

## The crystalline structure of poly(3-octylthiophene) at high pressure

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1995 J. Phys.: Condens. Matter 7 3501

(<http://iopscience.iop.org/0953-8984/7/18/014>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.179

The article was downloaded on 13/05/2010 at 13:04

Please note that [terms and conditions apply](#).

## The crystalline structure of poly(3-octylthiophene) at high pressure

J Mårdalen†, Y Cerenius‡ and P Häggkvist‡

† Swiss–Norwegian Beamline, ESRF, BP 220, F-38043 Grenoble Cédex, France

‡ Institute of Earth Sciences, University of Uppsala, S-75236 Uppsala, Sweden

Received 28 December 1994

**Abstract.** The crystalline structure of poly(3-octylthiophene) as a function of pressure up to 3 GPa (30 kbar) has been studied by energy dispersive x-ray diffraction. The distance between neighbouring thiophene chains in the direction normal to the thiophene rings,  $b_{\perp}$ , has been found to decrease with increasing pressure. This is believed to increase the planarity of the polymer main chains and explains why the thermochromic transition is inhibited under pressure. The crystallographic repetition distance  $a$  in the direction along the octyl side chains is found to be constant during increment of pressure. This shows how the alkyl side chains in cooperation act as rigid interchain spacers even if, independently, they are flexible and rather disordered. A lack of change in the interchain charge complex transfer integral can be understood from the pressure behaviour of  $a$ . The measurements indicate that the crystalline fraction of this paracrystalline polymer increases with pressure, and that the size of the crystalline domains increases slightly.

### 1. Introduction

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 as commercial devices [1]. The possibility of controlling the band gap of these polymers by varying their conjugation length has been emphasized. A quasi-one-dimensional (1D) approach is usually employed to describe the relation between the band gap and the chain conjugation, and models for polymer chain behaviour are often suggested on the basis of spectroscopic measurements such as optical absorption (OA) and photoluminescence (PL). However, it is obvious that the influence of neighbouring polymer chains will be decisive for each chain's internal structure. Without proper 3D structural information it is difficult to draw any specific and unambiguous structural conclusions.

The effects of pressure on the thermochromic behaviour of PATs have recently been reported [2–4]. Detailed studies of OA, 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 lower than about 1.4 GPa (14 kbar), indicating that pressure inhibits rotational defects caused by the increment of temperature. High-pressure studies of polydiacetylenes with long side chains [5–7] show mainly the same effects as for PATs: a conformational change in structure leading to a redshift in the optical absorption spectrum.

The aim of this work has been to study in more detail how pressure affects the crystalline structure of PATs. By performing diffraction studies under pressure it was possible to reveal more detailed structural information, not only about the internal chain conformation, but also about the 3D packing of the polymer chains in its crystalline phase. A combination of a

suitable pressure cell and the possibility of carrying out energy dispersive x-ray diffraction on a white beam synchrotron source was crucial for the experiments. In this paper we will report on the very first high-pressure diffraction experiments on poly(3-octylthiophene) (POT) and relate the structural changes to earlier spectroscopic measurements.

## 2. Experimental details

The synthesis and characterization of the POT sample, provided by Neste OY (Finland), have already been described in detail [8,9]. A mixture of POT and MgO was mounted between sapphire anvils in a high-pressure cell [10] as shown in figure 1, allowing measurements of scattering angles up to  $2\theta_B = 30^\circ$ . MgO was chosen as a pressure reference due to its well defined equation of state [11]. This arrangement allowed a variation of pressure up to about 3 GPa, but no temperature variation was used in this work.

