were run as 20% (w/w) solutions in 1,2,4-trichlorobenzene with benzene-d_6 as the lock material. The spectra were taken on a Nicolet NT 360 WB spectrometer operating at 90.55 MHz. The probe temperature was set at 110 °C. The free induction decays were stored in 8K memory addresses, zero-filled upon processing, with a spectral window varying from 4500 to 6000 Hz. Samples were run with a 70° pulse angle and 4-s delay.

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Conformation of Cyclic Paraffins and Polyethylene in the Solid State As Studied by ^{13}C CP/MAS NMR

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ABSTRACT: ^{13}C high-resolution NMR spectra of cyclic paraffins ($C_{24}H_{48}$, $C_{28}H_{56}$, $C_{32}H_{64}$, $C_{36}H_{72}$, $C_{40}H_{80}$, $C_{48}H_{96}$, $C_{64}H_{128}$, and $C_{80}H_{160}$), *n*-paraffins (*n*-$C_{19}H_{40}$, *n*-$C_{22}H_{46}$, and *n*-$C_{32}H_{66}$), and a crystalline polyethylene were measured in the solid state. It was shown that the ^{13}C NMR resonance lines of the folded structure region and the trans zigzag structure region in the cyclic paraffins $C_{40}H_{80}$, $C_{48}H_{96}$, $C_{64}H_{128}$, and $C_{80}H_{160}$ are chemically shifted from one another and that the chemical shifts of *n*-paraffins with an all-trans zigzag form in the solid state parallel those of the trans zigzag structure region in cyclic paraffins. Their difference is 4–12 ppm. These results demonstrate that cyclic paraffins assume a crystalline conformation with the shape of two parallel straight chains bridged at both ends, producing a freezing of molecular motion. Similarly, it is shown that the ^{13}C NMR signals of the crystalline component and the other component (folded structure or noncrystalline structure) in a dilute-solution-grown crystalline polyethylene are chemically shifted from one another. In this case the latter peak appears as a high-field shoulder on the signal due to the crystalline form. Their difference is about 2.3 ppm. These results are compared with those in cyclic paraffins, and the fold structure is discussed.

Introduction

It is known from X-ray diffraction studies[1,2] that cyclic 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 1. This form is closely related to the chain-folded morphology resulting from the crystallization process in polyethylene (PE). This knowledge is very useful when attempting to provide an insight into the chain-folded conformation of PE.

Recently, high-resolution NMR in solids has become possible with the development of the cross polarization/magic angle spinning (CP/MAS) technique.[3] This new technique has been successfully applied to a wide field of chemistry as a powerful tool to obtain information about solid-state structure and dynamics on the atomic level. It provides an opportunity to obtain information about polymer chain conformation in the crystalline state, which is one of the most important problems in polymer science.

From such a viewpoint, various research groups have observed the high-resolution NMR spectra of PE's with different crystalline structures and have discussed the solid-state structure.[4-6] Earl and VanderHart[5] reported that the ^{13}C NMR resonance lines of the crystalline and noncrystalline components in polyethylene are chemically shifted from one another. Such trends are explained in terms of trans and gauche conformational effects on the chemical shifts. This leads to a description of the conformation of crystalline and noncrystalline PE's. Möller et al.[7] have employed cyclic paraffins such as $C_{24}H_{48}$, which shows a single sharp ^{13}C resonance at room temperature. However, it is too small a cyclic paraffin to obtain information about the folded structure, because $C_{24}H_{48}$ apparently is conformationally mobile at room temperature.

The main purpose of the present work is to measure high-resolution ^{13}C NMR spectra of cyclic paraffins with a wide range of carbon atoms, varying from $C_{24}H_{48}$ to $C_{80}H_{160}$, *n*-paraffins, and crystalline PE. On the basis of

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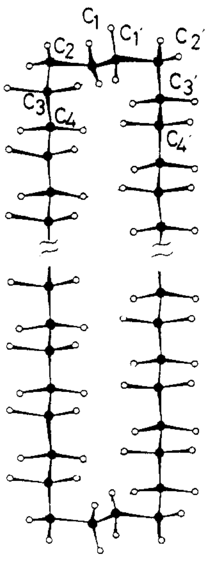

Figure 1. Schematic drawing of the conformation of a cyclic paraffin (ref 1).

these results, chain folding in PE is discussed.

