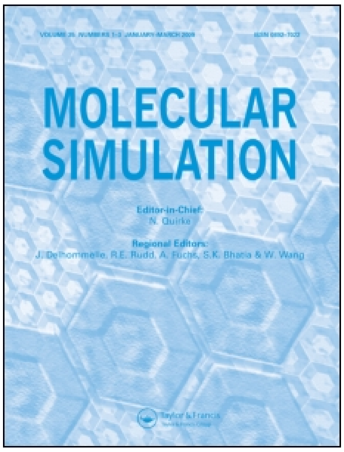

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A molecular dynamics simulation of the structure and properties of a self assembled monolayer formed from an amphiphilic polymer on a water surface

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A molecular dynamics simulation of the structure and properties of a self assembled monolayer formed from an amphiphilic polymer on a water surface

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The polymer poly (3-octyl-3′-oxanoyl thiophene) has alternating hydrophobic octyl and hydrophilic oxanoyl side chains in the "3" positions of the thiophene rings, rendering it an interesting amphiphilic electro-active material. The application of compression on the amphiphilic polymer (which forms self-assembled monolayers (SAMs) on a water surface) is investigated by molecular dynamics (MDs). It is found that there is a range of surface pressures in which the material possesses lattice order. As the compression is increased beyond a critical value breakdown occurs leading to the rupture of the surface layer. The results of the dynamics are interpreted via atomic plots, atom-pair radial distribution functions (RDF), torsional distribution functions and by monitoring some of the dihedral angles as functions of time.

Keywords: Amphiphilic polymer; Molecular dynamics; Self-assembled monolayer; Chain conformations

1. Introduction

Polythiophene in which the thiophene rings are linked in the 1- and 4-positions normally form large planar linear chains. In these structures, the rings adopt all-*anti* configurations, in which, as shown in figure 1, the sulphur atoms are alternately "up" and "down" along the chain direction [1]. If, in addition, the hydrogen atom in the 3-position of each ring is substituted with an aliphatic chain the resulting polymer retains the electro-optical properties of the unsubstituted polymer but in addition is soluble in non-protic solvents such as chloroform and tetrahydrofuran [2]. If now the 3-positions of alternate rings are substituted with an alkyl (hydrophobic) and with an oxanoyl (hydrophilic) chain the resulting amphiphilic poly(3-alkyl-3′-oxanoyl thiophene) shown in figure 1 is capable of forming a self-assembled monolayer (SAM) on the surface of a protic solvent such as water [3]. This polymer will be referred to as an alkyl-oxanoyl polythiophene (AOPT). The films formed by the AOPT essentially comprise 2D lattices, which also retain many of the characteristics of the polymer in its bulk form. They possess optical non-linear properties, and the electrical conductivity and thinness has resulted in the construction of electronic chips [4].

Bjørnholm *et al.* [3] have used several experimental techniques including grazing-incidence X-ray diffraction, X-ray reflectivity, NMR and other spectroscopic methods to investigate the structures of polythiophene derivatives in the water–vacuum interface. From various alkyl and alkanoyl chains as side-chain substituents they found that highly crystalline monolayer domains were formed only when both alkyl and alkanoyl were used in the 3 and 3′ positions so as to create an amphiphilic polymer. The requirement of having a regular polymer was shown by the fact that the crystallinity of the domains was low unless the main chains alkyl were highly regioregular. The observation that alkyl- and alkanoyl-substituted *dimers* produced disordered domains also shows the requirement to have an imposed regularity parallel to the interface. In order to maximise order in the alkyl chain sublattice the authors postulate that adjacent polymer chains have a mutual displacement of one thiophene unit along the chain direction. In this way, the alkyl chains of each polymer fits into the space between the alkyl chains of its immediately neighbouring polymer. This structural feature is also found in the bulk lattice regions of poly(3-alkyltyhiophene)s and has been used to explain the thermochromic properties of these materials [5].

Pressure-area isotherms on these systems [3] show the usual collapsing of the SAMs when the surface area becomes less than a critical value. We should like to investigate this collapse so as to obtain a description of the loss of structural

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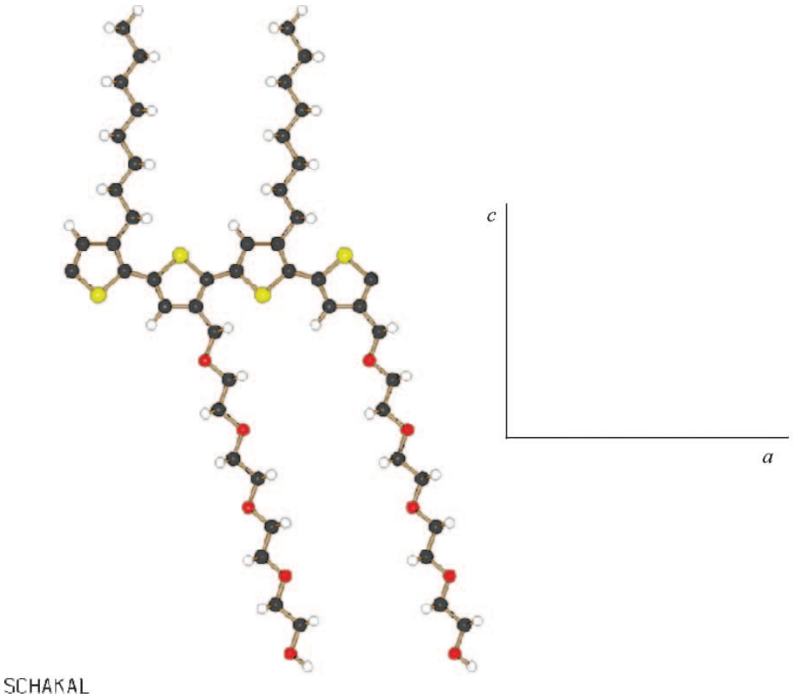


Figure 1. Two repeat segments of AOPT. (The red atoms are oxygen.)

order. In a molecular dynamics investigation of a hexagonal close packed particulate monolayer on a liquid surface Fenwick *et al.* [6] included the prediction of such pressure-area isotherms. They also applied a thermodynamic analysis to explain the collapsing of the monolayer by buckling. It would be interesting to compare the behaviour of this system with that of the amphiphile and to study the conformational changes in the two species of side chain.

