High-resolution solid-state ^{13}C nuclear magnetic resonance study of the combined process of ^{1}H spin diffusion and ^{1}H spin–lattice relaxation in semicrystalline polymers

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The combined process of spin diffusion and ^{1}H spin–lattice relaxation is measured for uniaxially oriented polyethylene films by high-resolution solid-state ^{13}C nuclear magnetic resonance spectroscopy with the ^{1}H–^{13}C cross-polarization method. The experimental data are compared with a numerical simulation of the diffusion equation containing the relaxation term in order to estimate ^{1}H spin-diffusion coefficients and ^{1}H spin–lattice relaxation times for crystalline, interfacial and amorphous regions. For these regions, the ^{1}H diffusion coefficients and the relaxation times are estimated as 6×10^{-12}, 6×10^{-12} and 2.5×10^{-12} cm^{2} s^{-1} and 4.0, 0.4 and 0.13 s, respectively.

(Keywords: phase structure; polyethylene; oriented films; high-resolution solid-state ^{13}C nuclear magnetic resonance; ^{1}H spin diffusion; diffusion equation)

INTRODUCTION

^{1}H spin-diffusion measurements, which were originated by Goldman and Shen[1], have been performed to analyse the microdomain structure of heterogeneous polymeric solids[2–6], because the spin-diffusion process is sensitive to the geometry of the microdomain structure. For quantitative analysis of the structure, however, it is necessary to know ^{1}H spin-diffusion coefficients D for the respective domains in a sample. Moreover, ^{1}H spin–lattice relaxation times T_{1H} should also be estimated for the individual domains since longitudinal relaxation proceeds at a rate comparable with the diffusion process: for a typical crystalline polymer, polyethylene, the diffusion time τ $(= L^2/D)$, where L is the lamellar size, is estimated to be of the order of a second, which is comparable to the spin–lattice relaxation time.

The combined process of relaxation and diffusion has frequently been analysed for decay curves of ^{1}H magnetization[2,3,5,6]. Each decay curve is decomposed into several exponential processes and their time constants are analysed to obtain geometric information on the microdomain structure. However, simple interpretation of the time constants in terms of the space parameters of the microdomain structure appears to be difficult because the decay curve is not always resolved into contributions from the respective domains[7,8]. On the other hand, separate measurements of T_{1H} or D will be possible only for systems in which the timescales of the diffusion and relaxation processes are far apart from each other[9,10].

In some polymers where different domains give different ^{13}C n.m.r. chemical shifts, the decay of ^{1}H magnetization of each domain can be measured individually as a change of ^{13}C magnetization by the cross-polarization (CP) technique. For these polymers the decay behaviour in each domain can be interpreted in terms of its T_{1H} and D as well as spatial parameters. In this paper, we develop the estimation method for the ^{1}H spin-diffusion coefficients and ^{1}H spin–lattice relaxation times for the respective domains of uniaxially oriented polyethylene films whose phase structure is well characterized as being composed of crystalline, interfacial and amorphous regions[11]. The ^{1}H spin-diffusion process coupled with ^{1}H spin relaxation is measured by combining the Goldman–Shen type pulse sequence with the CP technique and compared with a simulation considering the microdomain structure of the polyethylene sample.

METHOD

The combined process of longitudinal relaxation and diffusion of ^{1}H spins is described phenomenologically by the following diffusion equation:

$$\frac{\partial m_H}{\partial t} = D\frac{\partial^2 m_H}{\partial x^2} + \frac{m_H(\infty) - m_H}{T_{1H}} \qquad (1)$$

