

## Phase Structure and Molecular Mobility of Polyethylene Fibers by Broad-Line NMR Spectroscopy

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*Received May 15, 1977*

The phase structure of polyethylene filaments with different draw ratios is studied by broad-line NMR spectroscopy. The broad-line spectrum is analyzed in terms of contributions from three regions; a crystalline region (broad component), a noncrystalline region that has a liquidlike character (narrow component), and an intermediate region (medium component).

It is found that the mass fraction and molecular mobility of each region depend greatly on the degree of drawing.

- (1) The broad and medium components increase with decreasing narrow component as the degree of drawing increases.
- (2) The molecular mobility of the medium component decreases greatly with increasing degree of drawing.
- (3) The narrow component diminishes but a minor component with liquidlike mobility remains even at high degrees of drawing.

Such a change in the three components of spectra upon drawing is also reflected in the swelling effects in non-protonated solvent such as  $\text{CCl}_4$ . The results for such three components are discussed in relation to the morphological phase structure of samples.

### INTRODUCTION

Crystalline polymers are generally transformed into the so-called fiber structure by uniaxial stretching at temperatures between the glass and melting temperatures of the polymers. In such fiber structures X-ray diffraction and optical birefringence analyses reveal that molecular chains in both of the crystalline and amorphous regions are preferentially oriented parallel to the stretching direction. However, the detailed phase structure of those remains obscured, although it is of very importance in relation to the tensile and dyeing properties in the practical use.

We have shown that a refined broad-line NMR analysis renders important information of the phase structure in terms of molecular mobility for linear polyethylene samples. It was found that the phase structure of polyethylene depends greatly on the molecular weight as well as the crystallization modes, including crystallization from the pure melt and from dilute solution.<sup>1-4)</sup> For drawn polyethylene fibers, Fischer *et al.*<sup>5)</sup> have studied the effects of annealing and stress on the phase structure by analyzing the broad-line NMR spectrum. In this paper the NMR spectra of polyethylene fibers drawn to different degrees are analyzed over a very wide range of temperatures. The results serve to elucidate the effects of drawing on the phase structure and temperature dependence thereof.

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## EXPERIMENTAL

## Samples

A commercial whole polymer Sholex 6009M from Japan Olefin Chem. Ltd. was used as starting material. It had a viscosity-average molecular weight of  $8.0 \times 10^4$ . The polymer was extruded out through an orifice 2.0-mm diameter at  $220^\circ\text{C}$  by a spinning apparatus equipped with a screw of 15-mm diameter and wound up on a cylindrical bobbin at room temperature with a draft ratio of about 17. The filaments obtained were then drawn to different degrees with a continuous drawing machine in polyethylene glycol bath at  $100^\circ\text{C}$ . The samples are characterized by draw ratio, defined to be ratio of the drawn length to the original.

## Estimation of Molecular Orientation

The degree of orientation for molecular chain vectors can be described by the orientation factor<sup>6)</sup>

$$f = (3\langle \cos^2 \varphi \rangle - 1)/2 \quad (1)$$

Here  $\varphi$  is an angle of molecular chain vector to the stretching direction. The quantity associated with the crystalline region was evaluated by an X-ray diffraction scanning using a relation

$$f_c = \int_0^{\pi/2} I_{hkl}(\varphi) \cdot \frac{3\cos^2\varphi - 1}{2} \cdot \sin\varphi d\varphi / \int_0^{\pi/2} I_{hkl}(\varphi) \sin\varphi d\varphi \quad (2)$$

Here  $I_{hkl}(\varphi)$  is the diffraction intensity from the  $(hkl)$  crystal plane at an angle  $\varphi$  to the stretching direction. For samples with higher draw ratios, the diffraction from (002) crystal plane was used. For samples with draw ratios lower than 2 times, since the (002) diffraction could not be detected with sufficient precision, the orientation factors for  $a$  and  $b$  axes of the crystal lattice were first evaluated with diffractions from (200) and (020) crystal planes, respectively, and then the quantity for the molecular chain axis was obtained using the relation that the summation of all quantities for the  $a$ ,  $b$ , and  $c$  axes of the crystal lattice is zero.

The orientation factor for the amorphous molecular chains  $f_a$  was evaluated from a birefringence measurement with the  $f_c$  and the degree of crystallinity from density measurement, using the relation<sup>7)</sup>

$$\Delta n = X_c f_c \Delta_c^\circ + (1 - X_c) f_a \Delta_a^\circ \quad (3)$$

Here, the intrinsic configurational birefringence is neglected.  $\Delta n$  designates the birefringence measured,  $X_c$  the volume fraction of the crystalline material.  $\Delta_c^\circ$  and  $\Delta_a^\circ$  are the theoretical quantities<sup>8)</sup> for perfectly oriented crystalline and amorphous molecular chains, respectively;  $\Delta_c^\circ = 0.0572$ ,  $\Delta_a^\circ = 0.0428$  are adopted.

