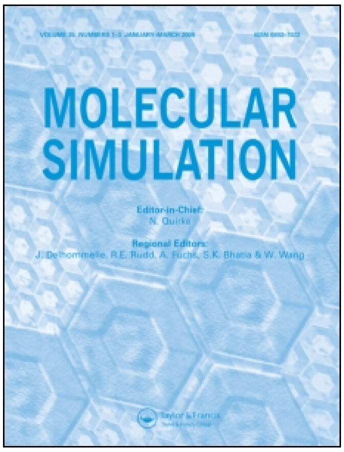

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

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Robert O'Farrell[a]; Sadhbh O'dwyer[a]; D. A. Morton-Blake[a]
[a] Department of Chemistry, Trinity College, Dublin 2, Ireland

To cite this Article O'Farrell, Robert , O'dwyer, Sadhbh and Morton-Blake, D. A.(2004) 'The Transport of an Ion through a Channel Formed by a Helical Electroactive Polymer', Molecular Simulation, 30: 10, 649 — 659

To link to this Article: DOI: 10.1080/08927020410001715355

URL: http://dx.doi.org/10.1080/08927020410001715355

Molecular Simulation, Vol. 30 (10), 30 August 2004, pp. 649–659

The Transport of an Ion through a Channel Formed by a Helical Electroactive Polymer

ROBERT O'FARRELL, SADHBH O'DWYER and D.A. MORTON-BLAKE*

Department of Chemistry, Trinity College, Dublin 2, Ireland

(Received April 2004; In final form April 2004)

The transport of a BF_4^- ion in helical poly(3-octylthiophene) is simulated by conducting molecular dynamics in the absence, and in the presence, of electric fields along the channel direction. Temperature-dependent diffusion simulations show that the ions encounter an energy barrier of about $7\,kJ\,mol^{-1}$. The effect of the degree of oxidation of the polymer (atomic charges on the inner walls of the channel) on the ion migration shows that the rate of the transport increases with oxidation level until the polymer is about 50% oxidised. Above this figure the resulting motion becomes hindered by the high charges on the channel, which result in ion congestion and "sticking". Also examined are the competing effects of solvent molecules in the channel and the radial distribution statistics which, in common with the migration studies, show that above 50% oxidation the polymer chain starts to undergo distortion from the helical configuration.

Keywords: Diffusion; Migration; Helical channel; poly(3-octylthiophene); Activated ion transport

INTRODUCTION

The electroactivity of ion-doped polythiophene is retained by the polymer when it is substituted in the "3" position of the thiophene ring by alkyl or other groups, and in addition the substituted polymers are soluble in common solvents [1,2].

Certain aspects of the electroactivity—the doping/undoping cycle for example, and the ability of the substance to function as an electrode—are associated with the migration of the dopant ions through the polymer material. A mechanistic description of this process on an atomic level requires the polymer to be in close association with solvent. Although the structure of such a system probably consists of regions of short-range order dispersed in a solvent medium, it may still be capable of a conformational description. The π-conjugated backbones in chains of polythiophene and its derivatives impose a degree of rigidity on them giving the main chains well defined conformations in the solid state and as mono- and multi-layers [3,4].

REGULAR CHAIN CONFORMATIONS OF POLYTHIOPHENES

Planar Main Chain

The commonest chain conformation of regio-regular polythiophene and its derivatives are ones in which the polymer backbone is planar and the adjacent thiophene units are in an *anti* arrangement; such a polymer chain is linear. This structure is retained when the thiophene "3" position is alkyl-substituted to produce a poly(3-octylthiophene) chain (P3OT), shown in Fig. 1, which describes a straight "hairy rod" polymer with the alkyl side chains directed approximately perpendicular to the direction of the backbone (the z axis).

Helical Polythiophene

Another conformation is the one that results from twisting each thiophene unit along the chain successively by a torsional angle ϕ around the inter-thiophene C–C bond to its left. Our definition of the torsional angle is that in which $\phi = 0°$ specifies the all-planar *anti* conformation described in the previous section while $\phi = 180°$ would describe

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*Corresponding author. E-mail: tblake@tcd.ie

ISSN 0892-7022 print/ISSN 1029-0435 online © 2004 Taylor & Francis Ltd
DOI: 10.1080/08927020410001715355

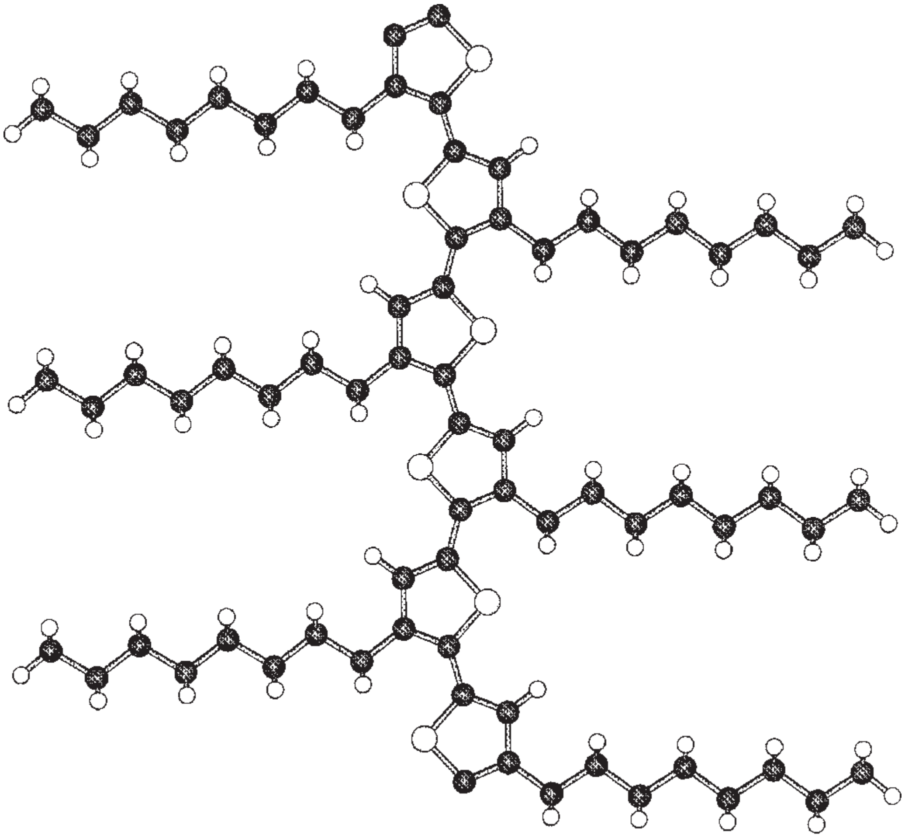

FIGURE 1 Poly(3-octylthiophene) in its all-*anti* conformation. The polythiophene main chain is planar and aligned along the z direction.

