Ultradrawing at Room Temperature of High Molecular Weight Polyethylene. 2. Effect of Annealing

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ABSTRACT: Annealed dry gel films of ultrahigh molecular weight polyethylene were stretched at room temperature. The maximum elongation ratio was about 30, which is considerably greater than that of unannealed samples reported in a previous paper. The nominal stress increased with elongation, while for unannealed specimens it remained nearly constant. The morphological properties of annealed samples were investigated by using wide-angle X-ray diffraction, small-angle X-ray scattering, and small-angle light scattering techniques in order to understand the origin of the difference of mechanical properties. The improvement of mechanical properties by annealing is thought to be due to an increase in the entanglement mesh that effectively transmits the drawing force.

Introduction

In a previous paper,[1] we reported studies of the structure and drawability of ultrahigh molecular weight (6×10^6) polyethylene films produced by gelation/crystallization from dilute solutions according to the method of Smith and Lemstra.[2–6] The dried gel films were composed of lamellar crystals oriented parallel to the film surface in a manner similar to mats of single crystals. Under ambient conditions, the dried gel film could be readily stretched up to a draw ratio of 20, which is a considerable improvement in comparison with the maximum elongation ratio of melt-crystallized samples.[7] The drawing process was nonuniform; the drawn film consisted of two alternating zones, namely, unoriented areas with a structure corresponding to that of the original undrawn specimens, and highly drawn domains oriented parallel to the drawing direction. As the draw ratio increased, the oriented regions were enlarged at the expense of the unoriented zones. The nominal stress remained constant throughout the drawing experiment.

In the present work, our interest is also concentrated on the effects of cold-drawing as opposed to the many experiments that have been carried out at elevated temperature.[2–6,8–12] The samples, prepared by the same method as in the previous work,[1] were annealed in a silicone oil bath at 110 °C, and the annealed samples were stretched to the desired elongation ratio at room temperature. When the specimens were stretched, many fine cracks appeared on the surface of the film drawn up to about 7 times. With further drawing up to a maximum draw ratio of 30, the cracks disappeared and the drawing process became uniform. The corresponding nominal stress increased with increasing strain. Such elongation behavior is quite different from the phenomenon observed in the previous work.[1] Therefore, in this paper we report on the drawability of the annealed samples in terms of morphological aspects by using small-angle X-ray scattering (SAXS), wide-angle X-ray diffraction (WAXD), small-angle light scattering (SALS), polarizing microscopy, and differential scanning calorimetry (DSC).

Experimental Section

The dried polyethylene films were prepared by using the linear polyethylene with a molecular weight of 6×10^6 (Hercules 1900/90209) that had been employed in the previous work.[1] The samples, which were produced by gelation/crystallization from dilute decalin solutions, the concentration being 0.5 wt % as in previous work, were cut into strips with dimensions of 50 mm × 10 mm and 40 mm × 3 mm. The former strips were employed to investigate the morphological properties under elongation and the latter strips to measure stress–strain behavior. All strips were annealed in a silicone oil bath at 110 °C and subsequently quenched at room temperature. The specimens were elongated at room temperature with an Instron tensile tester at the same cross-head speed (10 mm/min) as employed in the previous work.[1]

The various films were analyzed by polarizing microscopy, WAXD, SAXD, and SALS. X-ray patterns were obtained with Ni-filtered Cu Kα radiation produced by a Philips generator that was operated at 40 mA and 40 kV. A 15-mW He–Ne gas laser was used as a light source in recording light scattering patterns. Diffuse scattering was avoided by sandwiching the specimen between cover glasses with silicone oil (refractive index 1.533) as an immersion fluid. DSC measurements at heating rates of 20 °C/min were carried out on unconstrained specimens by using a Perkin-Elmer differential scanning calorimeter (DSC-1B).

Results and Discussion

Figure 1 shows the annealing-time dependence of the nominal stress–elongation curves for the dried polyethylene gel films annealed at 110 °C. It should be noted that in determining the stress corresponding to each elongation, the values of the tensile force were divided by the cross-sectional area of the original specimens. This figure evidently shows that under ambient conditions the remarkably high draw ratio of $\lambda = 30$ could be attained for the same ultrahigh molecular weight polyethylene as employed in the previous work.[1] This value should be compared with that of unannealed samples, which give maximum draw ratios of about 20. This means that the drawability is promoted by the annealing effect. It is also evident that an increase of the stress values occurs as a result of annealing.

