

On the deformation mechanisms of β -polypropylene: 1. Effect of necking on β -phase PP crystals

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PP samples containing β -phase crystals were prepared by doping with a β -nucleating agent. The β -PP specimens were tensile stretched at room temperature under various crosshead rates and the yielding behaviour was analyzed on the basis of Eyring's theory. After tensile testing, the β -phase was examined with WAXS and D.S.C. over the necking region and the deformation mechanisms were discussed. The β -phase was found to be mechanically stable at room temperature up to yielding point. However, once the samples were stretched to necking, the β -phase began to transform to the α -phase; this phase transformation continued over the necking region. The phase transformation implied that local melting and crystallization occurred during cold drawing and gave powerful support to Flory's model of the deformation mechanism of crystalline plastics. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

When subjected to a tensile load, some crystalline plastics exhibit a distinctive cold drawing phenomenon after necking. Accompanying the cold drawing process, the initial spherulite structure of the polymer converts to an oriented fibrous structure and its strength and modulus increase markedly in the stretching direction. The improvement of mechanical properties is attributed to molecular alignment along the drawing direction¹ and has been widely utilized to produce high performance polymer profiles, such as high modulus polymeric rod and pipe and many other articles^{2–4}, by solid-state extrusion^{5–7} or die-drawing^{8,9}.

Although necking and cold drawing are easily observed at a macroscopic level, the mechanism whereby the spherulite converts into the fibrous structure at the molecular level is still the subject of much debate. A lot of work on plastic deformation mechanisms of crystalline polymers has been published. Two distinct models on the conversion of spherulite into fibrous have been put forward by Peterlin^{10,11} and Flory and Yoon¹². The former considered that under the action of tensile load the initial lamellae of precursor materials disintegrate into mosaic blocks of several hundred angstroms width and then reorganize into the fibrous structure of the drawn materials, whilst the latter deem that under large plastic deformation, such as cold drawing, partial melting should be a consequence of applied stress because there are adequate connections between the neighbouring lamellae in melt-crystallized plastics. The formation of fibrous structure involves the melting of pre-existing lamellae and strain-induced crystallization in the melt phase.

Indeed, SANS results¹³ indicated that local melting might occur in HDPE when it was stretched above 70°C, and some melting and recrystallization traces were viewed in high molecular weight PE die-drawn at 115°C under

SEM¹⁴. When HDPE was drawn above its alpha transition temperature¹⁵, some continuous crystalline fibrils up to several μm long were observed in the drawn materials. These results suggested that melting occurred during plastic deformation at high temperature. However, whether the mechanism of melting does operate at room temperature is still controversial. The present work is designed to utilize the β -phase of PP as an indicator to clarify the debate on the conversion of spherulite into fibrous during cold drawing.

PP is a polymorphic material with three known possible crystalline phases¹⁶, namely monoclinic (α), hexagonal (β) and triclinic (γ). Considering the spatial distribution of chains in the PP crystals, Turner-Jones and others^{17–19} pointed out that a solid–solid transition of β -phase to α -phase is impossible and the transition has to destroy the β -phase and rewind some chains. Garbarczyk *et al.*²⁰ demonstrated, using WAXS with synchrotron radiation, that thermally induced transformation of β -phase to α -phase was preceded by the conversion of the β -phase into a disordered state, i.e. by a mechanism of melting and recrystallization. Therefore, when a PP sample containing β -phase crystals is stretched at room temperature and undergoes necking and cold drawing, if stress-induced melting occurs in the necking region the β -phase crystals should transform to α -phase after cold drawing because it is extremely difficult for PP to recrystallize into the β -phase at room temperature. Consequently, the amount of β -phase crystals would reduce, which can be detected easily by WAXS and D.S.C. On the contrary, if a breaking and recombination mechanism operates during cold drawing, the package pattern of the chain-folded mosaic blocks should not change after cold drawing, so that the relative amount of β -phase crystals would not vary largely. Hence, the mechanism of the conversion of spherulite to fibrous during cold drawing can be clarified by means of examination of the β -phase in β -PP before and after deformation.

