Molecular Structure and Some Related Properties of Polyethylene Stretched in the Amorphous and Crystalline States

HYONG-DONG CHU, RYOZO KITAMARU, and WAICHIRO TSUJI, *Institute for Chemical Research, Kyoto University, Takatsuki, Osaka, Japan*

Synopsis

The molecular orientation of stretched polyethylene has been estimated separately for the crystalline and amorphous phases by using x-ray and birefringence techniques. It is confirmed that if a lightly crosslinked polyethylene is highly stretched rapidly in the perfectly molten state and cooled to room temperature, a fibrous structure comprised of highly oriented crystallites and almost unoriented relaxed amorphous chains is produced. Some properties such as dynamic mechanical properties and thermodynamic property are discussed in relation to the molecular structure.

INTRODUCTION

It is reported by Judge and Stein[1] that if crosslinked polyethylene is supercooled from the molten and oriented states, the crystals grow with their c axis parallel to the stretching direction when the elongation exceeds about 200% but perpendicular to this direction when it is less than about 200%. Their results are of interest in clarifying the structural mechanism of crystal growth in the oriented state. Relatively high axial orientation of crystallites was observed by x-ray studies of samples elongated more than about 400%. However, the degree of the orientation was not so easily determined, probably due to the limited extensibility because of the presence of the large amounts of crosslinking.

Kitamaru and Mandelkern[2] have found in their study on the crosslinking efficiency of x-rays for linear polyethylene that an extremely high state of axial orientation of the crystalline phase can be obtained for a polyethylene film irradiated to the point of incipient gelation. A molded film of unfractionated Marlex 50 was first irradiated by x-rays to the gel point under high vacuum and a portion of the film was then stretched rapidly in the amorphous state at 150°C. in a silicone oil bath to about twenty times its original length and cooled to room temperature in the extended condition. The density of the fibrous sample thus obtained was 0.964 g./cc. at room temperature, and a high state of axial orientation of the crystallites was demonstrated by the wide-angle x-ray diffraction pattern shown in Figure 1 of their paper.[2]

In relation to this stretching technique for lightly crosslinked polyethylene, one may recall the racking process[4] of natural rubber and its properties.[5,6] Racked rubber can be obtained by a rapid stretching of natural rubber at an elevated temperature and quick cooling to about 20°C. in the extended condition.   Natural rubber can be stretched well beyond its normal limit of extensibility by this process and is capable of maintaining this state without the application of any external force.   The melting temperature of the racked rubber is reported to be in the range of 35–50°C., substantially higher than the equilibrium melting temperature assigned to natural rubber.[5] The above-mentioned stretching technique for crosslinked polyethylene and the racking process for natural rubber closely resemble each other and that the abnormally high melting temperature and the stable oriented state of the racked rubber doubtlessly must be attributed to its specially oriented crystalline state; therefore it may be worthwhile to investigate the molecular structure and related properties of the stretched polyethylene in more detail.

We have studied the molecular orientation both in the crystalline and amorphous phases for the stretched polyethylene and some related properties, such as mechanical properties, in a comparison with those of a fibrous polyethylene prepared by another technique.

EXPERIMENTAL

Materials

Linear polyethylene, Marlex-50 produced by Phillips Chemical Co., was used as a starting material.   A film of about 0.5 mm. thickness was molded from the polymer at 165°C. and quenched into water.   The density of this film was 0.943 g./cc. at 30°C., which corresponded to the crystallinity of about 65%.   In order to obtain a lightly crosslinked sample, the film was irradiated by γ-rays from a ^{60}Co source to 4 Mr at room temperature under vacuum.   The sol fraction of the irradiated sample was 0.852 and the number of the crosslinked units per molecule (based on the weight-average molecular weight) was evaluated as 1.14 from the critical dosage for the gelation and the total dosage irradiated.   A change in density by the irradiation was not observed within experimental error.

Elongation

The crosslinked sample was stretched rapidly in the amorphous state at 145°C. in a poly(ethylene glycol) bath and quickly cooled to room temperature in the extended state.   The rate of stretching was about 4000%/sec. and the degree of the stretching was 16 times the original length.   The crosslinked sample as well as the uncrosslinked original film was elongated also at a temperature of 80°C. in the poly(ethylene glycol) bath to 16 times the original length at a rate of 10%/sec. and cooled to room temperature.

