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Plastic Deformation of Polypropylene

Part 2 *The Influence of Temperature and Draw-Ratio on the Axial Long Period*[*]

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In a wide range of drawing temperatures (20 to 150° C) and draw-ratios λ (5 to 20) the axial long period L_T is a unique function of temperature. It is completely independent of the long period of the starting material which was varied within wide limits (125 to 350 Å). The gradual transformation of the long period observed at small draw-ratio (λ between 1 and 5) from the value L_0 of an undrawn sample to the limiting value $L_T > L_0$ of highly drawn polypropylene ($\lambda \geq 5$) could be demonstrated on samples with L_0 larger than L_T. The change of long period is abrupt, indicating a discontinuous step in the transformation from the original microspherulitic into the fibre structure.

These results may be interpreted in the same manner as in the case of polyethylene. During plastic deformation in the neck the lamellae are broken into small folded chain blocks which are then incorporated into the microfibrils, the basic building element of the fibre structure. The work of deformational forces must so mobilise the chains in the blocks that they get rearranged with a new long period, corresponding to the temperature of drawing.

1. Introduction

Small-angle X-ray scattering has proved to be an extremely powerful method for the investigation of plastic deformation and structure of deformed crystalline polymers. The most characteristic feature of the diffraction pattern is the occurrence of meridional maxima associated with the highly oriented lamella structure of the drawn or rolled sample. The position of the maxima yields the long period L in the draw direction (axial long period). In the case of rolled or drawn high density polyethylene (PE), which was systematically investigated in a wide range of draw-ratio λ, the high orientation of lamellae with only minor or no remains of the original spherulitic structure is found for all $\lambda \geq 3$. In this range the intensity of the diffraction maximum decreases with increasing draw-ratio and increases with increasing temperature of drawing [1, 2]. However, the most conspicuous feature is the dependence of long period on temperature of drawing, a very slight or even no dependence on draw-ratio, and complete independence from the long period of the material before the plastic deformation [3]. This fact, together with the information from electron microscopy of bulk material [4] of extremely thin layers (multilayer crystals) [5] and of single crystals [6], leads to the conclusion that during plastic deformation in the neck, not only the original approximately spherulitic structure is completely destroyed, but also every single lamella is broken up into small folded chain blocks [7, 8]. The blocks are then incorporated in long microfibrils, the basic element of the fibre structure of the highly drawn sample. Microfibrils pulled out in a narrow destruction zone from a single stack of favourably oriented lamellae have very nearly the same draw-rate and draw-ratio. Hence laterally the blocks tend to coalesce into wider lamellae and

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the microfibrils into very long fibrils extending for many tens or even hundreds of microns in the draw direction. The variation of draw-rate and draw-ratio from fibril to fibril causes the poor lateral fit between the stacked lamellae of adjacent fibrils, and favours the formation of longitudinal voids. Moreover, the heat generated during the destruction of lamellae which in the bulk sample cannot be removed fast enough, gives so much chain mobilisation in the blocks that they get rearranged with a new long period corresponding to or determined by the temperature of drawing [9]. This fact seems to explain the independence of the new long period from the old one before drawing.

We feel that this molecular model of plastic deformation in the neck is not a feature limited to PE but has a much more general significance, and indeed may apply, with minor modifications demanded by the specific chemical and morphological properties of the material, to all semicrystalline polymers. In order to check this speculation, we first investigated polypropylene (PP) which is very similar to PE chemically but has a helical instead of zig-zag conformation in the crystal lattice. On the other hand, PP is an important fibre material and therefore the elucidation of the deformational process is of more general interest than in the case of PE.

The study of the long period of mechanically deformed PP as a function of temperature of drawing and draw-ratio has been already reported. Zubov *et al* [10] have investigated the deformation of PP monofilaments which they drew to six and ten times the initial length. Their main conclusion is that the long period remains unaltered irrespective of the extension reached, and that the intensity of small-angle X-ray scattering decreases drastically with the draw-ratio. Samuels [11] has recently reported some experiments performed with material drawn at 110 and 135° C. The observed long period increases rather irregularly with the draw-ratio up to values of between 6 and 7 for λ and remains constant thereafter up to $\lambda = 8$, the maximum draw-ratio of his experiments.

