

Recrystallization of Polyethylene During Annealing

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INTRODUCTION

Recent studies¹⁻⁵ of the crystallization of polymers have been interpreted² in terms of the folding of the molecules within single crystal lamellae. Experiments have shown^{6,7} that the thickness of the lamellae of crystals of polyethylene is remarkably uniform in a given preparation. The thickness as measured in the electron microscope corresponds to the Bragg long-period spacing found in small angle x-ray diffraction patterns from aggregates of the crystals.

The long period, and thus the thickness of polyethylene lamellae, is dependent on the temperature of crystallization, increasing with increasing temperature.^{8,9} Similarly, polyurethane samples which had been quenched from the melt to a glassy state showed the development of a sharp long period spacing during crystallizing treatments; the spacing was largest for the highest annealing temperature.⁷

Some evidence has been presented that the long-period spacing of bulk polymer and of single crystal lamellae can be increased by annealing at temperatures below the melting point.⁸⁻¹⁰ In this paper we describe a detailed study of the recrystallization effect, occurring during the annealing of single crystals of polyethylene. Small- and wide-angle x-ray diffraction patterns from aggregates of the crystals and electron microscope and electron diffraction observations on isolated single crystals have been made. These results emphasize the earlier suggestion⁷ that polymer molecules have surprising mobility in crystals appreciably below their melting point.

EXPERIMENTAL

The crystals used for the x-ray investigations were grown by cooling dilute solutions of a higher density polyethylene in perchloroethylene. Several preparations were combined, and the crystals collected as a cake by filtering. Their lamellar nature provided a layered aggregate.⁶ Three orders of long-period diffraction were obtained when the x-ray beam was directed parallel to the surface of the cake. The Bragg spacings indicated a lamellar thickness of 104 Å. No long-period diffraction was obtained when the beam was directed normal to the surface of the cake.

The x-ray technique was standard for polyethylene studies in this laboratory:¹¹ 0.015-in. diameter pin hole collimators, 6 in. apart; a sample-film distance of 32 cm. in an evacuated box camera; Ilford G x-ray film; 8 hr. exposure (to record the intense first order) or 64 hr. exposure (to record the weaker second and third orders) from samples about 0.020 in. thick.

Portions of the crystalline aggregate were heated in air in a small furnace for 30 min. at the desired temperature, controlled to $\pm 1^\circ\text{C}$. A thermocouple near the sample registered the temperature. The samples were cooled by removing the glass dish holding the crystals from the furnace; the cooling rate would therefore be relatively high. The cooling rate was not critical, as shown by one experiment in which the crystals were cooled very slowly from 125°C. by leaving them in the hot furnace after the heating elements were turned off; no difference in results was found.

The electron microscope observations were made

on crystals from the above preparation, as well as on some that were recrystallized from dilute solutions in octane. The crystals were deposited from suspension onto glass slides which previously had been coated with evaporated carbon. The slides were then annealed at the desired temperatures in a vacuum oven and then shadowed prior to the observations. For the electron diffraction studies, the same crystal preparation was used, but the shadowing omitted.

The thickness of the lamellae in both the original crystals and the annealed crystals, as measured on the shadowed samples in the electron microscope, agreed well with the values obtained from the small-angle x-ray diffraction patterns. The original crystals were typical of polyethylene crystals¹⁻³ in having flat surfaces, rhombic shapes, and spiral overgrowths.

RESULTS

The x-ray results are summarized in Figure 1, and typical small-angle patterns are shown in Figure 2.