Estimation of Molecular Orientation

The total orientation of molecules both in the crystalline and amorphous phases of samples to the direction of elongation was evaluated from birefringence, and the orientation of crystallites was estimated by an orientation factor. In plotting x-ray diffraction intensity for the crystal plane (002) against the inclination angle of sample to the incident x-ray, if the half angular width is designated as H, the orientation factor of crystallites f_c can be obtained[3] as

$$f_c = (180 - H)/180 \tag{1}$$

Density

The density of samples was measured by a density gradient column of n-propyl alcohol and ethylene glycol and the value was converted to the degree of crystallinity (weight per cent of crystalline phase to total system) by utilizing the relation given by Chiang and Flory.[7]

Dimensional Change of the Stretched Samples with Temperature

The dimensional change in the direction of stretching was measured with increasing temperature in air at a constant load. The applied load was 10 g./mm.[2], and the dimensional change was followed by a cathetometer. The temperature was increased at the rate of 1°C./min.

Dynamic Mechanical Properties

The temperature dependency of dynamic modulus E' and dynamic loss E'' were measured by utilizing the Vibron DDV-2 (Toyo Measuring Instruments Co.), a type of forced vibrational method. The selected frequency for the measurements was 110 cps throughout the study and the values of E' and E'' were obtained in the range of temperature from -30 to $+120°C.$, increasing temperature at the rate of 1.5°C./min. The dimensions of the test piece were 30 mm. in length, 0.1–0.2 mm.[2] in cross section.

RESULTS AND DISCUSSION

Morphological Study

Figure 1 shows the wide-angle x-ray diffraction pattern for two samples; sample 1 was prepared by stretching the irradiated film to 16 times in the amorphous state at 145°C. and sample 2 was prepared by elongating uncrosslinked film to the same length in the low crystalline state at 80°C. The patterns demonstrate the high axial orientation of crystallites for both samples, particularly the pattern for the sample 1 exhibits very sharp diffraction. The x-ray diffraction pattern for sample 1 corresponds well in sharpness to the stretched crosslinked polyethylene prepared by Kitamaru and Mandelkern[2] by a similar technique, and it qualitatively indicates a very high state of axial orientation of the crystallites. The axial orienta-
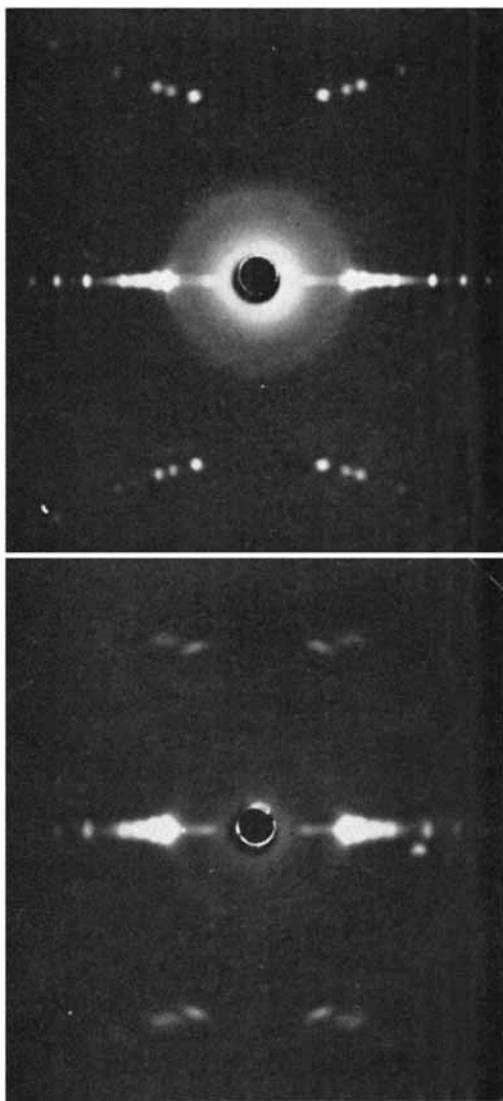
Fig. 1. Wide-angle x-ray diffraction patterns of stretched samples: (a) sample 1. (irradiated Marlex-50, stretched at 145°C. to 16×); (b) sample 2 (unirradiated Marlex-50, elongated at 80°C. to 16×).

