

Plastic deformation and subsequent crystallization of thin films of isotactic/atactic polystyrene (iPS/aPS) blends

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Thin films of crystallized and non crystallized isotactic polystyrene (iPS) and its blends with atactic polystyrene (aPS) were deformed below their glass transition temperature T_g . Deformation occurs in a very narrow 'deformation zone' ($\lambda=4$ nm) and the deformed material exhibits long range order independent of the crystallinity of the films till concentrations of aPS up to 15%. Films containing more than 20% aPS do not show long range order within the deformed material even after subsequent annealing above T_g . From these results, which were obtained by transmission electron microscopy and electron diffraction, the conclusion is drawn that the molecular processes of crazing in amorphous polymers and the high local deformation of polymer single crystals are obeying similar mechanisms.

(Keywords: plastic deformation; blends; crystallization; polystyrene)

INTRODUCTION

Thin films of blends of isotactic polystyrene (iPS) and atactic polystyrene (aPS) with different compositions were used to study the deformation process and the subsequent crystallization by transmission electron microscopy (TEM) and selected area electron diffraction (SAED). Primarily, the experiments were performed in order to obtain further information about the molecular deformation mechanisms in semi-crystalline polymers. At present, three different models exist describing the transformation of a single crystalline lamella into highly oriented drawn material. Peterlin¹ suggests that small crystalline blocks break off from the lamella and align parallel to the draw direction, Kobayashi² assumes a complete unfolding of chains from the lamella, and Petermann *et al.*³ propose an incomplete unfolding and bending of the molecule within a narrow disordered deformation zone.

The deformed material showed crystalline order in the as drawn state up to a concentration of 15% aPS (at a drawing temperature of 20°C), well below the glass transition temperature ($T_g=90^\circ\text{C}$). Deforming blends with concentrations of aPS more than 20% resulted in oriented but disordered molecules within the drawn region. Additionally, even annealing the drawn film well above T_g , did not lead to a crystalline order of the oriented molecules as followed by SAED. In contrast, in as prepared films of this composition crystallization occurred.

EXPERIMENTAL

The iPS used in the experiments was obtained from Polyscience, Inc., Warrington/PA, and had a molecular

weight $M_w=851\,000$ and $M_w/M_n=5.93$. The aPS was general purpose Polystyrol 168 N from BASF with the melt index MFI 200/5 of $1.2\text{ g }10\text{ min}^{-1}$. Both the polymers were dissolved in a 1 wt% solution of *p*-xylene at 135°C. Thin amorphous films were prepared according to the method of Patel⁴ and Kramer⁵. Briefly, a glass slide was placed vertically into the hot solution and drawn out of the solution with a velocity of 32 mm min^{-1} . The remaining polymer film was removed from the glass slide and bonded onto electron microscope grids, which subsequently were deformed at room temperature in uniaxial tension⁶. The electron microscope used was a JEOL JEM 200 CX operated at 100 kV.

RESULTS AND DISCUSSION

The uniaxial deformation of the films causes crazing in the iPS/aPS blends. *Figure 1(a)* shows a crazed region in pure iPS. Some of the films were heat treated before deformation in order to crystallize (1 h at 185°C). The crystal morphologies were plate like (single crystals) with the chains being perpendicular to the surface of the film. The lateral dimension of the crystals exceeded several micrometers. In *Figure 1(b)* a dark field electron micrograph is seen, inserted is the electron diffraction. The bright areas are crystal regions fulfilling the Bragg condition. The fine striations are moiré fringes due to multi-layered single crystals having a small orientation deviation. The black ribbon is the crazed material. This morphology was observed in all the films with the different concentrations. *Figure 2(a)* is a SAED of the crazed region in a pure iPS film. Crystalline order can clearly be seen. The same diffraction pattern are obtained in non crystallized deformed films of pure iPS⁷. As it was pointed out previously⁷, care has to be taken to radiation damage, because crystalline order

