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Structural Ordering in Phenyl-Substituted Polythiophenes

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ABSTRACT: Various substituted poly(phenylthiophene)s have been studied by X-ray diffraction. They are semicrystalline, with very different degrees of crystallinity. Those with para-substituted phenyl groups have a low degree of crystallinity, whereas those with ortho-substituted phenyl groups are more crystalline. The most crystalline materials in this study have two equally long substituents on the phenyl ring, one at the ortho position and the other at the ortho or meta position on the opposite side of the phenyl ring. Poly(3-(2,5-dioctylphenyl)thiophene) (PDOPT) was most thoroughly studied, and a structural model is proposed. The structure of PDOPT is quite different from previously studied substituted polythiophenes in that the octyl side chains are directed normal to the thiophene planes. In this way, the conjugated polymer chains are kept separated from each other. Solution-cast and spin-cast PDOPT films are anisotropic, with the octyl side chains oriented normal to the film surface in both cases. This is contrary to the situation for poly(3-alkylthiophene)s, where solution-cast and spin-cast films orient in different ways.

Introduction

Substituted polythiophenes are materials of great interest. Quite many of these semiconducting, conjugated polymers have been widely studied the past decade, both for fundamental reasons and because of their potential for applications, for instance in the field of electrooptics.[1] Their properties may be tailored by choosing proper substituents. The most studied subgroup of polythiophenes is poly(3-alkylthiophene)s (P3ATs), which have nonbranched alkyl groups as substituents.

A series of substituted poly(3-phenylthiophene)s were recently synthesized,[2] and the optical properties of this class of materials have been studied in great detail by Theander et al.[2,3] Some poly(phenylthiophene)s, in particular poly(3-(2,5-dioctylphenyl)thiophene) (PDOPT), are promising for electrooptical applications such as light-emitting diodes or lasers.[4]

Knowledge of the structure of a material is essential for understanding its properties. Previous structural studies exist only for one poly(phenylthiophene), namely poly(3-(4-octylphenyl)thiophene) (POPT).[5,6] The diffraction patterns of POPT powder and solution-cast film are shown in Figure 1 (from Fell et al.[5]). The existing structural model involves stacks of polymer chains, with a stacking distance $b = 5.06$ Å. The phenyloctyl side chains span the space between the main chains in the direction orthogonal to the stacking direction. This distance is $a = 28.4$ Å. The structure is basically similar to the established P3AT structure,[7] with larger interchain distances in order to give space for the phenyl unit.

The present work involves X-ray diffraction studies of seven poly(phenylthiophene)s with different substituent patterns. The polymers are presented in Figure 2. They are highly stereoregular, with around 90% head-to-tail couplings.

The most thoroughly studied compound in the present work is PDOPT. This particular material is notable for its exceptionally high luminescence yield,[3] and as will be shown in the present work, this property can be correlated with its particular crystalline structure which keep the conjugated polymer chains well separated.

Additional information from other experimental techniques is valuable when constructing structural models. For example, the band gap can be determined from optical spectroscopy. It is known to relate to the planarity of the backbone: a low band gap corresponds to a planar backbone. The observed band gap in P3ATs is around 1.9 eV,[8] and these polymers are believed to have planar thiophene backbones. Poly(3,3′-dioctyl-2,2′-bithiophene) has a band gap around 2.7 eV,[9] where the higher value is believed to be associated with a twisted backbone. Theander et al.[3] have measured optical spectra for several phenyl-substituted polythiophenes, which all have low band gaps, for example 2.0 eV for PDOPT. We therefore have good reason to assume planar thiophene backbones for the polymers of the present study.

Experimental Section

The synthesis of the polymers in this study is reported elsewhere.[2] All materials were studied by powder X-ray diffraction. Two polymers, PDOPT and POMeOPT, were also studied in the form of free-standing films, and PDOPT was also studied in the form of thin films on substrates.

The powder samples were pressed into pellets in a hole of a lead sample holder, and the measurements were carried out in transmission. The free-standing films were solution-cast from a mixture of chloroform and tetrahydrofuran, a mixture

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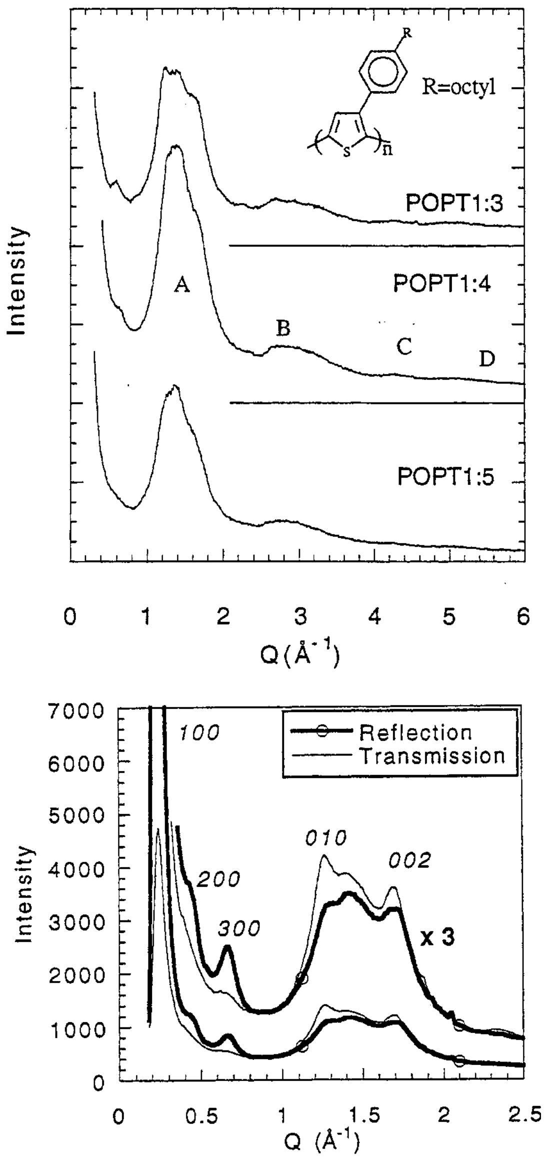

Figure 1. Diffraction patterns from POPT powder (above), synthesized under different conditions, and solution-cast POPT film (below), as a function of $Q = 4\pi \sin \theta/\lambda$. Reproduced with permission from ref 5. Copyright 1995 Elsevier.

known to enhance the anisotropy of solution-cast P3ATs.[10] These films were studied in both transmission and reflection. The measurements on both powders and free-standing films were carried out as $\theta-2\theta$ scintillation detector scans. The radiation was a graphite 002 monochromatized, slightly focused Cu Kα beam ($\lambda = 1.5418$ Å) from a rotating anode source at NTNU.

