Ultra-drawing of polystyrene by solid-state coextrusions: molecular weight dependence of properties and processing

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Solid-state coextrusion within polyethylene at 130° C has been shown to produce ultra-drawn polystyrene (PS). Six molecular weights of atactic PS of narrow molecular weight range were ultra-drawn. A strong influence of molecular weight and extrusion draw radio (EDR) on the efficiency of coextrusion was observed. The highest EDR of 27 and orientation achieved exceed values so far reported in the literature for PS. Bi-refringence reached $\Delta n = -4.2 \times 10^{-2}$, corresponding to 44% orientation, and the efficiency of chain extension as measured by elastic recovery was almost 100 %. The results are consistent with an entanglement deformation model for PS which facilitates molecular extension and concomitant orientation. Draw deformation of markers placed on the PS films prior to co-extrusion indicate the process is an effective elongational flow. The glass transition temperature and molecular weight did not change following draw.

1. Introduction

The ultra-drawing of many semicrystalline thermo-plastics, especially of polyethylene, has received considerable attention [1–3]. It has become possible to obtain semicrystalline thermoplastics of high orientation and enhanced tensile properties at high draw. For this purpose, several methods have been developed. The development of a solid-state coextrusion technique [4] has led to an efficient and general drawing process [5].

Ultra-drawing amorphous polymers such as polystyrene (PS) has so far received comparatively little attention even though they are some of the most widely used polymers. Drawing of polystyrene at temperatures just above the glass transition temperature, T_g, can produce high orientation [6–9]. Recently, it has been shown that solid-state coextrusion of amorphous polystyrene with high-density polyethylene [9], between T_g (PS) and 130° C, can produce highly orientated films. These films have the highest draw ratios reported for PS and exhibit quantitative recovery upon rapid thermal shrinkage.

Until recently, little attention has been paid to the influence of molecular weight on the drawing coextrusion process [10–13]. The limitations of this process due to the temperature and the nature of the billet coextrudate have been elucidated [9]. It is now of interest to investigate the molecular requirements for an efficient drawing (co-extrusion) process. A lower limit of molecular weight may be expected, below which chains will slip past each other resulting in inefficient orientation of chains. An upper limit of molecular weight may be reached when the apparent viscosity of the PS increases to a point where either no further deformation or fracture occurs. The limits may likely be modified by test conditions. For an investigation of this kind, polystyrene is an ideal polymer to test because of the wide variety of molecular weight standards of narrow mocelular-weight distributions (MWD) that are available.

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Previous studies on polyethylene [10–13] were always performed on samples of broad MWD.

2. Experimental procedure
2.1. Materials and extrusion
Polystyrenes with narrow MWD were obtained from Pressure Chemical Co., Pittsburgh (PCC) and from Toyo Soda Manufacturing Ltd, Tokyo (TSM). The molecular weights and corresponding polydispersities are listed in Table I.

Sample preparation was essentially similar to the method described earlier [9]. The polystyrenes were first compacted at room temperature in the barrel of an Instron rheometer and then mould-pressed into films of about 0.6 mm thickness at 180° C. The films were held at 180° C and 20 000 psi for ten minutes before quenching in ambient water.

Commercial high-density polyethylene rods, "Ultra Ethylux" from Westlake Plastics, Pittsburgh, were used as the coextrudate. The 3/8 inch diameter rods were split longitudinally with a slit saw and the plane surfaces were then grooved to accommodate the polystyrene films. The PS films were inserted into the split billets and press-fitted into the barrel of an Instron rheometer. The billet assemblies were then pushed through conical brass

dies of 20° included entrance angle at 127° C. The die draw ratios (DDR) (ratio of the cross-sectional areas of die inlet to die exit) were varied from 3.8 to 16.0. To achieve maximum draw, pre-extruded films were re-extruded with new polyethylene billets. In the two-stage process, films of an initial extrusion draw ratio (EDR) of 1.8 to 3.5 were used, whereas in the three-stage process, films pre-drawn to an EDR of 7 were employed. The EDR was determined from the ratio of the displacements of ink markers on the films before extrusion, L_0, and after extrusion, L_E, i.e. EDR = L_E/L_0. The marker displacement indicates that the deformation process is an effective elongational flow.

