Registry No. $Ti(OPr\text{-}i)_4$, 546-68-9; CNE, 109669-56-9; cyclohexene oxide (homopolymer), 25702-20-9; cyclohexene oxide (SRU), 32146-09-1.

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Received March 9, 1987

Single Crystals of Cellulose Tripropionate

The properties of aliphatic cellulose esters were reported more than 30 years ago by Malm et al.,[1] but very little progress has been achieved in our knowledge of the structures of cellulose derivatives, and the heterogeneously and homogeneously acetylated celluloses, the so-called cellulose triacetate I[2] and triacetate II,[3] are the only extensively studied cellulose derivatives whose structures have been determined. Recently, Zugenmaier reported that cellulose tripropionate crystallized in an orthorhombic unit cell with $a = 3.16$ nm, $b = 2.21$ nm, and c (fiber axis) $= 1.50$ nm, which contained eight chains.[4]

We wish to report ribbonlike lamellar single crystals of cellulose tripropionate grown from a mixture of dibenzyl ether and n-tetradecane at 205 °C. On the basis of the electron diffraction spots, we propose new orthogonal lattice parameters and the two-dimensional space group.

The cellulose tripropionate (CTP) was prepared by acylating an Avicel cellulose powder in the mixture of trifluoroacetic anhydride and propionic acid. The acylation was repeated to obtain trisubstituted cellulose propionate. The DS of the CTP was 3.0 from ^1H NMR spectrum and the weight-average molecular weight was 66 000 g·mol^{-1} from GPC data in which polystyrene was used as the standard.

The growth procedure followed the method reported in Chanzy and Roche.[5] The crystallization was achieved by cooling dilute CTP solutions (0.01 g/100 mL) in various mixtures of dibenzyl ether (poor solvent) and n-tetradecane (precipitant) at elevated temperatures. The best results were obtained when the CTP sample was dissolved in a mixture of 20% dibenzyl ether and 80% n-tetradecane at 205 °C, crystallized for 4 h, and slowly cooled. The crystals were recovered by repeated centrifugation and washing with ethyl alcohol and stored in ethyl alcohol.

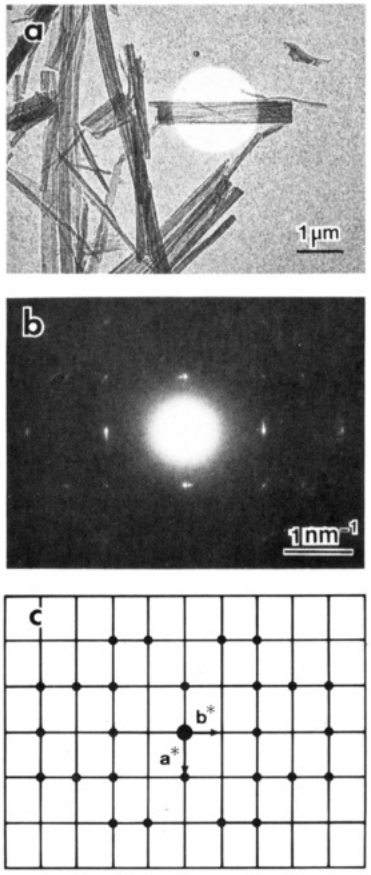

Figure 1. (a) Single crystal of cellulose tripropionate grown at 205 °C from a mixture of dibenzyl ether and tetradecane (20/80 v/v). Crystallization time, 4 h; polymer concentration 0.01%. (b) Corresponding electron diffraction diagram from the circled area. (c) Schematic drawing of the reciprocal lattice of the diffraction diagram. The dots show the diffraction spots actually observed.

Drops of the crystal suspension in ethyl alcohol were evaporated on carbon-coated grids. A JEM-2000ES electron microscope was used at 200 kV both for imaging and for diffraction. The electron diffraction diagrams were calibrated with the (111) plane of platinum ($d_{111} = 0.2266$ nm).

A typical electron micrograph of the CTP single crystal is shown in Figure 1a. The ribbonlike lamellar crystals are seen in this micrograph. Either increasing the volume ratio of dibenzyl ether against n-tetradecane or lowering the crystallization temperature resulted in smaller single crystals. The lamella is composed of finer rodlike crystals. Figure 1b shows a selected-area electron diffraction diagram obtained from the crystal shown in Figure 1a (see the encircled area), and Figure 1c shows an indexed schematic display of the diffraction diagram. The diagram contains all the ($hk0$) reflections of the CTP X-ray fiber patterns[4,6] which confirms that the diagram is a projection along the c axis: i.e., the polymer chains are perpendicular to the lamellar base of the crystal.

All the reflection spots can be indexed in terms of an orthogonal cell parameters, $a^* = 0.91$ nm^{-1}, $b^* = 0.65$ nm^{-1}, and $\gamma^* = 90°$. The two base plane dimensions are exactly half of the unit parameters proposed by Zugenmaier,[4] and accordingly the size of base plane becomes one-quarter.

Along the b axis only even-order reflections appear which suggests that the crystal possesses a pg two-di-

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mensional space group when projected along the *c* axis. From the systematic absence of the diffraction spots along the *b* axis, it is very likely that a twofold screw axis is present along the *b** axis, as is seen in the case of dextran.[7] The growth face of the crystal is {100} which is parallel to the longitudinal direction of the crystal.