The thin, deposited PDOPT films were spin-cast on glass and silicon substrates. They were studied by grazing incidence diffraction[11] at the surface diffraction beamline ID3 at the European Synchrotron Radiation Facility, Grenoble, France. The wavelength was $\lambda = 1.218$ Å, with an angle of incidence with the film surface of $\alpha_i = 0.15°$. The diffraction pattern was recorded with a scintillation detector, scanned both parallel with the plane of the film surface ("equatorial scan") and in the plane containing the surface normal and the direct beam ("meridional scan").

Structure modeling of PDOPT was carried out using the diffraction program package PowderCell.[12]

The densities of the free-standing films of PDOPT and POMeOPT were measured by the flotation method, using a mixture of water, ethanol and ethylene glycol, giving $\rho = 1.00$ g/cm^3 for PDOPT and $\rho = 1.03$ g/cm^3 for POMeOPT.

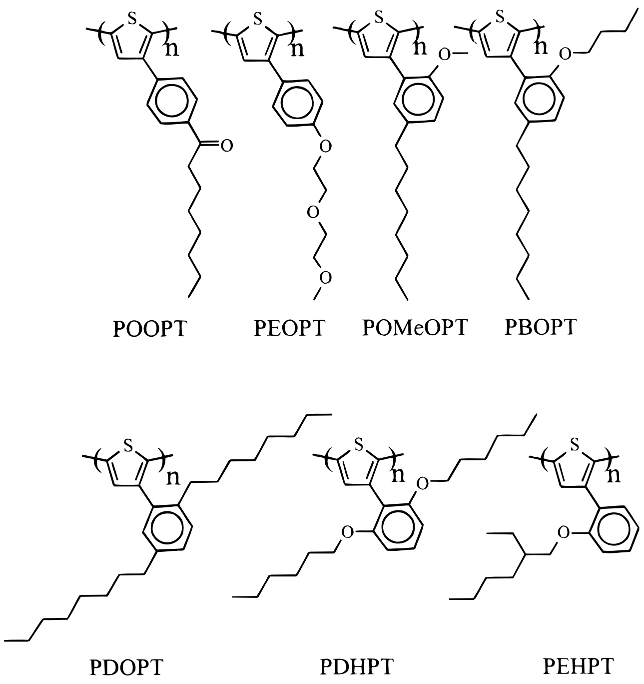

Figure 2. Molecular structures of the seven polymers of the present study.

Diffraction Results

We shall first present the overall results, and then discuss the different materials with a special emphasis on PDOPT.

Powders. Figure 3 shows powder diffractograms for the various polymers. From these one sees that all materials are semicrystalline, with crystalline diffraction features superimposed on amorphous scattering. The amorphous scattering consists of broad peaks, the most important one being centered around 20° for all polymers in this study. An amorphous peak at this position is observed for most polythiophenes.[7] The materials have very different degrees of crystallinity, as is seen from the varying distinctness of the Bragg peaks. We notice that those with the substituents of the phenyl ring at the para position are less crystalline, whereas those substituted at the ortho position (with substituents longer than a methoxy group) are more crystalline. The most crystalline ones in this study are PDOPT and PDHPT, which both have two long chains substituted on the phenyl ring. It is quite surprising that the polymers with the most bulky side groups are the most crystalline. Indeed, we had originally expected these polymers to be amorphous. By application of the Ruland method,[13] the crystallinity of PDOPT is estimated to be 40%.

The diffraction peaks are relatively broad, however. The fwhm of the powder diffraction peaks range from 1.2° (PDOPT) to 2.4° (PBOPT), corresponding to a crystallite size of 75 Å for PDOPT to 35 Å for PBOPT. For POMeOPT, and even more so for PEOPT, the peaks are weak and even broader than for PBOPT. In this context it is not unlikely that the *helical* configuration of the PEO chain may be an important factor to prevent order in PEOPT.

Films. Figure 4 shows the diffractogram from a solution-cast film of PDOPT. We observe the same peaks as for the powder sample. The film is moderately anisotropic, as can be seen by comparing transmission and reflection measurements. The peaks are narrower

