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Site Exchange Motion of Ends of Isolated Single Polyethylene Chains Tethered on the Poly(tetrafluoroethylene) Surface in Vacuum at 2.6 K

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Introduction. Numerous studies on the molecular motion of polyethylene (PE) chains in bulk PE have been reported. These reports indicate that the mobility of PE chains is frozen below the glass transition temperature because of the disappearance of a free space for the molecular motion. The isolated single PE chains tethered on the surface of poly(tetrafluoroethylene) (PTFE) were produced in vacuum at 77 K and had a large space around the chains. The rapid exchange motion between two α protons (H_α) and the site exchange motion between two sites at the end of the isolated single PE chains occur at 2.6 K, an extremely lower temperature than the T_g (=249 K[1]) of PE.

Experimental Section. The PE chains tethered on the PTFE surface in vacuum were produced[2−4] by the block copolymerization of PTFE with ethylene at 77 K in vacuum. This copolymerization was initiated by the PTFE mechano radicals,[2−5] which were produced by mechanical fracture of PTFE powder and were trapped on the surface of PTFE.[6] The tethered PE chain has an unpaired electron at the chain end. The detailed procedure of the block copolymerization has been described elsewhere.[2,4,5]

The ESR spectrometer (Bruker ESP 300E), equipped with a helium cryostat (Oxford ESR 900) was used to investigate the molecular motion at the ends of the tethered PE chains. ESR spectra were observed at X-band frequency at a microwave power level of 2 μW to avoid power saturation and with 100 kHz field modulation. The sample was cooled to 2.6 K in the cryostat and kept for 2 h; then the ESR spectra were observed at 2.6 K.

Spectral Simulation. Hori et al. have reported[7] a computer program based on a spin exchange due to ring inversion of the cyclohexyl and the cycloheptyl radicals, which have one H_α, in the respective thiourea complexes. The program employs the Liouvill density matrix theory derived by Heinzer[8] and is based on the assumption of two states.[7] Heinzer's equation is, as expected, identical with that derived from the modified Bloch equations.

We have modified the computer program developed by Hori et al. to simulate the ESR spectrum with the powder pattern of a chain end radical that has two H_αs with anisotropic hyperfine splitting (hfs) constants and two β protons (H_β) with isotropic hfs constants. The molecular coordinate system (x, y, z) based on the principal axis (A_x, A_y, A_z) of the hfs tensor of H_α is usually defined as follows: A_x is parallel to p_z occupied by the unpaired electron at the α carbon (C_α). A_z is along the direction of the $C_\alpha-H_\alpha$ bond. A_y lies in the $H_{\alpha1}-C_\alpha-H_{\alpha2}$ plane and is perpendicular to both A_x and A_z. When the hfs term is arising from two H_αs, a new coordinate system (1, 2, 3) can be based on the principal axes (A_1, A_2, A_3), which have a relationship with A_x, A_y, and A_z: $A = A_x \sin^2(\theta + \theta_0) \cos^2(\phi + \phi_0) + A_y \sin^2(\theta + \theta_0) \sin^2(\phi + \phi_0) + A_z \cos^2(\theta + \theta_0)$ where θ and ϕ are spherical polar angles for the applied static magnetic field to the coordinate system (1, 2, 3), and θ_0 and ϕ_0 are polar angles for the principal axis of the hfs tensor of H_α to axis 3 and 1 in the coordinate system (1, 2, 3). Axis 2 lies in the plane of $C_\alpha-C_\beta-C_\gamma$ and bisects the dihedral angle of 120° of $H_{\beta1}-C_\beta-H_{\beta2}$. Axis 1 is perpendicular to both the plane of $C_\alpha-C_\beta-C_\gamma$ and axis 2. Axis 3 is perpendicular to both axes 1 and 2 and is parallel to the chain axis of PE.

Two sites, which are called site 1 and site 2, are assumed for the end of the tethered PE chain. Site 1: Each A_x of $H_{\alpha1}$ or $H_{\alpha2}$ is parallel to p_z and tilts from axis 1 with an angle of $\phi_0 = 15°$. Each A_z lies in the $H_{\alpha1}-C_\alpha-H_{\alpha2}$ plane and has the angle of $\theta_0 = -90°$ to axis 3 for $H_{\alpha1}$ and $\theta_0 = 30°$ for $H_{\alpha2}$. Site 2: A_y and A_z are the same as those in site 1, except A_x tilts $\phi_0 = -15°$ from axis 1.