As in Langmuir monolayers and surfactants [7], the structure adopted by the AOPT polymers in the monolayer is decided by their amphiphilicity. The hydrophobic alkyl chains are directed away from the water, while the hydrophilic nature of the oxanoyl side chains results in their association with the molecules of the water layer. The similarity of the structures of oxanoyl chains to those of crown ethers suggests that this part of the polymer might show a similar ability to occlude positive ions from the aqueous layer.

In order to further an understanding of the nature of this potentially useful polymer monolayer we have performed a molecular dynamics (MDs) investigation of the system consisting of the AOPT monolayer in the water–vacuum interface. The response of the monolayer is investigated when the lattice **b** vector (that describing the stacking of the polymer backbone along the interface) is reduced, thereby simulating a lateral pressure applied in the plane of the water surface. A similar procedure was adopted to simulate the behaviour of discrete molecular species in monolayers [8] but we believe that this is its first application to a polymeric amphiphilic SAM.

2. Method of simulation

The AOPT film was simulated by extending the 2D lattice proposed by Bjørnholm *et al.* [3] to a 6 × 6 supercell shown in figure 2. It contained 12 polymer chains, each with 12 thiophene units. In accordance with figure 1, alternate thiophene rings were substituted with side chains of octyl C_8H_{17} or oxanoyl $-CH_2-(O-CH_2-CH_2)_4-OH$ which "dipped" into a slab of water molecules.

The polymer sublattice thus consisted of 5040 atoms. The plane of the polymer backbone was placed just below the upper surface of the water layer, in which the H_2O molecules had been created in sites that made them commensurate with the polymer sublattice. The spacing was chosen to give a density close to the correct value for liquid water but water molecules were eliminated to accommodate the protruding oxanoyl side chains, leaving 886 molecules in the water layer and making a total of 7698 atoms. For calculations involving a large series of deformed lattices to monitor the effects of monolayer expansion and contraction, a smaller (4 × 4) supercell was used, containing 3473 atoms.

The molecular geometries of the polythiophene backbone and of the octyl side chains are those used in earlier work on poly(3-alkylthiophene)s [5,9] and from an examination of the geometries of several ether molecules we selected a set of bond lengths and angles in the alkanoyl chain: $CC = 1.492$ Å, $CO = 1.435$ Å, $CH = 1.1$ Å, $CCO = 111.0°$, $COC = 111.0°$, $COH = 109.0°$, $HCH = 106.3°$. The partial atomic charges were those used in our previous published work.

The MDs were performed for 10,000–100,000 time steps (one time step was 10^{-15} s) at room temperature using the program DL_POLY [9]. Initially a Hoover constant-pressure thermostat was used to reach the best description of the relaxed AOPT monolayer lattice and the water medium, but this was replaced with an Evans constant volume thermostat when the monolayer was to be constricted.

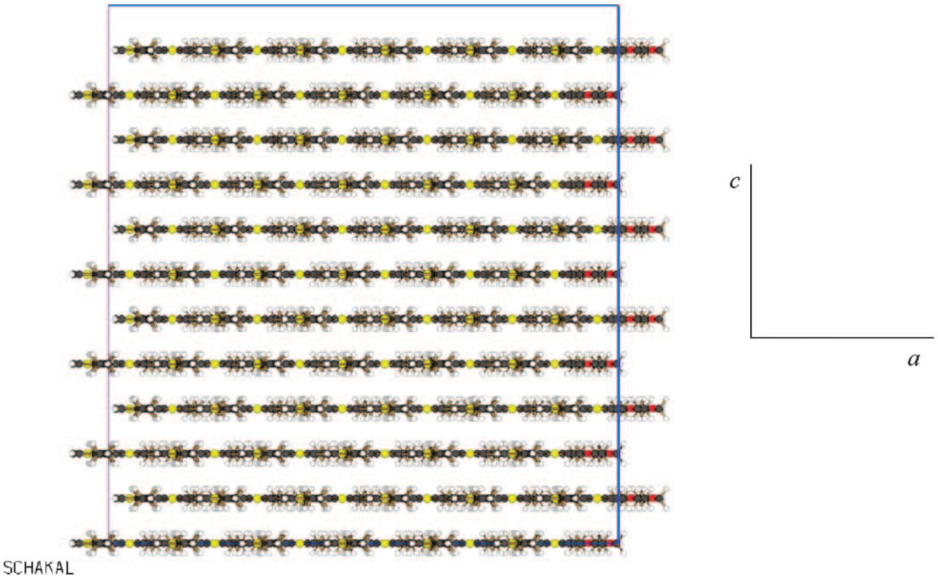


Figure 2. The cell used for the MDs simulation of the AOPT monolayer. The plane is that of the interface, the view being perpendicular to the **c** axis in figure 1. The polymer chains run horizontally along **a**. The yellow atoms are sulphur and the red atoms on the right (where they are unobscured by the polymer main chain) are the oxygens of the alkanoyl side chains. The molecules of the water layer are not shown.

3. Results of the simulations

3.1 Constant pressure

Figure 3 shows the result of a 10^5-time step constant pressure MDs simulation on the structure of an AOPT monolayer on the water surface in a cell in which there are eight polymer chains along the **b** axis. The **a** and **b** vectors of the relaxed MD cell are 30.72 and 32.46 Å, respectively, the former implying a mean stacking separation of 3.84 Å for the polythiophene chains in the interface. It is apparent that with no imposed lateral forces on the polymer interface, the intermolecular forces between the polymer chains preserve the stacking of the polythiophene backbone parallel to the water surface (**b** axis) with the planes of the thiophene rings perpendicular to the surface.

