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The structure and mechanical properties of syndiotactic polypropylene

Y. SAKATA*, A. P. UNWIN and I. M. WARD‡
IRC in Polymer Science and Technology, University of Leeds, Leeds LS2 9JT, UK

The drawing behaviour of several syndiotactic polypropylenes is examined as a function of molecular weight and initial morphology. It is found that these materials can be drawn to a much lesser extent than comparable isotactic polypropylene. This limited drawability is attributed to the absence of an effective crystalline *c*-slip process, a view supported by dynamic mechanical measurements. Highest draw ratios are achieved in gel spun high molecular weight material where the degree of molecular entanglement is low enough to suppress the undesirable increase in drawing stress with extension.

1. Introduction

Difficulties in its synthesis have meant that the syndiotactic form of polypropylene has historically received considerably less attention than the highly successful isotactic form. Recently, however, the development of the new metallocene catalyst systems [1] has made it possible to produce syndiotactic polypropylene, SPP, with high stereoregularity. The upsurge in interest in SPP stems in part from the possibility that alternate positioning of methyl groups may favour an extended chain conformation and thus lead to mechanical properties more akin to polyethylene than isotactic polypropylene. The crystal structures of SPP have been extensively studied but as yet there have been few reports [2, 3] on the physical and mechanical properties of SPP.

Here we report investigations into the drawing behaviour and mechanical properties of some syndiotactic and isotactic polypropylenes with different molecular weight characteristics and morphologies. Dynamic mechanical analysis has revealed the absence of an α relaxation in the syndiotactic form. The relatively poor drawing behaviour of this form, compared with isotactic polypropylene, is explained in terms of the restrictions imposed on the network by the lack of an effective crystal slip process.

2. Experimental details

2.1. Materials and sample preparation

The drawing and mechanical behaviour of predominantly syndiotactic but also some isotactic polypropylenes covering a range of molecular weights and morphologies are investigated here. The molecular weight characteristics of these grades, all produced using metallocene catalyst systems, are given in Table I. Isotropic sheets of approximately 1 mm thickness were obtained by compression moulding polymer pellets or powder between ~ 1.6 mm thick polished copper plates at a temperature of 170 °C (200 °C in the case of isotactic polypropylene). The molten product was then either quenched into iced water (– Q) or allowed to cool naturally to room temperature (– S) over a period of about 4 h. Cast films (– C) of S3 were prepared by gelation/crystallization from a 5% (w/w) decalin solution containing approximately 0.1% (w/w) of antioxidant (di-*t*-buthyl-*p*-cresol). The homogenized solution was prepared by heating the polymer/solvent mixture at 135 °C under nitrogen and then transferred to an aluminium tray surrounded by iced water. The decalin was allowed to evaporate from the gels under ambient conditions for about 2–3 days, after which, the nearly dried cast film was immersed in an excess of ethanol and subsequently air-dried to remove residual traces of the decalin–ethanol mixture. The thickness of a typical cast film obtained by this method was 0.06–0.07 mm. Gel sheets of the medium (S2) and low (S1) molecular weight material cracked while drying under ambient conditions and did not form a complete film. These materials did not draw at any temperature investigated, but failed in a brittle manner.

TABLE I Characterization of SPP and IPP

Sample	S1	S2	S3	I2	I3
M_w	69 800	152 000	490 000	135 000	465 500
M_w/M_n	2.2	2.0	2.4	1.9	2.1
T_{mp}	140 °C	139 °C	138 °C	151 °C	154 °C
Tacticity	syn	syn	syn	iso	iso

Dumbbell samples (2 cm by 0.5 cm) of quenched, slow cooled and cast material were drawn in air on an Instron tensile testing machine equipped with an oven.

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* *Present address*: Research Centre, Mitsubishi Kasei Corporation, 1000 Kamoshida-cho, Midori-ku, Yokohama 227, Japan
‡ To whom correspondence should be addressed.

Crosshead speeds of 5 and 0.5 cm min^{-1} and temperatures between 20 and 140 °C were used. The draw ratio, λ, was determined from the separation of the mid-points of ink marks on the sample surface initially spaced at intervals of 1 mm.

2.2. Sample characterization

Wide angle X-ray diffraction photographs were obtained using nickel-filtered CuK_α radiation and a flat plate camera. DSC measurements were carried out at a heating rate of 10 K min^{-1} on a Perkin-Elmer DSC-7 calibrated with an indium standard. Dynamic mechanical measurements were carried out over a range of temperatures from − 80 °C to 130 °C using equipment constructed in our laboratory, described in detail elsewhere [4]. The specimens, with a nominal gauge length of 5 cm, were mounted between the clamps of a special straining system. A sinusoidal uniaxial strain was applied to the samples by means of a vibrator driven by a Solartron 1250 frequency response analyser. Measurements were made using an oscillatory strain of 0.1% (peak-to-peak) with the samples under a dead-load sufficient to produce a strain of about 0.15%.

3. Results

3.1. Sample characterization

3.1.1. Chain conformation and packing

Three different chain conformations of SPP have been reported [5–7]. The most common and stable form has the helical conformation (TTGG)$_2$. A planar zigzag conformation, obtained by cold-drawing quenched material, has also been reported, as has a third conformation, (T$_6$GGTTGG), intermediate between the helical and planar zigzag forms. This last conformation can be obtained by exposing drawn samples containing the planar zigzag conformation to several kinds of organic solvent vapour. The last two conformations are easily transformed to the more stable helical conformation by annealing.

