Distribution of Molecular Orientation and Stability of Peroxy Radicals in the Noncrystalline Region of Elongated Polypropylene

Shigetaka Shimada,* Yasurō Hori, and Hisatsugu Kashiwabara

Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan.
Received July 22, 1987

ABSTRACT: The angular dependent ESR spectra of peroxy radicals in noncrystalline regions of elongated polypropylene are successfully observed following UV and γ-irradiation at low temperatures. The ESR spectra of mobile radicals obtained by subtracting the ESR spectra after annealing from those before annealing can be simulated from the calculated spectra of the partially oriented paramagnetic centers. The shape of the resulting spectrum changes drastically with the annealing temperature. It is found that the more mobile radicals have the lower degree of orientation. The degrees of orientation, $f_{S,M} = 0.42$ and $f_{S,L} = 0.31$, are determined for the peroxy radicals, which decay at the lowest temperature range, obtained by γ-irradiation at 195 K and UV irradiation at 77 K, respectively. The values of f are lower than those for the radicals in the crystalline region, $f_{S,H} = 0.536$ and $f_G = 0.968$, reported previously. Subscripts, S and G in the f-values mean skew and gauche conformations around the C–O bond, respectively, and L, M, and H mean low, medium, and high f-values in the skew case, respectively. The investigation of the stability of the radicals and the estimation of the degrees of orientation also lead to the conclusion that the less stable radicals are trapped in the less oriented molecular sites of the noncrystalline region. The peroxy radicals can be used to observe the distribution of molecular orientation in the noncrystalline region.

Introduction

We have developed spin label techniques in order to study the structure and dynamic behavior of polymer chains at a particular site or in a particular region.[1] When the label is stable, temperature dependence of the ESR spectrum can be observed over a wide temperature range. On the other hand, when an unstable label such as the peroxy radical[2–5] has chemical reactivity at low temperature, we can elucidate many kinds of local structures and molecular motions by exploiting the reactivities in the different regions. The spin label method may also offer some distinct advantages for the study of the mechanisms of chemical reactions, affected by the structure and molecular motion of the polymer chain. In our previous paper,[1a] it was reported that the conformational structure of peroxy radicals and the molecular disorder of a polymer chain in crystalline regions of elongated isotactic polypropylene can be determined from the angular dependences of ESR spectra of the radicals. The ESR spectra were composed of two spectra, arising from mobile peroxy radicals and rigid ones, which had skew and gauche conformations, respectively. It was also concluded that the former radicals were located in molecularly disordered sites of inner crystalline regions, although the latter were in highly ordered sites of the same regions.

We raise additional questions next. Can we observe peroxy radicals in noncrystalline regions? How different is the molecular disorder of the peroxy radicals in noncrystalline regions from those in the inner crystalline regions? In order to answer these questions, we must observe peroxy radicals generated at various sites by various methods and analyze the ESR spectra of the radicals by the same method mentioned in the previous paper.[1a] In this paper, we will compare the degree of orientation of the radicals in the noncrystalline region with that of a polymer chain in the same region estimated by other measurements and show that the ESR method is simple and effective for the determination of the orientation function of the polymer chain. We will also show that the ESR spectra reflect a distribution of molecular order in the noncrystalline region.

Experimental Section

An isotactic polypropylene, Noblen MA-4 (Product of Mitsubishi Petrochemical Co. Ltd., $\bar{M}_v = 40 \times 10^4$), was used for this study. The purification of the sample, the preparation of a film, and the elongation of the film were described in detail in our previous paper.[1a]

