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Electron diffraction of cellulose triacetate single crystals

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With 2 figures

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Cellulose triacetate single crystals can be prepared by the slow cooling of a solution of this polymer in a solvent - non solvent mixture as described by *Manley* (1), or by the film forming technique as shown by *Patel* and *Patel* (2). Due to the lack of reliable electron diffraction diagrams, there exists some uncertainty concerning the growth planes of these crystals: some arguments favor $\{210\}^1$ (1) whereas others give $\{100\}$ (2) as the growing planes. With X-ray techniques, it was shown recently by *Bittiger* and *Kuppel* (4) that these crystals had to contain a fair amount of mother liquor, to preserve their crystalline structure. Under vacuum such as the one found inside a vacuum X-ray camera or an electron microscope, a total decrystallization occurred and no diffraction could be obtained.

In order to record the electron diffraction of cellulose triacetate single crystals, a suspension of the crystals was prepared by the technique of *Manley*, using nitromethane as the solvent and n-butanol as the precipitant. A drop of this suspension was placed on a carbon coated grid already positioned on the specimen holder of a Philips EM 300 electron microscope. The specimen was then quickly frozen by immersion in liquid nitrogen and inserted into the microscope without raising the temperature. The specimen temperature was then slowly raised and n-butanol and the excess nitromethane sublimed inside the microscope column toward the anticontamination device. Around -50°C , the preparation cleared off and could be refrozen to a lower temperature without any change in the observed image. Electron diffraction of the crystals was recorded between -50°C and the liquid nitrogen temperature. If the temperature was raised above -50°C , decrystallization occurred readily due to the departure of crystallization solvent. Thus, the lack of electron diffraction of these crystals, as observed if the above precautions were not taken, was not due to destruction by the electron beam, but by the vacuum of the microscope. As a matter of fact, in this case, the observation of the disappearance of the diffraction diagram with irradiation time revealed that these crystals needed a fair amount of radiation to be decrystallized, the destruction dose being somewhat comparable to that of cellulose and polyethylene.

Fig. 1 represents a typical cellulose triacetate crystal and its diffraction diagram recorded at -120°C . The diagram, as explained on fig. 2, can be deduced from the two basic vectors D_1 and D_2 joining the origin to the most intense reflections. With most of the crystals, D_1 equals D_2 and corresponds to a d spacing of 10.5 \AA (gold calibration at room temperature, precision $\pm 0.2 \text{ \AA}$) while α , the angle between D_1 and D_2 measures 90° . In few cases, α decreases slightly to 89° and in the corresponding diagram, D_1 exceeds no-

ticeably D_2 by about 2%. With proper orientation of a crystal and its diffraction diagram, D_1 and D_2 are found to be parallel to the growth planes of the crystal. By direct measurement on the crystals, these growth planes were found by *Manley* (1) to make an