## Spectrometry and Analysis

The first derivative NMR spectrum was obtained over a wide range of temperature  $-80$ — $+40^\circ\text{C}$  for drawn polyethylene filaments randomly packed into a glass tube 18-mm diameter with a JNM-PW-60 NMR Spectrometer (JEOL Ltd.). The magnetic field

slowly swept was modulated at 35 Hz and amplitude of 0.4 G under a constant sub-field with a frequency of 60 MHz.

The spectrum observed was analyzed by a technique<sup>1-4)</sup> based on the method of Bergmann and Nawotki,<sup>9-12)</sup> decomposing into three parts; broad, medium and narrow components. The spectrum observed as a function of the field intensity was considered to be a spectrum  $y_{\text{cal}}$  constructed from three terms,

$$y_{\text{cal}}(H) = w_b y_b(H, \Delta H_b) + w_m y_m(H, \beta_{mg}, \beta_{ml}) + w_n y_n(H, \beta_n, H_m) \\ w_b + w_m + w_n = 1 \quad (4)$$

Here, the field intensity  $H$  is expressed by the deviation from the resonance center for convenience.  $y_b$ ,  $y_m$ , and  $y_n$  are the elementary spectra for the broad, medium and narrow components, respectively.  $w_b$ ,  $w_m$ , and  $w_n$  designate the respective mass fractions. The parameters  $\Delta H_b$ ,  $\beta_{mg}$  and  $\beta_{ml}$ ,  $\beta_n$  designate the respective elementary line shapes and  $H_m$  is the amplitude of modulation employed. All of the elementary spectra are normalized as

$$\int_{-\infty}^{\infty} \int_{-\infty}^H y_i dH = 2, \quad i = b, m, \text{ or } n \quad (5)$$

The  $y_b$  was obtained by changing the line-width of the spectrum at  $-160^\circ\text{C}$  for the  $\text{HNO}_3$ -treated polyethylene with a very high crystallinity but keeping the shape unchanged.  $\Delta H_b$  designates the line-width of the  $y_b$  thus constructed.

The  $y_m$  was taken as the product of Gaussian and Lorentzian distribution functions in integrated form.

$$y_m(H, \beta_{mg}, \beta_{ml}) = N \frac{\partial}{\partial H} [\exp(-H^2/2\beta_{mg}^2) \cdot \beta_{ml}^2 / (\beta_{ml}^2 + H^2)] \quad (6)$$

Here  $N$  is the normalization factor and  $\beta_{mg}$  and  $\beta_{ml}$  designate the broadness of the Gaussian and Lorentzian components, respectively.

The  $y_n$  was taken as a Lorentzian. However, a distortion of the line shape from the true Lorentzian due to the amplitude of modulation was theoretically taken into account, since it becomes enhanced as the line shape narrows. Accordingly, the  $y_n$  was taken as a function of the modulation amplitude  $H_m$  and  $\beta_n$  that designates the broadness of the Lorentzian.

$$y_n(H, \beta_n, H_m) = 2^{3/2} (\pi \beta_n H_m)^{-1} \cdot \frac{\zeta^{1/2} - \xi^{1/2}}{(\xi \zeta)^{1/2} [(\xi \zeta)^{1/2} + \eta]^{1/2}} \quad (7)$$

with

$$\xi = (H - H_m)^2 / \beta_n^2 + 1 \\ \eta = (H^2 - H_m^2) / \beta_n^2 + 1 \\ \zeta = (H + H_m)^2 / \beta_n^2 + 1$$

With use of the elementary spectra mentioned above the parameters in Eq. (4) were determined so as to minimize the sum  $\Phi$  of squares of the difference between the observed and calculated spectra over the full range of  $H$ ;

