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# Noncrystalline Contents in Linear Polyethylene Samples, Crystallized from the Melt and Dilute Solution as Revealed by Proton Dipole Decoupled/Magic Angle Sample Spinning $^{13}C$ NMR

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## Summary

It is certified from identification of a chemical shift coinciding with $\sigma_{iso}$, a motionally averaged chemical shift observed for this polymer in solution that noncrystalline contents in both melt- and solution-grown crystals are in a similar chain conformation to that in the melt or solution. Furthermore, examination of magnetic relaxation times of the $\sigma_{iso}$ line reveals that the local chain dynamics of the noncrystalline content are the same for both samples while a long range chain motion for the solution-crystal is somewhat restricted.

## Introduction

Since lozenge-shaped crystallites were observed for solution-grown polyethylene(Till 1957, Keller 1957, Fischer 1957), extensive studies have been carried out of the conformation and mode of molecular chains to participate in such crystallites with different techniques.* However, the final conclusion has been suspended because of the lack of a technique which could detect the chain conformation in noncrystalline materials in an order of molecule. Rather recently, however, new approaches to this problem have appeared with use of neutron scattering that principally can detect the chain conformation(Schelten et al. 1974). In relation to the chain conformation in solution-grown polyethylene, for instance, the mode of a molecular chain to participate in a given crystallite has been evaluated(Stamm et al. 1979, Yoon and Flory 1979, Sadler and Keller 1977). It is also concluded that the mean square radius of gyration of molecular chains in bulk-crystals is the same as in the melt (Stamm et al. 1979). These investigations have again stimulated researches of this problem with different techniques.

On the other hand, solid-state high-resolution $^{13}C$ nmr that has recently been developed can detect the chemical shift of methylene carbon in solid polyethylene as a tensor quantity that is definable for each local chain conformation. Therefore, information of molecular chains in an order of molecule is expected by this technique, together with information of chain dynamics through examination of magnetic relaxation

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* See, for instance, Faraday Discussion of the Chemical Society, No.68 "Organization of Macromolecules in the Condensed Phase", Roy. Soc. Chem., London, 1979

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times. This paper reports preliminary results of melt- and solution-grown polyethylene samples.

## Experimentals

**Samples** Fractionated and unfractionated samples of linear polyethylene were used. **Bulk-Crystals:** Molecular weight fractions with $\bar{M}_v$ of 31,800 and 248,000 were isothermally crystallized at 130°C for 2-4 weeks from the melt after melting at 160°C for 5h under vacuum. An unfractionated sample with $\bar{M}_v$ of $3\times10^6$ was isothermally crystallized at 129°C for 23 days after melting at 200°C for 1h under vacuum. **Solution-Crystal:** A molecular weight fraction with $\bar{M}_v$ of 106,000 was isothermally crystallized at 85°C for 24h from 0.08% toluene solution.

**$^{13}C$ nmr** Solid state $^{13}C$ nmr was performed with JEOL JNM FX-100 under a static field of 2.37T; Larmor frequencies of $^{13}C$ and $^{1}H$ are 25.05 and 99.61 MHz, respectively. Field strengths of $H_1$ were 6.0 and 1.5 mT for $^{13}C$ and $^{1}H$, respectively. The magic angle sample spinning was conducted throughout this work by the use of an Andrew type rotor of poly(chlorotrifluoroethylene) at a spinning rate of 3.2-3.5 kHz. The pulse sequences utilized are described in appropriate places of the text. $^{1}H$ decoupling of a field strength of 1.5 mT was only added for data-sampling in all sequences. The chemical shift was calibrated with use of $CH_2$ line of adamantane with a chemical shift of 38.7 ppm from tetramethylsilane.

