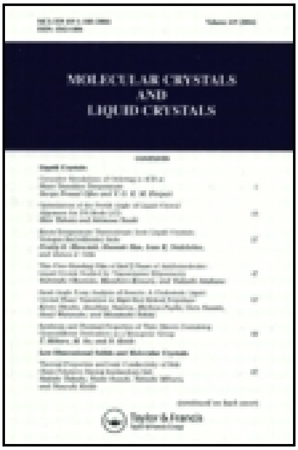

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Structure of Fully Oriented Crystalline Trans-$(CH)_X$

G. Leising [a], O. Leitner [a] & H. Kahalert [a]

[a] Institut für Festkörperphysik, TU Graz, Petersgasse 16, 8010, Graz, Austria

Version of record first published: 17 Oct 2011.

To cite this article: G. Leising, O. Leitner & H. Kahalert (1985): Structure of Fully Oriented Crystalline Trans-$(CH)_X$, Molecular Crystals and Liquid Crystals, 117:1, 67-70

To link to this article: http://dx.doi.org/10.1080/00268948508074597

Mol. Cryst. Liq. Cryst. 1985, Vol. 117, pp. 67-70
0026-8941/85/1174-0067/$10.00/0

STRUCTURE OF FULLY ORIENTED CRYSTALLINE TRANS-$(CH)_x$

G.LEISING, O.LEITNER, and H.KAHLERT
Institut für Festkörperphysik, TU Graz,
Petersgasse 16, 8010 Graz, Austria

Abstract Fully oriented highly crystalline films of trans-polyacetylene were synthesized by converting films of poly-(BTFM-TCDT) at elevated temperatures under applied stress. We report electron diffraction and X-ray diffraction experiments on these films, which allow to deduce the structural parameters of this fully oriented crystalline modification of trans-$(CH)_x$.

1. EXPERIMENTAL

The prepolymer poly- bis-(trifluoromethyl)-tricyclodeka-triene was cast from a solution in acetone onto a glass substrate and dried under argon flow. The prepolymer films were mounted into a stretching apparatus and stretched under dynamical vacuum and temperatures in the range between 80°C and 140°C. The attainable elongation depends on the size and the thickness of the prepolymer film and the applied stress and can presently be performed up to ratios of $l/l_0 = 20$, where l is the final length of the film and l_0 the length of the prepolymer film [1]. Films prepared at these temperatures are 100 % trans-$(CH)_x$ as was evidenced from the lack of the cis-C-H out-of-plane vibration at 740 cm^{-1} and the cis-C-C-C deformation vibration at 446 cm^{-1}. The films exhibit a compact, non-fibrous and fully dense morphology and smooth surfaces as found in the SEM [1].

2. ELECTRON-DIFFRACTION EXPERIMENTS

HEED-experiments were performed in a Philips EM420 electron microscope at a beam voltage of 120 kV on small pieces of films transferred to TEM grids. TlCl powder samples were used for calibration purposes. Fig.1 shows the diffraction pattern for a sample with a thickness in the range between 700 and 1000 Å, which was estimated from the maximum value of the optical density around 2.1 eV. It is a typical fiber pattern implying the existence of randomly oriented crystallites having all their c-axis aligned very precisely parallel to a preferred direction, which coincides with the stretching direction.

Fig.1 HEED pattern on a film with thickness < 1000 Å

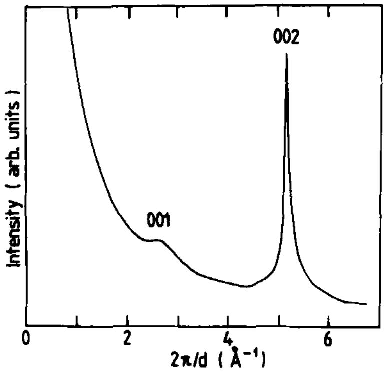

Fig.2 Microdensitometer scan ⊥ to the layer lines of Fig.1

Besides the sharp diffraction spots on the hk0, hk1 and hk2 lines we observe diffuse streaks, which can even be detected for the hk6 line. In Fig.2 we show a microdensitometer scan perpendicular to the layer lines through 000, which displays excess intensity at the position of a 001 reflection. Microdensitometer scans along the hk0,

