out on ion-beam thinned samples about 10 h after quenching, confirmed the main conclusions drawn from the X-ray small-angle analysis. In Fig. 2a, a uniform distribution of precipitates with Moiré patterns are present, as shown in greater detail in Fig. 2b. The appearance of the Moiré patterns and the invariance, by tilting the samples, of the contrast round the precipitates (i.e. there is not the typical elastic deformation of the coherent precipitate), lead us to interpret the precipitates as incoherent ones [8-10]. Moreover, micrographs and electron diffraction patterns show the two-dimensional nature of the precipitates. We emphasize that the thin platelets observed are equilibrium precipitates. In fact there is no evolution in their shape and distribution. At this stage the initial coherent structure has been transformed to another which is no longer coherent but which has a precise crystallographic orientation, thus producing the observed Moiré pattern.

On the basis of the electron microscopy observations, we have performed some preliminary theoretical calculations of small-angle X-ray scattering curves assuming the zones are disc shaped. By comparison with the experimental results we found that the mean "effective" radius of the Cd-rich platelets was about 20 Å. The interference maxima observed in the first ageing stages may be interpreted as interparticle effects due to a regular two-dimensional array ("superlattice") of the platelets themselves.

In conclusion we deduce that Guinier-Preston zones are present in Zn–Cd alloys. However, in order to have a complete characterization of the segregation phenomenon, we intend to correlate the lattice parameter measurements and the low-angle scattering with changes in mechanical and physical properties and in the electron micrographs and electron diffraction patterns of the specimen during the whole ageing sequence. These data are now being collected and will be reported in a following paper.

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GIANCARLO CELOTTI
PIER GIORGIO MERLI
Laboratorio di Chimica e Tecnologia dei
Materiali e dei Componenti per l'Elettronica
del CNR, Bologna, Italy
GIULIANO MARTINELLI
LUIGI PASSARI
Istitut di Fisica dell'Universitá,
Ferrara, Italy

Hydrodynamically-induced crystallization from an homogeneous solution of two polymers

Crystal nucleation is readily induced by mechanical agitation in melts or solutions of both low molecular weight and high polymeric substances. Under such conditions crystallization generally occurs at lower supercoolings than are otherwise necessary. Hydrodynamically-induced crystallization from polymer solutions was first extensively reported by Pennings [1] for high density polyethylene. Many studies have followed that report, the majority of the research carried out on polyethylene [2-8] although work has also been published on polypropylene [8], polyoxymethylene [9], isotactic polystyrene [10] and polyethylene oxide [11]. The general conclusion drawn is that the fibrillar crystals so produced have a "shish-kebab" morphology consisting of folded-chain lamellae overgrowing an extended-chain fibrillar or "row" nucleus.

It is known [12] from studies of crystallization from solution of low molecular weight materials, that the addition of a second solute

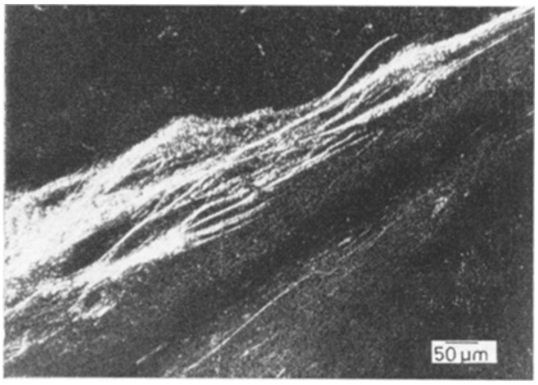

Figure 1 Optical micrograph of part of a fibrillar bundle.

often encourages the nucleation and growth of crystalline species. No such observation has been reported for the growth of polymer crystals from a solution containing a second polymeric solute. The reason for this is simply that even dilute ternary solutions cannot normally be made [13], most attempts resulting in two incompatible solutions containing a common solvent. One apparent exception [13] to this is the system (polyethylene–atactic polypropylene–diphenyl ether) where a quasi-ternary results at elevated temperatures.

A polymer which can be blended with many others, both in the melt and in solution [14, 15] is poly(ϵ-caprolactone) which has the formula $[-(CH_2)_5CO_2-]_n$. Presumably this ability to blend is a result both of its chemical structure and of its relatively low molecular weight (up to 80 000).

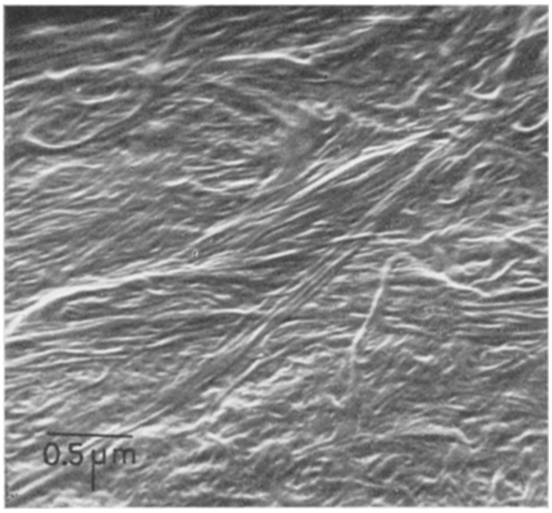

Figure 2 Scanning electron micrograph of the surface of a bundle obtained with Au–Pa shadowing.