The isotropic hfs constant (A_β) from H_β can be estimated by the McConnell equation:[9]

$$A_\beta = \rho_c B \cos^2(\lambda + \phi_{01})$$

where ρ_c is a spin density of C_α and B is an empirical parameter. λ is 30° of the projection angle between axis 1 and the $C_\beta-H_{\beta1}$ or $C_\beta-H_{\beta2}$ bond to the ABCD plane, which is perpendicular to the $C_\alpha-C_\beta-C_\gamma$ plane and $C_\alpha-C_\beta$ bond and has a 30° angle from the $C_\beta-H_\beta$ bond in the case of a trans zigzag chain of PE. ϕ_{01} is the projection angle between axis 1 and the p_z orbital axis to the ABCD plane (Figure 1).

Results and Discussion. *Isolated Single PE Chains Tethered on the PTFE Surface.* The tethered PE chains on the PTFE surface were obtained by the same procedure described elsewhere,[3−5] except for the low concentration of ethylene monomer introduced to the reaction system. It was confirmed by the disappearance of the wing peaks with the hfs constant of 45.4 mT[12] that all of the PTFE mechano radicals had completely initiated the block copolymerization with ethylene monomer and resulted in tethered PE chains.

The tethered PE chains are regarded as "isolated single PE chains" on the PTFE surface in vacuum because of the following reasons: The concentration of PTFE mechano radicals located on the PTFE surface was estimated at 6.8×10^{16} radicals/g;[4] i.e., the concentration of the tethered points of PE chains per gram of PTFE was 6.8×10^{16} points/g. The average degree of polymerization (D_p) of the tethered PE can be estimated at $D_p \leq 74$ from the concentration of the tethered points and amounts of ethylene monomer (1.43 $\times 10^{-5}$ mol) and PTFE powder (1.70 g). The spread of the tethered PE chain can be estimated by a root-mean-square radius of gyration (R_g),[10] which is calculated $R_g = (\langle R^2 \rangle/6)^{1/2}$ $\langle R^2 \rangle$ is a mean-square of the end-to-end distance of the polymer chain and is calculated by $\langle R^2 \rangle = nb^2$, where n is the number of bonds and b is the bond length. The spread of the tethered single PE chain was estimated at $R_g = 7.5$ Å by using the values $n = (2D_p - 1) = 147$ and $b = 1.524$ Å,[11] the bond length of PE, in which the Gaussian chain is assumed for simplicity. The

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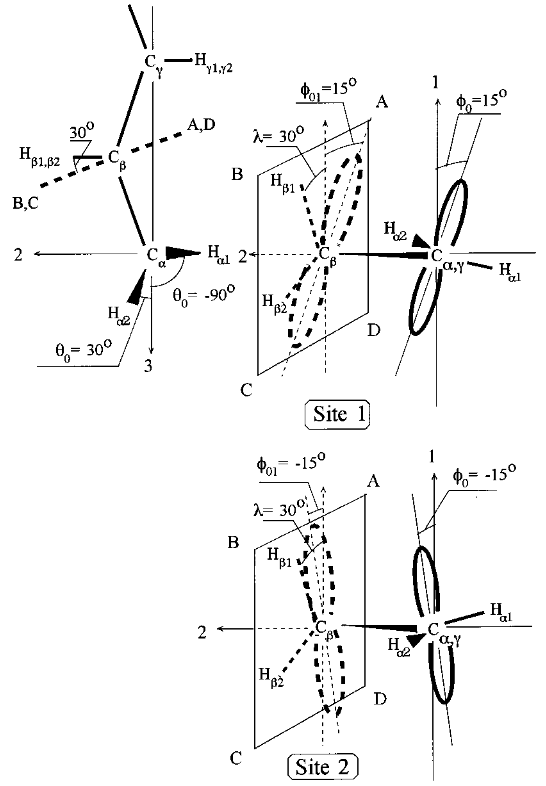

Figure 1. Two sites and the coordinate system at the ends of the isolated single PE chains.

surface area of the fractured PTFE was estimated at 2.1 m^2/g.[4] The surface area per tethered point (S_t) was deduced as $S_t = 3.1 \times 10^3$ Å^2/tethered point[4] by the concentration of tethered points and the surface area of PTFE.

We introduce an R_L value to evaluate a condition in which a tethered PE chain contacts and/or entangles with the neighboring chains or the PE chain is isolated from those. The R_L is defined as a ratio of twice the R_g value to the root-mean-square value of S_t, $R_L = 2R_g/S_t^{1/2}$. If $R_L < 1.0$, a tethered PE chain cannot contact and entangle with neighboring PE chains. In our experiment, R_L was estimated to be 0.27. Thus, contacts and entanglements with neighboring PE chains cannot take place. In addition, each chain does not aggregate because the chain is tethered to the PTFE surface by a covalent bond. Furthermore, PE is immiscible with PTFE. Thus, the PE chains tethered on the PTFE surface in vacuum can be regarded as isolated single PE chains tethered on the PTFE surface.

Site Exchange Motion. The five-line ESR spectrum of the isolated single PE chains was observed at 2.6 K (curve A, the solid bold line in Figure 2a,b). The simulated spectrum (curve B, the thin line in Figure 2) was obtained by assuming a frozen molecular motion. This simulated spectrum is a very poor fit to the observed spectrum.

