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Solid-state ^{13}C NMR investigation of the structure and dynamics of highly drawn polyethylene—detection of the oriented non-crystalline component

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Abstract

The structure and dynamics of highly drawn polyethylene samples were studied by solid-state ^{13}C NMR spectroscopy. The analyses of the ^{13}C spin–lattice relaxation time (T_{1C}) and the ^{13}C spin–spin relaxation time (T_{2C}) have revealed that at least three components with different T_{1C} and T_{2C} values, which correspond to the crystalline, less mobile non-crystalline, and rubbery amorphous components, exist for these materials, as in the case of isothermally crystallized samples. However, another component with a mass fraction of 0.13–0.18 exists which has a ^{13}C chemical shift very close to that of the orthorhombic crystalline phase but has an extremely small T_{1C}. Since this component is believed to have the all-trans conformation, it is termed fast all-trans. The chemical shift anisotropy (CSA) spectra for various samples that have small T_{1C} values have been recorded and resolved into those of the non-crystalline and fast all-trans components. As expected, the CSA spectra of the less mobile non-crystalline and rubbery amorphous components that have the smallest T_{1C} values display only a slight asymmetry. In contrast, the CSA spectrum of the fast all-trans component displays higher asymmetry. However, the spectrum is still much narrower than that of the normal orthorhombic crystalline phase, indicating a high degree of motional averaging. It is proposed that this component should be a highly oriented non-crystalline component, which may exist as taut tie-molecules traversing the non-crystalline region. To account for the narrow CSA, this component must undergo rapid fluctuation with large amplitudes at the torsional potential minimum in each C–C bond and possibly an additional random jump or diffusional rotation around the chain axis. Additional measurements obtained by aligning the draw axis of the sample parallel or perpendicular to the static magnetic field indicate that the fast all-trans component is oriented along the drawing direction and subjected to rapid motion around the chain axis.

Keywords: Drawn polyethylene; Solid-state ^{13}C NMR; Oriented non-crystalline

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1. Introduction

The structure and morphology of polyethylene, both in the isotropic and oriented states, have received much attention. The main reason for this is its simple chemical structure that can generally serve as a model for polymers. Despite its simple structure, it is possible to produce various physical states and structures for polyethylene. Several techniques that are specific to different components or structures have been employed in order to obtain sufficient information to deduce the structure and morphology of this polymer. Some of these techniques are simple mechanical measurements, dynamic mechanical analyses, DSC, optical and electron microscopy, electron and X-ray diffractometry, and Raman, Infrared, and NMR spectroscopy. To date, although new findings are reported regularly, such as the existence of the intermediate phase and the existence of the multicomponent crystalline phase, several questions remain to be solved. Solid-state ^{13}C NMR is one of the best techniques to provide structural information on solid polymers. Using this technique, a wealth of information can be obtained. In the simplest case, an isotropic chemical shift of a chemically identical polymer depends on conformation, packing, and relatively slow molecular motion of the constituent chains. Further, sophisticated pulse sequences and higher dimensional spectroscopy can provide more detailed structural information.

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In this paper, we investigate the detailed structure of solid-state drawn high-density polyethylene by solid-state ^{13}C NMR spectroscopy. This technique was used to identify the existence of four phases—two crystalline and two non-crystalline—that exhibit distinct ^{13}C chemical shifts, namely, the monoclinic crystalline phase (MCP), the orthorhombic crystalline phase (OCP), and the less mobile non-crystalline and rubbery amorphous phases, respectively [1–3]. Since these components can be identified by solid-state ^{13}C NMR, they were considered. Although, the highly mobile non-crystalline component [4,5] was identified as a separate component, it is not considered in this study. In addition to the above four phases, components that were classified as intermediate components having in-between ^{13}C chemical shifts were also observed [6,7]. They were assumed to be associated with the MCP/OCP interface [6,7] or the crystalline/amorphous interphase [7]. Such intermediate components have been the subject of many investigations; largely by Raman spectroscopy [8–11] and recently by NMR spectroscopy [12–14]. This study focuses on the intermediate component and describes the detection of the oriented non-crystalline component that has the all-trans conformation.

2. Experimental section

2.1. Samples

The material used in this study was a high-density polyethylene, grade 6200B, manufactured by Bangkok Polyethylene Pcl, Thailand. This material has a melt flow index of 0.5 g/10 min and $\overline{M}_w = 2.5 \times 10^5$ and $\overline{M}_w/\overline{M}_n = 6.58$. The sheets were compression molded from pellets at 160 °C and solidified by quenching in water. Dumbbell specimens were cut from these sheets and drawn in a hot-air oven set at 75 °C at a speed of 100 mm/min. The draw ratios were calculated using the separation of the ink marks printed on the samples. The samples were drawn to draw ratios of 9×, 12×, and 16×, and they were designated as DPE9, DPE12 and DPE16, respectively. Each drawn sample was cut into small pieces using a sharp razor blade and packed into a magic angle-spinning (MAS) rotor.

2.2. Solid-state ^{13}C NMR spectroscopy

Solid-state ^{13}C NMR spectra were primarily obtained using a Chemagnetics CMX-400 spectrometer operating under a static magnetic field of 9.4 T. The MAS rotor comprised a 7.5-mm diameter zirconia rotor and the rate was set at 4 kHz. The ^{1}H and ^{13}C field strengths $\gamma B_1/2\pi$ were 62.5 kHz and the contact time for the cross polarization (CP) process was 1.0 ms. ^{13}C chemical shifts were expressed as values relative to tetramethylsilane (Me_4Si) by using the CH_3 line at 17.36 ppm of hexamethylbenzene crystals as an external reference. Spin–lattice relaxations of the orthorhombic crystalline and non-crystalline phases were measured by the CPT1 [15] and solid-state saturation recovery [3,16] pulse sequences, respectively. The spin–spin relaxation of the non-crystalline phase was obtained by the solid-state spin–echo pulse sequence [3,16]. ^{13}C chemical shift anisotropy (CSA) spectra of components having smaller ^{13}C spin–lattice relaxation time (T_{1C}) values were obtained without MAS for each sample packed in a MAS rotor using the solid-state saturation recovery pulse sequence [3,16] by setting a short T_{1C} delay time.

CP/dipolar decoupling (DD) ^{13}C NMR spectra were obtained for drawn samples at different temperatures on a Chemagnetics CMX-200 spectrometer operating under a static magnetic field of 4.7 T. A JEOL CP/DD probe with a goniometer was employed by setting the draw axis of each sample parallel or perpendicular to the magnetic field. Most of experimental conditions were approximately the same as those for the measurements by the CMX-400 spectrometer, unless described specifically.

2.3. X-ray measurements

The degrees of crystallinity of the drawn samples were estimated using the X-ray diffraction patterns. The samples were cut into small pieces and diffraction patterns were recorded using a Nonius DIP2000 image plate system. A monochromatized X-ray beam with a wavelength of 1.54 Å produced by a rotating anode operating at 40 kV and 70 mA was used. Its intensity was integrated in the direction of the incident beam. Three crystalline peaks and a broad non-crystalline peak, all with Gaussian lineshape, were fitted to the diffraction patterns at approximately $2\theta = 15$–$30°$. The degree of crystallinity was calculated from the peak area of the crystalline peaks [MCP (001), OCP (110), and OCP (200)] and the total area.

3. Results

3.1. CP/MAS ^{13}C NMR spectra

Fig. 1 displays CP/MAS ^{13}C NMR spectra of highly drawn HDPE samples. It can be observed that the most prominent feature of the spectra is the CH_2 resonance line of the OCP at 33.0 ppm. Small fractions of the MCP and non-crystalline resonances are present downfield and upfield, respectively, from the main resonance line. The fractions of components cannot be deduced from the CP/MAS spectra due to differences in their CP efficiencies. However, it can be simply observed that the amount of the non-crystalline component at the upfield shoulder tends to decrease with increasing draw ratio.