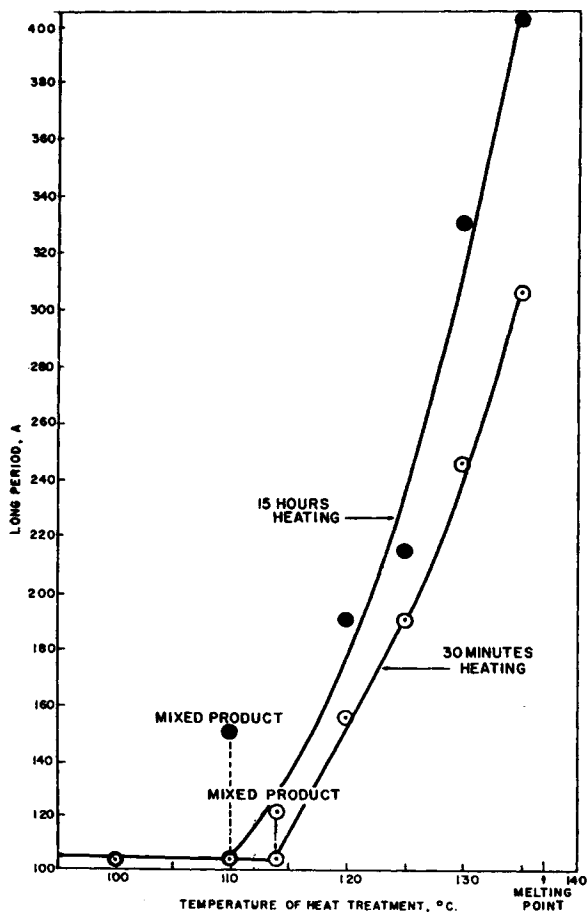


Fig. 1. Long-period x-ray diffraction from layered aggregate of polyethylene crystals after annealing.

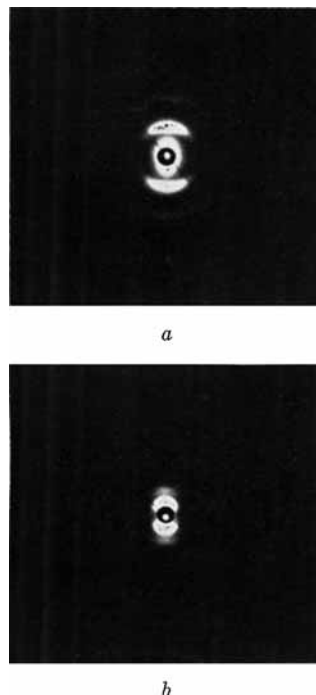


Fig. 2. Typical small-angle x-ray patterns of polyethylene crystal aggregate (*c* axis of platelets is vertical): (a) as prepared; (b) after heating at 130°C. for 30 min.

Table I lists a number of other measured parameters for the crystalline aggregate before and after the heat treatment. Especially noteworthy is the constancy of the gross dimensions of the aggregate.

The data in Figure 1 shows the effects of both temperature and time above 110°C. Equilibrium appears to be reached within 15 hr., since heating for 65 hr. at 125°C. produces no further change in the long period. Equilibrium may be reached more quickly if media other than air are used; this is currently being investigated. Below 110°C. no effect on the long period of temperature or of heating time (up to 15 hr.) is detected. However, after 15 hr. at 110°C. or 30 min. at 114°C., a mixed product is obtained. The diffraction patterns show the original long period of 104 Å., together with a discrete, larger, long period. Two orders of diffraction are obtained from the aggregates annealed above 114°C. It is apparent that some kind of transition occurs in the polyethylene crystals at approximately 110°C.

Polyethylene crystals obtained from a different solvent and at a different temperature have a different initial thickness.^{8,9} It is not yet known whether the transition temperature would similarly be different. A transition temperature of 110°C. was obtained, however, in a recent study of the

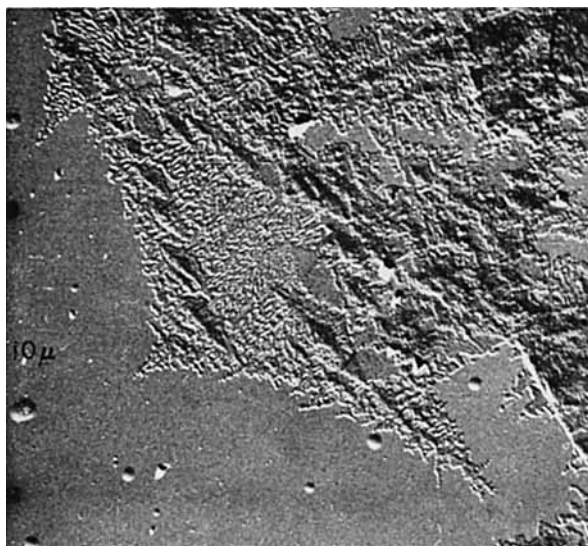


Fig. 3. Single crystals of higher density polyethylene crystallized from dilute perchloroethylene solutions and annealed at 125°C. for 30 min. The a and b axes are in the direction of the long and short axes, respectively, of the crystal. Pt-Pd shadowed at $\theta = \arctan 5/12$.

annealing of bulk polyethylene crystallized from the melt.¹⁰

The surprising x-ray results become more understandable when electron micrographs are studied. They show that recrystallization takes place during the annealing treatments at temperatures above 110°C. Figure 3 shows that many holes develop in single crystals in regions which were originally one lamella thick, and the lamellae increase in thickness.

