X-ray diffraction and infra-red spectroscopy studies of oriented poly(3-alkylthiophenes)

G. Gustafsson and O. Inganäs
Department of Physics, IFM, Linköping University, S-58183 Linköping, Sweden

and H. Österholm and J. Laakso
Neste Oy, Research R&D, POB 310, SF-06101 Porvoo, Finland

(Received 10 April 1990; accepted 5 June 1990)

Poly(3-octylthiophene) was stretched at 100°C to a final length up to five times the initial length. The degree of orientation in the crystalline and amorphous phases has been determined by means of X-ray diffraction and polarized infra-red spectroscopy. The value of the orientation function in the crystalline region was 0.72, which is comparable to the value 0.81 predicted from a theoretical calculation based on the draw ratio. The orientation of the amorphous phase was considerably lower, 0.47. Based on X-ray diffraction data from poly(3-alkylthiophenes) with different lengths of the side-chain, a tentative crystal structure for the poly(3-alkylthiophenes) is proposed.

(Keywords: poly(3-alkylthiophene); infra-red spectroscopy; X-ray diffraction; orientation)

INTRODUCTION

Orientation of conducting polymers has attracted a great deal of attention lately, mainly due to major breakthroughs in the synthesis of these materials. These include the preparation of fully oriented films of poly(phenylene vinylene) (PPV)[1] and polyacetylene (PA)[2] using soluble precursor polymers and the synthesis of processible conducting polymers like poly(3-alkylthiophenes) (P3ATs)[3–5] and polyaniline[6]. Films of PPV and PA can be produced by thermal treatment of precursor polymer films, cast from solution. If this conversion step is carried out in a stress field, highly oriented films can be achieved. The preparation of oriented fibres of conducting polymers by spinning from solution have been demonstrated by Andreatta *et al.*[6], who used a solution of polyaniline in concentrated sulphuric acid. In general, conjugated polymers exhibit melting points far above the decomposition temperature. The melting point and also the glass transition temperature (T_g) could, however, be lowered considerably by appending flexible side-chains to the conjugated backbone. This was demonstrated for the first time in the P3ATs, which show both solution and melt processibility. The low T_g of these materials make them suitable for stretching. Elongations up to five times the initial length upon stretching have been reported for poly(3-hexylthiophene)[7]. The processibility of this class of polymers is also reflected in their ability to form polymer blends with common commercial polymers and elastomers[8,9]. This gives new possibilities of achieving high extension ratios. This has successfully been demonstrated by Yoshino *et al.*[9], who stretched a P3AT/ethylene–propylene elastomer (EPR) composite to a stretch ratio of 12. However, it should be noted that in general there is no simple relation between the stretch ratio and the degree of orientation.

Preparing conducting polymers with highly aligned chains is important, not only to reach high conductivities or high mechanical strengths, but also for technological applications such as solar cells where highly anisotropic materials may be desirable. Furthermore, highly oriented films of conducting polymers allow studies of the anisotropic optical and electrical properties of these materials to be undertaken. The results of such experiments are very important for the understanding of fundamental properties of these quasi-one-dimensional materials. However, to be able to interpret correctly the information obtained from measurements on these films it is important to know the degree of orientation present in the material. Measurement of the degree of orientation is also important when optimizing orientation processes such as stress alignment, since it is well known that films drawn by the same amount can have different degrees of orientation due to relaxation processes.

In this paper we report a study of stretch-aligned poly(3-octylthiophene) (P3OT). From X-ray diffraction and infra-red measurements we have determined the degree of orientation in the crystalline and amorphous regions. Furthermore, we discuss possible crystalline structures of P3ATs based on X-ray diffraction data from P3ATs with different side-chain lengths.

EXPERIMENTAL

The synthesis and the characterization of the P3ATs have been reported elsewhere[10]. Free-standing films (thickness 100 μm) were prepared by compression moulding at 180°C. Orientation of these films was accomplished by stretch alignment in a home-made stretching apparatus at 100°C in a laboratory atmosphere followed by rapid cooling by means of dry ice.

X-ray diffractograms were obtained both in transmission and reflection by a Siemens D-500 wide-angle X-ray diffractometer. A Cu-anode tube was used. The reflection

0032-3861/91/091574-07

goniometer is equipped with a graphite monochromator and the transmission goniometer with a Ni filter in the diffracted beam. Azimuthal scans were obtained in transmission by rotating the sample at a constant speed (30° min^{-1}) and keeping the goniometer fixed at a certain Bragg angle. The data were recorded on a computer at 1° intervals between 0° and 360°.

*FT*i.r. dichroic measurements were performed with a Nicolet 510 *FT*i.r. spectrometer equipped with a Perkin Elmer wire grid polarizer. The spectra were taken with a resolution of 2 cm^{-1}.

