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## Structural Anisotropy of Poly(alkylthiophene) Films

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**ABSTRACT:** The structural anisotropy of various poly(alkylthiophene) films have been studied by X-ray diffraction, using both conventional methods and synchrotron radiation at grazing incidence. Solution-cast films orient with the side chains preferably normal to the film surface, whereas spin-cast films of nonstereoregular material orient with both the main and the side chains in the film plane. For thick (10–50  $\mu\text{m}$ ) solution-cast films, the degree of orientation depends strongly on the solvent used for casting, and on the stereoregularity of the polymer, films of stereoregular materials being more oriented than those of nonregular materials. The most oriented nonregular films are those cast from mixtures of chloroform and tetrahydrofuran. Thin (50–500 nm) solution-cast films are more oriented than the thicker ones, and the effects of different stereoregularity or different casting solvents are small. For spin-cast films, the degree of orientation is independent of substrate and solvent. Spin-cast films of stereoregular material have two different phases: One with the side chains normal to the substrate, and another where they are parallel to the substrate. The diffraction peaks of spin-cast poly(octylthiophene) narrow considerably upon heating.

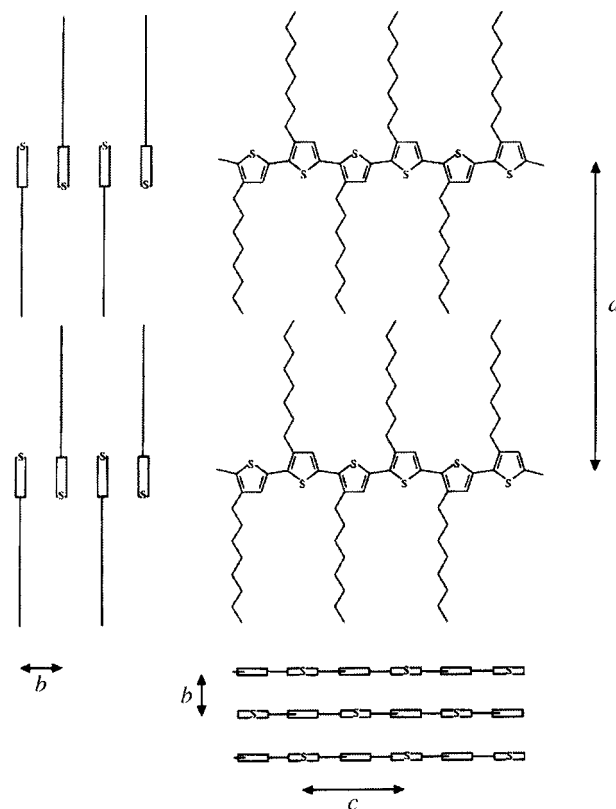
## Introduction

Poly(3-alkylthiophene)s (PAT) continue to be one of the most interesting groups among semiconducting, conjugated polymers. One reason for this is that substituted polythiophenes are promising for electrooptical applications such as light emitting diodes.<sup>1–2</sup> PAT were the first substituted polythiophenes to be synthesized and are the most studied in this class of materials.

Several workers have studied the structure of PAT, and a general agreement has been reached on basic points.<sup>3</sup> PAT are semicrystalline, with amorphous and crystalline fractions. The crystalline fraction consists of planar main chains stacked on top of each other, with a stacking distance around 3.8 Å. The alkyl side chains extend the space between neighboring main chain stacks, the separation distance depending on the alkyl side chain length. The structure is schematically shown in Figure 1. In conformity with common usage we denote the separation of main chain stacks as the *a* axis, the stacking distance of the main chains as the *b* axis, and the repetition distance along the polymer chain as the *c* axis.

PAT films have been observed to be anisotropic, with a different kind of anisotropy for different kinds of films. Bulk, solution-cast films have been found to orient with the *a* axis preferably normal to the film surface.<sup>4–5</sup> Thin, spin-cast films have on the other hand been found to orient with the *b* axis normal to the surface.<sup>6–7</sup>

In the present work, the anisotropic behavior of PAT films is studied in more detail, with varying parameters such as film thickness, solvent agent, substrate, and polymer stereoregularity.



**Figure 1.** Crystalline structure of polyalkylthiophenes. Note that this is a schematic figure, not claiming to show, e.g., the precise conformation of the side chains. The figure is taken from ref 3. Reproduced with permission. Copyright Wiley 1997.

## Experimental Section

$\text{FeCl}_3$ -polymerized poly(octylthiophene) (POT), with  $\sim 80\%$  h–t couplings and molecular weight  $M_n = 21\,500$ ,  $M_w = 43\,800$

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(and thus polydispersity  $D = 2.0$ ), was kindly supplied by Neste OY. Stereoregular poly(3-hexylthiophene) (R-PHT), with >98% h-t couplings, was purchased from Aldrich. Similar effects as reported here have also been observed for nonstereoregular poly(hexylthiophene) (PHT) synthesized at NTNU by P. H. J. Carlsen et al, for stereoregular poly(3-decylthiophene) (R-PDT) obtained from M. Trznadel, University of Mining and Metallurgy, Cracow, Poland, and for nonstereoregular poly(dodecylthiophene) (PDoDT) obtained from K. Levon, Brooklyn Polytechnic, New York.