In the present work we have systematically investigated the axial long period of mechanically deformed PP over a wide range of drawing temperatures (from 20 to 150° C) and draw-ratios (from $\lambda = 1$ to $\lambda = 20$ reaching the limit determined by break). Particular attention was given to the influence of the long period of the starting material on that obtained upon drawing.

2. Experimental

An isotactic 92.4% heptane insoluble polypropylene, Escon 502 (trademark of Enjay Chemical Co) with a weight average molecular weight of 426 000 was used. The pellets were pressure-moulded at temperatures between 180 [9] and 200° C to a 0.5 mm thick film, and the film was subsequently quenched in ice water. The resulting microspherulitic material possessed a density of 0.896 g/cm^3. The film was cut into strips of the usual dumb-bell shape (drawing region 30 × 5 mm). The sample, clamped in the table Model Instron tensile-testing instrument, was brought to the desired temperature by a thermostated hot-air oven and, after about 5 min when thermal equilibrium was reached, drawn, at a rate of 0.5 cm/min. In only a few cases was a lower draw-rate applied. If the drawing was performed during a short time, rather low λ values were obtained. With an increasing time of drawing, λ rapidly increases.

A minor permanent plastic deformation, between 5 and 10%, occurs in the whole narrowed section of the sample before a shallow neck starts with an intermediate reduction of cross-section. Two necks propagate in opposite directions along the entire strip length and transform the more or less isotropic, spherulitic film into a new highly oriented fibre structure with smaller cross-section and higher longitudinal tensile strength. Although the local draw-ratio does not vary much in the necked portion of the film, it was found advisable to determine it independently from the displacement of equidistant ink marks made on the sample before deformation.

High temperature and low draw-rate allow the achievement of higher draw-ratios. At low temperature (20 to 60° C for instance), the sample breaks before reaching a draw-ratio of about 10; while at high temperatures (120 to 150° C), values of between 20 and 25 for λ are easily obtained. Drawing sometimes drastically changes the appearance of the sample which may become cloudy, opaque, or white, indicating the formation of voids. Cloudiness depends on draw-ratio and temperature. At low temperatures ($T_d = 20°$ C) the samples become cloudy for $\lambda \geq 4$. At higher temperatures the cloudiness occurs at higher λ. At $T_d \geq 120°$ C, for instance, the samples remain transparent up to values of between 12 and 15 for λ. Annealing of the samples at high temperatures ($T_A \geq 120°$ C) before drawing, provoked brittleness. In order to achieve sufficiently high draw-ratios with annealed samples, very low draw-rates had to be used.

After drawing, the films were removed from the thermostat, unclamped, and allowed to cool at room temperature. The small-angle X-ray scattering (SAXS) photographs were taken at room temperature with a Rigaku-Denki small-angle camera and the RU-3 rotary anode tube. Cu Kα radiation with a Ni filter was used. The photographs were taken with the beam perpendicular to both the draw direction and the surface of the film. The working conditions were 60 kV, 100 mA, and a specimen film-distance of 200 mm. A distance of 300 mm was also occasionally used if higher resolution was needed. The small-angle X-ray diffractographs were analysed along the meridional direction with an automatic recording microdensitometer.

3. Small-angle X-ray Scattering Pattern

The unoriented quenched PP films used as starting material for all the experiments reported have a long period of 125 Å. The SAXS pattern is a relatively strong and broad ring with no tangential intensity variation. The drawn sample yields a diffraction pattern which varies very much with the draw-ratio: a rather complicated pattern in the range of small λ and a very simple pattern with a first-order meridonial maximum at higher λ. That means that the lamella orientation undergoes a drastic change during the first stages of plastic deformation which primarily occurs in the neck but later remains nearly unchanged in spite of the wide range of draw-ratios investigated.

The smallest draw-ratios ($\lambda = 2$, $\lambda = 3$) were obtained in the neck if the drawing was performed only during a short time. The corresponding small-angle diffraction pattern for $\lambda = 2$ is a superposition of an elliptical halo and a four-point diagram, which is to some extent similar to that obtained with PE [8, 12], polyvinyl alcohol [13], and polyoxymethylene [14]. The axial long period was derived from the position of the scattering maximum in the meridian which is the small axis of the scattering ellipse for drawing above 60° C. The four-point diagram yields a long period identical with that of the sample before drawing ($\lambda = 1$). It corresponds to stacked, undeformed lamellae oriented at an angle of about 50° to the draw direction.