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However, the α -phase predominates in PP whereas the β -phase occurs only sporadically under normal crystallization conditions. Fortunately, the β -phase can be stimulated by crystallization in the presence of certain nucleating agents¹⁶. Recently, a β -selective nucleating agent has been developed in this laboratory and PP samples containing various amounts of β -phase crystals can be prepared conveniently^{21,22}. So a study on deformation mechanisms by means of phase transformation can be conducted.

EXPERIMENTAL

Raw materials

The polymeric material used in present work was commercial isotactic polypropylene (Himont 6501 PP) supplied in powder form. The nucleating agent for β -phase was a mixture of pimelic acid and calcium stearate. The pimelic acid $\{\text{HOOC}(\text{CH}_2)_5\text{COOH}\}$ was Merck-Schuchardt P1072 (98%) and the calcium stearate $\{\text{Ca}[\text{OOC}(\text{CH}_2)_{16}\text{CH}_3]_2\}$ was an industrial grade product.

Preparation of PP samples

PP resin was moulded into 2 mm thick dumb-bell specimens with a working portion about 32 mm long and 6 mm wide, using a Bulter 10/60 injection moulding machine. The resin was heated gradually along the barrel to 205°C, then was injected into a mould at 123°C and hold in the mould for 2 min before being ejected. The mould temperature was controlled by running oil from a thermal controller.

To prepare the β -PP samples, the PP resin was doped with 0.6 wt% of β -nucleating agent in the ratio of pimelic acid to calcium stearate 1:2^{21,22}. Before moulding, the barrel of the machine was first purged with ordinary PP resin and then with doped resin. The prepared β -PP possessed an overall crystallinity of 59% and a percentage of β -phase of about 61%, as measured by D.S.C.

Tensile testing

The injection moulded samples were tensile tested on a Lloyd LR 50K tensile testing machine at room temperature with a crosshead speed ranging from 2.5 to 500 mm min⁻¹. When the specimens were stretched at low crosshead speeds, they exhibited necking and cold drawing after yielding. In this case, several marks over the necking region were made, the dimensions of the cross-sections of the deformed materials at the labelled portions were measured under load, and the actual strains of the materials in the neck were calculated on the basis of the ratio of the cross-sectional areas before and after deformation.

Identification of β -phase with WAXS

The WAXS experiments were performed in a Siemens D500 diffractometer. The Cu anode X-ray generator was operated at 35 kV and 30 mA and the Cu radiation was filtered by an Ni filter. The deformed specimen was set in a reflection arrangement and impinged with Cu K α radiation. The relative content of β -phase, K_β , was calculated according to equation (1), suggested by Turner-Jones¹⁸:

$$K_\beta = I_{\beta 1} / (I_{\beta 1} + I_{\alpha 1} + I_{\alpha 2} + I_{\alpha 3}) \quad (1)$$

where $I_{\beta 1}$ is the diffraction intensity of β {3 0 0} planes at diffraction angle $2\theta = 16^\circ$, $I_{\alpha 1}$, $I_{\alpha 2}$ and $I_{\alpha 3}$ are the diffraction intensities of the α {1 1 0}, α {0 4 0} and α {1 3 0} planes at diffraction angles $2\theta = 14.1^\circ$, 16.9° and 18.8° respectively.

Measurement of percentage of β -phase with D.S.C.

The neck of the cold-drawn β -PP sample was sectioned into films of 0.3 mm thickness perpendicularly to the stretching direction with a Leitz 1400 microtome. The melting behaviour of the thin films cut from different portions was analysed on a DuPont 910 D.S.C. at 10°C min⁻¹ in nitrogen atmosphere. The percentage of β -phase of a sample, ϕ_β , was determined by the relative crystallinities of α -phase and β -phase:

$$\phi_\beta = [X_\beta / (X_\alpha + X_\beta)] \times 100\% \quad (2)$$

where X_α and X_β are the crystallinity of the α -phase and β -phase respectively, based on specific fusion heats of the sample.

Because of the coexistence of α -phase and β -phase crystals in the samples, the β -PP sample exhibited both an α -fusion peak and a β -fusion peak on the D.S.C. curve, which overlapped partially. The specific fusion heats for α -phase and β -phase were approximated according to the following calibration method, developed in this laboratory.