**Solution-Cast Films.** Thick POT films were solution-cast on glass substrates from various solvents: chloroform, dichloromethane, carbon tetrachloride, tetrahydrofuran (THF), toluene, xylene, thiophene, Decalin, and various mixtures of those. The thickness of the films was around 20  $\mu\text{m}$ . POT films were also solution-cast on substrates of indium tin oxide-glass (ITO) and single-crystal silicon, using THF as solvent. A POT film was cast without contact with a substrate: It was made on a plate with a cavity, and removed while the cavity under the film still contained a concentrated solution of POT in chloroform. This particular film was 130  $\mu\text{m}$  thick.

The stereoregular R-PHT turned out to be poorly soluble in several of the solvents listed above. Chloroform is a good solvent; carbon tetrachloride and thiophene are poorer solvents, whereas the others hardly solve our R-PHT material. Films were solution-cast on glass substrates from chloroform, carbon tetrachloride and thiophene solutions, with thickness around 10  $\mu\text{m}$ .

All thick, solution-cast films were removed from the substrate by lifting with ethanol, and studied in the form of free-standing films.

Thinner submicrometer films of POT and R-PHT were solution-cast into an aluminum frame on glass slides. POT films were cast from chloroform and from chloroform/THF mixture, R-PHT films from chloroform. The film thickness could be varied by varying the concentration and/or the amount of solution. The thinner films were not homogeneous over the entire glass slide, but we chose areas with homogeneous thickness for X-ray diffraction. The thickness of the films was estimated by visually comparing with spin-cast samples of known thickness, where the thickness was known from combined use of profilometric and ellipsometric measurements. The two POT films to be presented were estimated to be 100–200 nm thick, and the two R-PHT films to be presented were estimated to be 50–100 nm and 300–500 nm thick, respectively.

**Spin-Cast Films.** Thin POT films were spin-cast onto substrates of glass, ITO, and onto single crystals of silicon, germanium and zinc selenide. The solvents used were chloroform, THF and a mixture of chloroform and THF. Thin R-PHT films were spin-cast from chloroform solution onto glass substrates.

The thickness of these spin-cast films was estimated by comparison, with other films of known thickness, to be around 100–200 nm, similar to the thickness of the thin, solution-cast films. The comparison was done both by a visual method and by comparing the preparation conditions (concentration of solution and spinning velocity) of the films.

**X-ray Diffraction.** All films were studied by X-ray diffraction.

The measurements on free-standing, solution-cast films were carried out as  $\theta$ -2 $\theta$  scintillation detector scans. The radiation was a graphite 002 monochromatized, slightly focused Cu K $\alpha$  beam ( $\lambda = 1.5418$  Å) from a rotating anode source at NTNU. The films were measured in transmission, in reflection and in intermediate geometries. The X-ray scattering vector  $\mathbf{Q}$ , defined as the difference between the scattered and the incident X-ray wave vectors, is parallel with the film surface for transmission measurements, and normal to the film surface for reflection measurements. We define  $\chi$  as the angle between  $\mathbf{Q}$  and the surface normal. For all scans,  $\chi$  was kept constant during the scan. The Laue condition, where diffraction peaks are observed when  $\mathbf{Q}$  is equal to a reciprocal lattice vector,<sup>8</sup> implies (for a pseudo-orthorhombic cell) that maximum intensity of a diffraction peak will be

observed when  $\mathbf{Q}$  is parallel with the preferred orientation of the corresponding lattice vector.

The thin films on substrates, both spin-cast and solution-cast, were studied by grazing-incidence diffraction,<sup>6–7,9</sup> to minimize the diffraction contribution from the substrate. These measurements were performed at the surface diffraction beamline BW2 at HASYLAB in Hamburg, Germany, with a wavelength of 1.540 Å and an angle of incidence with the film surface of 0.3°, and at the surface diffraction beamline ID3 at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, with a wavelength of 1.218 Å and an angle of incidence of 0.14°. In both cases the angle of incidence is close to the critical angle for total reflection against the substrate. The diffraction patterns were recorded by scintillation detectors. For scans in the plane of the film surface ("equatorial" scans), the scattering vector is almost in the plane of the film surface ( $\chi \approx 90^\circ$ ). For scans in the plane containing the surface normal and the direct beam ("meridional" scans), the scattering vector is close to being parallel with the surface normal ( $\chi \approx 0^\circ$ ). However, we do not obtain exactly  $\chi = 0^\circ$  (except at very small scattering angles), because of the nonsymmetric geometry due to the grazing incidence.

For temperature studies, the sample holder was enclosed in a Kapton container and flushed with dry nitrogen gas to avoid reactions with oxygen or water. Thin PAT films are very sensitive to damage from intense synchrotron radiation at elevated temperatures. The samples were therefore moved sideways in the beam between measurements at different temperatures, so that fresh material could be probed. Rapid scans (a few minutes) were performed in order to minimize the radiation damage.

**Quantifying the Anisotropy.** For moderately anisotropic films, all diffraction peaks are observed both in scans with  $\chi \approx 0^\circ$  and in scans with  $\chi = 90^\circ$ , but with different intensities. The degree of orientation can then be expressed by