SPP is also known to adopt different crystalline structures. Corradini *et al.* [5] proposed a *C*-centred orthorhombic unit cell (Cell-1) with axes a = 1.450 nm, b = 0.560 nm, and c = 0.740 nm. Recently, additional orthorhombic unit cells having chains in the helical conformation have been proposed [8, 9]. The first of these (Cell-2) has the same dimensions as Cell 1 but the molecules are placed on the *ac* faces rather than *C*-centred. In addition, the chain packing is antichiral along the *a* axis as opposed to the fully isochiral state in Cell-1. More recently the fully antichiral, body-centred unit cell (Cell-3) has been proposed. Here, the chains are packed in a fully antichiral manner along both the *a* and *b* axes. Cell parameters are a = 1.450 nm, b = 1.120 nm, and c = 0.740 nm.

X-ray diffraction measurements on the isotropic samples considered here confirm the presence of crystal structures with chains in the helical conformation although differences relating to the thermal history are observed. In quenched and cast materials the majority of crystals have the Cell-2 structure. In these materials the (0 2 0) reflection, typical of Cells-2 and -3, is observed but neither the (1 1 0) reflection, typical of Cell-1 nor the (2 1 1) reflection, typical of Cell-3, are present. Although weak, the (2 1 1) reflection is observed in the slow-cooled materials, indicating the presence of both Cell-2 and Cell-3 structures and suggesting that Cell-3 can be obtained by crystallization at higher temperatures.

The crystal structure of the drawn samples depends on the drawing temperature. Quenched samples drawn at 20 °C give an X-ray pattern typical of the planar zigzag conformation although relatively small amounts of the crystals having the helical conformation are also present. For samples drawn at higher temperatures (60–80 °C), there is no evidence of the planar zigzag conformation. Instead, X-ray patterns indicate the presence of helical conformation crystals, predominantly in Cell-1 and Cell-2 forms. Cell-3 becomes more prominent as the drawing temperature increases and at temperatures above 130 °C it is dominant. There is also no significant difference in the photographic patterns of quenched, slow cooled and cast materials drawn at these higher temperatures to comparable draw ratio.

The crystalline options for SPP are thus considerable, with three different orthorhombic unit cells with chains in the helical conformation as well as an orthorhombic unit cell with chains in the planar zigzag conformation. The particular crystal morphology displayed by a sample depends critically on its thermal history, but generally the helical conformation is adopted. The current results indicate that the most stable crystal structure is Cell-3 and that this becomes more dominant as crystallization or drawing temperature are increased.

3.1.2. Crystallinities

Values for the crystallinity of the isotropic SPP samples, shown in Table II, are obtained from differential scanning calorimetry at a heating rate of 10 °C min^{-1} using the value for the enthalpy of fusion of a fully crystalline sample (1.4 kJ mol^{-1}) suggested by Balbontin *et al.* [10]. Typically, values of ~ 20% for the quenched samples, ~ 30% for the slow-cooled samples, irrespective of molecular weight, and ~ 40% for cast films, are found.

TABLE II The fusion enthalpy of SPP samples

Sample	T_{mp} (°C)	ΔH (J g^{-1})	Crystallinity (%)
S1-Q	140.1	39.5	24
S2-Q	142.3	32.7	20
S2-S	146.2	47.4	29
S3-Q	143.6	34.1	21
S3-S	150.5	52.9	32
S3-C	147	71.0	43

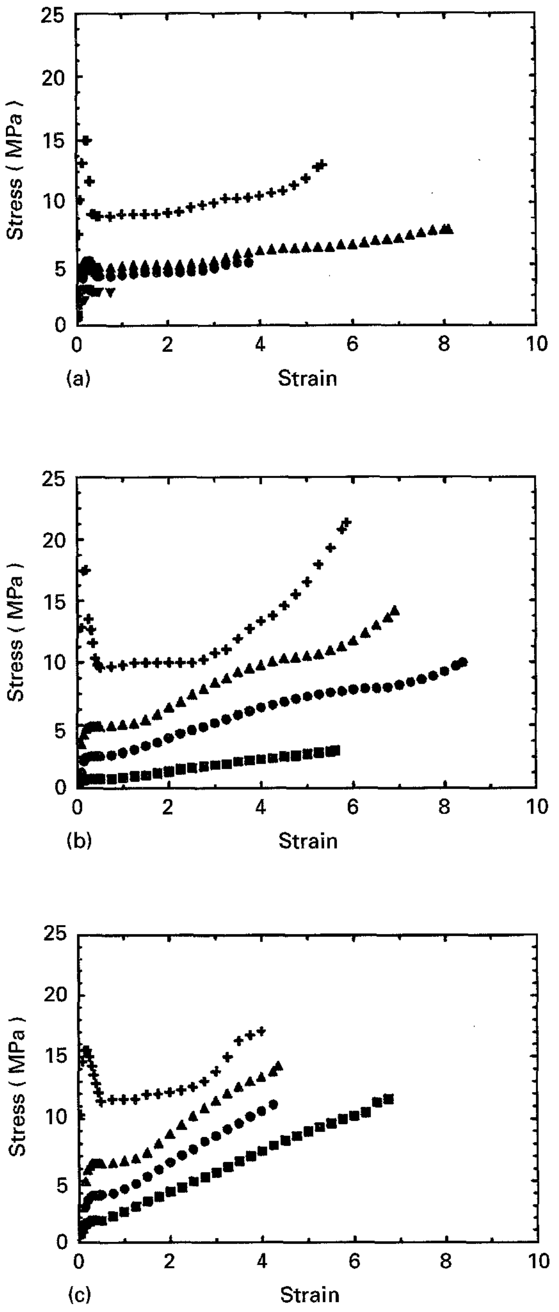

Figure 1 Stress–strain curves of quenched samples of syndiotactic polypropylene as a function of drawing temperature: (a) S1; (b) S2; and (c) S3. All samples drawn at 5 mm min^{-1}. Draw temperature:- +, 20 °C; ▲, 80 °C; ●, 90 °C; ▼, 110 °C, and ■, 130 °C.