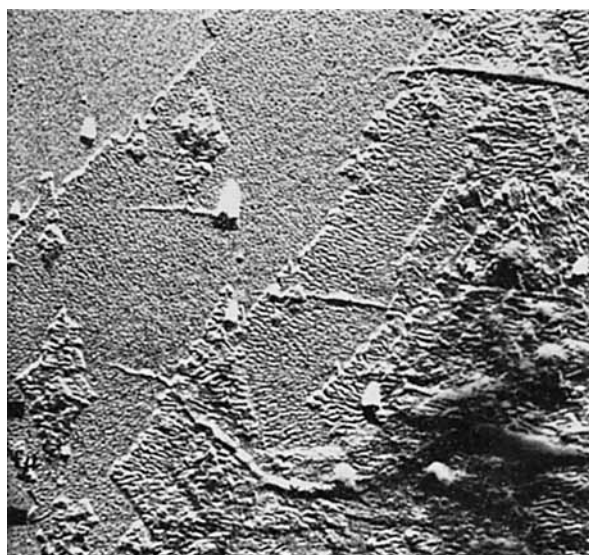


Fig. 4. Portion of a single crystal annealed at 116°C. for 30 min. Pt-Pd shadowed at $\theta = \arctan 5/12$.

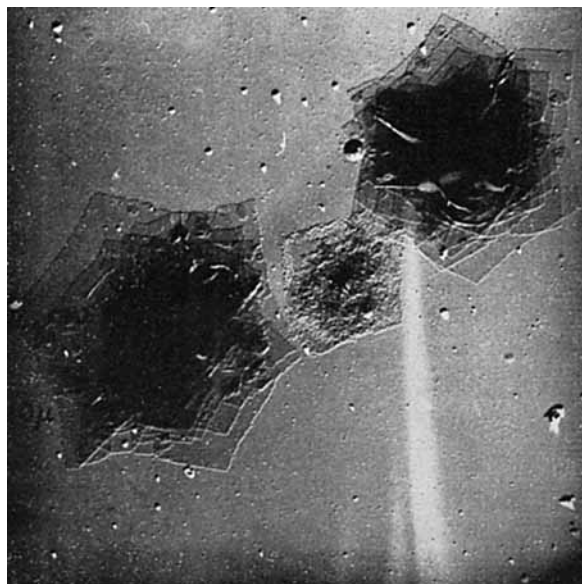


Fig. 5. Single crystals of higher density polyethylene crystallized from a dilute octane solution. Annealed at 120°C. for 12 hr. Only the smaller crystal has undergone recrystallization. The two larger crystals have developed wrinkles parallel to the b axis. Cr shadowed at $\theta = \arctan 4/7$.

The polymer required for the increase in thickness is drawn from localized regions of the same lamella; this is an indication of a heterogeneous transformation and explains the constant dimensions of the gross cake. As shown in Figure 4, the holes that develop in the lamellae are larger in regions where the crystal is more than one lamella thick. However, after higher annealing temperatures, the structure is obscure in regions which are more than one lamella thick.

If any solvent is still present at the time of the annealing, the crystals apparently dissolve and then reprecipitate as the solvent evaporates. Although the outline of the original crystal is retained, all evidence of the original lamellar structure disappears. The new structure resembles that found during crystallization from a hot solution by evaporation of the solvent.²

Since the single crystals are grown by cooling a dilute solution, it is possible that various crystals may be nucleated and start growing at different temperatures. The fold distance or thickness would be expected, therefore, to be different.⁸ Any subsequent annealing treatment might then be expected to affect the various crystals differently. Such was found after annealing crystals from octane solution; as shown in Figure 5, the smallest crystals underwent recrystallization while the larger ones in