3.2. Spin relaxation behavior

3.2.1. ^{13}C Spin–lattice relaxation behavior

In the CP/MAS spectra shown above, it can be observed that sufficiently large quantities of the crystalline and non-crystalline phases are present for spin relaxation studies. ^{13}C spin–lattice relaxation behavior was investigated for the resonance line at 33.0 ppm by the CPT1 pulse sequence to examine whether this line contains some components with different T_{1C} values as already reported for other polyethylene samples

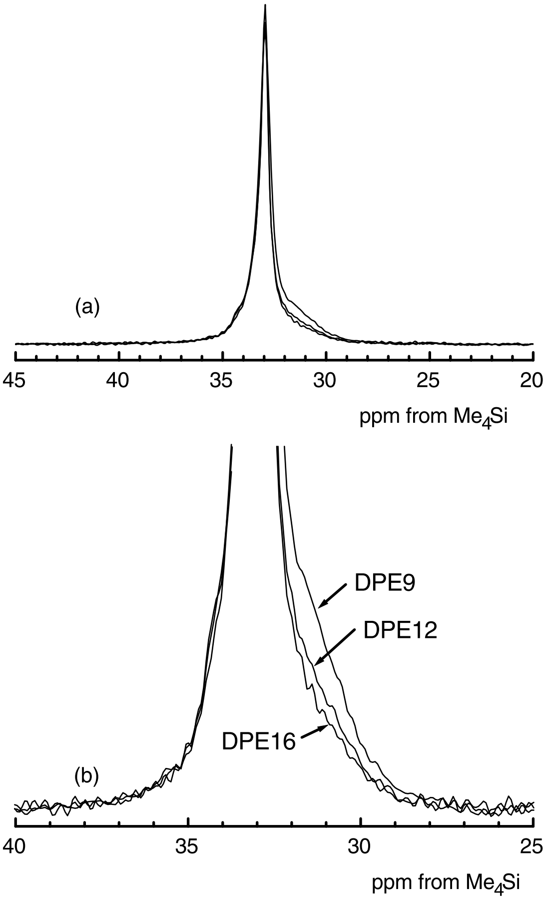

Fig. 1. (a) Comparison of CP/MAS ^{13}C NMR spectra of DPE9, DPE12, and DPE16; (b) enlarged spectra of (a).

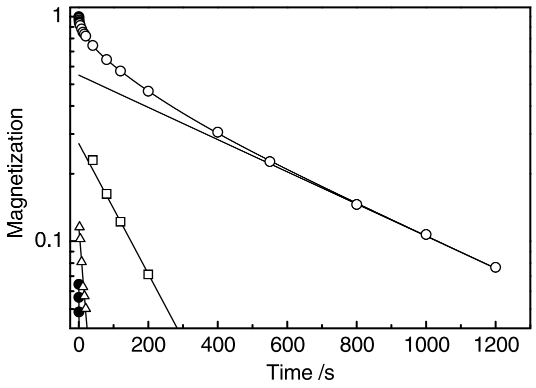

Fig. 2. ^{13}C spin–lattice relaxation behavior of the resonance line at 33.00 ppm for DPE16, which was obtained by the CPT1 pulse sequence. The peak intensities indicated by circles are plotted against the delay time for the relaxation.

Table 1
Apparent mass fractions (w) and spin–lattice relaxation times (T_{1C}) of components constituting the resonance line at 33.00 ppm

Parameters	DPE9	DPE12	DPE16
w_A	0.11 ± 0.01	0.06 ± 0.01	0.07 ± 0.01
T_{1C}^A (s)	1.39 ± 0.18	0.90 ± 0.18	1.10 ± 0.14
w_B	0.16 ± 0.02	0.10 ± 0.01	0.11 ± 0.02
T_{1C}^B (s)	18.9 ± 3.8	9.8 ± 3.0	22.7 ± 4.1
w_C	0.27 ± 0.03	0.29 ± 0.02	0.27 ± 0.02
T_{1C}^C (s)	126 ± 16	95 ± 12	150 ± 14
w_D	0.46 ± 0.04	0.55 ± 0.02	0.55 ± 0.03
T_{1C}^D (s)	519 ± 28	552 ± 20	606 ± 24

[3,16,18,19]. With regard to DPE16, the normalized peak height at 33.0 ppm is plotted against the T_{1C} delay time in Fig. 2. It is found that a single exponential decay cannot be fitted to the observed result, and, therefore, multiple exponential decay may be required [17]. As suggested by several previous studies [3,16,18,19], an attempt was first made to fit three lines of exponential decay to the results. An unsatisfactory fit was obtained since there is a low percentage of the intensity that remains unfitted in the short time region. A fit with four exponential decays was tried next, and the best fit was obtained as shown in Fig. 2. DPE9 and DPE12 were also found to exhibit similar behavior and required four exponential decays. The reliability of the four-component analysis is very high because the T_{1C} values obtained differ significantly from each other [17]. The results for all the samples are listed in Table 1. It can be seen that the ^{13}C spin–lattice relaxation behavior for the 33.0 ppm region requires four differential components with a wide range of T_{1C} values. The characterization of the smallest T_{1C} component will be made below and the other three components should be assigned to the orthorhombic crystalline components with different T_{1C} values detected by this T_{1C} analysis probably owing to the much less contributions of other co-existing components, as seen in Fig. 6 later, and the smaller T_{1C}s. It should be noted here that the fraction reported in the table was determined by the peak height in the CPT1 measurement. These values are not indicative of the real mass fractions of the respective components in the sample due to differences in the CP efficiency and line width.

The ^{13}C T_{1C} values for the resonance line at 33.0 ppm range from a few seconds to about 600 s. The largest T_{1C} value for each sample appears to increase with increasing draw ratio. On the basis of these T_{1C} analyses, lineshapes of three orthorhombic crystalline components, which can be described as Lorentzians with different chemical shifts and line widths, were determined by the subtraction method [20] for the partially relaxed spectra, which were obtained using different T_{1C} delay times and used for the multi-component lineshape analysis of fully relaxed spectra as described later.

The solid-state saturation recovery pulse sequence was employed for the non-crystalline phase appearing at 31.5 ppm due to its fast relaxation behavior. Each recovery process can be described by a single exponential as previously reported for isotropic polyethylene samples [3,16,18,19], and all the drawn samples were found to have a T_{1C} of 0.34 or 0.36 s, as shown in Table 3.

3.2.2. ^{13}C Spin–spin relaxation behavior

The ^{13}C spin–spin relaxation behavior was studied without ^{1}H decoupling during the relaxation only for the non-crystalline phase in each sample to examine the existence of the rubbery amorphous component in the drawn samples. The solid-state spin–echo pulse sequence [3,16] was used, and it

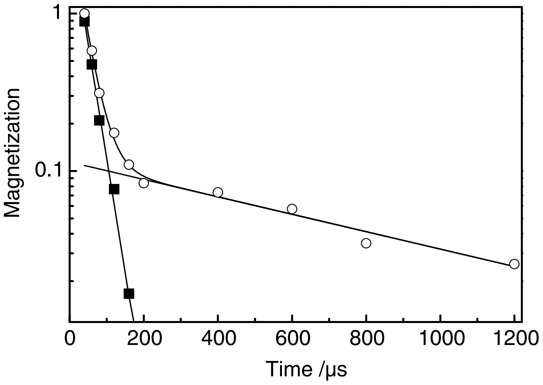

Fig. 3. ^{13}C Spin–spin relaxation behavior of the resonance line at 31.50 ppm for DPE16, which was obtained by the solid-state ^{13}C spin–echo pulse sequence. The peak intensities indicated by circles are plotted against the delay time for the relaxation.

was found that two components were required to describe the decay in magnetization of the non-crystalline phase. The spin–spin relaxation time, T_{2C}, of one component was about 30 µs, and that of the other was about 700 µs. According to previous studies for the isothermally crystallized isotropic samples [3,16,19], they correspond to the interfacial and rubbery amorphous components, respectively. However, the former component should be called the less mobile non-crystalline component compared to the rubbery amorphous component for the drawn polyethylene samples. An example of the results is shown in Fig. 3 for DPE16. Table 2 lists the results obtained for all the samples. It can be observed that the T_{2C} value of the less mobile non-crystalline component decreases slightly with increasing draw ratio while that of the rubbery amorphous component increases with increasing draw ratio. It should be noted here that some amount of the rubbery amorphous component is involved even in highly drawn polyethylene samples.

