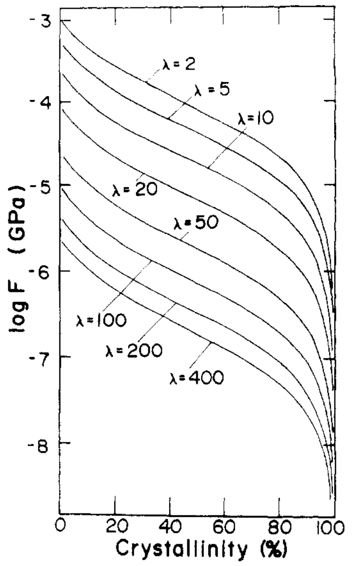

Figure 9. Logarithmic value of F calculated as a function of crystallinity for various draw ratios λ.

lattice modulus as measured by X-ray diffraction is independent of molecular orientation and crystallinity and that the Young's modulus approaches the crystal lattice modulus with increasing draw ratio at 100% crystallinity. These results support, on the whole, the experimental results measured for ultradrawn polyethylene films in previous work.[13] Furthermore, a slight discrepancy between the calculated and experimental results indicate that the Young's modulus is also sensitive to crystal defects, crystal disorder, and chain scission in addition to the molecular orientation and crystallinity. Accordingly, the simple relationship represented by eq 5 and 6 must be reconsidered in order to realize good agreement between the calculated and observed values. The effect of a number of parameters such as the defects, the disorder, and chain scission on mechanical properties are perhaps the most significant of the unknown contributions and must be taken into account in further studies.

Registry No. Polyethylene, 9002-88-4.

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On Deformation of Polyethylene: The Question of Melting and Recrystallization

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ABSTRACT: The question of melting and recrystallization of polyethylene on drawing is evaluated by using samples with a range of starting morphologies. They were prepared by crystallization at an elevated pressure of 460 MPa and at different temperatures to produce chain-extended polyethylene with lamellar thicknesses ranging from 270 to 480 nm. Chain-folded polyethylene was also prepared by quenching its melt. These samples were examined after being uniaxially drawn by solid-state extrusion at constant temperatures from 70 to 125 °C. Weak meridional intensity maxima were found in small-angle X-ray scattering patterns of the chain-extended polyethylene after drawing, which originates from the deformation of a small fraction of low molecular weight polyethylene rejected during crystallization. From thermal analyses and consideration of X-ray scattering patterns of both the drawn chain-extended and chain-folded polyethylene, the chain-extended lamellae do not appear to undergo melting and recrystallization for the draw conditions used.

Introduction

Several deformation mechanisms have been proposed to describe the morphological changes during drawing of semicrystalline polymers. The most widely accepted one and most suited for polyethylene (PE) is the model of Peterlin.[1] It involves shearing, rotation, chain tilt, and slip in the lamellae and their transformation into bundles of microfibrils. For many years, it has been disputed whether such morphological changes on deformation involve melting and recrystallization.

Advances in drawing have produced PE with uniaxial draw ratio many times above its "natural draw". This feature was thought to be possible only if the local strain

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energy during deformation is high enough to melt the chains, which could then be drawn to high ratios and recrystallized into extended chains giving ultrahigh tensile modulus fibers.[2] The shrinkage of drawn PE during annealing can thus be consistently explained.[3] The cold-drawn sample shrinks much more than PE obtained by hot drawing. It was rationalized that hot-drawn PE contains crystalline bridges which are formed during deformation, giving crystal continuity along the draw direction. These bridges are relatively stable to annealing, as opposed to the taut tie molecules of cold-drawn PE, which relax during annealing, and therefore the cold-drawn PE shrinks much more.

The strongest and often-cited evidence for melting and recrystallization on draw is that the lamellar long period of drawn PE, measured from small-angle X-ray scattering (SAXS), correlates with draw temperature, irrespective of initial lamellar thickness.[4] At each draw temperature, such long periods have been found to be independent of draw ratio, once the lamellae have been transformed into microfibrils. Indeed, the long period does increase with draw temperature, and in a way similar to its dependence on crystallization temperature.[5] Such comparable behavior has thus suggested that the long period must be produced by the same process, i.e., through recrystallization. The above observations apply to both tensile and compressive deformations.[6]

A melting and crystallization process during deformation is also considered a consequence of the proposed random switchboard model of chain folding in lamellae.[7] In this model, entanglements are trapped in the fold loops and the lamellae are interconnected such that their relative mobility is impeded during deformation. To transform them into the fibrillar structure of the drawn polymer, entanglements must be relieved through melting and recrystallize as folded chains in the fibrils.