Fig. 1 illustrates the dependence of the SAXS patterns on temperature and draw-ratio. Exposure times were increased with λ because the scattering intensity decreases drastically with increasing draw-ratio. Fig. 1a shows the SAXS photographs of PP drawn at 120° C for draw-ratios between 5 and 15. The long period as a function of deformation remains unaltered. For $\lambda \geq 8$, the SAXS pattern shows an equatorial scattering which for higher draw-ratios becomes more intense and extends to higher angles. Concurrently, the

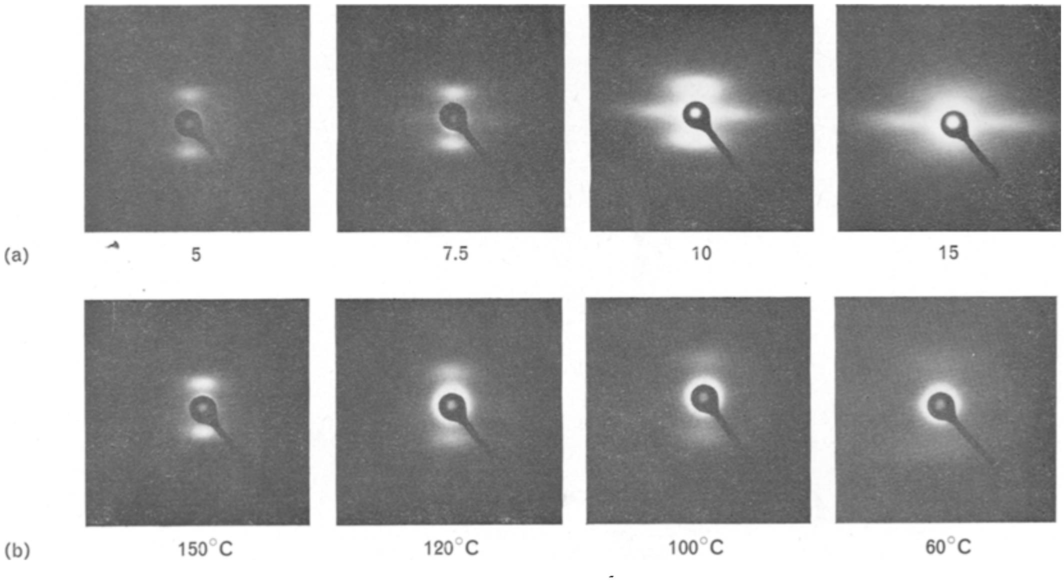

Figure 1 SAXS patterns of PP drawn (a) at 140° C for various draw-ratios; (b) for a draw-ratio $\lambda = 5$ at different drawing temperatures. Draw direction: vertical

lateral width of the meridional maxima increases. Fig. 1b shows the effect of the drawing temperature of PP drawn to $\lambda = 5$. Besides the conspicuous increase of long period and scattering intensity with the temperature of deformation, a concurrent decrease of the reflection width along the meridian and perpendicular to it is noticeable.

The drawing of PP at room temperature to $\lambda \geq 4$ gives rise to a milky appearance of the sample and to an unusually intense equatorial scattering which masks, nearly completely, the meridional maxima (fig. 2a). After gentle rolling, the cold-drawn sample becomes transparent and the equatorial scattering disappears so that one can see the two maxima clearly (fig. 2b). From these observations it can be concluded that by lateral pressing, both large voids of the order of the wavelength of visible light and the much smaller microvoids between the fibrils, disappear. As a consequence of efficient lateral packing of the fibrils and microfibrils without voids, the diffracted intensity originates only in the electron density difference between the crystalline lamellae and amorphous layers of the fibre structure.

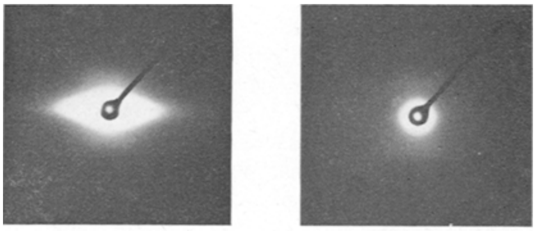
(a) (b)

Figure 2 SAXS patterns of PP drawn at room temperature ($T = 20°$ C) for $\lambda = 10$; (a) before rolling, (b) after rolling. Draw direction: vertical.