THEORY

In uniaxially oriented polymers, a measure of the average orientation of the polymer chains in the direction of the symmetry axis Z of the sample can be expressed as[11]:

$$f = (3\langle\cos^2\sigma\rangle - 1)/2 \tag{1}$$

where f is the orientation function and $\langle\cos^2\sigma\rangle$ is the average square cosine of the angle σ between the Z axis and the chain axis of the polymer (*Figure 1*). For random orientation of the chain axis the average square cosine is 1/3 and $f = 0$, while for complete orientation the average square cosine is 1 and $f = 1$. The orientation function may be computed either from X-ray diffraction measurements or from infra-red dichroism measurements. The former represents the orientation of the crystalline region while the latter could represent the orientation of the crystalline or the amorphous regions or the total orientation, depending on which bands are used in the calculation.

The dichroic ratio of an infra-red absorption band is defined by:

$$D = A_{\parallel}/A_{\perp} \tag{2}$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances when the polarization direction of the electric vector of the incoming light is parallel and perpendicular to the stretching direction Z, respectively. The dichroism is related to the orientation function by[11]:

$$f = \frac{D-1}{D+2}\,\frac{D_0+2}{D_0-1} \tag{3}$$

D_0 is the dichroic ratio when the chain axis is perfectly aligned with the stretching direction. This ratio is related to the angle α between the transition moment of the absorbing unit and the chain axis (*Figure 1*) through:

$$D_0 = 2\cot^2\alpha \tag{4}$$

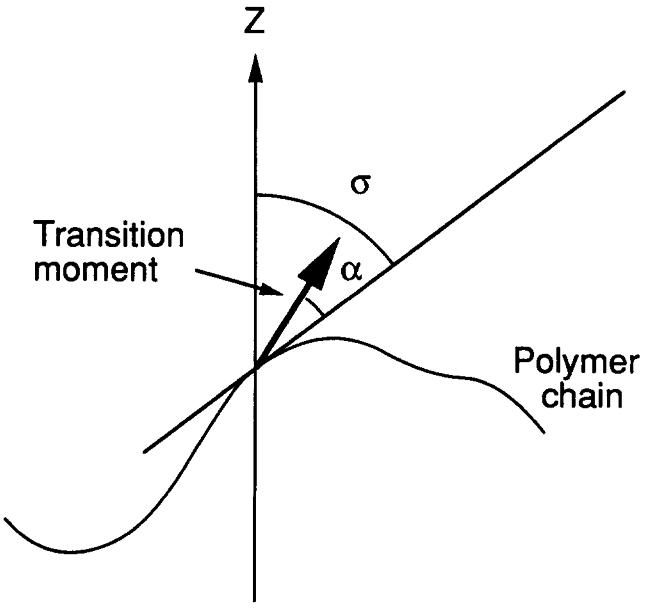

Figure 1 Illustration of the angles used in equations (1) and (4)

The orientation of a certain crystallographic direction of a crystal can be measured rather directly by X-ray diffraction if there are strongly reflecting planes perpendicular to that direction. In the case of uniaxial deformation the distribution of plane normals is proportional to the measured azimuthal variation of the diffracted intensity $I(\phi_{hkl})$ (corrected for background scattering). From such a measurement $\langle\cos^2\phi_{hkl}\rangle$ can easily be calculated as[12]:

$$\langle\cos^2\phi_{hkl}\rangle = \frac{\int_0^{\pi/2} I(\phi_{hkl})\cos^2\phi_{hkl}\sin\phi_{hkl}\,\mathrm{d}\phi_{hkl}}{\int_0^{\pi/2} I(\phi_{hkl})\sin\phi_{hkl}\,\mathrm{d}\phi_{hkl}} \tag{5}$$

where ϕ_{hkl} is the angle between the normal to the *hkl* planes and the symmetry axis Z. Equation (5) is valid for cylindrical symmetry about the Z axis, which is usually the case in uniaxial deformation. If there are suitable planes perpendicular to the chain axis the calculation of the orientation function is easily performed using equation (5). If such planes are absent or if the diffracted intensity is very weak it is possible to determine the chain axis orientation indirectly from planes parallel to the chain axis (*hk*0 planes) by the following expression[12]:

$$\langle\cos^2\sigma\rangle = 1 - 2\langle\cos^2\phi_{hk0}\rangle \tag{6}$$

where a random distribution of crystals about the c axis (chain axis) is assumed.

RESULTS AND DISCUSSION

FT*i.r. measurements*

The polarized *FT*i.r. spectra of a stretched film of P3OT is shown in *Figure 2*. The draw ratio $\lambda = l/l_0$ (l = final length, l_0 = initial length) of the film is 5.0. Owing to the thickness of the film, the bands at 2850–2960 and 1460 cm^{-1}, which are assigned to the octyl group, are too intense. However, measurements on thinner films show that there is no noticeable dichroism of the band at 2850–2960 cm^{-1} and that there is a weak dichroism of part of the band at 1460 cm^{-1}. The interpretation of this latter band is, however, complex since the band is superimposed on a ring mode of the main chain. The bands at 1306, 1184, 1150 and 1084 cm^{-1} and the broad band at 3500 cm^{-1} show quite strong dichroism. These bands are doping-induced bands, and the relatively high intensity of these bands shows that the polymer is lightly doped. This doping is probably due to remaining $FeCl_3$ from the polymerization process. The bands at 3058, 1510 and 824 cm^{-1} all show high anisotropy. The band at 1510 cm^{-1} can be assigned to a ring stretching mode. According to Hotta *et al.*[7] the transition moment of the corresponding mode in polythiophene is polarized in the