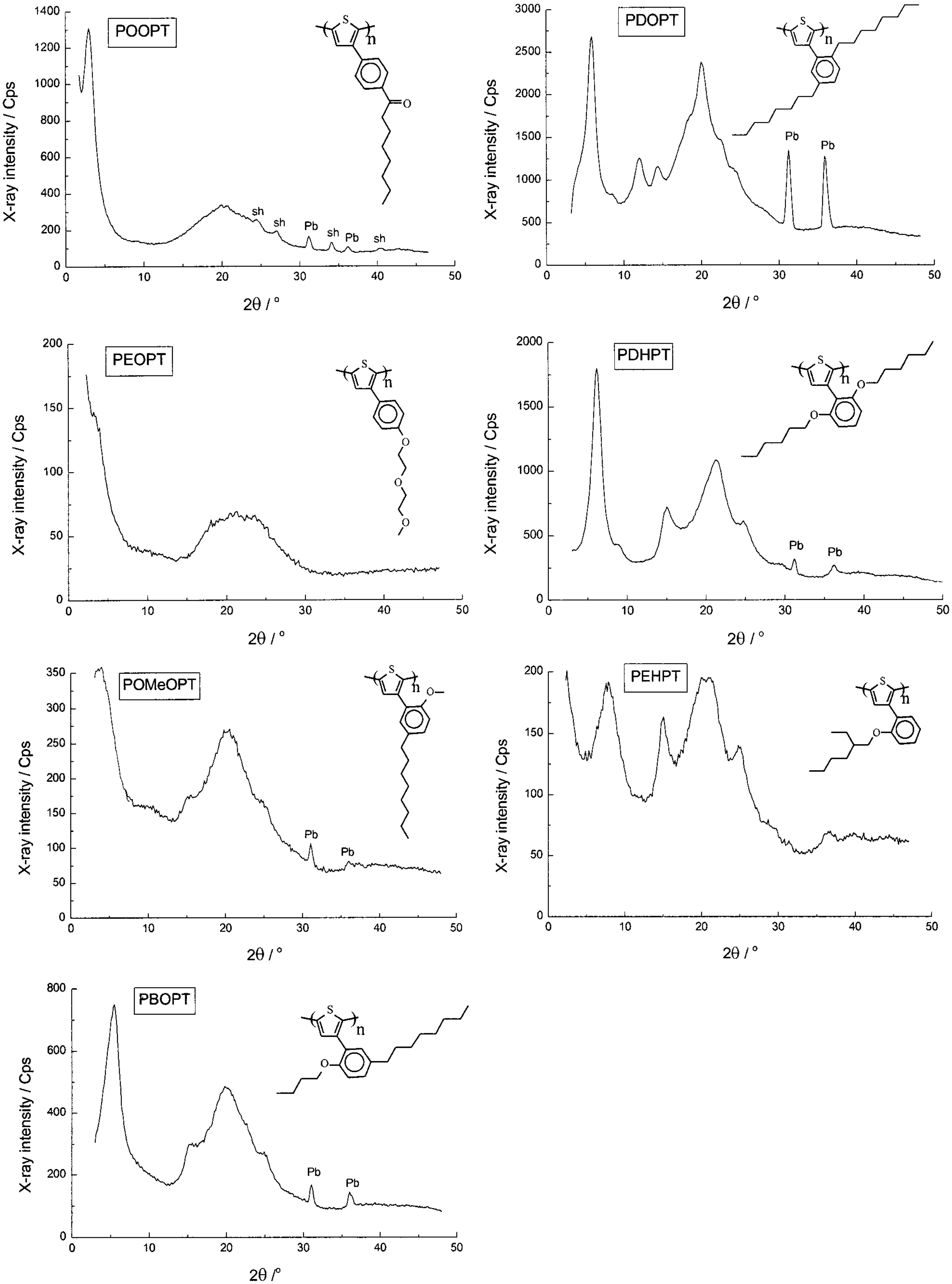

Figure 3. Powder diffractograms of the seven polymers of the present study, taken with an X-ray wavelength of 1.5418 Å. The peaks labeled "Pb" are diffraction peaks from the lead sample holder. For POOPT, the peaks labeled "sh" also arise from the sample holder, which in this case was not pure lead.

than for the powder sample, corresponding to a crystallite size around 120 Å for this case.

Figure 5 shows the diffractograms from thin, spin-cast films of PDOPT on various substrates, using

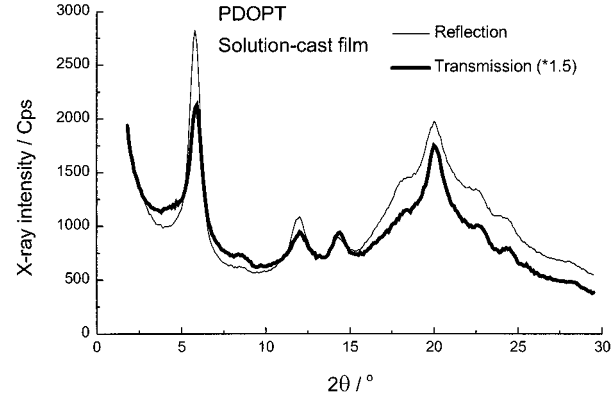

Figure 4. Diffraction pattern from solution-cast PDOPT film, reflection and transmission mode, taken with an X-ray wavelength of 1.5418 Å.

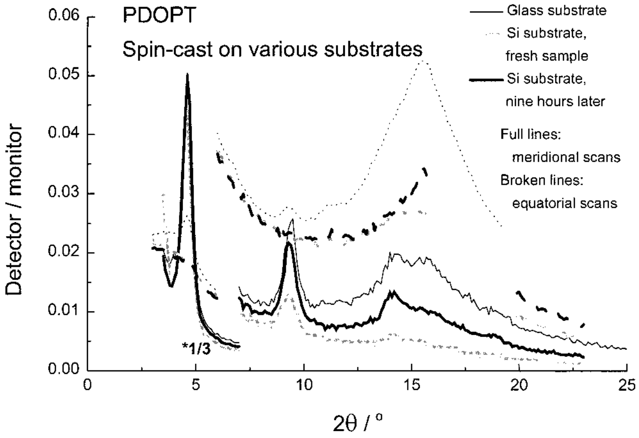

Figure 5. Diffraction patterns from spin-cast PDOPT films, taken with an X-ray wavelength of 1.218 Å. Notice the scale change at 7°! Meridional scans are plotted as full lines and equatorial scans as broken lines. In the equatorial scans for the film on silicon, the measurements between 15.7° and 19.8° were not reliable due to experimental problems.

grazing incidence. The meridional diffractogram has four equidistantly spaced peaks, which are interpreted as the first- to fourth-order reflections corresponding to a lattice spacing of 14.75 Å. The first three orders are seen also for the solution-cast film. For the film on silicon substrate, these four peaks are not observed in the equatorial scan, showing that this sample is very anisotropic. The sample on glass substrate is also anisotropic, but to a less degree: here, the first two peaks can be discerned also in the equatorial scan. The peak widths, and therefore the crystallite size, are comparable to the case for solution-cast film.

The film on silicon substrate was studied for a first time shortly after spin-casting and again 9 h later. The intensity *levels* need not be directly comparable for the two curves, because the sample had to be taken away and realigned between the scans, but the peak *widths* ought to be reliable. It is seen that the higher-order peaks were broad and diffuse in the first experiment but became narrower and more distinct in the repeated experiment, showing that the crystalline order increases with time. The same conclusion has previously been deduced from optical measurements.[14]

Also, POMeOPT was studied in the form of solution-cast film. The diffraction pattern in Figure 6 has more pronounced crystalline diffraction features than the powder diffraction pattern. However, the crystalline ordering is poor, compared to PDOPT. Also, the POMeOPT film is anisotropic, as seen by comparing transmission and reflection measurements.

