Chain conformation of polyethylene in the solid state as studied by ^{13}C cross-polarization/magic angle spinning nuclear magnetic resonance spectroscopy

Isao Ando, Tetsushi Sorita, Takeshi Yamanobe and Tadashi Komoto
Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Japan

and Hisaya Sato
Department of Material Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo, Japan

and Kenzo Deguchi and Mamoru Imanari
JEOL, Nakagami, Akishima-shi, Tokyo, Japan

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High-resolution ^{13}C nuclear magnetic resonance (n.m.r.) spectra of melt-quenched polyethylene and polyethylene single crystals are measured by the cross-polarization/magic angle spinning technique. Melt-quenched polyethylene and polyethylene single crystals have four small upfield peaks, a shoulder on the main peak and three small peaks, respectively. Based on the ^{13}C n.m.r. resonance lines of cyclic paraffin $C_{64}H_{128}$ reported previously, it is concluded that the main peak and the three upfield peaks arise from the *trans* zigzag structure region and the folded structure region, respectively. From these peak intensities, it is estimated that the stem length of polyethylene single crystals is approximately 125 Å. Taking into account an error in the estimation of the small peak intensities, the calculated stem length of 125 Å is consistent with the crystal thickness (120–150 Å) observed directly by electron microscopy. It can be concluded, therefore, that polyethylene single crystals mainly contain sharply folded structure. Melt-quenched polyethylene may contain sharply folded structure to some extent in addition to loose loops.

(Keywords: chain conformation; polyethylene; ^{13}C n.m.r.)

INTRODUCTION

Since Keller[1], Till[2] and Fischer[3] independently, in 1957, proposed a chain-folding hypothesis from electron diffraction of polyethylene single crystals, a lot of arguments on chain folding in a single crystal have been made by means of X-ray diffraction, Raman spectroscopy and other spectroscopies. Nevertheless, the configuration of the polymer chains in the folded structure region remains incompletely solved. The determination of the chain conformation of polyethylene in single crystals is one of the most important problems in polymer science, and its knowledge becomes fundamental for obtaining information about the conformation of a single polymer chain in the crystalline state. Several models have been proposed to depict the conformation in the folded structure region of polyethylene single crystal. *Figure 1* shows the three models: (a) sharp fold model[1]; (b) switchboard model[4]; and (c) loose loop model[5]. These models have been discussed from various aspects, but it has not been conclusively determined which model is the most reasonable for the folded structure region in polyethylene crystals.

The purpose of the present work is to clarify which model is the most reasonable for the folded structure region in polyethylene single crystals and melt-quenched polyethylene. Such an attempt will be carried out by means of ^{13}C cross-polarization/magic angle spinning (CP/MAS) n.m.r. spectroscopy, which has proved to be an excellent means for probing the conformation and dynamics of polymers in the solid state[6]. The results of ^{13}C CP/MAS n.m.r. of cyclic paraffin $C_{64}H_{128}$ (refs. 7–9) were used in an attempt to provide insight into the chain-folded conformation because such paraffins of long chain lengths assume a compact conformation in the solid state with the shape of two parallel straight chains bridged at both ends, as shown in *Figure 2*[10,11], and this form is closely related to the chain-folded structure.

EXPERIMENTAL

Materials

Polyethylene single crystals. For the preparation of polyethylene single crystals[12], fractionated Marlex 50 polyethylene with $M_w = 31\,000$ was used. The polyethylene was dissolved at 130°C in xylene at a concentration of 0.03%. The solution was kept at 80°C for 2 h for primary crystallization, and then at 102°C for 5 min for self-seeding. Next, the solution was kept at 82°C for 2 h again and then slowly air-cooled to room temperature. Deposited crystals were separated from solution by