## Results and Discussion

**Indentification of $\sigma_{ave}$ and $\sigma_{iso}$** Fig. 1 shows the DD/MASS $^{13}C$ nmr spectra of the bulk- and solution-crystals obtained by pulse sequences of $(\pi/4\text{-}1000s)_{64}$ and $(\pi/4\text{-}750s)_{84}$, respectively. These spectra are thought to reproduce completely contributions from all components in the structure.* The spectrum of the bulk-crystal evidently consists of two separable lines at chemical shifts of 34 and 32 ppm; the former coincides with $\sigma_{ave}$ ($=1/3\ \mathrm{Tr}(\boldsymbol{\sigma})$), the average of diagonal elements of the chemical shift tensor for trans-trans chain conformation (Fyfe et al. 1978, Earl and VanderHart 1979, Schröter and Posern 1981), and the latter coincides with $\sigma_{iso}$, a motionally averaged value observed for this polymer in solution. Hence, it is evident that the bulk-crystal contains a noncrystalline content, the chain conformation of which is similar to that in the melt or solution. On the other hand, the existence of $\sigma_{iso}$ in the spectrum of the solution-crystal is somewhat vague, though it may be seen as a shoulder at 32 ppm. Since $\sigma_{iso}$ represents noncrystalline contents in partially crystalline polyethylene, $T_1$'s at room temperature are

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* Since $T_1$ of the rigid crystalline component of this polymer is to be about 200-300s (Schröter and Posern 1981), the waiting times longer than 750s (at least 2.5 times $T_1$) are enough for the equilibrium magnetization to recover more than 98% after each $\pi/4$ pulse. Furthermore, since the cross-polarization which may predominantly enhance the $^{13}C$ magnetization of rigid components is not used here, contributions from the mobile noncrystalline component are thought to be fully reproduced.

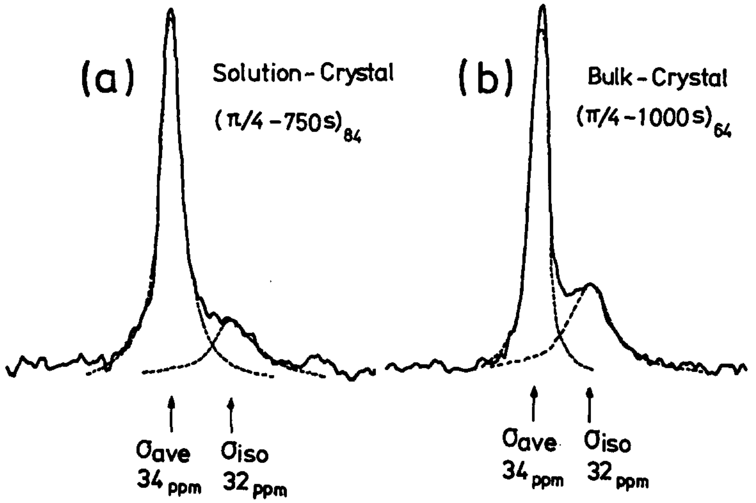

Fig. 1 DD/MASS $^{13}$C nmr spectra of polyethylene at room temperature. (a) the solution-crystal with $\bar{M}_v$ of 106,000. (b) the bulk-crystal with $\bar{M}_v$ of 3x10$^6$. Pulse sequences are described in each spectrum. Dotted lines indicate constituent lines decomposed with a curve resolver.

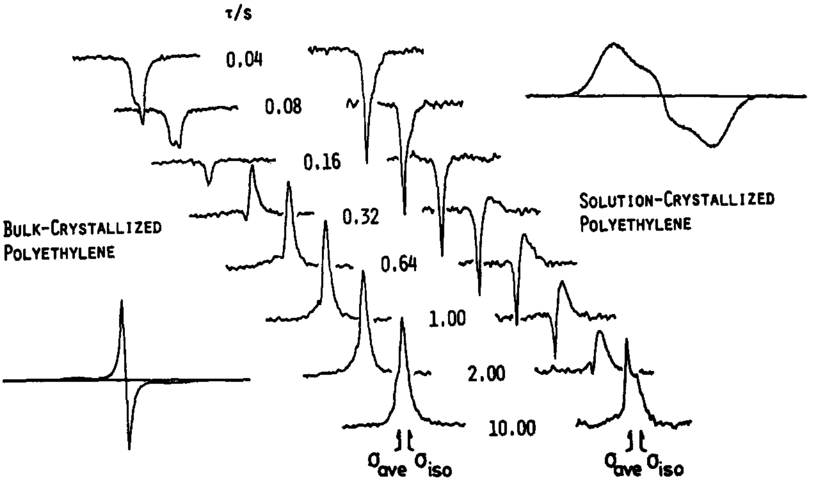

Fig. 2 Partially relaxed DD/MASS $^{13}$C nmr spectra obtained by $(\pi-\tau-\pi/2)_x$ sequences with different τ's, together with $^1$H broad-line spectra of the bulk- and solution-crystals. Samples are the same as for Fig.1.