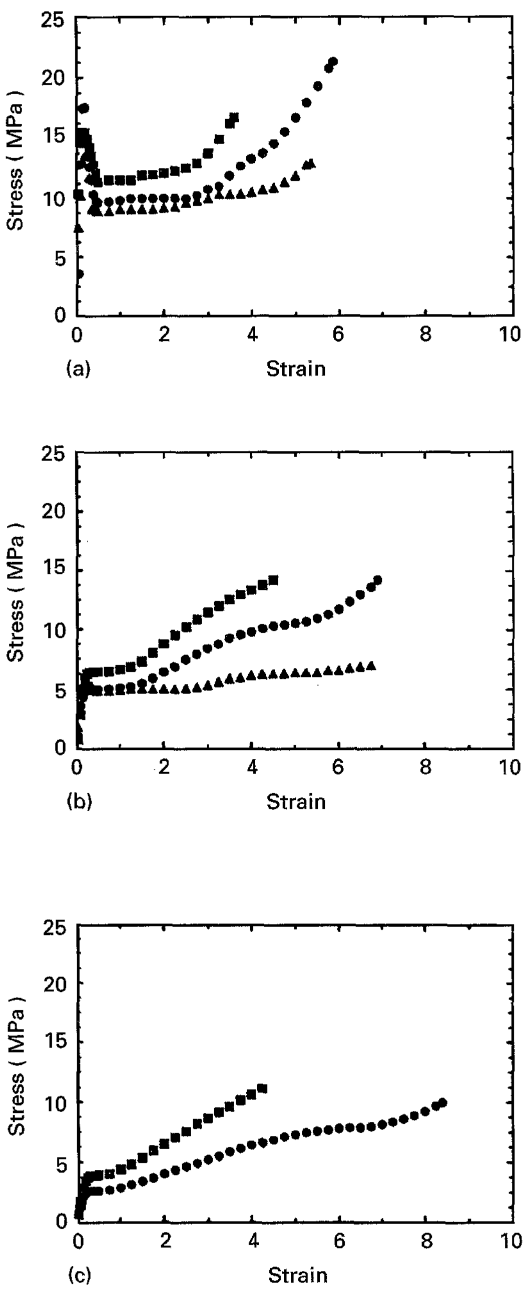

Figure 2 Stress–strain curves of quenched samples of syndiotactic polypropylene at three different drawing temperatures; (a) 20 °C; (b) 80 °C; and (c) 110 °C. All samples drawn at 5 mm min^{-1}. Grades:- ■, S3-Q; ●, S2-Q and ▲, S1-Q.

3.2. Drawing behaviour

Fig. 1a to c show stress–strain curves of quenched samples of SPP for a range of temperatures. As expected there is a general tendency for the drawability to increase with temperature. For the low, S1-Q, and medium, S2-Q, (Fig. 1a and b) molecular weight materials there is a temperature above which the drawability decreases. This turning point occurs at about 80 °C in S1-Q with the drawability becoming negligible at 110 °C and above. In S2-Q the drawability only starts to fall at a higher temperature (above about 130 °C). In the highest molecular weight material, S3-Q (Fig. 1c), the temperature has little effect on the drawability between 20 and 110 °C. Above 120 °C, it improves and the specimen can be drawn to an imposed draw ratio of 6–8. The drop in drawability at high temperature, seen in lower molecular weight materials, is not observed. Fig. 2a to c replot the data in Fig. 1a to c to allow a comparison of the drawing stresses. The higher molecular weight material shows a higher drawing stress, as might be expected from the higher melt viscosity associated with these materials.

The effect of morphology on drawing stress was examined by comparing samples produced under different initial thermal treatments. Obvious differences in the drawing behaviour of the quenched and slow cooled samples were evident in the initial stages of deformation. The low molecular weight S1-S would not draw under any conditions (at any temperature in the range 20 to 130 °C) whereas S2-S and S3-S both necked at a drawing temperature of 110 °C. In contrast, none of the quenched materials necked at this temperature. The true stress–strain curves for some of