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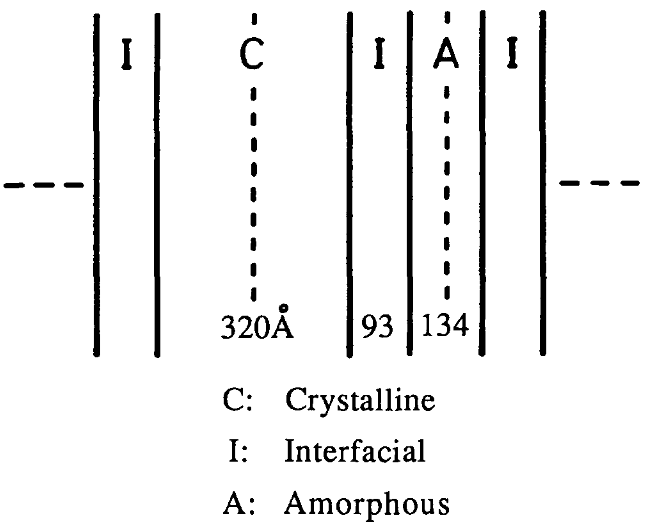

Figure 1 One-dimensional three-region model for the lamellar structure used in the simulation. The simulation is performed in the region between the two dotted lines. As for the thickness of each region, see 'Experimental' section

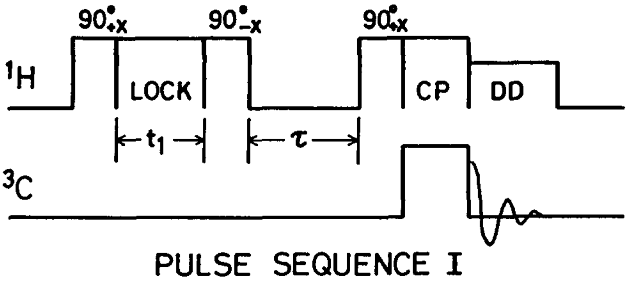

Figure 2 Pulse sequence used in this study

where m_H is the concentration of ^1H magnetization in position x at time t, which corresponds to a polarization per spin. The spin–lattice relaxation time T_{1H} and the diffusion coefficient D take different values depending on the domain indicated by x. Here, we use a one-dimensional, three-region model as shown in *Figure 1*, because the sample has a lamellar structure composed of crystalline, crystalline–amorphous interfacial and amorphous regions[11]. Each region is specified by thickness L^i, rotating-frame spin–lattice relaxation time $T^i_{1\rho H}$ and laboratory-frame spin–lattice relaxation time T^i_{1H} ($i = $ C, I, A), where C, I and A indicate the crystalline, interfacial and amorphous regions, respectively. For the polyethylene sample, it may be assumed that $T^A_{1\rho H} < T^I_{1\rho H} < T^C_{1\rho H} \ll T^A_{1H} < T^I_{1H} < T^C_{1H}$ at room temperature.

As seen from equation (1), the change of m_H caused by the diffusion term is minimized if the term $\partial^2 m_H/\partial x^2$ approaches zero. This condition may be realized when m_H is the same in the whole range of x. Under this condition, it will be possible to estimate the relaxation times without considering the diffusion effect. The pulse sequence to realize such a condition approximately is shown in *Figure 2*. The sequence is composed of three periods: (1) In the *preparation period* the concentration gradient of ^1H magnetization is created using the difference in $T_{1\rho H}$ values of the respective regions. At the end of this period, the average concentration $\underline{m}^i_H$ of each region is in the order $\underline{m}^A_H < \underline{m}^I_H < \underline{m}^C_H$. (2) During the *evolution period* relaxation and diffusion proceed in the laboratory frame. The ^1H spin system reaches thermal equilibrium at sufficiently long diffusion time τ, where $m^A_H = m^I_H = m^C_H$. Considering the condition that $\underline{m}^A_H < \underline{m}^I_H < \underline{m}^C_H$ at the beginning of this period and $\underline{m}^A_H = \underline{m}^I_H = \underline{m}^C_H$ in the final state as well as $T^A_{1H} < T^I_{1H} < T^C_{1H}$, it may be possible to find a certain τ^* at which $\underline{m}^A_H = \underline{m}^I_H = \underline{m}^C_H$. (3) In the *detection period* the ^1H magnetization of each region is transferred to the corresponding ^{13}C spin system through the cross-polarization and ^{13}C n.m.r. spectra are obtained for different τ values.