Experimental Section

Materials. Cyclic paraffins ($C_{24}H_{48}$, $C_{28}H_{56}$, $C_{32}H_{64}$, $C_{36}H_{72}$, $C_{40}H_{80}$, $C_{48}H_{96}$, $C_{64}H_{128}$, and $C_{80}H_{160}$) were synthesized according to the following procedure.[8] *cis,cis*-1,5-Cyclooctadiene and *cis*-cyclooctaene, which are starting compounds for preparing cyclic paraffins, were polymerized with $WCl_6/AlEtCl_2$ (1/5 molar ratio) as catalyst in chlorobenzene at room temperature under a nitrogen atmosphere. The reaction products were precipitated into methanol and oligomers were extracted from the products by acetone/methanol (1/1 volume ratio) as solvent. The oligomer mixtures having different molecular weight were separated by GPC into pure oligomers having general formulas of $\left[CH{=}CHCH_2CH_2\right]_n$ (n = 6–9) and $\left[CH{=}CH(CH_2)_6\right]_n$ (n = 5, 6, 8, and 10) with purities higher than 90%. The pure oligomers were hydrogenated by refluxing them with twice the theoretical amount of *p*-toluenesulfonyl hydrazide in xylene for 2–3 h.[9] The hydrogenated oligomers were precipitated into methanol and washed with methanol for 4 or 5 h.

n-Paraffins (*n*-$C_{19}H_{40}$, *n*-$C_{22}H_{46}$, and *n*-$C_{32}H_{66}$) were obtained from Tokyo Kasei Co.

High-density PE ($M_w = 8.7 \times 10^4$, $M_w/M_n = 10.3$) was obtained from the Rubber and Plastics Association. It was crystallized from 2% *p*-xylene solution.

NMR Measurement. ^{13}C CP/MAS NMR spectra were recorded at 50 MHz with a JEOL FX-200 spectrometer with a CP/MAS accessory. Samples (ca. 300 mg) were contained in a bullet-type rotor and spun as fast as 3–4 kHz. Contact time was 2 ms and repetition time 5 s. Spectral width and data points were 20 kHz and 8K, respectively. Powder pattern spectra were recorded with the same instrument without the magic angle spinning. The number of accumulations was 50–2000. The ^{13}C chemical shifts were calibrated indirectly through external benzene (128.5 ppm relative to tetramethylsilane ($(CH_3)_4Si$)).

Results

^{13}C CP/MAS NMR Spectra. Traces a–h of Figure 2 show ^{13}C CP/MAS NMR spectra of a series of cyclic paraffins in the solid state. $C_{24}H_{48}$ produces a sharp single peak, while $C_{28}H_{56}$ and $C_{32}H_{64}$ both present broad single peaks. The line width of the ^{13}C signal of cyclic paraffins increases with an increase in the number of carbon atoms. On the other hand, cyclic paraffins having more than 36 carbon atoms show high-field shoulders, or small peaks, on the main peak. It is seen from these spectra that the intensity of the shoulders, or small peaks, decreases with an increase in the number of carbon atoms. (The main signal and shoulders or small peaks are designated by I, II, and III, respectively, where the identification of III for some spectra is clear.) The chemical shifts of these peaks and their differences are listed in Table I. The difference in shielding between I and II increases from 4 to 7 ppm with an increase in the number of carbon atoms, and that between I and III is about 11.5–11.8 ppm except for the case of $C_{36}H_{72}$ (8 ppm). The fraction ratio of the intensity of I, II, and III, determined from resolution of the two peaks, is as follows: 5.8:1.7:1 for $C_{36}H_{72}$, 7.2:1.8:1 for $C_{40}H_{80}$, 8.5:2.3:1 for $C_{48}H_{96}$, and 14:2.6:1 for $C_{64}H_{128}$. Thus the fraction ratio of (II + III) to I decreases with an increase in the number of carbon atoms. Traces i and j of Figure 2 show ^{13}C CP/MAS spectra of one of the *n*-paraffins considered here, *n*-$C_{32}H_{66}$, and a dilute-solution-grown crystalline PE, respectively, in the solid state. The inner methylene carbons in *n*-$C_{32}H_{66}$ appear as a sharp single peak but in crystalline PE appear as a sharp main peak