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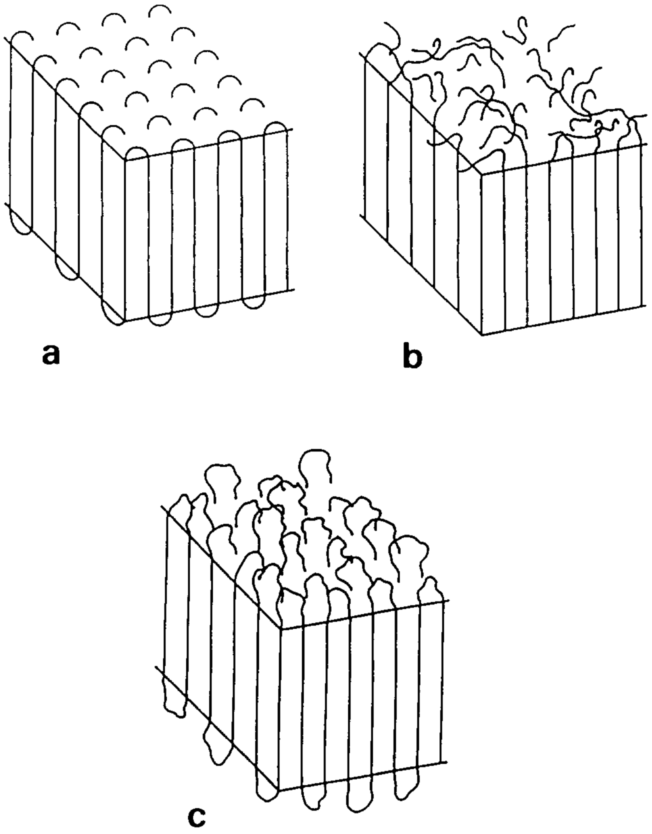

Figure 1 Schematic drawing of the conformation models of polyethylene single crystal: (a) sharp fold model; (b) switchboard model; and (c) loose loop model

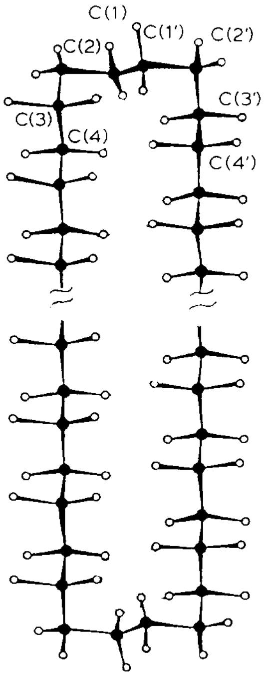

Figure 2 Schematic drawing of the conformation of a cyclic paraffin

filtration, washed with acetone and dried. This sample was composed of lamellar single crystals, as shown in *Figure 3*.

Melt-quenched polyethylene. Unfractionated polyethylene ($M_w = 128\,000$) was put into a glass tube and sealed off in vacuum. The glass tube was heated at 150°C and then quenched in dry-ice/methanol (about −70°C).

The crystallinity of the polyethylene single crystals and melt-quenched polyethylene was estimated from the density. The densities of the samples were measured in a mixture of n-hexane and carbon tetrachloride at 25°C (*Table 1*).

Methods

^{13}C CP/MAS spectra were measured by means of a JNM-FX200 (50 MHz) and GX 270 (67.5 MHz) spectrometers with a CP/MAS accessory. The sample (~ 300 mg) was contained in a bullet-type rotor and spun at 3000–4000 rpm. Contact time is 0.4–6 ms* and repetition time 5 s. Spectral width and data points were 20 kHz and 8 K, respectively. ^{1}H field strength was 12 mT for both CP and decoupling process. The number of accumulations was 50–1000. ^{13}C chemical shifts were calibrated indirectly through external benzene (128.5 ppm relative to TMS).

Electron micrographs of polyethylene single crystals were taken using a JEOL JEM-7 electron microscope (JEOL).

RESULTS AND DISCUSSION

Figure 4 shows ^{13}C CP/MAS n.m.r. spectra of cyclic paraffin $C_{64}H_{128}$, melt-quenched polyethylene and polyethylene single crystals. Each spectrum is normalized to the same total intensity and is plotted at amplification