$$\Phi = \sum_H [y_{\text{obs}}(H) - Ay_{\text{cal}}(H)]^2 \quad (8)$$

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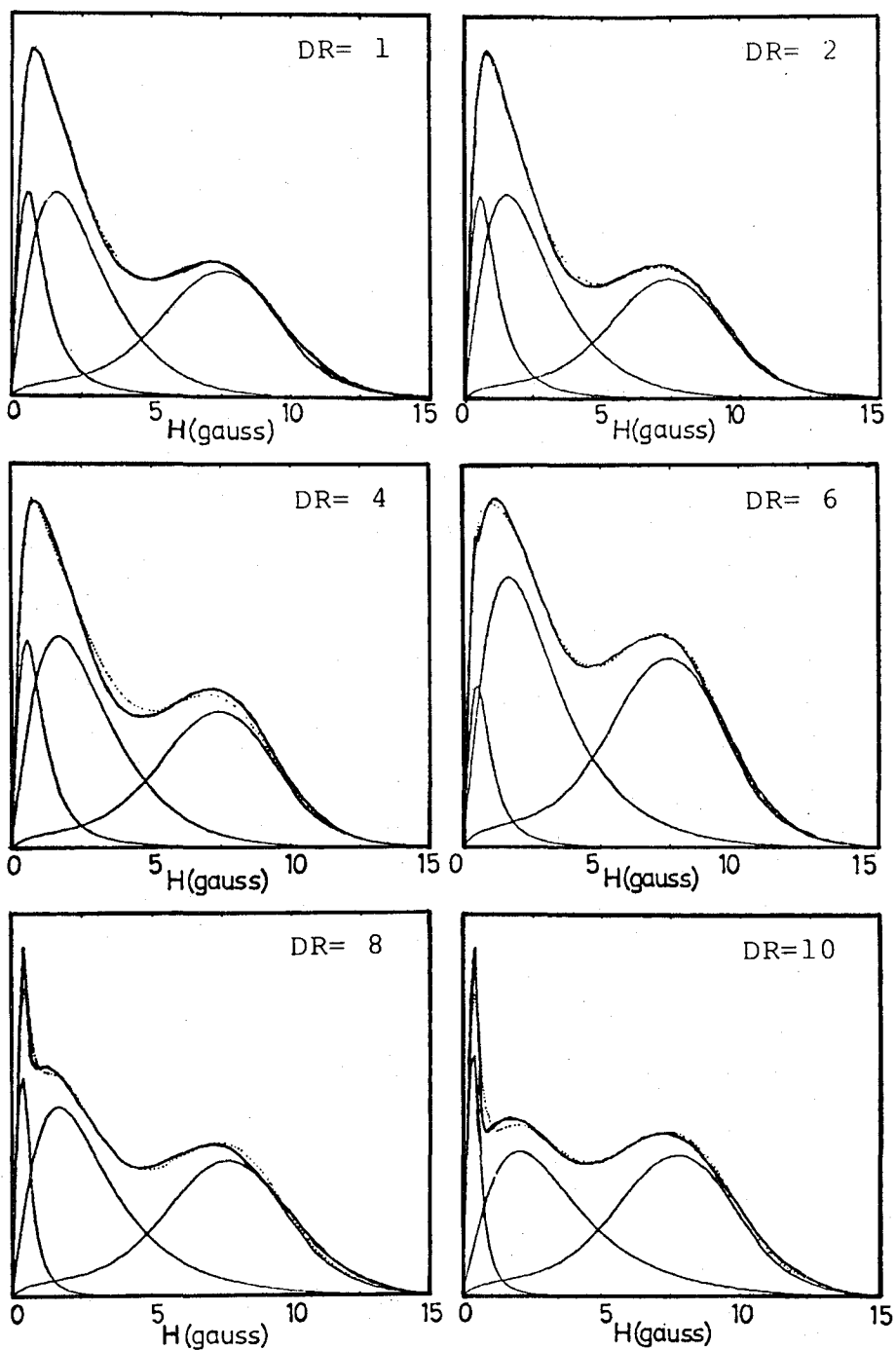


Fig. 1. Three-component analysis at room temperature for polyethylene fibers drawn to different degrees. The draw ratio (DR) is indicated in each figure. The thick solid and dotted lines indicate the experimentally observed spectra and the composite spectra the three components, respectively. Thin solid lines indicate the narrow, medium, and broad components, respectively, from the left side.

where  $A$  is a parameter which adjusts the amplitude of the spectrometry. More detailed procedure is given elsewhere.<sup>1,3)</sup>

## RESULTS AND DISCUSSION

### Spectrum Analysis at Room Temperature

Figure 1 shows the spectra for samples with draw ratios of 1, 2, 4, 6, 8, and 10 with the three-component analysis. It is shown that all spectra are well analyzed by the three components, although they differ in shape to a great extent depending on the draw ratio. In the spectra of the samples with higher draw ratios, three clear peaks can be explicitly recognized as reported for the stretched samples.<sup>13,14)</sup>

Table I summarizes the results of the three-component analysis, together with the densities of the samples measured at 30°C and orientation factors of the molecular chain vector in crystalline and amorphous phases. Here,  $w_b$ ,  $w_m$ ,  $w_n$ , and  $\Delta H_b$ ,  $\Delta H_m$ ,  $\Delta H_n$ , designate the mass fractions and the line-widths of the broad, medium and narrow components, respectively.  $\langle \Delta H^2 \rangle_m$  is the second moment of the medium component. It is shown that both of  $f_c$  and  $f_a$  increases with increasing draw ratio. This suggests that a typical fiber structure is produced by the drawing procedure. The molecular chains not only in the crystalline region but also in the noncrystalline region are preferentially oriented parallel to the stretching direction with increasing draw ratio.

