The question of whether specific $ABCO_6$ phases are actually compounds was considered by Blasse [2]. As regards the four tantalate compositions studied here, three immediately qualify as ternary oxide compounds since the individual oxide components to not exhibit similar structures – $AlHfTaO_6$, $YTiTaO_6$, and $YHfTaO_6$. Since $AlTiTaO_6$ has the cassiterite structure, it could be considered as a solid solution because TiO_2 (rutile) and TaO_2 have the same tetragonal structure; thus, Al^{3+} could be considered as substituting into this structure.

References

1. C. E. HOLCOMBE, M. K. MORROW, D. D. SMITH and D. A. CARPENTER, Survey Study of Low-Expanding, High Melting, Mixed Oxides, Y-1913, Union Carbide Corporation-Nuclear Division, Oak Ridge, Tennessee, February (1974).
2. G. BLASSE, *Mat. Res. Bull.* **2** (1967) 497.
3. *Idem, J. Inorg. Nucl. Chem.* **28** (1966) 1122.
4. D. E. WILLIAMS, Technical Report IS-1052, Ames, Iowa (1964).
5. C. E. HOLCOMBE, Determination of the Crystal System and Lattice Parameters of Previously Unreported Compounds, Y-1687, Union Carbide Corporation-Nuclear Division, Oak Ridge, Tennessee, September (1969).
6. O. W. HERMANN and A. L. COFFEY, INDOX Code for Orthorhombic Indexing, unpublished computer code at Oak Ridge National Laboratory.
7. R. W. G. WYCKOFF, "Crystal Structures" (Interscience, New York, 1965).

Received 28 November 1978
and accepted 5 January 1979.

C. E. HOLCOMBE
Development Division, Oak Ridge Y-12 Plant,
Union Carbide Corporation, Nuclear Division,
Oak Ridge, Tennessee, USA

A new method for the preparation of high modulus thermoplastic films

In the last decade much effort has been made to obtain fibrous crystals of polymers with ultrahigh tensile strength and tensile modulus [1–9]. Also, a great deal of work has been done to understand the morphology and the crystallization mechanisms of fibres prepared by strain induced crystallization [10–14]. Theoretical considerations [15–19] have shown that longitudinal flow gradients of solutions or melts are the most important factors involved in extending the polymer molecules during flow processes. Therefore, most of the methods for crystallization of fibres are necessarily based on this principle. In industrial methods longitudinal flow gradients are usually achieved by high spinning rates. It is the intention of this paper to report a method which yields an extremely high longitudinal flow gradient ($\epsilon = 4 \times 10^4 \text{ sec}^{-1}$) by relatively low take up speed ($V_1 = 4 \text{ cm sec}^{-1}$) and high quenching rate in a small flow region during the preparation process. It will be shown that the flow gradient obtained by our method is sufficient to induce fibrous crystallization to a large volume fraction. The method reported here is of general applicability to semicrystalline polymers and offers easy means for the preparation of polymeric materials with high tensile modulus and strength.

For preparing the films, polymer solutions (~ 0.3 to 1%) are prepared in suitable solvents. A glass slide having a smooth surface is placed on a heating plate and allowed to attain the particular preparation temperature. For polyethylene (Lupolen 5261 Z, MW = 3×10^5) the solvent used is xylene, and the preparation temperature ranges from 122° C to 130° C. Usually, the chosen temperature for the film preparation is just above the highest crystallization temperature of the relaxed undercooled melt. In order to avoid temperature fluctuations, the heating plate is placed in a specially prepared small cabinet. The solution is dispersed uniformly over the glass slide, and the solvent is allowed to evaporate. The resulting thin molten polymer film (thickness about $\leqslant 1\,\mu$m) is taken off from one end of the glass slide with the help of a glass rod coated with the respective polymer and simultaneously wound onto a glass slide for supporting the thin oriented film (Fig. 1).

For transmission electron microscopic (TEM) investigations, the oriented film is cut into pieces and mounted onto copper grids. The microscope used is a JEOL JEM 200A operated at 100 kV.