As in PE [3] a distinction can be made between "cold" and "hot" drawing of PP. Cold-drawing gives rise to meridional maxima in the form of two lines parallel to the equator, which very nearly have the appearance of a distorted four-point pattern. Hot-drawing, on the other hand, yields essentially two maxima in the form of oval or nearly circular spots (two-point pattern). However, the hot-drawn PP samples did not exhibit a second order maximum. This does not exclude the possibility that with longer exposure times such maxima eventually could be detected. The transition between the two types of drawing starts around 120° C as compared with 80° C for linear PE.

From our observations, four different states of perfection which depend on draw-ratio and drawing temperature can be distinguished:

(i) *low draw-ratios* ($5 < \lambda < 8$) and *hot-drawing* ($T_d \geq 140°$ C) yield a two-spot meridional diffraction pattern indicating a uniform orientation of relatively perfect lamellae perpendicular to the draw direction;

(ii) *high draw-ratios* ($8 < \lambda < 20$) and *hot-drawing* ($T_d \geq 140°$ C) yield a pattern between an oval spot and a line with an intense equatorial scattering. Thus, high draw-ratios provoke a distortion and disorientation of the lamellae and the formation of longitudinal voids between adjacent fibrils;

(iii) *low draw-ratios* ($5 < \lambda < 8$) and *cold-drawing* ($T_d \leq 100°$ C) give rise to a meridional broad line structure indicative of a large variation in lamellae orientation, with smaller lateral size of lamellae than obtained at high temperatures, and with a broad distribution of lamella thicknesses;

(iv) *high draw-ratios* ($8 < \lambda < 20$) and *cold-drawing* ($T_d \leq 100°$ C) yield a similar line structure with an intense equatorial scattering, indicating not only a large variation of lamella orientation, small lateral size, and a wide variation of lamella thickness, but also the formation of long, axial microvoids between the fibrils.

4. Axial Long Period *L*

The experimental results on axial long period obtained with drawing of quenched samples and derived from the position of meridional maxima are collected in fig. 3. The long periods reported by Samuels [11] for drawn PP Profax 651A (Hercules) at 110 and 135° C are also included for comparison. As in the case of PE [3] there is a conspicuous influence of drawing temperature on the long period. Drawing at temperatures higher than 60° C yields an increase of the long period whereas deformation below this temperature causes a decrease of L. The variation of the long period (either increase or decrease) as a function of draw-ratio λ proceeds rather smoothly between $\lambda = 1$ and $\lambda = 5$. Increasing the T_d towards higher values results in a more abrupt increase. For higher values of λ the long period remains practically constant (L_T). The long periods L_0 in fig. 3 for $\lambda = 1$ (i.e. undeformed material) refer to the portion of the strained sample before the neck which was held at the temperature of drawing during the whole

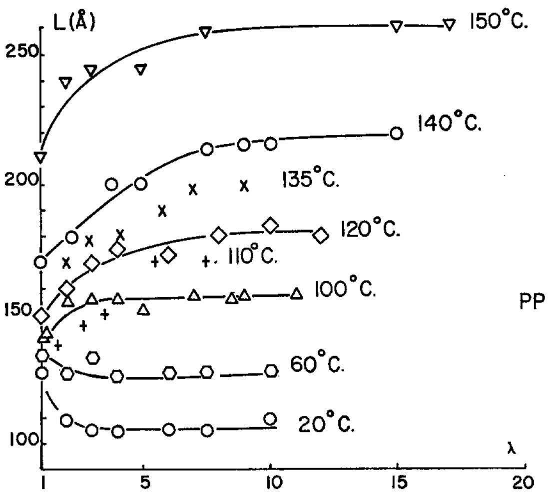

Figure 3 Variation of the axial long period *L* of drawn PP as a function of draw-ratio for different deformation temperatures.

