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Microscopic Observations of Unreported Crystalline Formations in Polycarbonate and Polysulphone

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Apparent crystalline entities, not previously reported, have been observed in both polycarbonate and polysulphone; these are described and compared to similar entities reported for other polymers.

1. Introduction

In view of the increasing interest in the crystalline behaviour of polycarbonate it seems pertinent to report briefly on what appears to be unusual types of crystalline entities which have been observed in thin films of polycarbonate and polysulphone.

Polycarbonate films were prepared from Makrolon (the polycarbonic ester of 2,2–bis (4 hydroxy phenyl) propane by techniques which have been adequately described previously [1–4]. Films, solvent-cast from xylene, were however prepared in a different manner. A saturated solution of polycarbonate in boiling xylene was prepared which contained a maximum of 0.1% polycarbonate. The boiling solution was immediately transferred to a bath thermostated at 70° C, when a slurry of polycarbonate and xylene was formed. After standing for several days, with the container tightly corked to prevent loss of xylene, the slurry was carefully and evenly spread onto a microscope slide and allowed to dry out. In this way a film containing large quantities of unusual crystalline entities could be obtained. Mechanical handling in spreading the slurry on the microscope slide was kept to a minimum as this tended to break up the crystals into very small pieces which were much more difficult to observe.

Films of polysulphone (the polycondensation product of 2,2–bis(4 hydroxy phenyl)propane with 4,4′–dichloro-diphenyl sulphoxide) were prepared from Union Carbide material by the techniques described in a previous note [1,2,5].

All these preparations were examined using a Gillet and Sibert polarising microscope, using polarised light and phase-contrast techniques. Melting point determinations were also carried out to check on the crystalline nature of the observed formations.

2. Needle-Shaped and Dendritic Crystals

2.1. Polycarbonate

Small numbers of needle-shaped objects have been noted from time to time in most films but these were regarded as accidental inclusions or arising from impurities in the material and it was not until very large numbers of these crystals were found in films prepared from a xylene slurry that it was concluded that they must be a form of the polymer itself. A picture of typical needle crystals is shown in fig. 1 but much more complicated crystals occur fairly frequently (fig. 2). Quite often the crystals appear to have formed at the periphery of a ring of material. The amorphous material in which the crystals

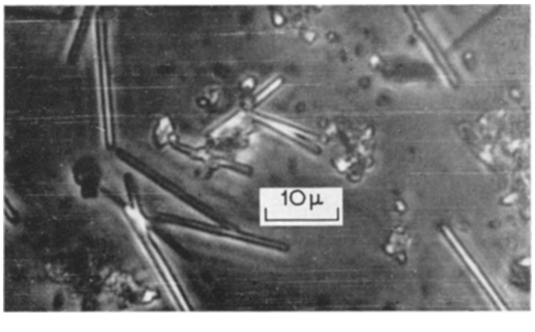

Figure 1 Polycarbonate. Simple needle crystals in film prepared from xylene slurry. Phase contrast.

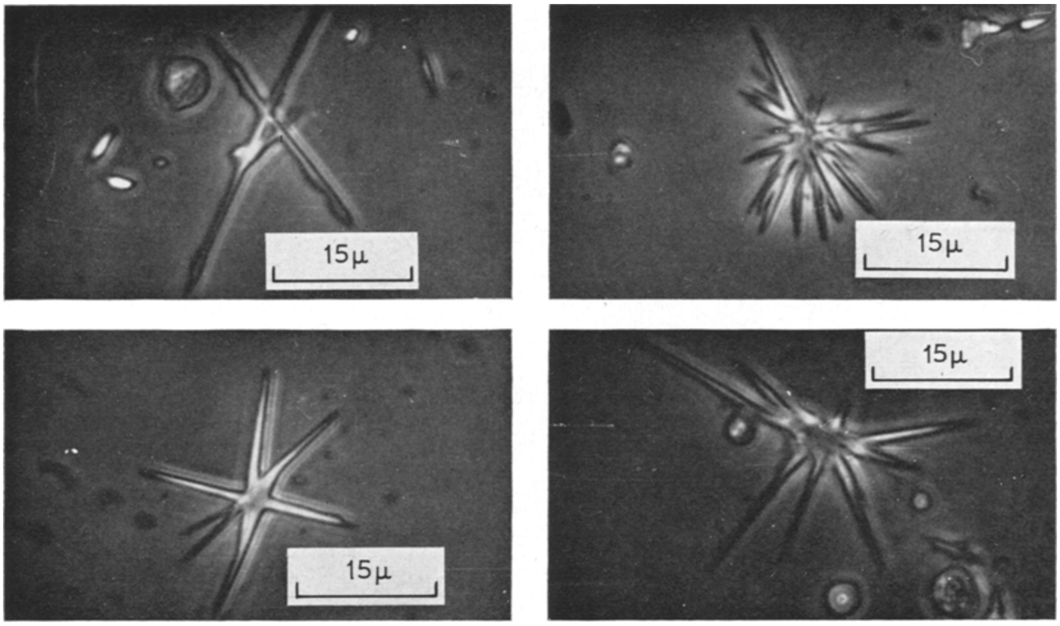

Figure 2 Polycarbonate. Complex needle crystals in film prepared from xylene slurry. Phase contrast.

are embedded was found to melt at 222° C, while for various crystals, melting points of 226, 232 and 239° C were recorded; whether these differences are due to variations in thickness or of molecular weight is not known. The fact that the crystals melted at a higher temperature than the amorphous phase suggests that they were not of very low molecular weight.