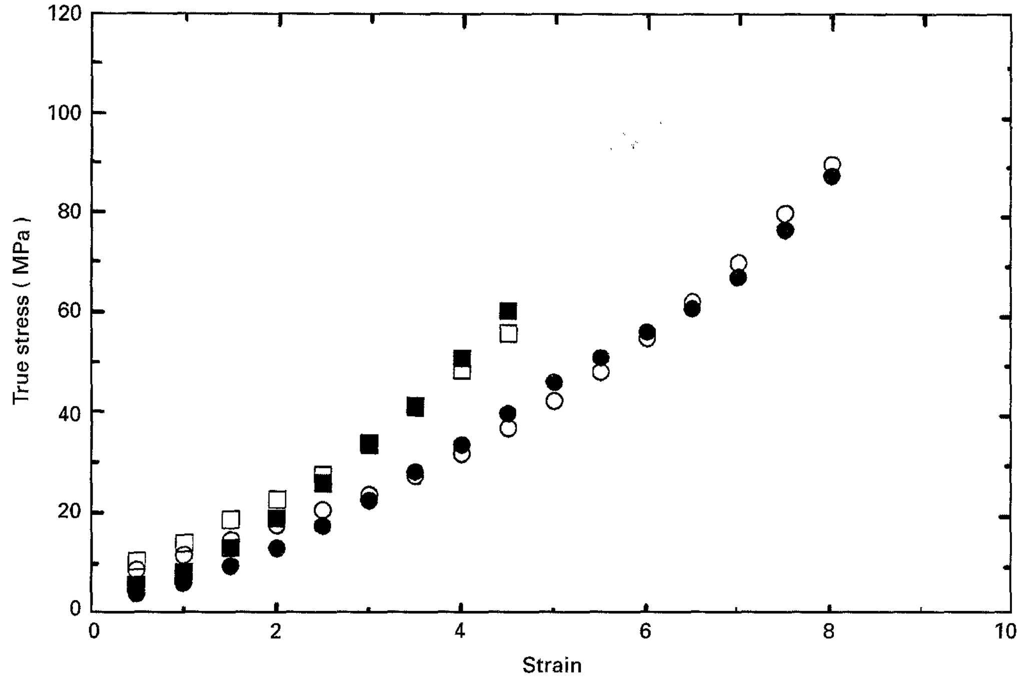

Figure 3 True stress–strain curves of syndiotactic polypropylenes with different initial morphologies, drawn at 5 mm min^{-1} and a temperature of 110 °C. □, S3-S; ■, S3-Q; ○, S2-S and ●, S2-Q.

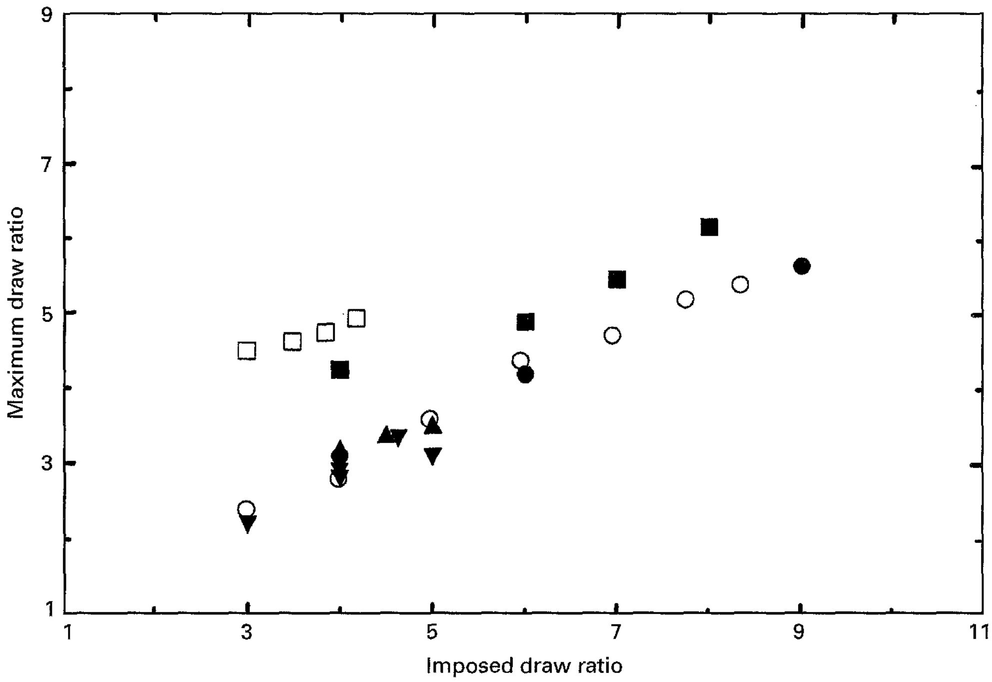

Figure 4 Relation between the final and the imposed draw ratios in samples of syndiotactic polypropylene drawn at 110 °C. ●, S2-Q; ■, S2-S; ▼, S3-Q and ▲, S3-S. Draw speed is 5 mm min^{-1} for closed symbols and 50 mm min^{-1} for open symbols.

these materials are shown in Fig. 3. Clearly, at low strains, the drawing stress is greater in the slow-cooled materials. At higher draw ratio the stress–strain curves converge and there is very little difference between the slow-cooled and the quenched materials. In addition, both materials gave approximately the same elongation at break. It therefore appears that differences in crystallinity, characterizing these different morphologies, do not have a significant effect on the high strain behaviour. Crystallinity affects the yielding process (i.e. the yield stress) but the strain hardening behaviour is dependent on different factors, of which the most important is probably the degree of molecular entanglement. Finally, the slow-cooled samples showed a sensitivity to draw speed (failure strain decreased with increasing draw speed) not shown by the quenched samples. This increased strain rate sensitivity in slow-cooled samples has also been observed in polyethylene [11], where it was concluded that in the slow-cooled more crystalline polymers there is a smaller activation volume for the thermally activated yield process.

Specimens of both quenched and slow-cooled materials showed a large degree of recovery immediately after removal of the drawing stress. Plots of the final ligament draw ratio as a function of imposed draw ratio, shown in Fig. 4, clearly indicate the extent of this elastic contribution to deformation. For example, the final draw ratio of S2-Q was found to be ~ 5 for an imposed draw ratio of ~ 8. Fig. 4 also shows the effect of initial thermal treatment on draw ratio for S2 and S3 drawn at a temperature of 110 °C. In the medium molecular weight S2 the curves for the slow-cooled samples lie above those of the quenched samples (i.e. the slow-cooled materials had less elastic deformation) but this difference is less pronounced in the case of higher molecular weight grade, S3. It appears that, particularly in the latter case, there is a large contribution to the stress from the deformation of a molecular network which is not broken down by drawing.