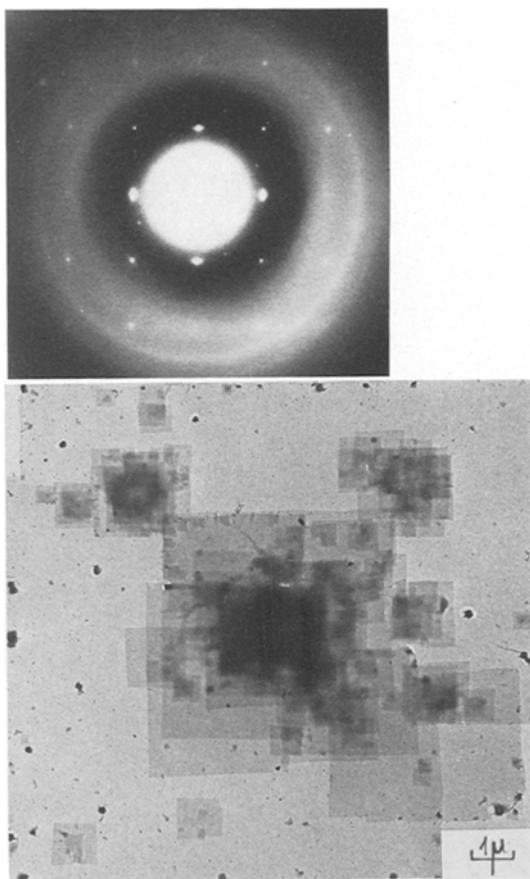


Fig. 1. Cellulose triacetate single crystal and its electron diffraction diagram

angle of 88° while *Patel* and *Patel* (2) showed that a slight variation existed in this angle, 90° being measured in most of the cases. The diffraction data presented here confirm that an angle of 90° exists between the growth planes of most of the crystals. If an attempt of indexation is made for the diffraction diagram, one cannot fit these data with the unit cell proposed by *Dulmage* (3) for cellulose triacetate II, assuming that the chain axis of this polymer is perpendicular to the base of the crystals, i.e. the diffraction spots seen in fig. 1 correspond

¹ These indices correspond to the unit cell and indexation of *Dulmage* (3) for cellulose triacetate II with $a = 24.5 \text{ \AA}$, $b = 11.56 \text{ \AA}$ and c (the chain axis) = 10.43 \AA .

to (hko) reflections. The discrepancy between the above spacing and the one proposed for the unswollen polymer by *Dulmage* (3) is certainly due to the presence of one or several molecules of solvent between the chains of cellulose triacetate, distorting the sides and angles of the lattice. Such an occurrence is common in the field of polysaccharides and certain X-ray data tend to prove that this is also the case for cellulose triacetate II swollen in various organic media (5).

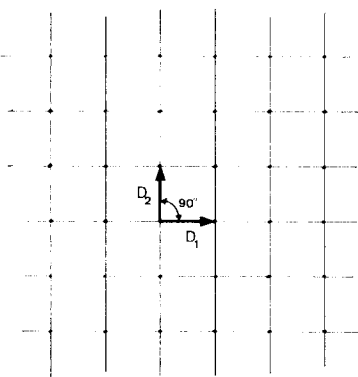


Fig. 2. Reciprocal lattice corresponding to the electron diffraction diagram of a cellulose triacetate single crystal

Up to this point, it has been assumed that cellulose triacetate crystals, precipitated from a solvent - non solvent mixture, contained the solvent (nitromethane) within their lattice with the exclusion of the non solvent (n-butanol). In order to prove this assumption, crystallizations were performed in various media. In each of these, the polymer was dissolved in nitromethane but the precipitating agent was varied from one case to the next. Thus, methanol, ethanol, toluene were successfully used as precipitants to produce cellulose triacetate single crystals. A crystallization method different from that of *Manley* was employed and consisted of exposing a 0.1% nitromethane solution of the polymer at room temperature to saturated vapors of the chosen precipitating agent. After 5 to 8 days, crystallization

occurred and gave a suspension of square crystals similar to that in fig. 1. It should be noted that with some precipitating agents more volatile than nitromethane (e.g. methanol, ethanol), the observation of the crystal presented some difficulty. As a drop of the suspension dried, the precipitant evaporated first, leaving an excess of nitromethane around the crystallized polymer. Because the crystals redissolved in this excess solvent, they could no longer be observed. This difficulty was overcome by displacing the nitromethane of the mother liquor by an excess of the precipitant or by freeze drying the preparation prior to observation. In each case, electron diffraction was performed, following the procedure described above. The diffraction diagrams were found to be exactly identical to those observed in the case of nitromethanebutanol. This seems to exclude the possibility of the presence of non-solvent within the crystalline lattice of the cellulose triacetate single crystals. Consequently, a crystal such as the one shown in fig. 1 appears to be built up from a complex of cellulose triacetate and nitromethane molecules.

Acknowledgments

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