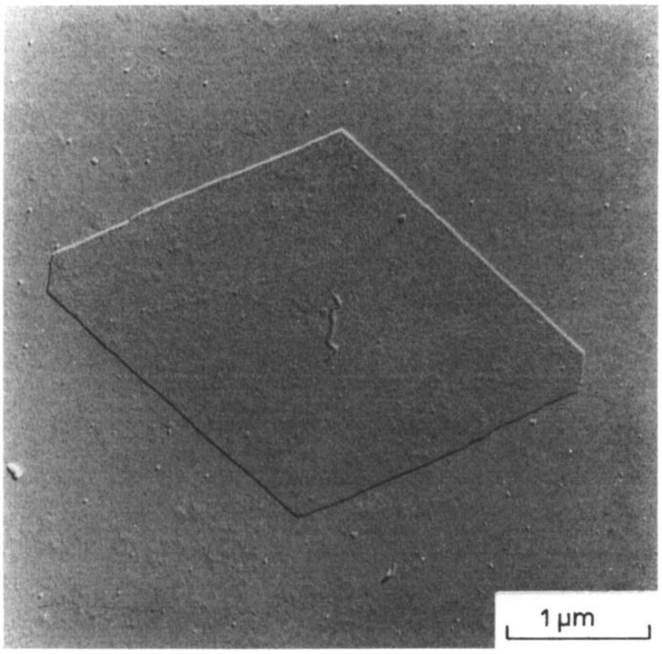

Figure 3 Electron micrograph of polyethylene single crystals with $M_w = 31\,000$. Chromium shadowing was done

Table 1 The crystallinity and density of polyethylene single crystals and melt-quenched polyethylene

Sample	Density (g cm^{-3})	Crystallinity (%)
Polyethylene single crystals, $M_w = 31\,000$	0.9814	94.1
Melt-quenched polyethylene	0.9456	70.4

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* The ^{13}C CP/MAS spectra of polyethylene samples were measured with various contact times in order to optimize the folded structure region. We found that contact times of 1 and 2 ms are better for obtaining a clear spectrum of the sample.

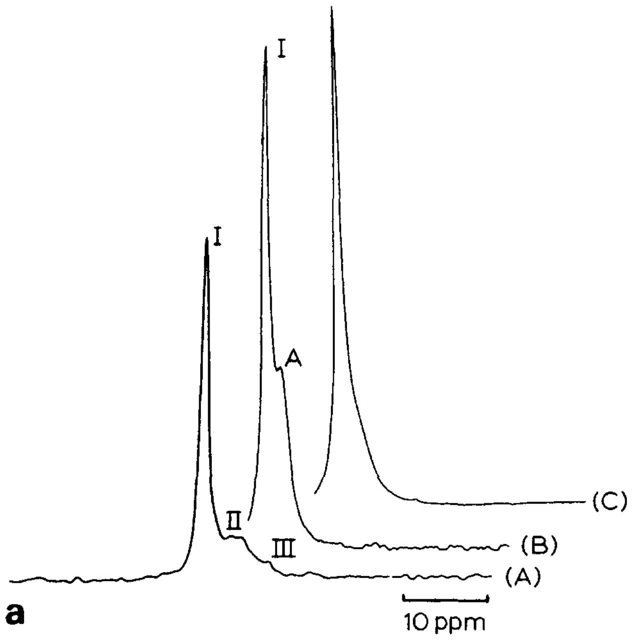
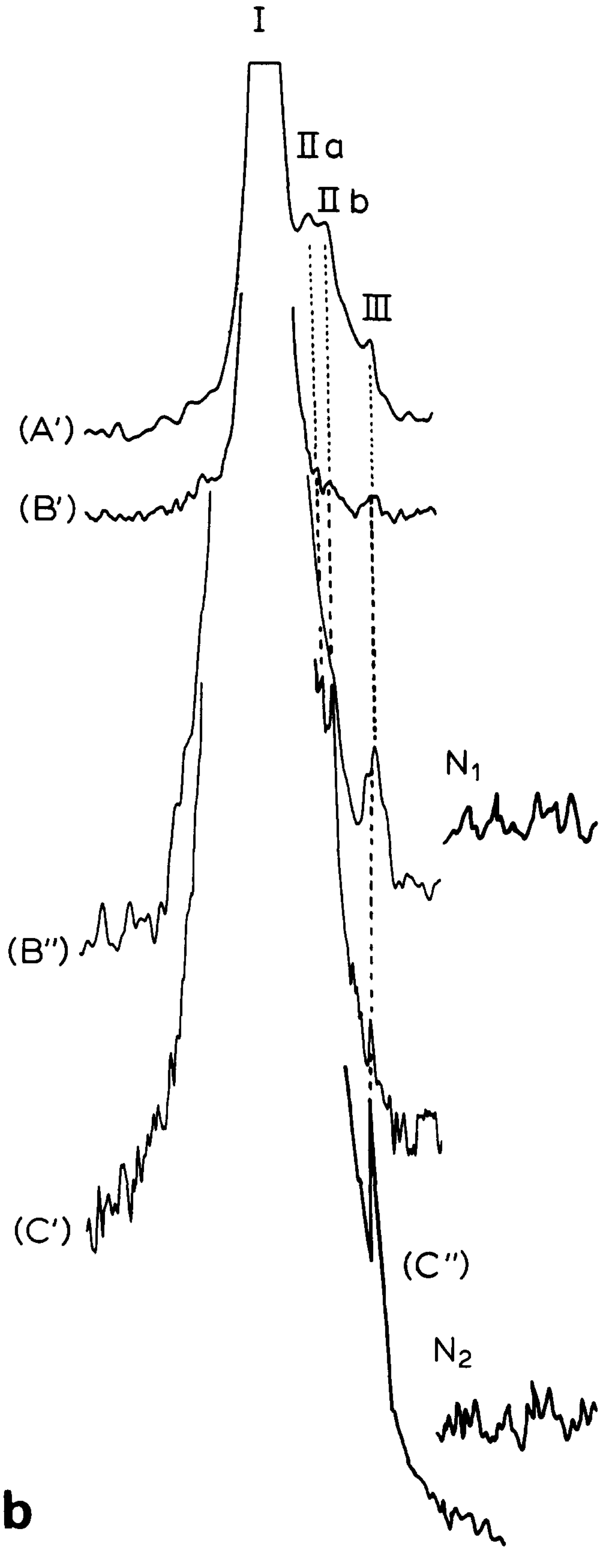