A sample having a stretch ratio of 6 was prepared and aligned with the stretching direction perpendicular to the axis of the sample tube. The sample was evacuated to 10^{-5} Torr and labeled with peroxy radicals in the following three ways. (A) After the sample was γ-irradiated in vacuo at room temperature, oxygen at a pressure of 200 torr was introduced at ~260 K for 55 h. This was coded as γ-irradiated in vacuo (GV) specimen. In our previous paper,[1a] it was concluded that the peroxy radicals produced in the GV specimen should be trapped in the crystalline cores. (B) After the sample was γ-irradiated in an oxygen atmosphere at 195 K, peroxy radicals were formed upon annealing the sample at ~260 K for 106 h. This was coded as γ-irradiated in oxygen (GO) specimen. (C) After the sample was UV irradiated in oxygen atmosphere at 77 K, peroxy radicals were formed upon annealing the sample at ~253 K for 27 h. The UV-irradiation was carried out with a H400-P mercury vapour lamp (Toshiba Denki Co.). This was coded as UV irradiated in oxygen (UO) specimen.

The GV and GO specimens were irradiated with ^{60}Co γ-ray to a total dose of ca. 4.0 Mrad. Into the GO and UO specimens, oxygen at a pressure of 200 torr was introduced before the irradiation at the low temperatures in order to observe the peroxy radicals trapped also in the noncrystalline region.[3,6] Many authors[5–7] reported that several carbon-centered radicals, precursors of peroxy radicals, were formed in polypropylene by UV and γ-irradiations. In the GV specimen, it was verified that only the tertiary alkyl radical of polypropylene ($\sim CH_2\dot{C}(Me)CH_2\sim$) was formed before the introduction of oxygen molecules. In the GO and VO specimens, the tertiary alkyl radicals should also be precursors of peroxy radicals, because diffusion of oxygen molecules into the film is very slow. We assume that unstable carbon-centered radicals should decay or convert to the tertiary alkyl radicals before the oxygenation. Other experimental details such as ESR measurements have been explained previously.[1a] The spectra were recorded with a MELCOM 70/25 computer connected to the spectrometer and the total relative concentration of the radicals was obtained by double integration of first derivative ESR spectra.

Simulation

The spectrum simulation for partially and uniaxially oriented peroxy radicals observed at 77 K was carried out by the method described in our previous paper.[1a]

1. We do not assume any motional mechanisms because ESR spectra of peroxy radicals in isotactic polypropylene observed at 4 and 77 K are identical as described in our previous paper.[1b]

2. We use the principal values $g_1 = 2.0021$, $g_2 = 2.0081$, and $g_3 = 2.0353$ and the line width that are obtained from

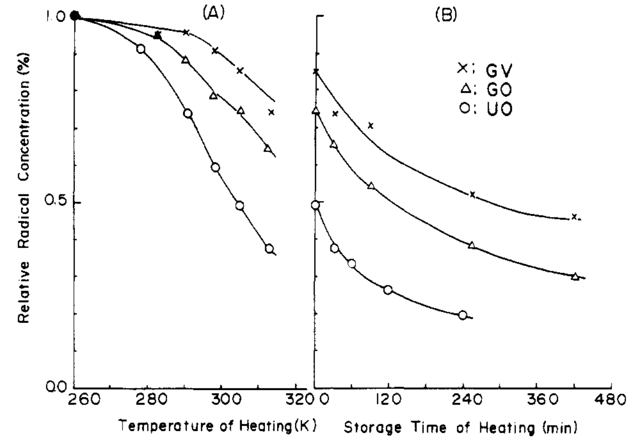

Figure 1. Change in peroxy radical concentration with annealing temperature (A) and with decay time at 313 K (B): (×) GV; (Δ) GO; (O) UO.

the simulation of the powdered sample.[1b] The spectrum in the powdered sample was well simulated by only one component when we used a Gaussian-Lorentzian product function as the line shape.

3. Several theoretical spectra for cases of both $\delta = 0°$ and $\delta = 90°$ were calculated by changing the values of λ_1, λ_3, and an orientation parameter a. δ is a rotation angle between the stretching direction and the external magnetic field. λ_1 and λ_3 can be defined as the angles between the principal directions of the g tensor and the polymer chain axis. The calculated spectra were recorded on an X–Y plotter and compared with the observed spectra in order to get the best fit. From the simulation, the angles λ_1 and λ_3, and the distribution function of the polymer chain, $\exp(a \sin^2 \alpha)$, the orientation function, f_α, can be obtained. The value of f_α is calculated as follows:

$$f_\alpha = \frac{\int_0^{\pi/2} [(3 \cos^2 \alpha - 1)/2] \exp(a \sin 2\alpha) \sin \alpha \, d\alpha}{\int_0^{\pi/2} \exp(a \sin^2 \alpha) \sin \alpha \, d\alpha}$$

where α is the distribution angle between the stretching direction and the polymer chain axis.