The deformation ratio is assessed using the gold

0022–2461/79/092260–05 $02.50/0

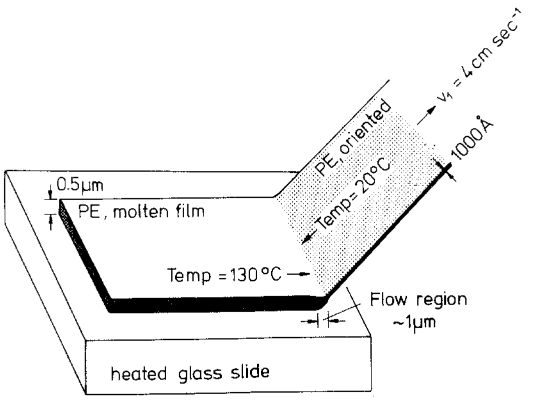

Figure 1 Schematic diagram for the method of preparing polyethylene oriented films.

decoration technique [20]. With selective preparation of the flow region (Fig. 1), the longitudinal flow gradient (dv_x/dx) is estimated by counting gold particles per unit length within the flow region. For tensile and DSC measurements, multilayered films are used having a thickness of approximately 10 μm. The tensile tester utilized is a conventional Instron machine and the DSC used is a Perkin Elmer II.

Apparently, there are two experimental ways for obtaining high longitudinal flow gradients, dv_x/dx;

(i) Using exceedingly high take up velocities, or

(ii) Building up the flow within an extremely short distance.

Our method is based on the second experimental variant in which high longitudinal flow gradients can be achieved by orienting the melt within an extremely short distance. Experimental observations suggest that the chosen spinning temperature just above the highest crystallization temperature of the relaxed melt provides a rapid crystallization rate within the flow region and avoids the relaxation of oriented polymer molecules. In order to keep the flow region small, it is necessary to use very thin films. Usually, the molten thin films of polymers adhere firmly to the glass substrate and hence provide the necessary condition for high deformation within a short distance. In polyethylene, it is observed experimentally that the flow region has a width which falls in the range of the molten layer thickness (Fig. 2). From the electron micrograph (Fig. 2), the abrupt change at the deformation boundary is noted. If one assumes a linear change in longitudinal velocity of the melt, then with a deformation zone of 1 μm and a take-up speed of 4 cm sec^{-1}, a longitudinal flow gradient of 4×10^4 sec^{-1} is obtained. This result is in agreement with a draw ratio, $\lambda = 5$, which is determined from the gold decoration technique for polyethylene. This flow gradient, even with the molecules spending a short time within the flow region [19], is sufficient to induce the high extension of polymer molecules. Depending on the preparation temperature, the highly oriented molecules become crystallized.

The morphology of polyethylene fibres prepared by the above discussed method is investi-

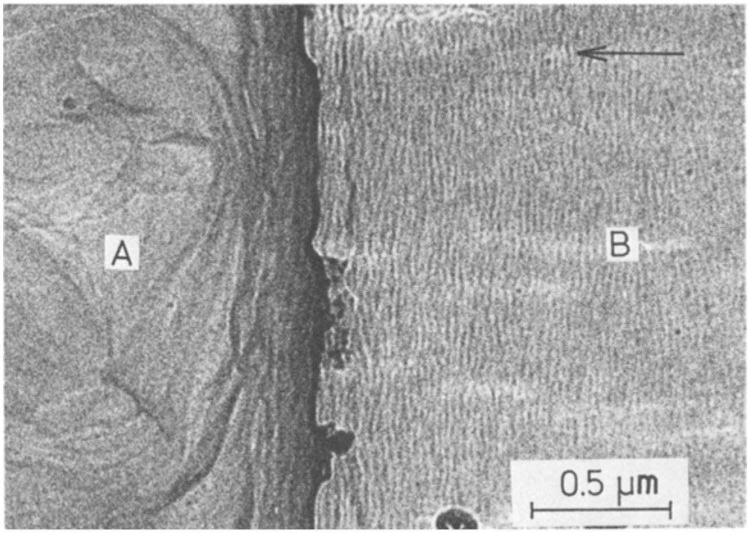

Figure 2 The flow region in the case of polyethylene. Part "A" is unoriented molten film while Part "B" is the oriented film. The arrow indicates the flow direction.