a chain in which the thiophene units lie on the circumference of a circle in a *syn* arrangement and is sterically precluded. Other torsions ϕ turn the main chain into a helix with the alkyls directed perpendicular to the helical axis. The power of BF_4^- ions to twist oligothiophene chains from their initial all-*anti* conformations into helical forms has been noted from DFT calculations on these systems [5]. Moreover alkyl-substituted polythiophenes, with the planes of adjacent rings almost parallel (ϕ nearly 180°), have long been identified as deposits on an electrode after synthesis using scanning tunnelling microscopy and diffraction methods [6–8]. More recently, however, they have been produced in solution [9] with 12 thiophene rings per turn of the helix, implying a torsional angle of about 175°. The planes of the adjacent thiophene units in the helical form are again almost parallel as they were in the rod-like chain, but they have a near-*syn* relationship, as demonstrated by the red shifts of their UV–visible bands when the helical chains are formed [9].

Which of the two conformations are obtained—planar chain or helix—depends on chemical conditions. In the solid both may be found in Refs. [6–8,10]. In solution while the most commonly reported conformation of poly(3-alkylthiophene) chains (P3AT) is that with a planar-backbone, the use of mixed solvents whose hydrophilic/hydrophobic ratio is adjusted promotes the production of helical chains [9]. Another method to produce a helical main-chain is to substitute the alkyl side chains by chiral chains [11–13]. Substituents with an aminoacid group result in backbones whose conformation changes from planar to helical depending on the pH of the ambient solution [14,15].

Atomistic lattice simulations have confirmed the stability of the helical chain with 11 or 12 thiophene rings per turn [16]. They showed that the planar (*anti*) and helical (*syn*) are conformers defined by minima in a torsional energy profile $E(\phi)$ which in an isolated polymer chain have similar energies, but are separated by an energy barrier of about 0.5 eV. When the helical chain forms part of a polymer *lattice*, however, the layer structure obtained when the backbone is planar ($\phi = 0°$, ring conformation *anti*) has more favourable lattice packing then that obtained when it is a helix ($\phi = 175°$, ring conformation nearly *syn*).

The two regular conformations are protected from interconversion by the energy barrier separating them which calculations [16] suggest is much higher than thermal energy. In the case of the oxidised polymer as is considered in this work (the positive charges on the chain are countered by BF_4^- dopant anions) quinoidal bonding stiffens the bonds between the thiophene rings, thereby enhancing the energy barrier. Thus a comparison of Raman bands for neutral and oxidised poly(3-chlorothiophene) at different temperatures by Chen *et al*. [17] showed that while the neutral polymer responded to the heating by changing from rod-like structure to a disordered one, the conformation of the oxidised polymer remained rod-like throughout.

Ion Migration

The above description forms a scenario for the motion of the "dopant" ions, which are the by-products of the oxidation of the polythiophene. This work will investigate whether and how the conformations of the polymer chains affect the ion migration.

In a recent molecular dynamics study of the mobility of BF_4^- ion dopants in a poly(3-octylthiophene) lattice of all-*anti* planar chains [18], the anions were predicted to be capable of lattice migration in zero-field conditions and even more readily when an electric field is applied. If the polymer were in a helical configuration generated by the $\phi = 175°$ torsions described above it would have a pitch (distance between successive turns of the coil) of 3.6 Å, which is small enough to confine the BF_4^- ions to either the inside or the outside of the channel (its strands would be too tightly wound to permit easy passage between these regions).

The passage of ions through a molecular channel is central to the functioning of a living cell, whose properties are sensitive to the concentrations of sodium and potassium ions in the aqueous medium on either side of the cell membrane [19]. The latter is a phospholipid chain bilayer with the phosphate groups forming the membrane's two exterior, hydrophilic surfaces. Since the interior of the membrane consists of hydrocarbon chains it does not provide a favourable environment for ions. Their ability to penetrate the membrane is due to single protein molecules embedded in the bilayer but with regions in contact with the aqueous media flanking the bilayer. These molecules possess ion-friendly hydrophilic channels which facilitate the passage of the ions between the two aqueous environments on either side of the membrane.

Few descriptions have been made of the detailed atomic-level dynamics of the ion transport in the channels just described. This is probably because of the complexity of the conformational changes occurring in the flexible protein chains forming the channel. In order to achieve some information on how ions migrate through such an environment we decided to perform molecular dynamics (MD) on the transport of BF_4^- ions through the channel in helical poly(3-octylthiophene) chains in a chloroform solvent. Although to our knowledge no experimental investigations have been reported on these systems it was felt that the established stability of helical P3ATs in solution merits an investigation of the manner in which ions could be transported along the central channel in field-free conditions and under the influence of electric fields.

STRUCTURAL MODEL AND COMPUTATIONAL TOOLS

As a model for an initial investigation of channel transport of ions we considered the migration of BF_4^- ions through the cylindrical channel in helical poly(3-octylthiophene) chains in a surrounding solvent medium. This was because such helices, doped with BF_4^- ions, are known [10] and because the solution would allow the model to represent ions moving through an ionophilic channel between fluids on either side of a biological membrane. The strong local electric fields that enable the ion transport in the real systems are effected in the simulation by applying uniform fields along chosen directions. For this purpose the polymer helix was secured in its solvent environment with its axis along the z direction by subjecting it to the periodic boundary conditions along z so that the helix becomes endless. In this work the electric fields are expressed in electric field units "efu" ($1\,\text{efu} = 100\,\text{Mv}\,\text{cm}^{-1}$) whose magnitudes are those of the *local* fields experienced by ions in electrolysis. (Experimentally these fields are difficult to measure, but calculations on simple electrical double layer models of nanometre separation show that ions in such environments can experience fields of $100\,\text{Mv}\,\text{cm}^{-1}$.) The work explores ion migration in field strengths of 0.01–10 efu.