Since the concentration profile in each of the regions is not flat in general even though flat at $\underline{m}^A_H = \underline{m}^I_H = \underline{m}^C_H$, the condition that $m^A_H(x) = m^I_H(x) = m^C_H(x)$ for all x does not hold exactly at τ^*. However, there should be a certain τ, in the vicinity of τ^*, where $\partial m_H/\partial x = 0$ at the boundary of the crystalline and interfacial regions (or of the amorphous and interfacial regions) because the order of the magnitudes for $\underline{m}^C_H$ and $\underline{m}^I_H$ (or for $\underline{m}^A_H$ and $\underline{m}^I_H$) is reversed after τ^*. Then, the effect of diffusion on the change of the average concentration should be minimized around τ^*. The analysis of the evolution curves around τ^*, therefore, gives estimations of the relaxation parameters T_{1H} of the individual regions.

The numerical analysis of equation (1) is performed using TWODEPEP, software available from IMSL Inc., which is designed to solve two-dimensional partial differential equations. The one-dimensional model shown in *Figure 1* is treated as a special case of two-dimensional problems. The boundary condition $\partial m_H/\partial x = 0$ is set at both boundaries shown by the broken lines in *Figure 1*. The initial values of m_H for the three regions are obtained by extrapolation of the experimental data to $\tau = 0$. The concentration profile of each region at $\tau = 0$ is not incorporated into the simulation: it is assumed that the initial concentration of each region is uniform throughout the region. T^i_{1H} and D^i ($i = $ C, I, A) are variable parameters that should be determined by fitting the simulation curve with the experimental data.

EXPERIMENTAL

Sample

Preparation and characterization of the uniaxially oriented polyethylene films were described elsewhere[11] in detail. The dipolar-decoupled cross-polarization (DD/CP) ^{13}C n.m.r. measurement revealed that the spectrum was resolved into three components assigned to the crystalline, interfacial and amorphous regions. Using the mass fractions of the respective regions and the value of the long period determined by small-angle X-ray scattering, the thicknesses of the crystalline, interfacial and amorphous regions were estimated to be 320, 93 and 134 Å, respectively (1 Å $= 10^{-10}$ m). The thickness of the interfacial region is very large compared to the thickness generally observed in isothermally crystallized samples[12]. A detailed discussion concerning this point was given in ref. 11.

^1H spin-diffusion measurements

DD/CP ^{13}C n.m.r. measurements were carried out at room temperature for the uniaxially oriented polyethylene films with the elongation axis set parallel to the static magnetic field on a JEOL JNM-FX200 n.m.r. spectrometer operating at 50 MHz for ^{13}C. The ^1H and ^{13}C radiofrequency field strengths $\gamma B_1/2\pi$ were 67.6 kHz for the cross-polarization, except for the dipolar-

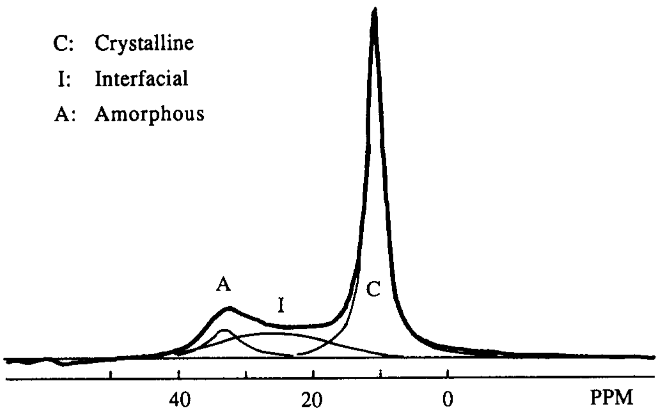

Figure 3 Lineshape analysis of ^{13}C n.m.r. spectrum at $\tau = 8$ s

decoupling processes where the ^1H field strength was reduced to 59.5 kHz. The pulse sequence used is shown in *Figure 2*, the repetition time being 8 s and the diffusion time τ ranging from 5 ms to 8 s. The interval t_1 was set at 10 ms in order to obtain the concentration gradient of ^1H magnetization among the three regions using the difference in their $T_{1\rho H}$ values.