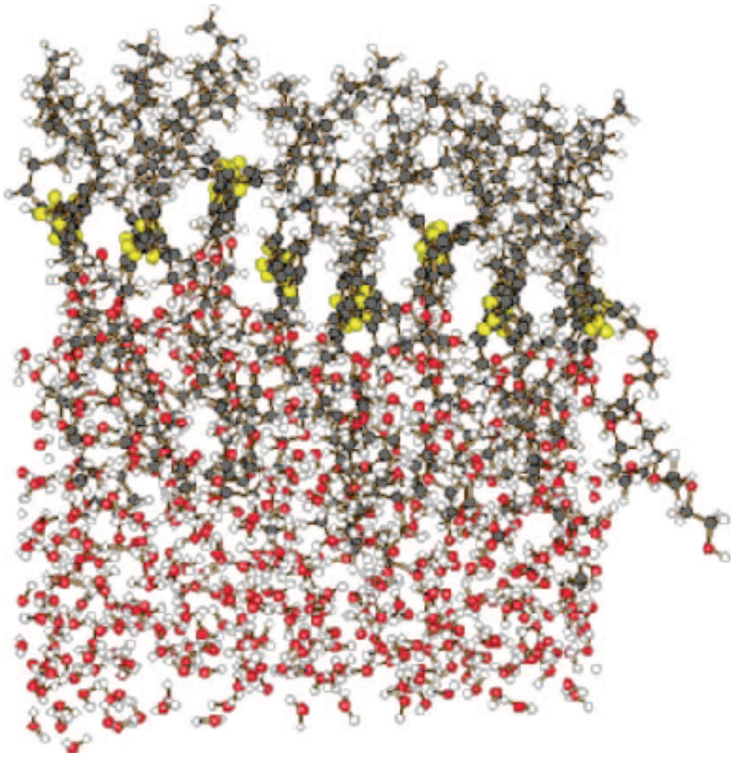


Figure 3. The result of relaxing an AOPT amphiphile monolayer on the water surface. The polymer backbone is identified by the yellow sulphur atoms of the thiophene rings, which are perpendicular to the paper (the polymer is directed along the **a** axis).

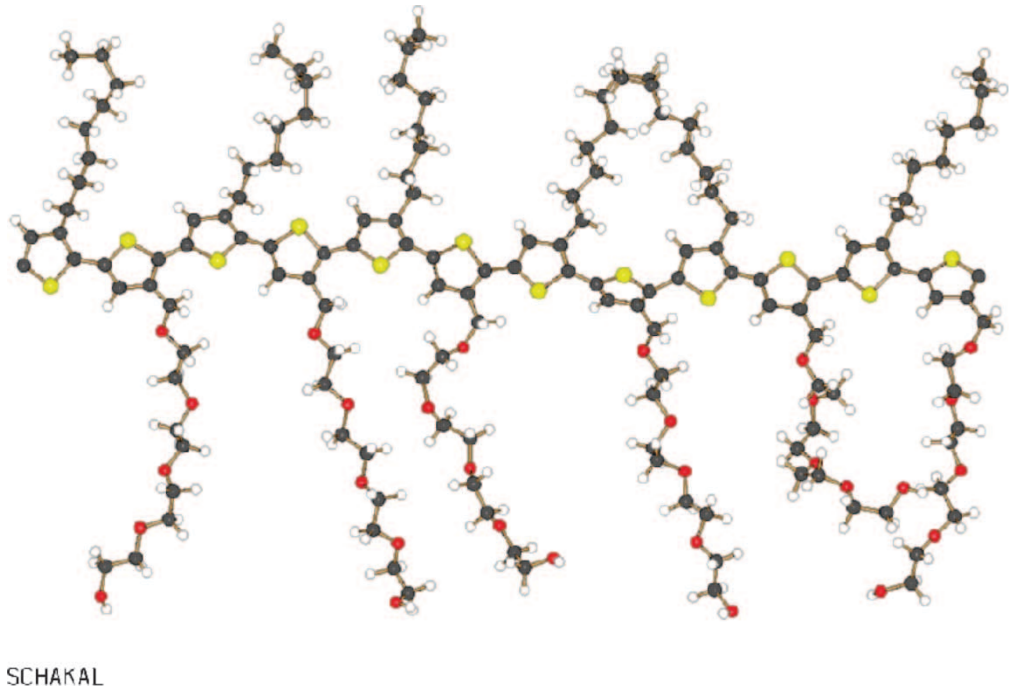


Figure 4. A typical single AOPT chain extracted from the relaxed cell. Some thiophene rings in the polymer main chain have twisted, but both species of side chain retain their original directions with the alkanoyl immersed in the water and alkyl in the vacuum.

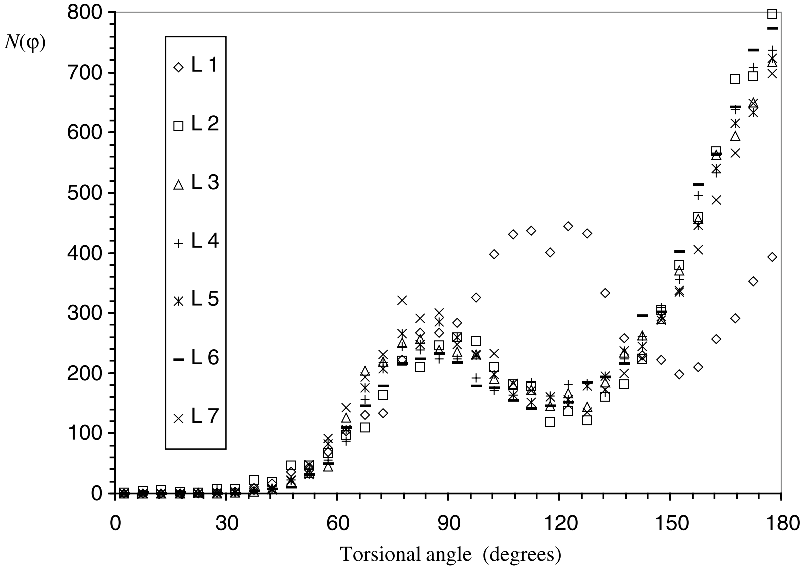
Although the octyl and alkanoyl side chains have lost some of the fully-extended order that was imposed on them prior to the dynamics, an examination of individual chains (as also shown for a typical one in figure 4) reveals that they are still largely perpendicular to the interface. The polythiophene backbone on the other hand, is not planar, the inter-ring C–C bonds showing torsions of about (±)40° from the original *anti* structure in either direction. Sometimes a greater twist brings a thiophene ring parallel to the interface (~90°), but no greater torsions were found, that might produce anything like a *syn* conformation of thiophene rings. Moreover, even when a thiophene ring does lie flat on the surface, the hydrophilic and hydrophobic side chains retain their respective directions into the water and into the vacuum.