Meinel and Peterlin[8] have calculated the microscopic conversion of deformation work into heat under adiabatic conditions. They find that the rise in temperature reaches only 110 °C and is insufficient to cause crystal melting in PE. Interest in this problem was revived when Juska and Harrison[2] proposed a deformation mechanism for PE which invokes melting at all draw temperatures for which the spherulitic lamellae are converted into microbrils through isolated deformation zones of crazes and shear bands.

Subsequently, Wignall and Wu[9] cleverly used the anomalous molecular weight segregation effect in small-angle neutron scattering (SANS) of a deuteriated PE and hydrogenated PE blend to study this problem. They found a large reduction in apparent molecular weight measured by SANS for deformation between 50 and 119 °C, which is similar to the phenomenon observed in melting and quenching. It was therefore concluded that reorganization of morphology during deformation is similar to melting and recrystallization. However, work by Wu et al.[10] on small-strain deformation of poly(ethylene terephthalate) at room temperature found the change in SAXS patterns does not indicate any melting and recrystallization.

The strongest experimental evidence of melting and recrystallization during deformation is the observed unique dependence of long period on draw temperature, yet in previous works this was evaluated only with initial lamellae <100 nm thick. In this paper we report on a study of this problem by uniaxial drawing using solid-state extrusion of chain-extended PE lamellar thicknesses in the region 10^2–10^3 nm. Chain-extended PE can only be crystallized under high pressure, >350 MPa.[11] Should melting occur, recrystallization would result in folded chains since the extrusion pressure is not high enough to cause recrystallization into chain-extended lamellae. The periodicity of recrystallized and folded chains along the draw direction can be followed by SAXS. Furthermore, the deformation induced by solid-state extrusion is so slow that heat transfer to the surrounding environment is maintained such that the system is virtually isothermal.

Table I
Crystallization Conditions and Lamellar Thickness Distribution of Initially Chain-Extended Polyethylene Billets

	crystallization		lamellar thickness distribution	
billet	temp, °C	press, MPa	L_n, nm	L_w, nm
1	221	460	480	570
2	216	460	350	500
3	207	460	270	330
4	198	460	280	320

Experimental Methods

High-density PE pellets (Du Pont Alathon 7050) with molecular weights M_w = 59 000 and M_n = 19 000 were crystallized at a constant pressure of 460 MPa and at the four crystallization temperatures 221, 216, 207, and 198 °C into chain-extended PE, as described previously.[12] Chain-folded PE billets were also prepared by quenching its melt from 160 °C at a constant pressure of 160 MPa. Each premorphology was solid-state-extruded at 100 °C through a conical brass die with a 20° entrance angle in an Instron capillary rheometer up to a draw ratio of 23.4. In addition, the chain-extended PE billet crystallized at 216 °C and the quenched chain-folded PE billet were also extruded at a constant draw ratio of 12.9 at constant temperatures from 70 to 125 °C, all at a plunger speed of 0.01 cm/min.

SAXS of the extrudates were measured with the Oak Ridge National Laboratory SAXS instrument at a 5-m sample-to-detector distance with Cu Kα radiation and a two-dimensional position-sensitive detector. Intensity was corrected for detector sensitivity, sample absorption, background, and dark current. The beam stop is circular with a 1-cm diameter such that the detector intensity is cut off at k = 0.008 Å^{-1} ($k = 4\pi \sin \theta/\lambda$). The long period is measured from the peak position of the intensity maxima and calculated by Bragg's equation. For undrawn samples, the intensities were Lorentz corrected.

Thermal analyses were made with a Perkin-Elmer differential scanning calorimeter DSC-II equipped with a data acquisition station. Indium was used for calibration. The heating rate was 2.5 °C/min to minimize superheating of the chain-extended crystals.

