# ESR Study on Molecular Motion of Chain End Radicals of Polyethylene Molecules Anchored on Fresh Surfaces of Polyethylene and Polytetrafluoroethylene

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*Received August 13, 1992; Revised Manuscript Received February 14, 1993*

ABSTRACT: The chain end radical of polyethylene molecules anchored on a fresh polymer surface was produced by block copolymerization of ethylene monomer which was initiated by mechanoradicals formed by mechanical fracture of a solid polymer and located on the fresh surface. The molecular motion of the radical of polyethylene molecule anchored on a fresh surface of polyethylene (PE) is induced by a spin exchange of $\beta$ protons between two equilibrium states at dihedral angles of 15° and 45°, and having spin exchange rates of $7.1 \times 10^7$ s$^{-1}$ at 77 K and $4.0 \times 10^8$ s$^{-1}$ at 104 K. This results in weak adsorption of the radical on the PE surface. The mobility of the radical is mildly inhibited by intermolecular forces holding the radical to the PE surface. On the other hand, the molecular motion of the radical anchored on the fresh surface of polytetrafluoroethylene (PTFE) allows free rotation around the $C_\alpha$–$C_\beta$ bond axis even at 77 K. The high mobility of the radical in this latter case is attributed to weak intermolecular forces between the radical and PTFE molecules and causes the radical to protrude from the PTFE surface. It is suggested that the polymer chain has relatively high mobility, even at temperatures as low as 77 K, if the chain is isolated from other molecules.

## Introduction

Numerous studies on molecular motion of polymer chains have been reported including, for example, molecular motion in the bulk of polymers,[1] effect of free volume on molecular motion,[2] and correlating molecular motion to miscibility of polymer blends.[3] In these systems, the polymer chains are surrounded by other molecules such as polymer chains and solvent molecules. Molecular motion of the polymer chain seems to be restricted by specific interaction with matrix molecules and/or intermolecular forces holding the chains in the matrix.

We have employed a novel technique to investigate the molecular motion in isolated and nonisolated systems. The present study reports the molecular motion of chain end radicals of polyethylene molecules anchored to solid surfaces of polyethylene (a nonisolated system) and on the solid surface of PTFE (an isolated system).

## Experimental Section

**Materials.** Polyethylene (PE) (Sholex 6050, Showa Electric Industry Co., Ltd.) was dissolved in boiling toluene, cooled, filtered, washed with acetone, and dried under vacuum at room temperature. This procedure was repeated three times. The PE powder sample was then dried in vacuo at room temperature for 2 days. Polytetrafluoroethylene (PTFE) powder (Aflon G 80, Asahi Glass Co., Ltd.) was used without further purification. Ethylene monomer (Takachiho Co., Ltd.) was purified by the freeze–pump–thaw method.

The chain end radical of polyethylene was produced under vacuum at 77 K by block copolymerization of ethylene monomer initiated by mechanoradicals, which were formed by mechanical fracture of the polymer, and then attached to a fresh surface.[4-10] Mechanical fracture of the polymer with, or without, ethylene monomer was carried out by milling in a home-made vibration glass ball mill[6] in vacuo at 77 K for 21 h. After the milling, the ESR sample tube connected to the glass ball mill was placed in liquid nitrogen, and the powdered sample was dropped into the ESR sample tube within 1 s by turning the glass ball mill upside down. ESR spectra at 77 K and higher temperatures were observed at a microwave power level of 0.04 mW to avoid power saturation and with 100-kHz field modulation using a JEOL JES-FE3XG ESR spectrometer (X-band) coupled to microcomputer (NEC PC 9801).

**Spectral Simulation.** Hori has reported[11] a computer program based on a spin exchange due to ring inversion of the cyclohexyl and cycloheptyl radicals, which have one $\alpha$ proton ($H_\alpha$) in the respective thiourea complexes. The program employs the Liouville density matrix theory derived by Heinzer[12] and is based on the assumption of two states.[11] We have modified the computer program developed by Hori to simulate the ESR spectrum of a chain end radical which has two $H_\alpha$ with anisotropic hyperfine splittings and two $\beta$ protons ($H_\beta$). The intramolecular coordinates based on the principal axes of hyperfine splitting tensor of $H_\alpha$ are defined as follows:[13] $A_x$ is parallel to the axis of p-orbital containing the unpaired electron at the $\alpha$ carbon ($C_\alpha$); $A_z$ axis is along the direction of the $C_\alpha$–$H_{\alpha 1}$ bond axis; and $A_y$ axis is perpendicular to both the $A_x$ and $A_z$ axes. It is assumed that $H_{\alpha 1}$ and $H_{\alpha 2}$ are at symmetric positions to the $C_\alpha$–$C_\beta$ bond axis with angles $\phi_1$ and $\phi_2$ of 60°, and the angle between $C_\beta$–$H'_{\beta 1}$ and $C_\beta$–$H'_{\beta 2}$ axes projected from $C_\beta$–$H_{\beta 1}$ and $C_\beta$–$H_{\beta 2}$ axes to the plane at $C_\beta$ is 120° (Figure 3).