tion of crystallites can be quantitatively estimated by the diffraction intensity distribution for the crystal plane (002). As shown in Table I, the orientation factor f_c of the crystallites was evaluated as 0.99 and 0.97 for samples 1 and 2, respectively. The value of 0.99 may imply that the axial orientation of the crystallites in the sample 1 is almost perfect. The birefringence of both samples is shown also in Table I. The values are 0.0462 for sample 1 and 0.0571 for sample 2. The results indicate that the total orientation of molecules for sample 1 is less than for sample 2, although

TABLE I
Degree of Orientation of Stretched Samples

Sample no.	Sample treatment	Orientation factor f_c (from x-ray data)	Birefringence Δ	Crystal-linity at 30°C., %
1	Irradiated Marlex-50, stretched at 145°C. to 16×	0.99	0.0462	80.1
2	Unirradiated Marlex-50, elongated at 80°C. to 16×	0.97	0.0571	80.6
3	Gel of irradiated Marlex-50, stretched at 145°C. to 5.5×	—	0.0421	67.0

the axial orientation of crystallites is higher for the former than for the latter, as shown by the orientation factors.

If we neglect the intrinsic configurational birefringence of samples, the birefringence for total system can be expressed as,

$$\Delta = X_c\Delta_c + (1 - X_c)\Delta_a \tag{2}$$

where Δ_c and Δ_a are birefringences for the crystalline and amorphous phase, respectively, and X_c is the volume fraction of the crystalline phase to total phase. For sample 1, $\Delta = 0.0462$ and $X_c = 0.77$, where X_c was calculated from the crystallinity and the density of the crystalline and amorphous phases. If the orientation of crystallites is assumed to be perfect for this sample, Δ_c can be taken as 0.0572, which has been assigned by Stein and Norris[8] to the crystal perfectly oriented to the stretching direction. Then the birefringence of the amorphous phase Δ_a is calculated from eq. (2) as 0.009. Such a small value of Δ_a indicates that the axial orientation of the amorphous phase is negligible although that of the crystalline phase is nearly perfect. Unless perfect orientation of the crystallites is assumed, the value of Δ_a may increase slightly. However, the conclusion would not be changed, because the orientation factor of the crystallites was estimated as 0.99, nearly equal to unity.

If subscripts 1 and 2 denote samples 1 and 2 respectively, the following equations apply for the two samples.

$$\Delta_1 = X_{c1}\Delta_{c1} + (1 - X_{c1})\Delta_{a1} \tag{3}$$

$$\Delta_2 = X_{c2}\Delta_{c2} + (1 - X_{c2})\Delta_{a2} \tag{4}$$

As shown in Table I, the crystallinity is fortunately almost equal for the two samples. Accordingly,

$$X_{c1} \cong X_{c2} = Xc$$

Then, it follows that

$$\Delta_{a2} - \Delta_{a1} = [1/(1 - X_c)](\Delta_2 - \Delta_1) + [X_c/(1 - X_c)](\Delta_{c_1} - \Delta_{c2}) \tag{5}$$

where $\Delta_1 = 0.0462$, $\Delta_2 = 0.0571$, $X_c \cong 0.77$.   The second term of the right-hand side of eq. (5) can be assumed to have a very small positive value from the x-ray diffraction patterns and the orientation factor of both samples. Hence,

$$\Delta_{a2} - \Delta_{a1} > [1/(1 - X_c)](\Delta_2 - \Delta_1) = 0.0474$$

Letting Δ_{a1} be 0.009, we obtain the value of Δ_{a2} as $\Delta_{a2} > 0.053$. This value indicates the highly oriented state of molecules in the amorphous phase of sample 2.   As a result, it is concluded that crystallites oriented highly in the stretching direction must coexist with almost unoriented amorphous chains for sample 1, which was prepared by stretching in the amorphous state, while both the crystallites and the amorphous chains are highly oriented parallel to the stretching direction for sample 2, which was prepared by stretching in the low crystalline state.

