

Effect of Orientation on Melting of Isotactic Polypropylene

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SYNOPSIS

The effect of uniaxial orientation on the melting of a commercial grade of isotactic polypropylene has been investigated by thermal analytical techniques. Orientation progressively shifts the onset of and the observed melting point to higher temperatures and increases the peak heights of differential scanning calorimetric (DSC) endotherms. The increase in melting point with orientation is attributed to the increase in configurational entropy of the extended melt into which the polymer crystallites melt.

INTRODUCTION

The thermal and mechanical properties of isotactic polypropylene (iPP), like those of many other semicrystalline polymers, are dependent on thermal history, orientation, and morphology.¹⁻³ Orientation alters the crystalline morphology, increases the modulus and the observed melting point, and decreases the elongation at break.^{4,5}

The morphology of iPP has been investigated by electron microscopy and wide- and small-angle X-ray scattering.⁶ The crystallinity of drawn iPP samples has also been investigated by Liu et al.⁷ and the melting behavior of melt and solution-crystallized samples studied.^{8,9} In this paper, the effect of orientation on the melting point of iPP is reported.

EXPERIMENTAL

Commercial iPP samples (Shell PP, KM 6001N) were supplied by Metal Box Plc, Wantage, U.K. The samples were about 47% crystalline with an optical melting point of 449 K. The weight and number average molecular weights were 103,000 and 22,000, respectively. Wide- and small-angle X-ray scattering studies show that the crystal unit cell is monoclinic. The spherulite diameter was about 0.15 mm, and the tacticity as determined by NMR spectroscopy was 98%.⁶

Drawing Procedure

PP granules were compression-molded at 473 K using a hydraulic press. Molded samples were quenched in ice water, and dumbbell-shaped specimens with 5 mm-distance ink marks along their gauge length were cut from the molded PP sheets and drawn uniaxially at 333 K at a draw rate of 5 mm/min using an Instron tensile tester. Drawing was carried out in a constant temperature room maintained at 295 K. An Instron environmental chamber provided an effective temperature range from 198 to 473 K, the system being cooled by the injection of liquid carbon dioxide into the chamber and heated when required.

DSC Measurement

The thermal properties of oriented samples were measured using the DSC-2 interfaced to an Apple 11GS microcomputer acting as a data station. The thermal response of the calorimeter was calibrated with the heat of fusion of ultrapure indium, 28.4 J/g, and the temperature from the melting points of indium, zinc, and tin. Experiments were conducted under a nitrogen atmosphere to prevent degradation.

The melting points of samples oriented to different draw ratios were measured at different heating rates from 5 to 20 K/min, while correction for thermal lag was achieved by zero heating rate extrapolation. As many runs as desired could be carried out on a single sample and an average melting temperature determined. The melting temperature was taken as the point corresponding to the last trace

Table I DSC Analysis of Oriented Polymer Samples

Ref. No.	Weight (mg)	Draw Ratio (λ)	T_m (K)	ΔH_f (J/g)
SH0	2.5	0	446	56.7
SH1	2.5	3	448.3	66.4
SH2	2.7	5	449.6	72.4
SH3	3.1	8	450.0	80.0
SH4	3.5	11	456.0	84.1
SH5	2.8	12	456.1	85.1
SH6	3.2	16	457.0	87.1
SH7	2.6	18	457.1	90.5
SH8	2.9	19	457.4	94.3
SH9	3.4	19	458.0	100.0

of crystallinity on the DSC trace. This is an established procedure for determining the T_m .^{10,11}

RESULTS AND DISCUSSION

The DSC analysis of oriented samples is summarized in Table I, while the scans of oriented and unoriented iPP samples and the effect of draw ratio on the melting endotherm is shown in Figure 1. The DSC melting endotherm and the temperature range over which melting occurred were dependent on the draw ratio. As the draw ratio increased, the endotherm shifted to higher temperatures and the peak height increased and became sharper (see Fig. 2), and, consequently, melting occurred at progressively higher temperatures. Nicolas et al.¹² pointed out that the relative heights of the melting endotherms could be used as an indirect measure of orientation. A constant T_m value of 458 K was obtained, corresponding to the maximum draw ratio obtained ($\lambda = 19$).

The melting point of drawn samples increased progressively with the draw ratio initially followed by a sharp rise (Fig. 3), while the heat of fusion increased in a rather gradual manner. The difference between the heat of fusion of oriented and unoriented samples was about 20 ± 4 J/g. For samples with identical thermal history, however, no significant change in the degree of crystallinity was observed.