The molecular geometries employed in this work were the same as those previously used in our P3AT investigations [16,18,20–23], but we give the chloroform C–H and C–Cl bond lengths, respectively, as 1.073 and 1.762 Å. The H–C–Cl and Cl–C–Cl bond angles are 110.9 and 108.0°. But since the translational periodicity of the helical chain along its axis depends critically on the bond lengths and bond angles used to describe the main chain, these values will be repeated here. The C–C bond lengths around the thiophene ring are 1.385, 1.442, 1.385 Å and the C–S and C–H lengths are, respectively, 1.1 and 1.686 Å. The inter-ring C–C length is 1.447 Å. The ring C–C–C bond angles are both 112.2°, C–C–S is $-110.25°$ and C–S–C is 95.1°. The exterior angle S–C–C where "C–C" is the inter-ring bond is 121.45°. The other geometries are not critical to the periodicity and may be found in our cited work [16,18,20–23].

When the all-*anti* polythiophene chain with the molecular geometry quoted is subjected to a series

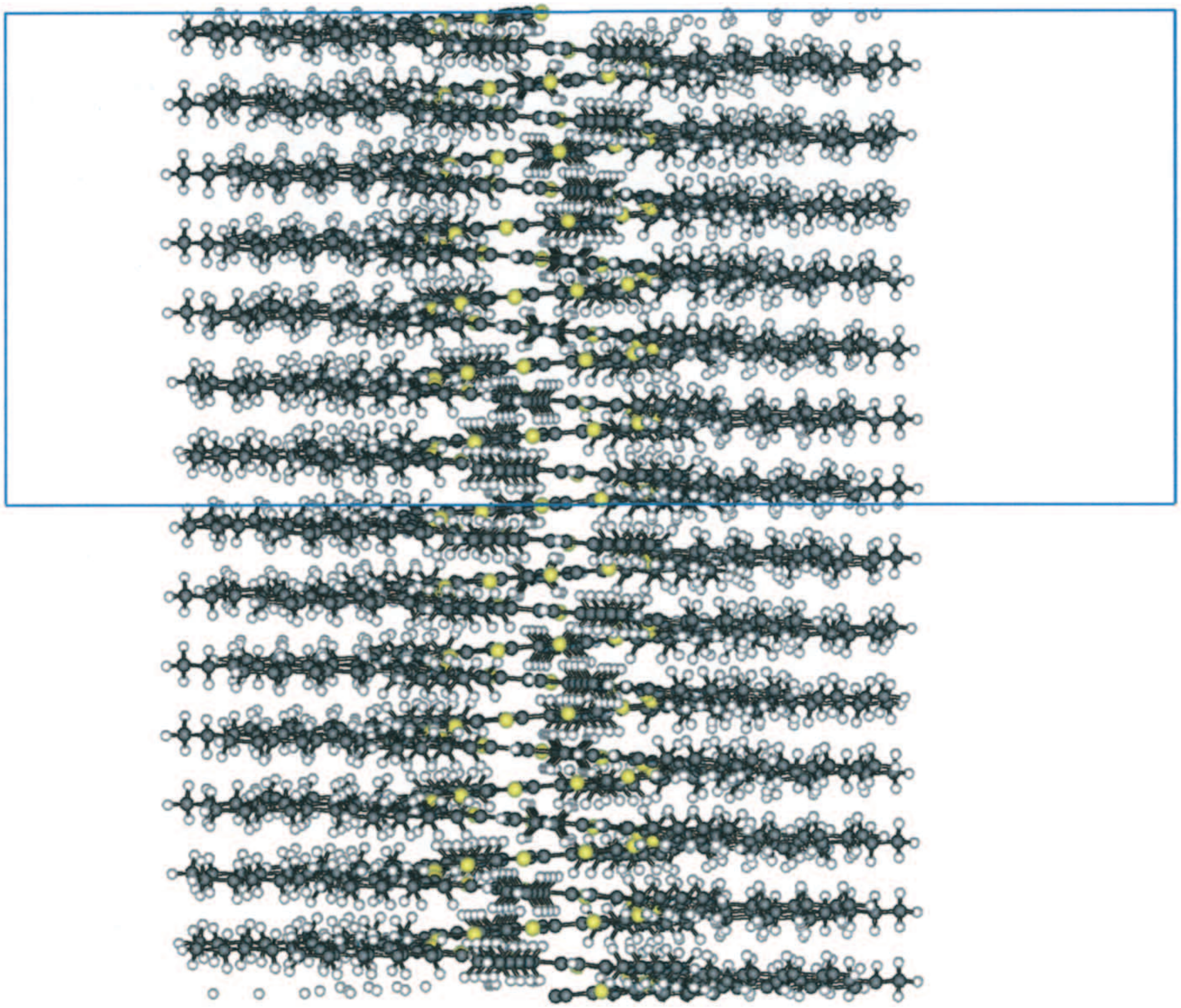

FIGURE 2 A section of helical poly(3-octylthiophene) derived from the all-*anti* chain by imposing the same torsion ϕ around each inter-thiophene C–C bond in turn. The box contains the length of the repeat segment. The chloroform solvent molecules, in which the polymer is immersed, are omitted for clarity.

of sequential torsions by rotating the portion of the chain to the right of the inter-thiophene-ring bond by $\phi = 177.33°$, a helical chain is generated. The result shown in Fig. 2 contains between 11 and 12 thiophene units for a complete rotation of the helix. After 78 rings translational periodicity is accurately established along the helical axis z. The pitch of the helix (the distance between adjacent turns) is 3.6 Å and its period along z is 26.98 Å, defining a P3OT chain containing 2418 atoms. The internal and external diameters of the helix of the initial model (i.e. prior to relaxation) are 5.73 and 38.57 Å, respectively, the latter being the distance from the helical axis to the tips of the octyl side chains. The "basic" cell used to illustrate the system in Figs. 2 and 3 consists of the 2418 atoms in the repeat segment of the polymer chain and 468 solvent molecules. The $2 \times 2 \times 2$ supercell used for the diffusion studies contains 8 times these numbers (19,344 polymer atoms and 18,720 atoms of $CHCl_3$).