It is to be noted here that the mass fraction of the broad component is not altered appreciably by drawing so that  $w_b \approx 0.689 \pm 0.009$  independent of draw ratio. On the other hand, the density increases from 0.9502 to 0.9662 with increasing draw ratio. If a constant density is assumed for the amorphous material, this result must imply the increase of the degree of crystallinity with stretching. However, the density of the amorphous material may be changed appreciably with stretching. For example, it was reported by Peterlin and others<sup>15)</sup> by X-ray scattering analysis that the density of the amorphous content was increased when stretched to high extents. If the unit-cell density is assumed to be 1.00 and the density of the amorphous region is assumed to change from 0.85 to 0.89 with drawing referring to their result, the degree of crystallinity is estimated to be unchanged within the experimental error such as  $0.698 \pm 0.04$ . This value is in good accord with the  $w_b$  obtained by the NMR analysis. If different values are assumed for the density of the amorphous region, the result may be changed appreciably. However, at the present time we may conclude that the degree of crystallinity is not changed appreciably by drawing

Table I. Three-Component Analysis for Drawn Polyethylene Filaments

Draw Ratio	Density at 30°C (g/cm <sup>3</sup> )	Orientation Factor		Mass Fraction			Line Width and Sec. Mom. in G and G <sup>2</sup> , resp.			
		$f_c$	$f_a$	$w_b$	$w_m$	$w_n$	$\Delta H_b$	$\Delta H_m$	$\langle \Delta H^2 \rangle_m$	$\Delta H_n$
1	0.9502	0.383	0.293	0.685	0.257	0.058	15.0	3.19	5.9	1.00
2	0.9512	0.615	0.494	0.679	0.263	0.058	14.8	3.06	6.3	0.98
4	0.9532	0.739	0.733	0.680	0.268	0.052	14.8	3.25	6.9	0.98
6	0.9546	0.855	0.835	0.691	0.288	0.021	14.9	3.28	8.4	0.80
8	0.9602	0.924	0.884	0.698	0.287	0.015	15.2	3.36	9.5	0.45
10	0.9662	0.972	0.898	0.698	0.289	0.013	15.2	4.06	11.3	0.40

and the  $w_b$  well corresponds to the crystalline fraction in a similar manner for undeformed samples.<sup>1-4)</sup>

On the other hand, the analysis results concerned with the noncrystalline components are greatly altered with drawing. A significant increase in  $\langle \Delta H_2^2 \rangle_m$  is recognized with increasing draw ratio. This is considered as a result of the fact that the molecular chains in the noncrystalline region are oriented as shown by the increase of  $f_a$  and the versatility of the conformation is confined upon stretching.

Furthermore, a significant decrease in both of the  $w_n$  and  $\Delta H_n$  is recognized with increasing draw ratio. It shows that some amorphous molecular chains with liquidlike mobility are stretched with macroscopic drawing and come to contribute to the medium component with losing the liquidlike mobility. Some narrow component remains even after drawing to the highest draw ratio. This will be contributed from protons that belong to methyl end-groups or methylene groups adjacent to them. Since those protons are thought to be insensible to the macroscopic stretching and to be mobile, the decrease of  $\Delta H_n$  with increasing draw ratio will be well understood.

In conclusion, the spectrum analysis at room temperature shows several important changes in the phase structure upon stretching at 100°C. Before stretching the sample filament has a phase structure approximately similar to the bulk-crystals previously discussed,<sup>1-3)</sup> although some preferential orientation of molecular chains parallel to the filament direction exists as suggested by the  $f_c$  and  $f_a$  larger than zero. It comprises the lamellalike crystallites and amorphous interfacial and interzonal materials. Such a phase structure is drastically changed with macroscopic stretching at the high temperature and the so-called fiber structure is produced.

In the fiber structure, molecular chains in the crystalline region are not only highly oriented parallel to the fiber axis but also a majority of molecular chains in the noncrystalline region are highly oriented so that the conformational versatility as well as the mobility of molecular chains are much limited. But even in highly drawn fibers a significant amount of amorphous material with a liquidlike mobility still exists if minor.

### Temperature Dependence of the Phase Structure

We have discussed the phase structure of the fiber samples as a function of the draw ratio in terms of molecular mobility by analyzing the spectrum at room temperature. We next consider the phase structure as a function of temperature by the three-component analysis of the spectrum in a wide range of temperature.

Figure 2 demonstrates the three-component analysis of spectra for the polyethylene fibers. Despite of the large difference in the overall line shape, the composite curve of the three components analyzed is in good accord with the spectrum observed in the wide range of temperature.

In Fig. 3 the mass fractions and the line widths or the second moment of the three components for samples with draw ratios of 1, 6, and 10 are plotted against temperature. It is evident that the temperature dependence of the three components can be essentially understood in terms of the  $\beta$ - and  $\gamma$ -relaxation phenomena recognized in mechanical and dielectric measurements as discussed for the bulk- and solution-crystallized samples.<sup>3,4)</sup> However, the detailed temperature dependence varies greatly with the draw ratio.