Truly dendritic crystal growth has only been observed once with polycarbonate; this was during the formation of a film by solvent casting and the crystalline entities were eventually lost in the general body of crystalline polymer.

2.2. Polysulphone

Needle-shaped crystals have also been observed in very thin solution cast films of this polymer. They usually occur in groups of bundle-like crystals (fig. 3) which are rather complicated and are reminiscent of the sheaving crystals illustrated by Keller for polythene [6, 7]. Simple many-spiked crystals (fig. 4) similar to those illustrated for polycarbonate are not common. Crystallisation approximately at the periphery of rings (fig. 5) is also found in polysulphone but the individual crystals are generally thinner and show a marked degree of orientation. This orientation is well illustrated in fig. 5 where the light and dark crystals illustrate different orientation colours under polarised light with

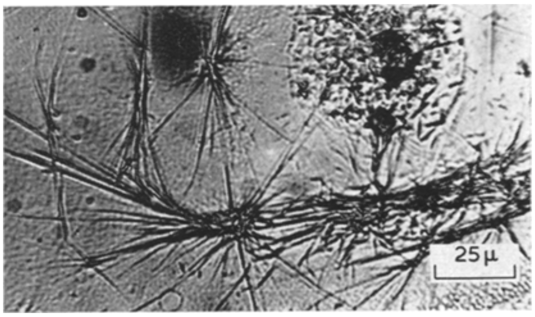

Figure 3 Polysulphone. Bundle of needle crystals. Film cast from chloroform, then treated with acetone. Phase contrast.

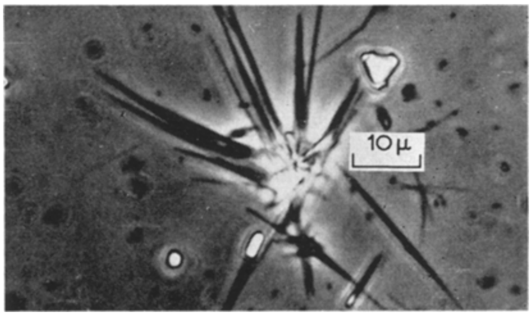

Figure 4 Polysulphone. Complex needle crystal. Film cast from chloroform and then treated with acetone. Phase contrast.

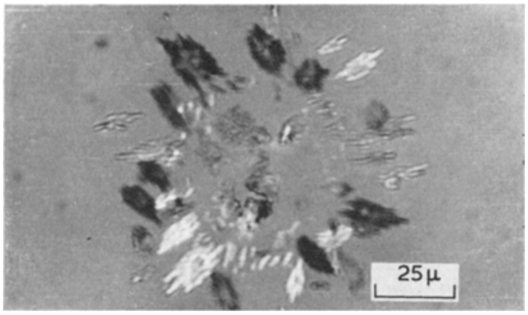

Figure 5 Polysulphone. Needle birefringent crystals oriented to form a ring. Polarised light, crossed polaroids, plus $\frac{1}{4}$ wave retardation plate.

crossed polaroids and 1/4 wave retardation plate.

Dendritic crystallisation is slightly more common with polysulphone than polycarbonate and a typical example is shown in fig. 6.

Neither the amorphous material, nor the crystals showed any sign of melting up to 370° C (the limit of the apparatus).

Finally a number of crystals of which fig. 7 is a typical example have been observed. These appear to be very similar in structure to those reported by Von Kampf [8] for polycarbonate although the scale differs since he was using an electron microscope. Keller has reported "four leaf" structured crystals for polyethylene [9,10] and these seem to be imperfect examples of the same type.

3. Rectangular Crystals

In various experiments with films of both polycarbonate and polysulphone what appear to be rectangular crystals, or crystals whose basic unit is a rectangle, have been observed. The first indication that such crystals might occur was seen in dissolution experiments in which very thin crumpled transparent sheets of material

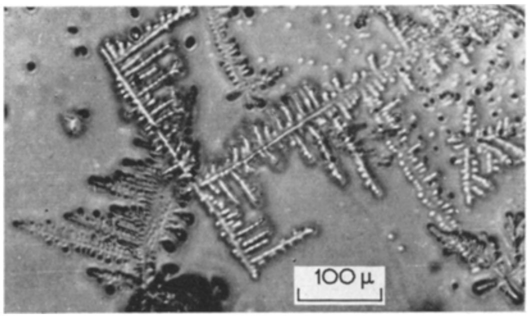

Figure 6 Polysulphone. Dendritic crystallisation. Polarised light. No analyser.