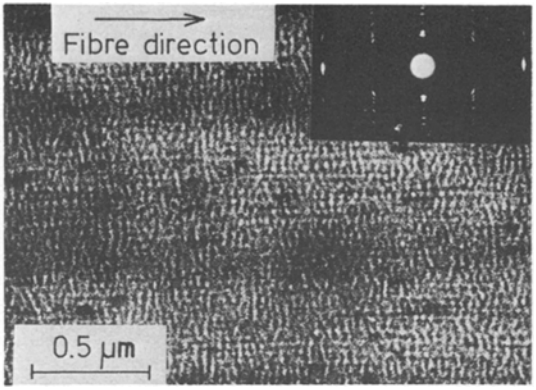

Figure 3 Electron micrograph of polyethylene fibrous crystals at room temperature indicating the lamellar overgrowth over the needle crystals.

gated by TEM. In fact, the fibrous product is in the form of thin films (~ 2000 Å thick and several cm wide) and can be utilized without any further treatment for the microscopic investigations. It is confirmed that any part of a film is representative of the whole preparation conditions. Fig. 3 shows the electron micrograph of such an oriented polyethylene film at room temperature. A "shish-kebab" like structure can be seen. The defocus image contrast electron micrograph (Fig. 4) of a polyethylene film photographed at 145° C shows the presence of long needle like crystals (shishs) more clearly with the kebabs being molten. The electron diffraction pattern inserted indicates a high orientation of molecules within the needle like crystals and a considerable volume fraction of those crystals. Fig. 5 shows a dark-field electron micrograph taken under the same conditions as in Fig. 4. Again long needle-like single crystals may be seen. The dark-field contrast suggests a periodic array of lattice disturbances along the needle like crystals.

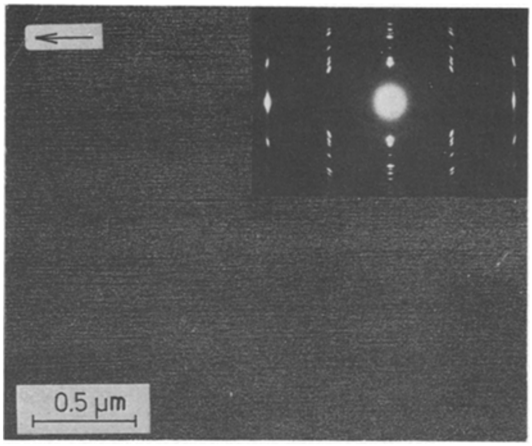

Figure 4 Defocus image contrast electron micrograph of an oriented polyethylene film at 145° C.

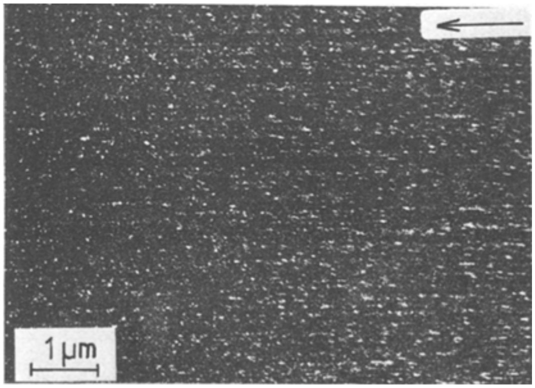

Figure 5 Dark-field electron micrograph of the needle crystals below its melting temperature (g = ⟨1 1 0⟩).

Below 124° C, polyethylene needle crystals are found to be always associated with lamellar overgrowth. It is noted that in all ranges of the preparation temperature of polyethylene films (122° C to 130° C) the lamellar overgrowth cannot be fully avoided. Also it is difficult to remove the lamellar overgrowth completely from the needle-like crystals by washing with xylene. When the film is heated in the hot stage of the electron microscope to 140° C, the stacks of lamellae (Fig. 3) disappear and only the needle crystals (Fig. 4) remain. On cooling the specimen to room temperature, the lamellar overgrowth reappears. The lamellar growth onto the needle crystals keeps the initial high orientation of molecules unchanged. The morphological results are confirmed by DSC measurements (Fig. 6). The melting peak at 130° C corresponds to melting of lamellar crystals while the broad high temperature shoulder of the DSC trace reflects the melting range of the needle-like extended chain crystals which are thermally stable up to 148° C.

Tensile test measurements are carried out using single layers as well as multilayered polyethylene films. The multilayers of polyethylene films are "sintered" by pressing the layers at a temperature just below the first melting peak of DSC trace.

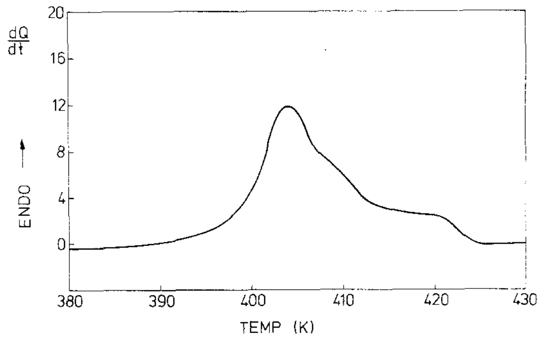

Figure 6 DSC scan of polyethylene oriented films taken with fixed ends. Note the endothermic tail at 148° C. The heating rate is 5° C min^{-1}.