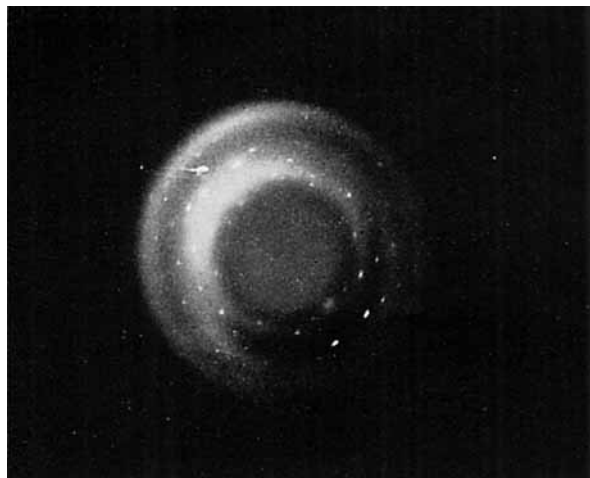


Fig. 6. Electron diffraction pattern from a single crystal of higher density polyethylene, crystallized from perchloroethylene and annealed at 132°C. for 30 min.

the same preparation did not. The smallest crystals are presumably those which are also the thinnest.

Two types of wrinkles are found in the crystals. The large ridges or pleats seen on the crystals in Figures 4 and 5 are similar to those described by Keller.² They develop during evaporation of the solvent and are more or less parallel to the *b* axis. Small wrinkles, also parallel to the *b* axis, develop

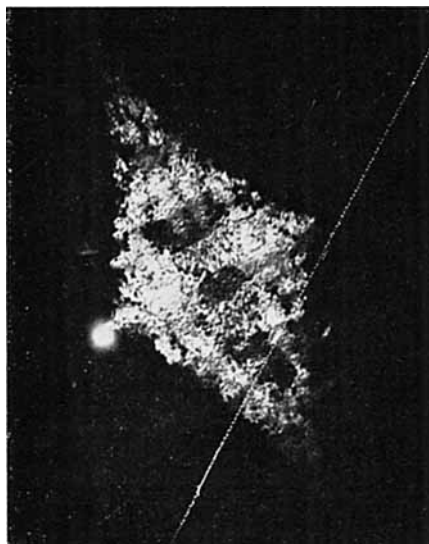


Fig. 7. Dark-field electron micrograph of the crystal used for the diffraction pattern shown in Fig. 6. The bright spot at one of the aspicies of the crystal is an overexposed image of the Bragg reflection used in taking the photograph. The entire crystal is scattering into the Bragg reflection, except for the regions where the substrate is warped.

on the larger crystals, as shown in Figure 5, during the annealing treatment. The latter type of wrinkle may result from the fact that the thermal expansion of the polyethylene lattice is primarily in the direction of the *a* axis.¹² The pleats result from the collapse of hollow pyramidal lamellae during solvent removal.¹³

X-ray diffraction patterns at wide angles indicate that the original molecular *c* axis orientation is maintained during the recrystallization. Electron diffraction patterns from isolated crystals, such as Figure 6, show that the alignment of the *a* and *b* axes, as well as the *c* axis, is maintained. The Bragg electron reflections are only slightly wider than those from the original crystals. The Bragg x-ray reflections are sharper after annealing; line-broadening measurements show an increase in crystallite length which corresponds to the increase in long period (Table I). Dark-field electron microscope observations, such as in Figure 7, also show that the annealed, recrystallized crystals retain the original orientation of the molecules since the entire crystal is bright.

TABLE I
Characteristics of the Polyethylene Crystalline Aggregate

Parameter	Before heating	After heating at 125°C.
Thickness of cake (through direction), mm. ^a	0.751	0.772 (3% expansion)
Width of cake (edge direction), mm. ^a	1.197	1.209 (1% expansion)
Density, g./cc.	0.979	0.978
Melting point, °C. (Kofler hot stage)	137	No change
Crystallite width, A. ^b	230	290
Crystallite length, A. ^b	120	300
Direction of x-ray beam to produce long-period diffraction	Parallel to platelets	No change
Crystallite orientation in aggregate	Chain axis well aligned perpendicular to surface of platelets	No change

^a Microscope measurements with calibrated eyepiece.