The total fusion heat, ΔH , was integrated from 80°C to 180°C on the D.S.C. thermogram. A vertical line was drawn through the maximum between the α - and β -fusion peaks and the total fusion heat was divided into β -component, ΔH_β^* , and α -component, ΔH_α^* . Because the less perfect α -phase crystals melted before the maximum point during heating and contributed to ΔH_β^* , the true value of β -fusion heat, ΔH_β , was approximated by multiplying ΔH_β^* by a calibration factor A :

$$A = [1 - (h_2/h_1)]^{0.6} \quad (3)$$

$$\Delta H_\beta = A \times \Delta H_\beta^* \quad (4)$$

$$\Delta H_\alpha = \Delta H - \Delta H_\beta \quad (5)$$

where h_1 and h_2 are the heights from the base line to the β -fusion peak and the maximum point respectively. After the specific fusion heats were obtained, the crystallinities of the α - and β -phases were calculated separately according to equation (6):

$$X_i = \Delta H_i / \Delta H_i^0 \times 100\% \quad (6)$$

where ΔH_i is the calibrated specific fusion heat of either the α -phase or the β -phase and ΔH_i^0 is the standard fusion heat of either α -phase or β -phase PP crystals, 178 J g⁻¹ for α -phase and 170 J g⁻¹ for β -phase²³.

RESULTS

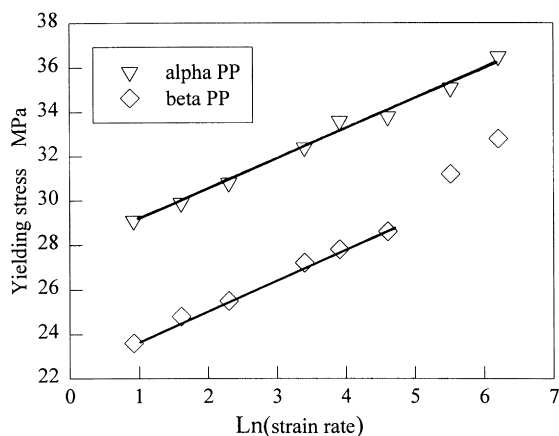
Yielding behaviour

When the injection moulded α -PP and β -PP were tensile stretched at 5.0 mm min⁻¹ (at 20°C), they yielded at a strain near 5% and 8% respectively. After the yield point, further stretching resulted in the specimens necking and cold drawing. The elongation of the samples before yielding was mostly recoverable at room temperature. After recovery for one week, the permanent elongation (plastic deformation) of the specimens stretched to the yield (maximum) load was about 0.5%. The yielding stresses were about 31 MPa and 26 MPa for the injection moulded α -PP and β -PP respectively. This is consistent with Jacoby's work²⁴ which showed that β -PP has a lower modulus, lower yielding stress and higher impact strength than α -PP. However, the yielding behaviour was rate dependent. If the injection moulded β -PP was stretched at higher strain rates, it could be broken with little cold drawing, as indicated in *Table 1*.

Table 1 Yielding stress of injection moulded PP at various strain rates

Strain rate (mm min ⁻¹)	2.5	5.0	10	30	50	100	250	500
α -PP	29.1	29.9	30.8	32.4	33.6	33.8	35.1	36.5
yielding mode ^a	C	C	C	C	M	B	B	B
β -PP	23.6	24.8	25.5	27.2	27.8	28.6	31.2	32.8
yielding mode ^a	C	C	C	M	M	B	B	B

Testing temperature: 23°C

^aC: cold drawing; B: all specimens broken without cold drawing; M: some specimens broken after a little cold-drawing**Figure 1** Effect of strain rate on the yield stress of injection moulded PP. Solid line: fitted linear regression result

The yielding stress of plastics is sensitive to temperature and strain rate and can be described by Eyring's equation²⁵, as shown below:

$$\frac{\sigma_y}{T} = \frac{\Delta U}{\nu T} + \frac{R}{\nu} \ln \left[\frac{2e'}{e_0} \right] \quad (7)$$