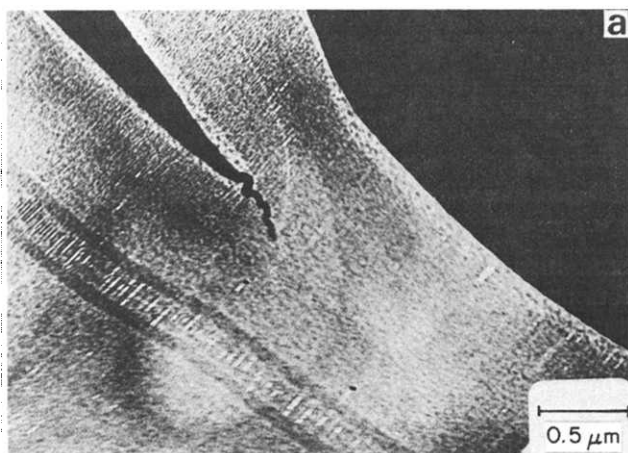


Figure 1(a) Bright field electron micrograph of a crazed region (bright area). The dark region is the undeformed material



Figure 1(b) Dark field electron micrograph of a crystallized region (bright) and deformed regions (dark ribbons). Inserted is an electron diffraction pattern of the crystallized region

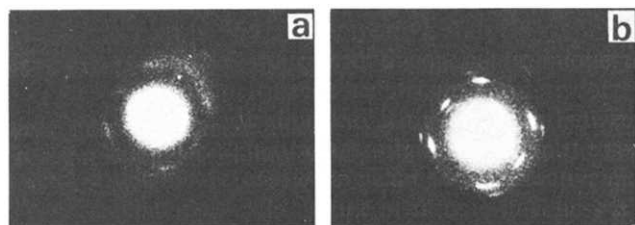


Figure 2 (a) Electron diffraction pattern from a deformed region in a crystallized iPS film; (b) electron diffraction pattern from a deformed region in a crystallized iPS film subsequently annealed 1 h at 185°C

gets destroyed by electron irradiation. Fibrillation of the crazed material can blur the SAED, too. Therefore, SAED was taken from continuous material (not fibrillated) within the crazes. *Figure 2(b)* shows the SAED of a crazed region, which was annealed 1 h at 185°C after the deformation. A considerable increase in the intensity of the diffraction spots is observed. Qualitatively the same results are obtained for the blends up to a concentration of 15% aPS, independent whether the films were crystallized or not before the deformation. Using films with concentrations more than 18% aPS, the SAED in the crazed region changes. *Figure 3a* shows the SAED in such a region of a film,

which was crystallized 1 h at 185°C before deformation and which exhibits single crystals in the non-deformed areas (*Figure 4*) similar as in the pure iPS films (*Figure 1(b)*). Non-long range crystalline order can be detected on the diffraction patterns in the deformed regions. Annealing the films after the deformation 1 h at 185°C does not change the SAED significantly (*Figure 3b*). The same observation was made when using non-crystalline films (as prepared). Again the crazed region shows only an amorphous halo, even when the film was subsequently annealed for 1 h at 185°C.

Two major conclusions may be drawn from the experimental observations:

(1) *Molecular process of deformation*

The observation that the amorphous and the crystallized films have the same morphology of the crazed regions and that the structures of the deformed material are identical for both the films leads to the conclusion that similar deformation mechanisms may occur.

The narrow deformation zones (interface between plastically deformed and non-deformed material) and the similar extension ratio^{3,8} ($\lambda \approx 4$) are further indications that craze formation and crystal deformation in thin films are obeying closely related molecular processes.

As pointed out by Fujiwara *et al.*⁹, the low extension ratio excludes the Kobayashi type of unfolding. For the regular unfolding of molecules at the deformation zone a much higher draw ratio of $\lambda = D/a$ (D = crystal thickness, a = nearest neighbour distance of molecules, see below) is expected, and the absence of lateral order

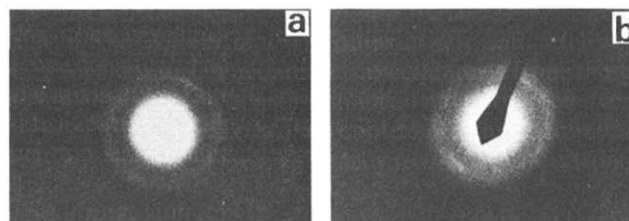


Figure 3 (a) Electron diffraction pattern of a deformed region in a crystallized iPS/18% aPS film; (b) electron diffraction pattern of a deformed region in a crystallized iPS/18% aPS film subsequently annealed 1 h at 185°C