The stress of all specimens, as shown in Figure 1, decreased with increasing elongation and reached a minimum value around $\lambda = 7$. Beyond $\lambda = 7$, however, the stress values increased with elongation. If the tensile force is divided by the cross-sectional area of the specimen at each elongation, the true stress, rather than the nominal stress, is obtained. The increase in true stress is, of course, more marked and attains 0.714 GPa at $\lambda = 30$ for the film annealed for 8 h. The stress–elongation curve in Figure 1 is quite different from that of the unannealed film,[1] where the nominal stress remained nearly constant throughout the drawing experiment.

The decrease in transverse specimen dimensions with increasing length occurred mainly in the direction of the film thickness, and much less in the film width. The final thickness of the 30-times-drawn film, for example, amounts to be about 8 μm (original thickness 150 μm), whereas the film width decreases by about 50%. This tendency is

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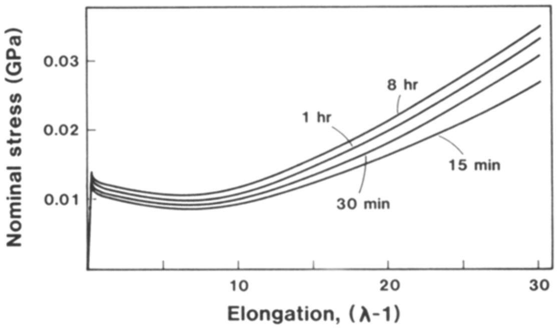

Figure 1. Annealing-time dependence of stress–elongation curves recorded at room temperature for dry gel films annealed at 110 °C. Elongation is defined as draw ratio (λ) − 1.

similar to the behavior obtained for elongation of the unannealed film.[1] Therefore, it is expected that a similar transformation from a folded to a fibrous structure must occur in the annealed films.

In order to clarify the difference between the deformation mechanism of annealed and unannealed samples, we shall discuss in detail the morphological changes observed when stretching annealed samples. Up to λ = 7 it was visually observed that the deformation process was nonuniform; fine cracks appeared in the film surface and the originally translucent specimen whitened owing to the formation of voids. Above λ = 7 the drawing process became uniform and the specimen assumed a fibrous appearance. In the polarizing microscope the development of the fibrous texture could be readily followed. Figure 2 shows the change in the appearance of a specimen with stretching after annealing at 110 °C for 15 min. At very low draw ratio (λ = 1.5) the texture is rather indistinct, but between λ = 3 and λ = 7 a random fibrous texture appears. At λ = 10 elongated birefringent regions can be seen predominantly oriented in the direction of stretching. With further increases in the draw ratio the elongated birefringent regions seem to be disruptively deformed into fine filaments, which are also highly oriented parallel to the drawing direction. This deformation mode is quite different from that of unannealed films,[1] for which the drawing process up to λ = 20 was nonuniform; the elongation occurred at the expense of the original unoriented zones and gave rise to highly oriented fibrils parallel to the drawing direction.

Figure 3 shows SAXS patterns from the original undrawn film as a function of annealing time when the X-ray beam was directed parallel to the film surface. The pattern from the specimen annealed for 15 s shows strong meridional scattering with two maxima, corresponding to the first two orders of a long period of about 10 nm. It is interesting to note that the second-order maximum becomes indistinct with increasing annealing time. This means that there is an increase in the orientational disorder and/or thickness fluctuations of the crystal lamellae that were oriented with their large flat faces parallel to the film surface. Moreover, the scattering maxima move closer to the center of the pattern as the annealing time increases, which indicates an increase of fold period (long spacing). This behavior is similar to the annealing effect of single-crystal mats.[13]

The increase of fold period and the orientational disorder and/or thickness fluctuations of crystal lamellae facilitate the drawability. Thus the probability of successfully drawing up to λ = 30 was highest when the sample annealed for 8 h was stretched, and the probability became lower with decreasing annealing time. This is probably due to an increase in the entanglement mesh (i.e., interpenetration of chains from neighboring crystals) that effectively transmits the drawing force. Therefore, it is assumed that the entanglement mesh in the unannealed films was not sufficient to avoid the slippage of polymer chains during the elongation process up to λ = 20 when the dry gel films were produced from 0.5 wt % solution in decalin. The increase of stress with increasing annealing time, as shown in Figure 1, supports the increase of the entanglement mesh. However, the relation between solution concentration, annealing time, drawability, and stress remains to be studied. In the present work we have restricted our attention to the morphological properties of the samples annealed for 15 min. The deformation properties of other specimens with different annealing times will be discussed elsewhere.[14]