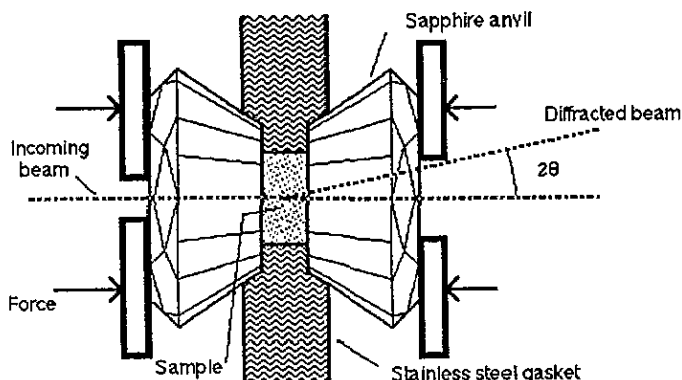


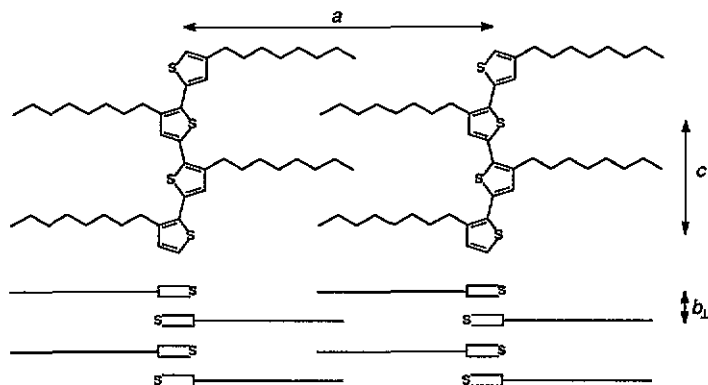
Figure 1. A schematic view of the sapphire anvil cell used for the high-pressure energy dispersive experiments. The  $400\ \mu\text{m}$  thick stainless steel gasket has a hole with diameter  $200\ \mu\text{m}$  where the sample is placed.

The diffraction experiments were performed on the Swiss–Norwegian Beamline (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble using the unfocused station with white beam x-rays. Scattered x-ray intensity was measured at  $2\theta_B = 3.10^\circ \pm 0.05^\circ$  through a slit arrangement allowing about 1 mrad horizontal divergence and detected by an energy dispersive Canberra low-energy Ge detector (LEGe, GL0110P).

The measured diffraction patterns revealed the main features known from angular dispersive diffraction at ambient pressure. The peaks 200 at about 22 keV, and 300 at about 33 keV, were clearly visible as well as the 010 reflection at about 62 keV. The very strong 100 reflection should have been seen around 11 keV but this low photon energy was absorbed by the sapphire anvils. The pressure on the sample was determined by the changes in the MgO 111 peak position [11] found at about 95 keV. An uncertainty of about  $\pm 1$  GPa is expected for pressures lower than 10 GPa. This is due to the fitting of the 111 diffraction peak, possible pressure gradients in the sample and uncertainty in the equation of state for MgO.

### 3. Results and discussion

The general structure of the crystalline phase of PATs has previously been reported in detail [12–16]. Even if there is some controversy surrounding such minor details as the various types of disorder, the structure in the amorphous part of the polymer and the possibility of side chain disorder, we will in this work concentrate on the main structural features.



**Figure 2.** A simplified pseudo-orthorhombic view of the POT crystalline structure projected along the  $b_{\perp}$  (upper) and  $c$  (lower) directions. For simplicity  $b_{\perp}$  will be used as a (pseudo-) unit cell parameter denoting the distance between neighbouring thiophene chains stacked on top of each other. It should however, be kept in mind that a parallel chain displacement along the  $c$  direction, implying a monoclinic unit cell with  $b = b_{\perp} / \sin \alpha$ , has been reported [15].  $a = 20.4 \pm 0.1 \text{ \AA}$ ,  $b = 4.80 \pm 0.06 \text{ \AA}$ ,  $c = 7.85 \pm 0.04 \text{ \AA}$ ,  $\alpha = 52 \pm 1^{\circ}$  and  $b_{\perp} = 3.76 \pm 0.03 \text{ \AA}$  for POT at ambient pressure.

The repetition distance  $c$  along the polymer backbone has been measured as  $7.85 \text{ \AA}$  for POT [15]. The backbone is considered to be close to planar in the crystalline part of the polymer and shows an alternating up–down configuration of adjacent thiophene rings as shown in figure 2 [12–16].

The thiophene chains are stacked on top of each other, separated by an interchain distance  $b_{\perp}$  normal to the thiophene ring plane.  $b_{\perp}$  varies only slightly with the length of the alkyl side chain. Stacks of thiophene chains form  $bc$  layers from which the alkyl side chains point out in either direction. The stacks are separated by the distance  $a$  and  $a$  is, in contrast to  $b$  (or  $b_{\perp}$ ) and  $c$ , strongly dependent on the length of the alkyl side chain.