In order to make a statistical description of the conformations adopted by the AOPT chains the distributions of the torsional angles φ in the two kinds of side chain and in the main chain were calculated and shown in figure 5 where $\varphi = 0$ and 180°, respectively, mean *cis* and *trans*. The alkyl chain C–C bonds give a set of distributions shown in figure 5(a). The unequal bimodal distribution shows that although about a quarter of the C–C links in octyl chains have undergone 90° rotations, there is still a strong component of linkages that are still *trans* ($\varphi = 180°$). The first link L1 (that connecting octyl to the thiophene ring) shows a different distribution from the others; it has bimodal peaks at 120 and 180°. (The range of φ is defined as 0–180°; values outside the interval are folded into the range.) The L1 twist indicates that about half the octyl chains are rotated to form the 'abutted' conformation that is like the diffraction structure originally proposed by Winokur and his co-workers for poly(3-alkylthiophene)s [11].

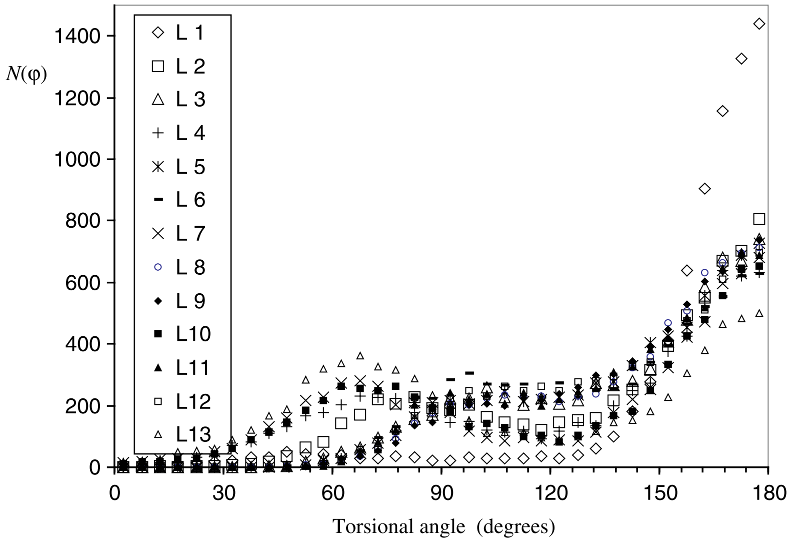
The dihedral angle distribution curves in the oxanoyl side chains shown in figure 5(b) are also bimodal, each of links showing a principal maximum at the *trans* conformation $\varphi = 180°$ and a smaller one at either $\varphi = 70$ or 110°. This result is consistent with the expectation that solvation by the water molecules twists the hydrophilic oxanoyl side chains more than the hydrophobic alkyl ones. Perhaps unexpectedly (considering the hydrophilic nature of the oxanoyl chains) the $\varphi = 180°$ maximum evidences these chains' retention of an appreciable degree of *trans* linkages.

The polythiophene main chains, whose inter-ring torsion angle distributions are shown in figure 5(c), tell a simpler story. While the occurrence of torsional angles that are $<90°$ is very low, the polymer backbone has largely lost the strict planarity that it possesses in the solid state, as the angles between most of the thiophene ring neighbours change from 180 to about 135°. This twisting of the backbone is consistent with the polymer chain extracted for depiction in figure 4, about which we remarked earlier that this (and randomly selected other chains) showed an alternating series of twists of about 40° from the *anti* (or *trans*) configurations.

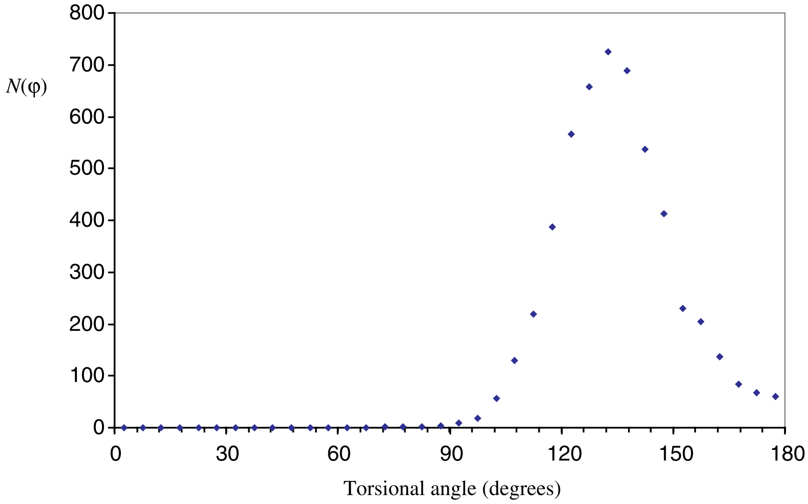
In figure 6, the dihedral angles around the eight C—C links in one of the 72 octyl chains in the MD cell are monitored over a 50,000 time step (50 ps) time interval. It was selected because, among its features of interest, it shows a "transition" involving links L2,–L4 between *trans* and *gauche* linkages, two of the linkages changing in one direction and the third in the other. That the changes



(a) octyl chains

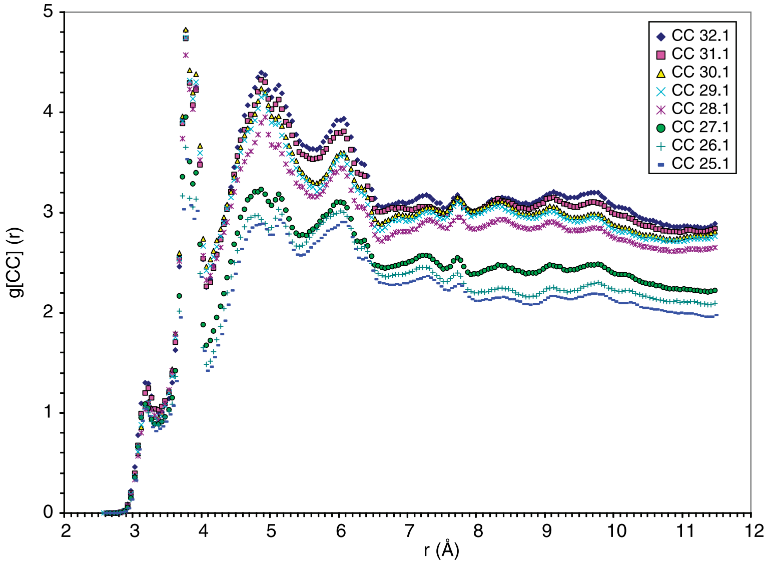


(b) oxanoyl chain



(c) main chains

Figure 5. The distribution of dihedral (torsion) angles in linkages L1, L2… in the octyl and oxanoyl side chains and in the polymer main chain, when the AOPT layer is in its most ordered configuration.


