

Ultradrawing and Crystallization of Isotactic Polystyrene and Blends with Atactic Polystyrene

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Synopsis

Pure isotactic polystyrene (iPS, $M_w = 8.89 \times 10^4$, $M_w/M_n = 4.89$) and its blends with an atactic polystyrene (aPS, $M_w = 3.9 \times 10^5$, $M_w/M_n < 1.13$) were subjected to draw by solid state coextrusion at 127°C within polyethylene. The content of amorphous iPS in these blends was varied from 100 to 24.4 wt %. The extent of draw-induced crystallization was found to depend on the draw ratio and on iPS concentration. The blend with 24.4% iPS was coextruded in two stages. The highest effective draw ratio (EDR) was 7.6 and 13.7 for one- and two-stage draw, respectively. The highest crystallinity of 33.2% was obtained for pure iPS at the maximum EDR of 7.6. Considerable crystallinity was induced in blends, requiring successively higher draw ratio to reach similar crystallinity with increased aPS content. The tensile modulus increased from 1.5 to 3.2 GPa, independent of iPS concentration. Thermal shrinkage results indicate that the elastic recovery of draw in the blends is near quantitative for an EDR < 8. For pure iPS, extrudate elastic recovery was dramatically altered by the draw-induced crystallinity.

INTRODUCTION

The crystallization of iPS and its blends has been previously studied as a function of annealing, solvent treatment, and draw.¹⁻⁵ Solid-state coextrusion within polyethylene^{6,7} has been shown to ultradraw aPS⁸ and to crystallize PS of 60% isotactic content.⁹ Crystallinity increases with EDR on coextrusion and is associated with enhancement of tensile properties.

EXPERIMENTAL

A polystyrene of nominal 100% isotactic content was obtained from Polymer Laboratory, Ltd., U.K. ($M_w = 8.89 \times 10^4$, $M_w/M_n = 4.89$). The isotacticity of this polymer was found by C¹³ NMR to be 98% isotactic dyads.¹⁰ Atactic narrow-distribution polystyrene (aPS, $M_w = 3.9 \times 10^5$, $M_w/M_n < 1.13$) was purchased from Polyscience Co., Inc., Warrington, PA.

Intimate binary blends with weight fractions iPS of 0.24, 0.50, and 0.73 were prepared by freeze drying from dilute benzene solutions. The powder obtained was dried *in vacuo* at 80°C for two days. For coextrusion, blends were then mold pressed into films of 0.6 mm thickness at 250°C and 20,000 psi. This temperature is higher than the melting point (T_m) of iPS and lower than for significant degradation.^{11,12} These films were subsequently quenched in ice water to avoid crystallization.

High-density polyethylene billets were used as coextrudate. The sandwich geometry for coextrusion draw has been described.⁹ In the two-stage process, films of an initial EDR ~ 3.5 were used. The EDR was measured by the ink

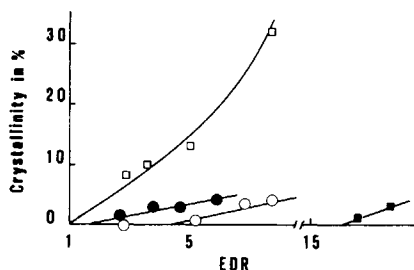


Fig. 1. Crystallinity as a function of EDR of iPS and iPS/aPS blends obtained by solid-state coextrusion at 127°C: (□) 100% iPS; (●) 73.6% iPS; (○) 49.6% iPS; (■) 24.4% iPS.

marker displacement on the sample after coextrusion. Thermal analysis (DSC 1-B at 20°C/min), elastic shrinkage, birefringence, and tensile tests were also carried out on the drawn samples by the methods given in ref. 9. The percent crystallinity was calculated from the area of melting peak using the known heat of fusion of Indium as a standard and taking the enthalpy of fusion of 100% crystalline iPS as 19.9 cal/g.¹² The T_g of these samples were also measured by DSC. Drawing of iPS by solid-state coextrusion within polyethylene leads to crystallization.⁹ Crystallization on solid-state coextrusion in highly isotactic iPS and in its blends with aPS has been investigated in this study. A coextrusion temperature of 127°C was chosen to ease processing and to minimize cold crystallization of iPS. This condition is also nearly equivalent to our prior coextrusion drawing study of atactic polystyrene.⁸

RESULTS AND DISCUSSION

The extent of draw, in terms of EDR, achieved for iPS and its blends at 127°C is shown in Figure 1. The crystallinity of iPS increased with both EDR and iPS concentration with the highest, 33.2%, obtained at an EDR of 7.6 for the pure iPS. Less crystallinity was achieved in blends, with higher EDRs required to attain equivalent crystallinity at even lower iPS content. The crystallinity of