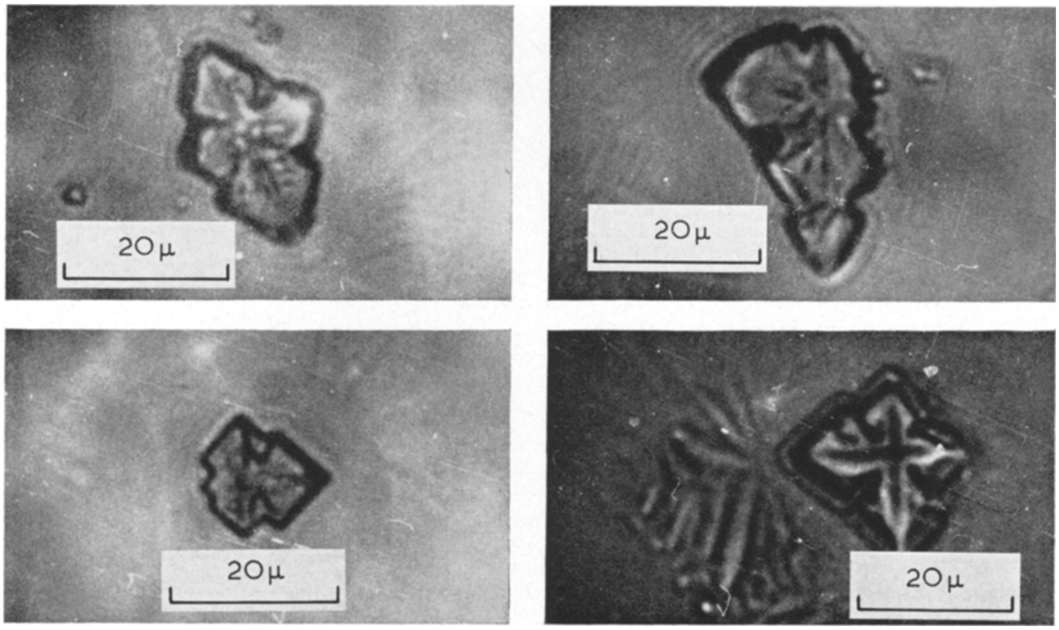

Figure 7 Polysulphone. Four-leaf crystals. Polarised light. Polaroids parallel.

were observed. When viewed perpendicular to their longest dimension these transparent sheets showed a high degree of orientation. Later, rectangular objects of a crystalline structure (fig. 8) were observed frequently, first in polycarbonate, and subsequently in polysulphone (fig. 9). The polycarbonate crystals were found to melt near 252° C, though in one case no change took place till 266° C was reached.

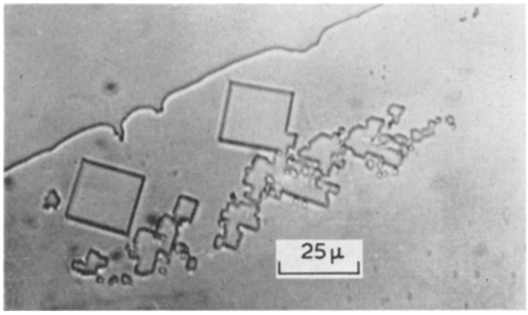

Figure 8 Polycarbonate. Rectangular crystals. Polarised light. Polaroids parallel.

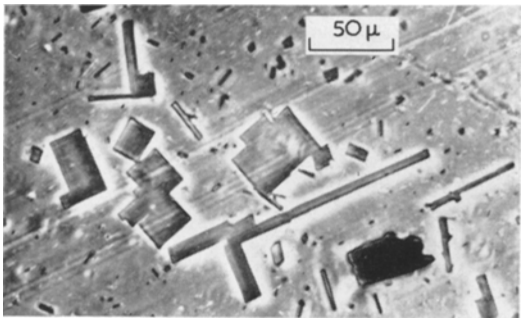

Figure 9 Polysulphone. Rectangular crystals. Polarised light. No analyser.

Originally it was considered that these entities might be window-frame crystals such as those described by Keller [9, 11] for 4-methyl-pentene-1. However during solvent-cracking experiments, rectangular crystals in the surface of a polysulphone preparation have been observed to become detached and float as a single entity. Further, these crystals appear to thicken when treated with stress-cracking agents and often during this process small quadrangular holes appear in them, indicating that the whole area is involved and not just the periphery.

When a polysulphone is treated many times with stress-cracking agent, cracks develop to a greater and greater extent until all stress in the material is relieved. Before this equilibrium state is achieved the forces at work often strip the area of film under treatment from the matrix, when it curls and wrinkles. Despite all these changes, the crystalline entities retain their shape and appear to stop cracks which in general do not break through the crystal edges.

All possible variations of crystal growth on the basis of a rectangular form appear to occur, and many as a result have a scalloped edge, at any rate in parts. Crystals in this form seem to be unstable as they often disappear rapidly during treatment with liquids. However it is not yet certain whether they in fact vanish or become incorporated in a general change which takes place through the body of the material.

The lath and square crystals recently discovered by Woodward and Morrow [12] for polybutane-1 seem to be similar to the polycarbonate crystals described here, not only in general morphology but also in their annealing behaviour.

Only preliminary results are given here. The work is continuing and will be reported fully at a later date.

Acknowledgement

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