The difference in the structure between these two fibrous samples must be attributed to the difference in the orientation mechanism of samples. If a crosslinked system is stretched in the perfectly amorphous state, chains between crosslinks are distorted from their most probable configuration. In particular if it is stretched as much as more than 16 times its original length, as in the above case, chains would be distorted to an almost perfectly extended configuration.   In this extended condition, if the system is super-cooled below its melting temperature, crystallization under the oriented state of polymer chains must take place.   It is a widely observed experi-mental fact that crystallites produced by stretching usually occur with their chain direction preferentially oriented parallel to the axis of elongation. In particular, when the extent of stretching is very large, the orientation of crystallites may be almost perfect.   An extremely high state of axial orientation of crystallites for the sample would thus be expected.   How-ever, the extended state of amorphous chains will be decreased, depending on the extent to which each chain participates in forming oriented crystal-lites, because chains in oriented crystallites take up a greater length in the direction parallel to the axis of elongation than do the chains in the amor-phous state, even if they are extended highly.   Consequently a fibrous structure comprised of highly oriented crystallites coexisting with amor-phous chains almost without orientation can be supposed to be produced.

On the other hand if a molded film of polyethylene is stretched at a lower speed at a temperature of 80°C. as is the case for sample 2, the trans-formation of isotropically partially crystallized structure of the sample to fibrous structure may be rather complicated because of the substantial existence of crystallites throughout the stretching.   If stretching is con-ducted in the presence of crystallites, crystallites can act as resistant points for stretching like crosslinked points in a network structure.   Hence, amorphous chains between crystallites will be extended and distorted from their most probable configuration in the first step of the elongation in a manner similar to rapid stretching of a network.   This increase in the stretched state of amorphous chains between crystallites must induce in a

second step an orientation of the crystallites, partial destruction of the lamellar structure, and the transformation to an oriented amorphous state, simultaneously with oriented crystallization. Furthermore, the stretching is continuing in this case throughout the oriented crystallization. Therefore, the relaxation of extended amorphous chains would not take place
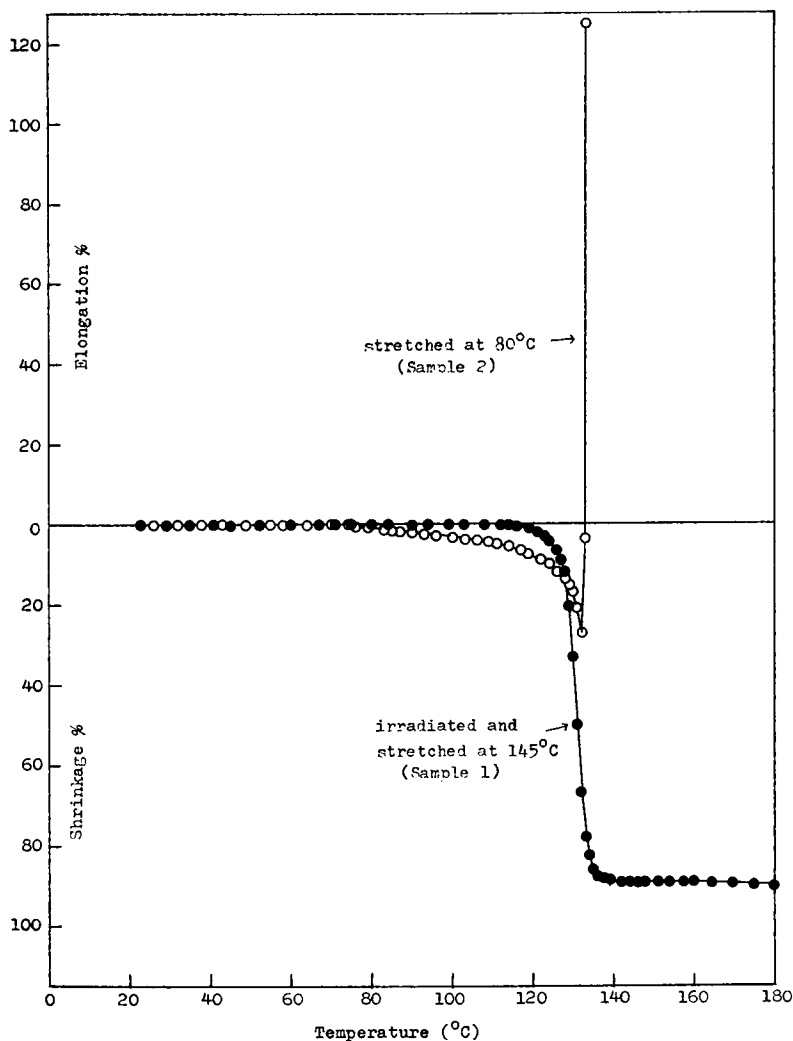