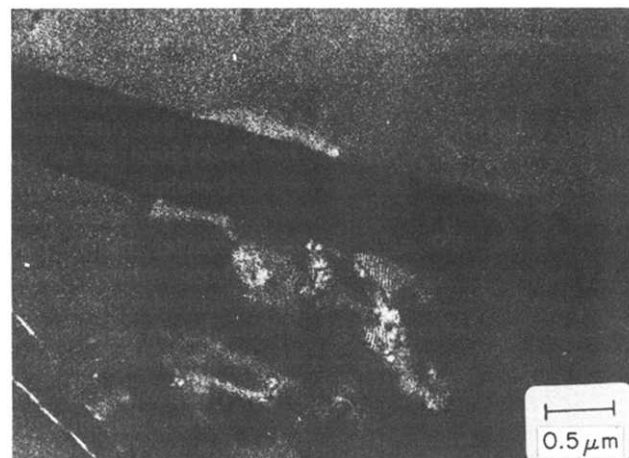


Figure 4 Dark field electron micrograph of crystalline parts (bright areas) in an iPS/18% aPS film

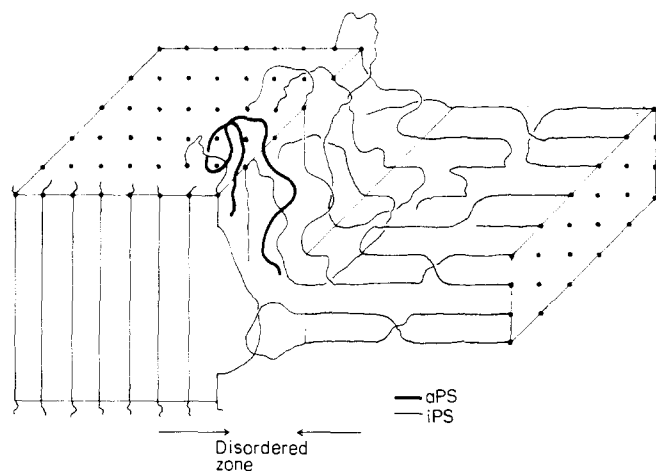


Figure 5 Schematic sketch of the deformation (disordered) zone, the non deformed crystal, and the deformed region

in the crystallized and deformed blends of 80% iPS/20% aPS excludes Peterlin's model. Bending and unfolding in a narrow deformation zone³ is the most likely molecular deformation mechanism in the crazing type of deformation (Figure 5).

The draw ratio λ may be estimated by

$$\lambda = \frac{D}{w}$$

where D is the crystal thickness and w the width of the deformation zone. The width w of the deformation zone depends on how far the force from a pulled molecule is transferred into the undeformed crystal. Highest draw ratios may be obtained from adjacent re-entry folding, in irregular folded crystals, the size of the loops may determine the width of the deformation zone and in entangled or crosslinked surfaces these forces may reach much further.

The question of the structure of the deformation zone still remains to be answered. Previous results on pure iPS⁷ and our results up to concentrations of 15% aPS show that lateral order in the deformed region appears, independent of lateral order (crystalline or amorphous) of the non-deformed material. A 'melt like'^{3,9} disordered zone could explain the loss of memory between the deformed and undeformed regions. A modification to a normal melt must be made, as stretched molten films of even higher iPS/aPS blends¹⁰ crystallize instantaneously, while non-lateral order is obtained in the craze fibrils of this blend even after annealing at 185°C.

(2) Crystallization of the deformed material

From the appearance of crystalline order in the deformed material it can be concluded that the molecules have reasonable mobility within the deformation zone. As the molecules have a very short resident time ($t < 10^{-2}$ s) during deformation in the zone, no long range diffusion can be expected and therefore aPS molecules may be incorporated into the crystals after deformation. With increasing concentration of aPS within the blends the lateral order of the crystals in the deformed region decreases as observed by the electron diffraction pattern. At 18% aPS, each iPS molecule has in the average one aPS molecule as a nearest neighbour (with six nearest neighbour chains in the pseudo-hexagonal packing of the iPS-crystal) and therefore the lateral packing is more liquid crystalline like. While in the blends with smaller aPS content annealing may cause a further perfection of the crystals by placing the molecules accurately into their periodic potential valleys given by the crystal structure (decreasing the *para* crystalline order¹¹), in the higher concentration no strongly periodic potential valleys exist due to the presence of aPS molecules. When crystallizing from a relaxed melt the separation of the molecules is obtained by a reptational motion¹² of the molecules, in the highly stretched conformation this type of motion in lateral direction seems to be hindered as a similar crystallization rate as from the relaxed undercooled melt is not observed.

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