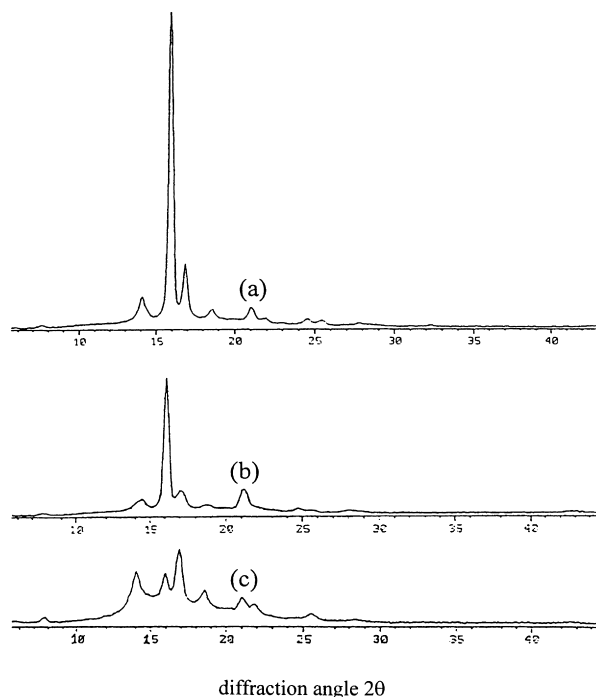
where σ_y is the yielding stress, T is testing temperature in K, ΔU is the activation energy of plastic deformation (flow), i.e. the height of the potential energy barrier of two adjacent equilibrium positions for element units to jump, ν is the activation volume of the element motion unit, e' is the strain rate and e_0 is the pre-exponential factor. According to equation (7), the plot of yielding stress (σ_y) versus $\ln(e')$ should be a straight line whose slope is related to the material itself (element motion unit) and the testing temperature:

$$\text{slope} = \frac{RT}{\nu} \quad (8)$$

The yielding stresses (at 23°C) of injection moulded α -PP and β -PP over a strain rate ranging between 2.5 and 500 mm min⁻¹ are listed in Table 1 and the plots of yielding stress (σ_y) versus $\ln(e')$ are shown in Figure 1. It can be seen that the plot for the α -PP is generally linear. On the other hand, the β -PP sample seems to exhibit a bilinear relation, which suggests that two activated flow processes are in operation. In fact, when higher testing temperatures were used, a bilinear relation was also observed on pure α -PP²⁶.

In both α -PP and β -PP, the slopes of the fitted linear regression lines (for β -PP samples only the section at low strain rates was considered) were found to be about 1.4 MPa and the calculated activation volumes were 3 nm³. A similar result was obtained by Liu and Truss²⁶ using a more precise two-stage Eyring equation. They found that for pure α -PP the activation volume was approximately 4 nm³.

The activation volume of PP is much smaller than the dimension of the mosaic blocks. The mosaic blocks

**Figure 2** WAXS patterns of β -PP, (a) before deformation; (b) yielded at 8% strain but without obvious necking; and (c) after cold drawing at 110% strain

suggested by Peterlin¹¹ were several hundred angstroms in width, while the thickness of the lamellae are approximately 10 and 20 nm for α - and β -PP respectively, as observed under TEM; thus, the magnitude of the mosaic blocks should be in thousands of nm³. On the other hand, the obtained PP activation volume seems to be close to the dimensions of chain segments of glassy plastics in dilute solution. For most glassy plastics the activation volume comes out to be the volume of several chain segments (typically between 2 and 10). It is believed that the plastic flow (yielding) of solid plastics involves more cooperative motion of chain segments than would be required for a conformation change in dilute solution²⁵. Evidently, the motion of chain segments in the condensed state would be affected more by adjacent molecular chains than in dilute solution. Nevertheless, the above result suggests that the yielding process (more precisely the onset of yielding) of PP mainly involves the motion of its chain segments.

Transformation of β -phase PP crystal over the neck

After tensile testing, the crystals of the deformed β -PP were identified with WAXS. Figure 2 shows the WAXS patterns of injection moulded β -PP at various strains. The undeformed sample (curve (a)) exhibited a prominent β -feature diffraction peak at $2\theta = 16.0^\circ$ and three evident α -feature diffraction peaks at $2\theta = 14.1^\circ$, 16.8° and 18.8° . On