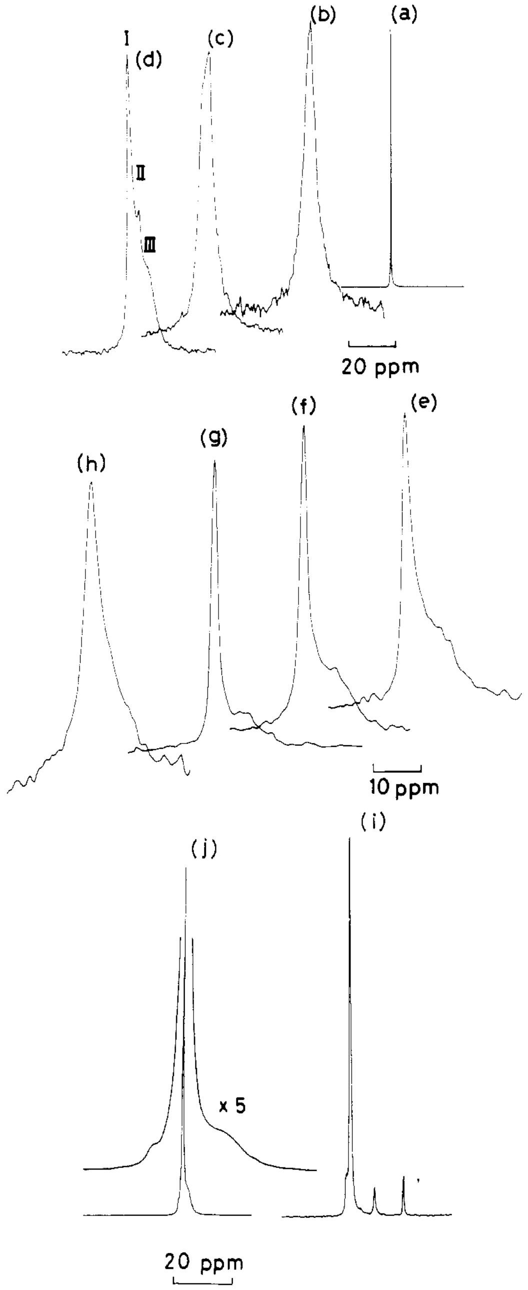

Figure 2. Observed ^{13}C CP/MAS NMR spectra of cyclic paraffins, *n*-paraffin, and polyethylene in the solid state: (a) $C_{24}H_{48}$, (b) $C_{28}H_{56}$, (c) $C_{32}H_{64}$, (d) $C_{36}H_{72}$, (e) $C_{40}H_{80}$, (f) $C_{48}H_{96}$, (g) $C_{64}H_{128}$, (h) $C_{80}H_{160}$, (i) *n*-$C_{32}H_{66}$, (j) polyethylene. I, II, and III correspond to peaks I, II, and III in the text, respectively.

Table I
Observed ^{13}C Chemical Shifts of Cyclic Paraffins, *n*-Paraffins, and Solution-Grown Polyethylene in the Solid State

	^{13}C chemical shift/ppm[a]				
sample	peak I δ_{I}	peak II δ_{II}	peak III δ_{III}	$\delta_{I} - \delta_{II}$	$\delta_{I} - \delta_{III}$
cyclic paraffin					
$C_{24}H_{48}$	30.0				
$C_{28}H_{56}$	29.7				
$C_{32}H_{64}$	30.7				
$C_{36}H_{72}$	34.0	30.0	26.0	4.0	8.0
$C_{40}H_{80}$	33.5	27.0	24.5	6.5	9.0
$C_{48}H_{96}$	33.7	27.0	22.0	6.7	11.7
$C_{64}H_{128}$	33.8	27.0	22.0	6.8	11.8
$C_{80}H_{160}$	34.0	~27	~22	~7	~12
n-paraffin					
n-$C_{19}H_{40}$	33.4				
n-$C_{22}H_{46}$	33.0				
n-$C_{32}H_{66}$	33.0				
polyethylene	33.0	30.7		2.3	

[a] Relative to $(CH_3)_4Si$.