Results

The characterization of the four chain-extended PE billets prior to drawing is shown in Table I. The number-average lamellar thickness, as measured from fracture surface replicas by electron microscopy, decreased systematically from 480 to 280 nm with decreasing crystallization temperature 221 to 198 °C. Figure 1 shows SAXS of one of these undrawn billets after Lorentz correction. No prominent maximum can be detected. A weak shoulder is seen at k = 0.02 Å^{-1}. The intensity fluctuation of this shoulder is within the error of measurement. However, repeated scans produced the same weak shoulder. Therefore, this feature is likely real and not the result of a statistical intensity fluctuation. The quenched chain-folded billet shows two orders of strong maxima (Figure 1), with a long period of 33.7 nm.

The first set of experiments was carried out by extrusion drawing of the chain-extended PE and the chain-folded PE billets at a constant temperature of 100 °C to various draw ratios up to the maximum draw before fracture occurs in the extrudates. After deformation, all four chain-

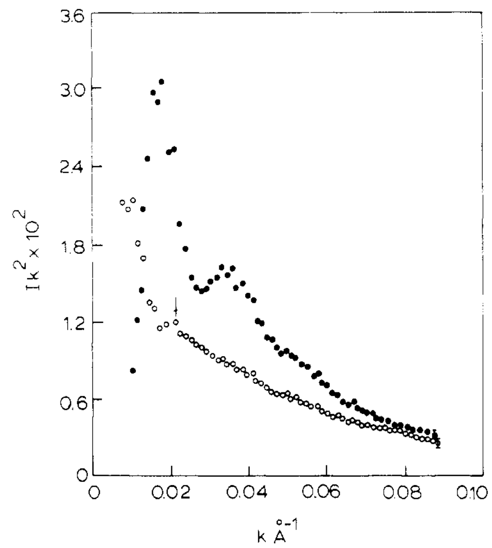

Figure 1. SAXS of undrawn chain-extended PE crystallized at 198 °C (○) and undrawn chain-folded PE (●) from quenching.

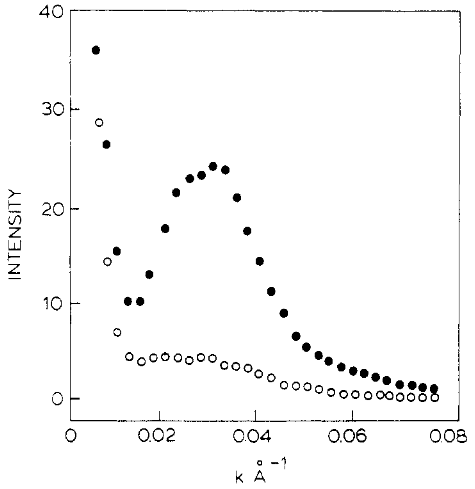

Figure 2. Meridional SAXS scans of chain-extended PE crystallized at 216 °C and extruded at 100 °C to draw ratio 16.4 (○) and chain-folded PE extruded to draw ratio 12.2 (●) under the same conditions.

Table II
Long Period of Chain-Extended and Chain-Folded PE Billets Extruded at 100 °C

Long Period (nm) from Extrudates of Chain-Extended PE Billets

draw ratio	1	2	3	4
4.1		29.4	31.3	30.1
4.9	22.3			
7.2	22.3	29.3	30.6	27.7
9.0	23.3	30.1	26.3	
11.4	25.7	24.4	25.7	27.0
16.4	24.5	23.8	25.1	25.0
23.4				22.4

Long Period (nm) from Extrudates of Chain-Folded PE

draw ratio	long period	draw ratio	long period
undrawn	33.7	12.2	23.4
5.8	31.1	14.8	27.0
9.1	25.7	16.2	21.4

