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The importance of molecular dynamics in the determination of crystalline structure of poly(3-dodecylthiophene)

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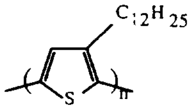
Molecular simulation of the crystalline structure of poly(3-dodecylthiophene), starting from the ideal 'alternating inverse comb' structure model, together with a consideration of thermal agitation in the main-chains and side-chains using molecular dynamics and diffraction simulation software provides good agreement of the calculated X-ray diffraction patterns with the experimental results for non-oriented and oriented samples.

(Keywords: poly(3-dodecylthiophene); X-ray diffraction; molecular dynamics)

Introduction

Polythiophene (PT) is an environmentally stable conjugated polymer, in both neutral form and doping form, having a conductivity as high as 500 S cm^{-1} (ref. 1), and it has been extensively investigated. Introducing a flexible side-chain, such as an alkyl group, with a carbon number of 4 or more on the 3-position of the thiophene ring causes the polymer to become soluble in common organic solvents, fusible and melt processable, yet retain a rather high conductivity of about 30–100 S cm^{-1} (refs 2–4). Extensive experimental and theoretical studies have been made on the structures and thermo- and solvatochromisms of poly(3-alkylthiophene)s (P3ATs). P3ATs are known to be partially crystalline and can be oriented, to some extent, by stretching[5–9] or by fibre spinning[6], allowing the polymer chains, both in the crystalline and amorphous phases, to align along the stretch direction[5]. During the melting transition, thermochromism could occur[10]. From their unit cell dimensions, determined by X-ray diffraction (XRD) patterns of oriented samples, it was proposed that the crystalline structure consisted of intraplanar layers formed by stacking of coplanar subchains while the side-chains, with nearly planar alternating zigzag (or nearly all-*trans*) conformation, lie between two neighbouring layers with partial interdigitation[5,6,8,9]. Here we designate this structure as 'planar structure with side chain interdigitation'. No confirmation by molecular simulation of this proposed structure has been made. An alternative model, the 'alternating inverse comb structure'[7], considers a re-orientation of the all-*trans* alkyl side-chain away from the direction of the coplanar main-chain; molecular modelling of this model was claimed to be in good agreement with the experimental XRD patterns of non-oriented and oriented samples at 23°C.

In this study, a modification of the alternating inverse comb model using a molecular simulation technique, and considering molecular dynamics (MD) to take account of effects of thermal motions of main-chain and side-chain, was employed to determine the molecular arrangement of poly(3-dodecylthiophene) (P3DDT)



in the ordered state.

Simulation technique

Simulations of the crystal structures of P3DDT were carried out using the programs POLYGRAF and CERIUS (Molecular Simulations Inc., Waltham, MA, USA). The force field used in POLYGRAF for molecular mechanics and dynamics calculations is the Dreiding force field[11]. POLYGRAF was used for the calculation of molecular dynamics, and CERIUS for XRD patterns. The parameters for thiophene rings, such as bond lengths and bond angles, were modified according to the structure of neutral PT[12]. The torsional potential curve of P3DDT was obtained from the calculation using extended Hückel theory based on the modified neglect of diatomic overlap (MNDO) to fully optimize the geometry[13]. The modules in CERIUS used for calculating XRD patterns are powder diffraction and Legendre two-dimensional (2-D) scattering for non-oriented and oriented P3DDT, respectively. For calculating Legendre 2-D scattering of the present oriented polymer samples, an averaging technique is used for a molecular cluster with 32 short chains, each containing 12 repeat units. The detailed logic used in POLYGRAF and CERIUS is in accordance with that in refs 14 and 15, respectively.

Results and discussion

Examination of the models proposed in the literature. We have regenerated the XRD patterns of the crystalline structures of P3DDT proposed in the literature, the planar structure with side chain interdigitation[5,6,9] and alternating inverse comb structure[7], using CERIUS. Both models consider perfectly aligned side-chains and main-chains. For the former model, the side-chains are

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*To whom correspondence should be addressed considered to have a planar all-*trans* conformation. The characteristic results are listed in *Table 1*. For the planar structure, the calculated relative intensity of the first order to the second order is reversed as compared to the experimental results. The strong second-order reflection results from the interdigitation of the side-chains, as found by comparison with the case without interdigitation. In addition, the reflection intensities of the calculated Legendre 2-D diffraction pattern deviate greatly from experimental results at several characteristic reflections: the first, second and third orders and 22.9°. For the alternating inverse comb[7] model (in which the conformation of alkyl side-chains is all-*trans*), the calculated Legendre 2-D XRD pattern deviates significantly from the experimental 2-D XRD pattern of oriented P3DDT[7] in most locations. For instance, in the diagonal direction, the former has a bright mosaic, but the latter has none; on the meridional axis at $2\theta = 15$–$20°$, the former has reflection intensities much higher than the latter. Thus it seems that these two models are not in satisfactory agreement with the experimental results. However, Prosa *et al.*[7] claimed that the alternating inverse comb model fits the experimental results of powder and Legendre 2-D XRD patterns, using their own computation program based on the same theory as used in CERIUS.

