Mechanical property and physical structure changes in highly hot-drawn polycarbonate

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The effect of hot stretching on the structure and properties of bisphenol-*A* polycarbonate was studied to determine if ordering and conformational changes occur, and their effect on the impact toughness of PC. The mechanical properties of hot-stretched PC were found to follow the same behavior observed for enthalpy changes, which showed (1) a drop at draw ratios between 2 and 5; (2) a plateau region extending out to a draw ratio of 45; (3) a further drop at draw ratios of 57 and 62. The enthalpy decrease at a draw ratio of 62 is comparable to that found for 15% solvent-crystallized PC; yet, wide-angle x-ray diffraction indicates that no crystallinity is present. Annealing of this highly hot-drawn PC increased the enthalpy by 7.5 kJ/kg, indicating that this highly hot-drawn PC must be in an ordered state.

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INTRODUCTION

A number of techniques are commonly used for the detection of structure and the characterization of glassy polymers. In this study, enthalpy changes during hot drawing of bisphenol-A polycarbonate (PC) have been determined through heat-of-solution measurements, which previous studies[1-5] have shown to be very sensitive to structural changes in glassy polymers. Mechanical properties of hot-drawn PC films were measured by conventional tensile testing at 0.00042 sec^{-1} and by instrumented tensile impact testing at 200 sec^{-1}. The structural changes, as determined by enthalpy measurements, were correlated with the changes in mechanical properties. Additional structural measurements, such as wide-angle x-ray diffraction (WAXD), birefringence, and differential scanning calorimetry (DSC) were also used.

Ito, Sawamura, and Saito[6] studied the effect of hot-drawing on the dielectric loss of PC. They found that hot drawing (1) first decreased, and then increased, the activation energy of the β (190 K) transition and (2) caused an initial drop, at low draw ratios, in the activation energy of the intermediate transition (333 K). They also found increasing birefringence and density with increasing draw ratio and explained their results in terms of a more compact packing and orientation of the molecular chains during hot stretching. Ito and Hatakeyama[7] studied the effect of hot-drawing on PC and found that the T_g increased with increased draw ratio up to a maximum, at a birefringence of 25×10^{-3}, and decreased at higher draw ratios. They also found, from infrared dichroism, that the molecular chains of PC became aligned and more densely packed with increased draw ratio, but that intermolecular regularity does not increase for birefringence above 22×10^{-3}.

Robertson and Buenker[8] reported that the tangent modulus of PC increased linearly with increasing birefringence. They also fitted their yield-strength data[9] with a smooth curve, which showed a constant yield strength at low birefringence and an increasing yield strength at higher values of birefringence. However, their tangent modulus data,[8] at low birefringence, could actually be better fitted with a horizontal line, which would indicate that the tangent modulus, in this low-orientation region, was not changed by hot-drawing. In a similar manner, their yield-strength data,[9] at low birefringence, could actually be better fitted with a smooth curve showing a small drop in the yield strength at low birefringence. Thus, the data of Robertson and Buenker indicates that the well-known increase in modulus and yield strength with increasing orientation may be present only at higher birefringence; at low birefringence the modulus may be constant and the yield strength may be decreased by hot stretching.

The PC data at high draw ratios follows the well-known behavior of increased properties with increased orientation; however, a number of interesting changes have been observed at lower draw ratios, which may indicate that different structural changes may be occurring at high and low draw ratios.

EXPERIMENTAL

Commercial M-50 grade Merlon bisphenol-*A* PC, obtained from Mobay Chemical Co. in a pellet form, was used in this study. From osmometry, this sample had a number-average molecular weight of 26000. As in most commercial polymers, this sample did contain small amounts of additive.

The PC pellets were initially dried at 383 K, under vacuum, for 36 h. PC films were extruded from a $\frac{3}{4}$-in extruder through a film die. The samples were hot-drawn directly from the film die and quenched on a stainless-steel chill-roll, with the amount of hot-drawing dependent on the extruder output and takeup roll speed. Regions of constant draw ratio were removed from the long film and used for further measurements. All sample films were observed to be clear and free from observable defects.