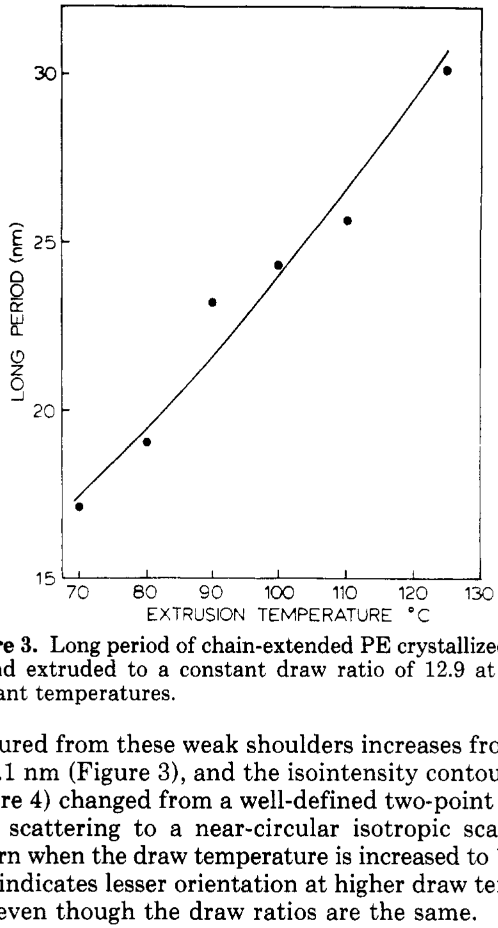

Figure 3. Long period of chain-extended PE crystallized at 216 °C and extruded to a constant draw ratio of 12.9 at several constant temperatures.

extended PE billets show two-point meridional scattering with weak intensity maxima (Figure 2). The measured long period decreases with draw to a constant value of ~24 nm (Table II). However, quenched chain-folded PE after drawing under identical conditions to the same draw ratio shows a contrasting scattering with strong intensity maxima, about 5 times the peak intensity of chain-extended PE (Figure 2). The long period also decreased with increasing draw ratio to ~23 nm, close to those found in extruded chain-extended PE and values previously reported at the same draw temperature by both tensile and compression drawing.[4,6]

The second set of draw experiments was carried out by extruding the chain-extended PE billet crystallized at 216 °C and the quenched chain-folded PE at a constant draw ratio of 12.9 at a series of constant temperatures from 70 to 125 °C. At this draw ratio, lamellae of the spherulites have been fully transformed into a fibrillar morphology and the draw temperatures cover both "cold" and "hot" (temperature above the α_c transition, ~100 °C) drawing.

SAXS shows weak meridional maxima for the drawn chain-extended PE, similar to those shown in Figure 2. Intensity of the maxima decreases to a small shoulder as the draw temperature is increased. The long period measured from these weak shoulders increases from 17.1 to 30.1 nm (Figure 3), and the isointensity contour plots (Figure 4) changed from a well-defined two-point meridional scattering to a near-circular isotropic scattering pattern when the draw temperature is increased to 125 °C. This indicates lesser orientation at higher draw temperature even though the draw ratios are the same.

DSC scans of the undrawn and drawn chain-extended PE billet crystallized at 216 °C are shown in Figure 5. The undrawn chain-extended PE has a small endotherm, about 4% of the total peak area, at a peak temperature of 130.5 °C. This low-temperature endotherm has been attributed to the low molecular weight PE fraction rejected during high-pressure crystallization,[13] which is able to crystallize into either fully extended or chain-folded lamellae during cooling. The presence of this small endotherm is interesting and is crucial to the conclusions of this study. The rejected low molecular weight fraction, when crystallized into fully extended form, gives a lamellar thickness of <100 nm. The shoulder observed in SAXS has a long period of 31–33 nm. This falls within the thickness expected from the rejected low molecular weight fraction.

On drawing, the low-temperature endotherm disappears, merging with the higher temperature endotherm at 136

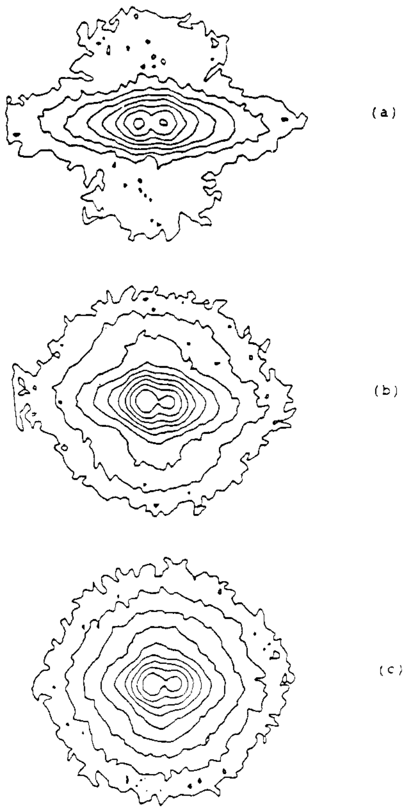

Figure 4. SAXS isointensity scattering patterns of chain-extended PE crystallized at 216 °C and extruded to a constant draw ratio of 12.9 at (a) 70, (b) 100, and (c) 125 °C.