^b Standard line-broadening measurements from appropriate diffractions in the wide-angle x-ray pattern; calculated by use of the Warren approximation of the Scherrer formula, $\pm 10\%$. Crystallite width is probably more correctly interpreted as the extent of crystallite perfection in a mosaic, since the individual single crystal lamellae are several orders of magnitude larger.

The recrystallization process appears to be irreversible in the solid state. Reannealing for 18 hr. at temperatures below the original annealing temperature produces no change in the long period. Reannealing at a higher temperature than the original does lead to a further increase in the thickness of the lamellae. However, if annealed crystals are dissolved and reprecipitated, the preannealed thickness (104 Å) is again obtained. If crosslinking is achieved by irradiation in an electron beam, the annealed crystals do not dissolve but form a gel in the solvent. When this gel is cooled to room temperature, it gives an unoriented long period of 120 Å. Thus, the crosslinking is sufficient to cause insolubility, but not sufficient to immobilize the molecules completely. This will require further experiments to be understood fully.

X-ray diffraction patterns obtained from the crystal aggregates before annealing are identical with those from highly crystalline polyethylene having an "amorphous" content of 15–20% by density. This result supports the suggestion¹⁴ that the "amorphous" content of crystalline high polymers arises from the chain folds, branch points, and gross imperfections within the single crystal lamellae.

The recrystallization process occurring during the annealing of the dry crystals apparently takes place by a refolding of the chains. The original orientation of the planar zigzag is maintained. Considerable molecular motion evidently occurs during recrystallization. The precise mechanism is unknown, but it must involve a movement of the entire chain in which the ends become closer together as the fold distance increases. It has been recognized for some time¹² that there are small oscillatory motions of the molecules in the crystalline regions of polymers. Furthermore, the premelting phenomenon has been interpreted in terms of a melting of the smallest and least perfect crystallites.^{12,15} However, the amount of motion that our results require is most surprising in the light of the generally accepted fringed micelle concept of crystalline high polymers. These results are another indication that many of the presently accepted theories concerning the nature of crystalline polymers need to be re-examined in terms of the lamellar structure of crystalline polymers.¹⁴

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Synopsis

The thickness of single crystal lamellae of polyethylene, crystallized from solution, is found to increase greatly during annealing at temperatures above 110°C. The change is observed with small-angle x-ray diffraction and electron microscopy. The increase in thickness of the lamellae takes place at the expense of their lateral perfection; holes develop within the lamellae. All evidence indicates that a major refolding of the molecules occurs; this emphasizes the need for a new concept of the amount of motion and freedom that polymer molecules can have in the solid state. A similar process apparently occurs during the annealing of bulk samples crystallized from the melt.

Résumé

On trouve que l'épaisseur d'une lamelle cristalline simple de polyéthylène, cristallisée au départ de sa solution, augmente considérablement durant la recuite à des températures supérieures à 110°C. La variation est suivie à l'aide de la diffraction des rayons-X à petit angle et par microscopie électronique. L'augmentation d'épaisseur des lamelles a lieu aux dépens de leur perfection latérale; des trous prennent naissance à l'intérieur des lamelles. Il est évident qu'un replissement des molécules a lieu; ceci confirme à nouveau le besoin d'un nouveau concept relatif au degré de liberté et de mouvement des molécules à l'état solide. Un processus similaire a lieu durant la recuite d'échantillons en bloc cristallisés au départ de la masse fondue.

Zusammenfassung

Es wird gefunden, dass die Dicke von Einkristalllamellen von Polyäthylen, wie sie durch Kristallisation aus Lösung erhalten werden, beim Tempern bei Temperaturen über 110°C stark zunimmt. Die Veränderung wird mit Röntgenkleinwinkelbeugung und elektronenmikroskopisch beobachtet. Die Dickezunahme der Lamellen geht auf Kosten ihrer seitlichen Ausbildung vor sich; innerhalb der Lamellen entwickeln sich Löcher. Alle Befunde sprechen dafür, dass eine grössere Umfaltung der Moleküle eintritt. Damit wird die Notwendigkeit eines neuen Konzepts für die Grösse der Bewegung und der Unabhängigkeit, die Polymermoleküle im festen Zustand besitzen können, nachdrücklich betont. Ein ähnlicher Vorgang findet offenbar beim Tempern von grösseren, aus der Schmelze kristallisierten Proben statt.

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