DISCUSSION AND CONCLUSIONS

Two distinct morphological units are produced in the Instron strands: the highly crystalline ribbons in the inner core and the less ordered 3000 Å diameter fibers of the outer sheath. Similar units have been observed by Pennings and Kiel[7] in the fibrous structures crystallized under the influence of shear in a dilute solution. They, too, described the morphological entities as being either ribbons or fibers having a lamellar overgrowth. The 3000 Å fibers may well be the melt-crystallized analog of the fibers grown from dilute solution by Pennings and Kiel.

Fibrous morphologies are not uncommon in crystalline polymers, especially if the polymer chain backbone is too stiff to accommodate chain folding. O'Leary and Geil[17] have described the fibrous textures in crystalline polytetrafluoroethylene in a manner similar to that used to define the polyethylene structure of this work. Crystal[18] has also described a fibrous morphology for crystalline poly-*N*-vinyl-carbazole, an apparently stiff molecule containing bulky pendant groups which inhibit free rotation about the polymer backbone. Because chain folding cannot be accommodated in poly-*N*-vinylcarbazole, this polymer apparently crystallizes into a fibrous structure containing weak interfiber bonds. While *c*-axis orientations were noted in these references, sharp-spot electron diffraction patterns were not reported.

Additional evidence for the existence of two distinct morphological units in the Instron strands was found in the fusion curves obtained from the melting of the strands in the Perkin–Elmer differential scanning calorimeter (DSC), Model 1-b. The DSC traces for two strands crystallized with the Instron procedure at 132°C are shown in Figure 11. It was noted that these strands appeared to be similar in structure to those examined in the above micrographs (crystallization at 136°C). One of the strands was exposed to 25 Mrad of irradiation in order to suppress reorganization during melting.[19,20] Both strands were found to have relatively high peak-value melting points, consistent with the presence of extended-chain crystals.[4] Furthermore, the irradiated strand showed a multipeak fusion curve indicative of two crystalline forms. A possible explanation for such behavior would be that the more perfect inner-core ribbon structure melted at the higher peak temperature, and the less ordered outer-sheath structure, containing chain-folded lamellae and defects, melted at the lower peak temperature. The primary effect of the radiation has been to resolve the single fusion curve, corresponding to the unirradiated sample, into low and high melting peaks for the irradiated sample. These observations are consistent with the hypothesis that the structure in the inner core of the strand appears to be dominated by an extended-chain crystalline structure, while that of the outer sheath is dominated by epitaxial chain-folded lamellae.

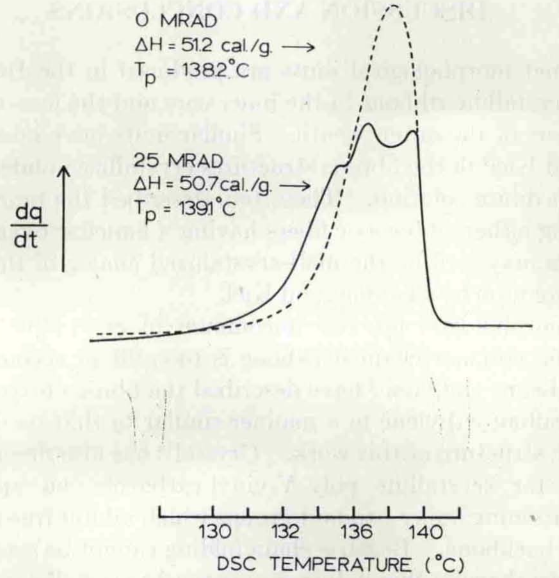

Fig. 11. Differential scanning calorimeter trace showing the effect of irradiation on the melting behavior of a transparent strand, produced at 132°C with a capillary of diameter 0.0762 cm and 1.0 cm/min plunger velocity.

The inner-core ribbon structure was the most perfect of the two crystalline units defined in this study. Well developed single-crystal electron diffraction patterns obtained from ribbons indicate that they are made up of extended-chain crystals. The eighth-order reflection along the *c* axis has been detected (see Fig. 10) by using a very small aperture achieved with the Phillips EM200 knife-type diffraction aperture. In order to obtain such an electron diffraction pattern, the crystalline order must have been in register over a considerable portion of the aperture opening. Otherwise, a more polycrystalline pattern would be expected. Note that a lamellar structure connected by tie molecules, such as the model proposed by Peterlin for drawn polyethylene,[15] would not result in sharp diffraction spots for the (0*kl*) planes over a 5000 Å length of the fiber. In the Peterlin model, the lamellae that stack together to form a fibril would be free to rotate around the *c* axis, thereby prohibiting the formation of coherent sets of diffraction planes for all except the (00*l*) planes. Figures 9 and 10 show the presence of other sets of diffraction planes. Only a well developed extended-chain crystal model which maintains a high degree of order and register across the aperture opening could account for the observed diffraction spots from the inner-core fibers.

The formation of an extended-chain structure by crystallizing from the bulk polyethylene is particularly significant from the aspect of improved mechanical properties. In addition to the transparency of the strands, the modulus of the central core containing the extended-chain crystal structure may well be extremely high in the direction of the strand length. If defect-