Single Crystals of Cellulose Triacetate

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Square, approximately square and rectangular single crystals of cellulose triacetate have been observed crystallizing from solutions in nitromethane or from mixtures of nitromethane and n-butanol, by the film formation method. {100} planes are suggested as the growth faces of single crystals instead of {210} planes, on the basis of density of different shaped single crystals and reticular density of growth planes. The origin of the striations has been suggested.

MANLEY[1] grew approximately square-shaped single crystals of cellulose triacetate by adding an appropriate amount of the non-solvent, n-butanol to dilute solutions in nitromethane since he could not grow the single crystals directly from nitromethane solution. The approximate square shape of the single crystals was explained by considering {210} planes as the growth faces because the angles between these planes are nearly equal to those of the single crystals. However, he did not present any experimental or theoretical evidence to support this claim and the observed shape of the single crystals can be explained on the basis of {100} planes as growth faces, if the growth of the planes is assumed to be proportional to their reticular densities.

It has been observed that one can easily grow single crystals of polymers by the film formation method[2]. Hence a detailed study of the growth of single crystals of cellulose triacetate was undertaken to study their morphology and the growth habit.

EXPERIMENTAL

The method of preparation of cellulose triacetate and its crystallization have been reported earlier[2]. Molecular weight ($\bar{M}_n$) of polymer was $2\cdot3 \times 10^5$ as determined from the viscosity measurements in chloroform at 25°C using the Howard and Parikh[3] relationship.

OBSERVATIONS

Single crystals of cellulose triacetate were obtained from its solution, either in pure nitromethane or in a mixture of nitromethane and n-butanol, by the film formation method[2].

Single crystals as shown in *Figure 1* obtained from 0·3 to 0·6 % solution in nitromethane, between 45 and 55°C, are less regular in shape and show overgrowth. Close examination of the overgrowth shows that it occurs in the directions perpendicular to the edges of the crystals: these are the directions of the striations. The overgrowth is less pronounced in the lamellae grown later on, as can be seen in *Figure 2*. It is observed that as the number of lamellae on the basal lamella increase, the overgrowth becomes less pronounced.

Well defined single crystals are obtained by adding *n*-butanol to its 0·05–0·5% solution in nitromethane so that the polymer is just on the verge of precipitation between 35 and 55°C. Spirals and closed loops are observed along with single crystal platlets. The spirals and the closed loops are not observed in the crystals grown from pure nitromethane.
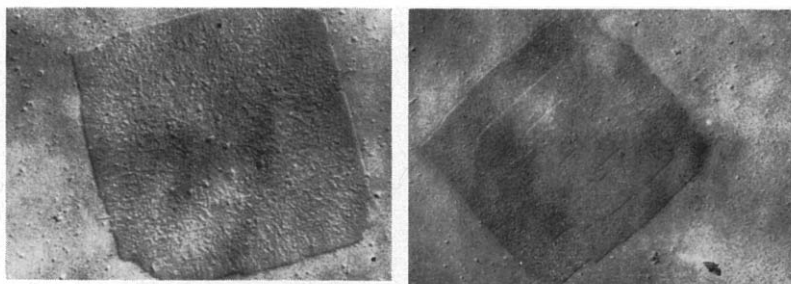
Figures *1* and *2*—Single crystal of cellulose triacetate grown from 0·4% solution in nitromethane at 55°C (Figure 1, × 5500; Figure 2, × 3300)
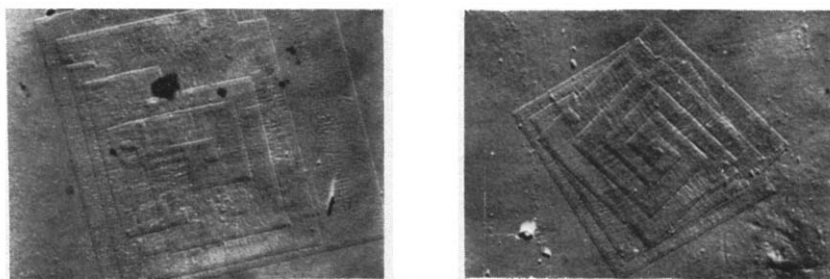

Figure 3—Single spiral of cellulose triacetate (× 8300)   *Figure 4*—Double spiral of cellulose triacetate (× 5500)

(Grown from 0·1% solution in nitromethane and n-butanol so that the polymer is just on the verge of precipitation at 55°C)

Single spirals of both senses developed on the basal lamella are shown in *Figure 3*. Double spiral of the same sense is shown in *Figure 4*. Out of these two spirals, one is diverging from its upper part. The proper reason for this divergence is not known at present but it may be due to twinning.[4] Two spirals of opposite senses form closed loops as shown in *Figure 5*. The closed loops are always observed at the edges of the lamellae.