Figure 4 shows WAXD patterns from the drawn specimens when the incident X-ray beam was along the film normal direction (through view). Interestingly, the pattern at λ = 10, corresponding to the maximum elongation ratio

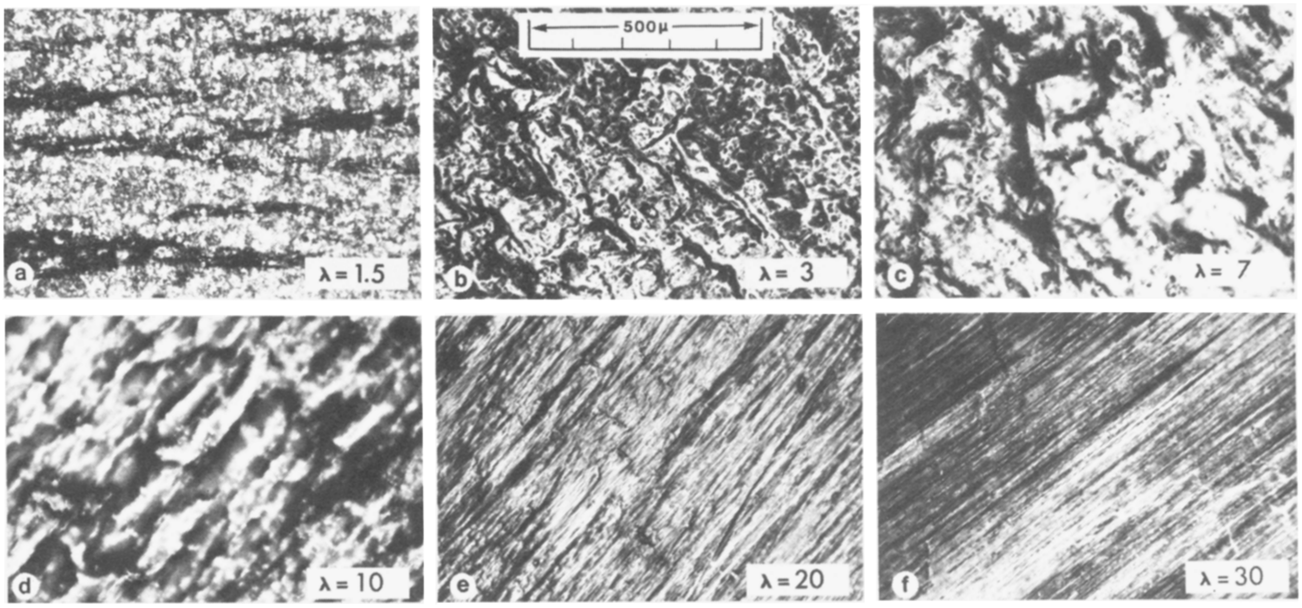

Figure 2. Optical micrographs of drawn polyethylene gel films annealed at 110 °C for 15 min. The stretching direction is along the diagonal. Crossed Nicols.