3.3. 90° Single pulse measurements

3.3.1. Partially relaxed spectra measured with a short recycle delay

In the spin–lattice relaxation behavior of the 33.0 ppm resonance line shown above, a component with very fast relaxation ($T_{1C} = \sim 1$ s) was observed. In order to confirm the existence of this component, a 90° single pulse measurement with a short recycle delay of 0.5 s was conducted. The spectrum displayed two peaks: one is close to the position of the OCP and the other corresponds to the non-crystalline component. The spectrum is dominated by the non-crystalline component. As the draw ratio is increased, the spectrum continues to exhibit two peaks; however, the amount of the non-crystalline component decreases. These results are shown in Fig. 4. For each spectrum, a Lorentzian curve at about 33.3 ppm can be fitted to all the samples. This Lorentzian lineshape at 33.3 ppm is used for the multi-component lineshape analysis of fully relaxed spectra, as described later. The lineshape of the non-crystalline component for each sample can then be obtained by the subtraction of the Lorentzian at 33.3 ppm from the total spectrum.

Table 2
Apparent mass fractions (w) and spin–spin relaxation times (T_{2C}) of the non-crystalline components appearing at 31.50 ppm

Parameters	DPE9	DPE12	DPE16
w_A	0.96 ± 0.02	0.96 ± 0.02	0.97 ± 0.02
T_{2C}^{A} (µs)	31.6 ± 1.6	30.1 ± 1.5	29.8 ± 1.5
w_B	0.04 ± 0.01	0.04 ± 0.01	0.03 ± 0.01
T_{2C}^{B} (µs)	684 ± 43	676 ± 40	786 ± 44

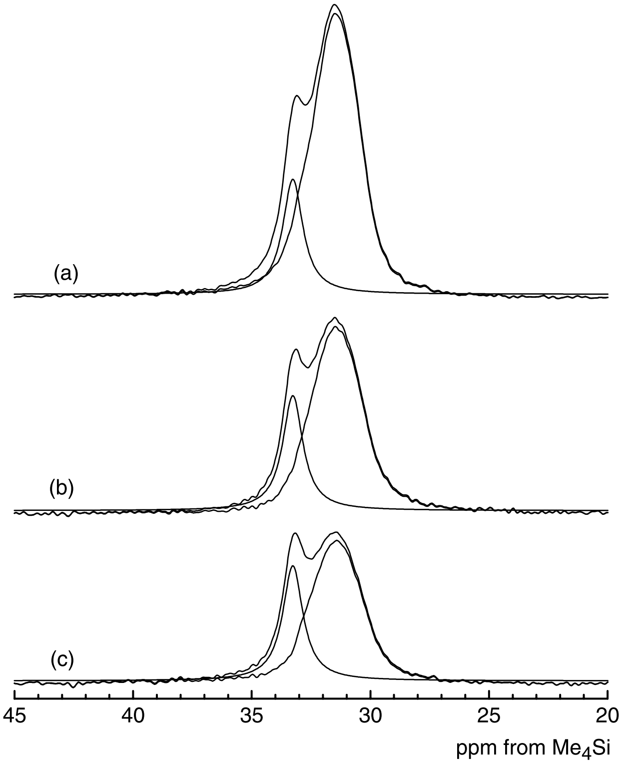

Fig. 4. Partially relaxed DD/MAS ^{13}C NMR spectra measured for DPE9 (a), DPE12 (b), and DPE16 (c) by the 90° single pulse sequence with a recycle delay of 0.5 s. A Lorentzian curve was fitted at about 33.3 ppm for each partially relaxed spectrum and a smooth lineshape was obtained for the non-crystalline component by subtracting the Lorentzian curve from each spectrum.

The non-crystalline lineshape thus obtained is found to be fairly broad and does not have a simple Lorentzian lineshape. Attempts to separate the broad peak into multiple Lorentzian peaks were not successful. To avoid complexities, the non-crystalline lineshape is retained; further, it is used for the multi-component lineshape analysis of fully relaxed ^{13}C NMR spectra, as described later. The non-Lorentzian lineshape of the less mobile non-crystalline component has also been previously observed in drawn polyethylene [18]. When we needed to determine the mass fractions of the less mobile non-crystalline and rubbery amorphous components, the non-crystalline lineshape was further separated into these components by the subtraction of the rubbery amorphous component from the total non-crystalline lineshape in each sample. Here, the lineshape of the rubbery amorphous component, which was well assumed as a Lorentzian, was obtained as a longer T_{2C} component shown in Fig. 3 for each sample by the solid-state spin–echo pulse sequence [3,16].

3.3.2. Fully relaxed spectra

In the relaxation results shown above, at least seven components constitute the ^{13}C NMR spectra of the samples; one Lorentzian corresponding to the MCP peak at 34.2 ppm, three Lorentzians with different half-widths forming the OCP peak at 33.0 ppm, one non-Lorentzian composed of two non-crystalline components similar to the cases of isotropic samples [3,16,19], and an additional Lorentzian at about 33.3 ppm in the drawn samples. The general procedure for obtaining the number of components and the spectra of the components is summarized in a flow chart shown in Fig. 5. The procedures to experimentally determine their lineshapes and chemical shift values were described above. In order to verify this finding and obtain the mass fraction of each component, fully relaxed spectra of the samples were recorded using a 90° single pulse with recycle delay times that were greater than five times of the largest T_{1C} values in the respective samples. The spectra are shown in Fig. 6 and multi-component lineshape analyses were conducted on them using the constituent components described above. The least-squares method was used to obtain best fits for the fully relaxed spectra. Here, the non-crystalline components, whose total lineshape is given as an upfield contribution in Fig. 4, were subtracted from each fully relaxed spectrum in advance, for simplicity. In each least-squares fitting, only the chemical shifts and intensities of the three crystalline components were fixed around their respective values that had been obtained by the subtraction method described above or by the T_{1C} analysis shown in Table 1 and several fittings were conducted by changing their fixed chemical shifts and