2.2. Thermal analysis
Differential scanning calorimetry (DSC) of extrudates was carried out in a Perkin–Elmer DSC-2 machine. The sample weights were between 10 and 12 mg, the heating rate was 10° C min^{-1} and the sensitivity was 2 mcal sec^{-1}.

Thermal shrinkage experiments were performed by floating 10 mm long strips of film in a glycerol bath. After reaching their equilibrium length, the films were cooled to room temperature and the dimensions redetermined. Shrinkage, S, is defined

T A B L E I Molecular weights and polydispersities for the ultra-drawing of polystyrenes[*] by solid-state coextrusion at 130° C.

Polystyrene sample	M_w before drawing ($\times 10^5$)	EDR	M_w after drawing ($\times 10^5$)	M_w/M_n
PCC	18	1	15.0	2.2
		5	15.9	1.95
		6	16.3	2.18
		7	15.7	2.03
TSM	12.6	1	11.7	2.0
		10.6	12.3	1.98
		19	11.4	1.83
PCC	6.70	1	6.23	1.77
		8.08	6.0	1.98
		18.6	6.47	1.76
PCC	6.0	1	5.68	1.19
		4	4.87	1.39
		12.2	4.43	1.44
		27	5.13	1.37
PCC	3.90	1	3.98	1.44
		13.9	3.80	1.44
		22.4	3.93	1.37
TSM	1.07	1	1.19	1.22
		3.3	1.08	1.36
		11.9	1.14	1.32

[*] Starting polystyrene samples were mould-pressed.

as $S = (L_E - L_S)/L_E$ and the recovery, R, as $R = (L_E - L_S)/(L_E - L_0)$.

2.3. Bi-refringence
Total bi-refringence was measured with a Zeiss polarizing microscope equipped with a Calcspar rotary compensator (manufactured by Zeiss). The thickness of the sliced samples was taken as the average of several micrometer measurements ($\pm 10\%$) along the films.

2.4. Gel permeation chromatography
Gel permeation chromatograms were obtained from a Waters 201 high-pressure GPC machine with an on-line, low-angle, laser-light scattering photometer (from Chromatix, Sunnyvale, CA). Four columns (μ-styragel: columns of 10^3, 10^4, 10^5 and 10^6 Å) with tetrahydrofuron (THF) as solvent at $25°$ C and a flow rate of 1 cm^3 min^{-1} were used. Molecular weights and distributions were calculated and corrected for instrumental spreading [14] by a method modified for the light scattering detector.

2.5. Tensile testing
Tensile properties of the polystyrene extrudates were determined with an Instron tester model TTM at room temperature. The modulus was calculated from the slope at 0.1% strain, the strain rate was about 1.7×10^{-4} sec^{-1}. All films were stressed-to-break and the corresponding strength computed. Some films tended to exhibit cold flow under these conditions. Yield was taken as the maximum of the stress–strain curve. All tensile properties are reported as engineering moduli and yield strength.

3. Results and discussion
Atactic polystyrene is one of the most widely produced non-crystallizable bulk polymers, because of its extensive commercial applications [15]. Notwithstanding the fact that it is probably the most extensively investigated polymer, a variety of aspects of polystyrene still provide scope for further work.

Atactic polystyrene has recently been subjected to solid-state coextrusion to produce films of high orientation [9]. This polymer thus provides an interesting system to elucidate the changes in physical and mechanical properties resulting from extreme deformation.

In the first stage of the coextrusion process, PS films were drawn to a draw ratio between 1.8 and 3.5. During the second and third stages of coextrusion the pre-extruded films were drawn to their maximum possible draw ratio of EDR > 20. A low limit was found for PS of $M_w = 1.07 \times 10^5$. Although it could be drawn to an EDR $\geqslant 17$, only brittle films of low bi-refringence were obtained. The upper limit for achieving high draw ratios seemed to occur for PS $M_w = 1.8 \times 10^6$, which could only be drawn to an EDR of 7. Attempts to draw this polymer further lead to fracture.

Results are consistent with the model of chain entanglements. The entanglements restrict the molecules from slipping past each other on extrusion, therefore facilitating chain extension and concomitant orientation. For the lowest molecular weight, the apparent bulk viscosity is sufficiently low to allow disentanglement and extensive chain slippage, resulting in inefficient draw. The highest molecular weight exhibits fracture, apparently resulting from its viscoelasticity.