RESULTS AND DISCUSSION

Figure 3 shows a DD/CP ^{13}C n.m.r. spectrum obtained by pulse sequence I with $\tau = 8$ s. On the basis of the lineshape analysis reported in a previous paper[11], this spectrum is resolved into three components corresponding to the crystalline, interfacial and amorphous regions. Though there is no theoretical justification for assuming a specific lineshape for each component of the spectrum, we assume Lorentzians for the crystalline and amorphous regions and a Gaussian for the interfacial region because the curve composed of these lineshapes gives good agreement with the observed spectrum. A Lorentzian function was suitably applied to the lineshape for the crystalline component of the DD ^{13}C n.m.r. spectrum measured for the same sample[11].

The resonance lines for the crystalline and amorphous components can be described by Lorentzians centred at 11.0 ppm with linewidth of 150 Hz and at 33.6 ppm with linewidth of 325 Hz, respectively. The lineshape for the interfacial component is approximately assumed as a Gaussian with linewidth of 850 Hz centred at 26.5 ppm, although the subtracted spectrum obtained by the subtraction of the crystalline and amorphous components from the total spectrum is somewhat asymmetric with up-field tailing[11]. This approximation may cause overestimation of the crystalline component and underestimation of the amorphous component, whereas almost no effect appears for the interfacial component owing to the cancellation of the low-field overestimation and the up-field underestimation. However, as will be shown later, such an approximation for the interfacial component does not significantly affect the analysis of T_{1H} and D values. Similar analyses were performed for the spectra obtained for different τ values.

In *Figure 4* is shown the time evolution of ^{13}C magnetization M_C obtained for each region by the lineshape analysis. The ^{13}C magnetization $M_C^i(\tau)$ in region i may be proportional to the ^1H magnetization $M_H^i(\tau)$ existing in region i at the end of the evolution period for every τ. Since $M_H^i(\tau)$ is the product of the average concentration $\underline{m}_H^i(\tau)$ and the volume V^i of region i, $M_C^i(t)$ is given by:

$$M_C^i(\tau) = K^i V^i m_H^i(\tau) \qquad (2)$$

where K^i is a constant, which is associated with the efficiency of the cross-polarization in region i. $m_H^i(\tau)$ may be evaluated directly if K^iV^i is known from a separate experiment. In this work, however, an alternative evaluation has been made. Since $\underline{m}_H^A = \underline{m}_H^I = \underline{m}_H^C$ for a sufficiently long τ, the following relations hold:

$$\frac{M_C^A(\infty)}{K^A V^A} = \frac{M_C^I(\infty)}{K^I V^I} = \frac{M_C^C(\infty)}{K^C V^C} \qquad (3)$$

where $M_C^i(\infty)$ is the ^{13}C magnetization of region i in the equilibrium state. If we assume $m_H^i(\infty) = M_C^i(\infty)/K^iV^i = 1$ in the equilibrium state for simplicity, $\underline{m}_H^i(\tau)$ can be obtained by dividing $M_C^i(\tau)$ by $M_C^i(\infty)$. The concentration evolution of ^1H magnetization thus obtained is shown in *Figure 5* where $\underline{m}_H^i(\tau)$ is plotted against $\tau^{1/2}$. It may be expected that errors produced by the Gaussian approximation for the interfacial compo-