Effect of Orientation on Melting Point

The increased melting point of deformed iPP samples is associated with the increase in entropy of the amorphous regions and the decrease with lower

heating rates as a result of the relaxation of the deformed melt increasing with time. Based on Flory's treatment of elasticity, Krigbaum et al.¹³ have derived the relationship

$$1/T_m = 1/T_m^0 - R/N\Delta H_f[(6N/\pi)^{1/2}\lambda - (\lambda^2/2 + 1/\lambda)] \quad (1)$$

which relates the equilibrium melting point, T_m^0 , at λ , and T_m^0 at $\lambda = 1$, to the heat of fusion, ΔH_f , and the number of statistical segments between entanglements. This equation is, however, inappropriate to describe the melting point of deformed samples. The increased melting point of deformed samples results from the decrease in configurational entropy on melting the crystals into an oriented melt rather than into a randomly organized melt. This decrease in configurational entropy is given from classical rubber elasticity theory¹⁴ as

$$-\Delta S_c = R/2n(\lambda^2 + 2/\lambda - 3) \quad (2)$$

where n is the base monomer units between entanglements and λ is the draw ratio. The melting has been related to the number of repeat units, r , in the thickness of the crystal for lamellar crystals of a monodisperse polymer, such that

$$T_m = T_m^0[1 - 2RT \ln(r)/r\Delta H_f - 2\sigma\Delta H_f] \quad (3)$$

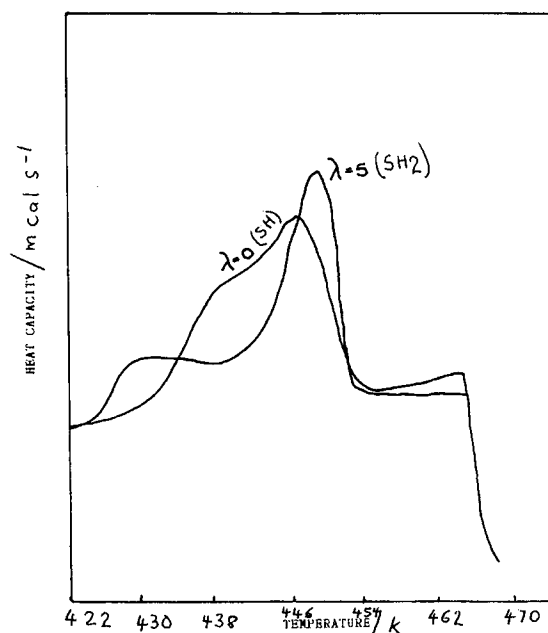


Figure 1 Effect of draw ratio on melting endotherm.