$$A = (I_{\max} - I_{\min}) / (I_{\max} + I_{\min}) \quad (1)$$

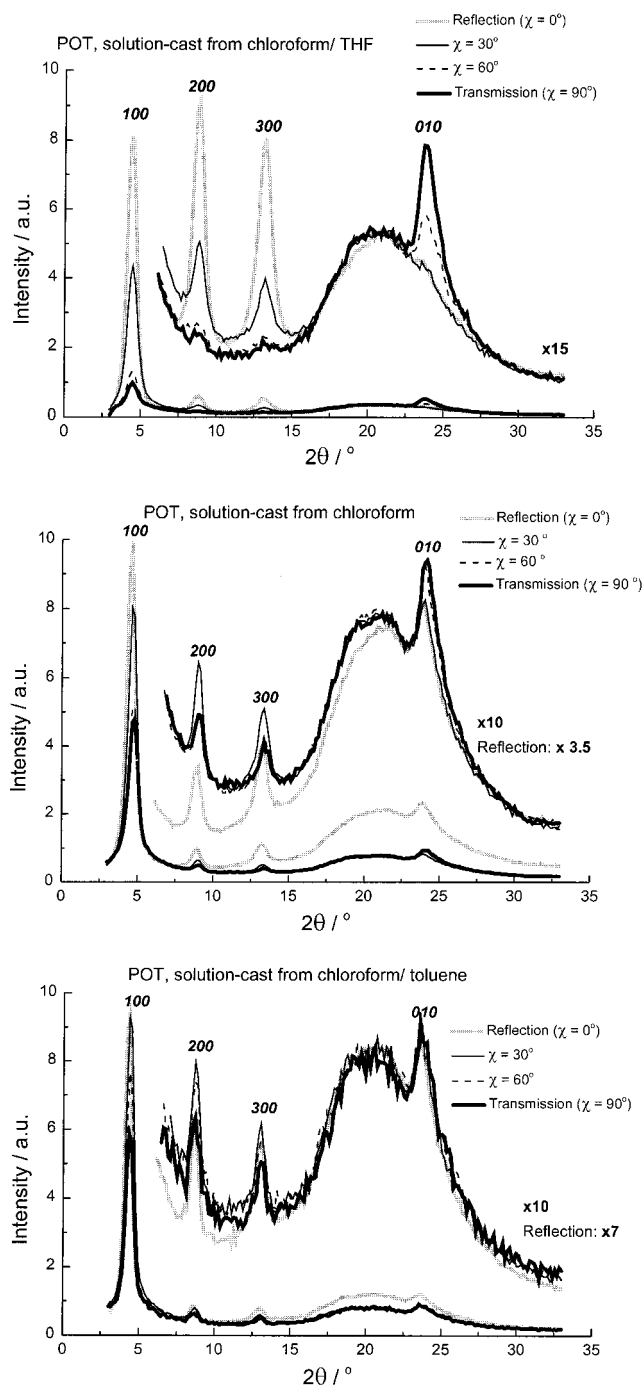
where  $I_{\max}$  and  $I_{\min}$  are the maximum and minimum intensities of a given diffraction peak in the two scans. Proper corrections must first be made for differences in scattering volumes and background signals for the two scans. The corrected anisotropy parameter  $A$  is zero for isotropic samples and unity for perfectly oriented ones.

For more anisotropic films, the diffraction peaks may be observable in just one of the two extreme scans. The  $A$  value is close to unity, but it is not suitable for describing the anisotropy, because of the large uncertainty in the determination of  $I_{\min}$ , and because of the inability to differentiate between different well-oriented films. One should then rather look at the diffraction peak intensity as a function of the angle  $\chi$ , which determines the "orientation distribution" of the material. The degree of orientation may be described by the difference  $\Delta\chi$  between the scan giving maximum intensity of a given diffraction peak and the one giving half that intensity. Note that  $\Delta\chi$  is not defined for films with a low degree of orientation.

$A$  and  $\Delta\chi$  both describe the average anisotropy of a film. For a given form of the orientation distribution, both parameters give the same information. If two samples have different forms of the orientation distribution,  $A$  and  $\Delta\chi$  give supplementary, but related, information. Increasing degree of orientation is reflected both in increasing  $A$  values and in decreasing  $\Delta\chi$  values. We shall, however, mainly restrict ourselves to the use of  $\Delta\chi$  for more oriented samples, and to the use of  $A$  for less oriented ones. In some cases, both values will be given.

## Results

**Solution-Cast POT Films.** All solution-cast POT films are found to orient with the  $a$  axis preferably normal to the substrate, in accordance with previous



**Figure 2.** Diffraction patterns of thick ( $\sim 20 \mu\text{m}$ ) POT films, with X-ray wavelength  $1.5418 \text{ \AA}$ . The films are cast from chloroform/THF mixture (upper graph), from pure chloroform (middle graph), and from chloroform/toluene mixture (lower graph). They are corrected for air scattering, and the different diffraction profiles are normalized to equal intensity of the amorphous background. For the two lower graphs, the reflection measurements are scaled according to the background at  $100$  for the nonmagnified view and according to the background at  $010$  for the magnified view.

reports. In contrast to what has been reported previously, we find very different degrees of orientation for different samples.

**(a) Thick Films.** The degree of anisotropy is found to depend strongly upon the solvent used for casting the POT films. This is illustrated by Figure 2, which shows diffraction patterns of POT cast from solvents giving very different degrees of anisotropy. The three low-angle

diffraction peaks indexed  $h00$ , which are known to be associated with the crystallographic direction along the side chains, are most intense in reflection, whereas the peak indexed  $010$ , associated with the stacking of the main chains, is most intense in transmission. This shows that the  $a$  axis is preferably oriented normal to the film surface. The degree of orientation of a sample is seen by comparing diffraction curves for different  $\chi$  values. The  $200$ ,  $300$ , and  $010$  reflections are all suitable for quantifying the anisotropy as described in the Experimental Section. Corrections for differences in effective scattering volumes for scans with different  $\chi$  values are done by normalizing the peak intensity to the intensity of the background (corrected for air scattering) as interpolated for the peak position. This is based on the assumption that the diffuse scattering is isotropic, and therefore a suitable measure of the effective scattering volume. For the free-standing films,  $100$  is not used for determining the anisotropy, because the determination of the background under that peak is very uncertain.