A new molecular coordinate system of axial symmetry due to a free rotation of the chain end around the $C_\alpha$–$C_\beta$ bond axis is assumed; the $A_\parallel$ axis is parallel to the $C_\alpha$–$C_\beta$ bond axis, and the $A_\perp$ axis is perpendicular to $A_\parallel$.

## Results

The ESR spectrum observed at 77 K (Figure 1a) was obtained from the powder of fractured PE without ethylene monomer under vacuum at 77 K. The ESR spectra observed at 77 K and higher temperatures (Figure 1b–f) were obtained from fractured PE with ethylene monomer in vacuo at 77 K. The peak intensity (shown by an arrow in Figure 1b) is larger than the corresponding peak from fractured PE without ethylene monomer (Figure 1a). This peak intensity decreased with increased observation temperature and decayed out at 162 K (Figure 1f) as the ESR spectrum changed to the spectrum of alkyl radical of PE.[14]

The sextet spectrum (the solid line in Figure 2a) was obtained by computer subtraction of Figure 1c from Figure

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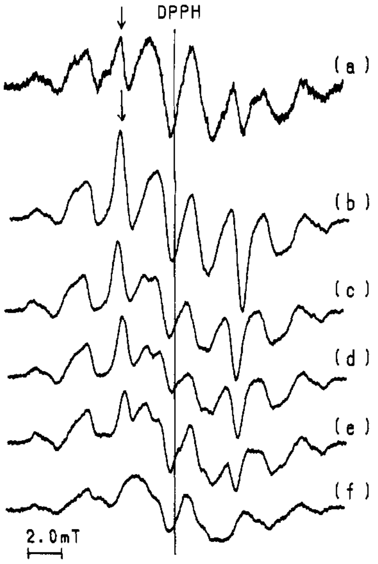

**Figure 1.** (a) ESR spectrum observed at 77 K from fractured PE without ethylene monomer under vacuum at 77 K. ESR spectra observed at (b) 77, (c) 96, (d) 104, (e) 132, and (f) 162 K, from fractured PE with ethylene monomer in vacuo at 77 K. 1,1-Diphenyl-2-picrylhydrazyl (DPPH) is used to calibrate the magnetic field position.

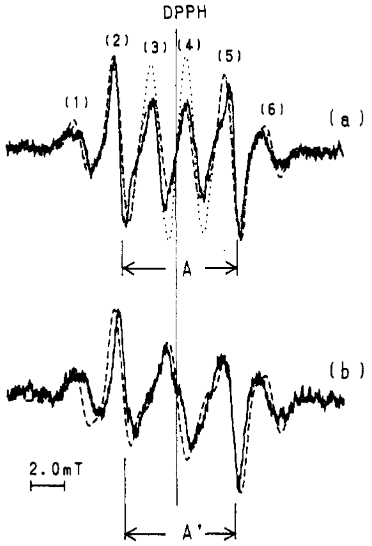

**Figure 2.** (a) Sextet spectrum obtained by spectral subtraction of Figure 1c from Figure 1b (—), the simulated spectrum without considering a spin exchange (···), and the simulated spectrum based on the spin exchange of $\beta$ protons between two equilibrium states at a rate of $7.1 \times 10^7$ s$^{-1}$ (- - -). (b) Quintet spectrum obtained by spectral subtraction of Figure 1e from Figure 1d (—) and the simulated spectrum based on the spin exchange of $\beta$ protons between two equilibrium states at a rate of $4.0 \times 10^8$ s$^{-1}$ (- - -).

