The Influence of Polytypic Structures on the Solid-state ^{13}C NMR Spectra of *n*-Alkanes

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Two polytypes for the monoclinic (M_{011}) modification of *n*-hexatriacontane (*n*-$C_{36}H_{74}$), single-layered structure Mon and double-layered structure Orth II, were studied by means of the solid-state CP/MAS ^{13}C NMR spectroscopy. The terminal methyl carbon showed clear differences in the chemical shift as well as spin-lattice relaxation time (T_1) between Mon and Orth II, in contrast to no marked difference for the other carbons.

The crystalline state of aliphatic long-chain compounds such as *n*-alkanes and *n*-fatty acids usually forms a layered structure.[1–3] Depending on the crystallization conditions, those compounds often show a variety of crystal structures, which can be categorized by the two concepts, polymorphism and polytypism.[4,5] Polymorphism refers to the structural variation within a molecular layer such as molecular inclination, conformation, and the lateral packing of hydrocarbon chains, so-called subcell.[6] Polytypism refers to the higher-order structural variation caused solely by the stacking mode of the molecular layer.[7,8] So far, two polytypic structures have been found for long-chain compounds, single-layered structure Mon and double-layered structure Orth II (Figure 1). It has been clarified that polytypism has a significant influence on thermodynamic stability,[9,10] mechanical properties,[11,12] solid-state phase-transition mechanism,[13–15] and so on.

High-resolution solid-state ^{13}C NMR spectroscopy has been used for the study on the polymorphism of *n*-alkanes. It has been clarified that the difference in subcell structure, chain inclination and dynamical properties are reflected sensitively in the chemical shifts and T_1 values of carbon atoms.[16–21] However, there is no report concerning the influence of polytypic structure on the ^{13}C NMR spectrum. Since polytypism gives rise to a large difference in lamellar interfacial structure, the methyl carbon might show some sort of difference between polytypic structures. In the previous study on *n*-$C_{36}H_{74}$, we clarified the occurrence conditions of the Mon and Orth II polytypes of the monoclinic (M_{011}) modification, which made a detailed comparison possible.[9]

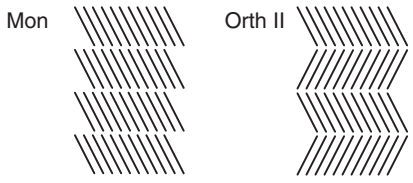

Figure 1. Two polytypes of M_{011} modification of *n*-$C_{36}H_{74}$: the single-layered structure Mon and double-layered structure Orth II.

The high-purity sample of *n*-$C_{36}H_{74}$ (>99% purity, purchased from GL Science Inc.) was used for the crystallization of the Mon and Orth II polytypes. According to the results of the previous study,[9] fine single crystals of Mon were grown in a solution whose supersaturation σ was larger than 0.30, and those of Orth II were grown under the supersaturation less than 0.16. The polytype of each powdery sample was confirmed with the IR band due to the methyl symmetric deformation around 1380 cm^{-1}.[22]

The solid-state ^{13}C NMR measurements were performed with a Chemagnetecs CMX-300 spectrometer at 75.5 MHz with a CP/MAS and a variable temperature accessory. The sample was sealed into a 5-mm bullet-type zirconium rotor and the spinning rate of rotor was set to 4 kHz. For the one-dimensional ^{13}C NMR measurements, spectrum width of 15 kHz and the number of data points of 8192 were applied. For the T_1 measurements of the terminal methyl carbon and other segments, the inverse recovery sequence (T1xcpir pulse sequence) and the Torchia sequence (T1xcp pulse sequence) were applied, respectively. The number of accumulation cycles and data points for measuring each spectrum were 32 and 4096, respectively. The $\pi/2$ pulse width was 3.50 μs. The cross-polarization (CP) contact time and the repeating time were 4.0 ms and 20 s, respectively. The signal of methyl carbons of hexamethylbenzene at 17.35 ppm was used as an external reference for chemical shifts.

The solid-state ^{13}C NMR spectra of Mon and Orth II measured at room temperature are depicted in Figure 2. Except the peak due to the methyl carbon, the two polytypes show almost identical spectra as summarized in Table 1. Reflecting the $O_\perp$ subcell structure, the peak assigned to the inner-CH_2 carbon is observed at 33.6 ppm.[19,20] The peaks due to α-CH_2 and β-CH_2 appear at 25.5 and 34.7 ppm, respectively.