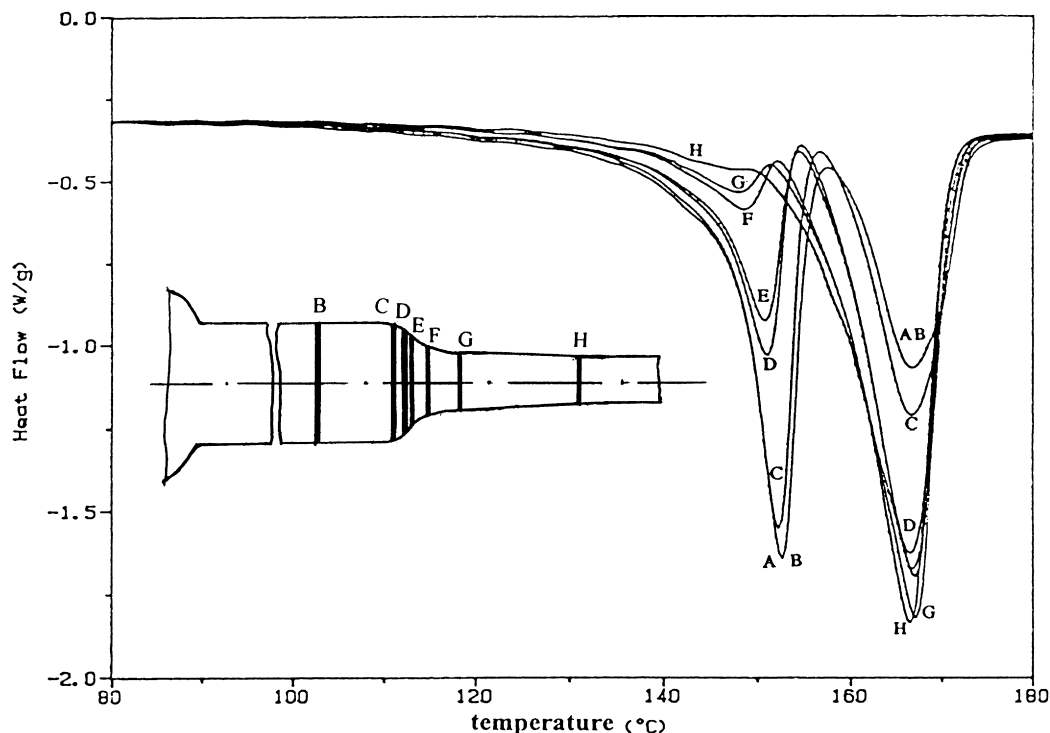


Figure 3 D.S.C. thermogram of undeformed and deformed material taken from different sections of the neck of β -PP. A: undeformed material; B: yielded materials with 8% elongation; C: upper shoulder of neck with 22% elongation; D: lower shoulder of neck with 55% elongation; E: 65% elongation; F: 110% elongation; G: cold-drawn section with 160% elongation; and H: 230% elongation

Table 2 Variation of α - and β -phase crystals over the neck of β -PP

Sample	Strain(%)	Starting fusion(°C)	β -melting point(°C)	α -melting point(°C)	$\Delta H_{\beta}(\text{J g}^{-1})$	$\Delta H_{\alpha}(\text{J g}^{-1})$	$X_{\beta}(\%)$	$X_{\alpha}(\%)$	$X(\%)$	$\phi_{\beta}(\%)$
A	0	106.0	152.5	166.9	61	41	36	23	59	61
B	8	105.5	152.5	166.7	61	41	36	23	59	61
C	22	106.3	152.3	166.6	56	46	33	26	59	56
D	55	113.0	151.2	166.5	36	66	21	37	58	36
E	65	114.0	150.9	166.8	30	70	18	39	57	31
F	110	119.0	148.8	166.8	13	83	8	46	54	14
G	160	120.5	148.0	167.2	9	86	5	48	53	9
H	230	121.0	147.0	167.2	2	88	1	50	51	2