3.2.1. Comparison with isotactic polypropylene

Fig. 5 shows the stress–strain curves for quenched samples of SPP and comparable molecular weight IPP at a drawing temperature of 110 °C. In IPP, an apparent yield point is observed, beyond which the stress increases gradually with increasing strain. On the other hand, SPP shows a less pronounced yield point and strain-hardening commences at a relatively early stage with the stress increasing more rapidly than in IPP. Moreover, it can be seen from Fig. 6 that the final draw ratio of IPP is approximately equal to the imposed draw ratio, unlike the findings in SPP.

3.2.2. Cast films

Cast films show a much greater drawability than quenched samples, reaching an imposed draw ratio of ~ 14 (~ 8 for quenched sheets) at a drawing temperature of 135 °C. Fig. 7 shows stress–strain curves for the cast film of S3 measured at a temperature of 110 °C compared with those of quenched and slow-cooled materials. Cast film and slow-cooled materials both necked at this temperature. The cast film has a lower drawing stress than either the quenched or the slow cooled materials at a strain in the range from ~ 1.5–4.5 despite its relatively high crystallinity (shown in Table II). This supports the view that the strain hardening behaviour depends not on the crystallinity but on the entanglement density.

3.3. Mechanical properties

3.3.1. Relaxation peaks

Figs 8 and 9 show the temperature dependence of the loss factor and the dynamic modulus at 10 Hz for differently prepared samples of polypropylene. The quenched samples of SPP in Fig. 8 show a broad peak at ~ 20 °C (the β peak) which corresponds to the relaxation of chains in the amorphous regions. At higher temperatures, above 60 °C, values of tan δ gradually increase but no other peaks are observed. In contrast, IPP shows a strong α relaxation (at ~ 100 °C), in addition to the β relaxation. The general features seen in quenched SPP are also seen in the cast films. The height of the β relaxation is less than in the quenched samples because of the higher crystallinity (Table II) and there is still no α-relaxation. The high crystallinity of the cast material suggests that the absence of the α-relaxation in SPP is not because of a lack of crystallinity.

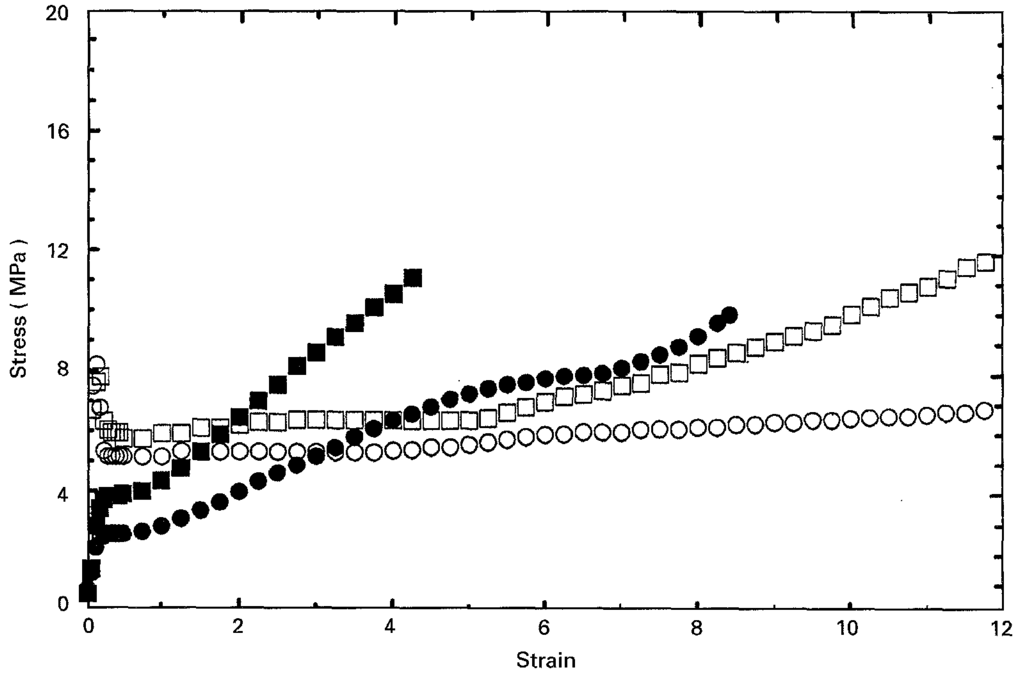

Figure 5 Comparison of stress–strain curves of quenched samples of syndiotactic and isotactic polypropylene drawn at 5 mm min^{-1} and 110 °C. ■, S3-Q; ●, S2-Q; □, I3-Q and ○, I2-Q.