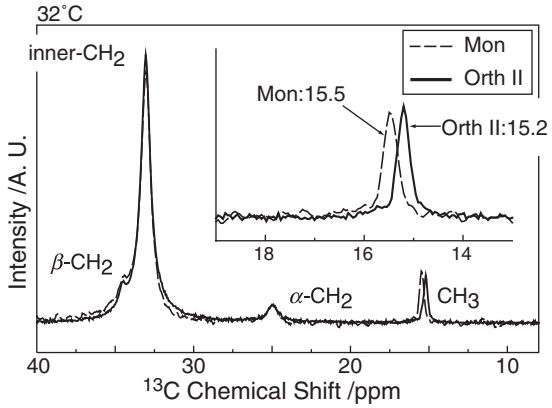

Figure 2. Solid-state ^{13}C NMR spectra of the two polytypic structures at room temperature: Solid line, Orth II; broken line, Mon.

The difference in the lamellar interface between the polytypes is clearly reflected in the chemical shift of methyl carbon. The methyl carbon gives a signal at 15.5 ppm in Mon and 15.2 ppm in Orth II, respectively. The difference in chemical

Table 1. Influence of the intra- and interlayer structural difference on the chemical shift of the inner-CH_2, α-CH_2, and terminal-CH_3 carbon peaks (abbreviated as $\delta_{\text{inner-CH}_2}$, $\delta_{\alpha\text{-CH}_2}$, and δ_{CH_3})

Polymorph (Polytype)	Subcell	$\delta_{\text{inner-CH}_2}$	$\delta_{\alpha\text{-CH}_2}$	δ_{CH_3}
Pseudohexagonal	Hex	33.66[a]	23.99[a]	14.81[a]
Triclinic	$T_{\parallel}$	34.92[a]	26.55[a]	16.02[a]
Orthorhombic	$O_{\perp}$	33.62[a]	25.59[a]	15.06[a]
Monoclinic	$O_{\perp}$	33.66[a]	25.53[a]	15.25[a]
Monoclinic (Mon)	$O_{\perp}$	33.6[b]	25.5[b]	15.5[b]
Monoclinic (Orth II)	$O_{\perp}$	33.6[b]	25.5[b]	15.2[b]

[a]VanderHart.
[b]this work.

shift is comparable to the difference observed between polymorphs, as shown in Table 1. In the previous study of VanderHart,[19] the methyl carbon of the monoclinic form showed a signal at 15.25 ppm. The specimen of the monoclinic form might have been of Orth II polytype. As can be seen in Table 1, it is now possible to distinguish the typical polymorphs of *n*-alkanes, including polytype, from the chemical shifts of *n*-alkanes.

Polytypic structures are also reflected on the spin-lattice relaxation time (T_1) of methyl carbon. As shown in Figure 3, Orth II shows longer T_1 values than Mon from the room temperature up to 70 °C. On the contrary, the internal-CH_2 carbon do not show such a clear difference. Since the methyl carbon is in the extreme narrowing limit, the longer T_1 means the larger mobility of the terminal methyl group. This agrees qualitatively with the result of our recent inelastic neutron scattering experiment that the potential barrier of the CH_3 torsion is lower by 0.4 kJ/mol in Orth II than in Mon.[23]

We consider that the local environment around the methyl group is the cause for the differences in chemical shift and T_1 of methyl carbon. The chemical shift of the methyl group has a tendency to shift to downfields as the packing of methyl groups becomes tight.[19,20] At the lamellar interface of Orth II, a methyl group is located just at the center of a dimple formed by four surrounding methyl groups of the flanked layer according to the requirement of crystal symmetry.[24] In Mon, the position of methyl group is deviated from the center along the b_s axis. As a result,

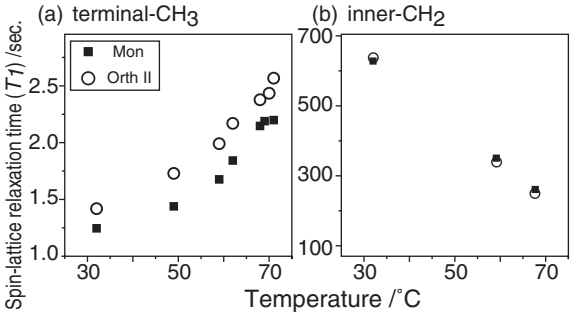

Figure 3. Temperature dependence of the spin-lattice relaxation time (T_1) of Mon (filled square) and Orth II (open circle) with respect to (a) the terminal-CH_3, and (b) inner-CH_2 component.

the distance to the nearest methyl group of the flanked layer shortens by 0.1 Å compared with that in Orth II, which may restrict the motion of methyl group. We infer that the increase in intermolecular interaction caused by the shortening results in the downfield shift and shorter T_1 values of methyl carbon in Mon.

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