Wide-angle x-ray diffraction (WAXD) patterns were taken, under high vacuum, using Cu-K_α radiation.

The enthalpy change during hot-drawing was measured by solution microcalorimetry, as has been described earlier.[1-5,10] However, a different sampling technique was used in which the films were held under

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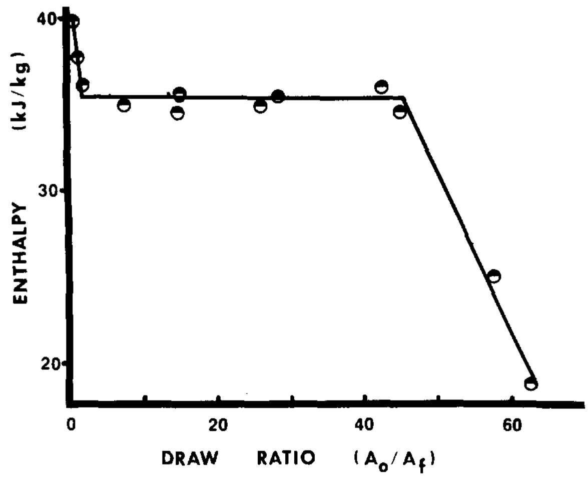

FIG. 1. The effect of hot-drawing on the enthalpy of M-50 grade Merlon PC at 307 K.

the mercury by two type 321 stainless-steel spring clips.[10]

Birefringence was measured with a L133A Babinet compensator with a 5.461×10^{-5}-cm light source.

Low-strain-rate testing was performed at 0.00042 sec^{-1}, with an Instron tensile testing machine. High-strain-rate tensile testing was performed at 200 sec^{-1}, with an instrumented tensile impact tester, using a Kistler Kiag Swiss type 902A SN1214 quartz transducer and a type 5001 Kistler charge amplifier. The gauge length of all specimens was arbitrarily set at 5 cm and was maintained at 5.00 ± 0.05 cm for all tests.

RESULTS

Enthalpies of PC films hot-drawn various amounts are illustrated in Fig. 1, where the enthalpy of the undrawn compression-molded PC is 39.7 kJ/kg. Upon hot-stretching, the enthalpy first decreases, to a plateau value of 35.4 kJ/kg, between draw ratios of 3 and 45, and, second, decreases again at draw ratios of 57 (25.2 kJ/kg) and 62 (18.7 kJ/kg).

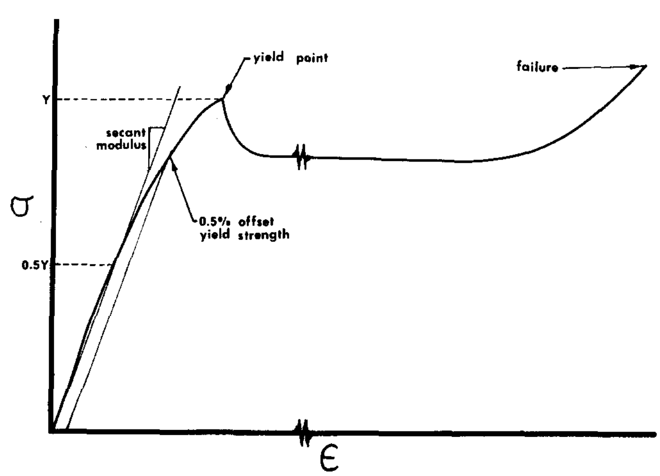

FIG. 2. A schematic illustration of our method of measuring mechanical property parameters from the engineering stress-strain curve of PC at 0.00042 sec^{-1} (300 K).