Fig. 2. Dimensional change of drawn film with temperature at constant load.

with the oriented crystallization and eventually a fibrous structure, comprised of highly oriented crystallites coexisting with amorphous chains highly oriented parallel to the axis of stretching direction, should be produced. The fibrous structure of synthetic fibers is thought to have this type of fibrous structure, which is in strong contrast to that of sample 1.

Dimensional Change with Increasing Temperature

The above-mentioned difference in the structure between two samples must be necessarily reflected in their properties. Therefore, we next examine some properties of the stretched samples. Figure 2 shows the dimensional change of the lengths of the samples with increasing temperature under a small load in air. Sample 1 does not show any appreciable change to about 120°C. and completes shrinkage or melting at about 135°C., whereas sample 2 begins to shrink gradually from about 70°C. and completes shrinkage at 132°C. The good dimensional stability of sample 1 must be caused by its relaxed amorphous chains and the perfection of the crystallites.

Oth and Flory[6] observed that the longitudinal dimension of racked rubber is maintained up to a temperature substantially higher than the equilibrium melting temperature under zero force and that rather abrupt shrinkage
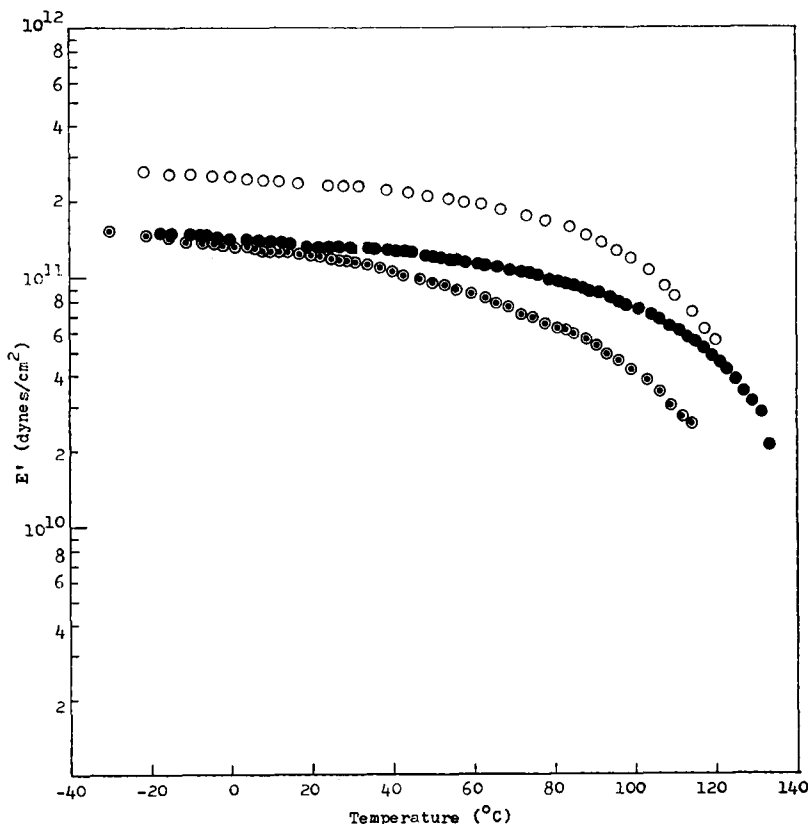

Fig. 3. Temperature dependence of dynamic modulus for drawn polyethylene films: (●) irradiated polyethylene drawn at 145°C. to 16× (sample 1); (◉) irradiated polyethylene drawn at 80°C. to 16× (sample 3); (○) unirradiated polyethylene drawn at 80°C. to 16× (sample 2).

takes place within a narrow temperature range in the vicinity of 35°C. It is to be noted here that the shrinkage curves of the stretched polyethylene and the racked rubber resemble each other in shape but the relations of the shrinking temperatures to each equilibrium melting temperature apparently differ.