Stress–strain curves for both the types of samples are the same and give a tensile modulus of 1.5×10^{10} N m^{-2} at liquid nitrogen temperature (−196° C) and a breaking strength of 3×10^{8} N m^{-2}. Similar results concerning the morphology, thermal and mechanical data have also been obtained for many other polymers. It should be noted that as an exception oriented films of poly(1-butene) do not show (Figs. 7a and b) any lamellar overgrowth at any temperature of preparation, ranging from 90 to 130° C. Dark-field electron microscopic results confirm the presence of only needle-like crystals. Detailed studies of the structure of the needle-like crystals and its correlation to mechanical properties especially with respect to their relatively low elastic moduli (compared with the ultrahigh modulus fibres) and crystalline perfection will be published elsewhere.

Acknowledgements

The authors gratefully acknowledge the support of this work by the "Deutsche Forschungsgemeinschaft" and "Alexander von Humboldt-Stiftung". One of us (Dr Gohil) is thankful to the Sardar Patel University, India, for granting the study leave.

References

1. A. KELLER and M. R. MACKLEY, *Polymer* **14** (1973) 16.
2. A. J. PENNINGS and A. M. KIEL, *J. Polym. Sci.* **C16** (1967) 1799.
3. E. H. ANDREWS, *Angew. Chem. Intern. Ed.* **13** (1974) 113.
4. A. KELLER and M. J. MACHIN, *J. Macromol. Sci.* **B1** (1967) 41.

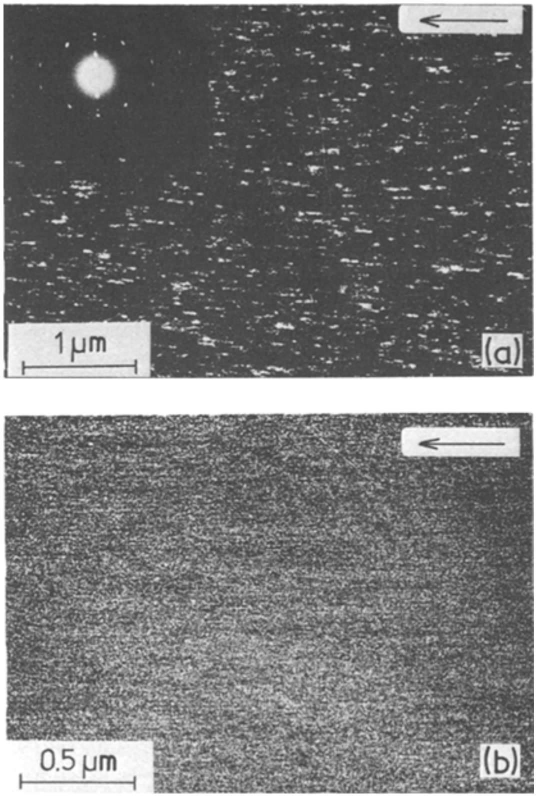

Figure 7 (a) Dark-field electron micrograph of an oriented poly (1-butene) film. (b) Defocus contrast electron micrograph of an oriented poly (1-butene) film.

5. A. J. McHUGH, *J. Appl. Polym. Sci.* **19** (1975) 125.
6. A. J. McHUGH and J. M. SCHULTZ, *Kolloid-Z.u.Z. Polymere* **251** (1973) 193.
7. G. S. Y. YEH, *Polym. Eng. Sci.* **16** (1976) 138.
8. A. PETERLIN, *Polym. Eng. Sci.* **16** (1976) 126.
9. J. H. SOUTHERN and R. S. PORTER, *J. Macromol. Sci.* **B4** (1970) 541.
10. M. J. HILL and A. KELLER, *J. Macromol. Sci.* **B5** (1971) 591.
11. D. LUCH and G. S. Y. YEH, *J. Appl. Phys.* **43** (1972) 4326.
12. A. J. PENNINGS, J. M. A. A.VAN DER MARK, and A. M. KIEL *Kolloid.-Z.u.Z. Polymere* **237** (1970) 336.
13. J. A. ODELL, D. T. GRUBB and A. KELLER, *Polymer* **19** (1978) 617.
14. J. PETERMANN, M. MILES and H. GLEITER, *J. Polym. Sci. Phys.*, in press.
15. A. PETERLIN, *Pure and Appl. Chem.* **12** (1966) 563.
16. F. C. FRANK, A. KELLER and M. R. MACKLEY, *Polymer* **12** (1971) 467.
17. M. R. MACKLEY and A. KELLER, *Phil. Trans. R. Soc. Lond. A* **278** (1975) 29.