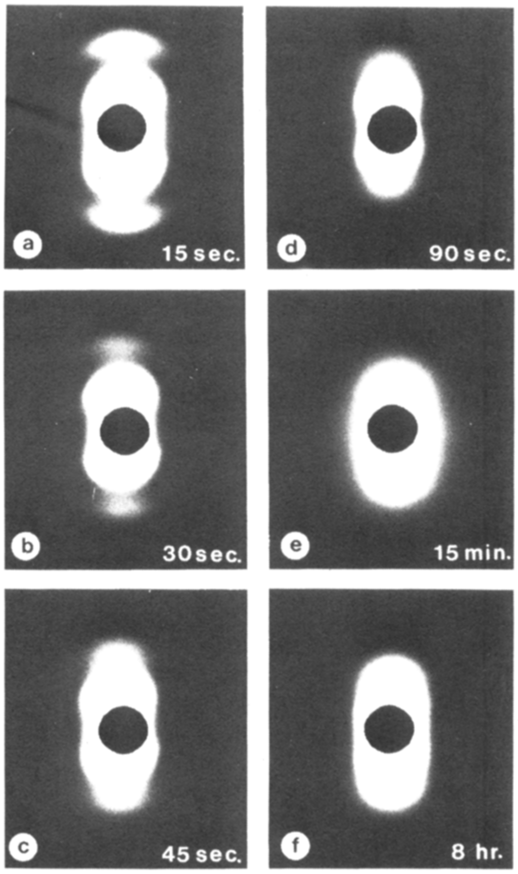

Figure 3. SAXS patterns of undrawn polyethylene gel films with changes in annealing time when the X-ray beam is directed parallel to the film surface.

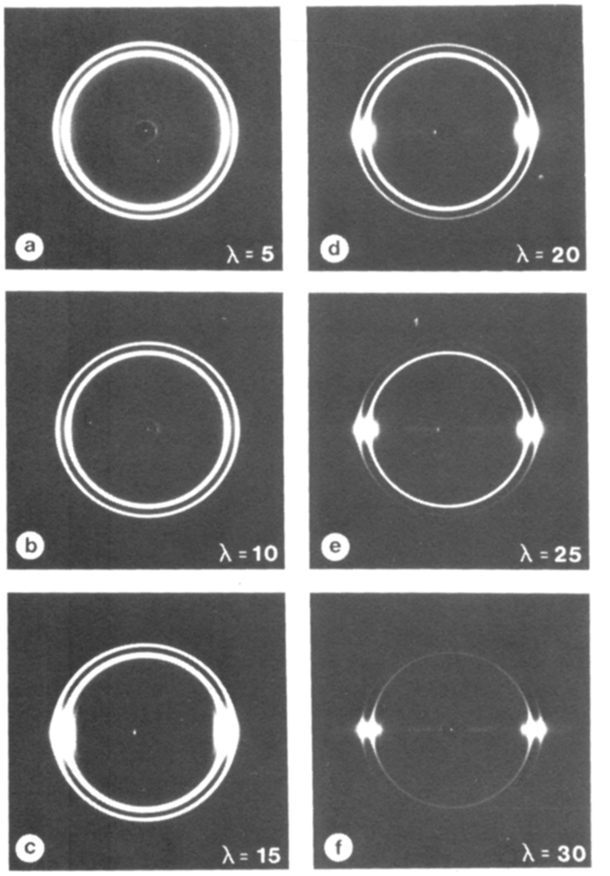

Figure 4. WAXD patterns from drawn polyethylene gel films annealed at 110 °C for 15 min (through view). The drawing direction is vertical.

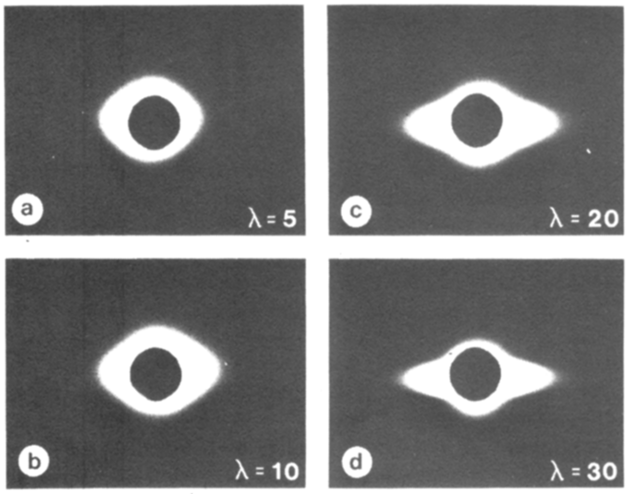

Figure 5. SAXS patterns from drawn polyethylene gel films annealed at 110 °C for 15 min (through view). The drawing direction is vertical.