Figure 4 Observed ^{13}C CP/MAS n.m.r. spectra of cyclic paraffin $C_{64}H_{128}$ ((A) and (A′)), melt-quenched polyethylene ((B), (B′) and (B″)) and polyethylene single crystals ($M_w = 31\,000$) ((C), (C′) and (C″)). The spectra in (b) are amplified, compared with the spectra in (a). The spectra (A), (A′), (B), (B′) and (C″) were recorded with a contact time of 2 ms at 50 MHz and the others with a contact time of 1 ms at 67.5 MHz. N_1 and N_2 indicate noise levels for spectra (B″) and (C″), respectively

level. The regions at the base of all of the lines are asymmetric.

Cyclic paraffin $C_{64}H_{128}$ has small upfield peaks on the main peak. The main peak and two small peaks are designated I, II and III, respectively. In a previous paper[7], these peaks were assigned using the *γ-gauche* effect concept; peak I, and peaks II and III arise from the methylene *trans* zigzag structure region and folded structure regions, respectively. These were interpreted in the following manner. As shown in *Figure 2*, cyclic paraffins of long chain lengths crystallize in a conformation characterized by two parallel all-*trans* zigzag strands connected by two *GGTGG* loops[10,11], where *G* and *T* denote *gauche* and *trans*, respectively. If this conformation is dynamically rigid in the solid state at room temperature, then, based on the γ-effect, we would expect loop carbons C(3), C(3′), C(4), C(4′), to resonate 1γ-effect upfield and loop carbons C(1), C(1′) to resonate 2γ-effects upfield from the all-*trans* carbons and from loop carbons C(2), C(2′), whose next nearest bonds are also both *trans*. Most recently, Möller *et al.*[9] showed that, for C(2) and C(2′) carbons, another contribution to the ^{13}C chemical shift is of importance, namely the 'vicinal *gauche*' (*V*) effect[13,14], and results in an upfield shift of about 6 ppm compared with that of the all-*trans* carbons. Here, we consider this effect in addition to the γ-effect to assign the loop carbon signal. To estimate the chemical shift position for the small peaks, we chose, as an example, γ of -4 to -6 ppm[15] and V of about -6 ppm. Thus, for cyclic paraffin $C_{64}H_{128}$, for which the spectrum has peaks I, II and III, we could obtain the values of 34, 28–30 and 22–26 ppm. The small splitting of peak II into IIa and IIb may be due to different values of the γ-effect for C(3) (C(3′)) and C(4) (C(4′)) carbons which arise from the distribution of the corresponding dihedral angles. If the 'vicinal *gauche*' effect is considered, C(2) and C(2′) carbons may appear at the ^{13}C chemical shift position for peak II. Thus, the peak for C(2) and C(2′) carbons may overlap with peak II† assigned by Möller *et al.*[9]. The ^{13}C chemical shift values of these peaks are listed in *Table 2*.