4. When the spectrum is calculated by assuming two components that have different conformations and degrees of orientation, we use the values of λ_1, λ_3, and a for rigid radicals, as obtained in our previous paper,[1a] and then we can get the values of λ_1', λ_3', and a' for another component and the relative concentration of the two fractions from the simulation.

Results and Discussion

1. **Decay of Peroxy Radicals.** In Figure 1A, the "decay curves" of total concentration of peroxy radicals are shown for the GV, GO, and UO specimens. The sample was annealed at a desired temperature for 30 min and subsequently plunged into liquid nitrogen. The ESR measurements were carried out at 77 K. The "decay curve" was obtained by repeating these procedures with increasing an annealing temperature. After the sample was annealed at 313 K for 30 min, the annealing time was changed at the constant temperature, 313 K, as shown in Figure 1B. The decay curves of the respective specimens were very different. For example, the peroxy radicals in the UO specimen began to decay at a lower annealing temperature, 280 K, than in the GV specimen.

Although only 20% of the radicals in the GV specimen decay at 313 K, 65% in the UO specimen decayed at the same temperature. In the GO specimen, the intermediate decay behavior of the radical was observed. As discussed in previous papers,[1,4] the ESR spectra observed in these experiments were composed of two spectra arising from chemically identical peroxy radicals having different mobilities and stabilities. One of the radicals, which was unstable, was called a mobile peroxy radical and the other was called a rigid peroxy radical.

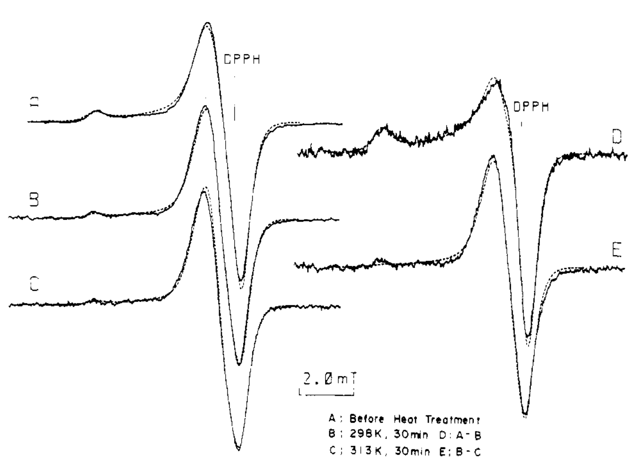

Figure 2. Variation of the observed (solid) and calculated (dotted) ESR spectra of peroxy radials trapped in elongated polypropylene (UO) with annealing temperature (B, 298 K: C, 313 K). The stretching direction is set to be parallel to the external magnetic field. ESR spectra were observed at 77 K. The calculated spectra A, B, and C are composed of two spectra although the calculated spectra D (A – B) and E (B – C) are one spectrum, as mentioned in the text. No significance should be attached to the relative intensity of these spectra.