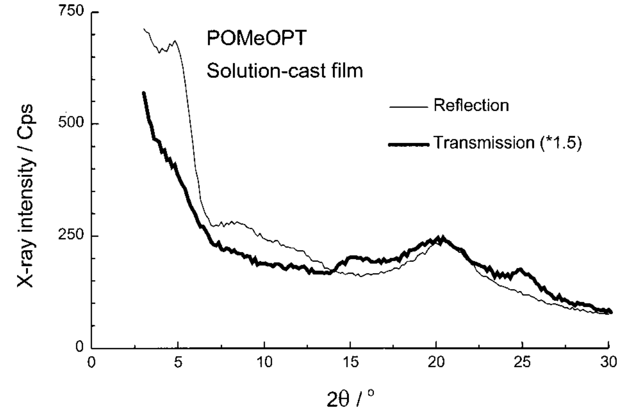

Figure 6. Diffraction pattern from solution-cast POMeOPT film, transmission and reflection mode, taken with an X-ray wavelength of 1.5418 Å.

Structure

General Assumptions. In the following, we discuss structure models of the various polymers, based upon the diffraction data and auxiliary information. For polymers with long flexible side chains, like the ones in the present study, there is a tremendously large amount of possible configurations. We shall be seeking the simplest conceivable models, which means that several assumptions must be made, so the structures can be described by a limited set of free parameters. In accordance with the optical data, we assume that the thiophene backbones are planar. The phenyl rings are taken to be oriented normal to the corresponding thiophene rings, which is a sterically favorable configuration. The alkyl or alkoxy side chains are supposed to be rather extended, but no a priori assumptions are made on their orientation. For PDOPT, where we propose a specific structure model, the assumptions for the side chains are more clearly specified: The octyl side chains are taken to be in all-trans configuration, whereas the torsion angles between the phenyl unit and the octyl chains have been subject to variation. These torsion angles are determined by the best fit to the experimental diffraction pattern.

We have chosen to work with unit cells with perpendicular crystal axes. For PDOPT, we also tried monoclinic cells, without improving the results. The pseudoorthorhombic unit cells we discuss may contain two monomers belonging to the same polymer chain or four monomers belonging to two different polymer chains. For the latter case, the two polymer chains are parallel, with one chain at the unit cell corner and the other at the center. Such unit cells will be referred to as "centered", although they are not necessarily centered in the crystallographic sense of the word. Cells with two monomers (a single polymer chain) will be referred to as "noncentered" or "simple". The orientation of the polythiophene backbones relative to the crystal axes is assumed to be the same for all polymers in this study: The main chains are directed along *c*, and the thiophene rings lie in the *ac*-plane. The length of the *c*-axis is assumed to be 7.8 Å, which is the main chain repeat distance found for stretched poly(3-alkylthiophene) films.[7]

We assume that the densities of the crystalline and amorphous fractions of the polymers are not very

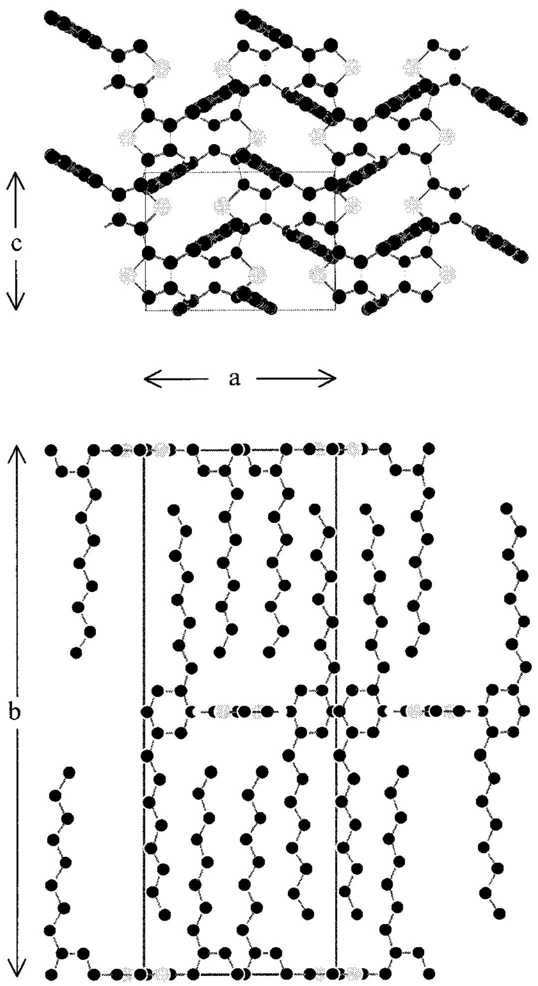

Figure 7. Structural model of PDOPT, in *b*-projection (above) and in *c*-projection (below). Sulfur atoms are gray and carbon atoms black. All atoms within the unit cell are shown. For clarity, selected polymer chains are shown outside the unit cell, the two projections showing the same chains.

different, but with the crystalline density somewhat higher than the amorphous one. The density calculated from given lattice parameters should therefore be comparable to, but slightly higher than, the measured, bulk density.

Polymers with Para-Substituted Phenyl Groups. The two para-substituted materials in this study, PEOPT and POOPT, both have monomers that are similar to the previously studied POPT. The length of the side chains is about the same for all the three. All show a diffraction peak at low angle (a shoulder in the case of PEOPT), which for POPT is indexed as the 100 reflection, corresponding to an *a*-axis of 28.4 Å. For POOPT, the low-angle peak is centered at 3.0°, corresponding to an interplanar distance of 29 Å. PEOPT has its low-angle diffraction shoulder at 3.6°, corresponding to an interplanar spacing of 25 Å. However, this determination is inaccurate, as the shoulder is very broad. The long interplanar spacings suggest that both POOPT and PEOPT have structures resembling that of POPT.