The medium component appears at a temperature higher than  $-100^\circ\text{C}$  and increases

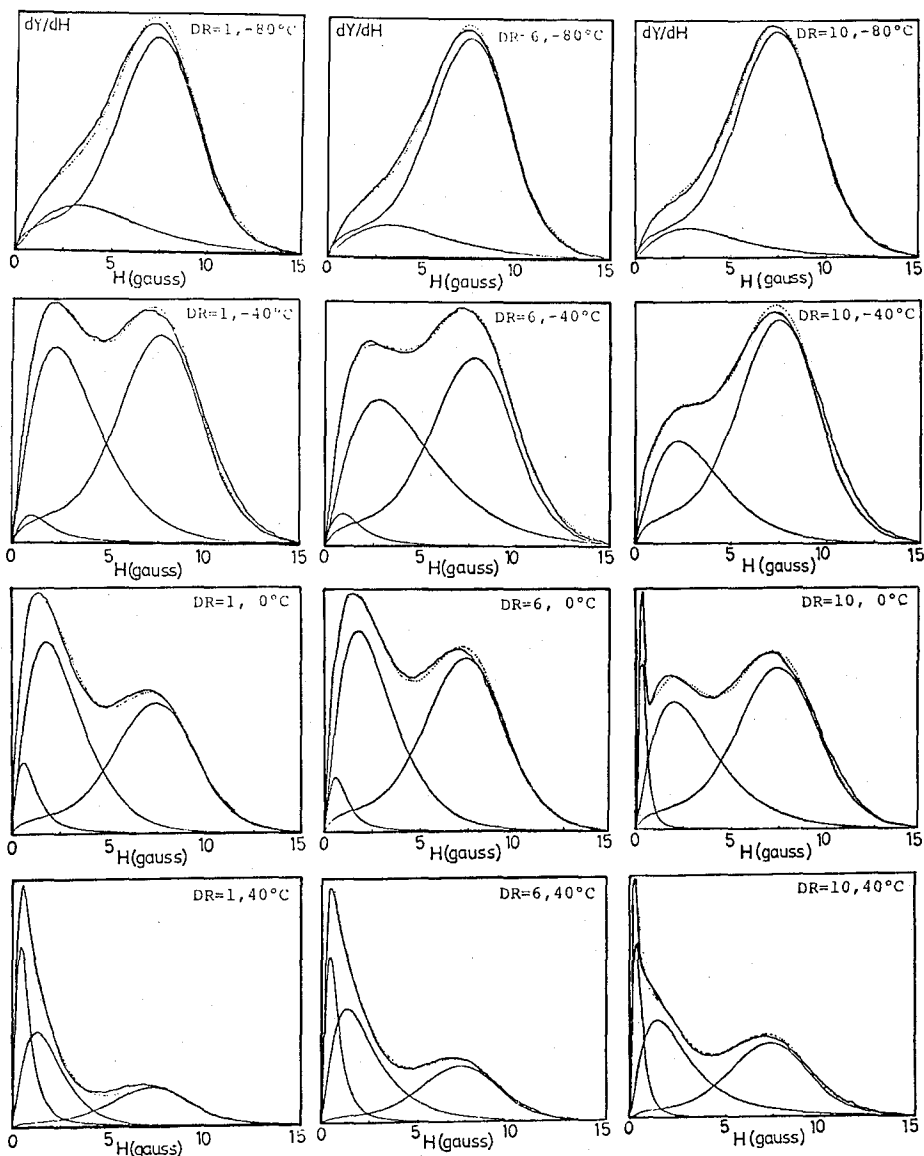


Fig. 2. Three-component analysis for drawn polyethylene fibers in a wide range of temperature. See the legend in Fig. 1 about the distinction of lines. For the spectra of the all samples at  $-80^{\circ}\text{C}$  and the 10-fold drawn sample at  $-40^{\circ}\text{C}$ , only the medium and broad components are plotted since no narrow component was detected.

with rising temperature, more gradually as the draw ratio increases. The mass fraction of the broad component decreases and reaches an asymptotic level as the temperature rises, but this decreasing of the broad component is retarded as the draw ratio increases. This suggests that the  $\gamma$ -relaxation temperature, in which a local motion of molecular chains is produced in the noncrystalline region, tends to shift to a higher temperature with increasing draw ratio. As a result, the temperature region in which the  $w_b$  actually

