A study of structure and properties of lightly cross-linked polyethylene, crystallized from the melt under uniaxially stretching

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A lightly crosslinked sample when stretched in a molten state, transformation to crystalline state first takes place from the stretched molecular chains. It is observed that this mode of crystallization produces a very unique phase structure associated with many characteristic properties which are advantageous for practical use.

Keywords: Crosslinked sample, Draw ratio, Uniaxially stretching, Polyethylene, X-ray diffraction

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At high temperatures below the melting point, linear polyethylene can be usually stretched uniaxially to high extent and produces a fiber structure. In this structure, molecular chains are predominantly oriented parallel to the stretching direction. On the contrary, even if it is stretched at temperatures above the melting point, such fiber structure can hardly be expected because of the rapid relaxation of stretched molecular chains. However, if the polymer has adequate intermolecular crosslinks, even when stretched in the molten state at temperatures well above the melting point, the molecular chains are stretched definitely according to the macroscopic deformation and, upon cooling the crystallization will take place by the stretched molecular chains with a very rapid rate and a structure with a high degree of molecular chain orientation is produced. At temperatures below the melting point, there necessarily exists some amount of crystalline material as crystallites due to very high crystalizability of the polymer. Hence, upon stretching in such a state below the melting point, molecular chains in the amorphous region will be first stretched and the orientation of crystallites will follow.

But, when a crosslinked sample is stretched in the molten state, since molecular chains are stretched according to the macroscopic deformation, upon cooling to lower temperatures, transformation to the crystalline state will first take place from the stretched molecular chains. It is observed that this mode of crystallization produces a very unique phase structure associated with many characteristic properties that are sometimes advantageous for the practical uses. In view of the above, the study of structure and properties of lightly crosslinked polyethylene has been undertaken.

Experimental Procedure

Molecular weight fraction of linear polyethylene with a viscosity average molecular weight of $3.8 \times 10^5$ was obtained by a liquid-liquid separation technique from an unfractioned polyethylene sample. Films of this sample, about 0.2 to 1.0 mm thick, were irradiated to a dosage of 8.5 Mrad in vacuum with [Cobalt-60] at room temperature.

The irradiated samples, thus, obtained were next extracted with boiling xylene with 0.5% 2,6-di-t-butyl-p-cresol added as an anti-oxidizing agent in order to remove the soluble fraction and dried in vacuum at about 60°C for least for 2.5 weeks. The soluble fraction $W_s$ was evaluated to be 0.18. The density of intermolecular crosslinks of the gel samples, thus obtained was approximately evaluated to be $2.2 \times 10^{-4}$. This was evaluated by using a relation from the theory of gel formulation for linear polymer.

$$\rho_g = \left(\frac{R}{R_c}\right)\left(\frac{M_0}{M_\eta}\right)\left(1+W_s\right)$$

Here, $R$ and $R_c$ are the dosage irradiated and critical dosage for the incipient gelation, respectively. $M_0$ and $M_\eta$ are fundamental molecular weight of methylene group and viscosity average molecular weight of the sample before the irradiation.

The samples were melted under a hydrostatic pressure in order to remove the voids produced by extraction with xylene and after cooling to room temperature these were uniaxially stretched with two kinds of procedures as described below:

(a) A piece of sample was uniaxially stretched to different extents at a rate of 500% per second after it...
melted perfectly in a silicon oil bath at 170°C and cooled to room temperature while holding the stretched length.

(b) A piece of sample was uniaxially stretched to different extents at a rate of 500% per second at 110°C and after keeping for 5 min it was cooled to room temperature.

The stretching was achieved in the molten state and in the partially crystalline state, respectively by using procedures (a) and (b).