This is also in good agreement with the recently suggested liquid–liquid transition temperature, T_{ll} [16] which is found at about $T_{ll} = 1.16 \, T_g$. The limited mobility of the network chains at temperatures between T_g and T_{ll} allows deformation of the PS films by coextrusion. At the same time, the relaxation times are long enough to enable preservation of the achieved orientation on cooling. The slight molecular-weight dependence of T_{ll} also explains the increased viscous slip for
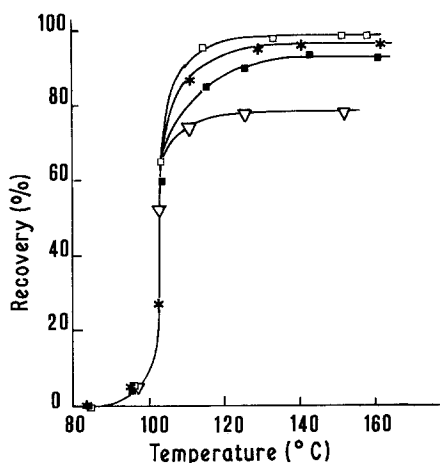

Figure 1 Elastic recovery as a function of shrinkage temperature for samples of different molecular weights but of similar draw ratios: (□) $M_w = 1.8 \times 10^6$, EDR = 13; (*) $M_w = 6 \times 10^5$, EDR = 16.8, (■) $M_w = 3.7 \times 10^5$, EDR = 13; (▽) $M_w = 1.07 \times 10^5$, EDR = 13.

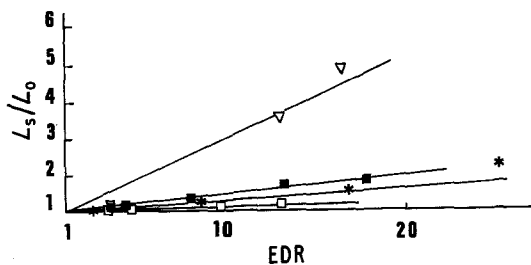*Figure 2* Chain slippage as a function of EDR for different molecular weights: (□) $M_w = 1.8 \times 10^5$, (*) $M_w = 6 \times 19^5$, (■) $M_w = 3.7 \times 10^5$, (▽) $M_w = 1.07 \times 10^5$.

the $M = 1.07 \times 10^5$ PS and the limited extrudability of the $M = 1.8 \times 10^6$ PS.

The efficiency of drawing was measured by the recovery upon rapid thermal shrinkage. A perfectly drawn amorphous specimen will retract to its original shape if heated to a temperature sufficiently above T_g. Such efficient drawing is reflected in Fig. 1 where the recovery is plotted as a function of temperature. For molecular weights greater than 1.07×10^5, with comparable draw ratio, almost total recovery (90–98%) is observed for temperatures of about 160° C. For the lowest molecular weight, however, at a comparable draw ratio (EDR = 13) only 78% recovery is observed, indicating that the drawing was less efficient. It is
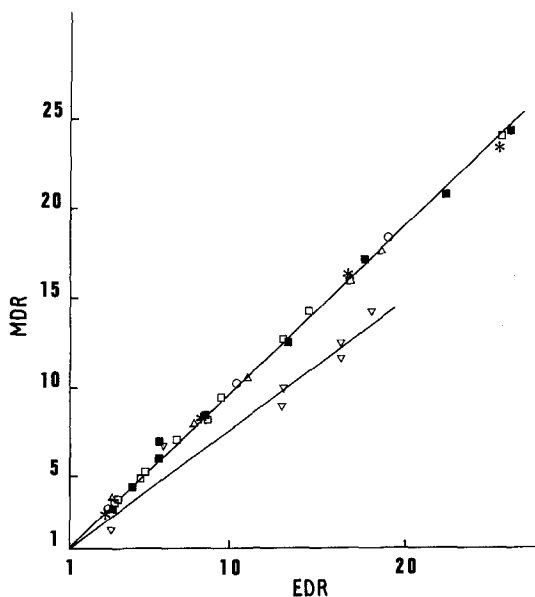
interesting to note that for the same polymer at lower EDR a more efficient coextrusion, i.e. a high elastic recovery is observed. The efficiency of draw, as expressed by recovery, is always greater for the higher molecular weights under comparable draw conditions.

