevan<sup>16</sup>. They observed only an A-

radical and no B-radical and therefore concluded that the C–O bond rotation with the O–O group undergoing two successive 180° jumps for a COO angle of 104°, and suggested that chain-axis motion is minimal due to the steric hindrance of the side groups. We do not agree with either of these two conclusions. For the A-radical, the 180° jumps of O–O around the C–O bond may explain the temperature dependence of  $g$  values, but we suggest that this result can be explained by assuming only a small vibration of the O–O group around the C–O bond. The existence of the B-radical does not support the minimum for the chain axis motion as will be shown in the following discussion.

For the chain axis motion, it is significant that the spectra arising from the B-radicals appear at higher temperatures. As can be seen in *Figures 2* and *5*, the temperature dependence of  $g$ -values of the B-radical is quite clear. From the experimental results, this B-radical is evidently a mobile peroxy radical and the motion of this radical becomes greater or faster with increasing temperature. If one assumes that there are only two modes of motion of the peroxy radicals, the O–O group rotation around the C–O bond and the C–O–O rotation around the chain axis, we can be clear which is the case. If O–O group rotation around the C–O bond occurs, the increase in  $g_1'$  should be greater than that for  $g_2'$ , since the principal direction of  $g_1'$  is perpendicular to the C–O bond. Clearly this is not the case as can be seen in *Figures 2* and *5*.

For the polyethylene peroxy radical, the temperature dependence of  $g_2'$  and  $g_3'$  have been explained by the chain axis rotation. Although for polypropylene there is a new result which differs in that the values of  $g_1'$  are different from those of  $g_1$ , the C–O–O rotation around the chain axis explains the experimental results when one considers that the structure of polypropylene is helical. The structure of the peroxy radical of polypropylene may be analogous to that of polyethylene particularly from the view point of conformation, and then the C–O–O plane can be thought of as being perpendicular to C<sup>1</sup>–C<sup>3</sup> direction when the radical is described as ( $\sim$ C<sup>1</sup>H<sub>2</sub>–C<sup>2</sup>(Me)(OO·)–C<sup>3</sup>H<sub>2</sub> $\sim$ ). The angle between  $g_1$  and the chain axis can then be estimated to be about 35° from the helical structure of polypropylene. The C–O–O rotation around the chain axis combined with the inclination of the  $g_1$ -direction from the chain axis explains the difference between  $g_1$  and  $g_1'$ , and the temperature dependences of  $g_1'$ ,  $g_2'$  and  $g_3'$  also. Other evidence for chain-axis rotation can be obtained if one observes the angular dependence of the e.s.r. spectra of stretched polypropylene film at room temperature. If C–O–O rotation around the chain occurs, the spectra observed at room temperature should be similar to those at 77 K in the case of the magnetic field parallel to the extension axis, although the spectra at room temperature should be different from those at 77 K in the perpendicular direction. Indeed, a preliminary study on a stretched film of isotactic polypropylene showed the above mentioned angular dependence<sup>20</sup>.

From the above mentioned discussion, the mobile fraction has been concluded to be rotating or rotationally vibrating around the chain axis. Intermolecular hydrogen abstraction can be suggested by considering both of the chain axis rotation and the instability of the B-radical at higher temperature mentioned previously.

Another feature of the peroxy radicals is that the

temperature dependence of  $g$ -values of isotactic polypropylene is similar to that for atactic polypropylene. Both the peroxy radicals in isotactic polypropylene (crystalline) and atactic polypropylene (amorphous) are rotating or rotationally vibrating around the chain axis, although the distribution of the rates of motions and the temperatures of the same mobility are different. This is similar to the case of polyethylene. Both the peroxy radicals trapped in the amorphous parts of polyethylene<sup>1</sup> and in the urea-polyethylene complex<sup>2</sup> (crystalline) are rotating or rotationally vibrating about the chain axis. Also the peroxy radicals trapped in the main chain of poly(tetrafluoroethylene) exhibit the same motion<sup>5,6</sup>. All these facts indicate that the peroxy radicals trapped in the main chain of the polymer are rotating or rotationally vibrating about the chain axis regardless of polymer phase or polymer structure (planar zigzag or helical) at the considerably high temperatures where the radicals are stable. Other indications are that the peroxy radicals trapped in the main chain are separated into two groups of less mobile and mobile states, and that the mobile fraction has a broad distribution of mobility in all polymers. These two hypotheses must, however, be proved in other polymers and we are planning to extend the study to these other polymers in the future.

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