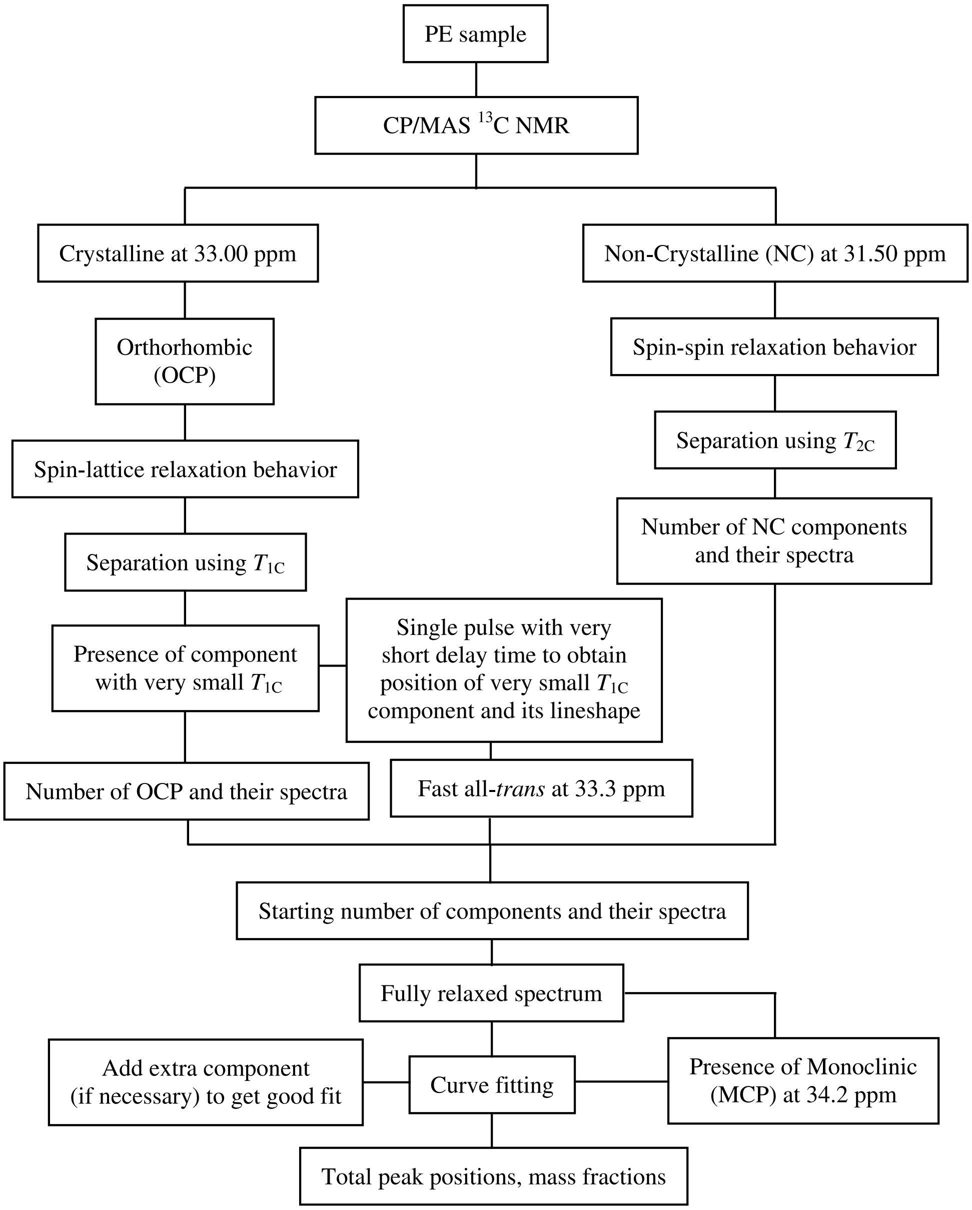

Fig. 5. Flow chart for a general procedure in determining the number of components and their own spectra for the lineshape analysis of a fully relaxed spectrum for drawn polyethylene.

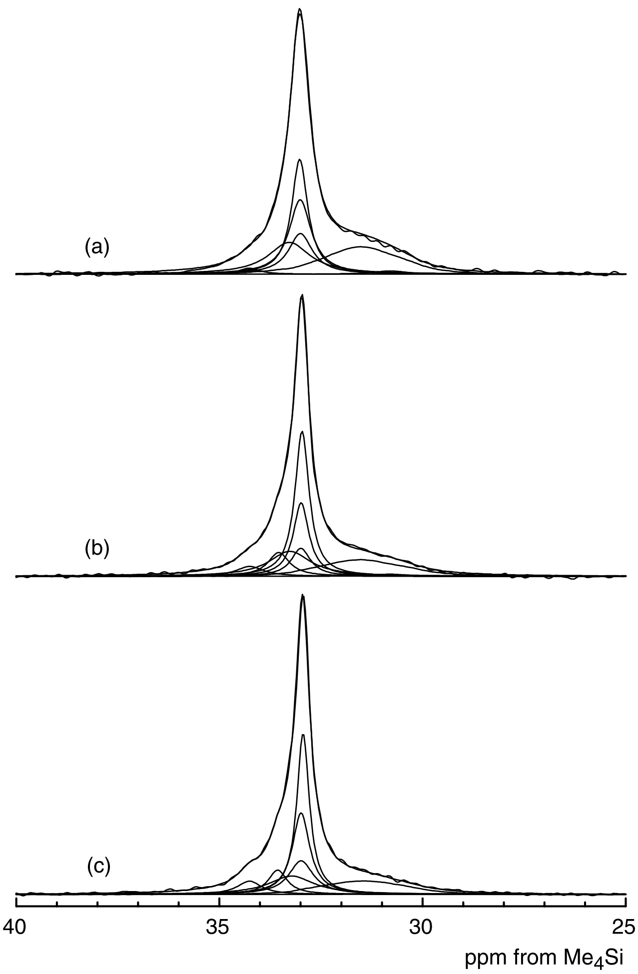

Fig. 6. Fully relaxed DD/MAS ^{13}C NMR spectra measured for DPE9 (a), DPE12 (b), and DPE16 (c) by the 90° single pulse sequence with recycle delay times longer than five times of the longest T_{1C} values for the respective samples. The mass fractions of the less mobile non-crystalline and rubbery amorphous components shown in Tables 3 and 4 were determined as described in the text.

intensities. If no good fit could be obtained, such a case was neglected. When several good fits were obtained, then an averaged value and its dispersion for each parameter were determined in these fits for each sample.

As shown as the best fit case in each sample in Fig. 6, a reasonably good fit was obtained in each drawn sample. The main difference among the samples lies in the non-crystalline region whose amount decreases as the draw ratio increases. Another notable difference is the existence of a new additional peak at 33.5 ppm, which is also described as a Lorentzian, for the samples with higher draw ratios. Eight peaks are required to satisfactorily fit the spectra of DPE12 and DPE16, while seven peaks are sufficient for DPE9. The parameters of the peaks are displayed in Table 3 [21]. The peaks that have known or published origins are stated explicitly as MCP, OCP, and less mobile non-crystalline and rubbery amorphous phases. The peaks that do not currently have clear origins at present are called all-trans. As evident from Table 3, these all-trans components appear at about 33.5 and 33.3 ppm for all the samples. The 33.5 ppm component is found only in DPE12 and DPE16, while the other peaks are observed in all the samples.

The mass fractions of the various components can be summarized as follows. The fractions of the MCP and the all-trans component at 33.5 ppm, if present, range from about 0.07 to 0.08. The mass fraction of the all-trans component at 33.3 ppm is as somewhat high as approximately 0.16 for all the draw ratios. The OCP mass fractions for DPE9, DPE12 and DPE16 are about 0.59, 0.57, and 0.63, respectively. The fraction of the less mobile non-crystalline component decreases from 0.20 to 0.14 and further to 0.11 with increasing draw ratio, while it remains as low as 0.01 for the rubbery amorphous component. These results appear to suggest that the entire OCP increases as the less mobile non-crystalline component decreases.