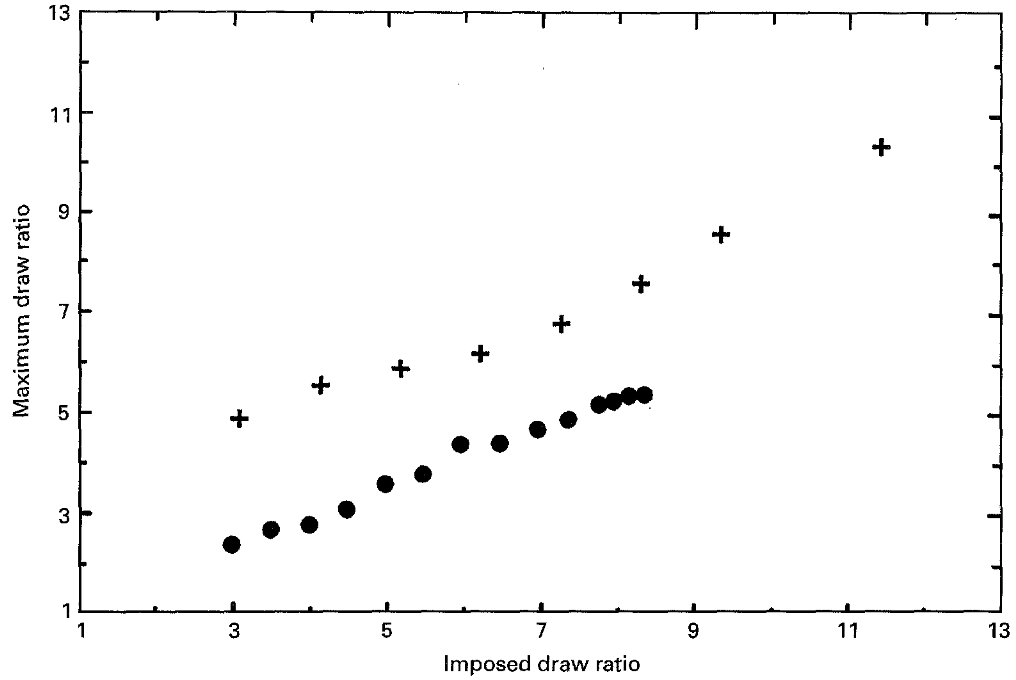

Figure 6 Comparison of the effectiveness of the drawing procedure on quenched samples of syndiotactic and isotactic polypropylene drawn at 5 cm min^{-1} and 110 °C. ●, S2-Q; +, I2-Q.

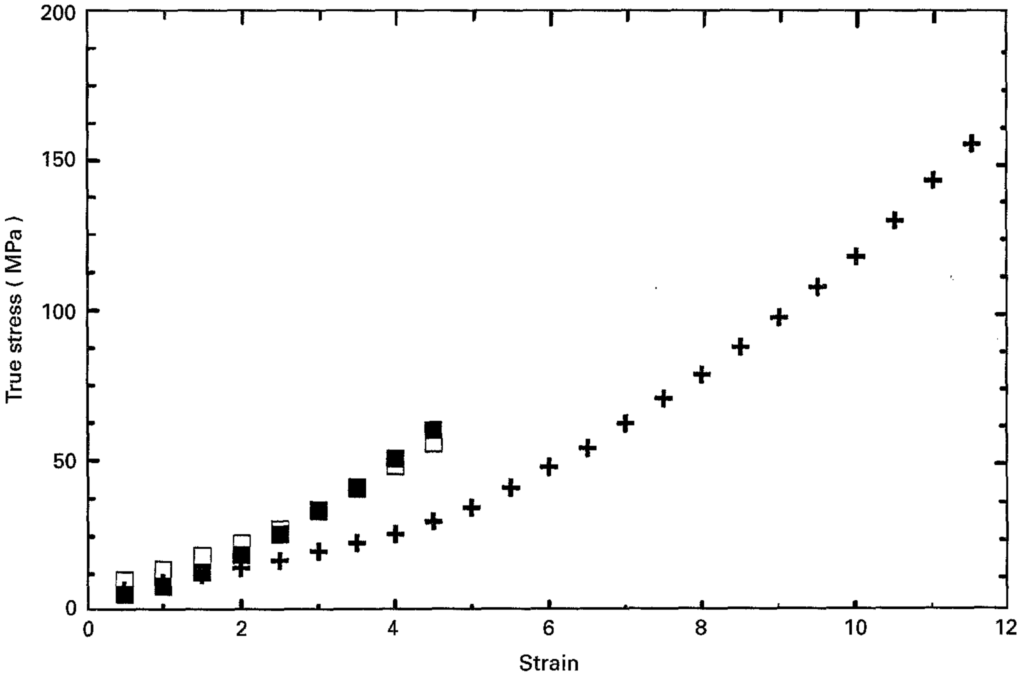

Figure 7 True stress–strain curves of high molecular weight syndiotactic polypropylene with different initial morphologies drawn at 5 mm min^{-1} and 110 °C. ■, S3-Q; □, S3-S and +, S3-C.

The modulus data, shown in Fig. 9 for SPP only, can be readily understood in terms of the different crystallinities and loss factor behaviour. The rapid fall in modulus, observed at room temperature in both the drawn and isotropic quenched samples coincides with the glass relaxation, and this is likely to be critical in samples of low crystallinity. The cast films which have a higher crystallinity, reflected in the lower intensity of the β relaxation, show a correspondingly lower sensitivity to temperature and there is a smaller decrease in the modulus. At 20 °C the maximum achieved modulus of drawn cast films is ~ 4 GPa (at a frequency of 10 Hz), while the modulus of the quenched samples is ~ 2.5 GPa. At − 80 °C, well below the β relaxation, these values rise to about 6.5 and 5.5 GPa, respectively, and there is little difference between the materials.