**Theory**

**Estimation of molecular orientation**

The molecular orientation of stretched samples has been estimated separately for the crystalline and amorphous phases by using wide angular X-ray and birefringence techniques.6,7,9

The degree of orientation for molecular chain vectors can be described by the orientation factor given by,

\[ f = \left( \frac{3 \cos^2 \phi - 1}{2} \right) \]  

...(1)

Here \( \Phi \) is an angle of a molecular chain vector to the stretching direction (1). The orientation factor \( f_C \) for C-axis in crystallites was obtained from an X-ray diffraction scan for the (002) crystal plane using a relation,

\[ f_C = \frac{\int_0^{\pi/2} I_{hk0} \left( \frac{3 \cos^2 \phi - 1}{2} \right) \sin \phi \, d\phi}{\int_0^{\pi/2} I_{hk0} \, (\phi) \sin \phi \, d\phi} \]  

...(2)

Here, \( I_{hk0} (\Phi) \) is the diffraction intensity from the (002) crystal plane when sample is fixed in a position such that the stretching direction makes the angle of \( \Phi \) to the inner bisector of X-ray incident and the (002) diffraacted beams.

The quantity for the amorphous molecular chain vectors \( f_a \) was evaluated from a birefringence measurement with the \( f_c \) and the degree of crystallinity from density measurement using the relation,

\[ \Delta n = \chi f_c \Delta_c^0 + (1-\chi) f_a \Delta_a^0 \]  

...(3)

Here, the intrinsic configurational birefringence is neglected. \( \Delta n \) designates the birefringence measured, \( \chi \) is the volume fraction of the crystalline material. \( \Delta_c^0 \) and \( \Delta_a^0 \) are the theoretical quantities for perfectly oriented crystalline and amorphous molecular chains respectively \( \Delta_c^0 = 0.0574, \Delta_a^0 = 0.0426 \) were adopted.

**Small angle X-ray scattering**

The small angle X-ray scattering (SAXS) patterns were obtained at room temperature with a point collimation small angle X-ray camera. Ni-filtered Cu-K\(_\alpha\) radiation was used. The working conditions were carried out under vacuum with 50 kV, 90 mA and 0.4 mm primary beam diameter and a specimen to film distance of 320 mm. A small angle camera with a Kratky collimation (Cu-K\(_\alpha\) scintillation counter) was used to obtain quantitative characteristics of small angle scattering. The long period, \( d = \lambda/2 \sin \theta \), was found from the position of maximum in the scattering curve after subtraction of the diffuse scattering. Here, \( \lambda \) is the Cu-K\(_\alpha\) wavelength and \( \theta \) is the scattering angle of the primary beam.

**Discussion**

**Orientation of molecular chains in crystalline and amorphous phases**

Figure 1A shows the wide angular X-ray diffraction patterns taken with a flat camera using a nickel filtered Cu-K\(_\alpha\) beam for samples uniaxially stretched to different degrees in the melt and cooled procedure. It is seen that for the 1.6 fold drawn sample the diffraction from the (020) crystal plane of the orthorhombic crystal form for this polymer locates on the equator whereas the (200) and (110) diffractions locate in azimuthal angles close to the meridian and intermediate directions as arcs separated into two, respectively. This implies that upon stretching to such a small extent a crystalline structure appears, in which the \( b \)-axis is perpendicular to the stretching direction while the \( a \)-axis orient parallel to the direction. This result is phenomenally in accordance with the morphological change for a crosslinked polyethylene, when it was stretched 2 fold and cooled after melting, reported earlier and discussed as “\( a \)-axis orientation”. However, it is noted here that upon stretching to such a low degree the \( b \)-axis orient perpendicular to the stretching direction while the \( a \)-axis does not orient parallel to the direction but in an intermediate angle.

Upon further stretching beyond 2 times the (200), (110) diffractions as well as (020) diffractions tend to gather on the equator and all diffractions from the
(hko) crystal planes such as (110), (200), (210), (020) etc. become to be sharp points when drawn to higher degrees. The result evidently indicates that, when the crosslinked sample is uniaxially stretched and cooled a very high degree of orientation of the C-axis in the crystallities appears in compliance with the macroscopic stretching.