1b. The simulated spectrum in Figure 2a (dotted line) was obtained for the polyethylene chain end radicals without considering a spin exchange of $\beta$ protons. The best-fit simulated spectrum (the broken line in Figure 2a) was obtained by using the parameters listed in Table I, in which there was spin exchange at a rate of $7.1 \times 10^7$ s$^{-1}$ between two dihedral angles $\theta_1 = 15°$ and $\theta'_1 = 45°$. Each dihedral angle is defined as the angle between $C_\beta$–$H'_{\beta 1}$ or $C_\beta$–$H''_{\beta 1}$ axes and an axis projected from the p-orbital axis to the plane at $C_\beta$ (shown in Figure 3)

$$A_\beta = \rho_C B_0 + \rho_C B_2 \cos^2 \theta^{15}$$

where $\rho_C$ is the spin density at the carbon atom and $\theta$ is the dihedral angle. In the spectral simulations, $\rho_C B_2$ is assumed to be 4.60 mT. $B_0$ is small compared to $B_2$ and is generally ignored in the calculation.

**Table I. ESR Parameters Used in the Spectral Simulations**

| | | | |
|---|---|---|---|
| $A_x$, mT | 2.00 | $g_{iso}$ | 2.0031 |
| $A_y$, mT | 3.20 | $\phi_1$, deg | 60 |
| $A_z$, mT | 1.34 | $\phi_2$, deg | 60 |
| $\Delta H_G$,[a] mT | 0.6 | | |
| site 1 of $\beta$ proton | | site 2 of $\beta$ proton | |
| $\theta_1$, deg | 15 | $\theta'_1$, deg | 45 |
| $A_{\beta 1}$, mT | 4.29 | $A'_{\beta 1}$, mT | 2.30 |
| $\theta_2$, deg | 45 | $\theta'_1$ | 15 |
| $A_{\beta 2}$, mT | 2.30 | $A_{\beta 2}$, mT | 4.29 |
| sextet spectrum | | | |
| $K$,[b] s$^{-1}$ | $7.1 \times 10^7$ | | |
| quintet spectrum | | | |
| $K$,[b] s$^{-1}$ | $4.0 \times 10^8$ | | |

[a] $\Delta H_G$ is a line of Gaussian shape function. [b] $K$ is spin-exchange rate of $\beta$ proton.

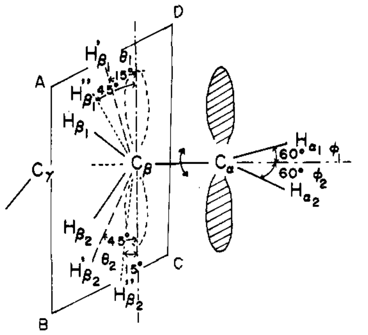

**Figure 3.** Schematic diagram of the chain end radical of polyethylene molecule.

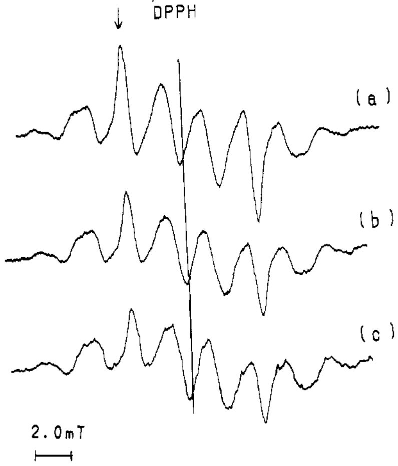

**Figure 4.** ESR spectra at 77 K from PE fractured with ethylene monomer at 77 K under vacuum after fracture: (a) as milled, (b) after 4 days, and (c) after 13 days.

The splitting, $A$, between peak 2 and peak 5 in Figure 2a is 6.82 mT.

The quintet spectrum (the solid line in Figure 2b) was obtained by computer subtraction of Figure 1e from Figure 1d. The splitting $A'$ (shown in Figure 2b) was 6.56 mT. Positions of the outer peaks, indicated by numbers 1, 2, 5, and 6 in the sextet spectrum (Figure 2a), were almost unaltered with an increase of observation temperature, but the inner two peaks (3 and 4) joined to form nearly one peak at the mid-position (the solid line in Figure 2b).

The simulated spectrum of the quintet (the broken line in Figure 2b) was obtained using the same parameters (Table I) but with a spin exchange rate of $4.0 \times 10^8$ s$^{-1}$.

Figure 4 shows spectral changes of the ESR spectrum obtained from fractured PE with ethylene monomer with increase in storage time at 77 K. The peak intensity (shown

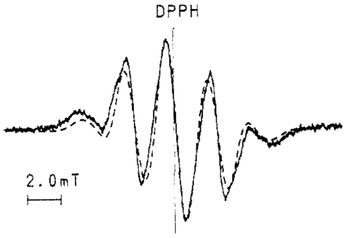

**Figure 5.** ESR spectrum from fractured PTFE with ethylene monomer in vacuo at 77 K observed at 77 K (—) and the simulated spectrum of the chain end radical of polyethylene molecule based on free rotation around the $C_\alpha$–$C_\beta$ bond axis (- - -).

by the arrow corresponding to peak 2 of the sextet spectrum in Figure 4) decreased with storage time. However, the total intensity of the radical, obtained by double integration of the ESR spectrum, did not change.