About 90% single crystals have all four sides almost equal and all angles of 90°. A typical example is shown in *Figure 6*: the remaining single crystals have various angles. The angles between the bounding faces at the ends of the long and the short diagonals of the crystals are found to vary from 83° to 90° and from 90° to 97°, respectively. Three typical examples are shown in *Figures 7, 8* and *9*. Measurements of the angles of the lozenges of polyethylene reported in the literature gave the variation in the angles as about 5°.
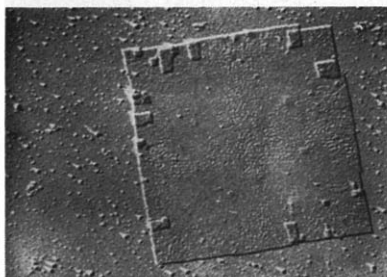
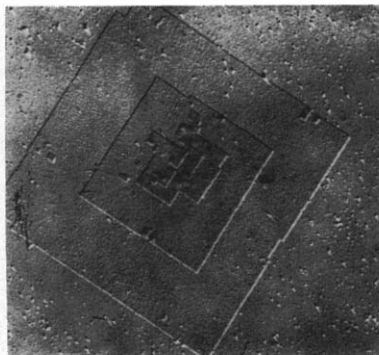Figure 5—Closed loops on cellulose triacetate single crystal (× 5500)

Figure 6—Square single crystal of cellulose triacetate (× 6600)

The striations running perpendicular to the edges of the crystals are more distinctly developed in the single crystals grown from the solution in a mixture of nitromethane and *n*-butanol. These crystals are similar to the crystals grown from the solution in pure nitromethane, the striations again being less pronounced on the lamellae grown later on.
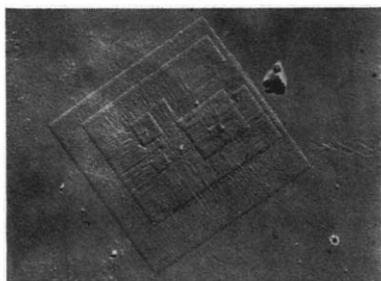

Figure 7—Single crystal of cellulose triace-
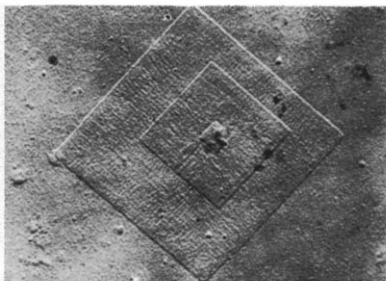tate having angles 91° and 89° (× 8300)

Figure 8—Single crystal of cellulose triace-
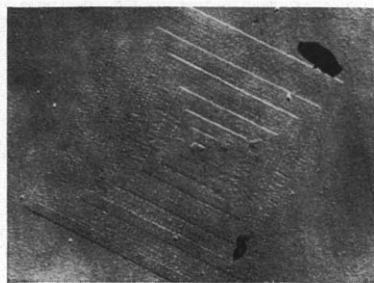tate having angles 92° and 88° (× 5500)

Figure 9—Single crystal of cellulose triace-
tate having angles 93° and 87° (× 8300)

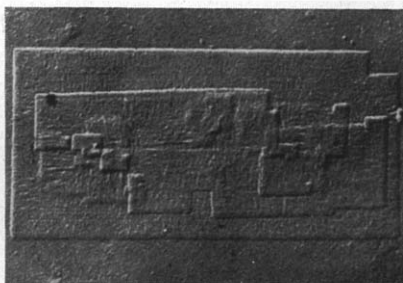

Figure 10—Rectangular single crystal of cellulose triacetate (× 11000)

Occasionally single crystals of a rectangular shape are also observed along with the square single crystals. A typical example is shown in *Figure 10*. The angle at each corner is 90° and the ratio of length of the longer side to the

shorter one is exactly equal to the ratio of the a ($=$ 2·46 nm; 24·6 Å) and the b ($=$ 1·18 nm; 11·8 Å) axes of the orthorhombic unit cell[1] of the polymer, within the limits of experimental error.

