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Analysis

Dipolar-Decoupled Carbon-13 NMR Study of Highly Oriented Polyethylene Films

Fumitaka Horii[1], Ryozo Kitamaru[1], Shiro Maeda[2], A. Saika[2], and Takehiko Terao[2]

[1] Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

[2] Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan

SUMMARY

High-resolution solid-state ^{13}C NMR spectra and ^{13}C relaxation times T_1 and $T_{1\rho}$ have been measured at 40-100°C for uniaxially oriented polyethylene films with the drawing direction parallel to the magnetic field; this sample has a unique morphological structure that the noncrystalline chains are nearly disordered irrespective of the high degree of drawing. A sharp resonance line(line A) appears at the position corresponding to the principal value σ_{33} of the chemical shift tensor for the CH_2 carbons with the *trans-trans* conformation. Another sharp line(line B) is observed at almost the same chemical shift as for the CH_2 carbons of polyethylene in solution. Although these observations are similar to those for a cold-drawn polyethylene sample reported previously, line B is much enhanced in intensity and the linewidth is narrower in the present sample, reflecting the disorientation of the noncrystalline component. It is found from T_1 measurements that line A contains two components with different molecular mobility, both being assigned to the crystalline components. On the other hand, the line B is composed of a single component assignable to the noncrystalline component with liquid-like molecular mobility.

INTRODUCTION

It is well known that high-resolution solid-state ^{13}C NMR spectra can be obtained for solid organic substances by employing combined techniques of proton dipolar decoupling(DD) and magic-angle sample spinning(MAS) usually together with a ^{13}C-^{1}H cross-polarization(CP) technique. In this case a sharp resonance line appears at the position corresponding to the mean of the principal values σ_{11}, σ_{22}, and σ_{33} of the chemical shift tensor. However, in a uniaxially oriented polyethylene or poly(ethylene terephthalate) sample a sharp line can be observed at the most-shielded component σ_{33} by setting the drawing direction parallel to the magnetic field B_0 without MAS(1-3), since the principal axis of σ_{33} for the samples coincides with the drawing direction. This technique for oriented samples is very useful in analyzing local chain alignments against B_0 and particular modes of motion such as a 180°-jump rotation about the molecular chain axis.

In this paper we report such ^{13}C NMR spectra for highly oriented polyethylene films with a very unique phase structure; the crystalline component is highly oriented, whereas the noncrystalline component is almost disordered(4). We have also measured ^{13}C spin-lattice relaxation times T_1 and $T_{1\rho}$ in the laboratory and rotating frames, respectively. On the basis of these results, we discuss the different components with different chemical shifts and relaxation times in connection with the phase structure of the sample.

EXPERIMENTAL

Sample. Uniaxially stretched linear polyethylene films were prepared as follows(4). The films of a molecular weight fraction($\bar{M}_v$ =3.8 x 10^5) were irradiated to 8.5 Mrad with γ ray from a ^{60}Co source at room temperature in vacuum. After the removal of the sol by extraction, the films were uniaxially stretched to 600% at 160 °C and crystallized from the stretched and molten state by cooling, holding the length of the fimls unchanged. Through this process a unique morphorogical structure was produced; large crystallites with molecular chains oriented highly parallel to the drawing direction coexist with a large amount of rather disoriented noncrystalline component. Such a unique disordered noncrystalline component was produced, unlike in the case of usual drawing, as a result of the relaxation of the drawing force accompanying with the crystallization because the crystalline *trans-trans* methylene sequences were longer than stretched methylene sequences. The degree of crystallinity obtained from density measurements was 0.64.

Dipolar-Decoupled ^{13}C NMR. Measurements were performed on the stretched films with its drawing direction set parallel to B_0 by a home-built spectrometer operating at 1.4 T. Radio-frequency field amplitudes $\gamma B_1/2\pi$ were 63.8 kHz for both CP and DD processes. The CP contact time was 2.5 ms and the waiting period after the acquisition of a FID was 2.0 s. The chemical shifts of the spectra were determined by using liquid benzene as a reference and then converted to the values relative to tetramethylsilane(TMS)(6).

RESULTS AND DISCUSSION

Figure 1 shows 15 MHz CP/DD ^{13}C NMR spectra obtained at 70°C and 100°C for the highly oriented polyethylene sample where the drawing direction is parallel to B_0. At both temperatures well-resolved resonance lines can be observed at 11.5-11.7 ppm and 32.0-32.4 ppm relative to TMS. Similar resonance lines have been already reported for a cold-drawn polyethylene sample(2). However, in our sample the downfield line appears more clearly, reflecting the disorientation of the noncrystalline component as described below.