Table II
Observed ^{13}C Chemical Shielding Anisotropy $\Delta\sigma$ of Cyclic Paraffins, *n*-Paraffins, *n*-Paraffin *n*-$C_{32}H_{66}$, and Polyethylene

sample	$\Delta\sigma$/ppm[a]
$C_{24}H_{48}$	-7
$C_{40}H_{80}$	-20
$C_{48}H_{96}$	-24
n-$C_{32}H_{66}$	-22
polyethylene	-25

[a] $\Delta\sigma = \sigma_{11} - (\sigma_{22} + \sigma_{33})/2$, which was determined from the theoretical powder pattern spectrum convoluted with a Lorentzian broadening function.[19]

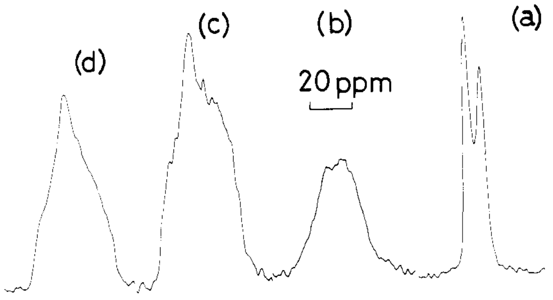

Figure 3. Observed powder pattern spectra of cyclic paraffins, *n*-paraffin and polyethylene: (a) $C_{24}H_{48}$, (b) $C_{40}H_{80}$, (c) *n*-$C_{32}H_{66}$, (d) polyethylene.

having a small high-field shoulder. These results agree with those reported by Earl and VanderHart[4] and Kitamaru et al.[6] on melt-crystallized PE. The two peaks correspond to those observed in cyclic paraffins and therefore the main peak and shoulder are designated by I and II, respectively, as in the case of cyclic paraffins. The chemical shifts of these peaks and their difference are listed in Table I. The difference in shielding between I and II is about 2.3 ppm and agrees with the value of 2.36 ppm reported by Earl and VanderHart[4] and that of 2.3 ppm by Kitamaru et al.[6] They should be considerably smaller than those found for cyclic paraffins.

Powder Pattern Spectra. Figure 3 shows the powder pattern ^{13}C NMR spectra of the cyclic paraffins $C_{24}H_{48}$ and $C_{40}H_{80}$, the *n*-paraffin *n*-$C_{32}H_{66}$, and PE. $C_{24}H_{48}$ gives two peaks representing the axially symmetric chemical shielding tensor: one peak corresponds to $\sigma_{\perp}$ $(=\sigma_{11} = \sigma_{22})$ and the other to $\sigma_{\parallel}$ $(=\sigma_{33})$, where $\sigma_{\perp}$ and $\sigma_{\parallel}$ denote shielding perpendicular and parallel to the symmetry axis, respectively, and σ_{ii} is a principal shielding element.[3] This signal is different from that of a typical axially symmetric powder pattern. On the other hand, PE appears as a typical tent-like powder pattern.

From these patterns the determined chemical shielding anisotropy $\Delta\sigma$ $(=\sigma_{11} - (\sigma_{22} + \sigma_{33})/2)$ is given in Table II. The value of $\Delta\sigma$ for $C_{24}H_{48}$ is very small compared with those for the other compounds. The value of -25 ppm for PE agrees with that of -25.7 ppm reported by Urbino and Waugh[20] and of -25.65 ppm given by VanderHart.[5] The values for *n*-paraffin and cyclic paraffin are somewhat smaller than that of PE. However, the powder pattern spectra of the former are not defined and so the experimental error is great. Thus, we cannot discuss in detail the difference in $\Delta\sigma$ between *n*-$C_{32}H_{66}$, $C_{40}H_{80}$, $C_{48}H_{96}$, and PE.