Our method of measuring the low-strain-rate mechanical properties of PC, at 0.00042 sec^{-1}, is illustrated schematically in Fig. 2. The mechanical property parameters that were measured at 0.0042 sec^{-1} are the 0.5% engineering offset yield strength and the engineering yield-point strength (Fig. 3) the engineering strain to failure and the engineering yield-point strain (Fig. 4); and the engineering secant modulus of elasticity, as measured from the origin to one-half the yield strength (Fig. 5). It can be seen in Figs. 3–5 that the yield-point strength, the strain to failure, and the yield-point strain can be described by a curve similar in shape to that observed for the enthalpy change during hot stretching, where there is an initial decrease, a plateau region, and a further decrease at high draw ratios. The 0.5% yield strength and the modulus can be described by a plateau region extending out to a draw ratio of 43 and a decrease at higher draw ratios.

The impact tensile strength (Fig. 6) can also be described by a plateau region (draw ratios 1–43) and a decrease at higher draw ratios. The impact plastic strain-to-failure (Fig. 7) and the area under the impact stress-time curve (Fig. 8) can be described by a curve similar in shape to that observed for the enthalpy change during hot-drawing. The area under the stress-time curve ($\int \sigma dt$) is a pseudoimpact toughness measurement, which can be converted to an impact toughness by multiplying by the strain rate, which could not be measured directly, but was estimated at approximately 200 sec^{-1}.

From Fig. 9, the birefringence of hot-drawn PC can be seen to increase linearly with increasing draw ratio, out to a draw ratio of 43. An increase in birefringence is noted at draw ratios of 57 and 62. It should be emphasized that the total amount of birefringence present in these samples is less, by about

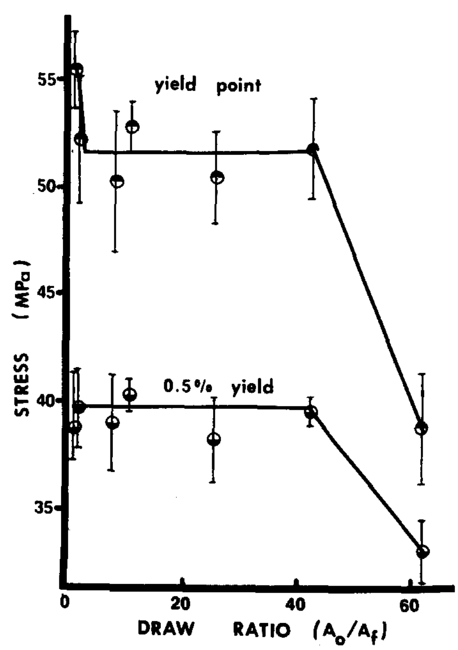

FIG. 3. The effect of hot-drawing on the 0.5% engineering offset yield strength and the yield-point strength of M-50 Merlon PC at 0.00042 sec^{-1} (300 K).