On the other hand, the X-ray patterns are shown in Fig. 1B for samples drawn at 110°C. The orientation of the c-axis appears in the beginning of the stretching and increases highly with stretching but to lesser degrees in comparison with that for sample made by stretching in the melt. The diffractions from (hko) planes in Fig. 1B (×6) are located on the equator but they are not so sharp as those in Fig. 1A (×6).

In Table 1, the orientation of the C-axis to the stretching direction is filled as the orientation factor $f_c$ for the two series of samples as a function of draw ratio.

It is seen that when drawn in the molten state, extremely high degree of orientation of the C-axis is attained, such as $f_c$ is 0.997 for 6 fold drawing. On the other hand, when drawn at 110°C $f_c$ could not exceed 0.986 even if highly stretched.

### Table 1—Characterisation of the crosslinked gel sample, uniaxially stretched in the molten state at 170°C and the partially crystalline state at 110°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>X</th>
<th>(1-$\lambda_d$)</th>
<th>$\Delta n$</th>
<th>$f_c$</th>
<th>$f_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drawn at</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>170°C</td>
<td>3</td>
<td>0.580</td>
<td>3.42×10^{-2}</td>
<td>0.974</td>
<td>0.111</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>3.72×10^{-2}</td>
<td>0.987</td>
<td>0.125</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td>3.92×10^{-2}</td>
<td>0.994</td>
<td>0.217</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td>4.05×10^{-2}</td>
<td>0.997</td>
<td>0.265</td>
</tr>
<tr>
<td>Drawn at</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>110°C</td>
<td>3</td>
<td>0.595</td>
<td>3.87×10^{-2}</td>
<td>0.970</td>
<td>0.328</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>4.24×10^{-2}</td>
<td>0.975</td>
<td>0.491</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td>4.5×10^{-2}</td>
<td>0.986</td>
<td>0.604</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td>4.75×10^{-2}</td>
<td>0.986</td>
<td>0.732</td>
</tr>
</tbody>
</table>

$X$—Draw ratio, (1-$\lambda_d$)—Degree of crystallinity, $\Delta n$—Total birefringence.

$f_c$—Orientation factor of molecular chain vector in the crystalline phase.

$f_a$—Orientation factor of molecular chain vector in the amorphous phase.
In Table 1, the birefringence $\Delta n$ and the degree of crystallinity $(1-\lambda_d)$ obtained from density measurement are filled. The last two columns show the values of $f_c$ and $f_a$ (evaluated from these quantities) for two series of samples as a function of draw ratio. Variations of $f_c$ and $f_a$ with $X$ (draw ratio) at 170°C and 110°C are shown in Figs 2A and 2B, respectively. Figure 2A shows the variation of $f_c$ with $X$ at 170°C and 110°C whereas Fig. 2B shows the variation of $f_a$ with $X$ at 170°C and 110°C. From figures 2A and 2B it is concluded that for the samples stretched in the melt, the value of $f_a$ stays very low such as less than 0.265 even if highly stretched while the $f_c$ increases rapidly and reaches a value very close to unity as the draw ratio increases. For the samples stretched at 110°C $f_a$ increases to a very high level with increasing draw ratio but $f_c$ is smaller than that one former series of samples. These results evidently show that when the crosslinked sample is stretched to a high degree in the melt and cooled to lower temperatures a very unique structure is produced, the crystallites, of which C-axis is highly oriented to the stretching direction, coexist with amorphous molecular chains not oriented appreciably to the direction. On the contrary, the sample stretched at 110°C has a structure, in which the crystallites, oriented highly but to lesser extent than for the former series of samples, coexist with highly oriented amorphous molecular chains.

Such a unique structure in which very highly oriented crystallites coexist with unoriented amorphous molecular chains was obtained only by the special mode of crystallization for the sample with a proper amount of crosslinks.

References
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