3.3.2. Room temperature modulus

The dynamic modulus (at 10 Hz and 20 °C) of drawn samples of SPP was, to a first approximation, found to

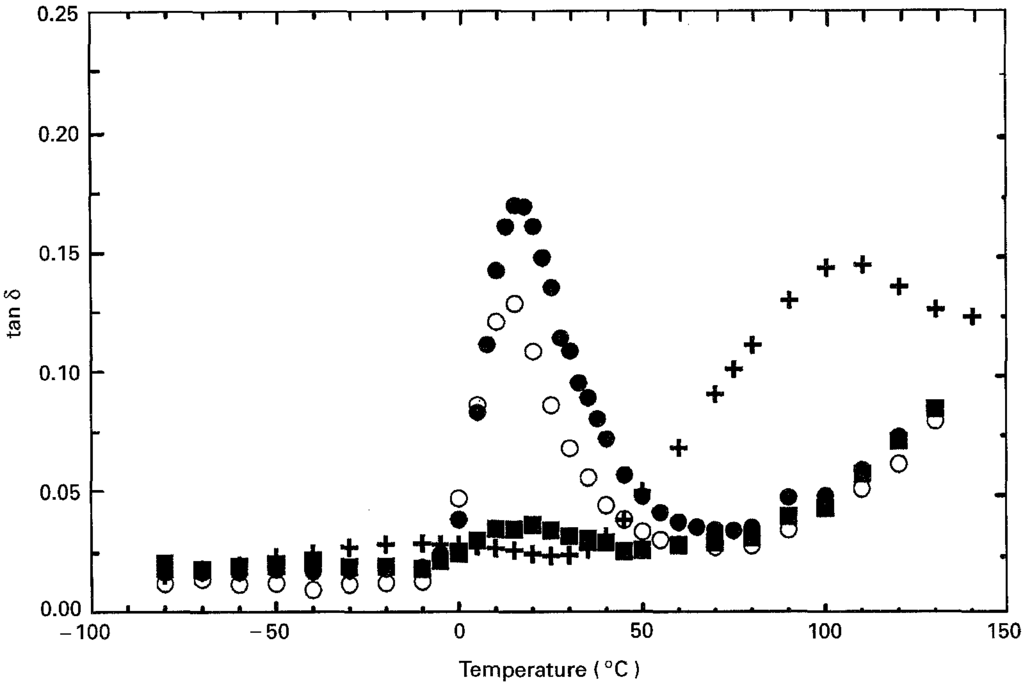

Figure 8 Temperature dependence of the dynamic loss factor in samples of syndiotactic and isotactic polypropylenes. ●, S2-Q; ○, S2-S; □, S3-C and +, I2-Q.

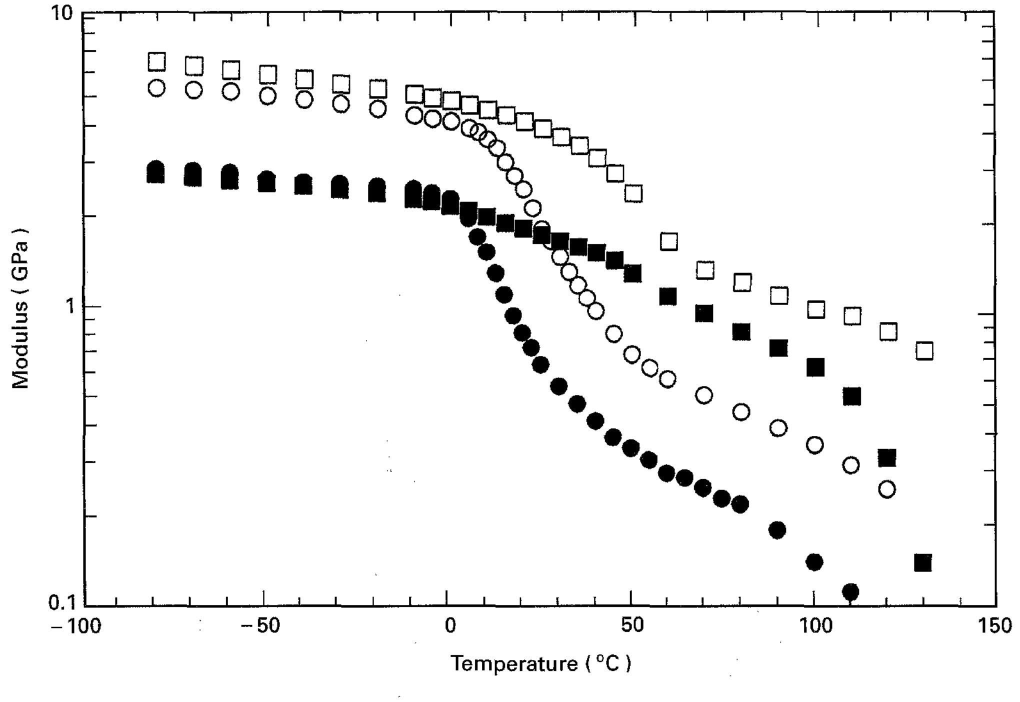

Figure 9 Temperature dependence of the dynamic modulus of isotropic and drawn samples of syndiotactic polypropylene. ●, S2-Q, $\lambda = 1$; ○, S2-Q, $\lambda = 5.25$; ■, S3-C, $\lambda = 1$ and □, S3-C, $\lambda = 10.5$.

depend only on the draw ratio (Fig. 10), as has been shown to hold previously for polyethylene and isotactic polypropylene [12]. Factors such as the drawing temperature, drawing speed, molecular weight and initial morphology were all shown to have an insignificant impact on the modulus. The maximum modulus, shown by cast film of draw ratio 11, is ~ 4 GPa. This compares with typical values of ~ 10 GPa shown by comparable isotactic material. In comparisons with isotactic material of comparable molecular weight and draw ratio, SPP always shows a considerably lower modulus.