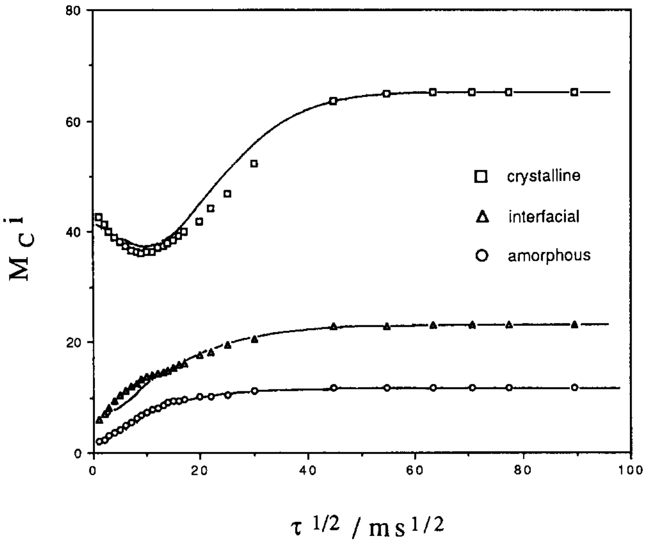

Figure 4 Time evolution of ^{13}C magnetization for each region plotted against $\tau^{1/2}$. Full curves represent the results of the simulation

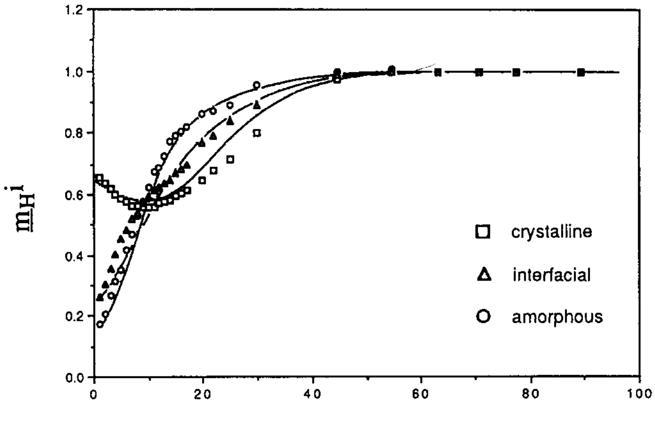

Figure 5 Time evolution of the concentration $\underline{m}_H^i$ of ^1H magnetization for region i plotted against $\tau^{1/2}$. Full curves represent the results of the simulation