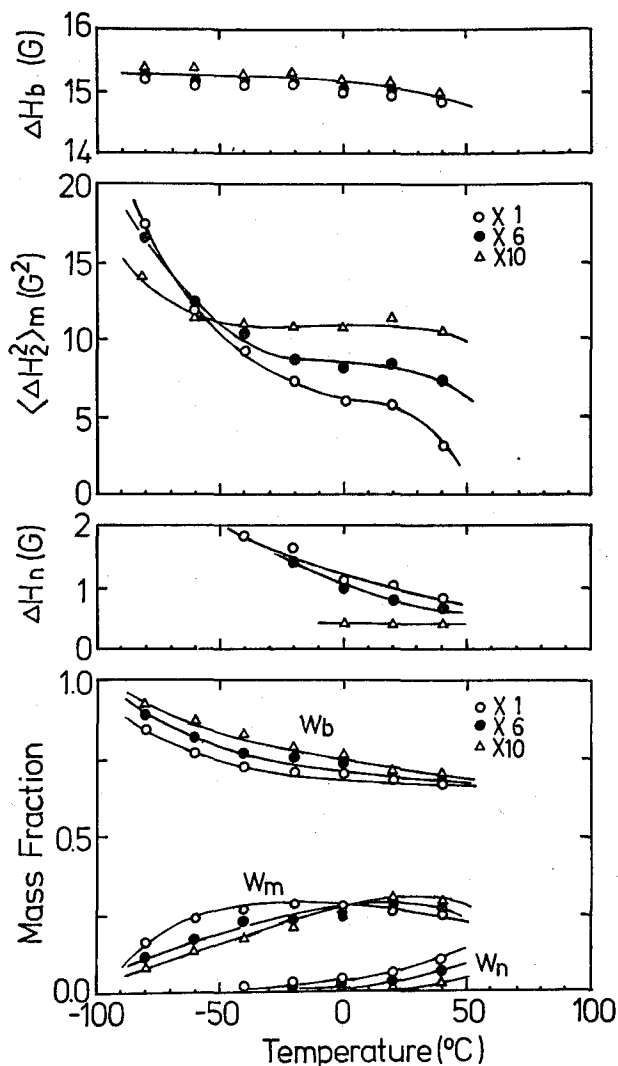


Fig. 3. Mass fractions, line-widths or second moment of three components as a function of temperature for drawn polyethylene fibers.  $\circ$ ,  $\bullet$ , and  $\triangle$  indicate the results for the undrawn filament, and the filaments drawn 6 and 10 times, respectively.

corresponds to the crystalline fraction is shifted to a higher temperature region such as above room temperature for the highly drawn samples, whereas the  $w_b$  well represents the crystalline mass fraction in a temperature range of  $-40$  to  $+50^\circ\text{C}$  for the bulk-crystallized samples.<sup>2,9)</sup> The similar effect of drawing is also evidently recognized on the behavior of the narrow component, implying that the  $\beta$ -relaxation process associated with the micro-Brownian motion of molecular chains in the noncrystalline region is shifted to a higher temperature with increasing draw ratio.

Such elevation of  $\gamma$ - and  $\beta$ -relaxation temperatures with increasing draw ratio will be due to the limited mobility of molecular chains in the noncrystalline region. As pointed out in the foregoing section the amorphous molecular chains align fairly well parallel to



the drawing direction. Therefore, the conformational versatility and mobility of such molecular chains are considered to be much restricted.

Such highly restricted molecular mobility is also suggested by a very characteristic change of the  $\langle \Delta H_2^2 \rangle_m$  with rising temperature. The  $\langle \Delta H_2^2 \rangle_m$  of 10-fold drawn sample decreases as the temperature in accord with the increase of the  $w_m$  as the temperature increases but it holds a very high level larger than  $10 \text{ G}^2$  in a temperature range of about  $-50^\circ\text{C}$  to  $+40^\circ\text{C}$  and again decreases above  $40^\circ\text{C}$ . This characteristic S-type behavior and the high values of  $\langle \Delta H_2^2 \rangle_m$  are approximately equivalent with those for the bulk-crystal with a low molecular weights.<sup>3)</sup> In this bulk-crystal the molecular chains that contribute to the medium component must be composed of short molecular chains that are excluded from the basal plane of lamella crystallites. Such molecular chains must be in a rather extended chain conformation and comprise a parallel intermolecular alignment perpendicular to the basal plane of the crystallite.<sup>3)</sup> The large values and characteristic temperature dependence of  $\langle \Delta H_2^2 \rangle_m$  recognized for the both kinds of samples may be associated with the highly extended molecular chain conformation in the amorphous region.

For the 10-fold drawn sample the  $\Delta H_n$  remains in a very low level such as about  $0.4 \text{ G}$  over the temperature range examined. As discussed already, the narrow component for such a highly drawn sample will be mainly contributed by protons belonging to methyl end-groups or adjacent methylene groups insensible to the macroscopic drawing. Such components will be rather mobile even at lower temperatures. The very small value of  $\Delta H_n$  for the highly drawn sample will be thus well understood.

#### Effect of Swelling Agent

If partially crystalline polymers are immersed in a proper swelling agent, the phase structure of the polymers may be more distinctly examined because the swelling heightens the molecular mobility preferentially in the amorphous region. Such an attempt for stretched polyethylene was carried out by Peterlin and Olf<sup>16)</sup> by NMR spectroscopy.