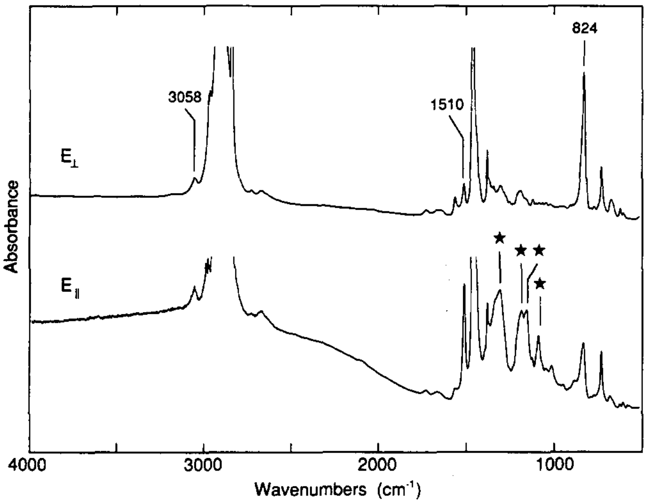

Figure 2 *FT*i.r. spectra of a stretched, free-standing film of poly(3-octylthiophene) for light polarized with the electric vector parallel, $E_{\parallel}$, and perpendicular, $E_{\perp}$, to the stretch direction. Peaks marked with asterisks are doping-induced bands. The draw ratio of the film is 5.0

thiophene ring plane and perpendicular to the symmetry axis of the thiophene ring. Assuming the same polarization of the 1510 cm^{-1} band in P3OT, α in equation (4) equals zero. The transition moment of the aromatic CH stretch mode (3058 cm^{-1}) is also polarized along the polymer chain; however, the dichroism of this band is lower than the dichroism of the 1510 cm^{-1} band, which shows that there is also a perpendicular component of the transition moment of this mode. As Hotta *et al.* have pointed out, the band at 820–830 cm^{-1} consists of two peaks, one at 824 cm^{-1} and another that appears as a shoulder at 830–835 cm^{-1}. The former can be assigned to the CH out-of-plane mode, which is polarized perpendicular to the thiophene plane. This means that $\alpha = 90°$ for this band. The dichroic ratio of a band is defined as the ratio between the integrated intensities measured with light polarized parallel and perpendicular to the reference direction (stretching direction) of the sample. However, since there is a considerable overlap between the 824 and 835 cm^{-1} bands it is not possible to integrate without performing a deconvolution; therefore the dichroic ratios are calculated from the peak intensities.

Table 1 summarizes the dichroic ratios and the orientation functions for the 1510 and 824 cm^{-1} bands.

X-ray diffraction

Figure 3 shows a diffraction scan measured in reflection mode of the P3OT film used in the *FT*i.r. measurements. As can be seen, the polymer is partly crystalline. An approximation of the degree of crystallinity X_c can be made by taking the ratio of the integrated intensity of the crystalline (sharp) peaks to the total intensity (corrected for background scattering)[13]. By doing a gravimetric integration of the peaks in *Figure 3* between $2\theta = 2$ and 50°, we obtain the value $X_c = 0.23$.

In *Figure 4* diffractometer scans parallel (meridional) and perpendicular (equatorial) to the stretching direction of the P3OT film are shown. The equatorial scan is characterized by a sharp reflection at low scattering angle (4.4°) together with its higher orders (8.8° and 13.1° respectively). This is typical for comb-shaped polymers in general and is due to an arrangement of the main chains in parallel planes, separated by the side-chains[14]. In *Figure 5* the azimuthal scans of these peaks are shown. Assuming a random distribution of crystallites about the chain axis and that the small-angle peak is due to reflections from planes parallel to the chain axis (*hk*0 planes), equations (1), (5) and (6) can be used to calculate the orientation function of the crystalline region of the P3OT film. In *Table 2* the results of these calculations are listed. The results obtained from the higher-order peaks are more uncertain than the result obtained from the first-order peak. This is due to the higher noise level of these scans, which makes the background correction more unreliable. Therefore, we take the value $f = 0.72$, obtained from the azimuthal scan of the first-order peak, as a measure of the orientation in the crystalline phase.