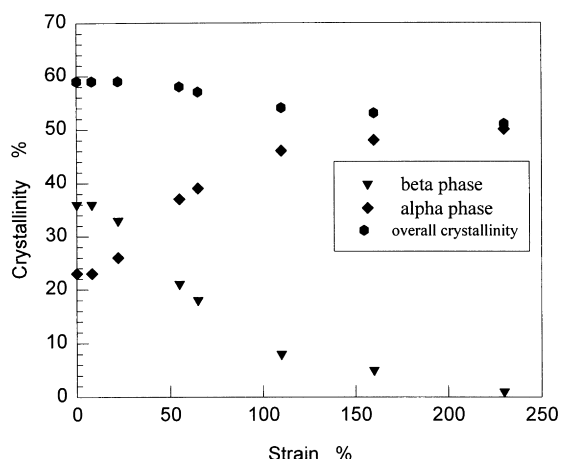


Figure 4 Effect of strain on crystallinity of α -phase and β -phase over the neck of β -PP

the basis of equation (1), the K_{β} value was calculated to be 0.73. Curve (b) shows the diffraction pattern of a sample which has just yielded at 8% elongation but before obvious necking has occurred. The β -diffraction peak at $2\theta = 16.0^{\circ}$

is still the most prominent one among other diffraction peaks, and the K_{β} value was calculated to be 0.74, almost the same as that of the undeformed materials. However, after the material necked and was cold drawn to an elongation of 110% (curve (c)), the β -feature diffraction peak at $2\theta = 16.0^{\circ}$ weakened significantly while the intensity of α -feature diffraction at $2\theta = 14.1^{\circ}$, 16.8° and 18.8° increased. The K_{β} value reduced to 0.21, indicating that many of the β -phase crystals have transformed to α -phase.

The phase transformation of β to α over the neck was extensively investigated with D.S.C. The fusion behaviour of materials from different sections of the neck is shown in Figure 3 and the analytical results are listed in Table 2. The undeformed material gave a β -fusion peak near 152.5°C and an α -fusion peak near 166.9°C . The specific fusion heats for β -phase and α -phase were 61 J g^{-1} and 41 J g^{-1} respectively. On the basis of equations (2) and (6), the crystallinities of β -phase and α -phase were calculated to be 36% and 23%, and the percentage of β -phase was 61%. The yielded material had a similar D.S.C. thermogram (curve B) to the undeformed material even though it underwent yielding stress and was stretched to 8%. No difference in melting behaviour has been identified by D.S.C., indicating that little phase transformation of β to α has taken place up

to the yield point. This is consistent with the WAXS results in Figure 2.

As the specimen began to neck, the phenomenon of phase transformation of β to α became apparent: the β -fusion peak diminished while the α -fusion peak enlarged as the material necked down. Curve C shows the fusion behaviour of material taken from the upper shoulder of the neck, i.e. the area just below the parallel section above the neck, where the elongation was approximately 22%. The β -fusion peak has diminished while the α -fusion peak has strengthened. It can be seen from Table 2 that there is a 3% drop in the crystallinity of the β -phase, X_β , which is accompanied by a corresponding increase in X_α , leaving the overall crystallinity, X , unchanged at 59%. At the lower shoulder of the neck, where the strain was about 55% (curve D), the reduction of X_β became rather substantial.

Figure 4 shows a plot of the various crystallinities versus the strain, from Table 2. It is apparent that much of the phase transformation took place between the upper and lower shoulders. The phase transformation did not stop beyond the lower shoulder but continued within the cold-drawn material of the neck, nevertheless at a much lower rate. It was also observed that the overall crystallinity of the samples dropped from 59% to 51% after cold drawing.

Furthermore, as the β -PP specimens necked down, not only did the β -fusion peaks diminish, but also the low temperature portion of the β -fusion peaks shifted towards higher temperature. The incipient fusion temperature (at which the D.S.C. graph diverged from the base line of 0.05 W g^{-1}) increased from 106°C before necking to 120°C after necking. Meanwhile, the β -melting point decreased from 152.5°C to 147°C monotonically, while the α -melting point reached a minimum (166.5°C) at the upper shoulder of the neck, where the β -phase crystals largely transformed to α -phase.

The above WAXS and D.S.C. results clearly indicated that the β -phase PP crystal was capable of mechanical stability up to the yield point. No obvious phase transition was detected by D.S.C. in the β -PP before necking. However, once the sample was stretched to necking, the β -phase transformed to α -phase and this phase transformation occurred over the whole necking region, but mainly between the upper and lower shoulder of the neck. Similar results were also found on the samples tested at different strain rates.