CC 32.1
CC 31.1
CC 30.1
CC 29.1
CC 28.1
CC 27.1
CC 26.1
CC 25.1
g[CC] (r)
0
1
2
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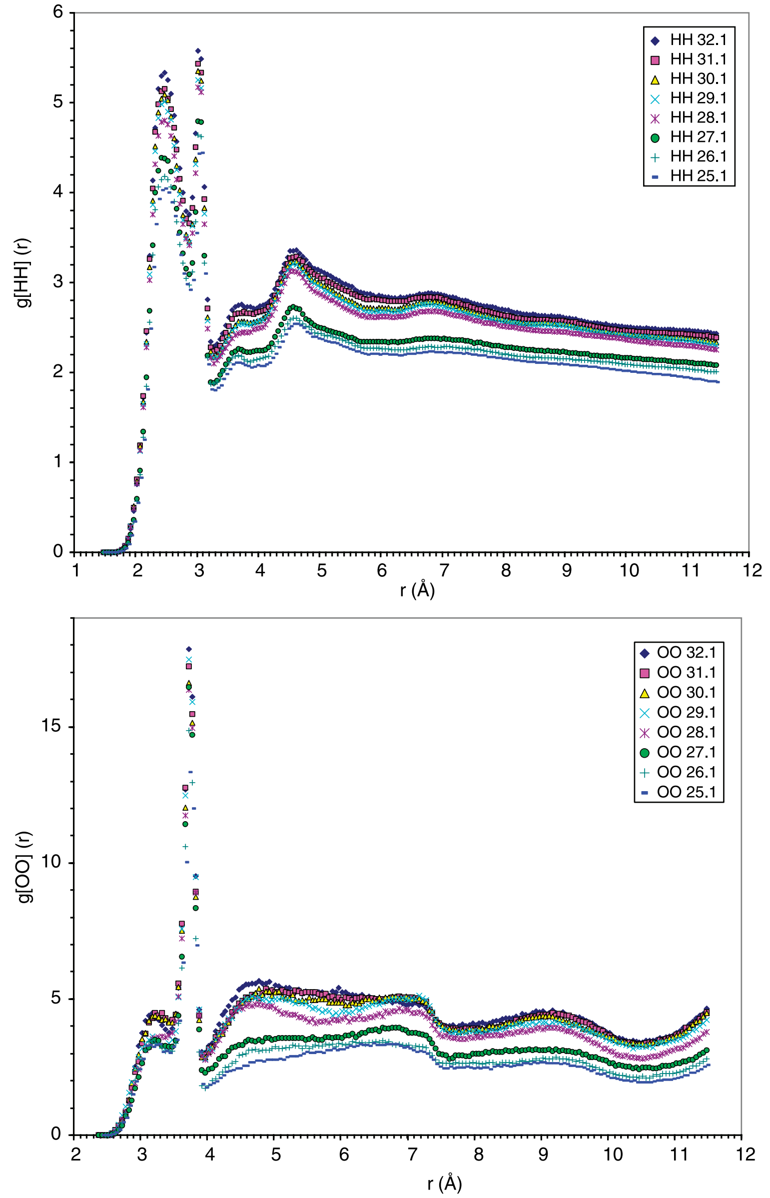
11
12
r (Å)

(a) C…C


HH 32.1
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HH 28.1
HH 27.1
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HH 25.1
g[HH] (r)
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7
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11
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r (Å)
OO 32.1
OO 31.1
OO 30.1
OO 29.1
OO 28.1
OO 27.1
OO 26.1
OO 25.1
g[OO] (r)
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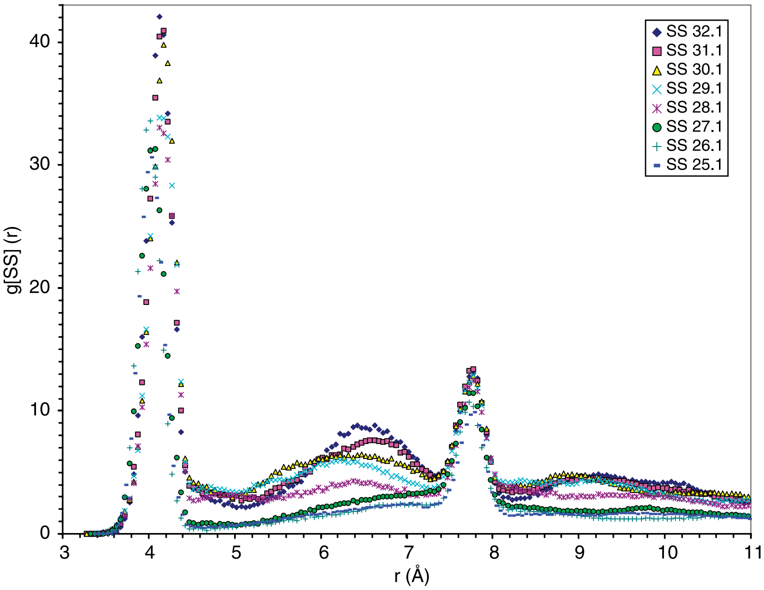
r (Å)

(c) O…O



(d) S…S

Figure 6. The time evolution of the torsion angles in the C−C links of one octyl side chains in the AOPT layer. The figure shows a transition from a *trans* to a *gauche* linkage in L2 (C_2−C_3) and one in the reverse sense in L3 (C_3−C_4) and in L4 (C_4−C_5).

occur almost simultaneously in the time interval is almost certainly not coincidental: simultaneous transitions were also found in several of the remaining side chains (both octyl and oxanoyl), strongly suggesting that the changes are concerted. It is interesting that when transitions like this occur they mainly involve the "lower level" linkages L1, L2, L3 and L4 which are closest to the polymer backbone. The other linkages seem either to maintain *trans* conformations or, like the "highest level" L8 (i.e. −CH_2−CH_3) in figure 6, the torsion motion occurs over a large φ range as might be expected for a relatively unhindered methyl internal rotation.