In the process of solution blending of this polymer with gutta percha (*trans*-polyisoprene) in benzene at room temperature, a polymeric material was observed to nucleate on the ends of the PTFE-covered magnetic stirrer. The solution was homogeneous, both components having completely dissolved, and the phenomenon has not been observed in simple gutta percha solution after many days of stirring. After collection and repeated washing the product was observed in an optical microscope using crossed polars (Fig. 1). Quite clearly a bundle of polymeric fibres had been produced. Scanning electron microscopy using gold-palladium shadowing confirmed the general fibrillar nature of the material (Fig. 2). These fibres were grown from a solution containing 2 wt % gutta percha (viscosity average molecular weight 385 000) and 0.2 wt % of poly(ϵ-caprolactone) in benzene at a temperature of 21 °C.

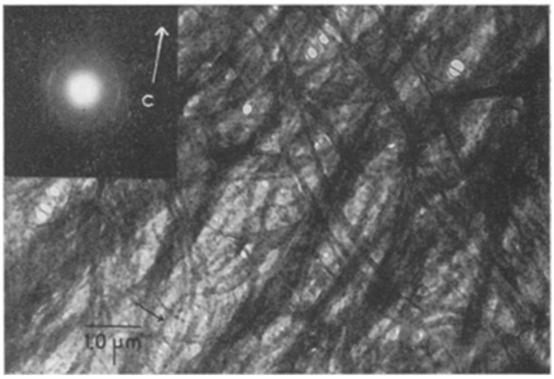

Figure 3 Transmission electron micrograph of part of a fibrillar bundle with electron diffraction pattern inset. Arrow indicates well-resolved lamellar structure. The insert is an electron diffraction pattern of a 1 µm square area close to the centre of the micrograph.

Transmission electron microscopy showed that the fibres (see Fig. 3) consist of row-nucleated structures ("shish-kebabs") of average diameter 70 nm, the lamellar thickness of the folded-chain overgrowths being 25 nm. It proved possible, through the use of selected area electron diffraction, to identify the crystal structure as that of the low-melting form of gutta percha (orthorhombic; $a = 0.784$ nm, $b = 1.187$ nm, $c = 0.475$ nm) [16, 17]. The equatorial arcs of the (1 2 0) and (2 0 0) reflections were present and

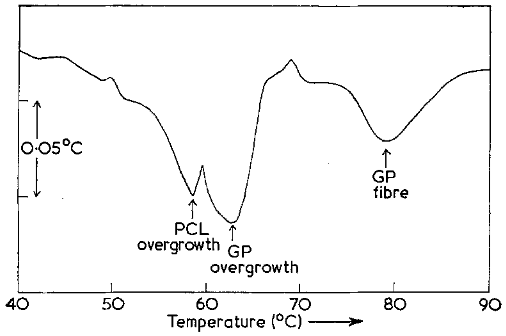

Figure 4 Differential scanning calorimetric trace of a bundle with overgrowth due to solvent evaporation.

the (002) reflection appeared in the meridional position indicating that the *c*-axis (molecular chain direction) was parallel to the fibre axis (see insert in Fig. 3).

Differential scanning calorimetry (DSC) was also informative. A DSC trace of a fibrillar bundle which had not been thoroughly washed (thereby allowing overgrowth to occur) is shown in Fig. 4. The two lower temperature peaks (58 and 63° C) are poly(ϵ-caprolactone) and spherulitic low-melting form gutta percha respectively, both due to overgrowth during evaporation of the solvent. The melting point of the gutta percha overgrowth is to be contrasted with the melting point of 79° C characteristic of the fibre. Even allowing for a superheating of up to 2° C (the DSC experiment was carried out at a heating rate of 5° C min^{-1}) the melting point is close to the equilibrium melting point [17] of 80° C characteristic of this crystal form of gutta percha.

Since this phenomenon was first observed we have conducted preliminary experiments on ternary solutions of poly(ϵ-caprolactone) with two other crystallizable polymers. These polymers, which are high density polyethylene and *cis*-polyisoprene (natural rubber), have behaved in a similar manner to gutta percha. The temperatures for these systems were, of course, different since the controlling variable is the supercooling and not the actual temperature.

The main purpose of this communication has been to report what we believe is the first observation of hydrodynamically induced crystallization in polymer solutions which would not exhibit this phenomenon in the absence of a second polymeric solute.

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B. C. EDWARDS
P. J. PHILLIPS
Department of Materials,
Queen Mary College,
University of London, UK