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Shish Kebabs
An Experimental Preparation

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With 3 figures

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In this note a new method for preparing shish kebab type fibrous crystals of polyethylene is reported. In addition to the interesting hydrodynamic aspects of the method, the samples produced have been found to be highly suitable for direct observation in the electron microscope avoiding previous difficulties and uncertainties associated with mechanical or ultrasonic stripping of the sample.

The method simply entails slowly rotating a fine gauze in a polyethylene solution maintained at a temperature below the dissolution temperature (112 °C) and above that at which single crystals would grow in the quiescent solution (90 °C). In an experiment a solution was made containing 1.5% by weight polyethylene (Marlex 6002) in xylene. The solution was introduced into a cylindrical vessel and maintained at 106 °C. A gauze, 2 sq. cm. in area, made from stainless steel wires 0.02 mm thickness and 0.1 mm spacing was rotated for five minutes at 20 rpm from an arm 1 cm. from the rod axis. It was noted that at this stirrer speed the flow was laminar throughout the vessel. Subsequent washing of the gauze was carried out by progressive dilution and removal of solution ensuring that the gauze remained immersed in hot solution until the concentration of polymer was below 10^{-4} grms/cc. To assist washing the gauze was rotated slowly at 2 rpm. After removal from the solution the gauze was cut into sections of convenient size for direct observation in the electron microscope. Figs. 1 and 2 are electron micrographs of the gauze where a network of finely dispersed shish kebab type crystals are clearly visible.

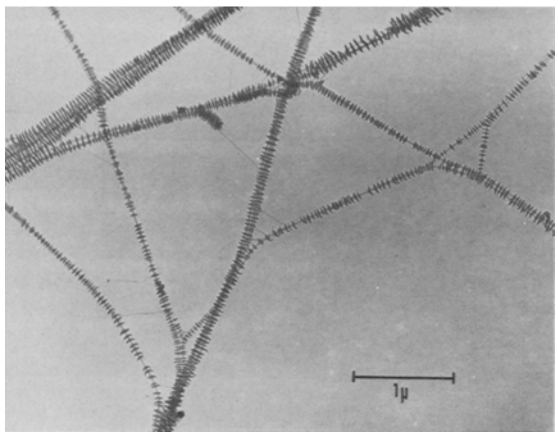

Fig. 1. Electron micrograph of shish kebabs crystallized and washed at $T = 106$ °C

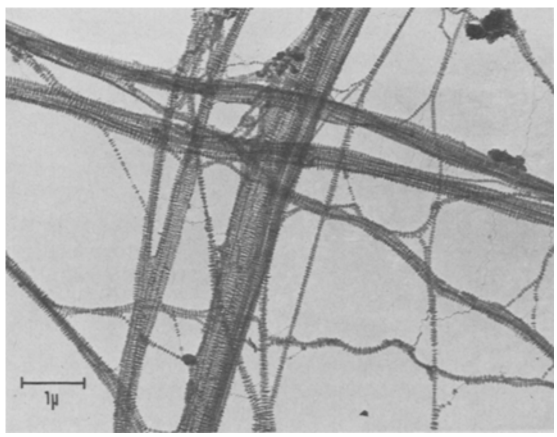

Fig. 2. Electron micrograph of shish kebabs crystallized and washed at $T = 106$ °C

Two aspects of the experiment will be considered, firstly, the hydrodynamics involved in the nucleation and growth of the

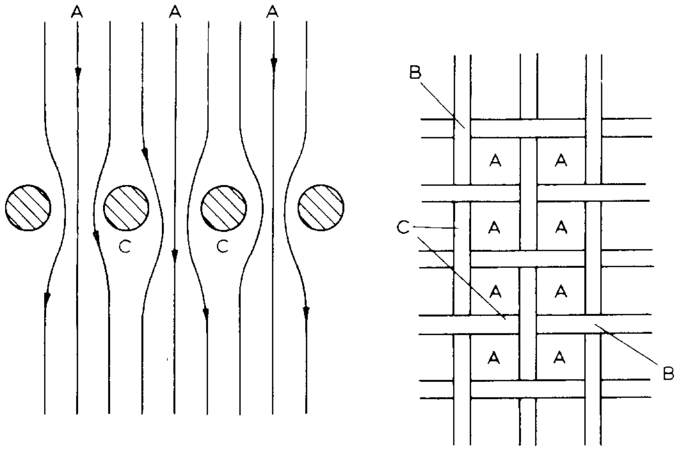

Fig. 3. Diagrammatic representation of laminar flow through a wire gauze

fibres and secondly, the morphological features observed from the electron micrographs.