Table 3
The numerical results obtained by the lineshape analysis of the fully relaxed spectra for different samples

	Peak 1 MCP	Peak 2 all-trans	Peak 3 all-trans	Peak 4 OCP 1	Peak 5 OCP 2	Peak 6 OCP 3	Peak 7 less mobile non-crystalline	Peak 8 rubbery amorphous
DPE9								
Chemical shift (ppm)	34.27±0.04	–	33.28±0.01	33.01±0.01	33.01±0.01	33.02±0.01	31.50	30.50
T_{1C} (s)	–	–	1.39±0.18	18.9±3.8	126±16	519±28	0.34±0.01	0.34±0.01
T_{2C} (μs)	–	–	–	–	–	–	31.6±1.6	684±43
Half-width (ppm)	0.60±0.11	–	1.24±0.20	0.71±0.13	0.65±0.11	0.48±0.10	∼2.26	
Mass fraction	0.02±0.005	0	0.18±0.02	0.13±0.02	0.21±0.02	0.25±0.02	0.20±0.02	0.01±0.005
DPE12								
Chemical shift (ppm)	34.25±0.03	33.54±0.02	33.27±0.01	33.00±0.01	32.99±0.01	32.97±0.01	31.50	30.50
T_{1C} (s)	–	<16[a]	0.90±0.18	9.8±3.0	95±12	552±20	0.34±0.01	0.34±0.01
T_{2C} (μs)	–	–	–	–	–	–	30.1±1.5	676±40
Half-width (ppm)	0.83±0.11	0.64±0.12	1.24±0.20	0.57±0.11	0.47±0.12	0.43±0.12	∼2.50	
Mass fraction	0.04±0.01	0.08±0.02	0.16±0.03	0.09±0.01	0.17±0.02	0.31±0.02	0.14±0.02	0.01±0.005
DPE16								
Chemical shift (ppm)	34.26±0.02	33.57±0.01	33.23±0.01	32.99±0.01	32.99±0.01	32.94±0.01	31.50	30.50
T_{1C} (s)	–	<16[a]	1.10±0.14	22.7±4.1	150±14	606±24	0.36±0.01	0.36±0.01
T_{2C} (μs)	–	–	–	–	–	–	29.8±1.5	786±44
Half-width (ppm)	0.72±0.06	0.56±0.15	1.35±0.22	0.73±0.14	0.52±0.11	0.37±0.10	∼2.53	
Mass fraction	0.05±0.01	0.07±0.02	0.13±0.02	0.12±0.02	0.21±0.02	0.30±0.02	0.11±0.02	0.01±0.005

[a] Estimated approximately using the delay time at which the peak disappears in the spectrum measured by the CPT1 pulse sequence.

As far as solid-state ^{13}C NMR is concerned, there are only two known positions for the crystalline region, i.e. 34.2 ppm for the MCP and 33.0 ppm for the OCP. This results in degrees of crystallinity of about 61, 61 and 68% for DPE9, DPE12, and DPE16, respectively. These values are very close to those (59, 65 and 69%, respectively) estimated by wide-angle X-ray diffractometry.

The appearance of two new peaks observed at 33.5 and 33.3 ppm in specific cases is notable since they are not generally observed. The 33.5 ppm peak, which is 0.5 ppm downfield of our OCP, is believed to be equivalent to the 33.4 ppm peak observed for the UHMWPE nascent reactor powder in which the OCP peak is observed at 32.8 ppm [7]. The 33.3 ppm peak, which is about 0.3 ppm downfield of our OCP, is believed to be equivalent to the 33.0 ppm peak observed for ultraoriented polyethylene in which the OCP peak is observed at 32.8 ppm [6].

The effects of temperature on the various components described above were studied in DPE12. The fully relaxed spectrum of the sample was recorded at 60 and 80 °C, and the lineshape analysis of the spectrum was carried out. The results are listed in Table 4. The results obtained at room temperature (23 °C) are incorporated in the table to facilitate comparison. At 60 °C, the fully relaxed spectrum can still be separated into eight peaks but with different mass fractions. When the temperature is increased to 80 °C, the fully relaxed spectrum can be separated into seven peaks: the peak at 33.5 ppm is found to disappear. Attempts were made to fit a curve assuming the presence of a peak at 33.5 ppm, but none resulted in a good fit. It can be, therefore, concluded that, as the temperature increases, the fraction of the all-trans component at 33.3 ppm increases, while that at 33.5 ppm decreases and finally disappears at 80 °C. As seen in Table 4, changes are also observed in other components; however, they will be investigated in another study.

3.4. Chemical shift anisotropy

From the above results, the component at 33.3 ppm was observed in all the drawn samples. This component was found to have a very small T_{1C} value of the order of 1 s. The chemical shift at which it appears suggests that this component should have the all-trans conformation. Its small T_{1C} value suggests that it may undergo rapid local fluctuation with rates comparable to the ^{13}C Larmor frequency. In order to obtain more detailed information about molecular motion of this component, the CSA spectrum of this component was evaluated.

Fig. 7 displays the CSA spectrum of DPE9 obtained by the solid-state saturation recovery pulse sequence [3,16] using a T_{1C} delay time of 1 s. The spectrum was resolved into the non-crystalline and fast all-trans components using the difference between their T_{1C} values. The latter spectrum (3) was obtained by the subtraction of the former spectrum (2) measured at a delay time of 0.2 s from the total spectrum (1). It can be observed that both components do not exhibit the static CSA powder pattern of polyethylene orthorhombic crystals [19]: the non-crystalline component (2) exhibits a nearly symmetric peak while the fast all-trans (3) displays a slightly larger contribution at a lower field [22]. A similar trend is observed for DPE16, as shown in Fig. 8; however, the CSA spectra of both the non-crystalline and fast all-trans components are broader than those of DPE9 [23].

The CSAs of the randomly oriented samples shown above can only provide an overview of the average motion of the fast all-trans component at 33.3 ppm in the samples. To obtain specific information regarding the orientation and the mode of

Table 4
The numerical results obtained by the lineshape analysis of the fully relaxed spectra for DPE12 at various temperatures

	Peak 1 MCP	Peak 2 all-trans	Peak 3 all-trans	Peak 4 OCP1	Peak 5 OCP2	Peak 6 OCP3	Peak 7 less mobile non-crystalline	Peak 8 rubbery amorphous
23 °C								
Chemical shift (ppm)	34.25±0.03	33.54±0.02	33.27±0.01	33.00±0.01	32.99±0.01	32.97±0.01	31.50	30.50
T_{1C} (s)	–	<16[a]	0.90±0.18	9.8±3.0	95±12	552±20	0.34±0.01	0.34±0.01
T_{2C} (μs)	–	–	–	–	–	–	30.1±1.5	676±40
Half-width (ppm)	0.83±0.11	0.64±0.12	1.24±0.20	0.57±0.11	0.47±0.12	0.43±0.12	∼2.50	
Mass fraction	0.04±0.01	0.08±0.02	0.16±0.03	0.09±0.01	0.17±0.02	0.31±0.02	0.14±0.02	0.01±.005
60 °C								
Chemical shift (ppm)	34.29±0.02	33.69±0.03	33.26±0.01	33.03±0.01	33.03±0.01	33.00±0.01	31.50	30.87
T_{1C} (s)	–	<16[a]	1.53±0.24	10.2±2.9	94.2±14	309±17	0.48±0.02	0.48±0.02
T_{2C} (μs)	–	–	–	–	–	–	34.1±2.2	684±48
Half-width (ppm)	1.46±0.15	0.86±0.16	1.27±0.15	1.10±0.14	0.92±0.12	0.92±0.13	2.19	1.97
Mass fraction	0.07±0.01	0.01±0.005	0.16±0.02	0.15±0.02	0.15±0.02	0.17±0.02	0.19±0.02	0.10±0.01
80 °C								
Chemical shift (ppm)	34.35±0.01	–	33.27±0.01	33.06±0.01	33.07±0.01	33.04±0.01	31.50	30.50
T_{1C} (s)	–	–	1.22±0.12	9.7±2.0	54.4±10	250±13	0.73±0.02	0.73±0.02
T_{2C} (μs)	–	–	–	–	–	–	38.1±2.3	838±50
Half-width (ppm)	1.62±0.14	–	1.45±0.15	1.25±0.13	1.22±0.13	1.18±0.14	2.30	1.53
Mass fraction	0.05±0.01	0	0.17±0.02	0.13±0.02	0.16±0.02	0.17±0.02	0.19±0.02	0.13±0.02

[a] Estimated approximately using the delay time at which the peak disappears in the spectrum measured by the CPT1 pulse sequence.