TABLE I
Crystallinity Increase on Coextrusion Draw in an Isotactic Polystyrene and in its Blends with an Atactic Polystyrene

Composition, %	EDR	Normalized crystallinity, %	Crystallinity, %
100 (iPS)	7.6	33.2	33.2
	5.0	13.2	13.2
	3.6	10.0	10.0
	2.9	8.1	8.1
73.6 (iPS)	5.9	5.8	4.2
	4.6	3.2	2.3
	3.8	3.6	2.7
	2.7	1.6	1.2
49.6 (iPS)	7.7	8.2	4.1
	6.8	7.4	3.7
	5.2	0.9	0.5
	2.8	0	0

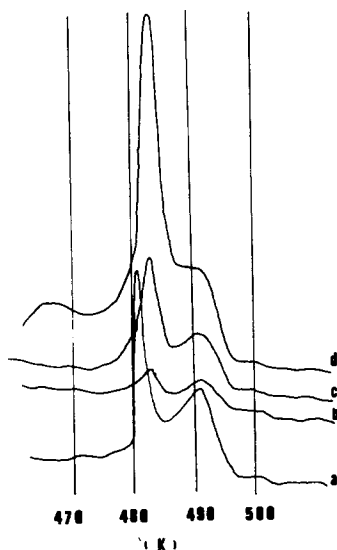


Fig. 2. Thermogram of extruded iPS/aPS (73.6/26.4; EDR 5.9) and its change during annealing at 127°C for different period: (a) first run; (b) annealing for 10 min; (c) 20 min; (d) 3.5 hr.

iPS in blends at the same EDR thus decreased with decreasing concentration (see Table I).

Double melting peaks were observed for the drawn iPS blends. These melting points were 222 and 208°C, close to literature values.¹³ Lemstra³ and Overberg^{14,15} suggest that this double melting involves a partial reorganization or recrystallization during heating.

The draw-induced crystallization was compared here with that produced by thermal treatment. This was done by heating samples in the DSC to about 230°C, above the highest melting point (T_m), followed by quick cooling to 177°C and annealing for different times. The area under the lower T_m increased with this annealing faster than that of the higher (see Fig. 2). In these experiments, the area under the higher T_m in the first run was always larger. Thus, draw- and thermal-induced crystallizations of iPS are clearly different. Also, the crystals induced by draw at 127°C were less stable, i.e., exhibited a lower T_m than that produced by annealing at the higher temperature, i.e., 177°C. For all compositions, the higher T_m changed with iPS content but not with EDR (see Table II). The T_m of crystals induced in pure iPS on coextrusions at 127°C gave the highest of all extrudate melting points. The blends with 25% iPS did not crystallize on single-stage coextrusion and had to be drawn to a EDR > 16 by a two-stage coextrusion before crystallization occurred.

TABLE II
Change in Higher of the Two Melting Points with iPS Concentration in Blends with aPS^a

iPS % in aPS	Higher T_m , °C
100	222
73.6	218
49.6	217
24.4	216

^a Measured by DSC I-B at a heating rate of 20°C/min.

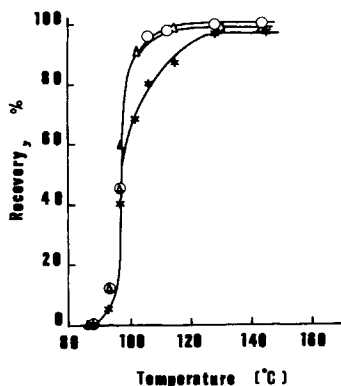


Fig. 3. Elastic recovery as a function of shrinkage temperature for iPS/aPS blends drawn at 127°C at EDR of: (O) 2.7; (Δ) 6.0; (*) 7.7.

The glass transition temperature, T_g , of these blends measured by DSC at 20°C/min was 96.9°C and apparently did not change with the composition and EDR, although annealing during the temperature programming to reach T_g was not excluded. For the extrudate of pure iPS at EDR > 5, T_g was not readily observed.