PDOPT. Structural Model. Figure 7 shows our structural model for PDOPT. It consists of a "centered" cell containing four monomers, with $a = 10.8$ Å, $b = 29.5$ Å, and $c = 7.8$ Å. The calculated density is 1.02 g/cm^3, which agrees very well with the measured bulk density 1.00 g/cm^3. The monomers belonging to the same polymer chain are related by a 2-fold screw axis along *c* ($P2_1$, no. 4). Thus, successive ortho-substituted octyl chains along the polymer chain are directed in alternating positive and negative *b*-direction. The two different polymer chains are related by the transformation $(x, y, z) \leftrightarrow (x + {}^1/_2, -y + {}^1/_2, -z)$. This ensures that the resulting structure is nonpolar and that hkl and $h\bar{k}l$ reflections have equal intensities.

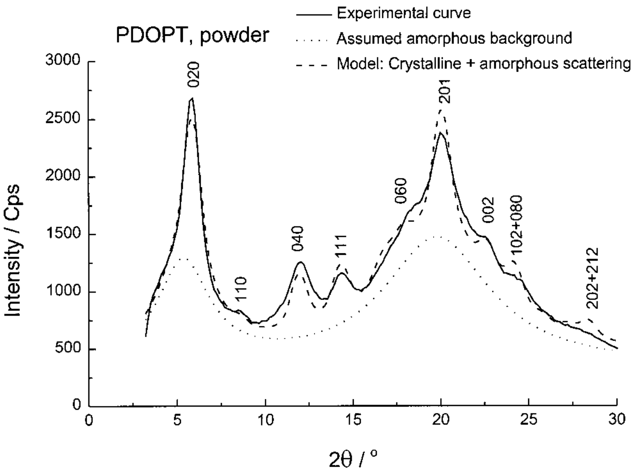

Figure 8. Calculated powder diffraction pattern of the proposed PDOPT model (dashed line) and experimental curve (full line).

In our model, both octyl chains lie in the plane of the phenyl ring. The octyl chains span the space between the thiophene backbones in the *b*-direction. The proposed configuration is appealing because of good space filling, with nonbonding interatomic C–C distances larger than 3.8 Å. Octyl chains from neighboring polymer chains interdigitate fully into each other in this direction. They are parallel and pack with a distance between nearest-neighboring octyl chains around 4 Å. Along the *a*-direction, the distance between neighboring main chains is spaced only by the phenyl rings, and there is almost no interdigitation.

Figure 8 shows the calculated powder diffraction pattern of the structure model, together with the experimental powder diffraction pattern. The hydrogen atoms are not included in the calculation. The calculated diffractogram is a sum of two contributions: the crystalline part, calculated from the structural model in Figure 7, and an amorphous background, assumed to consist of two broad, Lorentzian peaks. In the calculation of the crystalline scattering, we use pseudo-Voigt peaks with widths equal to the observed 1.2°. Thus, close-lying reflections merge into one peak. The agreement is very good: all observed peaks are reproduced with reasonable intensity. The four meridional diffraction peaks of the spin-cast film correspond to the 020, 040, 060, and 080 reflections. One should notice that the 002 reflection turns out to have significant intensity. This corresponds to the observed peak at 22.8°, in agreement with the previously assumed *c* value of 7.8 Å. For powder samples of P3AT, *c*-axis reflections are not observable due to overlap with *b*-axis reflections.

Disorder Effects. A simulated diffractogram like the one in Figure 8 is based on the assumption that the polymer consists of small but perfect crystals in an amorphous matrix. For a polymer with complex side groups such as PDOPT, it is not likely that the crystallites are strictly perfect. A realistic structure model should allow some disorder. Small deviations from the