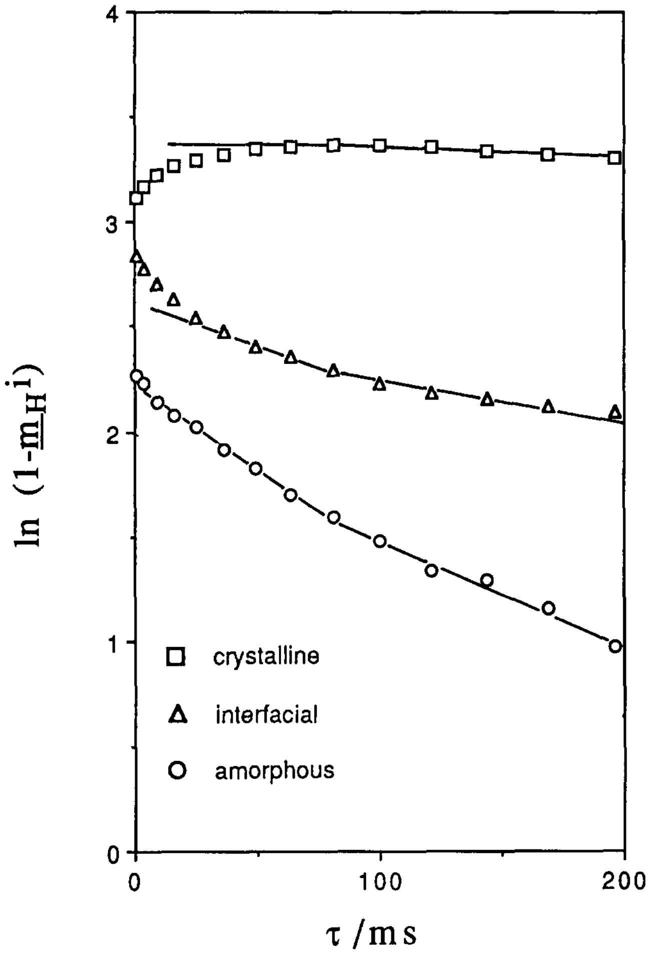

Figure 6 Semilogarithmic plot of $1 - \underline{m}_H^i$ against τ for shorter τ values. The ordinate value for each region i is shifted by a factor of $\ln M_C^i(\infty)$ for clarity of the figure

nent are reduced in the procedure described above because cancellation of the overestimation or underestimation occurs when $M_C^i(\tau)$ is divided by $M_C^i(\infty)$.

As seen from the initial value for the crystalline region in *Figure 5*, the decay for this region during the preparation period is about 35%. This value is extraordinarily large compared to the value due to the $T_{1\rho H}$ relaxation, which is estimated to be 8% using $T_{1\rho H} = 123$ ms measured for this sample. One of the reasons for this discrepancy seems to be attributed to spin diffusion during the preparation period. Suppose that, in the early stage of the spin-lock process, the magnetization in the interfacial and amorphous regions decays to zero while that in the crystalline region remains almost constant due to the long $T_{1\rho H}$ for this region. Then, the magnetization front, which is located at the boundary of the crystalline and interfacial regions, proceeds, during the preparation period, a distance d, which is estimated as $d = (Dt_1)^{1/2}$ where D is the diffusion coefficient and t_1 is the duration of the preparation period. The decrease in magnetization initially contained in the crystalline region is estimated by a factor of $L^C/(L^C + 2d)$, where L^C is the thickness of the crystalline region. The factor is 88% if we put $D = 6 \times 10^{-12}$ cm^2 s^{-1}, $t_1 = 10$ ms and $L^C = 320$ Å. Accordingly, the total decay in the preparation is estimated as 19%, accounting partially for the experimental value of 35%. Other causes for the discrepancy are probably attributed to the imperfectness of the ^{1}H $\pi/2$ pulse, and to the ^{1}H spin–spin relaxation during the period for the 0–$\pi/2$ phaseshift of the ^{1}H radiofrequency to spin-lock the ^{1}H magnetization along the y axis in the rotation frame in the preparation period.

We find in *Figure 5* that the evolution curve for the interfacial component is evidently located between the curves for the crystalline and amorphous components in the entire range of diffusion time. This indicates that the ^{1}H magnetization diffuses through the interfacial region from the amorphous region to the crystalline region for $\tau^{1/2} > 9$ ms$^{1/2}$, and from the crystalline region to the amorphous region for $\tau^{1/2} < 9$ ms$^{1/2}$. The assignment of the interfacial component is therefore confirmed by this observation.

In *Figure 6*, $\ln(1 - \underline{m}_H^i(\tau))$ is plotted against τ around $\tau = 80$ ms ($= \tau^*$) where the crossover of the three curves takes place. Since the diffusion effect is minimized at about τ^*, as mentioned before, we can estimate T_{1H}^i from the slope of the plot. The plot for each of three components, however, seems to be composed of two straight lines crossing around τ^*. The intrinsic T_{1H}^i for each region is, therefore, expected to be an intermediate value between T_{1H}^i values obtained from the slopes of these two straight lines, namely, $2000\text{ ms} < T_{1H}^C < \infty$, $250\text{ ms} < T_{1H}^I < 490\text{ ms}$, and $125\text{ ms} < T_{1H}^A < 200\text{ ms}$. The curvatures of the plots at τ^* indicate that the period in which the effect of diffusion is minimized is limited to a short range around τ^*.