The elastic recovery ratio on rapid heating of thin sections in a nonsolvent is used to estimate molecular draw. It is defined as:

$$R = \frac{L_T - L_S}{L_T - L_0}$$

where L_0 and L_T are the lengths of the PS film before and after coextrusion, respectively, and L_S is the length after subsequent elastic recovery. Thermal shrinkage indicated that all blends with EDR < 8 shrink abruptly above T_g for PS and that at 140°C quantitative maximum recovery is observed (see Fig. 3). The recovery measured here is consistent with that of amorphous polymer. The elastic recovery of these blends is thus equivalent to that for pure aPS,^{8,9} i.e., for samples exposed to lower EDR, a high percent recovery is obtained. This is due to the insignificant crystallinity in these blends. On solid-state coextrusion, pure iPS develops significant crystallinity. This leads to a markedly different elastic

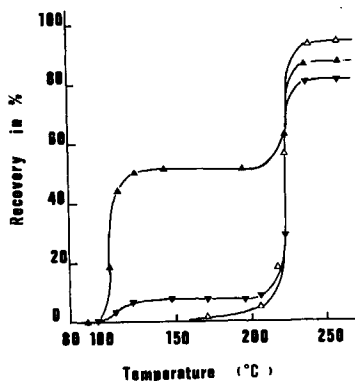


Fig. 4. Elastic recovery as a function of shrinkage temperature for iPS drawn at 127°C at EDR of: (▲) 5.0; (▼) 3.6; (Δ) 7.6.

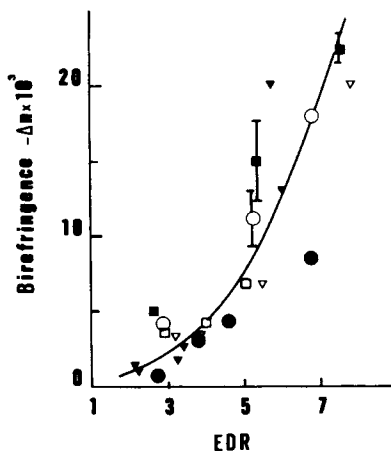


Fig. 5. Molecular draw ratio as a function of EDR for different compositions of blends, symbols as in Fig. 1.

recovery (see Fig. 4). On heating the crystalline samples, shrinkage is a distinct two-step process: the first stage above T_g , the second above T_m . The marked relaxation above T_g suggests an absence of a crystal continuum, consistent with only a modest increase in tensile modulus after coextrusion drawing.

The extent of deformation in solid state coextrusion can be expressed by a molecular draw ratio (MDR) as previously defined:¹⁵

$$MDR = \frac{L_T - L_S}{L_0} + 1$$

Figure 5 shows that efficiency of draw on coextrusion, i.e., $MDR/EDR \sim 99\%$ for all blends, independent of induced crystallinity and composition. This efficient segmental orientation and chain extensions were achieved by the action of basically extensional forces on the network of entangled polystyrene chains.

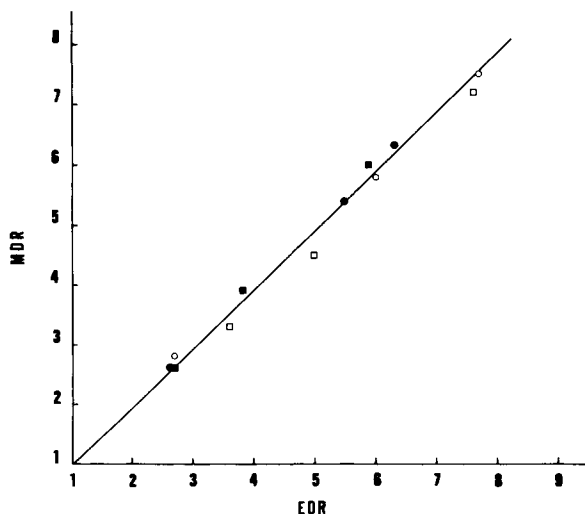


Fig. 6. Birefringence as a function of draw ratio, symbols as in Figure 1 and: (\blacktriangledown) 60% iPS extruded at 160°C; (∇) at 124°C obtained in previous work.⁹

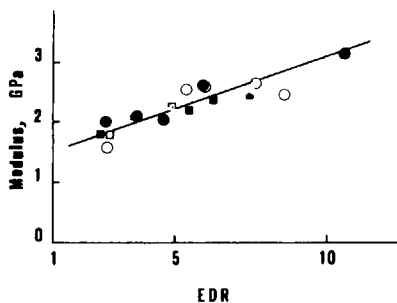


Fig. 7. Modulus as a function of EDR, symbols as in Fig. 1.

Birefringence measurements provide a combined measure for both amorphous and crystal orientations, with detailed explanations being complex.^{4,5} On drawing, birefringence for PS becomes negative and increases in absolute magnitude with EDR (see Fig. 6). This is because the pendant phenyl groups are basically transverse to the PS chain. The results are also consistent with an efficient draw for all blends. The dependence of birefringence on EDR is similar to that in our previous work⁹ (see Fig. 6).