In principle it is also possible to calculate the orientation function from the meridional peaks assuming that these peaks are due to scattering from planes that

Table 1 Observed dichroic ratios and calculated orientation functions (equation (3))

Peak (cm^{-1})	$D = A_{\parallel}/A_{\perp}$	f
1510	4.5	0.54
824	0.38	0.52

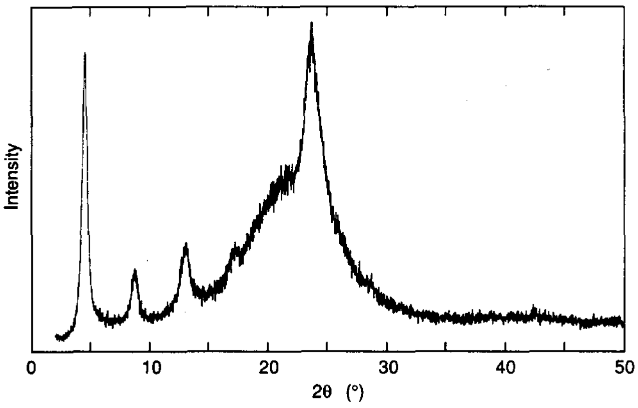

Figure 3 X-ray diffractogram measured in reflection mode of the poly(3-octylthiophene) film used in the *FT*i.r. measurement

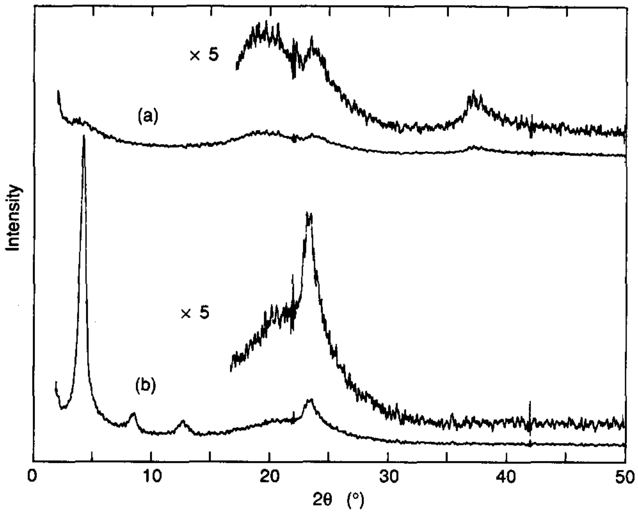

Figure 4 Diffractometer scan along the meridian (a) and the equator (b) of the poly(3-octylthiophene) film used in the *FT*i.r. measurement

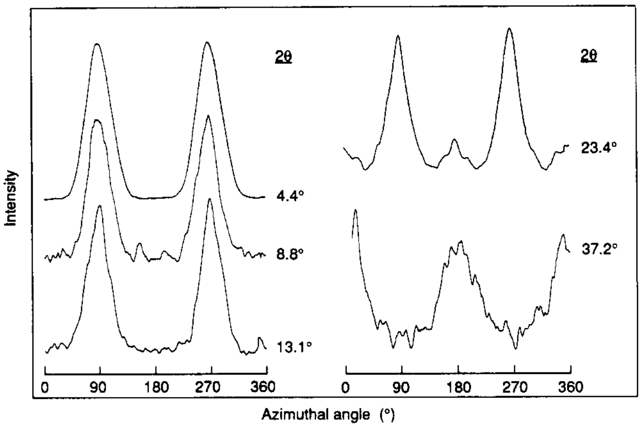

Figure 5 Azimuthal scans of the peaks observed in *Figure 4*

Table 2 Values of $\langle \cos^2 \sigma \rangle$ and f calculated (equations (1), (5) and (6)) from azimuthal scans of the small-angle diffraction peak and its higher orders[a]

Peak 2θ (deg)	$\langle \cos^2 \sigma \rangle$	f
4.4	0.81	0.72
8.8	0.83	0.75
13.1	0.83	0.75

[a] The integrals of (5) have been approximated by summations at 1° intervals

are perpendicular to the chain direction and using equation (5). However, the azimuthal scan of the peak at 23.4° is composed of both equatorial and meridional peaks, which makes the integration difficult to carry out. Calculating the orientation function from the second meridional peak (37.2°) is very unreliable because of the high noise level. However, performing the integration on a curve that was mathematically smoothed, we obtained the value 0.45 for the orientation function. This very low value is partly due to the smoothing, but the main reason is probably that the second meridional peak is attributed to planes with a non-unique direction, i.e. there are several sets of planes in different crystal directions that have the same interplanar distance.

If we assume that the transition moments of the two infra-red bands at 824 and 1510 cm^{-1} do not vary between the crystalline and amorphous phase, the value of the orientation function obtained from the dichroism of these bands can be taken as a measure of the average orientation of the two phases. Using the estimated value of the crystallinity we can then calculate the value of the orientation function of the amorphous phase according to:

$$f_a = \frac{f_{tot} - X_c f_c}{1 - X_c} \qquad (7)$$

where f_{tot} is the total orientation function and f_a and f_c are the orientation functions of the amorphous and crystalline regions, respectively. With $f_{tot} = 0.53$, $f_c = 0.72$ and $X_c = 0.23$, we get the value 0.47 for the orientation function of the amorphous domains.

Comparing the values of the orientation function presented above with the values 0 for a random orientation of the polymer chains and 1 if chains are perfectly aligned with the stretching direction, we see that the chains are oriented preferably parallel to the stretching direction. It is also clear that the crystalline regions are more aligned with the stretching direction than are the amorphous regions. In order to help to visualize the degree of orientation in the polymer, we can assume a distribution function where all the chains in the amorphous region are oriented at the angle σ_a and all the chains in the crystalline region are oriented at the angle σ_c. Then:

$$f_{a,c} = (3\cos^2 \sigma_{a,c} - 1)/2 \qquad (8)$$

and

$$\sigma_{a,c} = \cos^{-1}[(2f_{a,c} + 1)/3] \qquad (9)$$

With $f_a = 0.47$ and $f_c = 0.72$ we obtain $\sigma_a = 36°$ and $\sigma_c = 26°$. This should be compared with the value $\sigma = 54.7°$ for an unoriented sample.