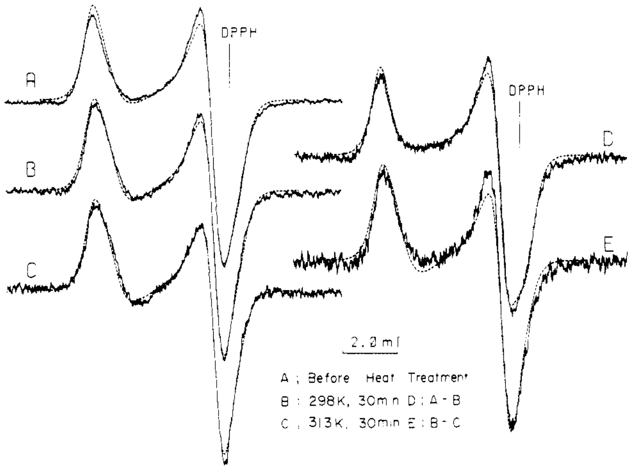

Figure 3. Variation of the observed (solid) and calculated (dotted) ESR spectra of peroxy radicals trapped in elongated polypropylene (UO) with annealing temperature (B, 298 K: C, 313 K). The stretching direction is set to be perpendicular to the external magnetic field. ESR spectra were observed at 77 K. The calculated spectra A, B, and C are composed of two spectra although the calculated spectra D (A – B) and E (B – C) are one spectrum, as mentioned in the text. No significance should be attached to the relative intensity of these spectra.

In all GV, GO, and UO samples, ESR spectra obtained after annealing for a long time at 313 K are very similar to that of the rigid peroxy radicals as shown in Figure 2C.

Consequently, the different behavior of the decay reactions in Figure 1 should have its cause in the various environments and the various sites of the mobile peroxy radicals.

2. **Distribution of Molecular Disorder of Peroxy Radicals.** Examples of the dependence of ESR spectrum shape on annealing temperature and angular dependence of the shape are shown in Figures 2 and 3, and the change

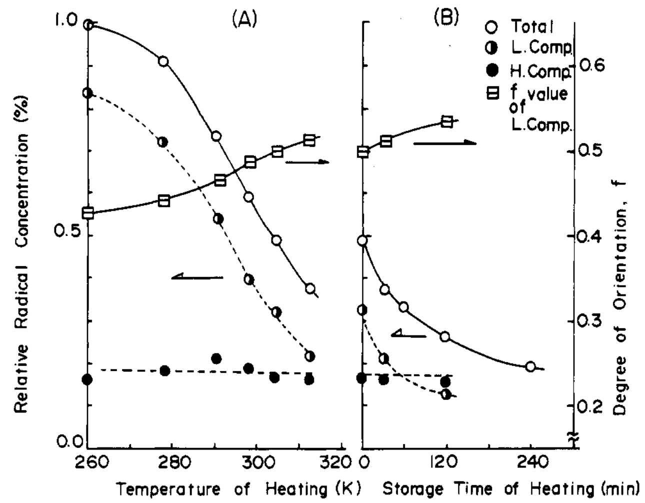

Figure 4. Change in total (○) and partial concentration of mobile (◑) and rigid (●) radicals with annealing temperature (A) and with decay time at 313 K (B) in the case of the UO specimen. Variation of orientation function, *f* of mobile radicals (⊟) is also shown.

of concentration of the peroxy radicals with the temperature is shown in Figures 1 and 4.

A very marked angular dependence of the ESR spectra suggests a preferential orientation of the polymer chain along the stretching direction. In order to elucidate the degree of orientation, spectral simulations for the ESR spectra of partially and uniaxially oriented peroxy radicals are performed. The shape of the spectrum changes with the annealing temperature as shown in Figures 2 and 3.

One of the main changes is reduction of the small peak at the lowest value of the external magnetic field along the stretching direction ($\delta = 0°$). The broad component for the field perpendicular to the stretching direction ($\delta = 90°$) also disappeared. These facts indicate that the spectra observed at any stage of reaction are composed of two components arising from mobile and rigid fractions.

It can be considered that the peak at the lowest magnetic field in the case of $\delta = 0°$ arises from the mobile component, which has a low degree of orientation. For instance, the mobile radicals can be considered to be trapped in molecularly disordered regions. One may then suppose that the decay of peroxy radicals shown in Figure 4 is due mainly to the mobile radicals and that the rigid radicals at those temperatures are very stable or at least decay only very slowly. In order to confirm these hypotheses, we simulated all of the spectra by assuming two components as shown in Figure 5. The simulated spectra are shown with dotted lines in Figure 2 and 3. The ratio of the concentration of the mobile peroxy radical to that of the rigid one was also obtained from the simulation.

