I. Introduction

The present paper deals with the electron microscopic examination, supplemented by some optical microscopy and low angle X-ray work, of crystals of the two-block copolymers poly(ethylene oxide) (PEO) and polystyrene (PS) the preparation and detailed light optical examination of which has already been described (1).

The scope and significance of the work is threefold. Firstly, it provides information on the morphology specific to the block copolymers in question; secondly, it aids the elucidation of the crystallography of PEO; thirdly, it touches upon morphological problems encountered but still partly unexplained in polymer crystallization in general.

In connection with the second point the following needs stating. As will be noted later and implied by Part I, the crystallography and morphology of the copolymers have much in common with that of pure PEO. The study of pure PEO, however, is rendered difficult by the fact that the crystals are mechanically and thermally (refolding - particularly under the effect of moisture) less stable than their eopolymer counterparts. Further, the copolymer crystals are more resistant to the electron beam owing to the protecting effect of the aromatic rings. For these reasons they proved to be good model substances for the study of the PEO homopolymers - their intrinsic interest as copolymers apart.

The PEO homopolymer itself has been studied electron optically previously in association with one of us (2, 3) [see also concurrent communication (4)]. The exploration of the copolymers and the pure PEO crystals has directly merged in the present research project when it was discovered that if seeded by copolymer crystals PEO homopolymer crystals could be grown which, surprisingly, were stabler than the pure PEO crystals which formed on their own. The seeding experiments will form part of a later publication. Nevertheless, here a few illustrations will be taken from the material on seeded PEO crystals, in cases where they feature effects which are equally typical of the copolymers but provide better examples for pictorial presentation.

II. Experimental

1. Light Optical Examinations

These observations are supplementary to the ones in Part I (1), to be quoted in order to maintain the continuity between the work with the light and electron microscopes.

Examination of crystal suspensions under phase contrast illumination showed two kinds of crystal population: individual layers floating separately and strings of splaying crystal platelets seen edge-on (to be referred to as shish-kebabs; fig. 1 in Part I (1)). These latter platelet aggregates were seen to break up during drying of the suspension: the more complex multilayer structures to be described and illustrated here will refer to the original components of such broken-up shish-kebabs. The former crystals were usually flat square tablets consisting of one or two contiguous layers (layer doublet) depending on chemical composition as will be described below.

2. Electron Microscopy

2.1. Sample Preparation

The samples were used in transmission as sedimented on a substrate, whenever diffraction effects were to be recorded. For clearer recognition of morphological features, particularly in multilayer structures the crystals were shadowed with gold-palladium and replicated with carbon. For both examination techniques the crystals had to be rinsed with ethyl benzene after sedimentation in order to remove non-crystalline sediment always present. Exposure to moisture had to be avoided whenever the original crystals were still present.

2.2. General Description of Crystals

The crystals fell into the two classes already indicated light optically: single tablets and complex multilayer aggregates mostly originating from shish-kebabs.
Tablets

These were used for the thickness measurements to be referred to. Figs. 1–3 show three examples. In fig. 1 the regular square is seen with sectorisation, the sector boundaries along the square diagonals corresponding to

Fig. 1

lines of depression. Two corners in particular are clearly truncated. These represent the beginnings of the hexagonal development referred to previously [figs. 4 and 18 in Part I (1) and present fig. 4]. There are small sectors associated with these truncating faces – as indicated by low contrast boundaries – confined to the crystal periphery. Closer examination reveals (unlikely to show in the reproduction) that there is a step in the crystals where these new sectors, consequently the truncating face development, starts. Thus growth conditions must have changed at that stage. Figs. 2 and 3 are variants with more or less elongated shapes from the same sample. The peculiar sectorisation effect in fig. 2 supports the suggestion (Part I) that such crystals grew from elongated fragments of another crystal where they were parts of one sector only, the sectorisation developing only beyond the original fragment shape. Fig. 3 shows in addition to the elongation also a halving effect manifest by a ridge. It is seen that these tablets are composed of two layers (see corners of fig. 3) a feature generally encountered with samples of high PS content.

As described in Part I, high temperature crystallisation yields additional crystallographic prism faces truncating the squares along one diagonal, which leads to hexagonal outlines. In such overall hexagonal crystals ($H_4$), new crystallographic prism faces may appear both sides of the long diagonal (fig. 4, also figs. 16–18). In the same preparation more complex shapes can also be observed in a few percent of the crystals, of which the overall pentagonal habits ($H_5$ in fig. 4) is one example.

Multilayer Structures

Out of a variety of multilayer features, two very specific ones will be referred to.

Shish-kebabs as seen edgewise reveal that they are composed of stacks of lamellae (fig. 5). More frequently a more or less haphazard agglomeration of lamellae are observed which are believed to be shish-kebabs broken apart, the individual layers lying flat (fig. 6). Here the layers cover each other more or less concentrically (right-hand side) or, being displaced on top of each other, lie as a sheared stack of cards (left of fig. 6). Further examination reveals multiterraced units which may be parts of shish-kebabs or may be individual entities all centred around screw dislocations. These contain