3.2 Contraction and expansion of the monolayer

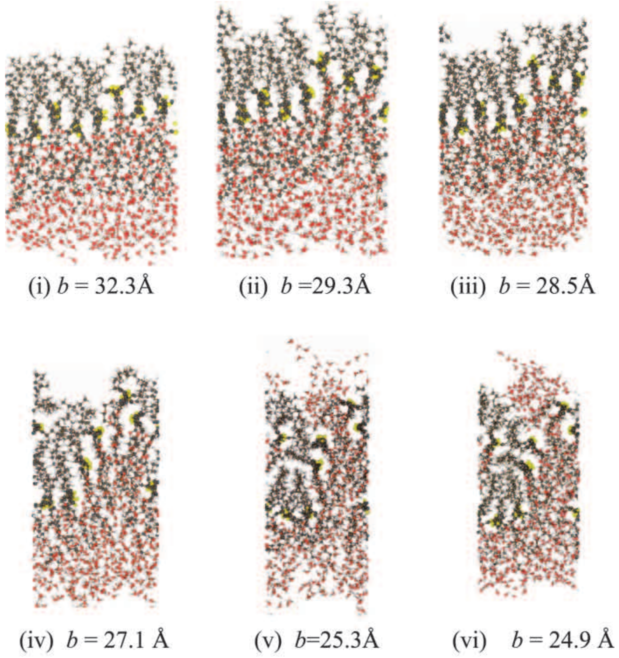
The contraction was applied along the **b** axis (the direction of the stacking of the polythiophene main chain) as a series of 6×10^4-time step constant volume dynamics. Pilot calculations with larger time steps established the sufficiency of this time interval; no gross structural changes in the monolayer occurred when the dynamics were run for longer times.

The monolayer was "contracted" by decreasing the length of the **b** axis in a series of 0.5 or 0.2 Å intervals, from 32.0 to 24.9 Å, beyond which the MD failed to produce a stable monolayer lattice. Atomic plots were made for each b value, some of which are selected for figure 7(a). They show that the stacked order of the interface monolayer is largely retained when the cell axis is contracted from 32 to about 27 Å but that the direction of the stacking, and the water surface below it, departs from the *ab* plane of the interface lattice. At greater contractions the stacking is lost as some of the polymer chains are ejected from the monolayer and the water molecules break through the polymer layer that formerly constituted the interface.

When the interface is *stretched* (by lengthening the **b** axis) the structural changes to the monolayer are less dramatic than those obtained by squeezing, but the atom plots in figure 7(b) again show a diminishing degree of order; the surface stacking of the polymer is lost and some thiophene rings even lie parallel to the surface.

It is instructive to use the changes in the atom-pair radial distribution functions (RDF) to monitor the response of the monolayer to the applied surface pressure. The value of this function $g_{AB}(r)$ when atoms A and B are separated by a distance r is a measure of the probability that a pair of A and B atoms occur at that separation. Although, the RDF peaks shown in figure 8 become broadened with the increasing compression of the monolayer, (with exceptions that will be explained) their maxima are not shifted, indicating that the principal conformation of most of the chains (which will be demonstrated to be *trans*) is retained during the compression. In the analysis we have concentrated on the $g_{AB}(r)$ peaks at short r: at large separations the decreasing order not only blunts the peaks but the RDF functions are complicated by contributions from a large number of intra- and inter-chain sources, generating incoherent peaks.

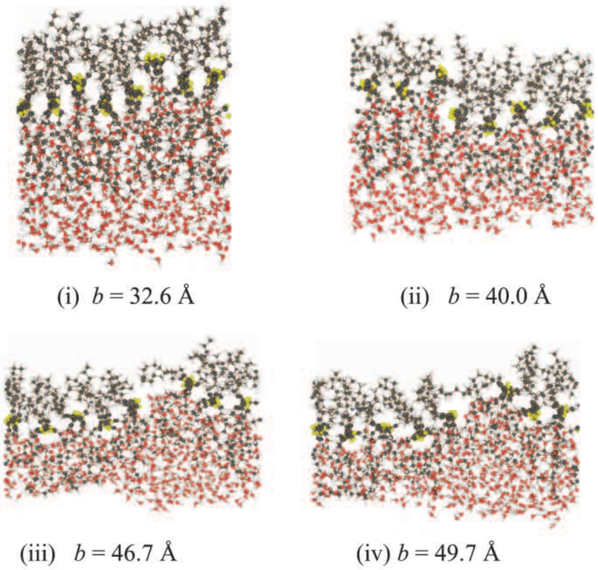
The shortest C…C separations that would indicate *trans* side chains are for a four-atom (butyl) segment $C^{(1)}H_2$−$C^{(2)}H_2$−$C^{(3)}H_2$−$C^{(4)}H_2$ in octyl where $C^{(1)}$ and $C^{(4)}$ are separated by 3.92 Å in the all-*trans* chains; in the same chain a $C^{(1)}H_2$−$C^{(2)}H_2$−O−$C^{(4)}H_2$ alkanoyl segment $C^{(1)}$ and $C^{(4)}$ are 3.70 Å apart. Shorter C pair separations are invariant to chain conformational changes. Any change in the torsional angle around the butyl segment's $C^{(2)}$−$C^{(3)}$



(i) $b = 32.3$ Å (ii) $b = 29.3$ Å (iii) $b = 28.5$ Å

(iv) $b = 27.1$ Å (v) $b = 25.3$ Å (vi) $b = 24.9$ Å

(a) contraction



(i) $b = 32.6$ Å (ii) $b = 40.0$ Å

(iii) $b = 46.7$ Å (iv) $b = 49.7$ Å

(b) expansion

Figure 7. The result of applying (a) increasing and (b) decreasing, surface pressure along the **b** axis of the AOPT monolayer. The values show the consequent lengths of the **b** axis. As in the former figures the polymer chains, viewed along their backbones, can be identified by the yellow sulphur atoms in the thiophene rings. Red denotes the oxygen atoms, which are present in the alkanoyl side chains and in the water layer.

bond would lose the *trans* description of the segment and decrease the $C^{(1)}\ldots C^{(4)}$ separation. An internal rotation of 180° around the bond would create the *cis* conformer, reducing the separation of the $C^{(1)}$ and $C^{(4)}$ atoms to 2.70 Å, while a rotation of 90° would bring the separation to 3.361 Å. Although minor $g_{CC}(r)$ peaks appear at shorter r values shown in figure 8(a) the RDF curves maintain the sharp peak at $r = 3.77$ Å, indicating that a substantial proportion of the side chains' *trans* links are largely retained during the compression.