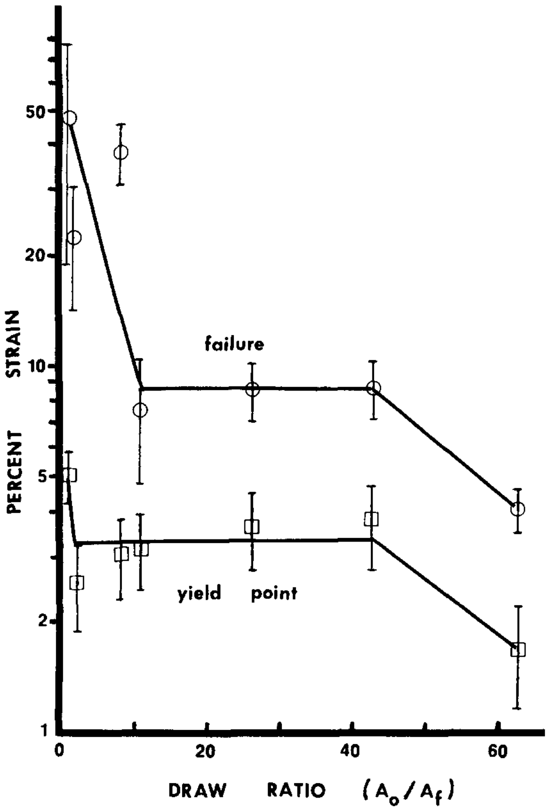

FIG. 4. The effect of hot-drawing on the engineering percent yield-point strain and the engineering percent strain to failure of M-50 grade Merlon PC at 0.00042 sec^{-1} (300 K).

a factor of 7, than is commonly observed for cold-drawn PC. This was a consequence of the relatively high temperature at which these samples were drawn.

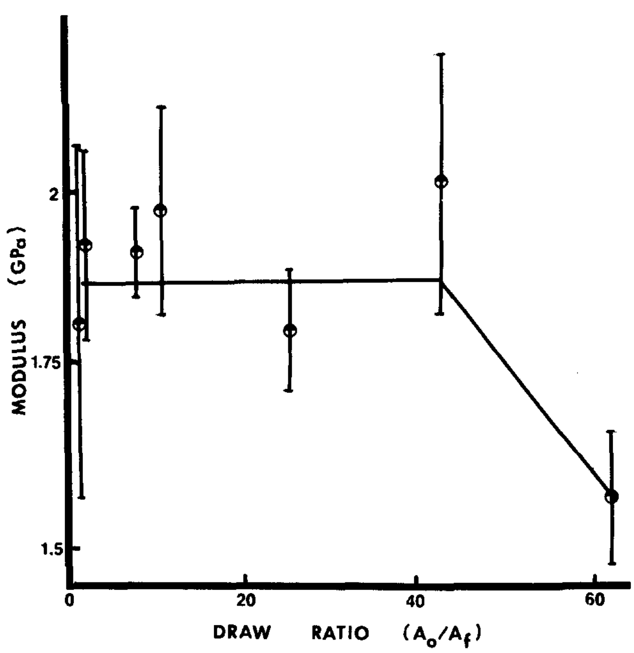

FIG. 5. The effect of hot-drawing on the engineering secant modulus of M-50 grade Merlon PC at 0.00042 sec^{-1} (300 K).

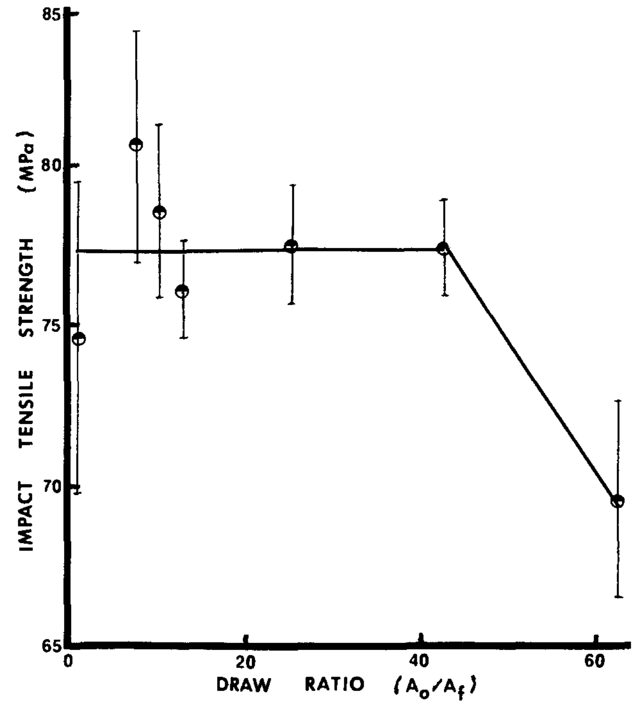

FIG. 6. The effect of hot-drawing on the engineering impact tensile strength of M-50 grade Merlon PC at 200 sec^{-1} (300 K).