The quintet spectrum (the solid line in Figure 5), was observed at 77 K from fractured PTFE with ethylene monomer in vacuo at 77 K. The intensity and line shape of the spectrum did not change with storage time at 77 K.

Spectral simulations of radicals anchored on the fresh surface of PTFE were achieved by assuming that the radical rotates freely around the $C_\alpha$–$C_\beta$ bond axis. The best-fit simulation spectrum (the broken line in Figure 5) was obtained with the parameters $A_\parallel$ = 3.19 mT, $A_\perp$ = 1.75 mT, and $A_{\beta 1} = A_{\beta 2}$ = 2.52 mT.

## Discussion

**Identification of Radicals.** We earlier reported that *mechanoradicals can initiate radical polymerization* of ethylene monomer in vacuo at 77 K and produce polyethylene chains which are bound to the molecules composing the fresh surface of a polymer.[7] The simulated spectrum from the chain end radicals (the broken line in Figure 2a) is in good agreement with the sextet spectrum (the solid line in Figure 2). The sextet spectrum can be assigned to a chain end radical of polyethylene molecule anchored on a fresh surface of solid PE.

It has been reported[14] that chain end radicals of PE can abstract hydrogen atoms from intermolecular chains (not intramolecular chains) and produce alkyl radicals of PE: $\sim CH_2\text{–}\dot{C}H\text{–}CH_2\sim$. The spectrum of Figure 1e is identical to that reported for the alkyl radical of PE.[14] Since the ESR spectrum for the alkyl radical of PE is stable, this spectrum shape does not change at temperature as low as 96 K. Furthermore, the alkyl radical of PE was not observed for the fractured PTFE with ethylene monomer. The apparent octet spectrum (Figure 1b) can be ascribed to the superposition of chain end radicals and alkyl radicals of PE which are produced by intermolecular hydrogen abstraction from PE composing the solid surface during milling under vacuum at 77 K.

**Spin Exchange of Chain End Radical of Polyethylene Molecule Anchored on Fresh Surface of PE.** The simulated spectrum shown by the dotted line in Figure 2 was obtained from the parameters in Table I without considering spin exchange, in which molecular motion of the radical is frozen. This is obviously a rather poor fit with the sextet spectrum for the chain end radical at 77 K. This poor fit suggests that molecular motion of the chain end radical occurs at 77 K.

The best-fit simulated spectrum based on spin exchange with the rate of $7.1 \times 10^7\ s^{-1}$ is shown by the broken line in Figure 2a. The simulated spectrum is identical with the sextet spectrum for chain end radicals. This result demonstrates that the molecular motion of the chain end radical of the polyethylene molecule anchored on the fresh surface of PE occurs even at 77 K and results in weak adsorption of the radical on the surface of PE (illustrated in Figure 6a, left).

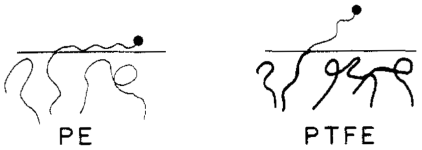

**Figure 6.** Schematic illustrations of the location of the chain end radical of polyethylene molecule anchored on a solid surface: (a, left) the chain end radical adsorbed on the surface of solid PE and (b, right) located above the surface of solid PTFE, where the thin wavy line is a polyethylene chain and the heavy wavy line is a PTFE chain.

The peak (shown by the arrow in Figure 4) corresponding to peak 2 of the sextet spectrum decreased with storage time. However, the total intensity of the radical did not change. These results indicate that the radical conversion of chain end radicals to the alkyl radicals of the PE by intermolecular hydrogen abstraction occurs at 77 K. This radical conversion also demonstrates that the molecular motion of the chain end radical takes place even at 77 K.

The simulated spectrum (the broken line in Figure 2b) was obtained by using the same parameters (Table I) except a spin exchange rate of $4.0 \times 10^8\ s^{-1}$. This simulated spectrum is in fair agreement with the quintet spectrum (the solid line in Figure 2b) from the chain end radical at 104 K. The spin exchange of $H_\beta$ at 104 K is more vigorous than that at 77 K.