DISCUSSION

A spiral will originate if there is an exposure or growth of a wedge shaped portion of a lamella[5-7]. Thus the single screw dislocation will give rise to a single spiral of either sense, as shown in *Figure 3*. Two screw dislocations of the same sense in a plane give rise to two spirals (double spiral) in the plane. Two screw dislocations of opposite senses will give rise to a closed loop at the edges of the crystal, if one of these is above and another is below the plane[1, 8, 9] and a plate if both are in the same plane[10].

Almost square (square crystals with angles of 90° and sides almost equal); approximately square (square-shaped single crystals with sides equal but angles not quite 90°) and rectangular single crystals of cellulose triacetate are observed using the film formation method. The observed shapes of the single crystals can be explained by considering either {210} or {100} planes as the growth faces as shown in *Figure 11*. No other plane can explain the observed shapes of the single crystals.

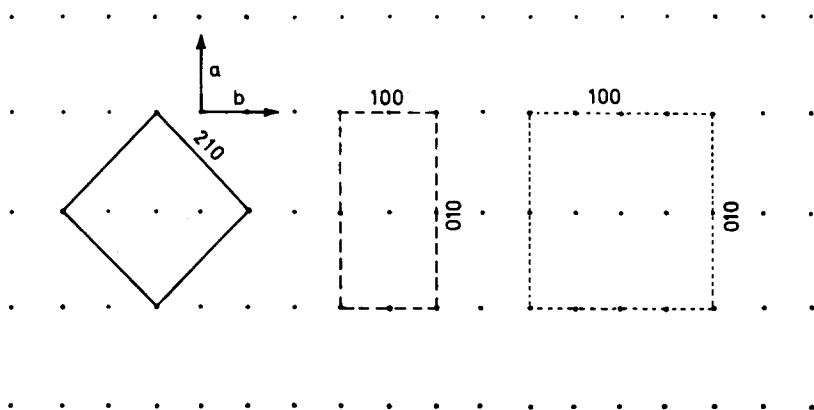*Figure 11*—Diagram of {001} plane of lattice of cellulose triacetate explaining the shape of almost square (dotted lines) and rectangular (dashed lines) single crystals with {100} and {010} planes and approximately square single crystals (continuous lines) with {210} planes.

If {210} planes are the growth faces, the shape of the single crystals should be approximately square with angles 87° and 93°. If {100} planes are the growth faces, the shape of the single crystals should be rectangular with the ratio of length of the longer side to that of the shorter one equal to a/b. *Figure 9* is a case where {210} planes can be considered as the growth faces while *Figure 10* is the case where {100} planes can be considered as the growth faces. Though the planes of the growth faces of the single crystals can be conformed by the selected area electron diffraction study, such a study proves to be extremely difficult in the case of cellulose triacetate single

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crystals due to sudden disappearance of electron diffraction spots since cellulose triacetate is highly sensitive to the electron beam. Now if {210} planes are considered to be the growth faces, growth of the rectangular single crystals remains unexplained, and if {100} planes are considered then it seems that the growth of the other single crystals cannot be explained. Therefore it is necessary to study other characteristics of the single crystals such as the shapes of the single crystals and their densities (number of particular shaped crystals per unit area) as well as the reticular density of the growth planes.

The density of single crystals having their angles 87° and 93° is very low, while that of the rectangular single crystals is even lower. One may be tempted to explain the almost square shaped crystals with {210} planes as growth faces, but assuming that the 3° variation in the angles is due to the external elongation (the elongation of the crystals may occur during replication and during transferrence of the replica onto the electron microscopic grids). If this is the case (single crystals having angles 87° and 93° deformed by external stress to form exact square shape), the density of the crystals having angles less than 93° and more than 87° should be at least approximately equal to the density of crystals having angles more than 93° and less than 87°. Observation showed that about 90% of the single crystals are almost square and among the remaining 10%, about 5% have angles of less than 93° and more than 87°. Thus from density considerations of single crystals, the shape of the single crystals is nearly square, rather than an approximate square with angles of 87° and 93° as was reported by Manley[1]. The measurements of angles of the single crystals reported by Manley indicate that the angles are nearly 90° (90° ± 1). Hence the possibility of {210} planes as the growth faces is almost ruled out.