WAXD patterns (Figs. 10 and 11) indicate no observable effects of orientation or crystallization as a result of hot-drawing.

Annealing of the highly hot-drawn PC (draw ratio 62) at 408 K (135C) for 24 h resulted in an enthalpy increase of 7.5 kJ/kg to a value of 26.2 kJ/kg. Thus complete recovery to the original value (39.7 kJ/kg) did not occur. Although it is possible that complete enthalpic recovery may have occurred if the annealing had been performed at a higher temperature, nonetheless, this behavior indicated that the highly hot-

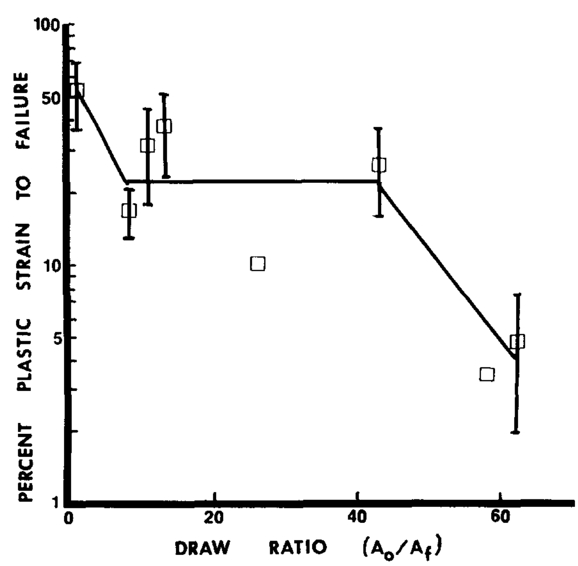

FIG. 7. The effect of hot-drawing on the engineering impact percent strain to failure of M-50 grade Merlon PC at 200 sec^{-1} (300 K).

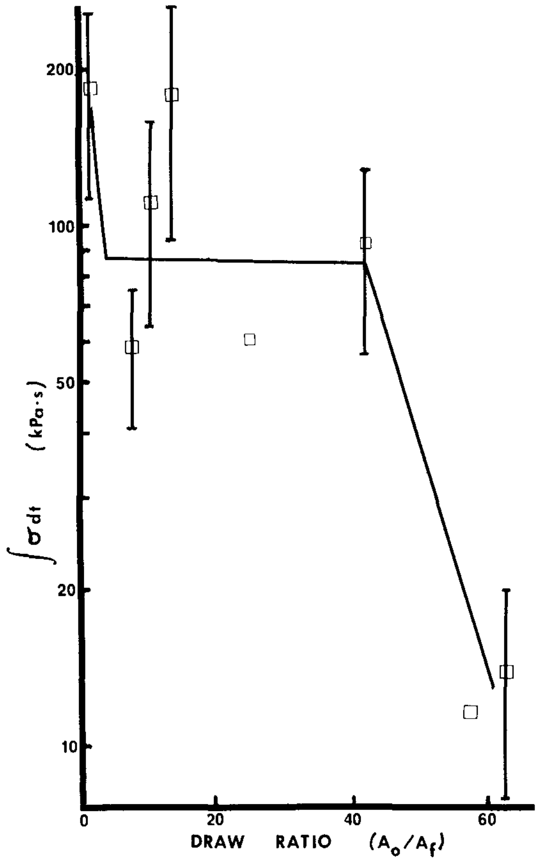

FIG. 8. The effect of hot-drawing on the engineering normalized impulse to failure for M-50 grade Merlon PC. Approximate strain rate is 200 sec^{-1} (300 K).

drawn PC is not in a stable state (e.g., crystalline). Furthermore, DSC studies indicated traces of a melt near the melting temperature of PC, but it was insignificant with respect to the melt observed for a solvent-crystallized PC sample (15% crystallinity).