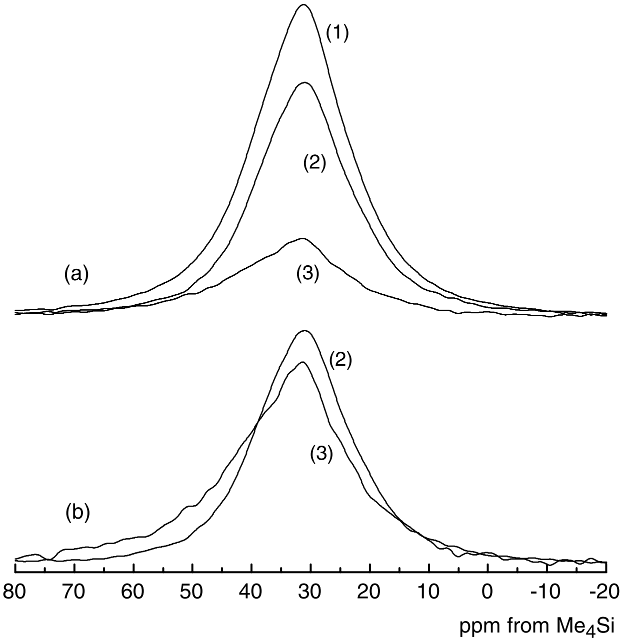

Fig. 7. (a) ^{13}C CSA spectra of DPE9 obtained without MAS by the solid-state saturation recovery pulse sequence with different delay times: (1) 1 s; (2) 0.2 s; (3) difference spectrum ((1) $-1.87\times$(2)), which should be the fast all-trans component. (b) ^{13}C CSA spectra of the fast all-trans component (3) and the non-crystalline component (2) as demonstrated with the same integrated intensity.

motion of this component, a CSA spectrum of DPE12 was measured further by aligning the draw axis parallel or perpendicular to the static magnetic field B_0 using a CP/DD ^{13}C NMR probe with a goniometer. The spectra were recorded at room temperature, 60 and 80 °C using the solid-state saturation recovery pulse sequtransence with short delay times of 0.5 and 2 s. Initially, the background contributions obtained by blank measurements were subtracted from the respective CSA spectra; then, the spectrum of the fast all-trans component was obtained by subtraction of the two spectra obtained for delay times of 2 and 0.5 s in a parallel or perpendicular setting.

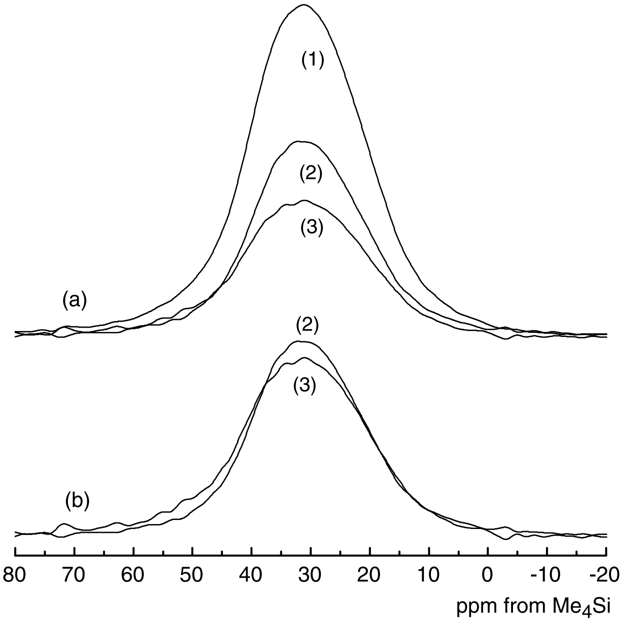

Fig. 8. ^{13}C CSA spectra of DPE16 obtained without MAS by the solid-state saturation recovery pulse sequence with different delay times: (1) 1 s; (2) 0.2 s; (3) difference spectrum ((1) $-1.45\times$(2)), which should be the fast all-trans component. (b) ^{13}C CSA spectra of the fast all-trans component (3) and the non-crystalline component (2) as demonstrated with the same integrated intensity.

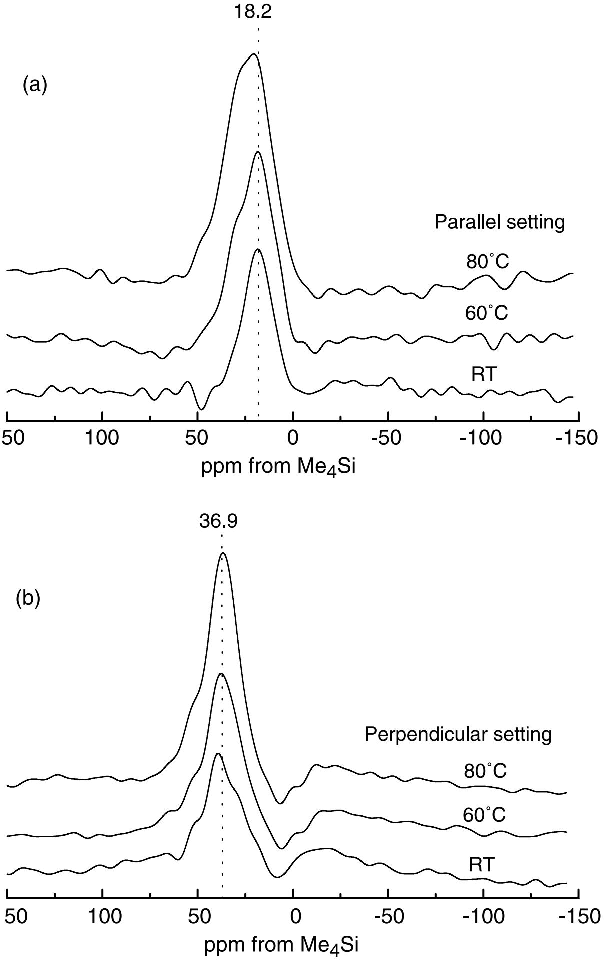

Fig. 9. ^{13}C CSA spectra of the fast all-trans component obtained for DPE12 at different temperatures by setting the draw axis of the sample parallel (a) or perpendicular (b) to the static magnetic field.

Fig. 9 shows the CSA spectra obtained for the fast all-trans component when the draw axis is aligned parallel (a) and perpendicular (b) to B_0 at different temperatures. In the parallel setting, a single peak is observed at 18.2 ppm, and it becomes slightly wider and more intense as the temperature increases. When the draw axis is perpendicular to B_0, a considerably broad singlet is observed at about 36.9 ppm at room temperature. As the temperature is increased, the peak becomes significantly narrower and more intense.

4. Discussion

It is worthwhile to summarize a few points at the beginning of this section. It was found that several components constitute the fully relaxed ^{13}C NMR spectra of highly drawn PE samples. These include MCP, all-trans at 33.5 ppm, all-trans at 33.3 ppm, three OCPs, and less mobile non-crystalline and rubbery amorphous components. The first six components are composed of segments that have the all-trans conformation. If they are regularly packed into three dimensional cells, they would form either the MCP or the OCP. The last two components, the less mobile non-crystalline and rubbery amorphous components, are really non-crystalline. It should be noted that the rubbery amorphous component in this case consists of a portion of chains, which adopt a statistically random conformation and undergo rapid *trans–gauche* exchange in each C–C bond. In contrast, the less mobile non-crystalline component is subjected to relatively restricted slower motion associated with a smaller T_{2C} value, and it contains a significantly higher fraction of *trans* conformation than the rubbery amorphous component [3,16,18,19]. It is important to recognize that similarity cannot be assumed between the interfacial component observed by Raman spectroscopy and the component mentioned above that is separately detected by NMR spectroscopy. It is known that the former contains chains, which adopt the all-trans conformation but lack lateral order. It is, however, important to acknowledge that there exists a critical sequence length that can be detected as a particular band. For example, the 1130 cm^{-1} band, which is associated with CH_2 in the all-trans conformation, may be observed if the sequence length is longer than 18 methylene units [25,26].