expected to be 0.2-0.3s from a scalar decoupled $^{13}$C nmr where only the rubbery component is detected(Kitamaru 1982). Furthermore, the $T_1$ of the rigid crystalline component which contributes to $\sigma_{ave}$ is to be 200-300s(Schröter and Posern 1981). Accordingly, the existence of a noncrystalline content that contributes to $\sigma_{iso}$ can be judged by examining partially relaxed spectra obtained by a sequence with a shorter waiting time $(\pi-\tau-\pi/2-10s)_x$ where only contributions of components with $T_1$'s shorter than 10s appear. Fig. 2 shows such partially relaxed spectra with different $\tau$'s together with $^1$H broad-line spectra of both samples. Here, the existence of the $\sigma_{iso}$ line and faster recovery of the magnetization are evidently confirmed for both samples. See, for instance, the spectra of the solution-crystal at $\tau$=1.00 and 2.00s. At $\tau$=1.00s the magnetization of $\sigma_{iso}$ has already recovered in the positive direction while that of $\sigma_{ave}$ is still in the negative direction. At $\tau$=2.00s only $\sigma_{iso}$ is detected in the positive direction.

Based on the existence of both $\sigma_{ave}$ and $\sigma_{iso}$ lines, each spectrum in Fig. 1 was decomposed into two Lorentzians as shown by dotted lines in each spectrum. The integrated fraction of the $\sigma_{ave}$ line is in accordance with the crystalline fraction of each sample estimated from density measurements as shown in Table 1. Hence, it is evident that the $\sigma_{ave}$ and $\sigma_{iso}$ are contributed from the crystalline and the entire noncrystalline components. This suggests that the entire noncrystalline component of both samples is in a similar local chain conformation to that in the melt or solution.

$^{13}$C magnetic relaxation times As was pointed out by Schröter and Posern(1981), the $\sigma_{ave}$ line comprises two components with $T_1$'s of about 1-2s and 300s whereas the $\sigma_{iso}$ line comprises one component with a much shorter $T_1$. Since it is difficult at present to measure exactly such a longer $T_1$ as 300s, we have estimated only $T_1$'s shorter than at least 10s with a pulse

TABLE I

Spin-lattice relaxation times of linear polyethlene samples obtained by DD/MASS $^{13}$C NMR$(\pi-\tau-\pi/2-10s)_n$ and $^1$H scalar-decoupled $^{13}$C NMR at room temperature

| | crystalline fraction | | $T_1$/s | |
|---|---|---|---|---|
| Samples | $(1-\lambda)_d$ 1) | $(1-\lambda)_\sigma$ 2) | $\sigma_{ave}$ 3) | $\sigma_{iso}$ |
| Bulk-Crystal | | | | |
| fractionated | | | | |
| $\bar{M}_v$= 31,800 | 0.922 | —— | 1.0 | 0.23 |
| $\bar{M}_v$=248,000 | 0.761 | —— | 3.6 | 0.26<br>(0.20) 4) |
| unfractionated | | | | |
| $\bar{M}_v$=3x10$^6$ | 0.620 | 0.61 | 1.6 | 0.23 |
| Solution-Crystal | | | | |
| $\bar{M}_v$=106,000 | 0.825 | 0.78 | 2.0 | 0.23 |

1. Crystalline fraction from density measurements. 2. Integrated fraction of $\sigma_{ave}$ line in the total spectrum. 3. Among $T_1$'s of $\sigma_{ave}$, $T_1$'s shorter than 10s are detected. 4. $T_1$ estimated from scalar-decoupled $^{13}$C nmr.