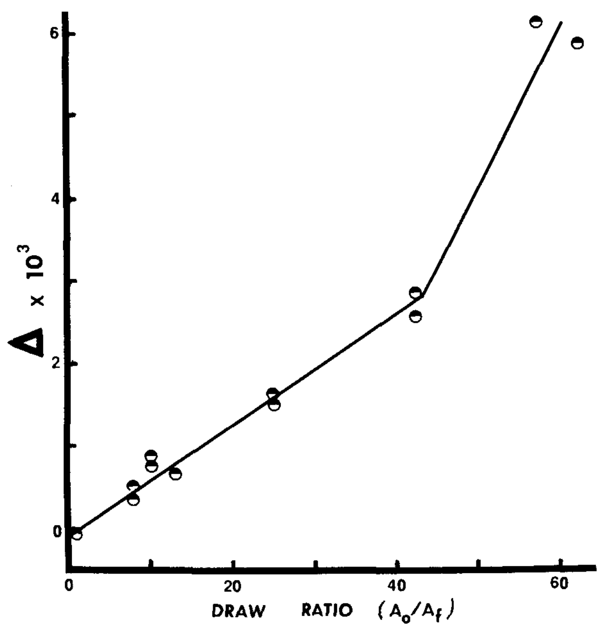

FIG. 9. The birefringence of hot-drawn M-50 grade Merlon PC (300 K).

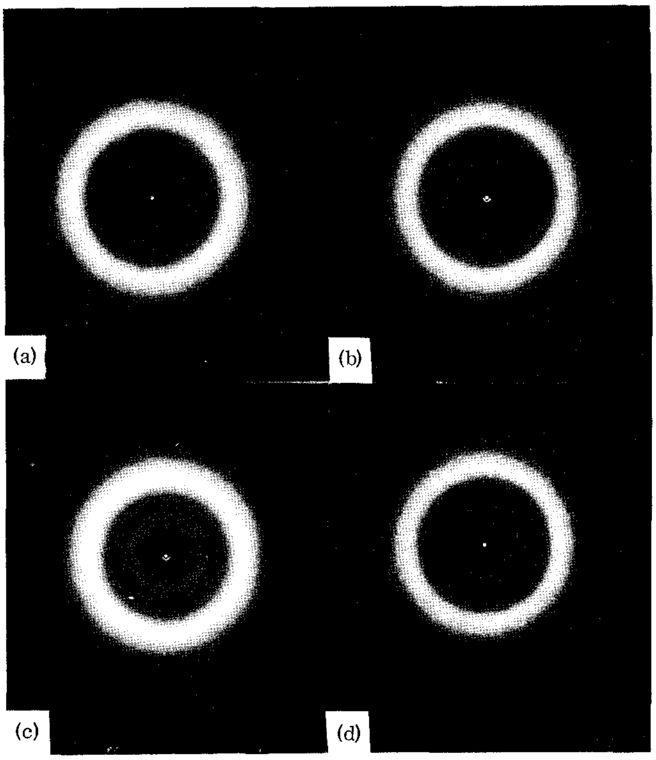

FIG. 10. Wide-angle x-ray diffraction patterns of M-50 grade Merlon PC (300 K). (a) As-compression-molded; (b) as-extruded, draw ratio (dr) = 1; (c) extruded and hot-drawn, dr = 15; (d) extruded and hot-drawn, dr = 43.