Melt-quenched polyethylene has four small peaks upfield of the main peak. The main peak and four small

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† The previous assignment[7] for C(2) and C(2′) may be replaced by the present one.

Table 2 Observed ^{13}C chemical shifts (relative to TMS) of cyclic paraffin $C_{64}H_{128}$, melt-quenched polyethylene and polyethylene single crystals in the solid state

	^{13}C chemical shift, δ (ppm)				
Sample	Peak I	Peak A	Peak IIa	Peak IIb	Peak III
Cyclic paraffin $C_{64}H_{128}$	33.8		28.7	26.9	22.0
Melt-quenched polyethylene	33.0	31.2	26.5	24.3	21.1
Polyethylene single crystals, $M_w = 31\,000$	33.0	31.5	26.5	24.5	20.9

peaks were designated by I, A, IIa, IIb and III, respectively. The spectrum (B′) was measured with a contact time of 2 ms at 50 MHz. In order to ascertain the existence of these small peaks, the ^{13}C CP/MAS spectrum of the same sample was measured with a contact time of 1 ms at 67.5 MHz, as shown in spectrum (B″). The signal-to-noise ratio for the upfield peaks II and III is very low. Nevertheless, as seen from spectrum (B″), peak III is obviously above the noise level (N_1). The existence of III is apparently identified. Peak II is at the foot of the intense main peak I and is a shoulder on peak A (several measurements on this sample show that peak II is a shoulder or a peak on peak A). Judging from the chemical shift position of these peaks, it is evident that peak A does not appear in the spectrum of cyclic paraffin $C_{64}H_{128}$, and the chemical shift positions of the other peaks agree with those of cyclic paraffin, respectively. It is noted that there is a difference of about 1 ppm in chemical shift of peaks I, II and III between cyclic paraffin $C_{64}H_{128}$ and polyethylene samples. We reported previously[16] that there is the difference of about 1 ppm in chemical shift of the *trans* zigzag carbons between n-paraffins and polyethylene, and cyclic paraffins, for which the crystallographic forms are orthorhombic and triclinic, respectively. We suggested that such a difference may be caused by a local change in intermolecular interaction which results in going from the orthorhombic to the triclinic forms[16]. However, for the carbons in the folded structure region, we cannot confirm at this stage whether this suggestion is true or not. Nevertheless, we consider that molecular packing may be one of several reasons for the effect on chemical shift.

Peak A appears upfield by 2.3 ppm from the main peak I. ^{13}C chemical shift values of peaks I and A agree with the respective values reported by Earl and VanderHart[17,18], Kitamaru *et al.*[19], Möller *et al.*[20] and Axelson *et al.*[21] on melt-crystallized polyethylene. As discussed by them, it is indicated that peak I is straightforwardly ascribed to the *trans* zigzag structure region and that the appearance of peak A arises from the methylene carbons in the amorphous state, which are undergoing rapid transitions between the conformers, contrary to the behaviour of the *trans* zigzag structure region. According to such a consideration, the fraction of methylene carbons in the amorphous state was estimated to be approximately 0.28 from the intensity of peak A. This value is very close to the value of 0.296 (*Table 1*) determined from the density of the sample.

Next we consider peaks II and III. Because the chemical shift positions of peaks of IIa, IIb and III agree approximately with those of cyclic paraffin $C_{64}H_{128}$, it is considered that the appearance of peaks II and III arises from the methylene carbons in the folded structure region. It may be therefore said that the melt-quenched polyethylene takes the 'adjacent re-entry' type of macroconformation in addition to loose and long loops in the fold surface, as shown in *Figure 5*. A most recent neutron scattering study[22] on the chain conformation of polyethylene in the crystalline state shows that an 'adjacent re-entry' folding is possible in the case of slowly crystallized polyethylene. These results do not conflict with our present results.