In monomeric and polymeric single crystals, it has been found that the high density (reticular density) planes are the habit planes. The low index planes are the high density planes. The single crystals of polymers like polyoxymethylene[6], poly-4-methylpentene-1[11], polybutene-1[12], poly-*p*-xylylene[13] have {100} planes as the growth faces (habit planes). {110} planes of polyethylene are more dense than {100} planes and hence {110} planes are the growth faces in true lozenges. Reports of {210} planes as growth faces are rare, except for poly(ethylene oxide)[14], where {120} planes are suggested as growth faces; however this has yet to be proved by selected area electron diffraction. The reticular density of various lattice planes of cellulose triacetate decreases in the following order, {001}, {100}, {010}, {110}, and {210}. Thus the probability of {210} planes being growth faces or habit planes is very low.

In the monomeric crystals it has been found that the low density planes grow faster than the high density planes and that the growth is generally proportional to the reticular density. To explain the square shape of the single crystals of cellulose triacetate, it is assumed that {010} planes are growing twice as fast as the {100} planes as the reticular density of {100} planes is twice that of {010} planes. The unit cell dimension along the *a* axis is also almost twice as great as that along the *b* axis. One must, therefore, expect the length of a crystal along the *a* and the *b* axes to be almost equal and hence the shape of the single crystal will also appear almost square.

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The approximately square shaped single crystals can be considered to be the elongation of square crystals. If, under certain conditions, the growth of {100} planes is not proportional to their density, then rectangular single crystals may be formed. Therefore we believe that single crystals of cellulose triacetate have {100} planes as the growth faces; but detailed investigation by selected area electron diffraction or some other means is still required.

Manley has also stated that the striations should be parallel to the edges of the crystals rather than perpendicular. This type of striation is now observed in many polymers[2, 13, 15, 16]. Quite recently, Geil and Garber[15] attempted to explain such striations in single crystals of polyoxymethylene. From the study of X-ray line width measurements; deformation; and dark and bright field electron microscopy of single crystals, they concluded that the single crystals are composed of folded chain blocks of about 100 Å (10·0 nm), aligned or oriented along the specific crystallographic directions over a relative large distance (as much as several micrometres): these appear as striations. They suggested two modes of origin of the block: (1) by internal stresses generated when the crystals collapse onto the substrate or (2) by growth. In the present case, the overgrowth observed on the single crystals grown from pure nitromethane is arranged in the directions of the striations. The striations are less pronounced in the lamellae grown later on and therefore it is believed that the striations are produced either by readjustment of the folded chains after the growth of the lamellae or by irregular folds present on the surface. The overgrowth may also be due to the irregular folds on the surface of the crystals.

The striations in polymer single crystals are always perpendicular to the growth faces. The directions of the striations can be explained if each fold domain is considered as a single crystal and the whole single crystal as a twinned (mimetic twinned) single crystal twinned along the fold domain boundaries. The single crystals of polymers are actually twinned (mimetic twinned). Mimetic twinning of this kind is frequently observed in the monomeric crystals[17] of orthorhombic pseudo-hexagonal substances. In these crystals the directions of the crystallographic axes particularly a and b are frequently marked by striations[17] in these directions. In the present case, the striations will be also in the directions of the a and b axes i.e. perpendicular to the growth faces, as observed. This observation can be taken in support of {100} planes as growth faces. Thus by considering the polymer single crystals as mimetic twinned crystals, one can explain the directions of the striations.

As about 90% of the single crystals are almost square, it is suggested that the growth faces of cellulose triacetate single crystals are the {100} planes rather than the {210} ones. This is further supported by the fact that the reticular density of the {100} planes is much greater than that of the {210} ones, and the direction of the striations is perpendicular to the {100} planes. The rectangular single crystals can also be easily explained by considering the {100} planes as the growth faces.

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