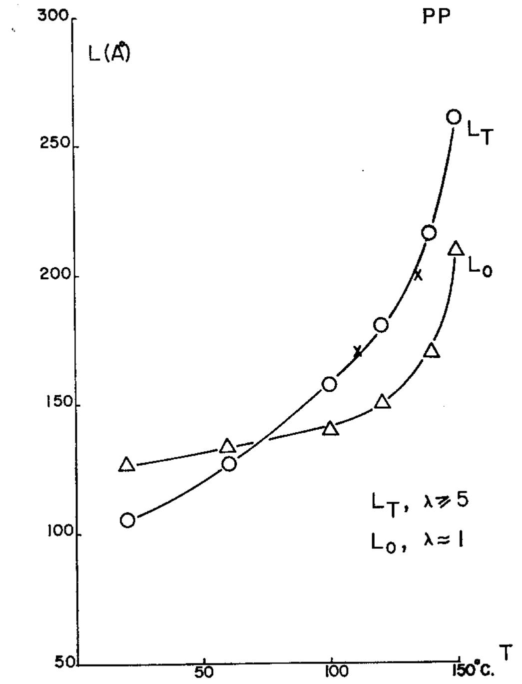

Figure 4 The limiting long period L_T ($\lambda \geq 5$) and the initial long period L_0 ($\lambda = 1$) as a function of temperature of drawing *T*. The crosses are the data of Samuels [11].

drawing process. More specifically, this material corresponds to a plastic deformation with a draw-ratio between 1.05 and 1.10. Note that as a rule $L_0(\lambda = 1)$ does not coincide with either the intermediate L or with the limiting L_T of drawn material.

If the final long period L_T of the highly deformed films with $\lambda \geq 5$ is plotted against the drawing temperature, an analogous increase as in the case of PE [3] is obtained (see fig. 4, curve 2). The long period L_T increases almost linearly with drawing temperature till values close to 130° C are reached; thereafter, the increase becomes more rapid. The long period L_0 of the material before deformation ($\lambda = 1$) is also plotted in fig. 4 (curve 1) as a function of temperature. Note particularly that at a drawing temperature below 60° C the final long period is smaller than the starting one. By comparing curves 1 and 2 in fig. 4, the same conclusion as in the case of PE can be reached; i.e. as a consequence of mechanical deformation, the PP film attains a final long period depending exclusively on the temperature of deformation. In this range of λ, within the error limits of our data, the influence of draw-rate and draw-ratio is undetectably small. The process of drawing may be thought of in exactly the same way as in PE, as breaking the original folded chain lamellae of the spherulitic structure into small blocks which are then incorporated into the microfibrils. The latter are the basic structural elements of the highly oriented fibres or film. The new final long period L_T is independent of the lamellae thickness of the starting material and is only related to the deformation temperature.

In order to demonstrate in a conclusive manner the characteristic influence of the drawing temperature on the final long period and its independence from the long period of the starting material, the same type of experiment as formerly reported for PE was carried out [3]. Polypropylene samples with a wide range of long period was prepared and subsequently drawn at 20 and 100° C respectively. Fig. 5 illustrates the results. Starting material with long periods between 125 and 350 Å was obtained by annealing quenched PP film at different temperatures in Wood's metal (curve 1). L_A values thus obtained differ a little from those corresponding to $\lambda = 1$ (L_0) in figs. 3 and 4. The difference is caused by the completely different treatment: heating of an unclamped, fully stress-free sample in contact with the metal in the first case (L_A) and heating in air under applied stress during the drawing process in the second case (L_0). By drawing the samples obtained in this way at 20 and 100° C with draw-ratios λ of 4 to 5 and 5 to 10, respectively, final long periods of 105 Å (curve 3) and

155 Å (curve 2) were obtained respectively. Thus, the limiting long period L_T of the highly deformed material is a function of drawing temperature only and absolutely independent of the initial long period of the undeformed starting material.