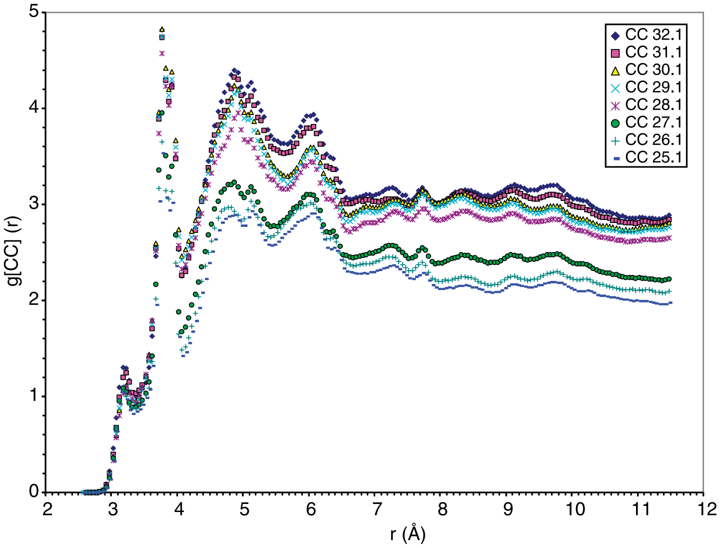
In the H…H RDF curves shown in figure 8(b) the sharp $g_{HH}(r)$ peaks at 2.5 and 3.0 Å come from the three sources: (1) the two H…H distances on the *trans* ethyl units $CH_2{-}CH_2$ (2.55 and 3.10 Å) in the octyl side chain, (2) the separations of the two H atom pairs on the methylenes on the 1 and 3 carbon atoms in the all propyl $CH_2{-}CH_2{-}CH_2$ segments in which each $CH_2{-}CH_2$ unit is *trans*, and (3) the corresponding $CH_2{-}CH_2$ and $CH_2{-}O{-}CH_2$ units on the oxanoyl chains (in the latter the separations are 2.37 and 2.95 Å). These H…H separations too are sensitive to torsion around the intervening C–C bonds. An internal rotation of 90° reduces the separations by 0.3 Å, which is within the resolution of the discernible $g_{HH}(r)$ peaks.

The sharp peak at $r = 3.73$ Å of the $g_{OO}(r)$ curves in figure 8(c) is at almost the exact separation of the closest pair of oxygen atoms in the oxanoyl chain (3.725 Å), indicating a strong retention of short term *trans* order in these side chains. The broad peak at $r \sim 7.2$ Å probably arises from the separation of next nearest O…O pair (7.19 Å in the *trans* polymer chain), but it is superimposed in a broad signal from intermolecular O pairs in adjacent polymer layers.

The $g_{CO}(r)$ RDF curves (not included in figure 8) also show a sharp peak at a distance corresponding to the separation of the $C^{(1)}$ and O atoms in the *trans* segment $C^{(1)}H_2{-}O{-}C^{(2)}H_2{-}C^{(3)}H_2{-}O$. Both the O…O and C…O RDF sets, therefore, indicate that the *trans* conformation persists to a greater extent in the alkanoyl, than in the octyl, side chains.

The $g_{SS}(r)$ curves shown in figure 8(d) describe the response of only the polythiophene main chains to the compressions. As the peaks from pairs of S atoms on adjacent rings on the polythiophene backbone would appear at 4.31 Å if these rings are *anti* and 3.21 Å if they are *syn*, the RDF peaks might be expected to provide information on the relative conformations and planarity of the main chains. Unfortunately, the prominent peak in this region is subject to interference from S atom pairs in the stacked backbones of adjacent polymer layers along the **b** axis interface (the stacking distances along **b** is in the region of 4 Å). The peaks from stacked chains, including those at ca. 6.5 and 9.2 Å can be identified by their shift to lower r with increasing compression along **b**. This feature can be seen also on the sides of the 4 Å peak, leaving a rather narrow unshifted main component at 4.2 Å, which would indicate that many rings have rotated by 40° from the imposed *anti* conformation. The RDF curves show no contribution from *syn* pairs of thiophene rings (at $r = 3.2$ Å), and may admit an appreciable proportion of *anti* pairs ($r = 4.31$ Å).

The peak at 7.73 Å, which is not subject to shifting with decreasing **b**, is close to the **a** axis repeat distance of 7.76 Å as expected from S atom pairs in next-nearest-neighbouring thiophene rings in a planar *anti* main chain, and would not change much with the rotation of the intervening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r (Å)
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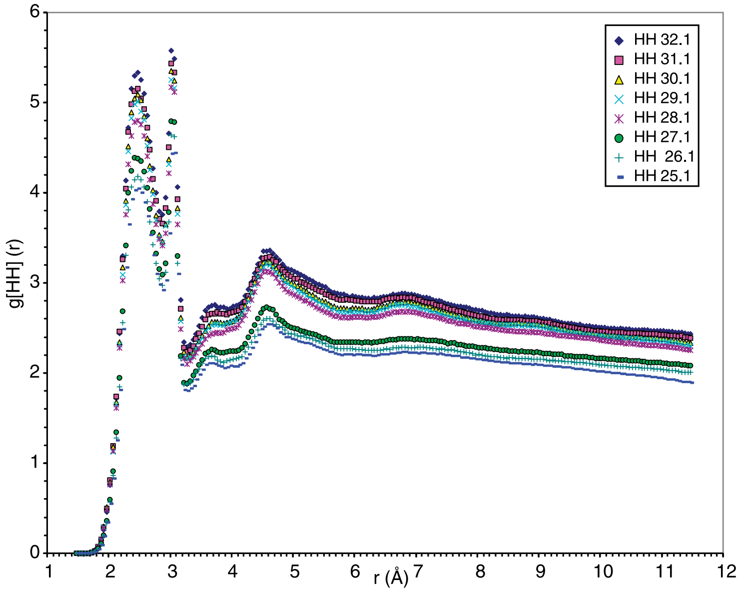
CC 28.1
CC 27.1
CC 26.1
CC 25.1