With the helix directed along the z axis of the local coordinate system three kinds of sites can be identified in the solution system: (1) a small number of solvent molecules are within the helical channel, (2) about the same number are between the octyl chains outside the channel and (3) the great majority of them form the bulk of the solution. They are distinguished on the basis of the distance of the carbon atom in each solvent molecule from the axis: a value less than the internal radius (2.87 Å) implies a channel site. If it is between this distance and the external radius (19.79 Å) it is a side-chain site. Distances outside this range describe a bulk solvent site. Anions of BF_4^- were then generated in two solution sites by selectively replacing the required number of $CHCl_3$ in the two kinds of site by BF_4^- ions. The MD was conducted for 10^4 and 10^5 time steps ($1\ \text{ts} = 0.001\ \text{ps}$), depending on the purpose of the dynamics, with a Hoover NPT (constant numbers of particles, pressure and temperature) thermostat.

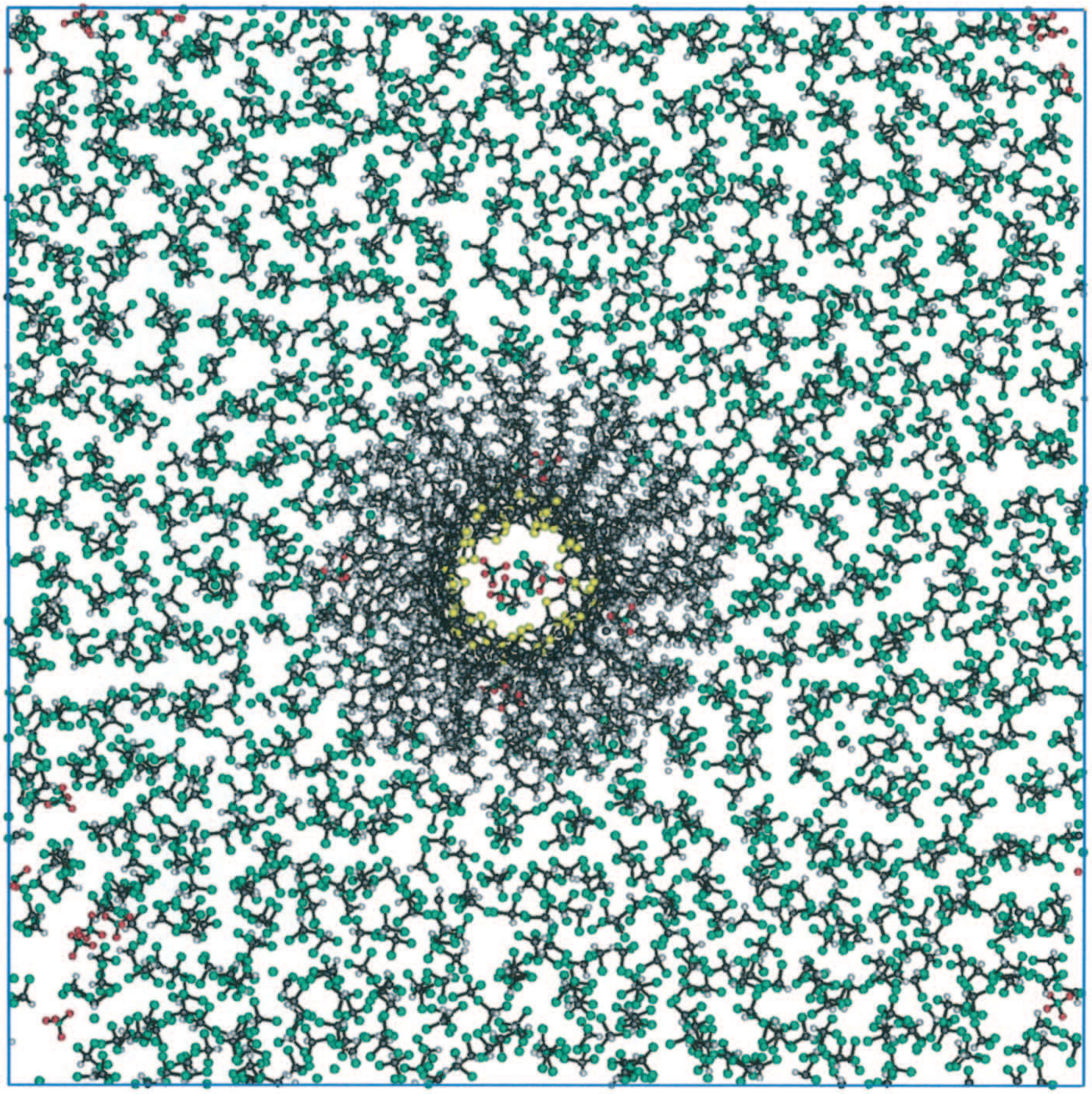

FIGURE 3 The simulation box (MD "unit cell") viewed along the helical axis of the P3OT chain or "z axis" after equilibration in chloroform. The *a* and *b* lengths of the box are 99.88 Å, and the length *c* along the channel (*z* axis) is 28.12 Å. The $CHCl_3$ solvent molecules are green and the BF_4^- ions are red.

We used the same force field parameters for the atom-pair bond stretch, bond angle deformation, torsional and atom-pair non-bonded potentials as in our earlier investigations [16,18,20–23], supplemented by the potential parameters for chloroform from the work of Chang *et al.* [24]. The partial atomic charges are taken from Yurtsever's B3LYP 6-31(d) calculations on thiophene oligomers [5]. Each BF_4^- ion was supposed to balance a positive charge transferred to the polythiophene main chain and spread evenly over the sulphur and four ring-carbon atoms. These were used by the Ewald method to calculate the lattice, Coulomb energy. The dynamics were conducted mainly at 300 K, but a range of temperatures was applied to estimate energy barriers to dopant diffusion.

Corish *et al.* [16] showed that an energy barrier as low as 0.5 eV (about 11 kcal mol^{-1}) for torsion around the C–C bond linking two thiophene rings was sufficient to stabilise the neutral polythiophene chain in its helical conformation. For the positively-charged *oxidised* chain (a polyelectrolyte with BF_4^- counterions) the quinoidal bonding in the π-bond order of the inter-ring bond would be larger than 0.5 eV and so also therefore would be the torsional barrier. Nevertheless, due to a lack of reliable quantitative data to describe this bond we assign a lower-limit torsional barrier of 0.5 eV to the inter-thiophene C–C bond. All other atomistic parameters not defined in this section are identical to those used in our other calculations on P3ATs.

The response of the ionic migration to changing the atomic charges within the helical channel was investigated. Although the great majority of these ions at any instant are in the bulk of the solution rather than within the channel, the observation of overall electroneutrality means that simply by increasing the number of BF_4^- ions in the bulk, increased positive charges are generated on the atoms of the channel.