The most anisotropic of the investigated films are the ones cast from a mixture of chloroform and THF. The film of Figure 2 (upper) is characterized by anisotropy values (defined in the Experimental Section)  $A = 0.91$  and  $\Delta\chi = 15\text{--}20^\circ$  from  $h00$ , and  $A = 0.83$ ,  $\Delta\chi = 20\text{--}25^\circ$  from  $010$ . A POT film cast from chloroform/THF by extremely slow evaporation of the solvent is even more anisotropic:  $A = 0.94$  from  $h00$ ,  $A = 0.88$  from  $010$ , and  $\Delta\chi \sim 15^\circ$  for all reflections. POT films cast from chloroform are moderately anisotropic, the film of Figure 2 (middle) have anisotropy values  $A = 0.43$ ,  $\Delta\chi \approx 60^\circ$  from  $h00$ , and  $A = 0.23$  from  $010$ . When POT is cast from a mixture of chloroform and toluene the resulting film is much less anisotropic, the lower diffraction pattern of Figure 2 gives  $A = 0.20$  for all diffraction peaks. Other solvents and solvent mixtures give varying degrees of anisotropy. Among the pure solvents studied, dichloromethane gives the most oriented films, approaching the anisotropy of chloroform/THF films, whereas films cast from toluene or mixtures containing toluene have the lowest anisotropy.

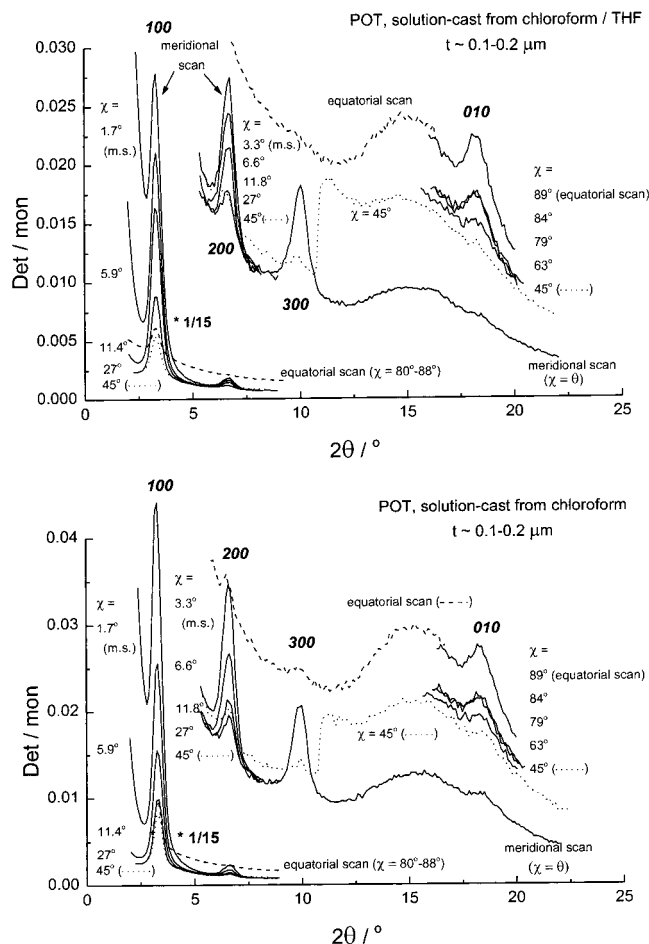
For films cast from chloroform/THF mixture, varying the mixing ratio does not have a great influence on the degree of anisotropy.

POT films cast onto substrates of ITO-glass, and onto single-crystal silicon, give similar results as the ones cast on glass. The film cast without contact with a substrate is slightly more anisotropic than those cast on substrates (from chloroform solution).

**(b) Thin Films.** Figure 3 shows diffraction patterns of thin POT films solution-cast from chloroform and from chloroform/THF mixture. The film thickness is around  $1/100$  of that of the thick films. From the diffraction patterns, we see that the films are well oriented with the  $a$  axis normal to the substrate. Contrary to the situation for thicker films, there is not a very big difference between the film from chloroform and that from chloroform/THF mixture. In fact, the  $h00$  peaks are more confined to the meridional scan for the chloroform film ( $\Delta\chi = 10^\circ$ ) than for the chloroform/THF film ( $\Delta\chi = 15\text{--}20^\circ$ ). For the  $010$  reflection, the two films yield the same value of  $\Delta\chi = 20^\circ$ .

However, for the chloroform sample, remnants of the  $h00$  peaks are observed in the equatorial scan, and a weak  $010$  peak is observed in the meridional scan. This