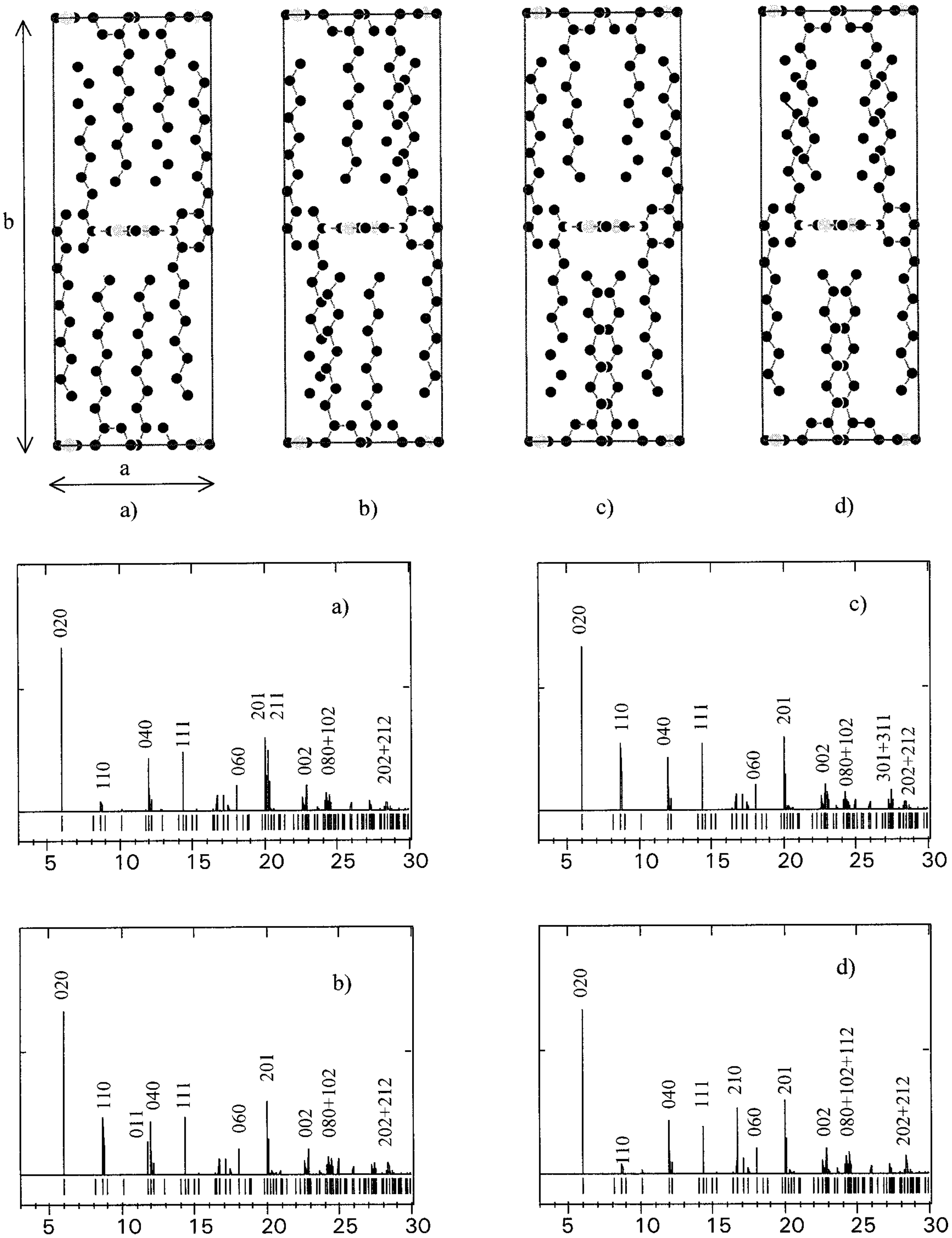

Figure 9. *c*-axis projections of PDOPT structure models with different relations between the four monomers of the unit cell and the corresponding calculated diffraction patterns with zero peak width.

idealized model should not have a big influence on the simulated diffractogram. For instance, there might be some disorder in the positioning of the octyl chains. This has been checked by varying the torsion angles around the bonds connecting the octyl chains to the phenyl ring. Varying these angles ±15° does not change the calculated diffraction pattern dramatically, so our model allows some disorder of the octyl chains.

Whether a given dioctylphenyl side group is oriented with its ortho-substituted octyl chain in positive (“up” configuration) or negative (“down” configuration) *b*-direction cannot be totally dependent on the orientation of its neighbors. In the crystallization process, the side groups may not have the freedom to orient into the most favorable configuration. For a planar polythiophene backbone, the 180° rotation of a side group around the bond connecting the phenyl and the thiophene rings is not possible due to steric hindrance. We should therefore allow some randomness in this orientation. This is modeled by introducing three new structure models with different relations between the orientations of the different side groups. A structure with random “up−down” configuration is represented by an intermediate between these four ideal models. Model b has the screw axis as its symmetry element, keeping the “up−down−up−down” conformation of the successive side chains along the polymer chain. The side groups on the polymer chain at the unit cell center are rotated 180° around the thiophene−phenyl bond, relative to model a. Models c and d have a *bc* glide plane with the glide vector along *c* (*Pc*, no. 7) as a symmetry element. Thus, the side groups on one polymer chain are all in “up” or all in “down” configuration. In model c, the side groups on the two different polymer chains in the unit cell are in the same configuration (“up” or “down”), whereas in model d they are in opposite configurations.

Figure 9 shows *c*-projections of the unit cells and calculated crystalline diffraction patterns for all models a−d. All the models have reasonable distances between the octyl chains. The major features are the same for all diffraction patterns. The main differences are the following: models b and c give a more intense 110 reflection than observed, model b gives a 011 reflection (which would merge with the 040 reflection), and model d gives a significant 210 reflection at 16.7°, where no peak is observed. The 211 peak is obtained only for model a. This peak would merge with the 201 reflection.

The similarities of the calculated diffractograms a−d show that a large amount of disorder in the orientation sequence of the side groups is compatible with the observed diffractogram. Our model a represents the best fit to the experimental curve. We therefore conclude that the basic structure is as in model a, but a large amount of disorder in the “up−down” configuration is allowed.

Preferred Orientation. Both solution-cast and spin-cast films of PDOPT are anisotropic, as discussed above. The 0*k*0 reflections are most pronounced in reflection measurements for solution-cast film (Figure 4) and in meridional scans for spin-cast films (Figure 5). This means that the *b*-axis is preferably oriented normal to the film surface for both kinds of film. Spin-cast films are strongly oriented, the film on silicon substrate more than the film on glass substrate. This difference may be caused by the different substrates, or it may be a thickness effect, as the film on glass is probably twice as thick as the film on silicon. The solution-cast film is less oriented.

According to this preferred orientation, the *h*0*l* reflections should be strongest in transmission measurement (solution-cast film) and in equatorial scans (spin-cast films). The *h*1*l* reflections should have their maximum intensity for scans between the two performed scans but closest to the transmission/equatorial scans. Indeed, for the solution-cast film, the *h*0*l* (201, 002, 102, and 202) and *h*1*l* (110, 111, and 212) reflections are all most pronounced in the transmission measurement. For the spin-cast film on silicon, the *h*0*l* reflections are not seen in meridional scans. The low-angle side of the 201 reflection is clearly seen in the equatorial scan for the 9 h “aged” sample. (The equatorial diffraction curve for this sample is not reliable in the rest of the angular range for *h*0*l* reflections, due to experimental problems.) For the spin-cast film on glass, the *h*0*l* reflections cannot be properly discerned from the amorphous scattering. The 110 and 111 reflections cannot be discerned in equatorial or meridional scans for the film on silicon, whereas for the less oriented film on glass, the two reflections are discerned in the equatorial scan. This agrees with those reflections having their maximum intensity between the two performed scans but closest to the equatorial scan.

Temperature Studies. Polythiophenes are known to show pronounced temperature effects such as anisotropic expansion and reversible or irreversible loss of crystallinity[7] and even temperature *contraction*.[15] For this reason also PDOPT was subject to a temperature study.