RESULTS

The positively charged P3OT chain in chloroform solution, stabilised by coulombic interactions with the BF_4^- ions and by the imposed periodic boundary conditions along the channel direction, keeps its helical conformation indefinitely during the molecular dynamics runs. Pilot MD calculations on short (1-turn) helical P3OT oligomers under the same conditions showed a tendency to become unravelled after a few thousand time steps, but those containing more than 3 turns preserved their helical shapes up to 10^6 time steps (10^{-9} s). The dimensions of the simulation box along both the z direction (that of the helical axis) and the perpendicular dimensions (decided by the width of the helical chain) increased by about 10% from the imposed length to initiate the MD runs. A typical result of an MD run on the polymer solution is shown in Fig. 3 where the solvent molecules (green) and the BF_4^- ions (red) may be seen both inside and outside the central channel. The dimensions of the basic cell shown in the Figure are $a = b = 99.98$ Å and $c = 28.12$ Å, but each of these are doubled for the diffusion calculation which is described below. The density profiles of the three constituent atomic species in a slice across a diameter of the helical polymer in Fig. 4 indicate that after the relaxation the overall diameter of the helix between the outermost tips of its alkyl chains is 38 Å, showing that this distance is almost unchanged from the diameter prior to relaxation (38.57 Å). This value may be somewhat larger than a more realistic diameter due to the instantaneous deformations of the helical main chain that are apparent from Fig. 3, but it shows that the octyl chains largely preserve their fully-extended conformations. The channel diameter is more sensitive to the same deformations, and if the 10 Å separation of the two sulphur density peaks are taken as a mean diameter, it must be concluded that the relaxation of the P3OT chain has increased the channel diameter from its value of 5.73 Å before the MD runs.

Field-migration of Ions

The "fixed" charges on the atoms inside the helical channel were varied by altering the total number of BF_4^- solute ions while requiring overall electroneutrality. In monitoring the mean square displacements of the mobile ions in the channel it

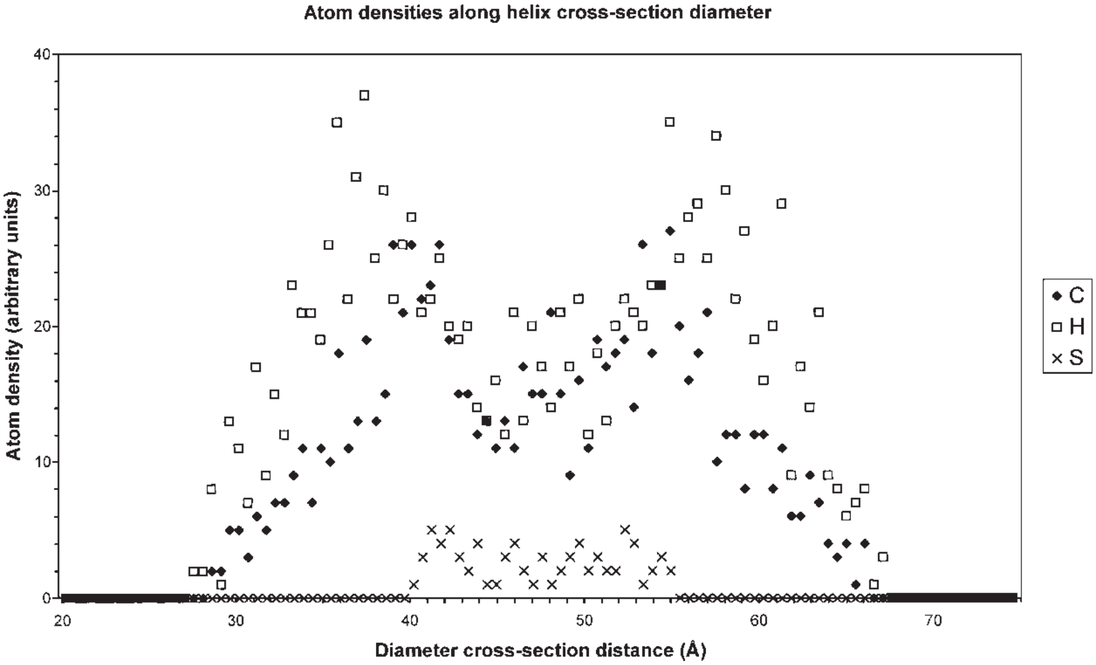

FIGURE 4 Atomic density profile along the cross-sectional diameter of the P3OT chain, perpendicular to the helical axis. The system in $CHCl_3$ solution has been equilibrated for 5000 time steps.

must be remembered that as the number of channel ions is necessarily very low (usually six or less) in comparison to the thousands of other particles in the simulation box, the consequent statistics for these BF_4^- ions of interest are not as substantial as would be the case for an MD investigation in which there were hundreds or more of these ions. Nevertheless, repeated calculations on the ion trajectories showed that the trends reported were quite reproducible even for such small numbers of migrant ions.

Figure 5(a) shows the mean square displacement (msd) of the BF_4^- ions in the helical channel when it accommodated six such anions with none in the surrounding solvent medium (since there are 78 thiophene units in the repeat segment the polythiophene main chain is here only weakly oxidised). The ions are therefore moving in a helical channel whose net charge balances those of the migrating ions. The figure shows the progressively greater ionic mobility with increasing electric field E_z applied along the helical axis. The result is as expected, but the muted response of the ionic mobility to increasing field at high field strengths (doubling the field after 5 efu has little effect on the mobility) will be commented on below. When more BF_4^- ions are introduced so that they occupy not only channel sites but also positions near the side chains and in the bulk of the solvent medium, more compensating fixed positive charges are added to the thiophene rings (that largely form the channel) so that the channel charge exceeds that of the BF_4^- ions occupying the channel. Figure 5(b) shows the effect of increasing the total charge on the thiophene atoms to 36, thus describing a polythiophene main chain that is about 50% oxidized. The lower rates of migration compared with those for the lightly-oxidised polymer may be attributed to the arresting action or "sticking" which the high charges associated with the thiophene rings exert on the migrating ions.