The experiment is of hydrodynamic interest because both nucleation and growth of the fibres occur in laminar flow, in contrast to the usual production of shish kebabs which involve turbulent flow (1). For nucleation of shish kebabs to occur in laminar flow it has been concluded (2, 3) that a longitudinal, as opposed to transverse velocity gradient is necessary. An examination of the laminar flow between the gauze wire, shown schematically in fig. 3 shows that areas of longitudinal velocity gradients do exist for this flow system. In the regions marked A in the diagram the flow will be that of uniaxial extension upstream of the gauze and uniaxial compression downstream of the gauze; similarly in regions marked B the flow will be uniaxial compression upstream and uniaxial extension downstream of the gauze. Areas marked C will be areas of pure shear. One or a combination of these sites must offer suitable conditions for shish kebab nucleation.

It is not certain whether fibres are attached to the gauze at nucleation or whether the fibres are nucleated without attachment and 'caught' by the gauze on subsequent rotations in the solution; however, fibres eventually do become attached to the gauze; subsequent growth then appears to continue due to the uniform streaming of solution past the fibres which are anchored with at least one of their ends freely trailing in the solution; this can be observed if crystallization times are increased and the crystal deposit becomes sufficiently large to be seen visually. Mechanisms to explain the nucleation of the chain extended backbone of the shish kebab in the presence of longitudinal velocity gradients have been previously proposed (2, 3, 4). Also mechanisms by which shish kebabs can grow when anchored in a uniform stream flow have been examined in the companion paper to this one (5).

Concerning the morphological features of the shish kebabs. The micrographs obtained from the preparation bear a striking resemblance to the higher magnificance micrographs of *Jamet* and *Perret* (6) where their samples were prepared by refluxing hot solvent over undissolved blobs of polymer supported on a carbon coated electron microscope grid. Morphological features which are common to both preparations are; (A) the existence of longitudinal central threads of diameter about 160 Å. (B) Intrinsic regularly spaced lamellar platelets of thickness ~250 Å. (C) Many examples of shish kebabs containing more than one equispaced longitudinal backbone thread can be seen; in particular fig. 2 shows an area where many threads appear to have associated giving rise to a resultant impression of a transverse lamellar structure where the longitudinal threads are obscured.

One feature which is not common to both preparations but is seen frequently in figs. 1 and 2 is that of structureless fibres of diameter ~180 Å which bridge neighbouring shish kebabs and appear to originate from the side faces, of the lamellar platelets, in some cases these fibres are observed to run along the edge of the lamellar platelets for some distance. Also they can appear buckled as seen clearly in fig. 2, which contrasts noticeably with the backbone fibres. This latter observation illustrates clearly that the structure of the interconnecting fibres must be intrinsically different to that of the backbone fibres. The rigidity of the backbone fibres is consistent with the belief that it is of a predominantly chain extended nature whilst the buckling of the interconnecting fibres, presumably caused by electron beam damage would be consistent with that of a predominantly chain folded fibre. It has been reported before (7) that the interconnecting fibres bear a close resemblance to fibres which can be pulled out from single crystals.

To conclude, the method reported offers

evidence of a simple and convenient method for studying both hydrodynamic and morphological features involved in shish kebab formation where major parameters such as temperature and flow field are well characterized and sample preparation for electron microscopy is minimized. In addition the experimental observation that crystal growth of anchored shish kebabs is observed to take place in a region of essentially uniform flow, supports the conclusions of the companion paper to this one (5).

Summary

The method of slowly rotating a fine gauze in a polymer solution has been found to produce both nucleation and growth facilities for shish kebab type crystals of polyethylene. When removed from the solution the shish kebabs form a finely dispersed network on the gauze suitable for direct observation in the electron microscope. Both hydrodynamic and morphological features of the experiment are examined.

Zusammenfassung

Rotation eines leichten Drahtgeflechts in einer Polymer-Lösung führt sowohl zur Keimbildung wie zum Wachstum von Polyäthylen-Kristallen vom Typ „shish kebab". Die „shish kebabs" bilden ein fein verteiltes Netzwerk auf dem Gazegeflecht, das direkte Beobachtungen im Elektronenmikroskop erlaubt. Sowohl hydrodynamische als auch morphologische Aspekte des Experiments werden untersucht.

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