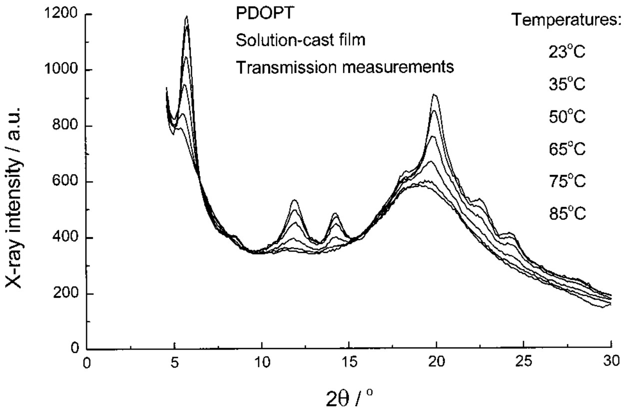

Figure 10. Transmission diffraction patterns of solution-cast PDOPT film at different temperatures, taken with an X-ray wavelength of 1.5418 Å. The curves are normalized to equal background intensities at 10° and 16°.

Figure 10 shows the diffraction profile of the solution-cast PDOPT film at different temperatures. The crystallinity decreases gradually upon heating, and at 85 °C almost all traces of the Bragg peaks have disappeared. The *b*-axis expands 3% upon heating from 23 to 85 °C. When lowering the temperature from 85 °C, the diffraction patterns does not reappear to any appreciable extent over a period of 2 days. Apparently, the kinetics is too slow for significant recrystallization. Such a lack of recrystallization is observed also for poly(3,3′-dioctyl-2,2′-bithiophene),[15] which also have a melting point close to that of PDOPT. The two polymers have in common that the octyl side chains interdigitate to a very high degree.

Structural Information for the Remaining Compounds. Lattice parameters as inferred from the observed Bragg peaks are collected in Table 1, which also shows observed and calculated densities.

For PDHPT and PBOPT two somewhat different models are given. For the first material they differ by the indexation of the interplanar distance of 9.8 Å (peak at 9.0°) being 110 or 100 in a centered or simple unit cell. For the second material it is a matter of interpretation of the interplanar distance of 16 ± 2 Å (peak at 5.4°), being either 100 or 020. The latter choice would corroborate with a structure similar to that of PDOPT.

PEHPT differs somewhat from the compounds above as it has only one, branched, side chain on the phenyl ring. The peak at 7.9° is very broad (fwhm 2.8°) compared to the peaks at 15° and 25° (fwhm 1.6°−1.7°), so it is taken as a double peak. The observed pattern is qualitatively reproduced by a choice of $a = 10.5$ Å and $b = 11.9$ Å in a noncentered unit cell containing one polymer chain (two monomers).

For POMeOPT the interplanar distance 17 Å (Bragg peak at 5.1°) is assumed to be the *a*-axis parameter. If so, the meta-substituted octyl chains must be twisted away from the backbone to keep the distance between neighboring polymer chains in the *a*-direction. The ortho-substituted methoxy group is placed between neighboring main chains in the *b*-direction. A *b* value around 7 Å is reasonable: In POPT[5] the phenyl rings alone span the *b*-axis, with a *b* value of 5.06 Å. An

Table 1. Lattice Parameters for the Polymers under Study, Together with POPT and P3OT[a]

name	*a* (Å)	*b* (Å) (simple cells), *b*/2 (centered cells)	calculated density (g/cm^3)	measured density (g/cm^3)
PDOPT (centered)	10.8 ± 0.1	14.75 ± 0.06	1.02 ± 0.01	1.00 ± 0.02
PDHPT, centered cell	10.5 ± 0.2	14.3 ± 0.3	1.02 ± 0.04	
PDHPT, simple cell	9.8 ± 0.2	14.3 ± 0.3	1.09 ± 0.04	
PEHPT	10.5 ± 0.7	11.9 ± 0.7	1.0 ± 0.1	
POMeOPT	17 ± 2	7[b]	1.06[b]	1.03 ± 0.02
PBOPT (a)	16 ± 2	9[b]	1.0[b]	
PBOPT (b)	9[b]	16 ± 2	1.0[b]	
POOPT	29 ± 2			
PEOPT	25 ± 3			
POPT (from ref 5)	28.4 ± 0.2	5.06 ± 0.01	not given	not given
P3OT (from ref 16)	20.3 ± 0.1	3.81 ± 0.05	1.06 ± 0.02	1.05 ± 0.05

[a] The crystal axes are defined such that the polythiophene backbone has the same orientation relative to the crystal axes for all materials. [b] Not based on diffraction peaks, but calculated from the densities, which for PBOPT is an assumed density.

additional spacing of 2 Å due to the methoxy group is not unlikely.

Discussion

Comparing the Structures. Table 1 shows lattice parameters *a* and *b* for the different polymers in this study and also for POPT and poly(3-octylthiophene) (P3OT). For centered cells, *b*/2 is given instead of *b*, because *b*/2 is the interplanar spacing between neighboring main chains. *c* is assumed to be 7.8 Å for all materials.

PDOPT, PDHPT, and PEHPT all have quite equal *a* values and *b* (*b*/2 for centered cells) values which depend on the length (and the number) of the side chains on the phenyl group. These polymers have in common that they all have a long side chain at the ortho position of the phenyl group. Their structures are quite similar: The alkyl/alkoxy side chains span the distance between neighboring main chains in the *b*-direction (the direction along the thiophene normal), whereas the main chains are spaced only by the phenyl units in the *a*-direction.

POMeOPT has a quite different structure, even if this material is, like PDOPT, substituted at the ortho and meta positions on opposite sides of the phenyl group. However, this polymer has its long side chain at the meta position. This side chain is twisted away from the polymer backbone and separates neighboring polymer chains along the *a*-axis. The structure of POMeOPT therefore resembles somewhat that of POOPT, PEOPT, and POPT, the polymers substituted at the para position of the phenyl unit. The *a*-axis of POMeOPT is much shorter than for those, however. This is because the rather large (~7 Å) distance between neighboring polymer chains in *b*-direction, caused by the ortho-substituted methoxy group, allows the octyl chains to interdigitate to a very high degree. Furthermore, whereas para-substituted side chains may orient parallel to the *a*-axis, meta-substituted side chains are more likely to orient tilted to the *a*-axis. This also contributes to a shorter *a*-axis for POMeOPT than for the para-substituted materials.