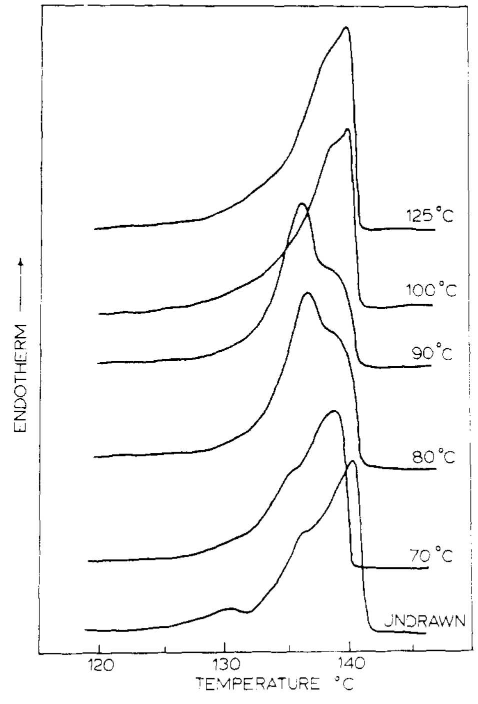

Figure 5. DSC scans of chain-extended PE crystallized at 216 °C and extruded to draw ratio 12.9 at several constant temperatures. The scans are shifted upward.

°C (Figure 5). The highest endotherm, with a peak melting point of 141 °C, also decreases in both peak temperature and magnitude as extrusion temperature is increased, while the 136 °C endotherm increases in magnitude and becomes dominant at a draw temperature of 90 °C. At higher draw temperatures, >100 °C, an endotherm with a peak maximum at 140 °C accompanied by a shoulder in close proximity at 139 °C was observed.

Discussion

SAXS results of both the chain-extended and chain-folded PE extruded at 100 °C to a series of draw ratios give long periods of ~24 nm at high draw, irrespective of the initial lamellar thickness. When the PE was extruded to a constant draw ratio, the long period increased with increasing draw temperature. These observations are consistent with the evidence often cited by advocates of melting and recrystallization during deformation. However, this conclusion is not as simple as it appears in light of thermal analyses and consideration of the X-ray scattering patterns.

The total integrated intensity of SAXS is proportional to the mean squared electron density difference, $\langle(\rho - \bar{\rho})^2\rangle$, between the amorphous and crystalline phase

$$\langle(\rho - \bar{\rho})^2\rangle = (\rho_1 - \rho_2)^2\varphi_1\varphi_2$$

where ρ_1 and ρ_2 are the electron densities of each phase, assuming sharp boundaries, and φ_1 and φ_2 are the respective volume fractions. It has been found that for solid-state-extruded PE[14,15] the electron density difference between crystalline and amorphous phases becomes smaller as draw ratio and orientation are increased, resulting in diminished intensity. However, the overall scattering patterns (Figure 4) and wide-angle X-ray photographs show at higher draw temperature the extruded chain-extended PE is less oriented due to relaxation after draw and/or less efficient orientation during draw.[12] Therefore it is unlikely that $(\rho_1 - \rho_2)$ decreases in this case. Then the decrease in SAXS intensity is due at least in part to a decrease in the fraction that gives scattering intensity maxima.

SAXS and DSC of the undrawn billet showed, even in chain-extended PE, that there is a small fraction of low molecular weight PE rejected during crystallization, characterized by a weak shoulder in SAXS and a long period of 31–33 nm. The observed SAXS maximum of extruded chain-extended PE is so weak that the scattering fraction must be small and likely originates from this fraction of rejected crystals.