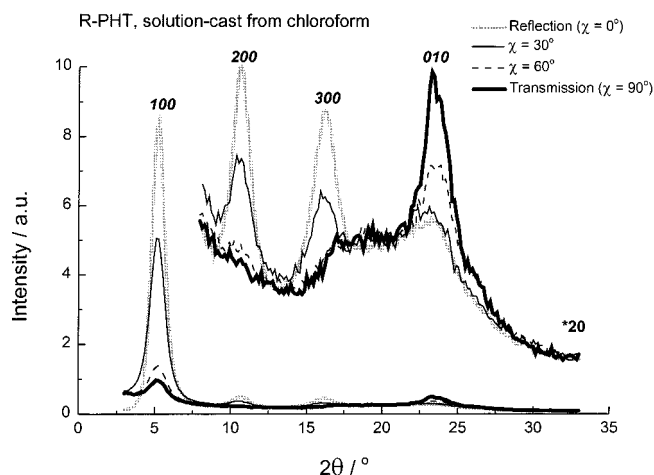




**Figure 3.** Grazing incidence diffraction patterns of thin ( $\sim 100$ – $200$  nm), solution-cast POT films, with X-ray wavelength  $1.218$  Å. The films are cast from chloroform/THF mixture (upper graph) and from pure chloroform (lower graph). The listed  $\chi$  values correspond to the angle between the X-ray scattering vector and the film normal at the peak positions. The anomalous jump in intensity at  $2\theta = 11^\circ$ , for the  $\chi = 45^\circ$ -scan, is an artifact of the diffractometer.

implies that even though most of the material is well oriented with the  $a$  axis along the surface normal, there is an observable amount of material oriented normal to this. In other words: The angular distribution of the  $a$  axes is narrow, but with significant tails. For the chloroform/THF sample, the  $h00$  peaks are much more suppressed in the equatorial scan, and similar to the  $010$  of the meridional scan. The angular distribution of the  $a$  axes is broader than for the chloroform sample, but the tails are less significant.

**Solution-Cast R-PHT Films.** Figure 4 shows the diffraction pattern from a thick ( $10\ \mu\text{m}$ ) film of R-PHT solution-cast from chloroform. Also this material is seen to be oriented with the  $a$  axis normal to the film surface. The anisotropy is stronger than for a similar POT film: The  $\Delta\chi$  value is around  $30^\circ$ , and the  $h00$  reflections are hardly observable in reflection. Similar strong anisotropy is observed also for the films cast from carbon tetrachloride and from thiophene. These two solvents give low anisotropy of POT films. Attempts to further enhance the anisotropy of R-PHT films by casting from chloroform/THF mixture were not successful, because the material is not sufficiently soluble in this mixture. Nor is it soluble in dichloromethane or other solvents that yield highly oriented POT films.



**Figure 4.** Diffraction pattern of a thick ( $\sim 10\ \mu\text{m}$ ) R-PHT film solution-cast from chloroform, with X-ray wavelength  $1.5418$  Å. The different diffraction profiles are normalized to equal intensity of the amorphous background.

Figure 5 shows diffraction patterns from thin films of R-PHT, solution-cast from chloroform. The anisotropy is of the same kind as for the thicker film, but even more pronounced. For the film with estimated thickness  $400$  nm, the  $\Delta\chi$  value is  $15^\circ$ ; for the one with estimated thickness  $100$  nm or below, the  $\Delta\chi$  value is  $7^\circ$ . The degrees of orientation of thin, solution-cast films of R-PHT and POT are thus comparable.

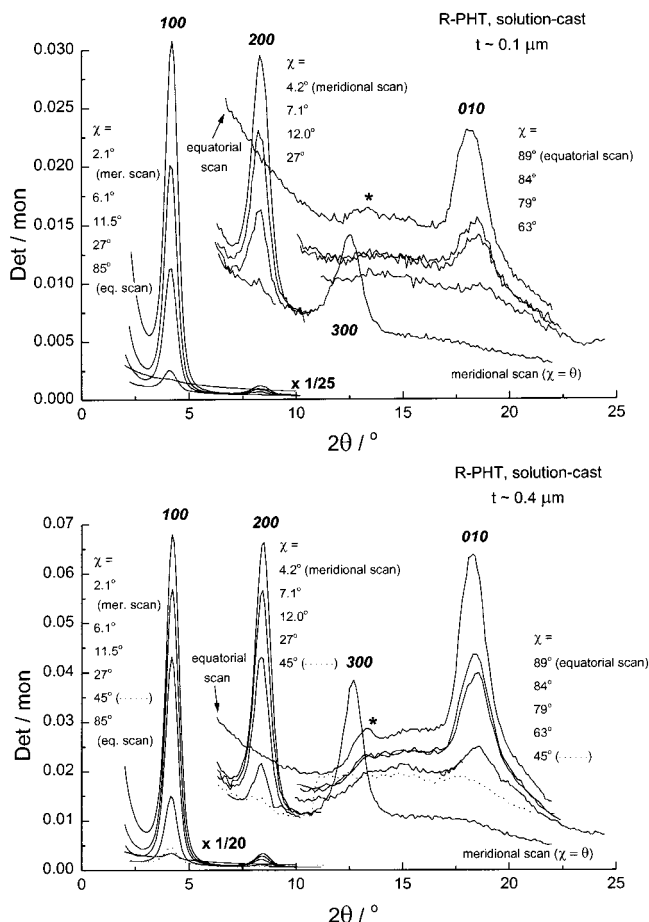
By checking with thick solution-cast films of nonregular PHT and R-PDT, we have settled that the different behavior of POT and R-PHT is caused by the different degrees of stereoregularity, not by the different side chain lengths. Reports in the literature also present very anisotropic solution-cast films of stereoregular R-PAT.<sup>10</sup>

**Spin-Cast POT Films.** Figure 6 shows the diffraction pattern of a spin-cast POT film on single-crystal silicon. The  $h00$  reflections are confined to the plane of the film, as observed previously for spin-cast POT on glass.<sup>7</sup> It is noteworthy that the  $010$  reflection is also observed, which has not been the case in previous work,<sup>6–7</sup> because of experimental limitations. As expected, this reflection is strongest for meridional scans.