18. R. J. GAYLORD, *J. Polym. Sci. Phys.* **14** (1976) 1827.
19. D. G. CROWLEY, F. C. FRANK, M. R. MACKLEY and R. S. STEPHENSON, *J. Polymer Sci. Phys.* **14** (1976) 1111.
20. P. J. HOLDWORTH and A. KELLER, *J. Polym. Sci.* **A-26** (1968) 707.

Received 5 December 1978
and accepted 21 February 1979.

J. PETERMANN
R. M. GOHIL
Werkstoffphysik und Werkstofftechnologie,
Universität des Saarlandes,
D-6600 Saarbrücken, West Germany

Discussion of "Effect of environment on stability of cracking in brittle polymers"

In a recent communication, Hakeem and Phillips [1] have commented on two very interesting problems concerning the effect of environment on stability of cracking in brittle polymers. The first problem deals with stick–slip crack propagation in epoxy resins. Because of the close resemblance between their experimental observations on cracking of PMMA in methanol and those by Yamini and Young [2] on epoxy resins, they suggested that the yet unresolved cause of crack instability in epoxy resins might be just an environmental effect. In replying, however, Yamini and Young [3] based on their most recent experimental findings felt that crack propagation in epoxy resins was principally controlled by the structure of the material and that any environmental effect was negligible. We do not wish to add anything further here at present but agree that much more work is needed to pin down the exact mechanisms of crack instability in epoxy resins. Although it has been suggested by Gledhill *et al.* [4] that the decrease of the specific work of fracture, R, with crack speed $\dot{a}$; i.e. $\mathrm{d}R/\mathrm{d}\dot{a}$ negative [5], is not the cause but rather the consequence of stick–slip cracking, from the crack mechanics viewpoint, we wish to stress that $\mathrm{d}R/\mathrm{d}\dot{a}$ or $\mathrm{d}R/\mathrm{d}a$ negative is a neccessary condition for crack instability [5, 6]. In conclusion, Yamini and Young mention that polystyrene is an example where unstable cracking occurs in the absence of an environmental effect. While this is so, the implication that similar processes are taking place at the crack tip in epoxy resins as in polystyrene to give stick–slip fracture seems questionable. Our initial experience [7] with double torsion polystyrene specimens pre-notched in the "normal" way with a razor blade show that in the cross-head speed range of 0.05 mm min^{-1} to 50 mm min^{-1} in the Instron machine the transition speed between stable continuous and unstable stick–slip cracking increases with increasing temperature (e.g. 0.5, 2 and 10 mm min^{-1} for 40, 60 and 80° C respectively) and that at a given temperature stable cracking occurs below this transition cross-head speed and stick–slip fracture occurs above. This latter behaviour is opposite to that in epoxy resins and the reason is not fully understood. A better example which gives stick–slip fracture in the absence of an environmental effect is TPX (poly(4-methyl-*l*-pentane)) [6]. The cause of instability has not been studied in details yet but it is probably due to crack tip blunting as a result of its very large fracture toughness value. A parallel study on TPX may thus give new insight into the mechanisms of fracture instability in epoxy resins.

The second problem that Hakeem and Phillips discussed concerns the apparently different fracture behaviour between PMMA–methanol and PMMA–ethanol systems. They found that the crack initiation (K_i) values of PMMA at 1 and 20 mm min^{-1} cross-head rates in methanol were always greater than the corresponding K_c values in air and that the K_i value was larger for the slower cross-head speed. However for the PMMA–ethanol experiments reported in [8], K_i was found to be less than K_c in air. They suggested that therefore it was possible that methanol was anomalous in its behaviour towards PMMA and that a five-fold increase in the corss-head rate of the Instron machine could cause an inversion from $K_i < K_c$ to $K_i > K_c$ (since K_i increased very rapidly with cross-head speed [8]). We have just finished an experimental investigation on the environmental

0022-2461/79/092264–04 $02.40/0