of melt-crystallized specimens,[7] exhibits diffraction rings from the (110) and 200) crystal planes, which indicates the predominance of random crystallite orientation. These rings are also observed in samples with maximum elongation ratio (λ = 30) in addition to the strong equatorial reflections indicating preferential orientation of crystal *c* axes in the direction of stretching. The random orientation is due to biaxial stress in the drawn specimens despite the uniaxial external strain. The occurrence of biaxial stress can be demonstrated by the dimensional changes of the specimens during elongation, the film width decreasing much less than the film thickness as described earlier. The two types of crystallite orientation could be observed in unannealed specimens drawn at room temperature.[1] However, such behavior has not been reported in dry gel films stretched near the melting point,[2,6] for which the WAXD pattern exhibited strong equatorial reflections of the (110) and (200) crystal planes. Apart from the typical (110) and (200) reflections of the orthorhombic polyethylene unit cell, all the patterns displayed a rather strong diffraction arc at an angle at 19.6° (twice the Bragg angle), due to the presence of the triclinic unit cell.[15] This reflection from the triclinic phase, corresponding to the unstable crystal modification,[16] has also been observed in unannealed specimens.[1] Figure 5 shows the SAXS patterns taken perpendicular to the draw direction (through view). The sequence shows an equatorial streak that may originate in scattering from elongated voids. The streak was extended with increasing elongation ratio.

Figures 6 and 7 show respectively WAXD and SAXS patterns from drawn specimens when the X-ray beam was directed along the stretching direction (end view). The WAXD pattern at λ = 5 is similar to that of the undrawn annealed film, which suggests that the crystallites retain the orientational mode in which the crystal *c* axes are perpendicular to the film surface. The corresponding SAXS pattern (part b in Figure 7), however, shows only circular diffuse scattering, indicating the disappearance of the crystal lamallae, which is presumably due to the disruption of the lamellae into fragments. With further increase of elongation ratio, the WAXD patterns (Figures 4 and 6) indicate that the crystal *c* axes become increasingly tilted toward the stretching direction, but around the stretching axis the *c* axes are almost randomly oriented. Judging from the X-ray patterns (Figures 3–7), one can conclude that the crystal *c* axes are oriented perpendicular

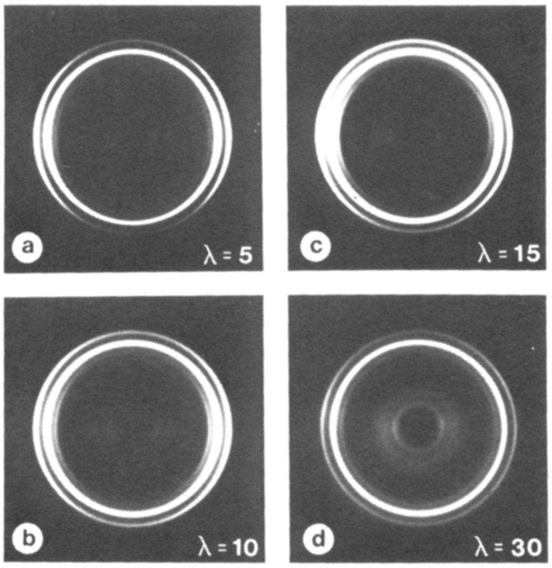

Figure 6. WAXD patterns from drawn polyethylene gel films annealed at 110 °C for 15 min (end view). The drawing direction is perpendicular to the plane of the figure.

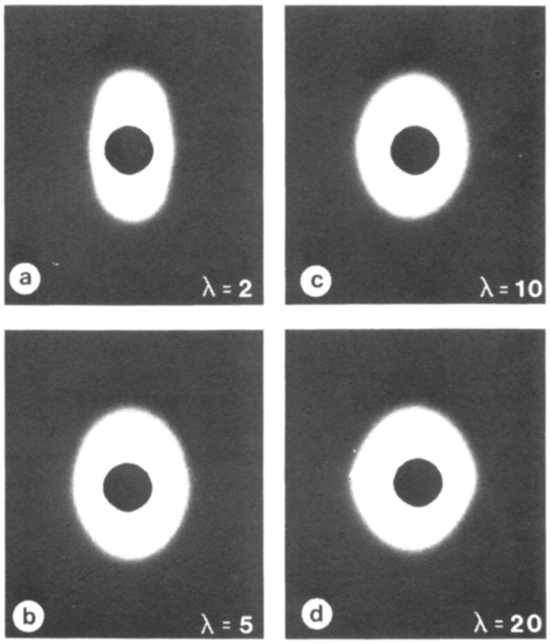

Figure 7. SAXS patterns from drawn polyethylene gel films annealed at 110 °C for 15 min (end view). The drawing direction is perpendicular to the plane of the figure.

to the large flat face in the original film and that during the drawing process they orient predominantly parallel to the stretching direction owing to the transformation from a folded to a fibrous structure.