All the studied thin, spin-cast POT films are found to orient with their  $b$  axis normal to the substrate, with a  $\Delta\chi$  value around  $10^\circ$ . This value is found both from  $h00$  and from  $010$  reflections. Neither the kind of substrate nor the type of solvents used seems to have significant influence on the degree of orientation for these spin-cast films.

**Spin-Cast R-PHT Films.** Figure 7 shows the diffraction pattern of a thin, spin-cast R-PHT film. All the peaks ( $h00$  and  $010$ ) are observed, both in meridional and in equatorial scans. Both the  $a$  and the  $b$  axis are therefore present in orientations in the film plane, and also normal to it. However, all peaks are weaker for intermediate scans. We interpret this as the presence of two kinds of orientations in the film: One with the  $a$  axis oriented normal to the film surface (similar to solution-cast films) and another with the  $b$  axis oriented in this way (similar to spin-cast POT films). Both kinds have narrow distributions: We find  $\Delta\chi$  values around  $10$ – $20^\circ$  for both cases.

In a work by Fell et al.,<sup>6</sup> spin-cast nonregular PHT was observed to orient similarly to POT. Also in this case, the different behavior of R-PHT and POT is

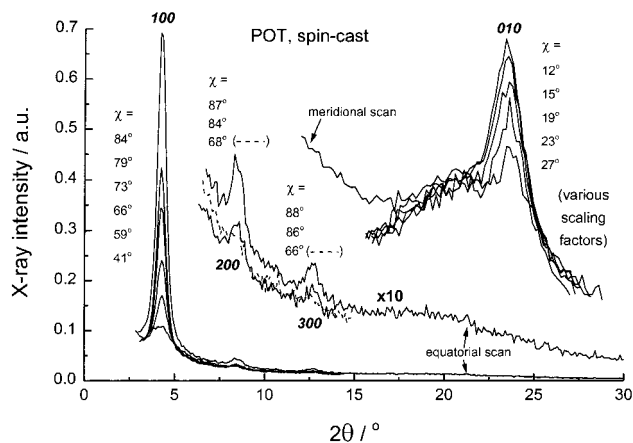


**Figure 5.** Grazing incidence diffraction patterns of thin, solution-cast R-PHT films, with X-ray wavelength 1.218 Å. The upper graph is from a thinner film than the lower graph, both films being cast from chloroform. The listed  $\chi$  values correspond to the angle between the X-ray scattering vector and the film normal at the peak positions. The peak marked with an asterisk is observed at  $2\theta = 13.2^\circ$  in the equatorial scan, and corresponds to a  $d$  spacing of 5.3 Å in a direction parallel with the film plane. This has not been observed previously for PHT, and may arise from an impurity. The anomalous jump in intensity at  $2\theta = 11^\circ$ , for the  $\chi = 45^\circ$ -scan, is an artifact of the diffractometer.

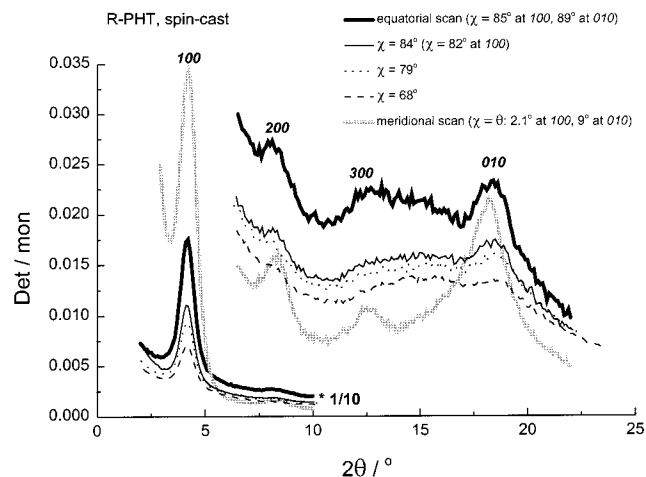
caused by the different stereoregularities and not by the different side chain lengths.

**Crystallite Sizes.** The width (in scattering angle  $2\theta$ ) of the diffraction peaks can be related to the size of the crystallites by the well-known Scherrer formula.<sup>8</sup> For the diffraction patterns presented above, the peaks of R-PHT are generally broader than those of POT, corresponding to average crystallite sizes of 80 Å for R-PHT and 110 Å for POT. Spin-cast and solution-cast films give similar results. In fact, we had expected the opposite behavior, that the more regular material should have the largest crystallite sizes. A possible explanation may be that our R-PHT material is more cross-linked than the POT material, which also may explain the poor solubility of R-PHT in commonly used solvents such as THF and toluene. Other workers have concluded that stereoregular PAT form larger ordered regions than nonregular PAT do.<sup>11</sup>

A spin-cast POT film was studied as a function of the temperature, the equatorial scans are shown in Figure 8. The diffraction peaks become narrower with increasing temperature, until the crystalline diffraction vanishes around 120 °C (a scan at 115 °C gave observable