For the estimation of the spin-diffusion coefficients D^i, we fit the numerical solution of equation (1) to the experimental data by varying six parameters, T_{1H}^i and D^i with $i =$ C, I, A, thereby referring to T_{1H}^i values estimated from *Figure 6*. As an initial guess of D^i, we take the value 6.2×10^{-12} cm^2 s^{-1} (ref. 13). In *Figures 4* and *5*, the results of the numerical analysis are shown as full curves, where we put $T_{1H}^C = 4000$ ms, $T_{1H}^I = 400$ ms, $T_{1H}^A = 130$ ms, $D^C = D^I = 6 \times 10^{-12}$ cm^2 s^{-1} and $D^A = 2.5 \times 10^{-12}$ cm^2 s^{-1}.

In the numerical analysis, we have assumed that the concentration of each region is uniform in the initial stage of the evolution period. However, as discussed previously, the concentration profile in the real system should not be uniform because of spin diffusion during the preparation period. The assumption that we have employed probably affects the shape of the simulated curves especially for short diffusion times, which leads to the estimation of somewhat different D^i values. The estimation of D^i based on the curve fitting will be affected accordingly. Though the effect of this assumption on the values of D^i is difficult to estimate at present, D^i obtained here is expected to be not far from the real values because the fitting is performed over the entire range of the diffusion time; the effect of the uniform assumption seems less effective at long diffusion times.

The D^C and D^I values obtained here are close to 8.3×10^{-12} cm^2 s^{-1} estimated by Cheung *et al.*[14] for the crystalline region of the polyethylene sample using the relationship:

$$D \simeq a^2/T_2 \qquad (4)$$

Here a is the distance between adjacent protons and T_2 is the ^{1}H spin–spin relaxation time. Since T_2 is in general increased with increasing mobility, the result obtained here that D^A is smaller than D^C and D^I is reasonable. One of the authors and his collaborators[12] reported that apparent ^{1}H spin–lattice relaxation times T_{1H}, which were measured by a combined pulse sequence of the ^1H inversion recovery method and ^{13}C–^1H CP technique, are of the same magnitude for the crystalline and interfacial regions, while the T_{1H} value is significantly decreased for the amorphous region. They concluded that there is a significant ^1H spin diffusion between the crystalline and interfacial regions. Our spin-diffusion analysis supports their conclusion because D^C and D^I are larger than D^A.

Finally it should be noted that the equi-concentration state created by the pulse sequence used in this study can also be realized in the initial state of a saturation recovery or inversion recovery experiment. The initial slopes in these experiments will give estimates of the intrinsic T_{1H} values for the regions. Though the concentration $m^i_H(x)$ of each of three regions become equal at a sufficiently long diffusion time, that is, near the equilibrium state, the estimation of T_{1H} using decay behaviour at this diffusion time may be difficult because the difference between $m^i_H(\tau)$ and $m^i_H(\infty)$ is so small to avoid large experimental errors.

CONCLUSIONS

We have developed an analytical method for the evaluation of the ^1H spin-diffusion coefficients and the spin–lattice relaxation times of the individual regions in semicrystalline polymers having a lamellar structure. The characteristic features of the method are summarized as follows:

(1) ^{13}C monitoring of the combined process of ^1H spin diffusion and relaxation by CP technique, which enables us to measure the ^1H decay behaviour for the individual regions separately.

(2) Realization of the equi-concentration state of ^1H magnetization for each region to evaluate the intrinsic relaxation times by suppressing the spin-diffusion effect.

(3) Fitting of the experimental data with a numerical simulation of the diffusion equation including the relaxation term to estimate the diffusion coefficients as well as relaxation times.

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