The chemical shift of the upfield line(hereafter referred to as line A) is in good accord with the value(12.9±1.3 ppm)(2) of the principal component σ_{33} of the chemical shift tensor(2, 7-9) for polyethylene and *n*-paraffins with orthorhombic crystal form. Since σ_{33} is the principal value along the chain axis, line A can be assigned to the CH_2 carbons with the *trans-trans* conformation whose molecular axis is parallel to B_0. On the other hand, the chemical shift of the downfield line(hereafter referred to as line B) well coincides with the value(31.0 or 29.67 ppm) of the central CH_2 carbons of *n*-$C_{17}H_{36}$ in liquid(2) or of polyethylene in

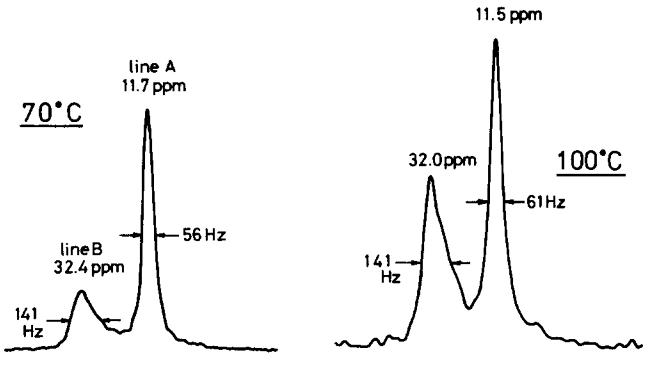

Figure 1 *15 MHz CP/DD ^{13}C NMR spectra of highly oriented polyethylene films at 70°C and 100°C. The drawing direction is parallel to B_0.*

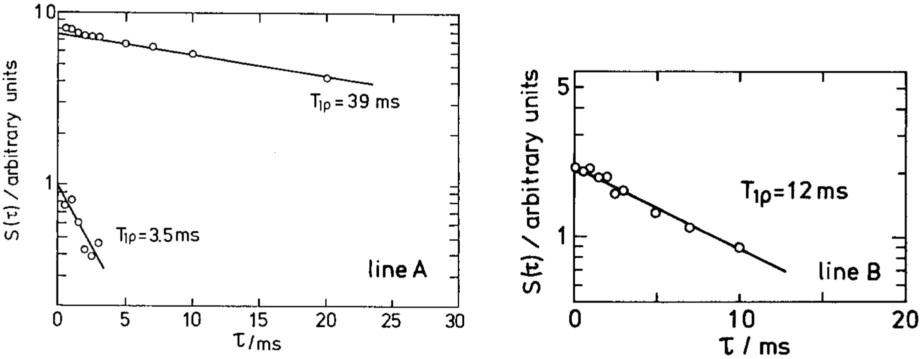

Figure 2 *^{13}C longitudinal relaxation decays in the rotating frame at 40°C.*

solution(10). This fact indicates that line B is assignable to the noncrystalline component whose chemical shift anisotropy is averaged out by rapid molecular reorientation.

We have measured ^{13}C spin-lattice relaxation times T_1(5) and $T_{1\rho}$ by use of the CP technique in order to inquire whether each line is composed of a single component. Figure 2 shows the longitudinal decay in the rotating frame for lines A and B at 40 °C. The magnetization of line B clearly exhibits a single-exponential decay with $T_{1\rho}$ = 12 ms. On the other hand, the decay of the magnetization of line A is described by two exponentials with the $T_{1\rho}$ values of 3.5 ms and 39 ms. Similar components were also observed at 70 °C for T_1 measurements of lines A and B as shown in Table 1. Therefore, it is concluded that line A is composed of two components with different molecular mobility, the mobile component keeping the *trans-trans* conformation and the rigid crystalline component, whereas line B complises a single component with liquid-like mobility.

VanderHart(2) also reported for a cold-drawn sample that a short T_1 component coexists with a long T_1 component in the resonance line at σ_{33} and classified the former component as noncrystalline. This classification

Table 1 Carbon-13 Chemical Shifts, T_1, and $T_{1\rho}$ of Highly Oriented Polyethylene Films

	chemical shift, ppm¹⁾	$T_{1\rho}$ at 40°C, ms	T_1 at 70°C, s
line A	11.5-11.7	3.5 39	1.6 80
line B	32.0-32.4	12	0.30

1) Chemical shifts relative to TMS.

may be valid in that case, because the noncrystalline chains in such a cold-drawn sample are considered to be highly stretched. On the contrary, in our sample most of the noncrystalline component is disoriented and undergoes liquid-like molecular motion as mentioned above. Hence, the short T_1 component seems not to be assignable to the noncrystalline component on the contrary to the case of the cold-drawn sample. In order to establish the assignment of this component, we tried to determine the mass fractions of the respective components and to compare them with the degree of crystallinity obtained from other methods. However, the CP technique is not applicable for this purpose because this technique does not reproduce the resonance intensities proportional to the number of concerned carbons for polyethylene sample unlike the case of cellulosic substances(22). Therefore, we have measured ^{13}C T_1 relaxation behavior at 40 °C using the saturation recovery method which allows us to determine each mass fraction from the equilibrium magnetization.