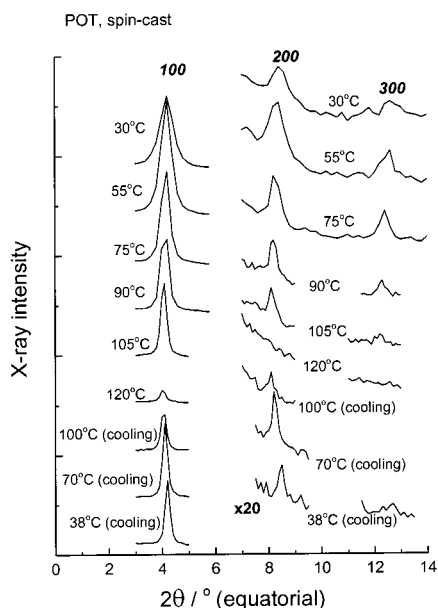
**Figure 6.** Grazing incidence diffraction pattern of a thin, spin-cast POT film, with X-ray wavelength 1.540 Å. The film was spun from chloroform solution on single-crystal silicon, other substrates and solvents gave similar results. The listed  $\chi$  values correspond to the angle between the X-ray scattering vector and the film normal at the peak positions. The curves showing the 010 reflection for  $\chi < 30^\circ$  are normalized to equal intensity of the amorphous background at the peak position, because of very large variations of the effective scattering volume seen by the detector for the different scans. The curves showing the  $h00$  reflections are on the other hand shown in absolute intensity.



**Figure 7.** Grazing incidence diffraction patterns of a thin, spin-cast R-PHT film, with X-ray wavelength 1.218 Å. For a similar sample, scans were performed for  $\chi < 45^\circ$ , and the intensity of all diffraction peaks was found to decrease with increasing  $\chi$ .

100, 200, and 300 peaks). The narrowing corresponds to an increase in crystallite size from 120 Å at 30 °C to 300 Å at 105 °C, using noncorrected peak widths. If the instrumental broadening is nonnegligible, the increase in crystal size is even larger. The diffraction peaks reappear upon cooling the "melted" polymer, and they are narrow at all temperatures (corresponding to 300 Å crystallite size). This shows that the peak narrowing is caused by some kind of annealing effect and not by a reversible phase transition.

Peak narrowing upon heating has previously been observed for thick solution-cast films of PDoDT,<sup>4,12</sup> but not for POT or other PAT with shorter side chains (to the best of our knowledge). We have looked for such peak narrowing for thick, solution-cast POT films, without finding significant effects. For thick, solution-cast films of PDoDT and R-PDT, we do observe peak narrowing upon heating.



**Figure 8.** Equatorial diffractograms during heating and cooling of a thin, spin-cast POT film, with X-ray wavelength 1.540 Å under grazing incidence. The film was spun from THF solution on glass.

For PDoDT, the peak narrowing has been attributed to a combination of annealing effects and a liquid crystalline polymer transition.<sup>4,13</sup> Prosa et al.<sup>13</sup> have performed detailed diffraction line-shape analysis of preannealed PDoDT films heated through this transition. By this approach, contributions from crystallite size, lattice parameter variations and disorder fluctuations could be separated. Our data on spin-cast POT are not sufficiently precise for a similar approach. The cited crystallite sizes should therefore not be taken as absolute values, but rather as relative indications of the crystalline coherence lengths.

Another consequence of the heat treatment is a great reduction in the anisotropy of the film. This was observed in a previous work,<sup>7</sup> by the presence of both  $h00$  and  $010$  reflections in the equatorial scan of a heated and cooled spin-cast POT film. This is verified in the present work, where all reflections ( $h00$  and  $010$ ) are observed in both meridional and equatorial scans after the heat treatment (not shown).

## Discussion

**Solution-Cast Films.** Thin, solution-cast films are much more oriented than thicker ones are, the effect being strongest for POT films from chloroform. This suggests that the orientation effect is associated with the interfaces between the solution and the substrate or the air. For thinner films, relatively more of the material is close to the interfaces, so interface effects will contribute more. A possible mechanism may be that the alkyl side chains tend to orient normal to one or both of the interfaces and that the polymer chains further inside the film adapt a similar orientation when the polymer crystallizes. Thus, the orientation is kept through the entire film, but with a stronger degree of orientation at one or both interfaces than in the interior of the film.

The different investigated substrates give similar anisotropy for solution-cast POT. The sample cast without contact with a substrate is somewhat more oriented, even though it is considerably thicker than those cast

on substrates. This indicates that the interface to air is more important than the substrate for the resulting anisotropy.

Whereas the studied thin, solution-cast films all have comparable degrees of orientation, this is not the case for the thicker ones. Thick films from stereoregular materials are more oriented than the ones from nonregular materials, and the choice of solvent used for the casting has major importance for the degree of orientation, at least for nonregular material. Since these differences are seen only for thicker films, the difference is found mainly in the interior part of the films.

**Spin-Cast Films.** For spin-cast films of nonregular POT, the anisotropy is of a different kind than for the solution-cast films: The polymer chains orient with both the main and the side chains parallel to the substrate. The kind and degree of orientation is independent of the solvent and of the substrate. It is the spin-casting process itself that yields the described anisotropy. It is natural to assume that the crystallization of spin-cast films starts at the substrate, and that the film grows outward as the solvent vanishes. The time scale is very different from that of solution-casting: spin-cast films form within a small fraction of a second, while solution-casting takes minutes or hours. The orientation obtained by spin-casting is probably forced by the short time scale and need therefore not be the thermodynamically most stable one. This is supported by the finding reported above, that the orientation obtained by spin-casting is not kept upon heating above the melting point, followed by cooling.