PBOPT can be regarded as an intermediate between PDOPT and POMeOPT. All three polymers have an octyl chain in the meta position. PBOPT have a butyloxy chain in the ortho position, intermediate between POMeOPT's methoxy group and PDOPT's octyl chain. Because of the large uncertainties in the lattice constants, it is not clear what kind of structure PBOPT has. It may have a structure similar to PDOPT, with similar lattice constants (which would imply a lower density than that of PDOPT), or it may have a structure more like that of POMeOPT. In the latter case, the *b*-axis should be long enough to accommodate the ortho-substituted butyloxy chain.

Crystallinity. The ortho-substituted polymers PDOPT, PDHPT, and PEHPT have resembling structures. They are also the most crystalline materials in the present study. Particularly PDOPT and PDHPT, which both are doubly substituted with two equal substituents on the phenyl unit, are well ordered. According to the PDOPT model, the octyl side chains form a rather regular lattice with interchain distances around 4 Å. This is a crucial feature for understanding the highly ordered structure of a polymer with such a bulky side group. Indeed, the ordering of the side chains is reminiscent of the crystalline structures of paraffins such as *n*-octadecane:[17] The octadecane molecules are parallel, also with intermolecular distances around 4 Å.

The polymers substituted at the para position of the phenyl group, together with POMeOPT, are less crystalline than the ortho-substituted ones. This is probably connected to the fact that the two groups of materials have quite different structures. The ortho-substituted side chains separating the main chains may have a stabilizing effect on the crystalline lattice. PBOPT, which above was described as an intermediate between PDOPT and POMeOPT, has a crystallinity between these two materials.

Our studies show that the structural order is improved upon film-casting, for both PDOPT and POMeOPT. In the work by Fell et al., POPT was found to be considerably more crystalline in the form of solution-cast films than in the form of powder.[5] Furthermore, it was concluded that spin-cast films of POPT show reduced band gap and increased crystallinity upon chloroform vapor treatment or heat treatment.[6] Optical absorption measurements by Theander et al. have demonstrated band gap reduction upon treatment with heat or chloroform vapor also for PEOPT and POOPT.[2,3] All para-substituted poly(phenylthiophene)s may therefore initially go into a metastable, poorly crystalline state in the "as-synthesized" form and then achieve a thermodynamically more stable form after appropriate treatment.

Preferred Orientation. We find that PDOPT films are anisotropic, with the *b*-axis preferably oriented normal to the film surface for both solution-cast and spin-cast films. Poly(3-alkylthiophene) films are also known to be anisotropic, but the crystal orientation is different in spin-cast and in solution-cast films: Spin-cast films orient with the *b*-axis normal to the film surface,[7,18] whereas solution-cast films orient with the *a*-axis normal to the film surface.[7,19] Solution-cast P3AT films cast from the same solvent mixture as used for the PDOPT film in the present study are much more anisotropic than the PDOPT film.[10]

Solution-cast films of POPT are previously found to orient similar to solution-cast P3AT films,[6] with the *a*-axis normal to the film surface. Our studies indicate that also solution-cast POMeOPT films take a similar orientation.

The different behavior of anisotropic films of P3ATs and PDOPT may be related to the different orientation of the alkyl chains relative to the polythiophene backbone. For P3ATs, the alkyl side chains lie more or less in the thiophene plane, whereas in our PDOPT model they are orthogonal to the polythiophene backbone. Thus, for spin-cast films of both polymers, the polythiophene backbone lies in the plane of the film surface. For solution-cast films of both polymers, the alkyl side chains are orthogonal to the film surface. Also for solution-cast POPT and POMeOPT films, the alkyl side chains are more or less orthogonal to the film surface.

Relation to Photoluminescence Yield. Photoluminescence studies by Theander et al.[3] show that PDOPT has a very high quantum yield: 0.37 in chloroform solution and 0.24 as thin, spin-cast films. Especially the value for PDOPT film is very high, compared to those for solid films of other polymers. The cited work includes photoluminescence studies of 22 substituted polythiophenes. The second most efficient is POMeOPT, with a quantum yield of 0.11 in the form of thin films. P3OT films, on the other hand, have a quantum yield of 0.04. The high quantum yield of PDOPT has been interpreted as caused by separation of the conjugated backbones due to the bulky side group. In this way, the photoinduced excitations cannot easily hop between the chains to find quenching sites.

Our structural models confirm this picture. The smallest distance between neighboring conjugated backbones in PDOPT is defined by the lattice vector *a*, 10.8 Å. This is indeed a long distance, compared to the shortest distance between the conjugated chains in P3OT and other P3ATs, where the stacking distance is 3.8 Å. For POMeOPT, the shortest interchain distance in our model is around 7 Å, in agreement with a quantum yield between that of PDOPT and P3OT. PDHPT, PEHPT, and PBOPT all have longer interchain distances than POMeOPT in our models. These materials were however not included in the list cited above.

Conclusion

We have performed X-ray diffraction studies on a series of substituted poly(phenylthiophene)s. They can be divided into two main groups: those with a long substituent at the ortho position of the phenyl unit and those without.

The materials of the first group (PDOPT, PDHPT, and PEHPT) have structures where the ortho-substituted side chains span the space between neighboring main chains in the direction along the thiophene normal (*b*-axis), and the phenyl units alone space the main chains in the orthogonal direction (*a*-axis). They are highly crystalline, despite their rather bulky side groups. The doubly substituted polymer PDOPT, with the phenyl group substituted both at the ortho and at the meta position, has been studied in detail. We propose a structural model, whose calculated diffraction pattern agrees very well with the experimental one. The octyl side chains form a rather regular lattice, with interchain distances around 4 Å. This is probably a major reason why a polymer with such a bulky side group can have a high crystallinity.

The materials of the second group (POMeOPT, PEOPT, POOPT, and the previously studied POPT) have structures where the para- or meta-substituted side chains are directed away from the polymer backbone. The main chains therefore pack closer along the *b*-axis but are spaced with longer distances along the *a*-axis. The para-substituted polymers have the largest *a*-parameters. The materials of this group are all poorly crystalline.

For PDOPT, we have developed a realistic structure model that reproduces the observed diffraction pattern well. For the other polymers, further work needs to be done in order to propose specific structure models.

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