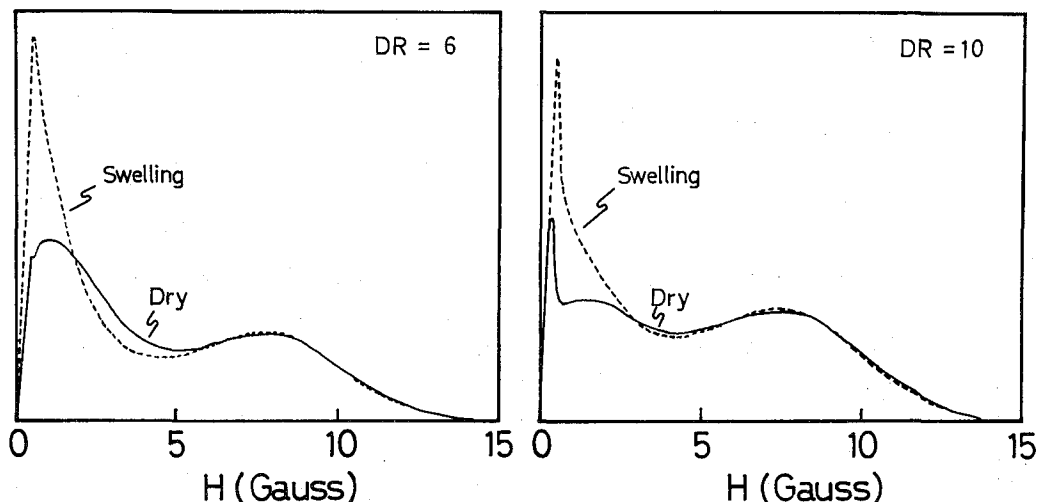


Fig. 4. The NMR spectra for 6 and 10-fold drawn filaments in the dry and swollen states in  $\text{CCl}_4$ . The solid and dotted lines indicate the results in the dry and swollen states, respectively.

They compared the NMR spectra of drawn and undrawn samples immersed in non-protonated solvents such as tetrachloroethylene ( $C_2Cl_4$ ). It was reported that an enhanced narrowing of the narrow component took place for the undrawn sample but no effect was recognized for the drawn sample while the broad component was held unaltered for both samples. It is thought that the swelling could not appreciably heighten the molecular mobility in the amorphous region in the drawn sample, because amorphous molecular chains are in a greatly stretched conformation for such a drawn sample.

We have analyzed the spectra for the samples with different draw ratios immersed in  $CCl_4$  at room temperature for 2 weeks. Figure 4 shows the spectra for 6- and 10-fold drawn fibers immersed in  $CCl_4$ . Enhanced changes are recognized by the immersion in the narrower components of the spectra, while no appreciable change is recognized in the broad component.

In Fig. 5 the mass fractions of the three components and the second moment of the medium component are plotted against draw ratio. The parameters in relation to the

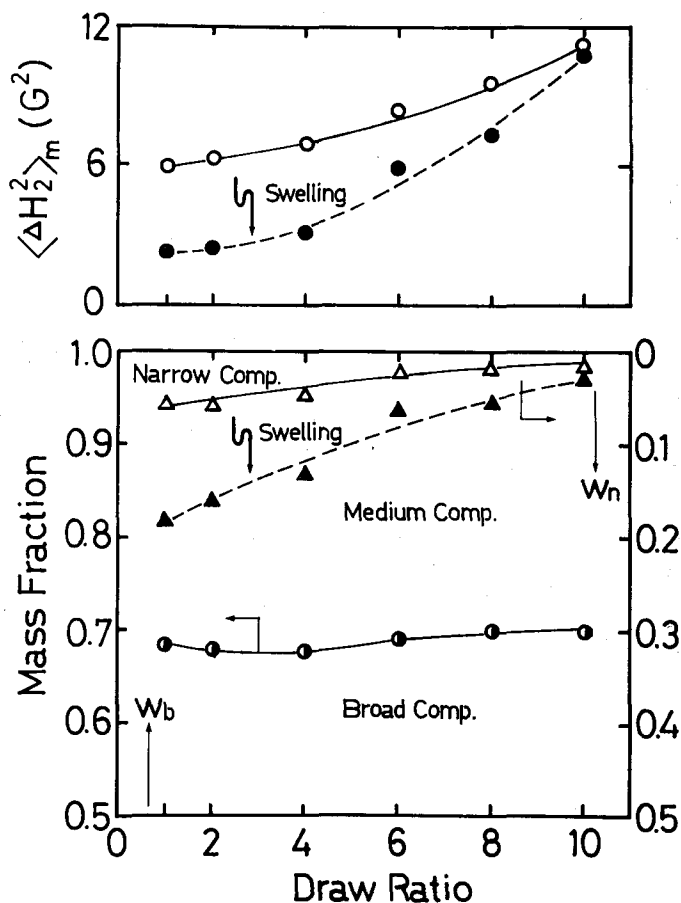


Fig. 5. Second moment of the medium component and mass fractions of the three components as a function of the draw ratio. The open and closed symbols indicate the data in the dry and swollen states, respectively. The half-closed circles indicate the data for the broad component, unaltered by the swelling.