The increase of tensile modulus with EDR is displayed in Figure 7. This is associated with orientations in the tensile direction and the increase of crystallinity on drawing during coextrusion. For the 25% iPS, i.e., the lowest concentration blend, for EDR < 7, no crystals were found, yet the tensile modulus was enhanced. Good agreement is found (see Table III) between measured moduli and a simple two-phase model for crystalline and amorphous components.

TABLE III
Comparison of Measured and Calculated Tensile Moduli for Semicrystalline Isotactic Polystyrene

iPS/aPS	EDR	E_{measured} (GPa)	$E_{\text{calcd.}}$ (GPa) ^a
100/0	2.9	1.8	2.0
	3.6	2.4	2.1
	5.0	2.3	2.1
	7.6		2.6
73.6/26.4	2.7	2.0	1.9
	3.8	2.1	1.9
	4.6	2.0	1.9
	5.9	2.6	2.0
49.6/50.4	2.8	1.7	1.9
	5.2	1.9	1.9
	6.8	2.2	1.9
	7.7	1.8	2.0
24.4/75.6	2.6	1.8	1.9
	5.5	2.2	1.9
	6.3	2.4	1.9

^a The modulus E of a semicrystallized polymer can be estimated by the equation:¹⁷ $1/E = V_a/E_a + V_c/E_c$. V_a, V_c = volume fraction of amorphous and crystallized part of the sample, respectively. E_a , measured in previous work is 1.9 GPa.⁹ $E_c = 10.9$ GPa.¹⁶

CONCLUSION

A 98% isotactic dyad polystyrene and its intimate blends with an atactic polystyrene have been drawn at 127°C by coextrusion in the amorphous state within billets of high-density polyethylene. The highest EDR attained was 7.6 and 13.7 for one- and two-stage coextrusions, respectively. The draw-induced crystallinity of iPS increases with both effective draw ratio and iPS concentration. The associated orientation was measured by birefringence. Its high and negative values are consistent with those in our previous article on only atactic polystyrene involving⁹ coextrusion in one stage. Two melting peaks, ~208 and ~222°C, for drawn iPS were observed by thermal analysis. No change of T_g with EDR was found by DSC. The maximum crystallinity for the maximum one-stage EDR of 7.6 was 33.2% for the pure iPS. The tensile modulus increased with EDR for all blends. The thermal elastic recovery and mechanical properties are considered in terms of the amount and type of crystallization induced on coextrusion draw as a measure of molecular draw and coextrusion draw efficiency.

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References

1. E. Martuseelli, G. Demma, E. Drioli, L. Nicolais, S. Spina, H. B. Hopfenberg, and V. T. Stannett, *Polymer*, **20**, 571 (1979).
2. H. D. Kieth and F. J. Padden, *J. Appl. Phys.*, **25**, 1286 (1964).
3. P. J. Lemstra, T. Kooistra, and G. Challa, *J. Polym. Sci. Part A*, **10**, 823 (1972).
4. W. R. Krigbaum and S. Maruno, *J. Polym. Sci. Part A-2*, **6**, 1733 (1968).
5. W. R. Krigbaum and T. Taga, *J. Polym. Sci. Polym. Phys. Ed.*, **17**, 393 (1979).
6. W. T. Mead and R. S. Porter, *Inter. J. Polym. Mater.*, **7**, 29 (1979).
7. W. T. Mead and R. S. Porter, *J. Appl. Polym. Sci.*, **22**, 3249 (1978).
8. A. E. Zachariades, E. S. Sherman, and R. S. Porter, *J. Appl. Polym. Sci.*, **24**, 2137 (1979).
9. B. Appelt and R. S. Porter, submitted.
10. L. F. Johnson, F. Heatley, and F. A. Bovey, *Macromolecules*, **3**, 175 (1970).
11. K. Arisawa and R. S. Porter, *J. Appl. Polym. Sci.*, **14**, 879 (1970).
12. J. Bandrup and E. H. Immergut, *Polymer Handbook*, 2nd ed., Wiley, New York, 1975, pp. v-60.
13. N. Overberg, H. Berhmans, and G. Smets, *J. Polym. Sci. Part C*, **58**, 237 (1972).
14. N. Overberg, H. Berhmans, and H. Regnaers, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 1177 (1976).
15. H. Berhmans and N. Overbergh, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 1757 (1977).
16. I. Sakurada, T. Ito, and K. Kanamae, *J. Polym. Sci., C*, **15**, 75 (1967).
17. N. J. Capiati and R. S. Porter, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 1427 (1977).

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