Figure 3 shows the variation of the crystal parameters  $a$  and  $b_{\perp}$  as functions of pressure. The interchain distance  $b_{\perp}$  decreases markedly with pressure. This can explain the earlier observed redshift of the OA spectrum and the lack of thermochromic effect in the following way. It is known from studies of the thermochromic effect that it is favourable for the thiophene chain to be rather planar at ambient pressure and temperature. It has in addition been shown how the chain quite easily twist out of planarity over the thiophene–thiophene bond when the temperature is increased. When pressure is applied, the increment of the steric interaction between neighbouring thiophene chains in the  $b_{\perp}$  direction entails an improved chain planarity. This is observed as the pressure-induced red shift.

A similar explanation is valid for the observed lack of thermochromism under high pressure. The transferred thermal energy is insufficient to introduce twists in the thiophene chain when the pressure is acting to squeeze neighbouring chains closer together with the  $b_{\perp}$  direction.

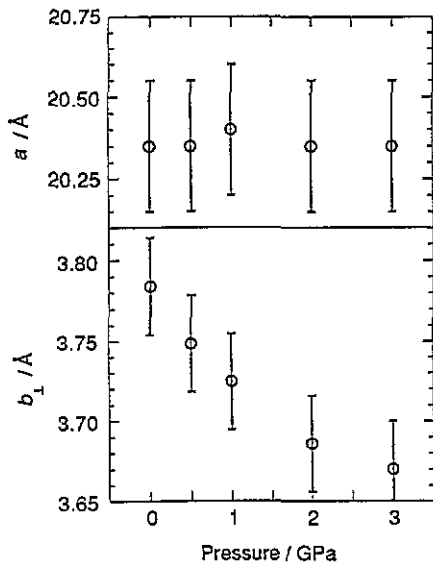


Figure 3. The variation of the two crystal parameters  $a$  and  $b_{\perp}$  as functions of pressure. The calculation of  $a$  is based on the two reflections 200 and 300, whereas the 010 reflection gives  $b_{\perp}$ . The pressure dependence of  $c$  could not be determined because no  $l \neq 0$  reflection was observed. The pressure is determined by the 111 reflection from MgO and an uncertainty of about  $\pm 1$  GPa is expected.

The most surprising observation from our measurements is probably the evolution of the unit cell parameter  $a$  (figure 3). Within the accuracy of the measurements,  $a$  is found to be constant for pressures of up to 3 GPa. This observation has several implications for the understanding of the crystalline structure of the PATs. First, it shows how alkyl groups act as very rigid spacers between the  $bc$  polymer layers. This is, to some extent, surprising since alkyl chains are known to be rather flexible and they are considered to be internally disordered even in the crystalline phase of the polymer [15]. It must thus be the collective effect of the side chains that results in this incompressibility.

Second, the constant  $a$  distance might also explain why PA measurements show constant covalent interchain coupling under pressure<sup>†</sup>. From the variation of  $b_{\perp}$  one might believe that the covalent interchain coupling expressed by the interchain transfer integral,  $t_{\perp}$ , should increase with pressure. This has been reported earlier for polyacetylene [17], but not for PHT [3]. If however, the long interchain distance  $a$  is the limiting factor for charge transfer in PATs, it is an obvious assumption that there is a direct relation between  $t_{\perp}$  and  $a$ . No change in the lattice parameter  $a$  gives no change in the covalent interchain coupling, and one can thus conclude that it really is the sidegroups that prevent an increase of  $t_{\perp}$ . This has previously been suggested for PHT [3], but the direct link to a constant value of  $a$  has hitherto been unknown.

No  $l \neq 0$  reflections were observed in the diffraction pattern. It is therefore difficult to conclude anything about the compressibility in the direction along the polymer main chains ( $c$  direction). However, since the general shape of the diffraction pattern stays the same and  $a$  and  $b_{\perp}$  behave as they do it is reasonable to draw two conclusions: (i) the main crystalline structure stays the same under pressure so our pseudo-orthorhombic cell is still valid and (ii)  $c$  is likely to be fairly incompressible for pressures up to about 3 GPa.

