



	Experiment title: Internal chain conformation in octyl-substituted polythiophenes under pressure	Experiment number: sc176
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Names and affiliations of applicants (* indicates experimentalists):

Jostein MÅRDALEN SINTEF Applied Physics, N-7034 Trondheim, Norway

Ove R. KONESTABO Department of Physics, Norwegian University of Science and Technology (NTNU), N-7034 Trondheim, Norway

Emil J. SAMUELSEN Department of Physics, Norwegian University of Science and Technology (NTNU), N-7034 Trondheim, Norway

Report:

The poly(3-alkylthiophene)s (PATs) have been studied thoroughly during recent years due to their interesting optical, thermal and structural properties, as well as their applicability in commercial devices. The possibility of controlling the band gap of these polymers by varying their conjugation length has been emphasized.

The molecular structure (3D) of poly(oktylthiophene) (POT) at ambient pressure is well established, and the polymer chains are known to align in a planar fashion. The situation for POTs regioregular counterpart, the poly(di-oktylthiophene) (PDOT₂), differs somewhat from that of POT. Steric interactions caused by the collective effect of two side chains is believed to cause inter-chain twisting [1,2]. One of the major goals for the present work has been to find whether the influence of hydrostatic pressure could transform the twisted PDOT₂ chains into a planar POT-like conformation.

The effects of pressure on the thermochromic behaviour of PATs have recently been reported [3-5]. Detailed studies of optical absorption (OA) and photoluminescence (PL), picosecond photoinduced absorption (PA) and electric conductivity indicate a conformational change in the polymer chain under pressure, leading to an increased conjugation length. In addition no thermochromic transition was observed for pressures higher than about 1.4 GPa indicating that pressure inhibits rotational defects caused by increased temperature. The compressibility of POT has earlier been studied in a dispersive diffraction experiment using white synchrotron X-rays at pressures up to about 3 GPa [6].

The measured a - and b - distances for POT and PDOT₂ as functions of pressure are plotted in figure 1. These new results differ somewhat from those obtained by dispersive diffraction. The reason for this conflict is probably related to the excessive heat load of the white beam, which may give rise to deterioration of the sample. A remarkable large initial anisotropy of the compressibility of POT is found from figure 1. (0.08 GPa⁻¹ in the a -direction and 0.035 GPa⁻¹ for b at pressures below 1 GPa) The corresponding figures for PDOT₂ are 0.02 GPa⁻¹ for a and 0.04 GPa⁻¹ for b . For higher pressures the POT curves level off and POT becomes virtually incompressible for pressures above 5 GPa. PDOT₂ on the other hand is compressible, with a decreasing compressibility up to about 6 GPa at which pressure the diffraction peaks vanish.

It is noteworthy that the anisotropy of the compressibility for POT resembles that of its thermal expansion behaviour. The a -axis direction is in both cases the soft one. However, it is not possible to conclude whether the suppression of the thermochromic transition is due to the reduction of a or b , but evidently the reduced free space of the polymer under pressure above 1.4 GPa prevents efficiently the main chain twisting to take place, a mechanism believed to be crucial for the blue shift of the band gap.

There were found no indication that the twisted PDOT₂ molecular structure were transferred into a planar POT like structure under pressure.

This experiment was carried out using monochromatic beam, a high pressure diamond anvil cell with Si-oil as pressure medium, and a CCD-based 2D detector system enabling azimuthal integration. This experimental setup was crucial for the collection of data with a reasonable signal-to-noise ratio from polythiophenes, which are poorly scattering samples.

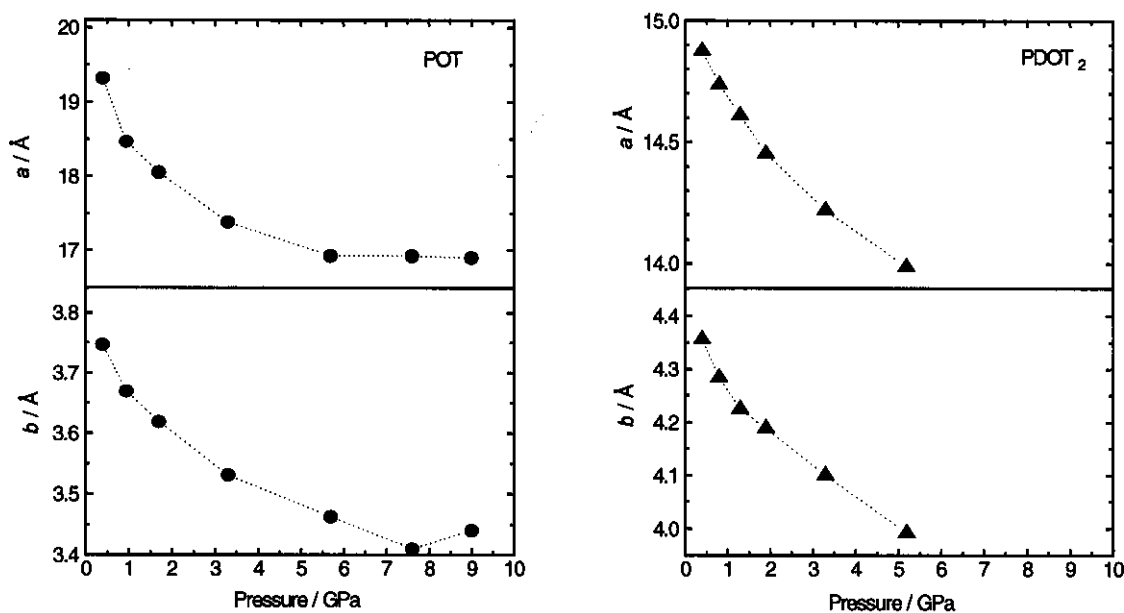


Figure 1 The hydrostatic pressure dependence of the a and b axes of POT and PDOT₂.

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