The L_S/L_0 ratio is a measure of the chain slippage on deformation; see Fig. 2. The ratio increases as the EDR is increased and as the molecular weight is decreased. The efficiency of coextrusion is thus dramatically reduced by chain slippage.

The efficiency of drawing in achieving chain extensions can also be expressed in terms of the molecular draw ratio (MDR)

$$MDR = \frac{L_E - L_S + L_0}{L_0} = \frac{S(EDR)}{100} + 1$$
$$= \frac{(EDR - 1) \times R}{100} + 1, \qquad (1)$$

which represents the actual molecular draw process. (The definition of MDR given in a previous paper [13] is incorrect.) The MDR data for all the samples are displayed in Fig. 3. Again it can be seen that, up to the highest attainable draw ratio, a highly efficient deformation has been achieved (upper line). A less efficient draw was observed for the lowest molecular weight, 1.07×10^5 (lower line), presumably due to more prominant intermolecular slip on draw.

An efficient drawing process results in extended molecules with a higher degree of orientation; the bi-refringence sample, Δn, provides a measure of
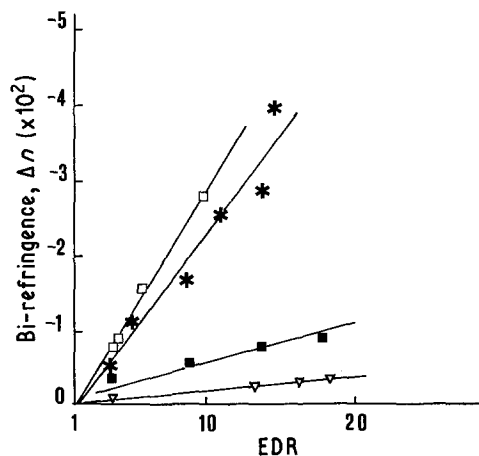

Figure 3 Molecular draw ratio as a function of effective draw ratio for different molecular weights: (□) $M_w = 1.8 \times 10^6$, (○) $M_w = 1.26 \times 10^6$, (△) $M_w = 6.7 \times 10^5$, (*) $M_w = 6 \times 10^5$, (■) $M_w = 3.9 \times 10^5$, (▽) $M_w = 1.07 \times 10^5$.

Figure 4 Bi-refringence as a function of the draw ratio for different molecular weights. (□) $M_w = 1.8 \times 10^5$, (*) $M_w = 6 \times 10^5$, (■) $M_w = 3.7 \times 10^5$, (▽) $M_w = 1.07 \times 10^5$.
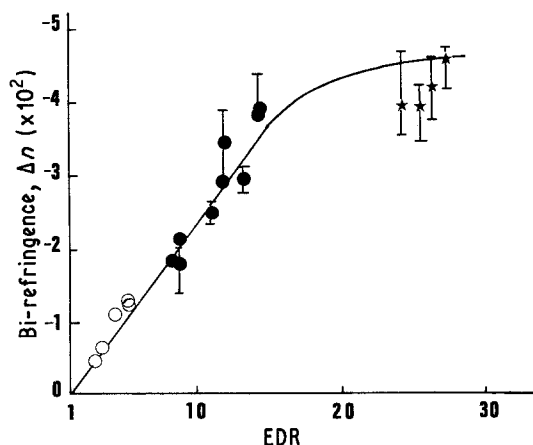
Figure 5 Bi-refringence as a function of the draw ratio for molcular weights of 6×10^5: (o) first stage; (●) second stage and (*) third stage.

this effect. As expected, efficiently drawn samples exhibit pronounced bi-refringence (Fig. 4) showing a systematic increase with both draw ratio and molecular weight of polystyrene. For the purpose of obtaining the highest possible orientation, a sample with a molecular weight of 6×10^5 was extruded in several stages, see Fig. 5. During the first and the second stage coextrusion, bi-refringence increases linearly with EDR but, during the third stage, the bi-refringence levels off to a maximum value of about -4.2×10^{-2}. This is probably due to the lower draw rates (cross-head speeds) at the third stage of coextrusion, allowing more elastic recovery in the barrel of the Instron machine. A four-fold increase in residence time in the barrel reduced bi-refringence by about 80%, as shown in separate tests. Nevertheless, a maximum bi-refringence for polystyrene of $\Delta n = -4.2 \times 10^{-2}$; apparently, the highest value yet reported. This value is also more than twice that reported [9] for a PS of broad MWD extruded at $100°$ C. A Δn value of -1.3×10^{-2} for draw ratio of 13.3 at $130°$ C has been reported [6] with slightly higher values at lower temperatures. Jasse and Koenig [7] reported that $\Delta n = -3 \times 10^{-2}$ for a draw ratio of 11 at $110°$ C. The maximum Δn value obtained in this work is also more than those given by Gurnee [17]. From his theoretical orientation correlation we compute a 44% orientation for the highest bi-refringence obtained.