Incorporation of molecular dynamics in the alternating inverse comb structure. The XRD pattern of a non-oriented sample of P3DDT is taken from a previous report[10]. The XRD pattern of the crystalline region is obtained by fitting the experimental XRD pattern after subtraction of the amorphous background, by use of the sum of several Gaussians. The result is shown in *Figure 1a*. In the previous report[10] it was found that the corresponding d-spacing of the first-order reflection increases with increasing length of the alkyl side-chain; the same trend also appears for the second- and third-order reflections. For P3DDT, these reflections are located at $2\theta = 3.5°$ ($d = 25.5$ Å), $6.7°$ ($d = 13.2$ Å) and $10.6°$ ($d = 8.3$ Å), respectively. Hence, these reflections must indicate that the space between two neighbouring coplanar subchains on the same plane (or interplanar spacing) must be filled with the side-chains. In the wide-angle region, in addition to the amorphous peak, a peak at $2\theta = 22.9°$ with moderate to weak intensity also appears. The corresponding value of the d-spacing is 3.9 Å for P3DDT. As the numbers of carbon atoms in the alkyl side-chains are 4 and 8, a wide-angle diffraction peak, corresponding to a d-spacing of 3.8 Å, also appears; this d-spacing, which is independent of side-chain length, has been attributed to the spacing between two successive stacking planes of coplanar subchains (or intraplanar spacing), as was also assigned to poly(3-hexylthiophene) (P3HT) by others[16].

To start the molecular simulation, an orthorhombic unit cell for P3DDT is first assumed. From an analysis of XRD patterns[9,16] and infra-red absorption spectra[9] of P3ATs, it has been inferred, respectively, that a planar *trans* conformation of the main-chain is preferred, and that major fractions of *trans* conformation appear in the alkyl side-chains at room temperature[9]. The sulfur atoms of two neighbouring stacked thiophene rings probably lie in opposite directions so that the steric repulsion between the H atoms of the alkyl side-chains of the two stacking main-chains can be released. Thus, the repeat intraplanar spacing is taken as twice the evaluated d-spacing of 3.9 Å, that is 7.8 Å. So the unit cell dimensions are taken as $a = 51.0$ Å, $b = 7.8$ Å and $c = 7.7$ Å (the length of two thiophene rings). As done by Prosa *et al.*[7] in their alternating inverse comb model, we also varied the dihedral angle ϕ about the C–C bond which connects the thiophene ring (as defined in *Figure 1b*) from 0° to 180°, while the rotational angle of the coplanar main

Table 1 Comparison of characteristic reflections of the calculated and experimental XRD patterns

					Legendre diffraction pattern						
	Powder diffraction pattern				Equatorial axis				Meridional axis		Diagonal direction
Item	1st	2nd	3rd	$2\theta = 22.9°$	1st	2nd	3rd	$2\theta = 22.9°$	$2\theta = 15$–$20°$	$2\theta = 20$–$25°$	$2\theta = 15$–$20°$
Experimental results[a]	intense	weak	weak	weak	intense	moderate	moderate	weak & broad	very weak	weak	very weak
Planar structure with side-chain interdigitation[b]					weak	intense	weak	moderate to intense			
Alternating inverse comb model[b]					intense	intense	weak	moderate	moderate	intense	moderate
All-*trans* side-chain model with $\phi = 0°, 15°, 30°$[c]	intense	weak	weak	weak	intense	moderate	moderate	weak	moderate	weak	moderate
Proposed molecular models with MD[d]	intense	weak	weak	weak	intense	moderate	moderate	weak	very weak	weak	very weak

[a] Experimental results of powder diffraction are taken from ref. 10 and those of Legendre 2-D diffraction pattern from ref. 7

[b] The software CERIUS is used to simulate XRD patterns of the planar structure with side-chain interdigitation model proposed in refs. 5 and 6 and 9, and alternating inverse comb model proposed in ref. 7