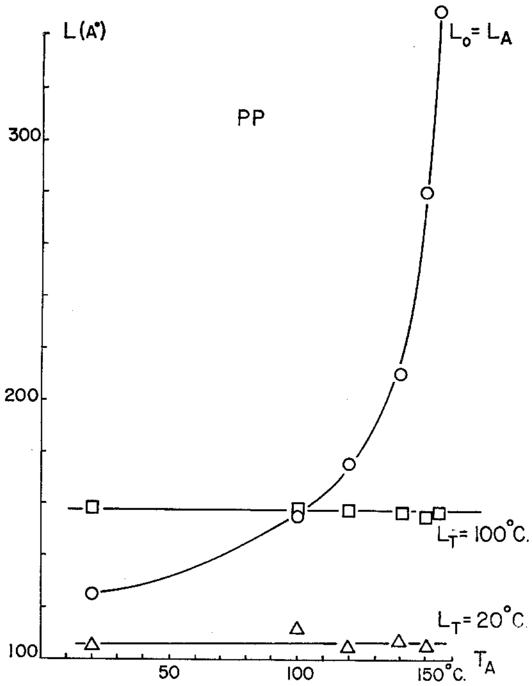

Figure 5 Long periods of melt-crystallized PP after annealing at T_A (L_A) and subsequent drawing at 20° C (L_{20}) and 100° C (L_{100}).

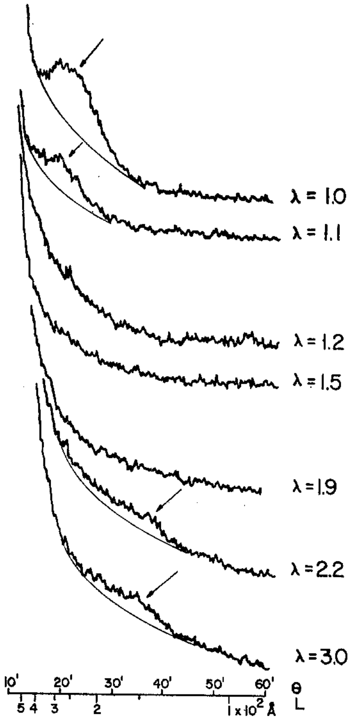

Figure 6 Microdensitometer curves of meridional scattering intensity versus $\theta = \lambda/L$ for annealed ($T_A \sim 150°$ C) PP samples with typical λ values drawn at 100° C. The arrows indicate the location of the maxima.

It is quite interesting to follow up the transition of long period from the starting $L_0 = 205$ Å and $L_0 = 260$ Å to the final value $L_T = 155$ Å ($T_d = 100°$ C) as a function of draw-ratio as shown in fig. 6 (microdensitometer curves of SAXS patterns) and fig. 7 (L as a function of λ). At sufficiently small draw-ratios the axial long period first increases very nearly linearly with λ (fig. 7). In the first sample ($L_0 = 250$ Å), the increase slows down at $\lambda = 1.4$. Beyond $\lambda = 1.7$, the meridional maximum completely disappears so that no long period can be determined. The second sample ($L_0 = 260$ Å) shows the linear increase up to $\lambda = 1.1$. Beyond this value no maximum is observable. At $\lambda = 2.5$ and $\lambda = 2.2$ for the first and second samples, respectively, the meridional maximum reappears. The new long period is exactly the limiting value $L_T = 155$ Å of fig. 4. Note that the new period in both cases appears at λ only slightly above 2 in very good agreement with the drawing from $L_0 = 140$ Å shown in fig. 3. This also means that as far as one may judge from the meridional long period, the mechanism of plastic deformation transforming the spherulitic into the fibre structure is independent of the long period.

The initial increase of long period is most easily explained by a nearly affine displacement of lamellae oriented perpendicular to the draw direction. The thickness of every single lamella remains constant but the spacing between them and hence the observed period in the draw direction increases with λ. The spacings thus produced are certainly not identical and also not proportional to λ over a wide range. With increasing irregularity, the definition of the scattering maximum is progressively impaired until it completely disappears. As soon as the new fibre structure is produced, one observes the new meridional maximum which is in no way related to the maximum at very small deformation ($\lambda < 1.7$ and $\lambda < 1.2$ in fig. 7).