Figure 4 shows how the integrated intensity over background for each of the diffraction peaks 010, 200 and 300 varies with pressure. The integrated intensities indicate the amount

<sup>†</sup> According to the theory of strictly 1D systems the density of states diverges at the top of the valence band and at the bottom of the conduction band [17, 18]. To avoid this unphysical singularity in a real 3D solid a weak interchain transfer integral,  $t_{\perp}$ , transverse to the chain direction, is introduced.

of crystallinity in the polymer. Within the uncertainty of the measurements one can conclude that the crystallinity in the  $a$  direction (200 and 300 reflections) increases slightly up to about 1 GPa and thereafter stays constant. The change in intensity for the 010 reflection is significantly larger than for the two  $h00$  reflections and is observed to increase up to about 2–3 GPa. These observations fit the general picture obtained from the absorption measurements and the  $a$  and  $b_{\perp}$  values in figure 3. An increased planarity of the main polymer chain induced by pressure results in increased crystallinity in both directions and a denser crystalline packing along  $b_{\perp}$ .

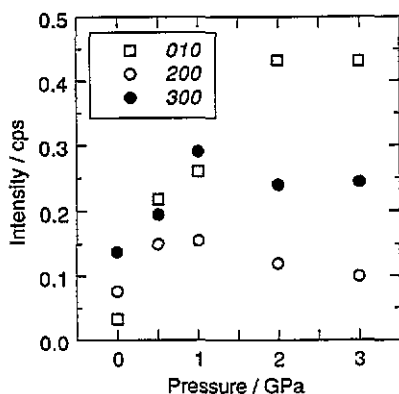


Figure 4. The integrated intensity over background for the three distinct reflections 010, 200 and 300 as functions of pressure. The crystallinity increases with increasing pressure in particular in the  $b_{\perp}$  direction (010 reflection). For convenience, uncertainty in pressure is not indicated in the figure, but is expected to be about  $\pm 1$  GPa.

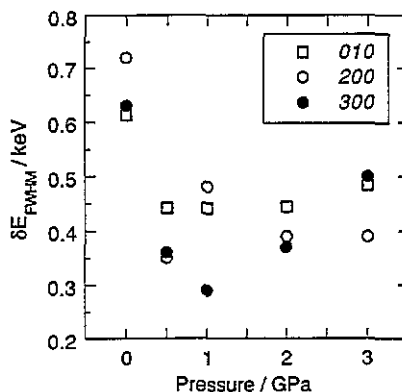


Figure 5. Diffraction peak widths,  $\delta E_{FWHM}$ , for the three reflections as functions of pressure. Decreasing peak widths correspond to larger crystalline domains. Under moderate pressures up to about 0.5–1 GPa the size of the crystalline domains seems to increase both in the  $a$  and  $b_{\perp}$  directions. The uncertainty in pressure is about  $\pm 1$  GPa.

The increment of the 010 intensity, as well as of the 200 and 300 intensities, agrees well with earlier suggested models for the amorphous part of PAT [16]. The polymer chains tend, even in the so-called amorphous phase, to order as relatively straight chains in a nematic-like fashion. From this model it is likely that pressure will increase chain planarity and imply stacking of more chains, especially in the tighter-bound  $b_{\perp}$  direction, leading to the observed increment of intensities (figure 4). The increased 010 intensity can to some extent also explain the redshift in the OA spectrum.

The size of the crystalline domains is, according to Scherrer's formulae [19], approximately inversely proportional to the diffraction peak width,  $\delta E_{FWHM}$  (full width at half maximum), for a fixed scattering angle,  $2\theta_B$ . Employing this principle one can from figure 5 conclude that the domain size generally increases under pressure. For pressure up to 0.5–1 GPa the crystallite size increases markedly. On increasing the pressure further the crystallite size becomes constant and maybe even decreases slightly. Comparing these observations with the crystallinity (figure 4) one finds a correlation between increasing crystallite size and increasing integrated intensity along the crystallographic  $a$  direction. Along  $b_{\perp}$  this correlation is not as pronounced, indicating the uniqueness of the polymer chain packing in this direction.