[c] Structures are the same as shown in *Figure 1*

[d] Molecular structures after thermal equilibrium is reached (by performing molecular dynamics) with the initial guesses of the dihedral angle $\phi = 60$–$120°$, which are the same as those used for XRD patterns in *Figure 2a*

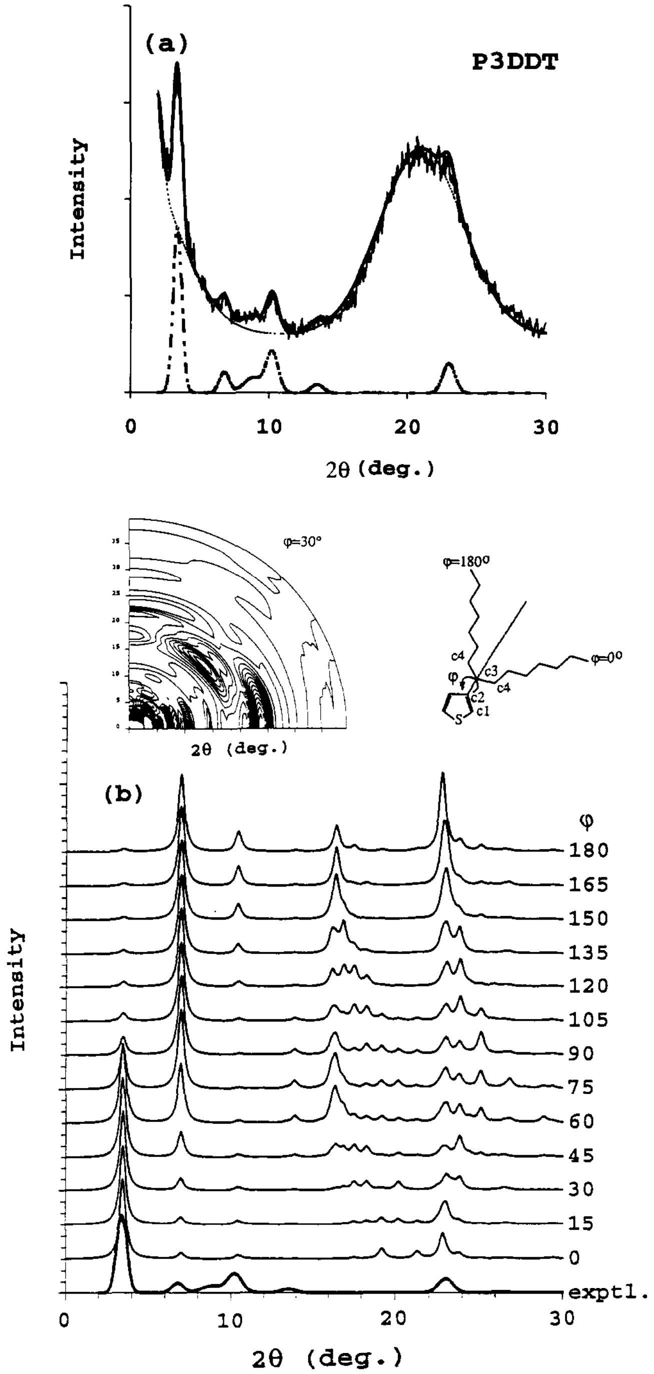

Figure 1 (a) Experimental X-ray diffraction pattern of P3DDT; (b) X-ray diffraction patterns of non-oriented P3DDT at various side-chain dihedral angles ϕ, calculated using the software CERIUS and obtained experimentally. The insert shows the simulated 2-D Legendre diffraction patterns of oriented P3DDT at the initial guess of the dihedral angles, $\phi = 30°$, without performing molecular dynamics

chain was retained at zero. Note that in the work of Prosa *et al.*, ϕ and the rotational angles of the coplanar main-chain with the a axis are 82° and 13°, respectively. The results of the calculation in *Figure 1b* show that the intensity of the first-order reflection decreases with increasing dihedral angle ϕ, but that of the second-order reflection increases; also, the calculated XRD patterns are close to the experimental result at $\phi = 0$–30°. However, the calculated 2-D XRD patterns for the oriented P3DDT (the same as in the insert of *Figure 1b* for $\phi = 30°$) at $\phi = 0$–30° have large deviations from the experimental result reported in the literature[7]; for instance, the calculated patterns show bright mosaic at $2\theta = 15$–23° in the diagonal direction and intense reflections at $2\theta = 15$–20° on the meridional axis, which are not found in the experimental patterns (*Table 1*). Note that in the calculation of the Legendre 2-D XRD pattern of P3DDT, a molecular cluster with 32 short chains, each composed of 12 repeat units, is considered.