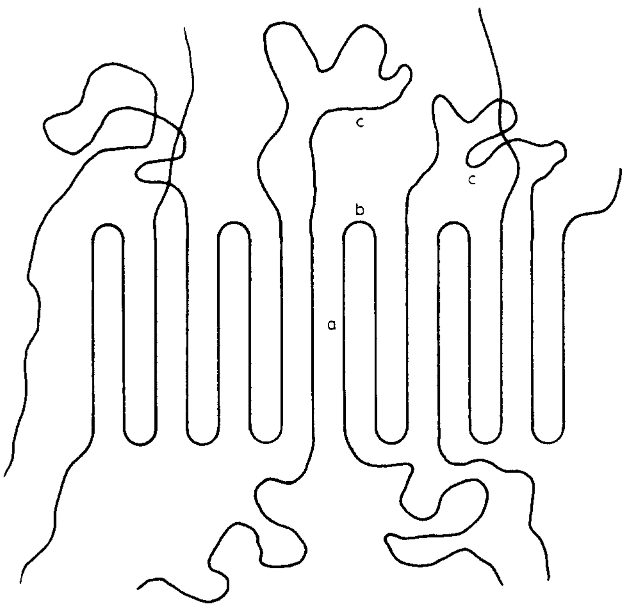

Figure 5 A schematic illustration of folded chain conformation for melt-quenched polyethylene[23]. The present work indicates that regions a (*trans* zigzag), b (sharp fold) and c (loose and long loops) contribute to peaks I, II + III, and A, respectively, in the ^{13}C CP/MAS spectra shown in *Figure 4*

Next, let us consider the case of polyethylene single crystals. As seen from ^{13}C CP/MAS n.m.r. spectra of polyethylene single crystals, the intensity of peak A decreases considerably, appearing as a shoulder in comparison with the case of melt-quenched polyethylene. This is in accord with the result that the percentage of crystallinity for polyethylene single crystals (94.1%) is considerably higher compared with melt-quenched polyethylene (70.4%). If we look carefully at the amplified spectrum of polyethylene single crystals ($M_w = 31\,000$), we can identify the small upfield peaks II and III on the main peak, for which the chemical shift positions agree approximately with those of cyclic paraffin $C_{64}H_{128}$ and melt-quenched polyethylene.‡ The signal-to-noise ratio for the upfield peaks II and III is very low as well for the case of melt-quenched PE spectrum. Nevertheless, as seen from the spectrum (C″), peak III is obviously above the noise level (N_2). Thus, the existence of peak III is apparently identified. Also, peak II is identified irrespective of the difficult case that peak II is on the foot of the intense main peak. This means that the existence of sharp-folded structure in polyethylene single crystals as well as in cyclic

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‡ We must note the previous results on ^{13}C CP/MAS n.m.r. spectra of polyethylene grown from a concentrated solution (2%) as compared with the present work (0.02%). Owing to the absence of small upfield peaks on the main peak, we concluded in the previous paper[7] that the fold carbons would not be in a sharp-folded structure with the freezing of molecular motion, but would be in the mobile state.

paraffin $C_{64}H_{128}$ can be identified by ^{13}C CP/MAS spectroscopy. It is not denied, however, that there exists a small amount of amorphous chain segments in the single crystal, as well as in the case of melt-quenched polyethylene, as is evident from the existence of peak A. By using such information about the intensity of the main peak and the small upfield peaks II and III, we can roughly estimate the stem length for polyethylene single crystals where the fractions of peaks I, II and III are about 0.94, 0.04 and 0.02, respectively. In the calculation we assume that all folds are tight folds. The *trans* zigzag methylene carbons contribute to the main peak I and the two methylene carbons (C(1), C(1')) for the sharp folded structure region to peak III. According to this assignment, the number of carbon atoms in the *trans* zigzag chain from one fold to the next is estimated to be approximately 100, and thus this leads to an estimate of the stem length being about 125 Å. This magnitude is consistent with the crystal thickness (120–150 Å) measured directly for polyethylene single crystals by electron microscopy.

Finally, it is worthy of note that ^{13}C CP/MAS n.m.r. information on the folded structure region and *trans* zigzag structure region leads to the estimation of the thickness of the stem length in polyethylene single crystals.

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