The splitting of $A'$ with 6.56 mT (shown in Figure 2b) is slightly smaller in comparison to the splitting of $A$ with 6.82 mT (shown in Figure 2a). If the spectral change from the sextet to the quintet is due to the spin exchange alone, the splittings of $A$ and $A'$ should be equal. The small deviation of the simulated spectrum from the quintet spectrum may be due to neglect other modes of molecular motion such as oscillation around each equilibrium state.

**Free Rotation of Chain End Radical of Polyethylene Molecule Anchored on Fresh Surface of PTFE.** We have reported[7] that the radical polymerization of ethylene monomer under vacuum at 77 K is initiated by PTFE mechanoradicals which are produced by mechanical fracture of solid PTFE, producing polyethylene molecules bound to the fresh surface of the PTFE. The best-fit simulated spectrum (the broken line in Figure 5) was obtained by the parameters based on free rotation of the chain end radicals around the $C_\alpha$–$C_\beta$ bond axis. Therefore, the observed spectrum can be assigned to chain end radicals of polyethylene molecule anchored on a fresh surface of PTFE, and the chain end radical rotates freely around the $C_\alpha$–$C_\beta$ bond axis even at 77 K.

Despite the free rotation at 77 K, the spectrum shape and the concentration of radicals did not change at 77 K with storage time. The high mobility of the radical is attributed to weak intermolecular forces between the radicals and the PTFE molecules and causes the radical to protrude from the PTFE surface as illustrated schematically in Figure 6b, right. Thus, the high mobility of the chain end radical results in specific isolation from the PTFE surface; i.e., there is a large specific volume around the radical.

On the other hand, in spite of the same chain end radicals being adsorbed on the fresh surface of PE, the exchange motion takes place at 77 K. Intermolecular forces between the chain end radicals and PE molecules composing the surface seem to be relatively strong in comparison to that for the chain end radicals and PTFE molecules.

In conclusion, polymer chains may have relatively high mobility, even at low temperatures such as 77 K, if the chain is isolated from other molecules.

## References and Notes

(1) For example: (a) Smith, P. M.; Boyer, R.; Kumler, P. L. *Macromolecules* **1979**, *12*, 61. (b) Bullock, A. T.; Cameron, G. G.; Smith, P. H. *J. Phys. Chem.* **1973**, *77*, 1635. (c) Pilá, J.; Labský, J. *J. Phys. Chem.* **1986**, *90*, 6038. (d) Hori, Y.; Shimada, S.; Kashiwabara, H. *Polymer* **1977**, *18*, 567. (e) Sakaguchi, M.; Kashiwabara, H. *Polymer* **1982**, *23*, 1594.

(2) Sueishi, Y.; Nishimura, N.; Hirata, K.; Kuwata, K. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 4253.

(3) Shimada, S.; Hori, Y.; Kashiwabara, H. *Macromolecules* **1988**, *21*, 2107.

(4) Sakaguchi, M.; Yamakawa, H.; Sohma, J. *J. Polym. Sci., Polym. Lett. Ed.* **1974**, *12*, 193.

(5) Sakaguchi, M.; Kodama, S.; Edlund, O.; Sohma, J. *J. Polym. Sci., Polym. Lett. Ed.* **1974**, *12*, 609.

(6) Sakaguchi, M.; Sohma, J. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 1233.

(7) Sakaguchi, M.; Sohma, J. *J. Appl. Polym. Sci.* **1978**, *22*, 2915.

(8) Sakaguchi, M.; Yokono, T.; Sanada, Y.; Sohma, J.; Kashiwabara, H. *Fuel* **1981**, *60*, 136.

(9) Kurokawa, N.; Sakaguchi, M.; Sohma, J. *Polym. J.* **1978**, *10*, 93.

(10) Sakaguchi, M.; Kashiwabara, H. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 563.

(11) Hori, Y.; Shimada, S.; Kashiwabara, H. *J. Phys. Chem.* **1986**, *90*, 3073.

(12) Heinzer, J. *Mol. Phys.* **1971**, *22*, 167.

(13) McConnell, H. M.; Heller, C.; Cole, T.; Fessenden, R. W. *J. Am. Chem. Soc.* **1960**, *82*, 766.

(14) Shimada, S.; Kashiwabara, H.; Sohma, J. *J. Polym. Sci., Polym. Phys. Ed.* **1970**, *8*, 1291.

(15) Heller, C.; McConnell, H. M. *J. Chem. Phys.* **1960**, *32*, 1535.