In order to investigate whether thermal agitation in the side-chains and main-chains could affect the diffraction pattern, the molecular dynamics (MD) method in POLYGRAF is used to simulate the probable structure of P3DDT at 300 K. The initial structure assumed for the simulation is that it has a cell containing two, four, and six repeat units in the a, b and c axes, respectively,

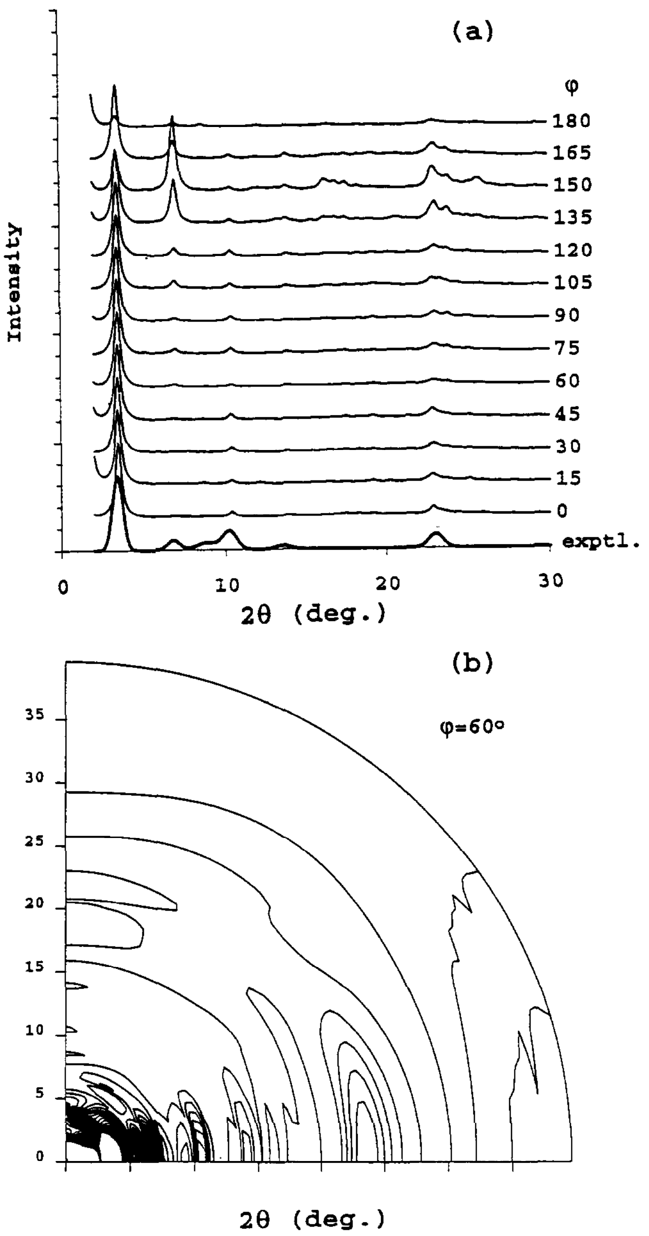

Figure 2 (a) Powder X-ray diffraction patterns of P3DDT with molecular dynamics performed at various initial values of the dihedral angle ϕ; (b) Legendre 2-D diffraction patterns for oriented P3DDT with molecular dynamics performed at the initial guess of the dihedral angle of $\phi = 60°$