In Figure 3 logarithmic integrated intensities $S(\tau)$ are plotted against time τ for lines A and B. These decay curves were analyzed by assuming two components for line A and one component for line B, respectively:

$$S_A(\tau)=S_1(\infty)[1-\exp(-\tau/T_{11})]+S_2(\infty)[1-\exp(-\tau/T_{12})], \quad (1)$$

$$S_B(\tau)=S_B(\infty)[1-\exp(-\tau/T_1)], \quad (2)$$

where $S_1(\infty)$, $S_2(\infty)$, and $S_B(\infty)$ are the equilibrium magnetizations of the respective components. Since it is very time-consuming to measure $S_1(\infty)+S_2(\infty)(=S_A(\infty))$ for this sample, the least-squares method was employed to determine the parameters in eqs.(1) and (2) using the simplex algorithm(11). As shown in Figure 3, the calculated curves given by eqs.(1) and (2) well coincide with the observed values for both lines A and B. The T_1 values thus obtained are 2.3 s and 272 s for line A and 208 ms for line B, and the fractions of these components are 0.16, 0.46, and 0.38, respectively. Since the sum(0.62) of the two components in line A is in good accord with the degree of crystallinity(0.64) obtained from density measurements, it is concluded that both components in line A are the crystalline components. Thus, the short T_1 component can be assigned to the mobile crystalline component with the *trans-trans* conformation.

A similar mobile component with the *trans-trans* conformation has been also observed for disoriented polyethylene samples using CP/MAS ^{13}C NMR

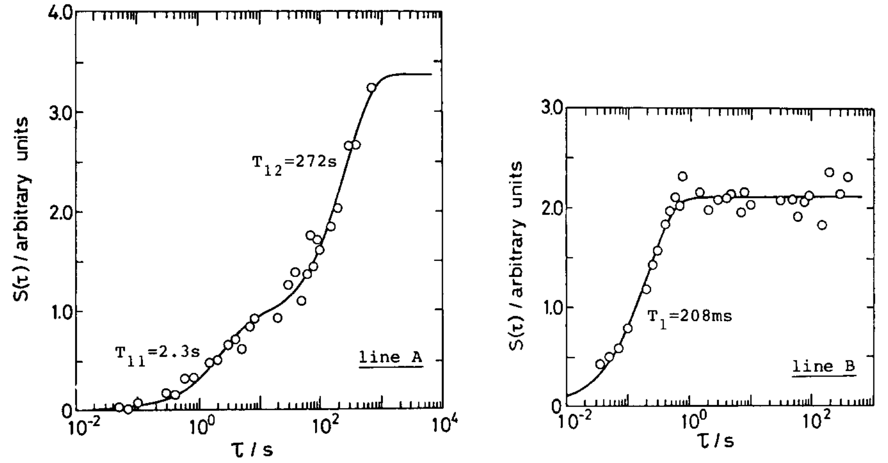

Figure 3 *^{13}C longitudinal relaxations in the laboratory frame measured by the saturation recovery method. The solid curves indicate the calculated results obtained by the least-squares method according to eqs. (1) and (2) in the text.*

spectroscopy by several authors (9, 12-16). In these cases this component appears at the position of the mean $\bar{\sigma}$ of the principal values together with the rigid crystalline component and has very short T_1's in an order of a few seconds in comparison with the T_1 values of 100-5000 s for the latter component. Although there was a controversy about the assignment of the component(14), we(15, 16) assigned it to the crystalline component by comparing the integrated fraction of the resonance intensity at $\bar{\sigma}$ with the degree of crystallinity obtained from density measurements. Thus, the conclusion obtained in this study for the oriented sample is consistent with the conclusion for the disoriented samples.

Although the assignment of the short T_1 component has been made, the motion leading to such a short T_1 value is not clear at present. One possible motion is a 180°-jump rotation or flip-flop screw jump(17-19) about the molecular chain axis which occurs in *n*-paraffins in a particular temperature region before melting. In fact, it has been confirmed that the 180°-jump rotation occurs in an ultraoriented polyethylene sample above room temperature(3). However, the order of the T_1 value associated with such a motion has not been determined. We are now trying to measure T_1 values of CH_2 carbons undergoing such a 180°-jump rotation using *n*-paraffins as model compounds.

Finally, we briefly note the contents of the noncrystalline component of the polyethylene samples. In our previous line-shape analysis of ^1H broad-line spectra(20, 21), we deconvoluted the contribution from the noncrystalline region into two components: the medium component with a hindered rotation and the narrow component with liquid-like mobility. The present ^{13}C T_1 results seemingly conflict with the ^1H broad-line results. However, this inconsistency may stem from the difference in time scale for the measurements; ^{13}C T_1 is associated with the motion with the correlation time in the order of 10^{-8} s, whereas ^1H linewidth(or spin-spin relaxation time T_2) depends on the motion with the correlation time shorter than 10^{-4}-10^{-5}s in the system. Thus, the noncrystalline region can be assumed to be homogeneous in relatively high frequency molecular motion but inhomogeneous in the slower motion probably due to the effect of the interface connecting the crystallites. An asymmetric line-shape appearing as upfield tailing in line B shown in Figure 1 may support this model, because the medium component with limited molecular mobility may contribute to such tailing. The detailed ^{13}C line-shape analysis will be published elsewhere together with the results in the case where the drawing direction is perpendicular to B_0.

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