The fact that polyethylene contains multiple components has been reported in many studies. It has been shown that T_{1C} of the OCP increases with lamellar thickness. It has been suggested that the OCP with the smallest T_{1C} may either represent segments in crystalline regions that are closer to interfaces, or it should be ascribed to very thin or defective lamellae if they exist. The component with the largest T_{1C} is the core of lamellar crystallites [19,20,27].

Recently, the concept of chain diffusion as a mechanism for spin–lattice relaxation was proposed [28]. Although supporting experiments have been documented [17,29–31], there is a discrepancy between the observed relaxation and that predicted by one-dimensional chain diffusion [19,20]. In addition, using a very large number of samples, it was demonstrated that two OCPs with distinct dynamics exist in polyethylene [6]. It was not clarified if these two OCPs are related to two of the three components with different T_{1C}s that are generally observed in polyethylene [3,16,32–34]. In our study, it was found that the resonance line at 33.0 ppm can be separated into four components. The fourth component, which has not been observed before, was found to have a very small T_{1C} ranging from 0.9 to 1.39 s and a chemical shift of about 33.3 ppm. This peak will be focused upon as it is fairly large and its nature is unclear.

The conformation of the fourth component will be considered first although the all-trans conformation was previously assumed. It is known that an isotropic chemical shift depends on the conformation as well as the packing of chains. Since the chemical shift of this component is higher than that of the OCP and any deviation from the conformation in this state would lower the chemical shift, this component is understood to have the same all-trans conformation as the OCP but with different packing. As the T_{1C} value of this component is very small, ranging 0.90–1.39 s, it appears to have a very high mobility. This observation is consistent with its narrow CSA spectrum, which will be discussed later.

As already mentioned, this component at 33.3 ppm has been previously observed in ultradrawn PE fiber and is tentatively suggested to be associated with the monoclinic/orthorhombic interface [6]. However, in this study, the mass fraction of this component was estimated to be much higher than that of the MCP. Therefore, the component at 33.3 ppm cannot be attributed to the monoclinic/orthorhombic interface. It is possible that the component at 33.3 ppm can be assigned to chains that have the all-trans conformation but without lateral order, i.e., the highly oriented non-crystalline component having the all-trans conformation. However, for the NMR to recognize the all-trans conformation, the sequence length should preferably be greater than about 10 nm (or about 80 methylene units) because the introduction of about 5% of the gauche conformation would be sufficient to induce an upfield shift of less than approximately 0.25 ppm due to the motional average of the γ-gauche effect [35] that is produced by the rapid migration of the gauche conformations along each sequence.

A similar all-trans component with a small T_{1C} value may be deduced from the spectrum of the non-crystalline component of stretched UHMWPE [1]. The chemical shift of this component is very close to that of the OCP, but it was not determined. Moreover, no comments were provided for the all-trans component. Recently, this component was also observed in isotropic polyethylene [12], gel-spun polyethylene fibers [13,14], and ultradrawn polyethylene fibers [5] at a fraction of about 0.20, 0.30, and 0.05, respectively. However, the chemical shift values in these cases were reported to be the same as the value of the OCP. We cannot explain these observations; however, careful inspection of a particular spectrum in Fig. 10 of Ref. [14] reveals slight asymmetry on the downfield shoulder of the OCP peak. This asymmetry appears to be caused not by the MCP peak but by another peak at a slightly downfield than the OCP. This issue can only be resolved by the lineshape analysis of spectra that were newly developed on the basis of the detailed T_{1C} and T_{2C} analyses in this study.

Additionally, it should be noted that there exists a difference in the meaning of ‘intermediate phase’ employed by Wunderlich’s group [12–14] and our all-trans non-crystalline component. The former was deduced from a fast relaxing orthorhombic crystalline peak that may have had a T_{1C} of the order of 1–20 s. This ‘intermediate phase’ has been suggested to have a structure similar to that of the OCP with the exception that the chains are able to reorient themselves around their axes at high rates. It should also be noted that such a fast relaxing OCP has been observed previously [3,16,19,20,32,35]; however, it was treated as an OCP and not as an ‘intermediate phase.’ Thus, it would be useful to compare it with a recent finding by one of the authors [36]. In that research, as-received and annealed ethylene ionomers were studied by solid-state ^{13}C NMR. Although not discussed in that work, the OCP in the former ionomers was found to exhibit a chemical shift of approximately 33.4 ppm. After annealling, the peak shifted about 0.3 ppm upfield to the position that is generally observed for the OCP. This may be partially related to the packing, as discussed above.

The fast motion of the all-trans non-crystalline component is confirmed by the significantly narrow CSA spectra, as shown in Figs. 7 and 8. The CSA spectrum of the non-crystalline component in DPE9 is slightly asymmetric and very similar to that observed in the drawn PE [18] with the exception that its half width is about twice as that observed in the present study. There is slight anisotropy in the non-crystalline component. This observation can be easily understood by recognizing that such anisotropy is greatly reduced in this component because *trans–gauche* exchanges are induced along with large-amplitude fluctuation around the torsional potential minima. The non-crystalline region in the present samples is primarily composed of the less mobile non-crystalline component. It should be noted that our non-crystalline CSA lineshape is very different from that reported by Hughes et al. [37] and Liu et al. [38] in which the CSA was very large. The CSA spectrum of the fast all-trans component displays slightly higher anisotropy than that of the non-crystalline component. When the draw ratio is increased to 16, the CSA spectra of both the non-crystalline and fast all-trans components become wider. Following the above reasoning regarding the shape of the CSA spectrum, it can be concluded that both the non-crystalline and fast all-trans components in DPE16 have higher structural distributions and anisotropy. In other words, both non-crystalline and fast all-trans components become more oriented. This is in good agreement with the observation of Pigeon et al. [10] who showed, by Raman spectroscopy, that the orientation of the all-trans component increases with the draw ratio. The fact that the CSA spectrum of this all-trans component is much narrower than that of normal orthorhombic crystalline phase suggests a high degree of motional averaging in this component. However, as mentioned by Hu et al. [17] and demonstrated by our recent CSA simulation [39], the CSA spectrum is not greatly averaged when the chains having the all-trans conformation undergo diffusional rotation around the chain axis even under the fast limit condition. It should be, therefore, assumed that rapid fluctuation with fairly large amplitude may be allowed in the torsional potential minimum in each C–C bond for the fast all-trans component. Consequently, this fast all-trans component should be non-crystalline and may exist as taut tie-molecules.

To clarify the above issue, the orientation and mode of motion of the fast all-trans component at 33.3 ppm will now be considered. In the CSA spectra shown in Fig. 9(a), a singlet is observed at approximately 18.2 ppm for this component in DPE12; the draw axis of this sample was set parallel to the static magnetic field B_0. This value is very close to the principal value σ_{33} of the chemical shift tensor for orthorhombic crystals of polyethylene [40], indicating that the chain axis of the fast all-trans component may be aligned along the drawing direction. As the temperature is increased, the peak becomes wider and more intense. An increase in the intensity of the peak can be interpreted as an increase in the amount of the fast all-trans component with increasing temperature. The greater width of the peak suggests a slight deviation in the chain axis of the component away from the draw axis. Such a situation is likely since highly oriented polymers are known to have a negative thermal expansion coefficient in the drawing direction (or *c*-axis). Such contraction as a result of heating would allow greater off-axis motion.

