polymer reports

X-ray diffraction and electron diffraction studies melt extruded poly(N-vinyl carbazole)

P. R. Sundararajan* and J. Zamin
Xerox Research Centre of Canada, 2480 Dunwin Drive, Mississauga, Ontario L5L 1J9, Canada

The orientation in films of poly(N-vinyl carbazole) (PVK) prepared by melt extrusion was recently reported by Penwell and Prest[1]. It was observed that films of high molecular weight PVK, extruded at stresses exceeding 10^6 dyn cm^{-2}, produced highly ordered one-dimensional structure, as confirmed by X-ray diffraction and infrared dichroism. From the low-angle light scattering patterns, it was concluded that the film possessed rod-like morphology. Further studies on the melt-extruded films, using X-ray and electron diffraction, are reported here which redefined the base-plane dimensions of the unit cell and show that the lateral order produced during extrusion is comparable to that observed earlier[2] with single crystals of PVK.

The experimental conditions for the preparation of the films were described previously[1]. Some of the films were further annealed under slight tension at 260°C for 8 h. The X-ray patterns were recorded using a flat-plate camera *in vacuo*, with the beam normal to the plane of the film.

* Address correspondence to this author

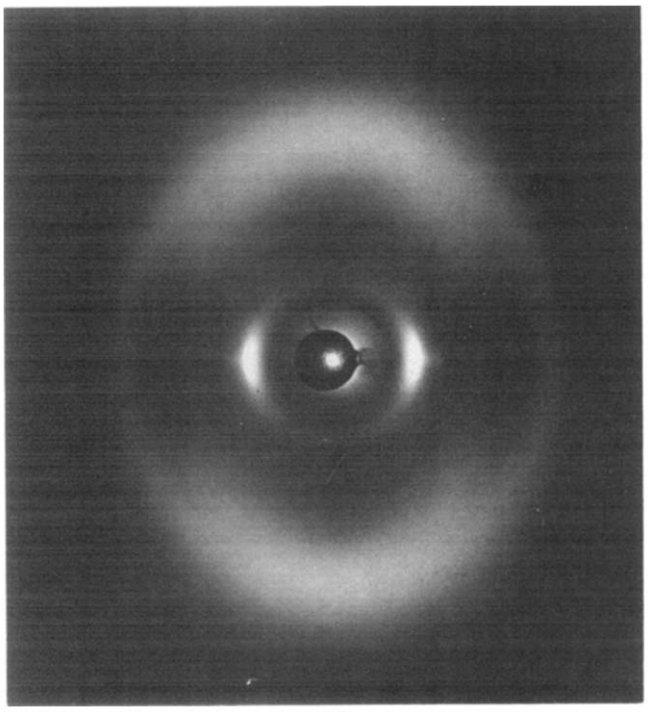

Figure 1 X-ray diffraction pattern of PVK film with the beam normal to the surface of the sample. The axis of the film is vertical

The electron micrographs and diffraction patterns were recorded using a Philips EM400 scanning–transmission electron microscope. The films were embedded in epoxy and microtomed to a thickness of 1 000–1 500 Å, in such a way that the patterns could be recorded (a) with the beam parallel to the surface of the film and normal to the direction of extrusion, and (b) with the beam parallel to the surface as well as the direction of extrusion of the film. These two modes of recording the patterns and the configuration used for X-ray diffraction are conventionally known as 'edge', 'end' and 'through' views, respectively[3].

The X-ray diffraction pattern for the annealed sample is shown in *Figure 1*. The film without the annealing treatment showed a similar pattern, although the reflections were slightly broader. In addition to the sharp and intense reflection corresponding to a spacing of 10.8 Å, faint but well-defined reflections are observed on the equator, with spacings of 21.5, 8.44 and 6.15 Å.

Crystal[2] indexed the 10.8 and 6.15 Å reflections as $\{01\bar{1}0\}$ and $\{11\bar{2}0\}$, using a hexagonal unit cell proposed by Kimura *et al.*[4], with $a_1 = a_2 = a_3 = 12.3$ Å. The 21.5 and 8.44 Å reflections, however, were not observed in previous studies on PVK[2,4,5] and cannot be indexed using the hexagonal base plane dimensions given above. On the other hand, an orthorhombic unit cell, with base plane dimensions a = 21.6 Å and b = 12.5 Å can be used to index the 21.5 and 8.44 Å reflections as (100) and (210). The 10.8 and 6.15 Å reflections then correspond to indices (200) and (020) respectively. A reflection at 9.2 Å is not reproducible. Its origin is uncertain and hence is not considered here. Thus, it would seem that the unit cell of PVK is orthorhombic, with pseudohexagonal packing of the chains. The schematic of the unit cell is shown in *Figure 2*.

A blob of intensity is seen in *Figure 1* corresponding to what might be termed the first layer line. The layer line, however, is not well developed due to the lack of order along the chain direction[4,5]. This is similar to the case of polyacrylonitrile[6].