From the bi-refringence for PCC of $M_w = 6 \times 10^5$ a levelling-off of segmental orientation is indicated during the third stage of coextrusion (Fig. 5). Chain extension, on the other hand, as reflected by the molecular draw ratio (obtained from thermal shrinkage tests, see Fig. 3), still increases linearly with EDR during the third stage of coextrusion. Apparently, at these high levels of chain extension and segmental orientations, the two quantities partially decouple. It seems that a limited segmental relaxation (short-range order) is allowed whereas the long-range order cannot dissipate under these coextrusion conditions, i.e. disentanglement of the tie points. This has also been the conclusion of Benoit [18] who observed a reduction in bi-refringence of a drawn sample upon annealing under tension; subsequent thermal shrinkage of the same sample exhibited total recovery.

The ultimate extrusion ratio (UDR) of a linear PS (planar zig-zag conformation) may be calculated for a given molecular weight, M_w from [9]:

$$UDR = 0.06686 \, M_w^{1/2}.$$

For the PCC, of $M_w = 6 \times 10^5$, an $UDR = 51.8$ is computed; this value is still twice the maximum MDR we have so far achieved. This serves to emphasize the role of the entanglement network which allows chain extension, but may also be responsible for its limit on drawing.

Differential scanning calorimetry, for the highest molecular weight sample, indicated no change in T_g with EDR. This implies that changes in conformation or density do not show up at T_g other than in the on-set of elastic contraction. If orientated amorphous chains are more closely packed, i.e. if they are of lower free volume, the difference must dissipate to warming to T_g.

Gel permeation chromatography was performed on most polystyrene samples at each stage of processing. Degradation occurred only during mould pressing of the films, leading mainly to broader MWD. However, no PS degradation could be detected for the coextrusion drawing process even after three stages of draw and for an EDR as high as 27, see Table I.

The tensile modulus and the strength show no major influence of molecular weight or EDR, except in the case of the lowest molecular weight sample which produced brittle films. The tensile moduli averaged 2.8 GPa and the strength averaged about 65 MPa. Obviously, therefore, atactic PS is not a candidate material for a high-modulus polymer as it shows little improvement in mechanical properties even under extreme orientation.

4. Conclusions

Polystyrenes of narrow MWD have been coextruded

efficiently, by a multiple stage process, with poly-ethylene up to an EDR of 27. Bi-refringence values Δn and elastic values, from recovery rapid thermal shrinkage tests, both exhibit a pronounced dependence on molecular weight and draw ratio. In general, the chain orientation and extension increase with EDR and molecular weight. For a sample of molecular weight 6×10^5 it was possible to achieve the maximum EDR of 27 and a corresponding $\Delta n = -4.2 \times 10^{-2}$, equivalent to 44% orientation, the highest values yet reported. The lowest molecular weight sample, 1.07×10^5, could be drawn to an EDR of 17, but the resulting films were brittle, reflecting their less-efficient draw, as shown by bi-refringence and elastic recovery measurements. The highest molecular weight sample, 1.8×10^6, on the other hand, was drawable only to an EDR fo 7. Here draw is highly efficient until fracture prevents further extension.

Deformation on solid-state coextrusion may be interpreted in terms of molecular entanglements. Chain entanglements provide the necessary inter-molecular network which facilitates molecular extension and the concomitant orientation, as shown by elastic recovery measurements and by bi-refringence measurements, respectively. For very high molecular weight samples the visco-elasticity of the network reaches a point where fracture readily occurs. For low molecular weight samples the entanglement network is vastly reduced and the resulting extensive chain slippage leads to less efficient orientation and extension.

Acknowledgement

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