It is also of interest to see how the migration of the BF_4^- ions depends on the concentration of the ions in the channel. Accordingly we maintained the field in the channel at $E_z = 0.5$ efu and kept the charges on the channel wall constant by conserving the number of BF_4^- ions in the total system in such a way that the only variable was the number of ions occupying the channel. Figure 5(c) compares the msd curves for a series of configurations, each of which contains a total number of 20 ions in the system, but in which the number inside the channel is 1, 2, 3 and 6, the remainder being outside the helix. The plots show a progressively faster migration as the number of BF_4^- ions increases. The slower migration at low ion concentrations may be attributed to the impeding effect of the $CHCl_3$ solvent molecules in the channel. This conclusion is supported by the contrasting behaviours of the one-ion case in Fig. 5(c), which show that when the solvent molecules are present and when they are removed. When the BF_4^- ion is the sole occupant of the channel in the unit cell its migration rate increases by an order of magnitude.

Structural Statistics

The departure of the order of the msd curves from that of the applied electric fields might be due to congestion effects in the channel at high fields, when the transported ions respond to increasing fields by blocking the channel. If this is so, the congestion might be revealed by $g(r)$, the pair correlation function or radial distribution function (rdf) between an atom of the polymer forming the channel and an atom of the migrating BF_4^- ions.

The two families of curves plotted in Fig. 6 are for the structure with six BF_4^- ions in the channel and various numbers outside the helix. Figure 6(a) displays $g_{SF}(r)$ for the (S, F) pair, selected as they are central to the interaction between the migrant ion and the channel wall. The sharp peak at $r \approx 3.3$ Å is close to the sum of the van der Waals radii for sulphur and fluorine (3.2 Å) and if the BF_4^- ion were to "dock" temporarily with a linear B–F––S configuration then the broader peak at $r \approx 5.1$ Å can be readily ascribed to the (S, F) pairs for the fluoroborate's other three F atoms. As the polymer becomes more highly oxidised, "fixed" charges on the channel atoms become more positive and the heights of the $g_{SF}(r)$ peaks at $r \approx 3.3$ and 5.1 Å decrease without appreciable shifting. This shows that BF_4^- channel sites in which the F atoms of the migrant ion occupy these separations from the S atoms of the chain still maintain their general positions which become less well defined with increasing anion concentration. A contributory factor to this result is seen from Fig. 6(b) which plots the $g_{SS}(r)$ function for the channel (S, S) atom pair, thus monitoring the conformational order of the polymer host. The figure shows that if the charge in the cavity walls of the unit cell segment is less than about 20 the helix is not distorted from that of the neutral (unoxidised) P3OT chain. Above this figure small torsions occur around the inter-thiophene bond in the direction of unwinding of the helix, so that although the position of the first sharp peak at $r = 3.5$ Å (corresponding to S…S separations in adjacent rings) is not much affected, the separation in next-nearest rings has increased from 6.8 for the neutral chain to 7.3 Å for the more heavily oxidized ones. The peak has also broadened, confirming the lower translational order in the more oxidized P3OT chains. The peak shown at $r = 4.3$ Å for the lightly doped chains is for pairs of thiophene S atoms in adjacent turns of the helix, and separated by 11 inter-thiophene C–C bonds. Consequently even a small amount of torsional

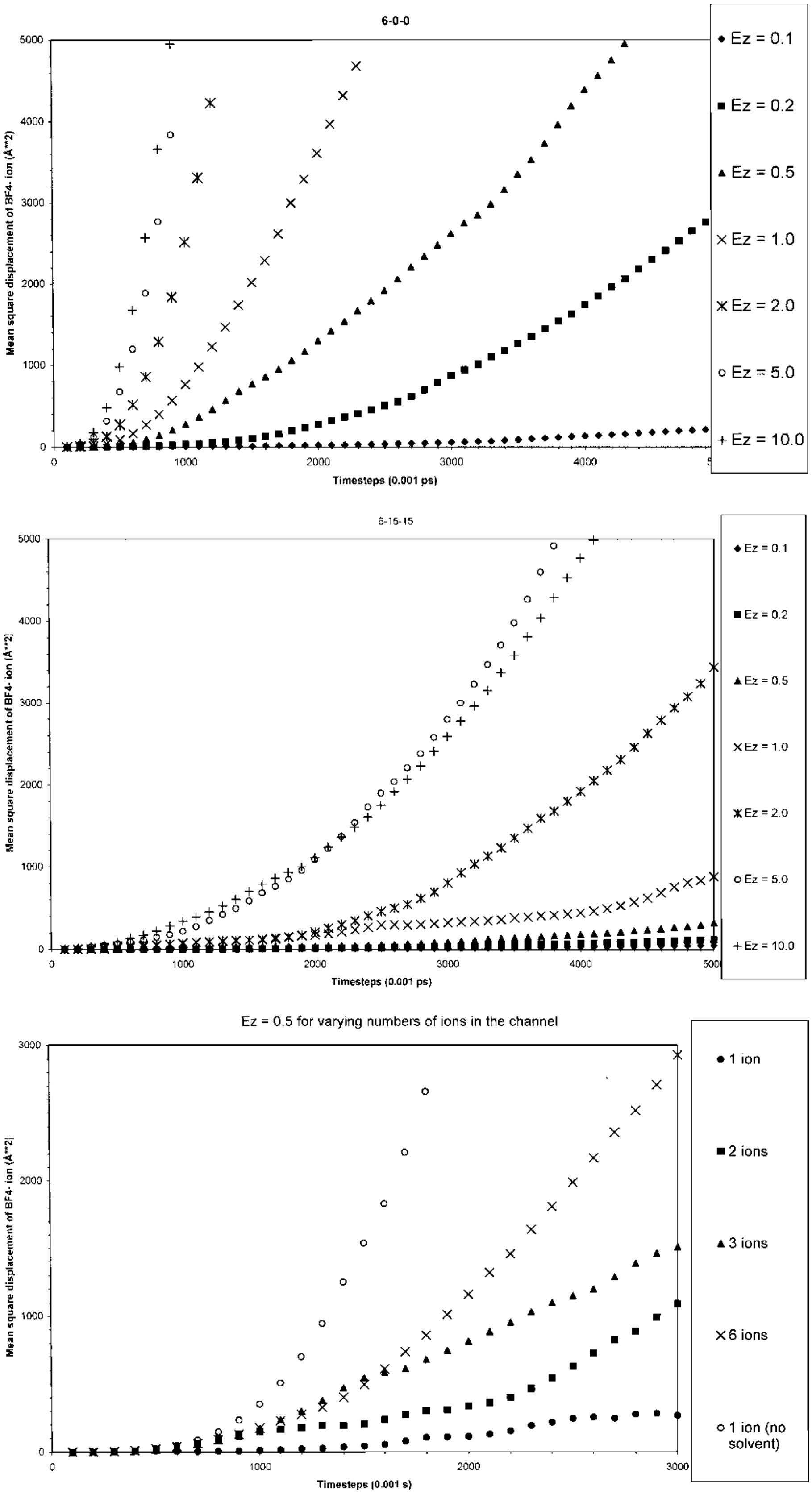

FIGURE 5 Mean square displacements (msd) of six channel BF_4^- ions migrating in an electric field $E_z = 0.5$ efu applied along the channel direction when the surrounding medium contains (a) 0 and (b) 30 BF_4^- ions. In (c) the channel contains l, 2, 3, 4 and 6 ions, (together with $CHCl_3$ solvent molecules), and also one ion migrating with no solvent molecules in the channel.