Results of the present study suggest that chain-extended PE crystals do not melt and recrystallize during deformation. Upon comparison of the SAXS of drawn chain-extended PE with that of chain-folded PE, the former exhibits weak intensity maxima. Should melting have occurred, the drawn chain-extended PE would have crystallized into chain-folded lamellae because the extrusion pressure was <180 MPa, which is insufficient for recrystallization into the chain-extended morphology. Also, on melting and after the material recrystallized, the observed intensity maxima should at least be of the same magnitude as that of the chain-folded PE extruded under the same conditions. The above conclusion corroborates the electron microscopy work of Attenburrow and Bassett,[16] who showed that there is an extensive sliding motion of the chains and the majority of chain-extended lamellae survived drawing.

A possible reason the chain-extended crystals apparently do not melt during deformation is that they have thickness of the same order as the molecular chain length and therefore have few folds per chain and consequently reduced entanglements. The deformation of such thick lamellae with reduced entanglements can be different from the chain-folded lamellae, which are profusely entangled. Disruption of the thick lamellae still occurs during deformation, as shown by a decrease in magnitude and temperature for the highest endotherm in DSC (Figure 5).

However, chains are easily unraveled when the draw temperature is high. Above the α_c transition temperature, the interchain dispersive force is drastically reduced. Slipping of chains can occur in the (hk0) crystallographic planes when the applied stress reaches the critical resolved shear stress. Such intralamellar shear was reported to occur on two slip systems: (010) ⟨001⟩ and (100) ⟨001⟩, both along the chain direction.[17] The slipped chains can then be incorporated into the drawn microfibrils without the necessity of melting. Indeed, transmission electron micrographs of fracture surface replica of a chain-extended PE drawn 4.9× show the shearing of stacks of the thick lamellae along the chain direction for incorporation into the generated microfibril.[12]

In the analysis of Meinel and Peterlin,[8] normal melting is excluded even under an adiabatic condition. On deformation, the crystalline blocks can be broken into sizes so small that they can be considered as "liquid" with well-ordered chains in contrast to the random chains of a normal liquid state. The accompanied increase in entropy, ΔS, is thus very small. However, the change in the enthalpy, ΔH, could be of the same magnitude as in normal melting. Under such conditions, the thermodynamic equilibrium melting point, $T_m = \Delta H/\Delta S$, is much too high to be reached.[18] The long extended chains make longitudinal sliding much easier such that in no time the thickness of the crystal blocks adjust to the temperature of the environment. Thus there is no true melting in this case and therefore no new long period arising from the deformed chain-extended crystals.

The study of in situ deformation of thin polyethylene film in a transmission electron microscope by Adams et al.[19] showed that when the stretched direction is along the chain axis of a stack of chain-folded lamellae, deformation is initially accommodated by interlamellar separation. The tie chains were stretched into extended chains and were followed by the shearing of the lamellae into smaller blocks. Up to this stage, there is no discerning feature of melting of the crystalline blocks. Further stretching caused them to be broken to below a critical size in which the crystal feature could not be distinguished under the resolution used; the blocks were described as "decrystallized". It is likely that the ordered liquid state described above was reached in this observation. Thus it is not suitable to describe this transformation of the lamellae into microfibrillar structure as melting since the chains are not randomized. The event is perhaps best described as quasi-melting.

It is concluded in the present study that the deformation of chain-extended PE with high chain extension does not involve melting and recrystallization.

Conclusions

The SAXS of solid-state-extruded chain-extended polyethylene shows weak intensity maxima along the meridian whether drawing is carried out at a constant temperature to various draw ratios or at a constant draw ratio with different draw temperatures. The corresponding long period increases with increasing draw temperature. When drawn at 100 °C, all four chain-extended PE billets with varying initial lamellar thickness showed a long period which decreases to a constant ~24-nm periodicity at high draw. This was also obtained in the chain-folded PE drawn under similar conditions.

From thermal analyses and consideration of the overall X-ray scattering patterns, the observed long period from the weak maxima is thought to originate from the deformed small fraction of low molecular weight PE which was rejected during high-pressure crystallization. However, the chain-extended lamellae do not melt and recrystallize during the draw conditions, which had been thought to be critical for the evaluation of melting and recrystallization process during deformation.

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