The deformation of a semicrystalline polymer can be described by the Kratky model[11,15]. In this model it is assumed that the material consists of a network of rigid units whose symmetry axes rotate on stretching, in the same way as lines joining pairs of points marked on the bulk material, which deforms at constant volume. Based on this model, Zbinden has derived an expression for the distribution function as a function of draw ratio[16]. From this expression the orientation function can be calculated and the result is:

$$f = 1 - \frac{3}{2}\left[1 - \frac{\lambda^3}{\lambda^3 - 1} + \frac{\lambda^3}{(\lambda^3 - 1)^{3/2}}\cos^{-1}\left(\frac{1}{\lambda^{3/2}}\right)\right] \qquad (10)$$

For $\lambda = 5$ we get the value 0.81 for the orientation function. The orientation of the crystalline phase ($f = 0.72$) is thus quite well described by the Kratky model. The orientation of the amorphous regions could, however, not be described by this model since the value of f_a is considerably lower than 0.81. This is frequently observed in semicrystalline polymers for relatively low stretch ratios and is expected since, in the amorphous domains, the 'rigid units', connecting the network points, consist of flexible chain segments with many possible conformations, at least for low stretch ratios. Furthermore, measurements of crystalline and amorphous orientations done on polyethylene drawn at varying temperatures showed a decrease in the amorphous orientation with increasing temperature while the crystalline orientation remained on a very high level[17]. This was attributed to the high mobility of amorphous chain segments at high temperatures. The low degree of orientation in the amorphous phase of the P3OT film could thus partly be due to a too high draw temperature. To obtain a higher degree of orientation in these films it is thus necessary to optimize the drawing conditions in such a way that the stretching rate and the rate of subsequent cooling exceed the rate of relaxation of the polymer chains. Furthermore, the melt processing of the films used for stretching is performed at a temperature where crosslinking is likely to occur. Such crosslinking, together with physical crosslinking by the crystallites, would probably also be one reason for reduced stretchability and low degree of orientation in the amorphous parts.

Morphology of poly(3-alkylthiophenes)

Owing to the conjugated backbone of P3OT and other conducting polymers a folded-chain model describing the crystalline state of these polymers is probably not plausible. Furthermore the large side-groups of the P3OTs makes such a model even more unlikely for this class of polymers. A more realistic model for the morphology for these polymers is the fringed micelle model, which describes the polymer as consisting of a continuous amorphous region with dispersed crystallites. Each chain passes in and out of many crystallites[18]. A stress field applied to this structure would cause the crystallites to orient by rotations and the amorphous phase to orient as an amorphous polymer with the restriction that many of the amorphous chains are physically crosslinked by the crystallites. To determine whether the fringed micelle model is appropriate or to find better models, more experiments are needed. Measurements of orientation of the different phases as a function of draw ratio would probably give valuable information concerning this matter.

Crystalline structure of poly(3-alkylthiophenes)

As can be seen in *Figures 4* and *5* the diffractogram of P3OT consists of four equatorial peaks at 4.4° (20 Å), 8.8° (10 Å), 13.1° (6.8 Å) and 23.4° (3.8 Å) and two meridional peaks at 23.4° (3.8 Å) and 37.2° (2.4 Å), the intensity of which are lower than the intensity of the equatorial peaks. The strong reflection at low angle together with its higher orders indicates a layered structure where the main chains are stacked on top of each other forming parallel planes separated by the alkyl side-chains. In *Figure 6* the interplanar distances d corresponding to the first and fourth maxima in the diffractogram are plotted *versus* the number of carbon atoms in the alkyl side-chain, n. As can be seen in the figure, the layer spacing (curve (a)) increases with increasing number of methylene groups in the side-chains. The relationship is, however, non-linear: the slope decreases with increasing length of the side-chains, being 2.1 Å per CH_2 unit between $n = 4$ and $n = 6$ and 1.4 Å per CH_2 unit between $n = 8$ and $n = 10$. This indicates that the alkyl chains of neighbouring polymer chains are non-interdigitating (two-layer packing) for short side-chains (the increase in d-spacing per CH_2 unit for interdigitating (one-layer packing) structures is expected to be no higher than 1.27 Å). Furthermore, the fact that the increment decreases with increasing number of methylene groups suggests that the overlap between neighbouring side-chains increases as the length of the side-chains is increased. This behaviour could be rationalized by a simple geometric calculation. The unit-cell parameters in close-packed triclinic paraffins (with parallel zig-zag planes) are 4.3, 4.8 and 2.5 Å for the a, b and c axis, respectively[19]. The width of two, close-packed, alkyl chains (9.6 Å) thus exceeds the distance between neighbouring side-chains attached to the same main chain (7.8 Å). An interdigitating structure would thus be impossible for short side-chains. However, for longer side-chains there is a possibility that the end segments of the side-chains are overlapping, giving rise to a partially interdigitating structure as illustrated in *Figure 7*. A further increase of the side-chain length would