When the draw axis is aligned perpendicular to B_0, a fairly broad single peak is observed at room temperature at about 36.9 ppm, as shown in Fig. 9(b). The spectrum does not exhibit a doublet at the principal values σ_{11} and σ_{22} of the chemical shift tensor [40]; this suggests that the fast all-trans component undergoes enhanced molecular motion around the chain axis, which in turn is perpendicular to B_0. As the temperature is increased, the peak becomes narrower and more intense. As in the case of parallel alignment, an increase in the intensity of this peak is also attributed to an increase in the amount of the fast all-trans component. However, the sharper peak that is observed when the temperature increases may be due to faster motion of this component around its chain axis. These results clearly indicate that the fast all-trans component is highly oriented in the drawing direction.

The fact that the amount of the fast all-trans component increases with temperature may require further examination. In this section, we consider the results of the lineshape analysis for the fully relaxed spectrum of sample DPE12 listed in Table 4. As indicated in the ‘Results’ section, the fraction of the fast all-trans component increases with temperature while that of the all-trans component at 33.5 ppm decreases with increasing temperature and disappears at 80 °C. Therefore, it is likely that the all-trans component at 33.5 ppm would transform into the fast all-trans component at 33.3 ppm as the temperature increases.

In the above discussion, it should be noted that the fast all-trans component at 33.3 ppm is associated with isolated chains that have the all-trans conformation. These chains are not crystalline, and they can be considered as taut chains that traverse the non-crystalline region. Since it has been previously suggested that these all-trans sequences should be longer than 10 nm to be detectable by NMR spectroscopy, these taut chains may be in the interfibrillar region. Further, it is likely that these chains are located in the lateral intercrystallite region since drawn polyethylene is known to have long crystallites with lateral dimensions of approximately 10–13 nm [41]. However, adequate information is not available for the all-trans component at 33.5 ppm. A separate estimation using the CPT1 pulse sequence indicated that this component appears to have a significantly larger T_{1C} value than the fast all-trans component, as seen in Table 3. Therefore, it can be proposed that this component may be a cluster or group of chains having the all-trans conformation. The packing of these chains may not be as regular as in the case of the OCP or the MCP. Upon heating, the molecular motion will be greatly enhanced, and contraction in the chain axis and expansion in the transverse direction may cause dissociation of this cluster, leading to isolated chains. Such dissociation would result in an upfield shift of the resonance line. Consequently, the all-trans component at 33.5 ppm will disappear and the behavior of the corresponding chains will be identical to that of the fast all-trans component at 33.3 ppm.

In addition to the above discussion regarding the nature of the fast all-trans component, structural transformation clearly occurs during the drawing. The mass fraction of the less mobile non-crystalline component decreases and that of the OCP increases. As the samples are composed of many components, deducing the transformation route is presently very difficult. Finally, it should be noted that the lineshape analysis in terms of the seven or eight components developed for the PE samples in this study would be unambiguously available for the spectra obtained under a static magnetic field higher than 9.4 T due to the resulting higher resolution.

5. Conclusions

The structure and dynamics of several components, particularly those of the oriented non-crystalline component, present in highly drawn polyethylene samples were studied by solid-state ^{13}C NMR spectroscopy. In general, the degree of crystallinity increases with the draw ratio. Each longitudinal relaxation decay curve of the resonance line at 33.0 ppm is found to be composed of four components that have different T_{1C} values, while the transverse relaxation decay of the non-crystalline component is composed of two components having different T_{2C}s. The drawing appears to mainly affect the T_{1C} values in a manner such that these values increase with the draw ratio. The fully relaxed spectra have been resolved into seven or eight components. In addition to the six resonance lines that are generally observed in the isotropic samples as one monoclinic, three orthorhombic, and two non-crystalline components, two additional peaks are found to exist 0.3 and 0.5 ppm downfield from the orthorhombic resonance line. By examining the broad half-width, small T_{1C} value, and narrow CSA of the former peak as well as by comparing the mass fractions with the degree of crystallinity determined by X-ray diffractometry, the former peak is assigned to the non-crystalline component with the all-trans conformation that probably exists as taut-tie molecules. It is suggested that the lack of lateral order may allow those chains to undergo rapid random jump or diffusional rotation around the chain axis. Moreover, it can be assumed that each chain may be subjected to rapid fluctuation with fairly large amplitudes around the torsional potential minimum in each C–C bond as deduced from the narrow CSA. Additional experiments also confirmed that these fast all-trans chains are aligned in the draw direction and that rapid motion occurs around their chain axis. The results of the component that appears 0.5 ppm downfield from the orthorhombic resonance line suggest that the component can be considered to be a cluster or a group of chains that have the all-trans conformation. At room temperature, they appear downfield due to packing. As a result of increased motion at higher temperatures, they may dissociate themselves and behave in the same manner as isolated chains having the all-trans conformation and, namely, as the fast all-trans component.

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[17] Hu et al. (Hu, J. Z.; Wang, W.; Bai, S.; Pugmire, R. J.; Taylor, C.M. V.; Grant, D.M. Macromolecules 2000, 33, 3359) reported by using the two-dimensional magic angle turning (MAT) method that the CSA spectra of the crystalline components with different T_{1C} values in polyethylene samples crystallized from the melt have almost the same powder pattern in the rigid state even when the T_{1C} decay curve could be analyzed in terms of plural components. This fact implies that the non-exponential decay curve could not be interpreted by the existence of different T_{1C} components but mainly by the segmental exchange between the crystalline and non-crystalline regions through the so-called chain diffusion. However, possible rapid fluctuation with a small amplitude around the potential minimum in each C–C bond does not contribute to the change in CSA line shape, although such motion greatly reduces the T_{1C} value. Moreover, the respective components obtained by the T_{1C} decay analysis have their own line widths for their MAS-averaged resonance lines and their T_{1C} values evidently differ 4–21 times from each other, as seen in Table 3 in this paper. These facts indicate that the crystalline components with different T_{1C}s should be really different in structure and molecular mobility associated with T_{1C} although their observed values are partially subjected to the average by the chain diffusion. In addition, these values may be averaged values for differently oriented chains against the static magnetic field, which may have slightly different T_{1C} values.
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[21] The stability of the 9.4 T magnet was 0.0196 Hz/h, which corresponds to 1.98×10^{-4} ppm/h. Since it took about 24 h to measure the fully relaxed ^{13}C NMR spectra shown in Fig. 6, a chemical shift drift is estimated to be 0.0047 ppm during the measurements. This order of the drift does not significantly affect the chemical shift values of the respective components that are listed in Tables 3 and 4.

[22] The isotropic chemical shifts calculated from the first moment [24] of the CSA spectra for the non-crystalline and the fast all-trans components in DPE9 are 30.94 and 33.24 ppm, respectively. The isotropic chemical shift of the latter component is very close to that observed in the corresponding MAS spectrum (33.25 ppm). Since the shape of the non-crystalline peak in the MAS spectrum is not symmetric like a Lorentzian, its top position cannot be simply compared with the 30.94 ppm calculated above.

[23] The isotropic chemical shifts calculated from the first moment of the CSA spectra for the non-crystalline and the fast all-trans components in DPE16 are 30.67 and 32.01 ppm, respectively. The value estimated for the fast all-trans is slightly different from its chemical shift of 33.25 ppm obtained under MAS. This disagreement may be due to macroscopic anisotropy that will still exist for the sample packed in a MAS rotor after cutting into small pieces in the case of higher-level drawing.

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