Spin-cast R-PHT films have the interesting property that there are two kinds of orientations present, one with the side chains in the plane of the substrate and another where they are normal to the substrate, both kinds being well oriented. We propose that the material close to the substrate orients with the side chains in the plane of the substrate (the "normal" spin-cast orientation), whereas the material close to the solution-to-air interface orients with the side chains normal to the substrate (the orientation observed for solution-cast films). The proportion of the two kinds of orientation is then a result of a competition as they extend into the interior of the film from each side. It may well be that both kinds of orientation exist also in spin-cast films of nonregular POT. If this is so, that with the side chains normal to the substrate, assumed to be located close to the air interface, does not extend sufficiently long into the sample to be observable. For the film from stereoregular material, however, the two kinds of orientation exist in proportions of the same order of magnitude. The discussion of solution-cast films above concluded that the stereoregular material has a better ability than the nonregular material to retain that kind of orientation to macroscopic thickness. It is probably the same property that is responsible for the large proportion of solution-cast-like orientation in spin-cast R-PHT films.

**Anisotropy of Other Substituted Polythiophenes.** Also films of several other substituted polythiophenes have been observed to be anisotropic. Solution-cast films of poly(3-(4'-octylphenyl)thiophene) (POPT),<sup>14</sup> poly(3-(2',5'-dioctylphenyl)thiophene) (PDOPT),<sup>15</sup> and poly(3,3'-dioctyl-2,2'-bithiophene) (PDOT<sub>2</sub>)<sup>16</sup> orient to varying extent with the octyl side chains preferably normal to the film surface, similarly to the situation for PAT. Poly(3,4-ethylenedioxythiophene) (PEDOT) films orient with



the side groups normal to the substrate.<sup>17</sup> The latter films are made by polymerization of the monomer in the form of films. The ordering probably takes place during the polymerization process, with a time scale of minutes. This time scale is comparable to that of the solution-casting process.

To the best of our knowledge, PDOPT and PDOT<sub>2</sub> are the only polythiophenes different from PAT where the structural anisotropy of spin-cast films has been studied. Spin-cast PDOT<sub>2</sub> has a low anisotropy,<sup>16</sup> whereas spin-cast PDOPT is well oriented,<sup>15</sup> but with the octyl side chains normal to the substrate, as for solution-cast films. However, the side chains of PDOPT are orthogonal to the main chain, so the plane of the polythiophene backbone is parallel with the substrate for spin-cast films both for PDOPT and for PAT. PDOT<sub>2</sub> does not have a planar thiophene backbone, which may explain the lack of orientation for this polymer.

**Consequences of the Anisotropy.** The anisotropy of a film may have consequences for the light absorption and emission properties of the polymer film, especially for polarized light absorbed or emitted. However, these properties depend mainly on the direction of the conjugated main chains. For both spin-cast and solution-cast PAT films (as well as for the other anisotropic films listed in the previous section), the main chains are oriented parallel with the plane of the surface.

The conductivity is presumably highest in the direction of the main chains, and should therefore be higher in the film plane than normal to it for all samples. The conductivity is presumably significantly higher along the *b* axis, the direction of stacking of main chains, than along the side chains (the *a* axis), because of the small separation of conjugated chains in the *b* direction. Spin-cast PAT may therefore have a higher conductivity normal to the film surface than solution-cast PAT. This may be of importance in the construction of various devices based on PAT, where a current normally is passed perpendicular to a thin PAT film.

Literature reports are scarce on anisotropic properties of PAT films. That is, many reports exist on optical and electrical anisotropy of the more obviously oriented stretched films, but anisotropy relative to the film normal has to a large degree been ignored. Reports exist on anisotropic conductivity of Langmuir–Blodgett PAT films<sup>18,19</sup> and on electrodeposited POT films,<sup>20</sup> in both cases claiming that the conductivity is several orders of magnitude larger in the film plane than along the film normal. Also electrodeposited unsubstituted polythiophene has been reported to have the same kind of anisotropic conductivity.<sup>21</sup> Furthermore, PEDOT has been revealed by spectroscopic ellipsometry to behave as a metal in the film plane and as a dielectric along the film normal,<sup>22</sup> a behavior explained by our previously proposed structure model for this polymer.<sup>17</sup> Reports on measurements of anisotropic conductivity for solution-cast or spin-cast PAT are not known to us. The conductivity of spin-cast films is reported to be 2 orders of magnitude larger than for solution-cast films,<sup>23</sup> but it is not clear whether this is the conductivity in the film plane or normal to it, as anisotropy is not considered in the cited article.

Anisotropic films are very useful in the determination of unknown polymer structures. An anisotropic diffraction pattern can be indexed more precisely than an isotropic powder pattern, and different peaks resolved in an anisotropic pattern may overlap in an isotropic

one. Spin-casting or solution-casting with various solvents may give anisotropic films of various polymers subject to structural study. Indeed, the preparation of anisotropic films has been important in the work to propose structural models of PEDOT,<sup>17</sup> PDOPT,<sup>15</sup> POPT,<sup>14</sup> and polypyridine.<sup>24</sup>

## Conclusion

We have studied the structural anisotropy of poly(alkylthiophene) films, as a function of preparation technique, polymer stereoregularity, film thickness, solvent, and substrate. Solution-cast films orient with the alkyl side chains normal to the film surface, whereas spin-cast films of nonregular PAT orient with both the main and the side chains in the plane of the film surface. For spin-cast films of stereoregular PAT, both kinds of orientations are present.

The degree of orientation of solution-cast films depends on the film thickness, on the solvent used for casting, and on the polymer stereoregularity. We have attempted to explain this as an effect starting with orientation of polymer chains at the interface of the solidifying solution, followed by a similar ordering of polymer chains further inside the crystallizing film. The ability of polymer chains to orient in the same way as those closer to the interface depends on the stereoregularity of the polymer, and on the interactions with the actual solvent used for casting.

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