The electron micrograph of the edge view of the PVK film is shown in *Figure 3(a)*, and the corresponding diffraction pattern in *Figure 3(b)*. The orientation of the fibrils in *Figure 3(a)* is evident. The diffraction pattern in *Figure 3(b)* shows the intense equatorial reflection with a spacing of 10.8 Å, as in the through view pattern given in *Figure 1*. The similarity of the patterns in the through view and edge view shows that a high degree of orientation, through the depth of the film, is created parallel to the draw direction,

0032–3861/79/121567–02$02.00

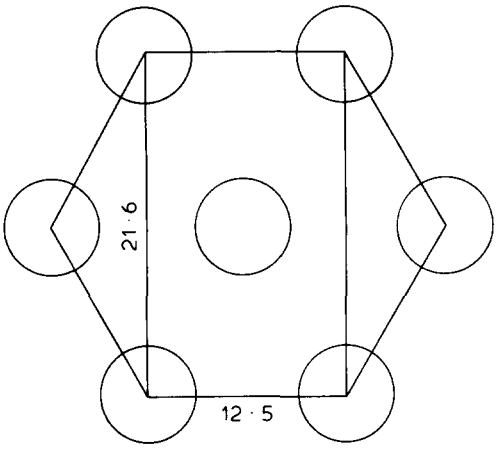

Figure 2 Schematic representation of the base plane of the unit cell of PVK, showing the relationship between the hexagonal and orthorhombic cells

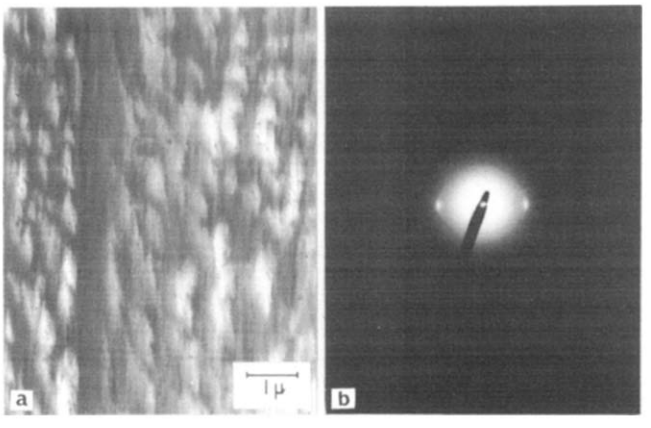

Figure 3 The edge view of the PVK film (a) and the corresponding diffraction pattern (b)

due to the high stress used for extrusion.

The end view of the PVK film and its diffraction pattern are shown in *Figures 4(a)* and *4(b)*, respectively. The former is essentially the cross section of the film. The pseudo-hexagonal symmetry exhibited in the diffraction pattern (*Figure 4b*) is striking. The spacing of the reflection corresponds to 10.8 Å. This pattern is identical to that obtained[2] from lamellar single crystals of PVK, although the reflections are slightly arced. This shows that the lateral order developed during the melt extrusion under high stress is comparable to that in the lamellar single crystals.

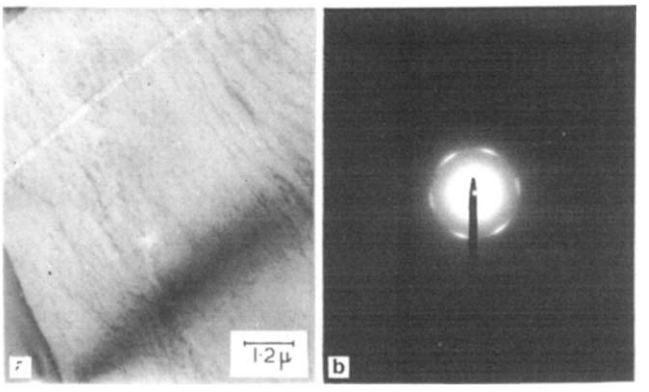

Figure 4 The end view (cross section) of the PVK film (a) and the corresponding diffraction pattern (b)

Acknowledgement

The authors are indebted to Drs. R. C. Penwell and W. Prest, Jr., for providing the melt-extruded PVK films used in this study. The X-ray patterns were recorded by Mr. L. Campbell.

References

1 Penwell, R. C. and Prest, W. M. *Polymer* 1978, **19**, 537
2 Crystal, R. G. *Macromolecules* 1971, **4**, 379
3 Statton, W. O. and Godard, G. M. *J. Appl. Phys.* 1957, **28**, 1111
4 Kimura, A., Yoshimoto, S., Akana, Y., Hirata, H., Kusabayashi, S., Mikawa, H. and Kasai, N. *J. Polym. Sci., Part A* 1970, **8**, 643
5 Griffiths, C. H. *J. Polym. Sci., Polym. Phys. Ed.* 1975, **13**, 1167
6 Bohn, C. R., Schaefgen, J. R. and Statton, W. O. *J. Polym. Sci.* 1961, **55**, 531