The calculated relative concentrations of mobile and rigid radicals are plotted against annealing temperature and reaction time at 313 K in Figure 4. One characteristic feature of Figure 4 is that the concentration of the rigid radicals is nearly constant throughout the decay process.

The orientation functions *f* of the mobile and rigid radicals can be also obtained from the simulation. In the previous paper, orientation of the O–O group around the C–O bond with respect to the adjacent C–C bond in the C–C–O–O• peroxy radical was discussed and it was concluded that the rigid and mobile radicals took the gauche and skew conformations, respectively. In the present study, the same conclusion was obtained from the simulation, and then the orientation functions of the rigid and mobile radicals were coded as f_G and f_S, respectively.

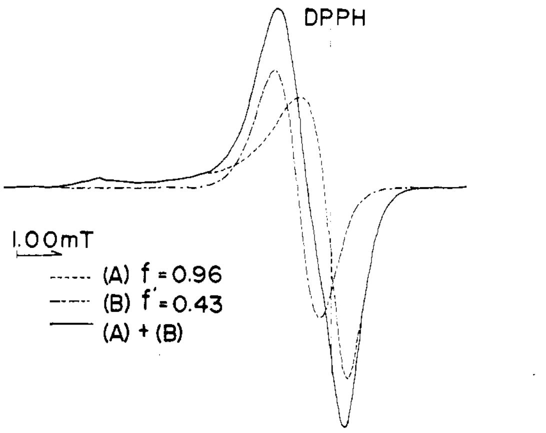

Figure 5. Example of an ESR spectrum of peroxy radicals, assuming that the spectrum is composed of two spectra from two different values of the orientation function. Solid line is a superposition of two patterns.

Subscripts, G and S in the *f* values mean skew and gauche conformations around the C–O bond. That of the mobile one increases with the annealing as shown (⊟) in Figure 4, although that of the rigid one, $f_G = 0.96$, is estimated to be constant. This fact suggests that the mobile radicals should be trapped in various disordered regions, which have various degrees of molecular orientation. It is also suggested that the more mobile radicals in the more disordered region should decay at the lower temperature.

In order to confirm these suggestions, the more mobile and the less mobile radicals, which decay at the lower and higher temperature regions, respectively, must be analyzed by the same method.

Figures 2D,E and 3D,E show the ESR spectra of the mobile radicals obtained by subtracting the ESR spectra after annealing from those before annealing. For example, Figure 2D was obtained by subtracting Figure 2B from Figure 2A. The shape of the subtracted spectrum changes drastically with the annealing temperature. In the case of $\delta = 0°$, the peak at the lowest magnetic field being more intense in Figure 2D than in Figure 2E suggests that the more mobile radical has a lower degree of orientation. As shown in Figures 2D,E, the profiles of the experimental spectra (solid lines) show good agreements with the spectra (dotted lines) calculated for the values of the orientation function, $f_{S,L} = 0.31$ and $f_{S,H} = 0.54$, respectively.

The small value of $f_{S,L} = 0.31$ in comparison to the value of $f_{S,H} = 0.54$ indicates that the more mobile radicals should be trapped in the more disordered region. In the case of $\delta = 90°$ as shown in Figure 3D,E, the spectra obtained by subtraction can be simulated with the same values of $f_{S,L} = 0.31$ and $f_{S,H} = 0.54$.

The subtracted spectra for the GV and GO specimens were also simulated by the same method. Comparison of the ESR spectra of peroxy radicals which decay in a lower temperature region for the three specimens is shown in Figure 6. The orientation functions for the GV, GO, and UO specimens are calculated to be $f_{S,H} = 0.54$, $f_{S,M} = 0.42$, and $f_{S,L} = 0.31$, respectively. From these analyses, it is evident that the mobile peroxy radicals generated by the different methods are trapped in the different disordered regions of the polymer substance as shown schematically in Figure 7. Symbols, L, M, and H in $f_{S,L}$, $f_{S,M}$, and $f_{S,H}$ mean low, medium, and high degrees of orientation, respectively.