Figure 8 shows small-angle light scattering (SALS) patterns under H_v polarization conditions as a function of elongation ratio. Pattern a of the undrawn film displays four lobes of a diffuse x-type, characteristic of the scattering from rodlike textures.[17,18] This suggests that in localized areas of the sample the lamellae are organized into large rodlike structures. This pattern is quite similar to that for unannealed specimens,[1] which indicates that the size and shape of the rods are hardly affected by the annealing process. As discussed in the previous paper,[1] the pattern appears at a very low scattering angle in comparison with the ones that had been reported previously for collagen and poly(tetrafluoroethylene),[19,20] and, in addition, the notch of the four lobes is less clearly defined.

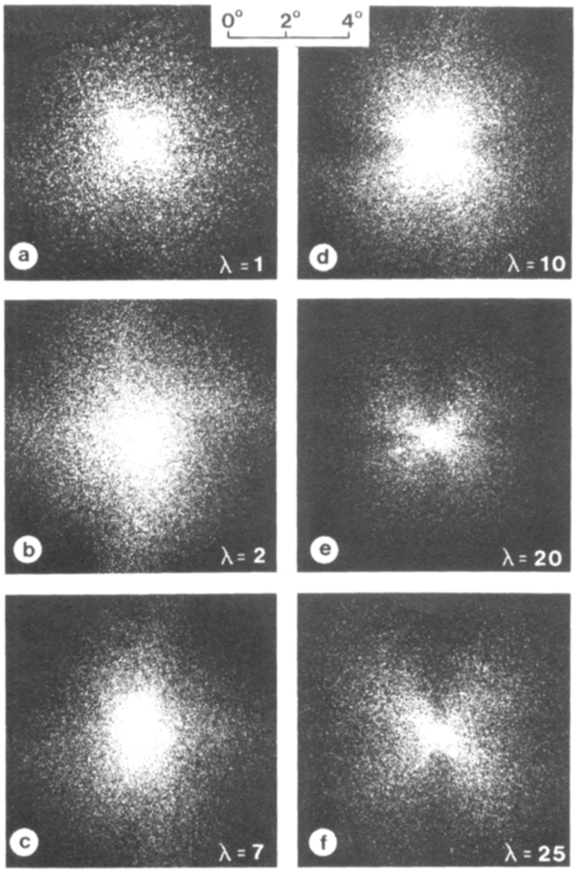

Figure 8. SALS patterns (under H_v polarization) from drawn polyethylene gel films annealed at 110 °C for 15 min. The drawing direction is vertical.

Such a pattern presumably indicates the existence of large-size rods with finite length and width[21], the optical axes being oriented normal to the film surface but showing orientation disorder with respect to the rod axis.[22]

For samples drawn up to λ = 7 the SALS pattern was distorted. This indicates that the rods assume an irregular orientation due to the disruptive deformation to a random fibrous texture as discussed above in relation to Figure 2a–c. Above λ = 10, the patterns show symmetrical lobes. The appearance of such an x-type pattern was not observed in the drawing process for unannealed samples.[1] As shown in Figure 8d–f, during the drawing process up to λ = 25 there was no change in the symmetrical lobe pattern. This strange and interesting phenomenon has not previously been reported. It is expected that the scattering lobes showing x-type patterns should become extended in the horizontal direction with increasing elongation ratio. The explanation for this effect remains for further investigation.

Figure 9 shows DSC thermograms of undeformed samples annealed for various periods of time. The thermal characteristics were found to depend on the annealing time. The DSC curve of the unannealed sample shows two peaks around 142 and 146 °C. With increasing annealing time, the interval between the peak positions decreased and finally the curve exhibited a single peak around 145 °C. Furthermore, with increasing annealing time the heat flow decreased sharply beyond the peak maximum. The origin of this interesting effect is not presently understood.