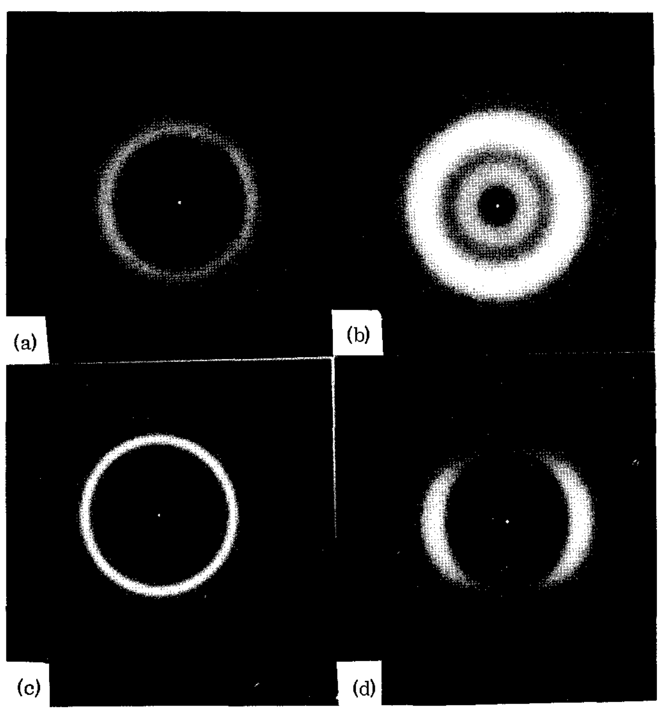

FIG. 11. Wide-angle x-ray diffraction patterns of M-50 grade Merlon PC (300 K). (a) Extruded and hot-drawn, dr = 57; (b) extruded and hot-drawn, dr = 62; (c) solvent-crystallized, 15% crystallinity; (d) extruded and cold-drawn to neck. Note: (b) and (c) exhibit similar enthalpies.

DISCUSSION

Figure 1 shows that hot-drawing, under the conditions indicated here, can have a pronounced effect on the enthalpy of polycarbonate. The decrease of 4.3 kJ/kg at low draw ratios is somewhat puzzling, but a similar behavior has been observed for poly(vinyl chloride)[11] and atactic polystyrene.[3] It cannot be explained by macroscopic inhomogeneities which may be introduced into the sample since these would raise and not lower the enthalpy. It is also unlikely that this decrease is a result of density changes,[12] or strain-induced crystallinity[13] since the amount of drawing is small and greater amounts of drawing show no additional decrease (except at very high draw ratios). One possible explanation is that the extrusion and low degree of drawing results in an increase in the number of trans conformations by the biasing effect of the drawing during cooling. Why this would occur only at low draw ratios is yet unknown.

The plateau region of enthalpy, from draw ratios of 3—45, suggests that either no substantial changes are occurring in conformational states or ordering, or opposing effects of drawing and annealing may be occurring which eliminate any changes. The latter effect has been reported on by Matsuoka[14] for annealed and cold-drawn samples. Yet, as shown in Fig. 9, the birefringence does linearly increase over this region. This suggests the possibility that reorientation of preexisting structural units may be occurring during this stage of drawing or that the enthalpy changes associated with this orientation are too small to detect. However, Matsuoka showed that enthalpy changes associated with small amounts of cold-drawing are certainly well within our detectability.[14]

The decrease of 21 kJ/kg from the compression-molded PC for the sample with a draw ratio of 62 is about the same magnitude as observed for solvent-crystallized PC. This large drop implies that a large structural change must be taking place within these samples. However, DSC studies failed to show a melting endotherm for these samples and x-ray studies indicated no difference between the compression molded and highly hot-drawn PC. Thus, although the possibility exists that strain-induced crystallization may be occurring, x-ray and DSC studies failed to show any evidence for it.

The fact that the yield-point stress, 0.5% yield stress, log percent yield-point strain, percent strain to failure, and modulus can all be fitted by a curve similar in shape to the enthalpy—vs—draw-ratio curve suggests that a possible relationship may exist between these various mechanical parameters and enthalpy. Similar correlations exist between impact strength, impact plastic strain to failure, normalized impulse to failure, and enthalpy. Until the exact molecular parameters responsible for the enthalpy changes and the mechanical property changes can be clarified, we are not able to conclude from this study the importance or significance of these correlations.