3. Location and Trapping Site of Mobile Peroxy Radicals. In the previous paper,[1a] it was concluded that both rigid and mobile peroxy radicals in the GV specimen should be trapped in the crystalline region. It could also

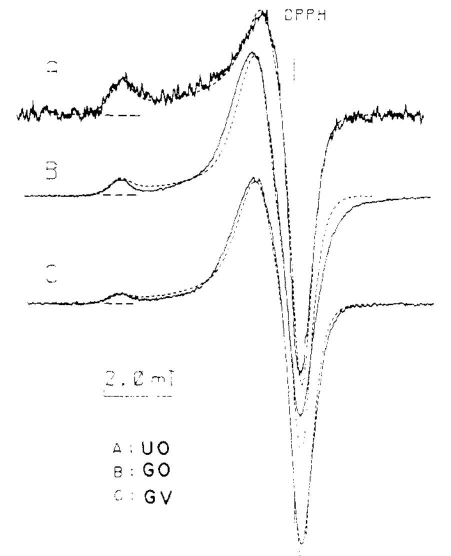

Figure 6. Comparison of the observed (solid) and calculated (dotted) ESR spectra of peroxy radicals which decayed by the heat treatments at lower temperature for three specimens UO (A), GO (B), and GV (C).

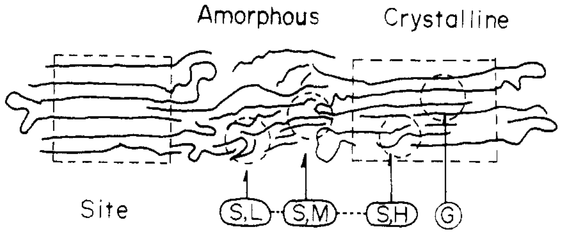

Figure 7. Schematic illustration of the molecular disorder in the semicrystalline polymer.

be reasonably concluded that the low orientation function, $f_{S,H} = 0.54$, of the mobile radicals points to molecularly disordered sites such as defects in the crystals, including conformational distortion, caused by the bonding of oxygen molecules. The next question is whether the location of the mobile peroxy radicals in the GO and UO specimens is the inner crystalline region or the noncrystalline region including the crystalline surface. Figure 8 shows orientation functions obtained in this study in comparison with those determined by using the X-ray diffraction method. The marks ×, Δ, and O indicate variations of orientation function of the mobile peroxy radicals in the specimens GV, GO, and UO, respectively, as a function of the annealing temperature. The f-values could be obtained by the simulations, assuming that the experimental spectrum was composed of only two components from the rigid and mobile radicals.

Although the orientation function of the mobile radicals in the GV specimen is not dependent upon the annealing temperature, those in the GO and UO specimens increase with the annealing temperature. These facts suggest that the mobile peroxy radicals in the GO and UO specimens include the radicals trapped in the noncrystalline region, the orientation function of which is lower than $f_{S,H} = 0.54$ in the GV specimen, and the more mobile radicals decay at the lower temperature. On the other hand, the values of $f_{S,M} = 0.42$ and $f_{S,L} = 0.31$ obtained for the subtracted spectrum in the cases of the GO and UO specimens, respectively, are close to the orientation functions of the noncrystalline region, 0.34–0.39, determined by the X-ray diffraction method.[8]