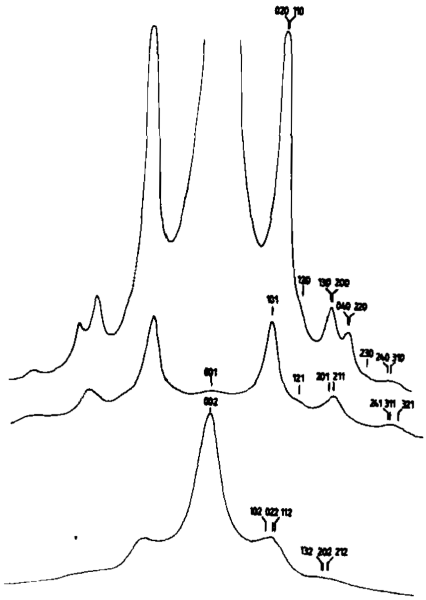

Fig.3 Microdensitometer scans along the layer lines of Fig.1

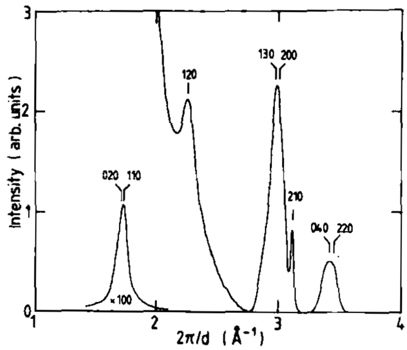

Fig.4 Scattered X-ray intensity for a scan in a plane containing the c-axis

hk1, and hk2 layer lines are shown in Fig.3. The marked positions are the calculated locations using the parameters derived in the discussion.

3. X-RAY-DIFFRACTION EXPERIMENTS

X-ray diffractometer data were recorded with CuK_α radiation. Fig.4 shows the diffracted intensity as a function of $2\pi/d$ for a scan in a plane containing the orientation direction. An almost identical pattern was obtained for a scan in a plane perpendicular to the stretching direction. Only the hk0-reflections are observed proving that the c-direction is oriented parallel to the stretching direction.

4. DISCUSSION

Starting with the assumption of a monoclinic lattice [2] we first deduced a value for $c\sin\beta = 2.42(9)$ Å from the distance of the layer-lines in the HEED pattern of Fig.1. Values for $a\sin\beta$ and b were derived from the splitting of the strongest hk0 reflection, were we observed 2ϑ-values of 24.25^0 and 24.5^0. Since it cannot be immediately decided, which is the 020 and the 110 reflection, we have tested both possibilities and have calculated the value of $\Sigma|d_{calc} - d_{obs}|$ for eleven HEED spots as a function of the monoclinic angle β for both choices. The result is shown in Fig.5. Both fits definitely improve for angles $\beta > 90^0$ with a remarkably better fit for the choice d(020)> d(110) and a minimum of the deviations at $\beta = 90.5^0$. As final result, we obtain the following parameters for the monoclinic lattice from our purely geometrical con-

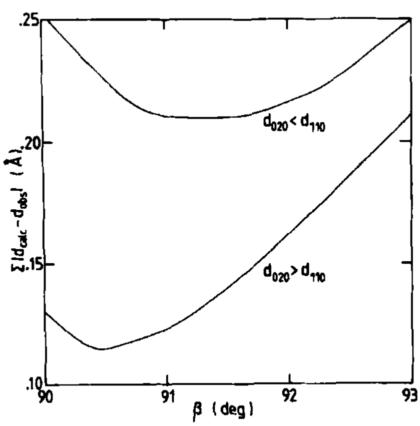

Fig.5 Quality of fit of the calculated lattice spacings to the observed ones as a function of β

siderations: a = 4.18(1) Å, b = 7.34(0) Å, c = 2.42(9) Å, $\beta = 90.5^0$. A decision about the space group can only be obtained after a proper calculation of the intensities, which is difficult for the HEED data because of the possibility of dynamical effects, which may alter the relative intensity of certain reflections. A clear evidence for the proper space group will come from a measurement of X-ray intensities for the 001 and 002 reflections, which we are presently attempting to perform.

REFERENCES

1) G.Leising, Polymer Bulletin 11, 401 (1984)
2) C.R.Fincher, Jr., C.E.Chen, A.J.Heeger, and A.G.MacDiarmid, Phys.Rev.Lett. 48, 100 (1982)