Annealing of the highly hot-drawn PC (draw ratio 62) for 24 h at 408 K (135 °C) produces an enthalpy increase of 7.5 kJ/kg. From a simple $\Delta F = \Delta H - T\Delta S$ relationship, the entropy of the highly hot-drawn PC must *increase* upon annealing, which indicates that the highly hot-drawn PC must be in a more ordered state. Williams and Flory[15] give the energy of the cis form of PC relative to the trans as being 5.4 kJ/mole. If the highly hot-drawn PC were entirely trans, then the amount of cis conformation could increase to a maximum of 50%,[15] which would mean a maximum enthalpy change of 10.5 kJ/kg. Thus our observed enthalpy increase may at least in part be due to conformational considerations. However, if the material had a high trans content or was in a low conformational energy state, a large endotherm may be observed in a DSC trace at T_g. Such an endotherm was not observed. However, it is possible that effects of stretching and annealing[14] can eliminate this effect.

Enthalpy measurements indicate a large "structural" change is occurring in highly hot-drawn PC, yet WAXD indicates no crystallinity. Comparison of the WAXD patterns for hot-drawn PC (draw ratio 62), Fig. 11(b), and solvent-crystallized PC, Fig. 11(c), both which have nearly the same enthalpy, clearly demonstrates the lack of x-ray detectable crystallinity in the highly hot-drawn PC. Thus if order or crystallinity does exist in this sample, it must exist in a morphology substantially different from the crystallinity in the solvent-crystallized sample.

Although WAXD may be unable to detect these low degrees of orientation, birefringence measurements clearly indicate that orientation increases during hot stretching. Although the orientation in the sample with draw ratio 62 is significant ($\Delta = 6\times10^{-3}$), it is small in comparison with many reported results[6-9] on cold-drawn samples where Δ may be as high as 45×10^{-3}. Robertson[9] showed that while the yield strength of PC increases at high orientations, it may decrease or remain the same at low orientations. Thus his results in the low-orientation region are not inconsistent with ours. However, our results on highly hot-drawn PC are not consistent with those reported for an orientation of $\Delta = 6\times10^{-3}$. This may be due in part to the differences in sample preparation: our samples were drawn more, at a higher rate and temperature, and quenched quicker than commonly reported in the literature.

Most hot-drawing studies are performed near T_g (150 °C) where melt viscosities are substantially higher and molecular mobilities much lower than in our drawing which was performed at 260 °C. Thus in our studies greater amounts of molecular relaxation presumably occurred resulting in the relatively low levels of orientation as determined by birefringence. However, the drop of enthalpy and corresponding decrease of mechanical properties for samples with draw ratios above 45 would be consistent with crystallization occurring. However, neither DSC studies nor x-ray studies indicated that crystallization occurred. Further, the fact that the enthalpies of the highly hot-drawn samples increased upon annealing suggests that the structure induced by the drawing is certainly not in an equilibrium state.

Two hypotheses may be advanced to explain the consistent enthalpy and mechanical property decreases in the highly hot-drawn PC: (1) they may be due to large void fraction or (2) they may be due to the presence of an ordered structure which possesses a smaller-than-normal number of entanglements and/or structural units that physically restrict the local yielding of PC. Hypothesis (1) can be rejected since we have found, with powdered samples, that surface free energy contributions to the enthalpy are very small, and Kolbeck, Fujimoto, Uhlman, and Calvert[16] have found that the presence of a large number of gas bubbles (voids) in PC has only a small effect on mechanical properties. Furthermore, similar behavior for the enthalpy of hot-drawn atactic polystyrene has been observed,[3] and along with the results of previously mentioned DSC and x-ray studies, we must conclude that crystallization of any sort, including strain induced, is probably not occurring. Thus we must conclude that some type of ordering is occurring which possesses a smaller-than-normal number of entanglements and/or structural units which somehow restrict local yielding in PC.

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