DISCUSSION

It is normally claimed that the β -phase PP crystal is mechanically and thermally unstable, transforming to α -phase during heating^{16,19,27}. An attempt to prepare oriented β -phase fibre through drawing a β -PP sample failed and only oriented α -phase fibre was obtained¹⁸. This study has shown that the β -phase PP crystal is mechanically stable up to the yield point but transforms to α -phase after necking. This is in agreement with the yield stress analysis based on Eyring's theory. The yielding process of crystalline PP is mainly associated with the movement of the chain segments rather than that of the mosaic blocks of the lamellae as a whole. As necking occurs, however, large-scale deformation within the crystals is expected and this may lead to phase transformation.

On the basis of electron or X-ray diffraction patterns and minimum energy calculation of PP¹⁶⁻²⁸, it has been recognized that the molecular chains in both α - and β -phase crystals take the same threefold helical conformation,

either right-handed or left-handed. However, the helical chains arrange in a different chiral arrangement in the two crystals. In α -phase crystals the molecular chains arrange in alternating right-handed and left-handed chain layers, while in β -phase crystals the same directional helical chains pack together to form crystalline domains with the same directional helical chains. The difference in helix chirality in the different crystalline phases was verified by Bunn *et al.*²⁹ and Gomez *et al.*³⁰ using solid-state ^{13}C N.M.R. and further clarified by Meille *et al.*¹⁷ using precise electron diffraction. Therefore, in PP polymorphs the change of packing pattern from hexagonal to monoclinic cannot be achieved by simple adjustment of the relative positions of the neighbouring chains through slipping but has to come about through rewinding of some helices from right-handed to left-handed or vice versa. This means that the transformation of β -phase to α -phase certainly involves the destruction of the original β -phase crystals and rearrangement of the chains to form new α -phase crystals. Hence, the above WAXS and D.S.C. results are considered to be a solid proof to Flory's model of plastic deformation of crystalline plastics: the conversion of spherulite structure into fibrous structure during cold drawing involves melting of pre-existing crystals and recrystallization in melted phases.

However, it should be pointed out that the 'melt' in the neck may be very different from normal thermal melting. Although there was an increase in temperature at the neck, it is unlikely that the temperature was anywhere near the normal melting temperature (approx. 152°C) of β -PP, due to the slow strain rate used in the tensile test. Indeed, necking was observed even in creep tests at room temperature; in such a case the temperature of the neck should be very close to room temperature. Juska and Harrison³¹ pointed out that applied mechanical energy may weaken van der Waals bonds between chains in polymer crystals and enhance the potential (internal) energy of the system during tensile testing. When the internal energy reaches a critical value the melt phase may be equally as stable as the crystalline phase and chain randomization will occur at the draw temperature. Using a deformation calorimeter, Rudnev *et al.*³² noted that less than 50% of the input mechanical work actually converted to heat during deformation and the rest was stored in the deformed material. Their study showed that the stored energy in crystalline PET was considerably higher than that in the amorphous PET. The stored energy may be more related to the local distortion of lamellae. Brady and Thomas¹⁵ studied the deformation of textured HDPE films with a shish-kebab structure and found that the stressed kebabs broke up and fed into the shish core to form fibrils through a mechanically induced 'decrystallization' process. Decrystallization occurred via chain slip, crystal shear and defect generation. Reduction in crystal size could lead to thermodynamic destabilization of the crystallites, reducing their melting point to the extent that melting would occur at the deformation temperature. Indeed, the term 'decrystallization' was used to avoid association with thermally induced melting.

Since the phase transformation was found to continue within the cold-drawn region, it is believed that the 'melting' or 'decrystallization' process did not occur simultaneously throughout the whole neck but, rather, was localized at areas where stresses were particularly high. In fact, using TEM combined with the RuO_4 staining technique, some decrystallized spots have been observed among β -lamellae which were parallel to the stretching

direction in the deformed β -PP even before necking. Perhaps the necking phenomenon is the consequence of local decrystallization of some lamellae. The decrystallization of lamellae may initiate from defects in the lamellae, because the low temperature portion of the β -fusion peak shifted towards higher temperature and the incipient fusion temperature increased as the material necked down.

Flory and Yoon¹² put forward the theory that the large irreversible deformation of crystalline plastics, such as happens in cold drawing, must involve local melting of pre-existing crystals at the drawing temperature. Here, the experimental results demonstrated that this viewpoint on plastic deformation is true at room temperature.

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