Figure 10 shows DSC thermograms of specimens drawn to various extension ratios after annealing for 15 min. The DSC curve of the specimen drawn up to λ = 5 exhibits a single peak around 145 °C. On comparison of the DSC curves in Figures 9 and 10, it is apparent that the double

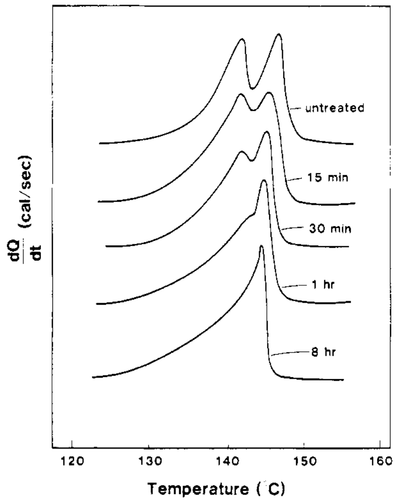

Figure 9. DSC thermograms of undrawn polyethylene gel films annealed for various periods of time. Heating rate is 20 °C/min.

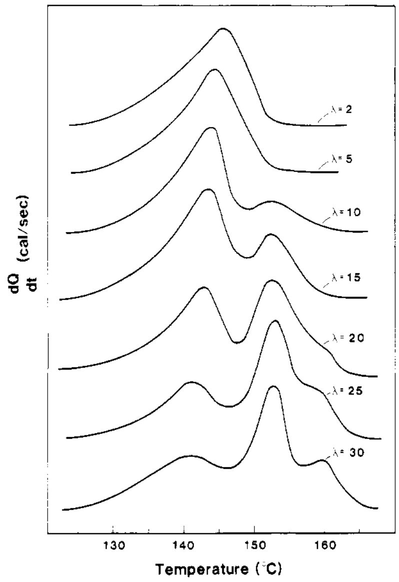

Figure 10. DSC thermograms of drawn polyethylene annealed gel films annealed for 15 min. Heating rate is 20 °C/min.

peak appearing in the original sample changes into a single peak. Beyond $\lambda = 10$, a new peak appeared around 152 °C. The new peak became larger as the elongation ratio increased, while the original peak around 145 °C became smaller. This tendency is quite different from the result reported by Smith and Lemstra[2] for samples drawn up to $\lambda = 31.7$ at 120 °C. According to their data,[2] the profile of the DSC curve exhibited only a single peak for the sample drawn up to $\lambda = 15.7$, and this peak shifted to a higher temperature with increasing elongation ratio, eventually appearing around 152 °C for $\lambda = 31.7$.

As illustrated in Figure 10, however, the peak around 152 °C became very large for our sample drawn beyond $\lambda = 25$ and a third small peak appears around 160 °C. The third peak was not observed in the drawn sample of Smith and Lemstra.[2] The second and third peaks have been observed by Pennings and Zwijnenburg,[23] who suggest that the second peak is probably due to a solid–solid transformation from the orthorhombic to a hexagonal crystalline phase, while the third peak is made up of two contributions: the melting of the hexagonal phase and the endothermic heat resulting from the trans-gauche conformational change that occurs following stress relaxation.

Here the question can be raised why the second peak is very pronounced in our drawn sample. Let us compare Figure 10 with Figure 4. As discussed before, the WAXD patterns in Figure 4 show random orientation of the (110) and (200) crystal planes in specimens drawn up to $\lambda = 10$, and although the intensity of the equatorial reflections was intensified beyond $\lambda = 10$, predominantly random orientation was still evident up to $\lambda = 30$. This is a very unusual phenomenon because normally at this level of elongation highly oriented crystallites are expected. The effect in this case is almost certainly due to internal biaxial stresses in spite of the externally applied uniaxial extension, as mentioned previously.

Now it may be noted that the second peak of the DSC curve became pronounced with increasing intensity of the equatorial reflections in the X-ray diagrams. Accordingly, it seems reasonable to ascribe the first ($T_{m_1} \simeq 145$ °C) and second ($T_{m_2} \simeq 152$ °C) DSC peaks respectively to contributions from the randomly oriented crystallites and those that are highly oriented in the stretching direction. These randomly oriented and highly oriented crystallites are probably connected together by amorphous chains so as to form a complex three-dimensional network. In such a system the randomly oriented crystallites are not constrained and therefore can melt easily, but the highly oriented crystallites must be restrained in some way so that instead of adopting the random coil conformation there is a transformation to the hexagonal rotator phase around 152 °C, which is beyond the normal melting point. This analysis is clearly consistent with the experimental results, but a detailed understanding of what limits constraint to the highly oriented crystallites must await further studies.