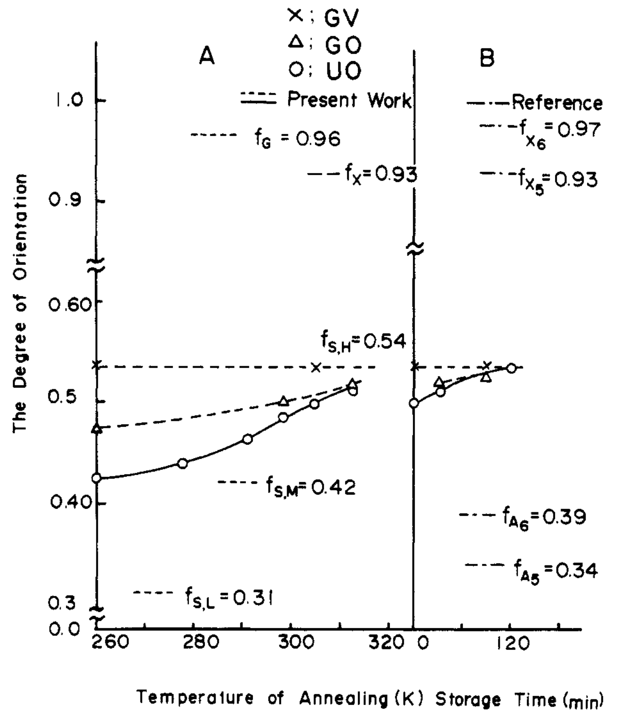

Figure 8. Variations of orientation function, f, obtained by simulations of ESR spectra, with annealing temperature (A) and with decay time at 313 K (B). × (GV), Δ (GO), and O (UO) are obtained for the mobile radicals and f_G is for the rigid radicals. $f_{S,L}$, $f_{S,M}$, and $f_{S,H}$ are obtained for the subtracted spectra, A, B, and C, respectively, in Figure 6. f_x is a orientation function of a good crystalline part, obtained for the material GV by the X-ray diffraction method.[1a] X and A in the reference data (- - -) mean crystalline and noncrystalline, respectively and the subscript numbers means the stretched ratio of the film.

Consequently, it is concluded that large numbers of mobile peroxy radicals in the GO and UO specimens are located in the molecularly oriented sites of the noncrystalline region in elongated polypropylene samples. The difference in the orientation functions, $f_{S,M} = 0.42$ and $f_{S,L} = 0.31$, should have its cause in the various locations and the various sites in the noncrystalline region. In other words, the various degrees of orientation of the peroxy radicals obtained in this study should reflect the various molecularly disordered structures of the polymer in the vicinity of the peroxy radicals and the distribution of the relaxation time of the radicals.

Registry No. Isotactic polypropylene, 25085-53-4.

References and Notes

(1) (a) Shimada, S.; Hori, Y.; Kashiwabara, H. *Macromolecules* **1985**, *18*, 170. (b) Hori, Y.; Makino, Y.; Kashiwabara, H. *Polymer* **1984**, *25*, 1436 and references cited in these papers.

(2) For example: Carlsson, D. J.; Dobbin, C. J. B.; Wiles, D. M. *Macromolecules* **1985**, *18*, 1791.

(3) Eda, B.; Nunome, K.; Iwasaki, M. *J. Polym. Sci., Polym. Lett. Ed.* **1969**, *7*, 91.

(4) Hori, Y.; Shimada, S.; Kashiwabara, H. *J.* Polym. *Sci., Polym. Phys. Ed.* **1984**, *22*, 1407.

(5) Alonso-Amigo, M. G.; Schlick, S. *Macromolecules* **1987**, *20*, 795.

(6) Tuji, K. *Rep. Prog. Polym. Phys. Jpn.* **1972**, *15*, 569.

(7) For example: (a) Iwasaki, M.; Ichikawa, T.; Toriyama, K. *Polym. Lett.* **1967**, *5*, 423. (b) Dunn, T. S.; Epperson, B. J.; Sugg, H. W.; Stannett, V. T.; Williams, J. L. *Radiat. Phys. Chem.* **1979**, *14*, 625. (c) Gvozdic, N.; Basheer, R.; Mehta, M.; Dole, M. *J. Phys. Chem.* **1981**, *85*, 1563. (d) Faucitano, A.; Buttafava, A.; Martinotti; Gratani, F.; Bortolus, P. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 635.

(8) Takahara, H.; Kawai, H.; Yamada, T. *Sen-i Gakkaishi* **1967**, *23*, 102.