Discussion

As shown by X-ray diffraction studies,[1,2] cyclic paraffins of long chain lengths take a folded structure (as shown in Figure 1). Thus it should be possible to obtain different chemical shifts for the methylene carbons arising from the folded and trans zigzag structures by means of ^{13}C CP/MAS NMR. The corresponding peaks are observed in all the cyclic paraffins with the exceptions of $C_{24}H_{48}$, $C_{28}H_{56}$, and $C_{32}H_{64}$. On the other hand, the observed sharp single signals for $C_{24}H_{48}$, $C_{28}H_{56}$, and $C_{32}H_{64}$ suggest that they have a given molecular structure without the freezing of molecular motion. In the powder pattern of $C_{24}H_{48}$ the presence of two peaks suggests that molecular motion of the paraffin is anisotropic because the principal shielding tensor elements, $\sigma_{\perp}$ and $\sigma_{\parallel}$, are observed. (If the motion is isotropic, the axially symmetric tensor components are not observed.) This implies that all of the methylene carbons within the cyclic paraffin are exhibiting identical gauche–trans populations with fast transitions between the conformers in the ring plane and so the transition occurs anisotropically. As the number of methylene carbons increases, the cyclic paraffins may take any specified cyclic structure due to the freezing of molecular motion. This is verified by the observation of peaks I, II, and III.

Let us discuss the origin of the appearance of peaks II and III. The three peaks I, II, and III can be assigned by means of the γ-gauche effect concept.[11,14] The methylene carbon appears at high field by 4–6 ppm if any carbon atom three bonds away is in a gauche, rather than a trans, conformation. This has been justified by both experiment and theory and been successfully used to predict the chemical shift of each stereosequence of polymers.[15] From this point of view, it is shown that peaks I, II, and III can be assigned to the methylene carbons arising from the trans zigzag structure region and folded structure region, respectively. These can be more effectively interpreted in the following manner. As shown in Figure 1, the cyclic paraffins crystallize in a conformation characterized by two parallel all-trans (T), planar zigzag strands connected by two GGTGG loops. If this conformation is dynamically rigid in the solid state at room temperature, thus based on the γ-gauche 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' 2γ effects upfield from the all-trans carbons and loop carbons C_2,C_2', whose next-nearest-neighbor bonds are also both trans. Thus, for $C_{36}H_{72}$ we would expect 24 carbons with 0γ's, 8 carbons with 1γ, and 4 carbons with 2γ's, leading to a 6:2:1 ratio of peaks, each separated by a γ-gauche effect. Similarly, for $C_{40}H_{80}$ the ratio is 7:2:1, for $C_{48}H_{96}$ 9:2:1, and for $C_{64}H_{128}$ 13:2:1. To estimate the chemical shift position for these peaks, we chose, as an example, -4 to -6 ppm as γ.[5,15] Thus, for example, for

$C_{36}H_{72}$, of which the spectrum has clearly peaks I, II, and III, we could obtain the values of 34, 28–30, and 22–26 ppm for peaks I (0γ), II (1γ), and III (2γ), respectively. On this basis we would interpret the spectrum of $C_{36}H_{72}$ as consisting of peaks I (34 ppm), II (30 ppm), and III (26 ppm) in the expected intensity ratio of 6:2:1 as compared with the observed ratio of 5.8:1.7:1. This interpretation appears to be at least as consistent with the spectra as our above assignment I and II plus III and certainly makes more conformational sense in terms of γ-gauche effect in hydrocarbon paraffins. Similarly, we would interpret the spectra of $C_{40}H_{80}$, $C_{48}H_{96}$, and $C_{64}H_{128}$ in the same manner.