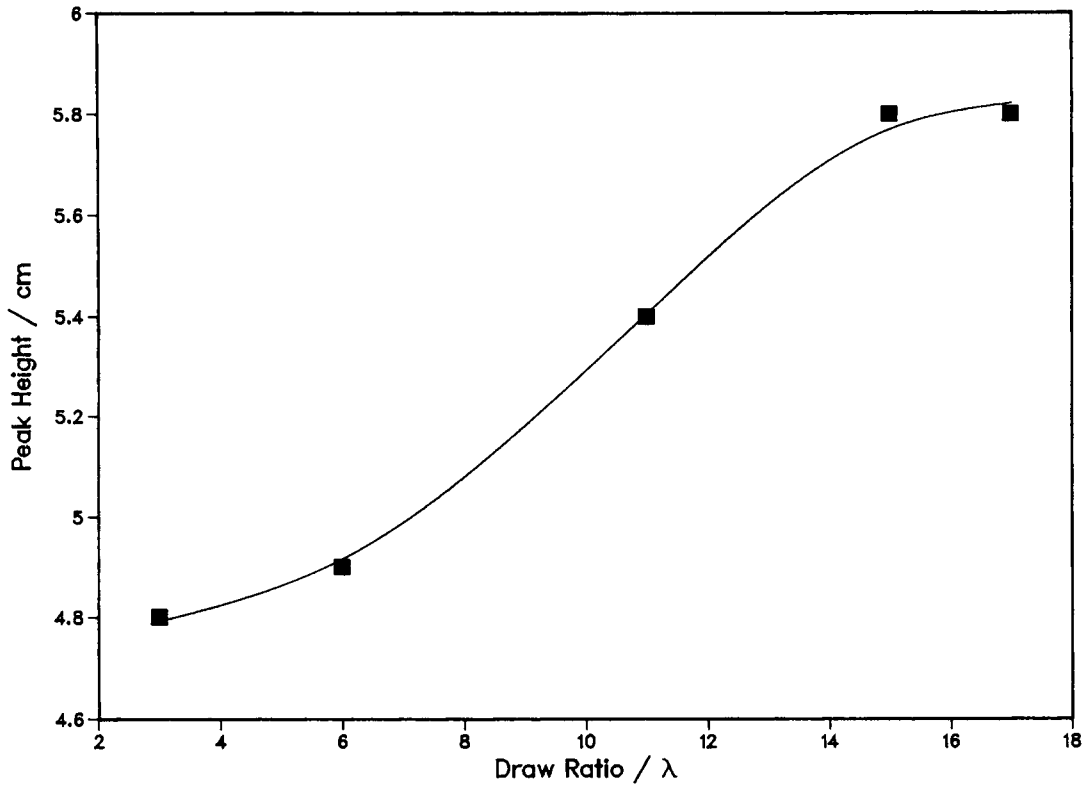


Figure 2 Peak height against draw ratio.

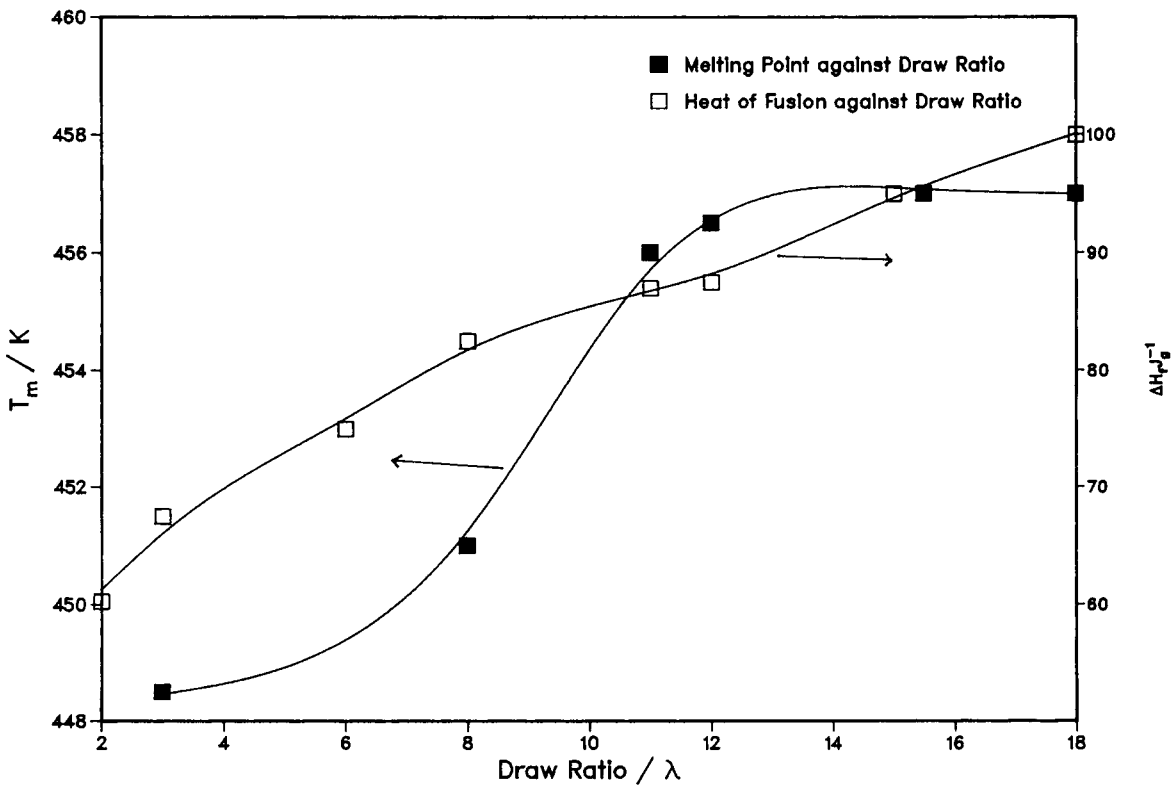


Figure 3 Melting point against draw ratio.