The result indicates that the crosslinked polyethylene has been by no means racked to its extended state as in the case of the racked rubber although the extended state is much more stable than for the polyethylene oriented in the partially crystalline state of 80°C.

Dynamic Mechanical Properties

In Figure 3 dynamic modulus is plotted against temperature for three samples; two of them are those already described above and the third is a sample of irradiated polyethylene elongated at 80°C. to 16 times of its original length. It is easily ascertained that the value of modulus for
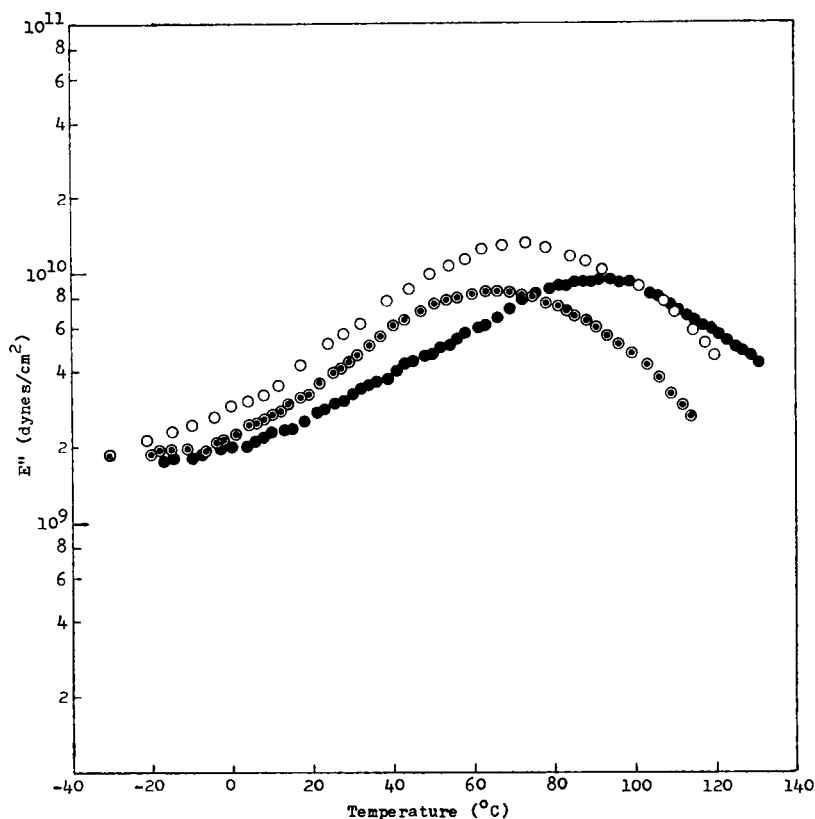

Fig. 4. Temperature dependence of dynamic loss for drawn polyethylene films: (●) irradiated polyethylene drawn at 145°C. to 16× (sample 1); (◉) irradiated polyethylene drawn at 80°C. to 16× (sample 3); (○) unirradiated polyethylene drawn at 80°C. to 16×.

sample 1 prepared by stretching in the amorphous state is smaller in the lower range of temperature than for sample 2 prepared by stretching in the crystalline state. This may be a result of the fact that the axial oriented state of amorphous chains between crystallites is higher for the latter sample than for the former. It is also seen that the dynamic modulus of sample 2 decreases at a higher rate with increasing temperature than sample 1. This difference may be due to the presence of very stable crystallites and relaxed amorphous chains in sample 1. In Figure 3 data are shown also for sample 3 prepared by stretching the irradiated sample at 80°C. The absolute value is shown to be lowest in all of the temperature range examined but it is recognized that the shape of the curve is quite similar to that of sample 2. This lower value of dynamic modulus of sample 3 must be caused by its lowest degree of crystallinity as shown in Table II, but it is supposed that the structure of its amorphous phase is similar to that of sample 2.