Conclusions

The results in this work show that lamellar polyethylene crystals in annealed samples can readily be destroyed by elongation even at room temperature. At this temperature, the polymer crystals in annealed specimens do not seem to act as rigid bodies, and the polymer chains exhibit the transformation from a folded to fibrous texture without specimen rupture. Obviously, the chain mobility at room temperature is much less than at elevated temperatures, where drawing is usually performed. Accordingly, the degree of orientation of crystal c axes is not so pronounced in comparison with that for specimens stretched at 120 °C.[2] Even in the film drawn to $\lambda = 30$ there is random orientation of crystallites, leading to internal biaxial stress within the specimen. The second and third peaks of the DSC curves for the specimens drawn beyond $\lambda = 10$ are probably due to a solid–solid transformation from the orthorhombic crystal form to the hexagonal modification.

In the previous work,[1] we were able to stretch the unannealed dry gel film of polyethylene up to 20 times at room temperature, although Smith and Lemstra had failed. Such a high draw ratio achieved at room temperature was concluded to be due to the extremely high molecular weight ($\bar{M}_w = 6 \times 10^6$) of the polyethylene used, which exceeded by 4 times the $\bar{M}_w$ of the sample employed by Smith and Lemstra.[2-5] As reported before in this paper, we could also succeed to stretch up to $\lambda = 30$ at room temperature by using specimens annealed at 110 °C. The question can be raised why the annealed specimens can be stretched up to a higher elongation ratio in comparison with the unannealed specimens used in the previous work.[1] In our opinion the effect is due to the increase of entanglement mesh that acts as interlamellar cross-links and effectively transmits the drawing force without chain slippage. The increase of entanglement mesh through annealing processes can be deduced from the SAXS patterns (Figure 3), which indicate an increase of the orientational disorder and/or thickness fluctuations of crystal

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lamellae oriented with their large flat faces parallel to the film surface, as well as in increase of fold period (long spacing). The increase of stress with annealing time (Figure 1) also supports the idea of an increase in entanglement mesh.

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Ultradrawing at Room Temperature of High Molecular Weight Polyethylene. 3. Theoretical Analysis of SAXS Patterns of Unannealed and Annealed Samples

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ABSTRACT: Thermoreversible polyethylene gels were produced by rapidly quenching hot solutions of ultrahigh molecular weight polymer. On drying, the gel forms a film composed of large lamellar crystals stacked on top of one another to form a periodic crystalline–amorphous structure perpendicular to the plane of the film. The SAXS patterns of these dry gel films show sharp meridional maxima up to the fourth order. After the films are annealed for a short time at 110 °C, the SAXS patterns show considerable changes: viz., all the scattering maxima become broader and are displaced toward the center of the pattern, the second-order maximum becomes particularly diffuse, the third-order maximum becomes extremely weak, and the fourth-order maximum disappears completely. In order to interpret the observed changes in terms of the structure of the annealed films, the SAXS patterns were computed in terms of a two-dimensional model of periodic crystalline–amorphous structures in which there are orientational fluctuations. By analysis of the theoretical expressions and comparison with the observed intensity distribution, conclusions are drawn as to the origin and significance of the changes in the SAXS patterns on annealing.

Introduction

It is well-known that sedimented mats of lamellar polyethylene single crystals undergo recrystallization when annealed at temperatures between 110 °C and the melting point.[1-6] The recrystallization process can be followed by small-angle X-ray scattering, which reveals that the Bragg spacings, corresponding to the diffraction maxima, increase considerably during annealing. This implies that the annealing process causes the polymer chains within the lamellae to refold into a longer fold period.

In our earlier paper[7] we reported that the small-angle X-ray scattering (SAXS) patterns from dry gel films of polyethylene, produced by gelation–crystallization from dilute solutions according to the method of Smith and Lemstra,[8-12] showed strong meridional maxima in several orders corresponding to a long period of about 10 nm. The patterns were interpreted as indicating that the dry gel films are composed of a stack of lamellar crystals that are highly oriented with their large flat faces parallel to the film surface. The SAXS patterns from these gel films are thus similar to those obtained from a sedimented mat of single crystals. When the dry gel films were stretched uniaxially at room temperature, a draw ratio of about 20 was attained and the stress remained nearly constant throughout the drawing process. On the other hand, when the dry gel film was annealed for 15 min at 110 °C, the first-order maximum became diffuse and moved closer to the center of the scattering pattern, corresponding to an increase of the fold period.[13] These changes in the SAXS

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