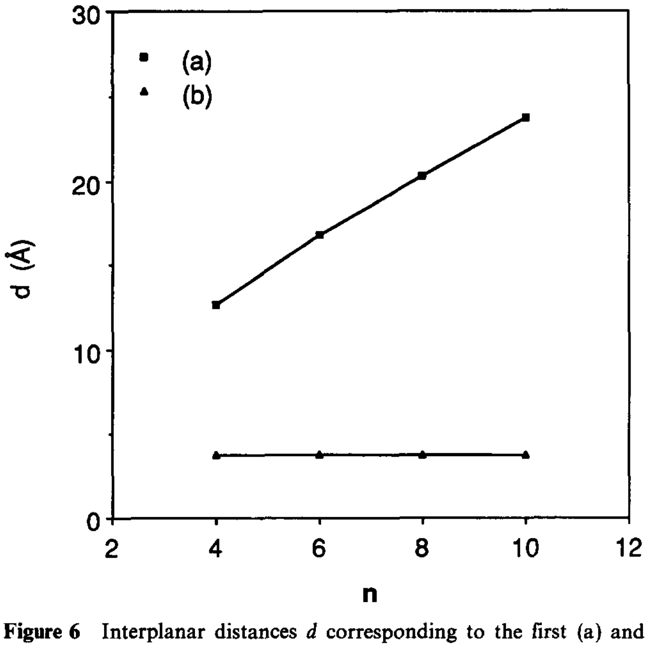

Figure 6 Interplanar distances d corresponding to the first (a) and the fourth (b) maxima in the diffractogram *versus* the number of carbon atoms in the alkyl side-chain, n. The values of d for $n = 4$ and 6 are taken from data presented by Winokur *et al.*[21]

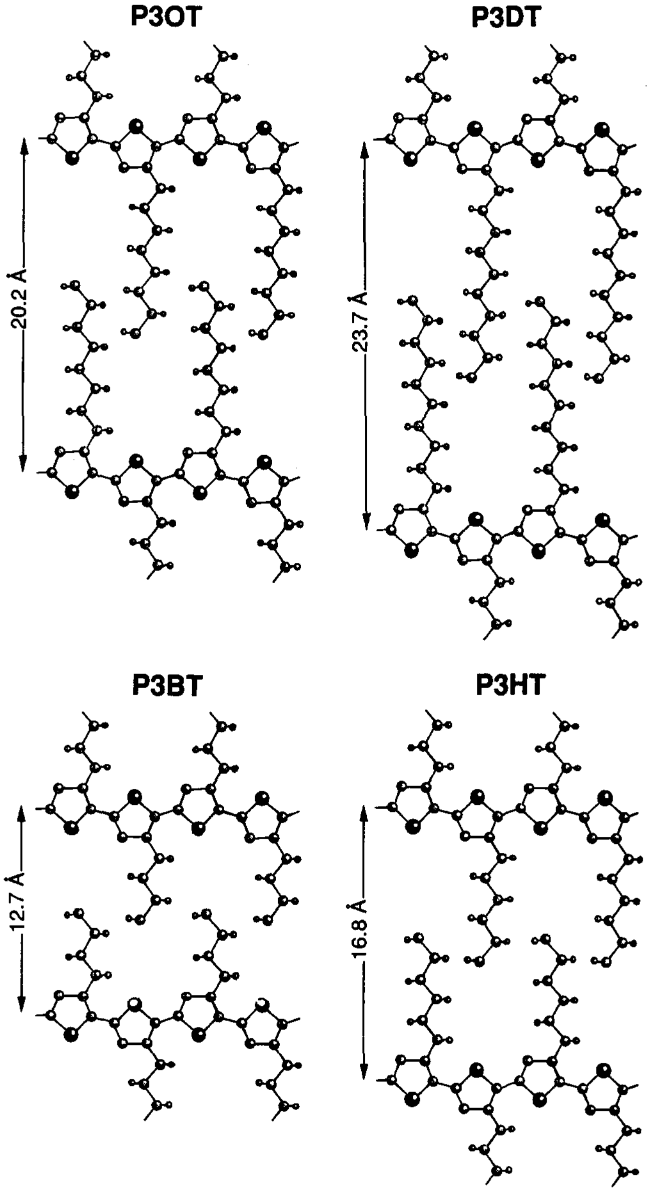

Figure 7 Illustration of a possible lateral arrangement of two polymer chains in crystals of poly(3-alkylthiophenes) with different lengths of the side-chains. The distance between the polymer chains is taken from the experimental data presented in *Figure 6*

probably increase the fraction of the side-chain segments that are overlapping and for long enough side-chains the increase in *d*-spacing per CH_2 unit should approach the value 1.27 Å.