#### 4. Conclusion

It has been shown that the compressibility of POT is strongly anisotropic. The straight thiophene chains packed on top of each other are compressed in the direction normal to the thiophene ring plane whereas the alkyl side chains act as spacers between stacked layers of thiophene and are not compressible up to a pressure of 3 GPa. This observation explains why PATs show a redshift under pressure, why thermochromic transitions are inhibited under pressures higher than 1.4 GPa and probably also why the interchain transfer integral  $t_{\perp}$  remains unchanged under pressure.

On the experimental side this high-pressure diffraction experiment on PAT, the very first of its kind, shows that this type of experiment on a white beam synchrotron source is feasible. It is also very promising for the future development of the high-pressure experimental set-up on the Swiss–Norwegian Beamline. In more general terms the experiments show the importance of relating various spectroscopic and conduction experiments to crystallographic data obtained through diffraction experiments in order to reveal more detailed structural information.

#### Acknowledgments

The authors would like to thank the rest of the SNBL staff in Grenoble (France) for excellent support, Neste OY in Kulloo (Finland) for providing the sample, and Professor S Saxena in Uppsala (Sweden) for kindly lending us the high-pressure cell. Financial support from the Research Council of Norway and the Swedish Natural Science Research Council are gratefully acknowledged. This is contribution No 95-1 from the Swiss–Norwegian Beamline at ESRF.

#### References

- [1] See for example the proceedings from ICSM'90, 1991 *Synth. Met.* **41–43**, and ICSM'92, 1993 *Synth. Met.* **55–57**
- [2] Iwasaki K, Fujimoto H and Matsuzaki S 1994 *Synth. Met.* **63** 101
- [3] Hess B C, Kanner G S and Vardeny Z 1993 *Phys. Rev. B* **47** 1407
- [4] Yoshino K, Nakao K, Onoda M and Sugimoto R 1989 *J. Phys.: Condens. Matter* **1** 1009
- [5] Aime J P, King H E, King M W, Kim M W and Chance R R 1991 *Synth. Met.* **41–43** 203
- [6] Lacey R J, Batchelder D N and Pitt G D 1984 *J. Phys. C: Solid State Phys.* **17** 4529
- [7] Variano B F, Sandroff C J and Baker G L 1991 *Macromolecules* **24** 4376
- [8] Tamao K, Kodama S, Nakajima I, Kumada M, Minato A and Suzuki K 1982 *Tetrahedron* **38** 3347
- [9] Österholm J-E, Laakso J, Nyholm P, Isotalo H, Stubb H, Inganäs O and Salaneck W R 1989 *Synth. Met.* **28** C435
- [10] Ming L C, Manghnani M H and Balogh J 1987 *Geophysical Monograph No 39: High-Pressure Research in Mineral Physics* ed M H Manghnani and Y Syono (Tokyo: Terra) p 69
- [11] Jamieson J C, Fritz J N and Manghnani M H 1982 *High-Pressure Research in Geophys.* ed S Akimoto and M H Manghnani (Tokyo: Center for Academic Publications) p 27
- [12] Gustafsson G, Inganäs O, Österholm H and Laakso J 1991 *Polymer* **32** 1574
- [13] Winokur M J, Wamsley P, Moulton J, Smith P and Heeger A J 1991 *Macromolecules* **24** 3812
- [14] Prosa T J, Winokur M J, Moulton J, Smith P and Heeger A J 1992 *Macromolecules* **25** 4364
- [15] Mårdalen J, Samuelsen E J, Gautun O R and Carlsen P H 1992 *Synth. Met.* **8** 363
- [16] Mårdalen J, Fell H J, Samuelsen E J, Bakken E, Carlsen P H J and Andersson M 1995 *Macromol. Chem. Phys.* **196** 553
- [17] Moses D, Feldblum A, Ehrenfreund E, Heeger A J, Chung T-C and MacDiarmid A G 1982 *Phys. Rev. B* **26** 3361
- [18] See for example Devreese J T and van Doren V 1979 *Highly Conducting One-Dimensional Solids* (New York: Plenum)
- [19] See for example Kakudo M and Kasai N 1972 *X-Ray Diffraction by Polymers* (Tokyo: Kodansha) p 329