In Figure 4 dynamic loss of three samples is plotted against temperature. There is observed a peak of E'' in the temperature range of 60–100°C. for the samples. The absorption of polyethylene in this temperature range is usually assigned as an energy loss induced in the crystalline phase.[9] Hence, the position of the peak would reflect the structural state of crystallites. In Table II, the temperature T_c where E'' goes through the maximum is shown for three samples. For sample 1, the highest value 97°C. is indicated. Such a high temperature has not been observed in measurements at a frequency of 110 cps for oriented polyethylene hitherto. It must indicate the very stable crystalline structure of the sample. In Table II the values of T_c are also shown for isotropic bulk samples crystallized isothermally from the melt. It is worthy of note that T_c of sample 1 is equal to that of a sample isothermally crystallized at 129°C. from the melt

TABLE II
Summary of Dynamic Mechanical Properties of Drawn Polyethylenes

Sample	Density at 30°C., g./cc.	E' at 20°C. $\times 10^{10}$, dynes/cm.^{2}	Max. value of E'' $\times 10^9$, dynes/cm.^{2}	Peak temp. T_s, °C.
Irradiated Marlex-50, stretched at 145°C. to 16× (sample 1)	0.964	13.1	9.38	97
Irradiated Marlex-50, elongated at 80°C. to 16×	0.955	12.0	8.40	65
Unirradiated Marlex-50, elongated at 80°C. to 16×	0.965	23.5	12.80	72
Bulk Marlex-50, crystallized isothermally at 129°C. from the melt	0.983	1.95	0.53	97
Bulk Marlex-50, crystallized isothermally at 115°C. from the melt	0.958	1.58	0.51	87

for a very long period of time. The high temperature of T_c for these two samples may be well explained by the fact that well-grown crystallites are thought to coexist with relaxed amorphous chains in the samples.

References

1. J. T. Judge and R. C. Stein, *J. Appl. Phys.*, **32**, 2357 (1961).
2. R. Kitamaru and L. Mandelkern, *J. Polymer Sci. B*, **2**, 1019 (1964).
3. I. Sakurada, Y. Nukushina, and T. Ito, *Kobunshi Kagaku*, **19**, 285 (1962).
4. H. Feuchter, *Kautschuk*, **1**, 6 (1925); *ibid.*, **4**, 8, 28 (1928).
5. D. E. Roberts and L. Mandelkern, *J. Res. Natl. Bur. Std.*, **54**, 167 (1955).
6. J. F. M. Oth and P. J. Flory, *J. Am. Chem. Soc.*, **80**, 1297 (1958).
7. R. Chiang and P. J. Flory, *J. Am. Chem. Soc.*, **83**, 2857 (1961).
8. R. S. Stein and F. H. Norris, *J. Polymer Sci.*, **21**, 381 (1956).
9. M. Takayanagi, T. Aramaki, M. Yoshino, and K. Hoashi, *J. Polymer Sci.*, **46**, 531 (1960).

Résumé

L'orientation moléculaire de polyéthylène étiré a été étudiée par les techniques de rayons-X et de biréfringence pour les phases cristalline et amorphe. On a pu confirmer qu'une structure fibreuse intermédiaire entre des cristallites hautement orientées et des chaînes amorphes non-orientées est obtenue si le polyéthylène légèrement ponté est fortement et rapidement étiré dans l'état fondu et refroidi ensuite à température de chambre. Quelques propriétés, telles que les propriétés dynamiques et thermodynamiques ont été discutées par rapport à la structure moléculaire.

Zusammenfassung

Die Molekülorientierung in gerecktem Polyäthylen wurde getrennt für die kristalline und amorphe Phase mit Röntgen- und Doppelbrechungsmethoden bestimmt. Es wird gezeigt, dass bei starker, rascher Reckung eines schwach vernetzten Polyäthylens im völlig geschmolzenen Zustand und nachheriger Abkühlung auf Raumtemperatur eine Faserstruktur aus hochorientierten Kristalliten und fast nicht-orientierten, relaxierten amorphen Ketten erzeugt wird. Eine Diskussion gewisser Eigenschaften, nämlich dynamisch mechanischer und thermodynamischer Eigenschaften, in Beziehung zur Molekülstruktur wird gegeben.