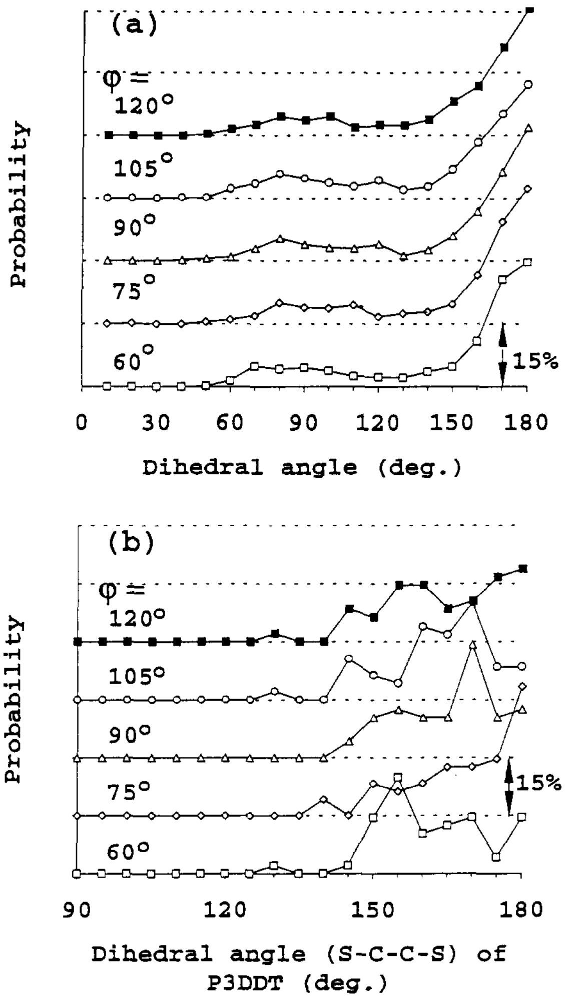

Figure 3 Dihedral angle distribution of P3DDT in the cell with molecular dynamics performed at various initial guesses of the dihedral angles ϕ: (a) alkyl side-chains; (b) main-chains (between two neighbouring thiophene rings)

with a specific dihedral angle between the alkyl side-chain and main-chain. The dimensions of the unit cell are held constant, and the temperature is maintained at 300 K. The time-step of the simulation is 0.001 ps and it takes 12 ps to reach thermal equilibrium. In order to assure that thermal equilibrium is really attained, the dynamic simulation is continued for 12 ps more in all cases. The criterion for thermal equilibrium is that the potential energy and temperature of the unit cell fluctuate stably within small ranges. At the end of the dynamics simulation, the resulting structures obtained from various initial conformations were examined by comparing their XRD patterns with the experimental result in order to determine the more probable structure. The powder diffraction patterns of the resulting unit cell structures of P3DDT at various initial ϕ values were calculated and then compared with the experimental result (*Figure 2a*, *Table 1*). This shows that the unit cell structures with initial dihedral angles of $\phi = 60$–$120°$ all give the best fit with the experimental powder XRD pattern. The typical corresponding Legendre 2-D diffraction pattern with $\phi = 60°$ is shown in *Figure 2b*, which is in good agreement with the experimental result of Prosa *et al.*[7]; for instance, an intense first-order reflection and moderate second- and third-order reflections exist on the equatorial axis, there is a weak reflection at $2\theta = 20$–$25°$ on the meridional axis, and bright mosaic is absent in the diagonal direction (*Table 1*). As can be seen, these initial dihedral angles are different from the best fit values without consideration of thermal agitation ($\phi = 0$–$30°$), and the Legendre 2-D diffraction patterns are also different at the meridional axis and in the diagonal direction, as shown in *Table 1*.

In order to explore the conformational identity of the cell structures with $\phi = 60$–$120°$, the dihedral angle distributions of the alkyl side-chains (based on 12×48 ($= 576$) data for each curve) and that between two neighbouring thiophene rings (based on 48 data for each curve) were calculated and are shown in *Figures 3a* and *b*, respectively. The probability of a specific dihedral angle is defined as the number of occurrences at that angle with 2.5° variation for all ϕ values divided by the total number of occurrences for all ϕ values. It is found that the distribution curves of various initial angles ϕ are very similar for the side-chains, and follow the same trend, but fluctuate more, for the main-chains. The greater fluctuation in distributions for the latter is probably due to insufficient statistical data. It can be concluded that only one equilibrium statistical conformation is determined by a dihedral angle distribution for side-chains and for main-chains.

The effect of thermal agitation of side-chains of P3AT has also been considered by Mårdalen *et al.*[8]. They found that even in the crystallites (or ordered phase) there is some degree of disordering, as was inferred from two observations: (1) no *hk*0, *h*0*l*, *hkl* reflections were observed; (2) the shape of the reflection arcs for $l = 2$–7 in the intensity maps of stretched P3HT and poly(3-octylthiophene) (P3OT) deviates from being arcs of circles. They also observed that the crystalline structure of P3OT before and after orientation remains unchanged. Thus, the calculated Legendre 2-D diffraction pattern of the structure established from a simulation of the powder diffraction data can be taken as that of the oriented polymer, as we did in the previous section. From the well fitted XRD patterns (as shown in *Table 1* and *Figures 2a* and *b*) corresponding to the proposed structures, with thermal agitation in the main-chains and side-chains, it is obvious that in the ordered phase at room temperature, ring distortion does exist in the main-chains, and that both *trans* and *gauche* conformations exist in the side-chains.

It can be concluded that in the ordered phase, the thermal agitation at room temperature causes the generation of *gauche* conformation in addition to *trans* conformation in the alkyl side-chains and a presence of ring distortion in the main-chains.

Acknowledgements

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