Adrian et al. reported[13] that H$_\alpha$ of the *n*-propyl radical in an argon matrix occurred at the exchange motion between two H$_\alpha$s at 4 K. Moreover, Kasai reported[14] the similar exchange motion of H$_\alpha$ of the trimethylene oxide anion in an argon matrix at 4 K, in which the ESR spectrum revealed six lines.

According to the assumption of the rapid exchange motion of H$_\alpha$, the simulated spectrum (curve C, the broken line in Figure 2a) was obtained. However, this simulated spectrum shows six lines and is a very poor fit to the observed spectrum.

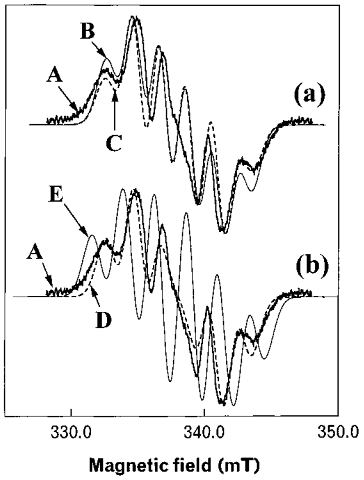

Figure 2. (a) Curve A with the solid line, observed spectrum at 2.6 K. Curve B with the thin solid line, simulated spectrum based on the frozen molecular motion. Curve C with the broken line, simulated as in curve B except for the rapid exchange motion between two H$_\alpha$s. (b) Curve D with the broken line, simulated by assuming both the rapid exchange of H$_\alpha$s and the site exchange motion at a rate of 67 MHz. For clarity, curve A is shown in (b) and is the same as in (a). Curve E with the thin solid line, simulated spectrum as in curve C using the typical values of hfs constants given in ref 15.

The best fit simulated spectrum (curve D, the broken line in Figure 2b) was obtained by assuming both the rapid exchange motion of H$_\alpha$ and the exchange motion between two sites at the end of the isolated single PE chain at a rate of 67 MHz. The site exchange motion can be induced by the 30° jump around the C$_\alpha$−C$_\beta$ bond axis. The hfs parameters are $A_x = 1.95$ mT, $A_y = 3.13$ mT, $A_z = 0.98$ mT, $\theta_0 = -90°$ for H$_{\alpha1}$ and 30° for H$_{\alpha2}$, $\lambda = 30°$, $\phi_0 = \phi_{01} = 15°$ for site 1 and $\phi_0 = \phi_{01} = -15°$ for site 2, and $\rho_C B = 4.07$ mT.[15] In the trans zigzag chain of PE, the projection angle of ϕ_{01} is identical with the tilt angle of ϕ_0. The simulated spectrum is in good agreement with the observed spectrum. The result demonstrates that the rapid exchange motion of H$_\alpha$ and the site exchange motion occur even at 2.6 K.

We conclude that the high mobility of the ends of isolated single PE chains tethered on the PTFE surface in vacuum is attributed to a free chain from the neighboring PE chains.

In previous reports,[4,5] the six-line ESR spectrum from the ends of PE chains tethered on the PTFE surface indicated that the site exchange motion was frozen at 2.8 K. The similar five-line ESR spectrum was observed at 30 K with the site exchange rate of 56 MHz. The D_p of these tethered PE chains was probably higher than that of the isolated single chains in this paper because the monomer concentration was about 40 times higher than that in the case of the isolated single chains. Thus, entanglements with the neighboring chains probably restricted the site exchange motion.

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(15) Initially, we made various trials using typical values of hfs constants of H_α ($A_x = 2.2$ mT, $A_y = 3.5$ mT, $A_z = 1.2$ mT) and $\rho_c B = 5.00$ mT[14] in primary alkyl radicals to simulate the ESR spectra at 2.6 K. However, we failed to get any appropriate simulation spectrum. For example, the simulated spectrum with typical values with the rapid exchange motion of H_αs gave a very poor fit spectrum (curve E in Figure 2). In contrast, the best-fit simulated spectrum was obtained by the hfs constants ($A_x = 1.95$ mT, $A_y = 3.13$ mT, $A_z = 0.98$ mT) and $\rho_c B = 4.07$ mT. However, these values are too small compared to the typical hfs constants and $\rho_c B = 5.0-5.38$ mT.[13,14,16] Generally, these values are dependent on ρ_c, which is affected by the substituent on the radical and a matrix surrounding the radical. In our case, the radicals at the ends of PE chains are tethered to the PTFE surface, which is composed of fluorine atoms with a large electron affinity (3.401190 eV).[17] Thus, those small values seem to be due to low ρ_c, which may cause leaking to the fluorine atoms comprising the PTFE surface.

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