(a) C…C


g[HH] (r)
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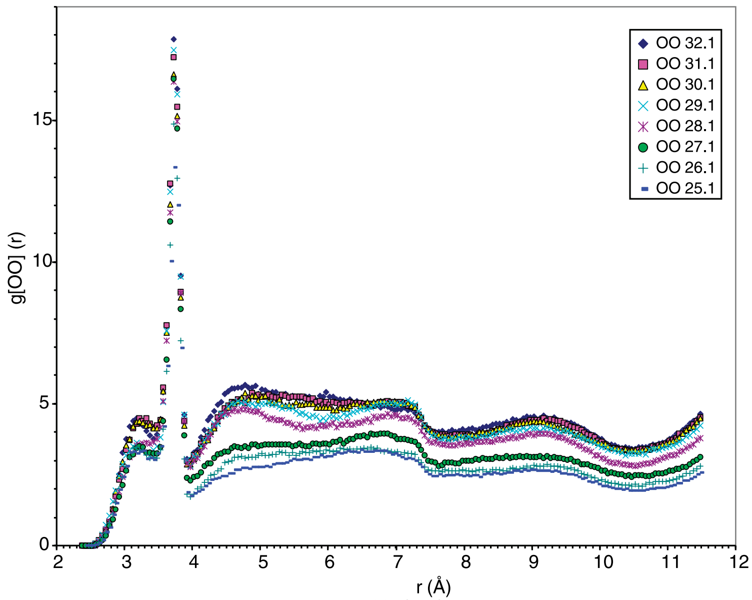
(b) H…H


g[OO] (r)
r (Å)
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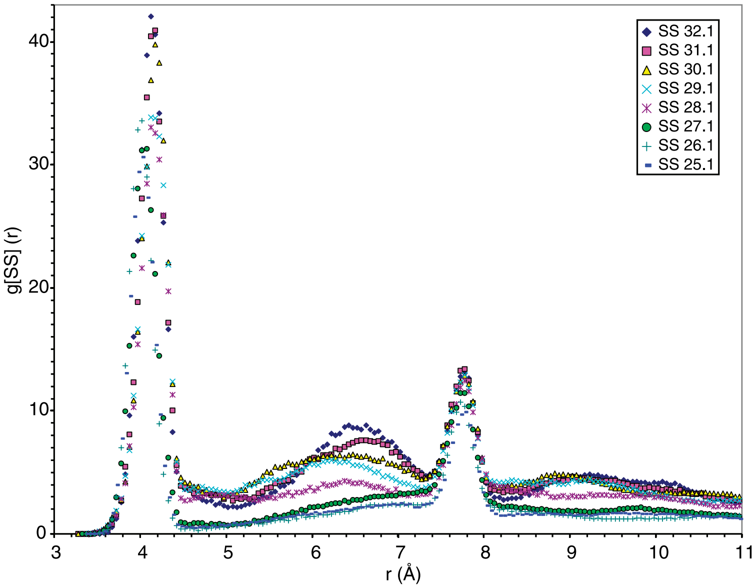
(c) O…O



(d) S…S

Figure 8. (a) to (d) Radial distribution functions at various **b** axis compressions for the atom pairs indicated. The figures in the legend show the changing length b of the **b** axis as it is compressed.

thiophene ring. Unlike the other RDF curves in figure 8 the positions of some of the peaks shift with compression.

Another feature evidenced by the RDF curves in figure 8 is the sudden change in the AOPT order at a certain compression. The curves monitor the structural response of the AOPT interface when b is reduced in monotonic intervals of 1 Å from 32.1 to 25.1 Å. Each set of $g_{\mathrm{AB}}(r)$ in figure 8, particularly those (a)–(c) describing the side chains, shows a discontinuity between $b = 28.1$ and 27.1 Å, indicating an abrupt decrease in structural order of the interface at this compression. This is matched by the molecular plots in figure 7(a) where, in the interval between 27.1 and 25.3 Å, the monolayer is ruptured, allowing the passage of water molecules into the region above the polymer layer. Figure 8(d) shows that the main chains respond to the compression at an earlier stage than do the side chains.

4. Discussion

The series of structure snapshots in figure 7 shows that the effect of contracting the monolayer in the direction perpendicular to the polymer chains was twofold: the order of the polymer main chains was initially reduced, and at more severe compressions the underlying liquid molecules broke through the polymer layer. The first of these might be interpreted as similar to the ‘buckling’ that was described by Fenwick *et al.* [6]. However the very different structural natures of the components of the present system would not lead us to expect parallel behaviour. The eruption of the liquid through the monolayer may be the result of the severe compression (25% reduction in area) and the fact that in our simulation the water slab as well as the monolayer is being compressed along the **b** axis. These latter response of the AOPT monolayer is reminiscent of the behaviour of phospholipid monolayers when laterally compressed in pure water [12]. That investigation found that the monolayer fractured resulting in loss of material to the liquid component.

The molecular “snapshot” plots in figures 3 and 7, the radial distribution curves in figure 8 and the torsion distributions and time-evolution in the chain links in figures 5 and 6 all show that the chains contain a range of non-planar linkages in the polythiophene backbone and in the octyl side chains. However, even when compression is applied to the monolayer we find in both species of side chain the retention of a substantial proportion of *trans* linkages. The resilience of the *trans* linkage in octyl chains is a structural feature of bilayer membranes that constitute living cells [13], and may support the mechanism of ion transport across such membranes. It also plays a role in the functioning of lubricants on nano-scale surfaces [14]. The *trans* contribution does not necessarily imply that the chains are “fully extended”—indeed the conformations in individual polymer chain “snapshots” in figures 3 and 4 show that many of the octyls and oxanoyls are far from such a description. We find merely that a near-*trans* conformation of the CH_2–CH_2 segment is favoured, but the additional presence of non-*trans* links precludes the side chains from attaining overall fully-extended conformations.

The rather regular twisting of the polythiophene backbone in alternating directions by about 45° is probably the result of a compromise between the chain’s hydrophilicity (the charges on the atoms in the thiophene rings would favour contact with the water layer) and the opposing drive by the side chains in alternate rings for hydration (association with the water) and to be aligned into the vacuum. The RDF curves in figure 8 show that many of the links in the oxanoyl chains have linkages that are more twisted than those in the octyl chains, suggesting the hydration of the former.

The time-evolution curves of the linkages in figure 6 show that they can jump between *trans* and *gauche* conformations, and that these two conformations correspond to those in maxima of torsional angle distribution curves in figure 5.

Unlike the behaviour of single-molecule alkanoate amphiphiles on a water surface, where a sharp drop in the surface diffusivities is monitored as the monolayer is compressed [8], in the system investigated in the present work the motions of the atoms in the interface are restricted by their being part of a polymer layer. This fact may enable the electrical charging the monolayer through the electro-active polymer backbone to lead to interesting physical and chemical properties.

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