The X-ray powder pattern of the CTP single crystal is identical with that of the oriented CTP sample which was annealed in an autoclave at 205 °C in the presence of water. No change of ^{1}H NMR spectra was noticed during the CTP single-crystal preparation, which proves that the CTP single crystal is chemically identical with the initial CTP sample.

Acknowledgment. We are greatly indebted to Dr. Henri D. Chanzy, C.N.R.S., Grenoble, France, for his invaluable suggestion and discussion on the crystallization procedure.

Registry No. CTP, 39320-19-9.

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Received May 14, 1987;
Revised Manuscript Received July 1, 1987

Ferroelectric Properties of Form I Perdeuteriated Poly(vinylidene fluoride)

In a recent paper,[1] two of us (R.E.C. and J.M.K.) reported the synthesis of perdeuteriated poly(vinylidene fluoride), d-PVF$_2$, which contained fewer chemical defects compared to the commercially available protonated PVF$_2$, H-PVF$_2$. The low level of chemical defects, which include head-to-head and tail-to-tail (H–H, T–T) linkages from reversed-monomer units, internal unsaturations, branching, and cross-links, was suggested as being the reason for the high melting point and high density (or crystallinity) observed in D-PVF$_2$.[1]

Since the ferroelectricity of PVF$_2$ originates in the polar form I crystals, the reduced chemical defects in the deuteriated polymer can be expected to have important bearings on ferroelectric properties. For example, in a related study[2] on copolymers of vinylidene fluoride and tetrafluoroethylene, TFE, the Curie temperature was found to decrease with increasing fraction of TFE (which is equivalent to introducing extra head-to-head defects into the H-PVF$_2$ molecules). However, while these copolymers crystallize naturally into the polar phase I, the natural form of PVF$_2$ crystals is nonpolar (form II); therefore, to render it ferroelectric, the polymer is usually mechanically stretched to convert the crystals to the polar form I. In this solid-state phase transformation, the final crystal structure can be expected to be highly sensitive to chain defects because of the severe lattice distortion involved in stretching. In fact, it has long been suspected that the presence of chemical defects in the commercial resins may be responsible for the low crystallinity (<50 vol %) observed in the uniaxially oriented films regardless of their preparation conditions. For this reason, the deuteriated polymer offers a unique opportunity for probing the effects of chemical defects on the stress-induced phase transformation and the ferroelectric properties of the resulting samples. In this paper, we describe the highlights of a study made on the *D*–*E* (i.e., electric displacement vs. electric field) hysteresis behavior and other properties of D-PVF$_2$ and compare them with those of H-PVF$_2$.

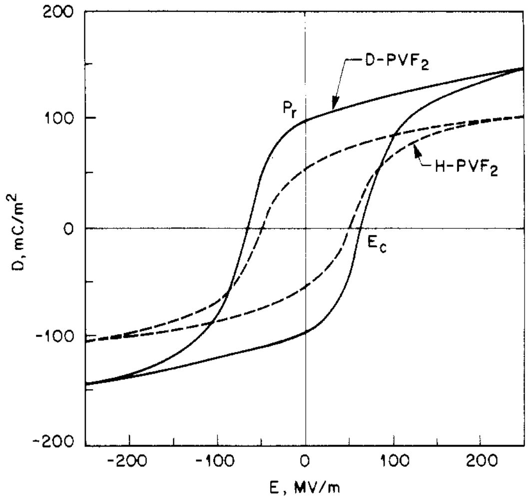

Figure 1. Comparison of *D*–*E* hysteresis curves obtained under a signal frequency of 0.01 Hz at room temperature from the deuteriated and protonated form I PVF$_2$ films.

Deuteriated PVF$_2$ was synthesized according to the procedure described in ref 1. Films of D-PVF$_2$ were prepared by casting them from a solution in dimethyl formamide. As with protonated PVF$_2$, these films contained only the nonpolar form II crystals. To convert them to the polar form I crystals, the films were uniaxially stretched at 70 °C to 4 times the original length and then annealed at 120 °C for 2 h in the stretched state. Complete conversion of crystal form was confirmed by X-ray diffraction patterns. Final thicknesses of the films were about 10 μm. Samples of H-PVF$_2$ were uniaxially oriented 7-μm-thick unpoled films supplied by Kureha Chemical Co. They were used without further treatments.

The *D*–*E* hysteresis curves were obtained by measuring the current responses across the film thickness while the film was being subjected a triangular or saw-tooth pattern electric field *E* with a frequency of 0.001 Hz. The current was then computer integrated to yield polarization *P* or displacement *D*. The contribution from dc conductivity was removed by numerical subtraction on the assumption that the dc conductivity is independent of *E*. Sample temperature, which was varied between −100 and 200 °C, was controlled to within 1 °C by using a thermostat. Linear dielectric relaxation was measured by using an impedance analyzer (Hewlett-Packard 4192A). Thermal properties were measured by differential scanning calorimetry, DSC (Perkin-Elmer DSC-4), the scanning rate being 40 °C/min to avoid crystal transformation during the heating measurements.

Typical *D*–*E* data of D-PVF$_2$ and H-PVF$_2$, measured under a field amplitude of 250 MV/m at room tempera-

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