Next, we consider the ^{13}C chemical shift for peak I in cyclic paraffins and *n*-paraffins. The ^{13}C chemical shifts for $C_{24}H_{48}$, $C_{28}H_{56}$, and $C_{32}H_{64}$ appear at higher field by about 3–4 ppm than those for $C_{36}H_{72}$, $C_{40}H_{80}$, $C_{48}H_{96}$, $C_{64}H_{128}$, $C_{80}H_{160}$, and *n*-paraffins as shown in Table I. This can be interpreted in the following manner. $C_{24}H_{48}$, $C_{28}H_{56}$, and $C_{32}H_{64}$ apparently are conformationally mobile at room temperature as mentioned above. Therefore, for example, for $C_{24}H_{48}$ we would expect each carbon to resonate $\Delta\sigma = [12(0\gamma) + 8(1\gamma) + 4(2\gamma)]/24 = (2/3)\gamma$ upfield from the internal methylene resonances in the all-trans cyclic paraffins or *n*-paraffins, and if $\gamma = -4$ to -6 ppm, $\Delta\sigma$ becomes -2.7 to -4 ppm. This is in good agreement with the observation. Similarly, we would interpret the results of $C_{28}H_{56}$ and $C_{32}H_{64}$ in the same manner. To prove further the origin of such chemical shift behavior, theoretical calculation of the ^{13}C chemical shifts, based on the molecular electronic structure obtained from quantum chemical methods,[16] is necessary. Such an attempt is in progress and will be published soon.

Therefore, the above-mentioned results show that the observed ^{13}C shifts of cyclic paraffins with longer chain lengths provide useful information about chain folding in PE. From this point of view, we consider the ^{13}C chemical shifts of dilute-solution-grown crystalline PE in the solid state. As shown in Table I, the chemical shift of peak I in PE nearly agrees with those of cyclic paraffins, which assume an all-trans zigzag chain form in the crystalline state, as indicated by X-ray diffraction. This shows that peak I in PE may be ascribed to the trans zigzag structure. On the other hand, peak II in PE appears at lower field by 2–5 ppm than that observed in cyclic paraffins. This indicates that the methylene carbons which contribute to the appearance of peak II are undergoing rapid transitions between the conformers, which is contrary to the behavior of the trans zigzag structure region. As discussed by Earl and Vanderhart,[4] we can obtain information about trans–gauche populations from the position of the chemical shift, δ_{II}, for peak II by using

$$\delta_{II} = \delta_0 - 2\gamma f_g \qquad (1)$$

where f_g is the equilibrium fraction of gauche bonds, δ_0 is the chemical shift for peak I in cyclic paraffins and *n*-paraffins or that for the all-trans zigzag structure region in PE, and the value of γ is attributed entirely to the trans to gauche change. At room temperature the probability that any internal bond in a long *n*-paraffin or PE chain in the liquid state is gauche (+ or −) is 0.357 (corresponding to the energy difference between the gauche and trans state $\Delta E = 500$ cal/mol). Thus, each carbon experiences $2(0.357) \times \gamma = 0.714$ γ-gauche interactions and would be expected to resonate 2.9–4.3 ppm upfield from its solid-state, all-trans conformation. We would expect the noncrystalline or fold carbons in PE to resonate upfield from the crystalline carbons by the same amount if they were conformationally amorphous. However, if the fold carbons in PE are in a sharp-folded structure in a lozenge-shaped PE with the freezing of molecular motion, they resonate about 5–10 ppm upfield from the all-trans carbons as shown in the case of cyclic paraffins. On the other hand, the observed shift is 2.3 ppm. This shows that the fold carbons are not in a sharp-folded structure with the freezing of molecular motion but are in the mobile state with slightly less gauche character than truly amorphous or molten PE. Thus, it seems that the above-mentioned conclusion conflicts with the result[18] predicting a sharp-folded structure in a lozenge-shaped PE single crystal grown from solution.

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Registry No. PE, 9002-88-4; *c*-$C_{36}H_{72}$, 297-50-7; *c*-$C_{24}H_{48}$, 297-03-0; *c*-$C_{28}H_{56}$, 297-24-5; *c*-$C_{32}H_{64}$, 297-39-2; *c*-$C_{40}H_{80}$, 297-54-1; *c*-$C_{48}H_{96}$, 36355-90-5; *c*-$C_{64}H_{128}$, 91686-93-0; *c*-$C_{80}H_{160}$, 63217-77-6; *n*-$C_{22}H_{46}$, 629-97-0; *n*-$C_{19}H_{40}$, 629-92-5; *n*-$C_{32}H_{66}$, 544-85-4.

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