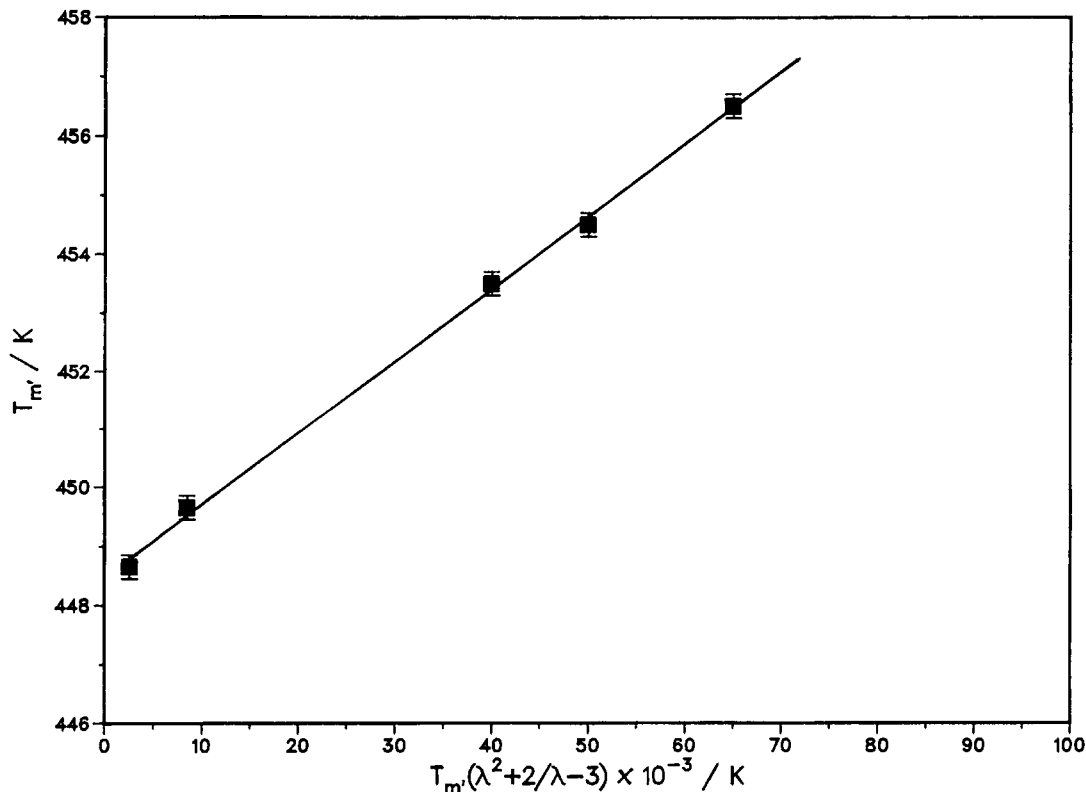


Figure 4 Melting point against configurational entropy.

where σ is the lateral surface energy. The entropy term in eq. (2) has been incorporated into eq. (3) to give

$$T'_m = T_m^0 [T'_m \Delta S_c / r \Delta H_f + 1 - 2RT'_m \ln(r) r \Delta H_f - 2\sigma / n \Delta H_f] \quad (4)$$

Equation (4) is the expression for the melting point of an oriented material.

Redefining T_m for $\lambda = 1$ and T'_m for all other values of λ , then

$$T'_m = T_m^0 (RT_m^0 T'_m / 2nr \Delta H_f) (\lambda^2 + 2/\lambda - 3) \quad (5)$$

or

$$1/T'_m - 1/T_m^0 = (RT_m^0 / 2nr \Delta H_f) (\lambda^2 + 2/\lambda - 3) \quad (6)$$

In the derivation of eq. (6), the assumption was made that only the amorphous regions are oriented with a draw ratio identical to the macroscopic draw ratio. Equations (5) and (6) were applied to the melting data presented in Figure 3.

The plot of T'_m against $T'_m (\lambda^2 + 2/\lambda - 3)$ is shown in Figure 4. The intercept, T_m , from the plot, that is, 452 K, is within the range of the T_m for undeformed samples, which is 449 K. The slope of the plot, 11×10^{-5} , is equal to $RT_m^0 / 2\Delta H_f nr$. Using the literature¹⁵ values of T_m^0 of 460.7 K and a ΔH_f value of 2.31 kJ/mol for iPP, an nr value of between 170 and 190 was obtained.

The ratio, n/r , is equal to the ratio of crystalline to amorphous sequences and, consequently, to the crystalline/amorphous content in the polymer. The observed heat of fusion of 100 ± 10 J/g fixes this ratio as 3 : 2, and this is consistent with the density crystallinity of about 50–60%. This implies that n is between 16 and 19, and an r value between 7 and 10 is expected from crystals formed under this condition. Accordingly, the model of deformable amorphous regions constrained by nondeformable crystallites accounts for the observed melting-point dependence on the draw ratio.

CONCLUSION

The relative degree of orientation in iPP can be determined to a high degree of accuracy using DSC. If

the samples have identical thermal history, no appreciable change in the degree of crystallinity is expected. It will remain virtually unchanged with the draw ratio.

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