broad component are not altered by the immersion but those in relation to the medium and narrow components are enhancedly changed by the immersion, depending on the degrees of drawing. For the samples with smaller draw ratios the medium component decreases and the narrow component increases with immersing in  $\text{CCl}_4$ . The  $\langle \Delta H_2^2 \rangle_m$  also decreases. These results evidently show that upon immersing in  $\text{CCl}_4$  the molecular chains in the interfacial region become to be mobile so as to exhibit a liquidlike mobility. The mobility of the molecular chains that still contribute to the medium component is also heightened by the immersion. Since the molecular conformation in the interfacial region is rather versatile for such samples with smaller draw ratios,  $\text{CCl}_4$  molecules will penetrate rather deeply in the region if the amount is minor. On the other hand, the effects of  $\text{CCl}_4$  become to be negligible with the increase of draw ratio in good accord with the result of Peterlin and Olf.<sup>16)</sup> In such samples because of the unversatile molecular conformation in the amorphous region,  $\text{CCl}_4$  molecules will not penetrate in the amorphous region so as to give no appreciable effects on the spectra.

Thus, the spectroscopy of the samples in  $\text{CCl}_4$  further supports the conclusion obtained in the foregoing sections that the molecular chains in the amorphous region of the drawn samples are in an unversatile conformation due to the high degree of molecular orientation.

### CONCLUSION

The NMR spectrum analysis shows that the phase structure of the drawn fibers is quite different from that of undeformed samples. The undrawn filament obtained by a melt-spinning has an approximately similar phase structure to the bulk-crystals with corresponding molecular weight. However, the structure is drastically changed with drawing. The highly drawn filaments comprise the crystalline material as well as a noncrystalline component more than 25% in a similar manner as undeformed bulk-crystals. Nevertheless, the molecular mobility and conformation of molecular chains in the non-crystalline component are quite different. The majority of molecular chains are almost fully extended parallel to the fiber axis and associated with a very limited molecular mobility over a wide range of temperatures. The swelling agents such as  $\text{CCl}_4$  hardly heighten the mobility of such highly extended molecular chains in the noncrystalline region. However, a noncrystalline material with liquidlike mobility evidently exists if the amount is minor even in the 10-fold drawn sample.

### REFERENCES

- (1) R. Kitamaru, F. Horii, and S.-H. Hyon, *J. Polym. Sci. Polym. Phys. Ed.*, **15**, 821 (1977).
- (2) R. Kitamaru, F. Horii, and S.-H. Hyon, *ACS, Polym. Prepr.* **17**, 549 (1976).
- (3) R. Kitamaru and F. Horii, "NMR Approach to the Phase Structure of Linear Polyethylene", *Adv. Polym. Sci.*, Springer-Verlag, Heidelberg, in press.
- (4) F. Horii and R. Kitamaru, *J. Polym. Sci. Polym. Lett. Ed.*, submitted.
- (5) E. W. Fischer, H. Goddar, and W. Piesczek, *J. Polym. Sci.*, **C32**, 149 (1971).
- (6) J. J. Hermans, P. H. Hermans, D. Vermeas, and A. Weidinger, *Rec. Chim. Trav.*, **65**, 427 (1946).
- (7) R. S. Stein and F. H. Noriss, *J. Polym. Sci.*, **21**, 381 (1956).
- (8) R. S. Stein, *J. Polym. Sci.*, **31**, 327 (1958).
- (9) K. Bergmann and K. Nawotki, *Kolloid-Z. Z. Polym.*, **219**, 132 (1967).

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- (10) K. Bergmann, *Ber. Bunsenges. Phys. Chem.*, **74**, 912 (1970).
- (11) K. Bergmann, *Kolloid-Z. Z. Polymer*, **251**, 962 (1973).
- (12) K. Bergmann and K. Nawotki, *Kolloid-Z. Z. Polym.*, **250**, 1094 (1972).
- (13) D. Hyndman and G. G. Origlio, *J. Polym. Sci.*, **39**, 556 (1959).
- (14) J. Loboda-Čačković, R. Hosemann, and W. Wilke, *Kolloid-Z. Z. Polym.*, **235**, 1253 (1969).
- (15) W. Glenz, N. Morosoff, and A. Peterlin, *J. Polym. Sci. Polym. Lett. Ed.*, **9**, 211 (1971).
- (16) A. Peterlin and H. G. Olf, *J. Polym. Sci.*, **A-2**, **4**, 587 (1966).