sequence $(\pi-\tau-\pi/2-10s)_x$. The data of samples with different molecular weights and modes of crystallization are filed in Table 1. As can be seen, the $T_1$'s of $\sigma_{iso}$ are virtually equivalent for all samples regardless of molecular weights and modes of crystallization.* These $T_1$'s are in good accordance with $T_1$'s obtained by a scalar-decoupled $^{13}C$ nmr for this polymer at room temperature. This coincidence is meaningful because it suggests that all noncrystalline contents can be detected also by the scalar-decoupled $^{13}C$ nmr at least at room temperature. In any case, it is concluded that the entire noncrystalline content in crystalline polyethylene samples is not only in a chain conformation similar to that in the melt but also it is associated with an equivalent spin-lattice relaxation time, whether they are crystallized from the melt or dilute solution. However, this does not necessarily mean that the chain dynamics of the noncrystalline content are the same independent of the morphology. See, for instance, the $^1H$ broad-line spectra of the bulk- and the solution-crystal shown in Fig. 2. The linewidth of the noncrystalline component of the solution-crystal is much wider than that of the bulk-crystal.** It is also confirmed that the linewidth of scalar-decoupled $^{13}C$ nmr spectrum of the solution-crystal is much wider than that of the bulk-crystal. These results suggest that the noncrystalline content is associated with an equivalent $T_1$ but different $T_2$'s depending on the morphology of samples; the $T_2$ of the solution-crystal is much shorter than that of the bulk-crystal.

In regard to shorter $T_1$'s of $\sigma_{ave}$ in an order of 1-3s, they will stem from some mobility within the crystalline region, because the integrated fraction of the $\sigma_{ave}$ line coincides with the crystalline fraction estimated from density measurements for both samples. It should be assumed that such a chain motion as 180°-jump rotation of crystalline sequences somewhat occurs at room temperature, by the anology of the case of n-hydrocarbons prior to melting(Strobl 1977).

Chain dynamics of noncrystalline contents The noncrystalline contents of the bulk- and solution-crystals are associated with an equivalent $T_1$ and different $T_2$'s. This apparently contradicts the suggestion from the single-correlation-time theory(Kubo and Tomita 1954, Solomon 1955) where the internuclear vector connecting coupled $^{13}C$ and $^1H$ is assumed to fluctuate spherically at random with one correlation time. So far as we persist in this theory, this contradiction cannot be solved even if a wide distribution in the correlation time is introduced. However, as will be discussed in detail elsewhere, if we assume plural correlation times at least more than three, this contradiction is easily solved and important information of the chain motion is obtainable(Kitamaru et al. 1982).

The equivalent $T_1$ of $\sigma_{iso}$ for both bulk- and solution-crystals indicates a similar local chain motion of the noncrystalline contents in addition to a similar local chain con-

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* Such an independence of $T_1$'s on morphology of samples is also confirmed by Komoroski and Mandelkern(1977) for $T_1$'s obtained by a scalar-decoupled $^{13}C$ nmr.

** For detailed analysis of the broad-line nmr spectrum of this polymer, see the article by Kitamaru and Horii(1978).

formation to those in the melt. Different $T_2$'s indicate a difference in a long range chain motion between two samples; the long range motion of noncrystalline molecular chains in the solution-grown sample is restricted because the both ends of chains are terminated by crystalline sequences in a given crystallite.

It is proposed from neutron scattering analysis of solution-grown samples that a molecular chain participates repeatedly in a given crystallite, forming "a stacked sheet" in the direction parallel to the (110) crystal plane(Stamm et al. 1979). Regardless of validity of this stacked model, if a molecular chain is assumed to participate in a given crystallite with a thickness of about 100Å, noncrystalline sequences in samples with a crystalline fraction of 0.8 must consist of methylene sequences of about 20 $CH_2$ repeating units, both ends of which are terminated with crystalline sequences. How are the conformation and dynamics of such a short noncrystalline sequence? It is significant that such a short methylene sequence can involve rather variable chain conformation as has been suggested by this nmr work.

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