The wide-angle equatorial peak at 3.8 Å, which does not vary with the alkyl chain length (*Figure 6*), can probably be attributed to the regular packing of the stacked main chains and their side-chains in the direction of stacking. The exact stacking pattern is difficult to predict since the interaction energy between conjugated chains depends on how the chains are stacked[20]. However, a 3.8 Å reflection is also observed in diffractograms of close-packed triclinic paraffins and has been attributed to the spacing between 1 0 0 planes[19]. If we assume that alkyl side-chains of neighbouring polymer chains are packed in the same way as triclinic paraffins ($a = 4.3$ Å, $\beta = 110°$ and $\gamma = 108°$), along the direction of stacking, we get the crystal structure shown in *Figure 8*. This structure would give rise to an equatorial peak at 3.8 Å. The strong peaks at 4.56 and 3.55 Å observed in diffractograms of triclinic paraffins would, however, not be present since these peaks are attributed to reflections in the 0 1 0 and 1 1 0 planes, respectively, and the spacing between side-chains along the polymer chain in the structure shown in *Figure 8* (7.8 Å) is much different from the spacing between neighbouring chains in triclinic paraffins ($b = 4.82$ Å). The interplanar distance corresponding to the first peak in the meridional direction ($\sim$3.8 Å) is of the order of the length of the thiophene monomer unit and could eventually be due to scattering from planes of side-chains stacked on top of each other as in *Figure 8*. For P3ATs with longer side-chains there should be a possibility for substantial overlap between the side-chains (cf. *Figure 7*) and thus a possibility that the side-chains from neighbouring polymer chains crystallize in a triclinic structure. However, those crystals should be very limited in size due to the mismatch with the thiophene repeat distance and thus gives rise to very broad peaks in a diffractogram if they can be observed at all. The peak in the azimuthal scan of the second meridional reflection ($\sim$2.4 Å) is very broad and the orientation function determined from this peak, assuming that the planes causing the reflection are perpendicular to the chain axis, shows an unreasonably low value. This can possibly be explained if this peak is attributed to a reflection in planes of the side-chain crystallites, which must not necessarily be perfectly perpendicular to the main chains.

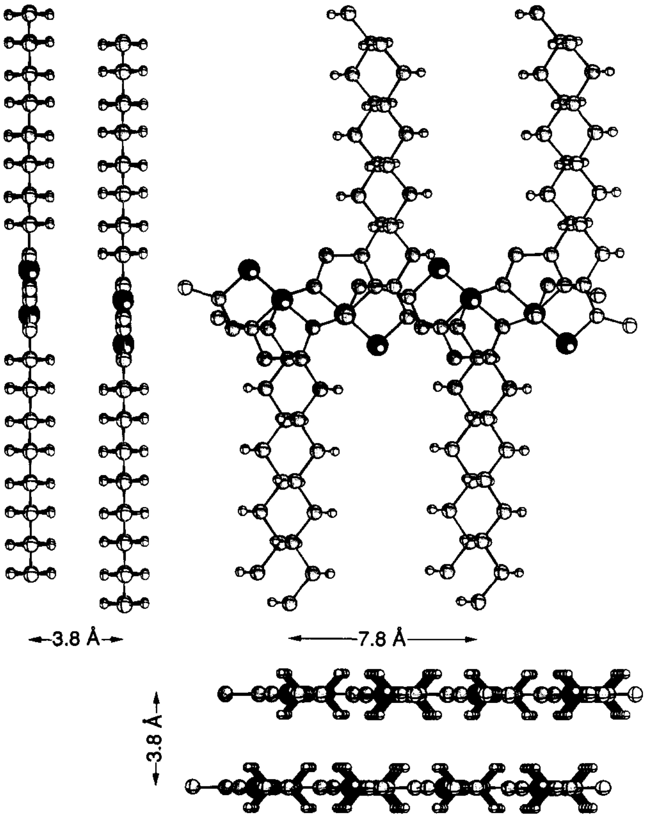

Figure 8 Illustration of a possible vertical arrangement of two polymer chains in crystals of poly(3-octylthiophene). The structure was obtained by packing the side-chains in a similar way as close-packed triclinic paraffins, along the direction of stacking. The packing of the side-chains in the direction of the polymer chain is determined by the repeat distance of the thiophene monomers ($\sim$3.9 Å)

Winokur *et al.*[21] proposed a model where successive main chains are stacked on top of each other and tilted alternately, forming a staggered structure along the stacking direction. However, in such a structure, the distance between the side-chains along the stacking direction should increase with an increase in the alkyl side-chain length. This is not observed. In fact, the position of the wide-angle equatorial peak is constant (3.8 Å) for all P3ATs measured (cf. *Figure 6*).

The crystal structure shown in *Figure 8* is very different from the structure of polythiophene where a rectangular *pgg* symmetry (herring-bone structure) has been suggested for the lateral packing of the chains[22]. This type of packing is typical for many conducting polymers but is not very probable in comb-shaped polymers due to the long side-chains. Instead the crystal structures of many comb-shaped polymers are determined by the crystallization of the side-chains[14] as suggested for P3OT in *Figure 8*. This implies that new properties can be obtained in conducting polymers simply by using different side-chains.

It should be noted that the model proposed above is based on a very limited number of experiments and that more data, especially from P3ATs with longer side-chains, are needed to verify the model.