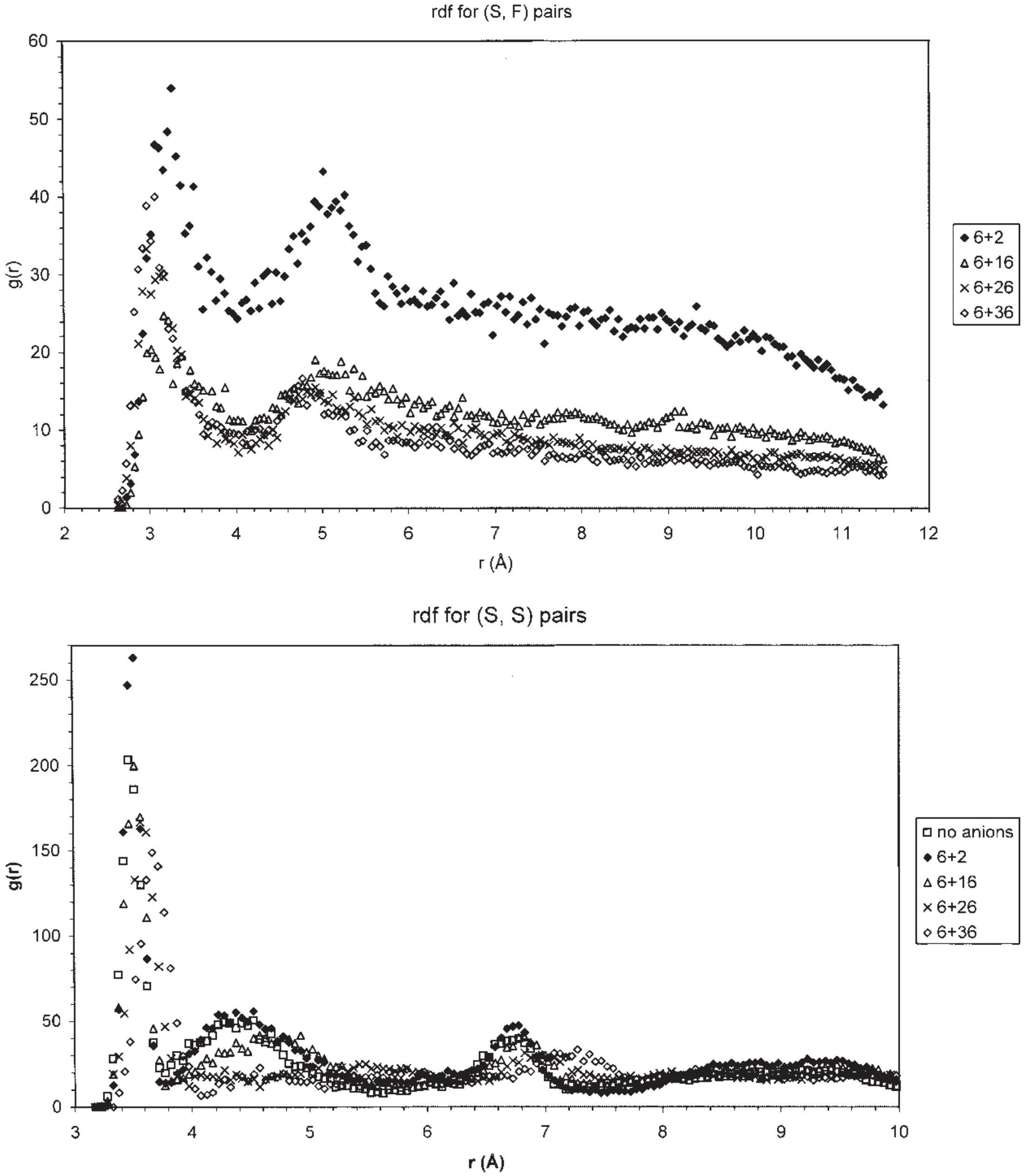

FIGURE 6 Radial distribution functions for atom pairs (a) (S, F), and (b) (S, S). The symbols legend indicates the ion configuration so that $6+2$ means that there are six BF_4^- ions in the helical channel and two in the bulk solvent. The legend thus indicates a sequence of increasing oxidation of the polymer chain.

disorder around these bonds would result in the severe broadening of the peak, as is observed in the distribution function $g_{SS}(r)$.

Energy Barriers

Until now the channel transport has been facilitated by the application of an electric field along the channel. The motion of the ions by thermal energy alone can be monitored by conducting field-free molecular dynamics at different temperatures. In order to improve the poor statistics associated with the necessarily small number of ions inside the helix channel a $2 \times 2 \times 2$ supercell was used to define a 38064-atom cell containing a total of 48 BF_4^- ions.

The MD of a thermally equilibrated P3OT/chloroform system corresponding to a 50% oxidised polymer was conducted at different temperatures, and in Fig. 7(a) the average diffusivity (diffusion coefficient) is plotted as a function of temperature. Despite the scattered nature of the plots (the 48 ions inside the helix channel is still rather few), they show a mobility that starts to increase with temperature from about 230 K when the solvent becomes liquid.