If L_T is larger than L_0 as is the case with all samples of fig. 3 drawn above 60° C, then within

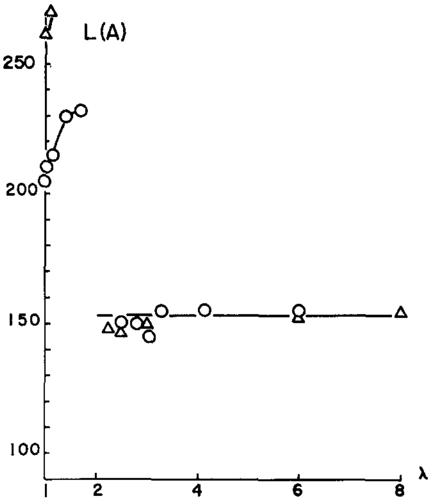

Figure 7 The axial long period L of two PP samples with different initial long periods ($L_0 = 205$ Å and $L_0 = 260$ Å) both drawn at $T_d = 100°$ C as a function of draw-ratio λ.

the error limits of the experiment, the initial increase in L, caused by the increased spacing of the original lamellae (and not by the transformation of the blocks in the destruction zone), makes L increase smoothly from L_0 to L_T. In this case one may not notice that there is a discontinuity between L values still corresponding to the original spherulitic structure and those at higher λ, which belong to the newly formed fibre structure. This discontinuity, however, is apparent when $L_T < L$ as in fig. 7. It will be obvious that the rising L values at small λ, hence the discontinuity itself, would have been missed if the measurements had not been made at sufficiently closely spaced λ values. This may well be the reason why it is not noticeable in fig. 3 for drawing below 60° C.

Moreover with relatively small differences between L_0 and L_T, the corresponding broad SAXS maxima partially overlap. Hence if both the initial spherulitic structure and the final fibre structure coexist in the sample – which is indeed to some extent the case in the neck – the superposition of the corresponding maxima cannot be resolved but yields a new maximum which gradually shifts in the direction of the prevailing structure. That means that at the start of the neck with merely a spherulitic structure one obtains L_0, at the end of the neck with a fibre structure one obtains L_T, and in the intermediate region one obtains a rather smooth transition from L_0 to L_T.

This analysis of experimental data in figs. 3, 5, and 7 seems to prove convincingly that the smooth transition of L from L_0 to L_T at small λ is an artifact and does not reflect the actual deformational mechanism. The true dependence of L as a function of λ is best demonstrated in fig. 7. First, we have here a slight increase of L with λ, corresponding to the initial step of plastic deformation which still preserves the spherulitic structure. After a certain gap in λ, we have a new and constant L_T characteristic for the new fibre structure.

One may therefore conclude that the change in the axial long period is an abrupt and discontinuous process and not a gradual transition in good support of the mechanism of plastic deformation as described in the introduction. The decisive step in the basic mechanism of drawing of bulk samples of crystalline polymers is the fracturing of folded chain lamellae into small blocks, which most probably proceeds in the same manner as observed with single crystals. The main difference is the geometry of removal of heat generated by the destruction of lamellae, which leaves unchanged the block thickness (long period) in the case of single crystals and modifies it according to the temperature of drawing in bulk samples. During this drastic discontinuous transformation, the new long period L_T of the fibre structure gets established. As a rule, its value seems to be very little affected by eventual subsequent deformation of the highly oriented fibre section as may be deduced from the constancy of $L = L_T$ over the wide range of draw-ratio between 4 and 17 in fig. 3.

5. Conclusions

The true axial long period of drawn polypropylene exhibiting the highly oriented fibre structure is a function of temperature of drawing and independent of draw-ratio and of the long period of starting material.

At the beginning of plastic deformation which does not yet markedly destroy the original spherulitic structure, the meridional long period increases nearly linearly with λ as a consequence of increased spacings between lamellae oriented perpendicular to the draw direction. One may imagine that in the linear strain field these lamellae are displaced as in an affine transformation. The irregularity of the displacement increases with λ and hence makes the corresponding meridional maximum disappear rather soon – for instance at λ between 1.2 and 1.7 if the drawing is performed at 100° C.

The transition from the original long period L_0 to the final L_T is discontinuous just as the transformation from the original spherulitic to the final fibre structure. The smooth transition usually observed is an artifact caused either by the above-mentioned initial increase of L (this applied to the case $L_0 < L_T$), and/or by eventual coexistence of spherulitic and fibre structure in the neck with corresponding meridional maxima overlapping, so that the resulting scattering maximum is shifted in the direction of the prevailing structure present.

As mentioned in the introduction the eventual, quite substantial change in long period during drawing, be it increase or decrease, may be explained in exactly the same manner as in the case of PE, by the geometry of heat removal from the extremely thin destruction zone where it is generated by the work of plastic deformation of lamellae.

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