CONCLUSIONS

Poly(3-octylthiophene) has been stretched at elevated temperature to a final length up to five times the initial length. By means of X-ray diffraction and polarized infra-red spectroscopy the degree of orientation in the crystalline and amorphous phases has been determined. The value of the orientation function in the crystalline region was 0.72, which is comparable to the value 0.81 that was predicted from a theoretical calculation based on the draw ratio. The orientation of the amorphous phase was considerably lower, 0.47. This is probably in part due to relaxation of the polymer chains, since the polymer is drawn at elevated temperature.

To reach a higher degree of orientation in the P3ATs the drawing process must be optimized. Furthermore, the number of crosslinks in the starting material should be kept at a minimum since these probably lower the degree of orientation in the amorphous regions. Since crystallites could be considered as physical crosslinks, quenching of the starting material, to reduce the crystallinity, could eventually also increase the stretchability and the degree of orientation. However, to obtain very highly oriented conjugated polymers the best way is probably to prepare the polymer by the precursor route since the conversion step in this route leads to an increase in unsaturation, which acts as an added driving force for the orientation. This is clearly demonstrated in the case of PPV where the orientation obtained for $\lambda = 5$ ($f = 0.94$)[1] is considerably higher than predicted by the Kratky model ($f = 0.80$), which is usually considered to give an upper limit for the orientation.

Based on X-ray diffraction data from P3ATs with different side-chain lengths and restricted pole figure measurements on P3OT a tentative crystal structure for the P3ATs is proposed. In this structure the side-chains are in the planar zig-zag form and confined to the plane of the thiophene backbone. The proposed crystal structure consists of a layered structure where the main chains are stacked on top of each other, at a distance of 3.8 Å, forming parallel planes, separated by the side-chains, which are partly interdigitated. The fraction of the side-chains that overlap is increased with increasing length of the side-chain.

ACKNOWLEDGEMENTS

This work was supported by Neste Oy. We are grateful to Dr Bo Liedberg and Professor Ingemar Lundström for critically reading the manuscript.

REFERENCES

1 Bradley, D. D. C., Friend, R. H., Lindenberger, H. and Roth, S. *Polymer* 1986, **27**, 1709
2 Leising, G. *Polym. Bull.* 1984, **11**, 401
3 Jen, K. Y., Miller, G. G. and Elsenbaumer, R. L. *J. Chem. Soc. Chem. Commun.* 1986, 1346
4 Sato, M., Tanaka, S. and Kaeriyama, K. *J. Chem. Soc. Chem. Commun.* 1986, 873
5 Hotta, S., Rughooputh, S. D. D. V., Heeger, A. J. and Wudl, F. *Macromolecules* 1987, **20**, 212
6 Andreatta, A., Cao, Y., Chiang, J. C., Heeger, A. J. and Smith, P. *Synth. Met.* 1988, **26**, 383
7 Hotta, S., Soga, M. and Sonoda, N. *J. Phys. Chem.* 1989, **93**, 4994
8 Laakso, J., Österholm, J.-E. and Nyholm, P. *Synth. Met.* 1989, **28**, C467
9 Yoshino, K., Onoda, M. and Sugimoto, R. *Jpn. J. Appl. Phys.* 1988, **27**, L2034
10 Österholm, J.-E., Laakso, J., Nyholm, P., Isotalo, H., Stubb, H., Inganäs, O. and Salaneck, W. R. *Synth. Met.* 1989, **28**, C435
11 Ward, I. M. 'Structure and Properties of Oriented Polymers', Applied Science, London, 1975
12 Wilchinsky, Z. W. 'Advances in X-Ray Analysis', Plenum Press, New York, 1963, Vol. 6, p. 231
13 Miller, R. L. 'Encyclopedia of Polymer Science and Technology' (Eds H. F. Mark, N. G. Gaylord and N. M. Bikales), John Wiley & Sons, New York, 1966, Vol. 4, p. 481
14 Platé, N. A. and Shibaev, V. P. 'Comb-Shaped Polymers and Liquid Crystals', Plenum Press, New York, 1987
15 Kratky, O. *Kolloid-Z.* 1933, **64**, 401
16 Zbinden, R. 'Infrared Spectroscopy of High Polymers', Academic Press, New York, 1964
17 Koenig, J. L., Cornell, S. W. and Witenhafer, D. E. *J. Polym. Sci.* 1967, **5**, 301
18 Herrmann, K., Gerngross, O. and Abitz, W. *Z. Phys. Chem. (B)* 1930, **10**, 1371
19 Turner-Jones, A. *J. Polym. Sci.* 1962, **62**, S53
20 Danielsen, P. L. and Ball, R. C. *J. Phys. (Paris)* 1985, **46**, 131; Baeriswyl, D. and Maki, K. *Phys. Rev. (B)* 1983, **28**, 2068
21 Winokur, M. J., Spiegel, D., Kim, Y., Hotta, S. and Heeger, A. J. *Synth. Met.* 1989, **28**, C419
22 Brückner, S. and Porzio, W. *Makromol. Chem.* 1988, **189**, 961