This behaviour contrasts that predicted for the migration of BF_4^- ions in a lattice of *fully-extended*

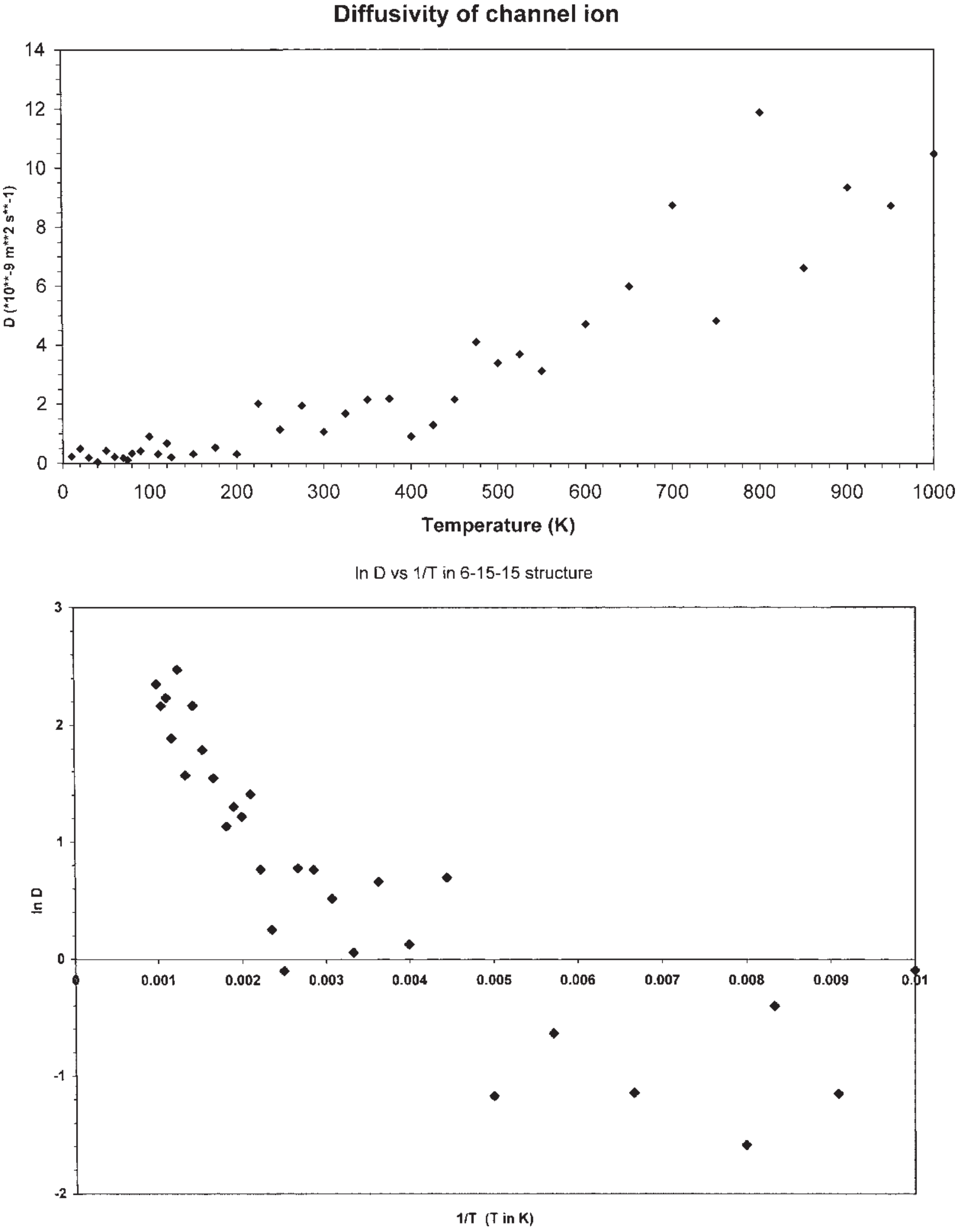

FIGURE 7 Temperature dependence of the zero-field diffusivities of the channel BF_4^- ions. (a) The diffusion coefficient D in units of $10^{-9}\,m^2\,s^{-1}$ is plotted against temperature T, (b) $\ln D$ is plotted against $1/T$.

P3OT chains [1,2]. In the latter case, where the ionic diffusivities were an order of magnitude lower than those in the helical channel, the mobility increased with temperature to a maximum at around room temperature, declined and increased again. This was ascribed to the changing contributions of the thermal modes involving the main and side chains at various temperatures. For the *helical* P3OT solution of the present case, recall from Figs. 2 and 3 that the side chains are on the outside of the channel and so presumably have less influence on the ion trajectories, and the lower flexibility of the helical main chain (compared to the fully-extended conformation) also implies a smaller influence from the backbone modes. Plotting the diffusivities in logarithmic form against T^{-1}, shown in Fig. 7(b), gives an energy barrier for the diffusional motion in the channel as $6.6\,kJ\,mol^{-1}$, which is similar to the high-temperature value of $8\,kJ\,mol^{-1}$ calculated for the same ion migrating in the solid state P3OT lattice.

CONCLUSIONS AND DISCUSSION

To our knowledge the diameter 5.73 Å calculated for the channel has not been measured directly by experiment, but its value is decided by the torsional angle around the C–C bonds linking the thiophene rings which in turn fix the overall width of the helix and the number of thiophene rings per turn. Our calculated overall diameter of 38 Å for P3OT compares with 35 to 50 Å reported for poly(3-hexylthiophene) from the interpretation of atomic force micrograms [9] and both results suggest the preservation of largely all-*trans* conformations by the alkyl side chains. Although our simulations and the experimental results cited [9] imply tightly wound helix coils the mean pitch of 3.6 Å is not sufficiently small to preclude the possible escape of such small ions as BF_4^- from the coil during their migration or diffusion. Sulphur atomic density profiles suggest that the thermal distortions of the channel result in a nearly two-fold variation of the channel diameter, whose average is about 7 Å.

The loss of the correlation of the migration rate with applied field is interpreted in terms of molecular congestion in the channel, particularly at high oxidation levels, where the positive charge on the thiophene rings (mainly the sulphur atoms) exhibit a sticking effect on the migrating ions. However the statistics that describe the necessarily small number of ions are inadequate to distinguish the (presumably higher) energy barrier from that derived from Fig. 7(b).

As the purpose of this paper has been to investigate the ion transport in the P3OT helical channel no observations have been made on the motion of the BF_4^- ions in the solution bulk and in the region of the alkyl side-chains. First results of such ion transport studies show that for lightly oxidized polymer chains the motion of the ions is faster in the channel than in the bulk of the solution, but that for chains that are oxidized more than about 30% the passage of the ions is slower than in the bulk. The causes of these effects are complex and will be discussed in a forthcoming paper.

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