4. Discussion

The complex stress–strain behaviour of SPP shown in Figs 1 and 2 can be explained in terms of the competition between the relative changes in the flow stress and the strength. Failure of this material at low extension arises because the rapid increase in the flow stress with

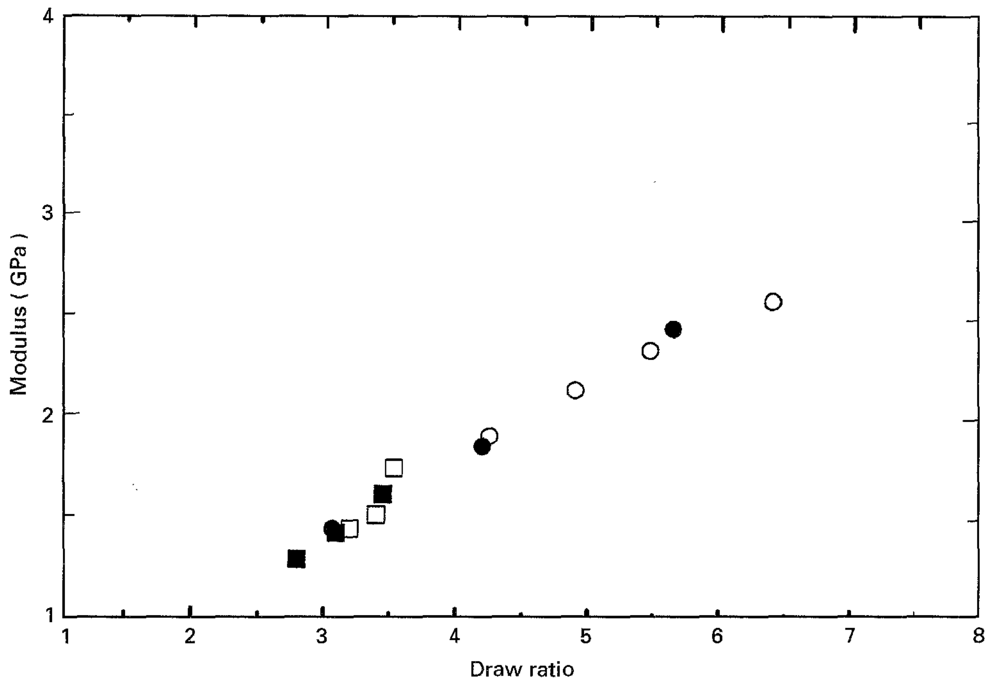

Figure 10 Relation between the modulus and draw ratio in different syndiotactic polypropylenes drawn at 110 °C and a crosshead speed of 5 mm min^{-1}. □, S3-S; ■, S3-Q; ○, S2-S and ●, S2-Q.

strain and the lack of development in the intrinsic strength means that the failure stress envelope is encountered at a relatively low draw ratio.

The stress–strain curves for SPP, shown in Fig. 3, are very characteristic of rubber-like behaviour, as is the high recovery shown by these samples after removal of the drawing stress. The crosslinks in this material, however, are not chemical in nature but instead probably arise from a combination of physical entanglements and crystallites. Consequently, the rate at which the stress develops with strain is expected to depend on both the number of crystallites and the molecular entanglement density. The lack of an effective α process seriously restricts slippage of chains through the crystals in response to the imposed macroscopic deformation, and therefore the crystals behave as permanent junction points. This anchoring of the chains means that the stress in the material will rise as the network is stretched until molecular rupture occurs. The strain hardening is not influenced significantly by changes in the crystallinity, as is shown in Fig. 3. This is probably because these changes do not necessarily equate to changes in the number of crystals. The strain hardening is, however, sensitive to molecular weight. This is attributed to changes in the entanglement density, a view supported by the much lower strain hardening of the gel cast material. It is interesting to contrast the drawing behaviour with that of IPP which does have a strong α process allowing crystal slip to relieve the build up of stress.

Reducing the entanglement density by using lower molecular weight material is not profitable because the basic strength is also reduced to too large an extent. The most effective way of reducing the entanglement density, and thereby the strain hardening, without drastically affecting the strength is by gel casting. However, satisfactory gels can only be obtained for high molecular weight material. The gel casting approach does produce a second benefit. Use of a high molecular weight results in a strength which permits operation at elevated temperatures, approaching the crystal melting point where the crystals no longer act to lock in the network.

Fig. 10 shows that the modulus of SPP depends, to a very good approximation, only on the draw ratio achieved and therefore it is essential to attain a high draw ratio. However, even when a high draw ratio is achieved, the modulus is considerably lower than in IPP of comparable molecular weight. This is believed to be due to the lower crystal modulus of SPP [13].

5. Conclusions

Because the modulus of SPP depends primarily on draw ratio, effective drawing is essential. However, the drawability of this material is significantly less than that of its isotactic counterpart because of the absence of an effective crystal slip process. As a consequence the crystals act as permanent crosslinks and the drawing stress rises rapidly with extension until the failure stress is encountered. Surprisingly, the degree of crystallinity does not affect the strain hardening behaviour, probably because the number of crystallites remains unchanged. A second contribution to the strain hardening, arising from the entanglement density, can be controlled by using different molecular weight grades. A reduction in entanglement density is most effectively achieved by gel casting, but only successfully if high molecular weight material is used. The highest final draw ratio of 14 was achieved by drawing gel cast high molecular weight material at elevated temperatures. Even at these high draw ratios the modulus of SPP is considerably lower than in comparable IPP. This is attributed to the low crystal modulus of SPP.

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