Ordering in Crystalline Short-Chain Polymer Electrolytes

ANTI LIIVAT
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Abstract

Polymer electrolytes are the most obvious candidates for safe "all-solid" Li-ion batteries and other electrochemical devices. However, they still have relatively poor ionic conductivities, which limits their wider adoption in commercial applications. It has earlier been the conventional wisdom that only amorphous phases of polymer electrolytes show usefully high ionic conduction, while crystalline forms are insulators. However, this has been challenged in the last decade by the discovery of highly organized, low-dimensional ion-conducting materials. Specifically, the crystalline phases of LiXF₆/PEO exhibit higher ionic conductivities than their amorphous counterparts, with the Li-ion conduction taking place along the PEO channels. Polymer chain-length and chain-end registry has emerged as potentially significant in determining ionic conduction in these materials.

Molecular Dynamics simulations have therefore been made of short-chain, monodisperse (M₉~1000), methoxy end-capped LiPF₆/PEO to examine relationships between ion conduction and mode of chain-ordering. Studies of smectic and nematic arrangements of PEO chains have revealed that ion-transport mechanisms within the smectic planes formed by cooperative chain-end registry appear to be more suppressed by ion-pairing than in-channel conduction. Disorder phenomena in the chain-end regions emerge as a critical factor in promoting Li-ion migration across chain-gaps, as does the structural continuity of the PEO channels.

Simulations incorporating ~1% aliovalent SiF₆²⁻ dopants further suggest an increase in Li-ion conduction when the extra Li-ions reside within the PEO channels, with the anion influencing charge-carrier concentration through enhanced ion-pair formation.

XRD techniques alone are shown to be inadequate in ascertaining the significance of the various short-chain models proposed; atomistic modelling is clearly a helpful complement in distinguishing more or less favourable situations for ion conduction.

Though providing valuable insights, it must be concluded that this work has hardly brought us significantly closer to breakthroughs in polymer electrolyte design; the critical factors which will make this possible remain as yet obscure.

Keywords: polymer electrolytes, molecular dynamics, ionic conductivity, crystalline ordering, polymer chain length, smectic, nematic

Anti Liivat, Department of Materials Chemistry, Box 538, Uppsala University, SE-75121 Uppsala, Sweden

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List of Papers

This thesis is a summary based on the following papers, which are referred to in the text by their Roman numerals:

I. Development of a force-field for Li$_2$SiF$_6$

II. Molecular dynamics simulation of the crystalline short-chain polymer system LiPF$_6$·PEO$_6$ (M$_w$~1000)

III. A molecular dynamics study of short-chain ordering in crystalline LiPF$_6$·PEO$_6$
    A. Liivat, D. Brandell, A. Aabloo and J.O. Thomas,
    Submitted to *Electrochim. Acta*.

IV. A molecular dynamics study of ion conduction mechanisms in crystalline low-M$_w$ LiPF$_6$·PEO$_6$
    A. Liivat, D. Brandell and J.O. Thomas,
    Submitted to *J. Mater. Chem*.

Some comments on my own contribution to this work:

**Papers I, III and IV:** The majority of the work in all its phases.

**Paper II:** A significant part of the project planning, model preparation and data analysis.

**Thesis:** I was helped with the writing of the *Populärvetenskaplig Sammanfattning* by my supervisor Dr. Daniel Brandell.
Other papers not included in this thesis:

**Molecular dynamics simulation of the LiPF$_6$·PEO$_6$ structure**
D. Brandell, A. Liivat, H. Kasemägi, A. Aabloo and J.O. Thomas,

**Conduction mechanisms in crystalline LiPF$_6$·PEO$_6$ doped with SiF$_6^{2-}$ and SF$_6$**
D. Brandell, A. Liivat, A. Aabloo and J.O. Thomas,

**Molecular dynamics simulations of Li- and Na-Nafion membranes**
D. Brandell, A. Ainla, A. Liivat and A. Aabloo,

**Molecular dynamics studies of the Nafion®, Dow® and Aciplex® fuel-cell polymer membrane systems**
D. Brandell, J. Karo, A. Liivat and J.O. Thomas,
Submitted to *Journal of Molecular Modeling.*
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### Abbreviations

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<tr>
<td>ADF</td>
<td>Atomic Displacement Factors</td>
</tr>
<tr>
<td>CN</td>
<td>Coordination Number</td>
</tr>
<tr>
<td>EO</td>
<td>Ethylene Oxide</td>
</tr>
<tr>
<td>HF</td>
<td>Hartree-Fock theory</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular Dynamics</td>
</tr>
<tr>
<td>MP2</td>
<td>Møller-Plesset second-order perturbation theory</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Molecular Weight</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>PEO</td>
<td>Poly(Ethylene Oxide)</td>
</tr>
<tr>
<td>PE</td>
<td>Polymer Electrolyte</td>
</tr>
<tr>
<td>RDF</td>
<td>Radial Distribution Function</td>
</tr>
<tr>
<td>TFSI</td>
<td>bis-(TriFluoroMethylSulphonyl)Imide</td>
</tr>
</tbody>
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Introduction

A weak link in energy storage technologies

Electrical energy is the most universal form of energy used today because it can be readily converted to other usable forms. Electrical energy now represents ca. 13% [1] of the total energy consumption in the World, with power plants supplying stationary locations with electricity through their distribution networks. A somewhat overlooked but critical contribution in the development of this technology was made by the English scientist Stephen Gray, who invented electrically conducting wire in 1729.

It took until 1799 and the invention of the first battery by Alessandro Volta for the importance of a “closed circuit” to emerge [2]. This evolution peaked with Michael Faraday’s discovery of the solid ion conductors (PbF₂) in 1839 [3] – “ion-conducting wire” or solid electrolytes. The significance of this discovery resurfaced during recent decades with the rapid development of portable electronics, which has shaped the lifestyle of a whole generation. This has led to the parallel development of small and medium-size batteries to supply this wide diversity of electronic equipment with safe portable power. While energy densities of the best Li-ion based batteries are today high enough for most applications, and the prospect of reducing the price of the materials involved is promising [4], the batteries still contain volatile (unsafe) liquid or gel-type electrolytes. This is a result of the poor ionic conductivity and mechanical brittleness of known dry solid electrolytes, which makes “all solid” wiring in batteries still a challenging task. This, indeed, remains the weak link in electrochemical energy storage technologies.

Polymer electrolytes

Polymer-based materials are the most obvious battery electrolytes by virtue of their mechanical strength combined with elasticity, making them easily formable to any desired shape. In principle, polymers offer unlimited possibilities in functionality, while still being a cost effective solution. A small subset has been found to solvate salts such as LiPF₆, LiClO₄, LiBF₄, Li-bis(trifluoromethylsulphonyl)imide (“Li-TFSI”), etc.; salts which are used in
today’s Li-ion batteries and show usable Li-ion conductivity. The most prominent polymer host for alkaline ion salts is Poly(Ethylene Oxide) (PEO) – a polymer with repeat unit –(CH₂-CH₂-O)- [5].

Ion conductivity in PEO-based polymers was discovered by Wright in 1973 [6], and their potential for use in “all-solid-state” batteries was later proposed by Armand in 1979 [7]. In fact, this property of PEO actually dates back to the 1960’s, when Pedersen discovered that crown-ethers – a ring-like relative of PEO – could form complexes with alkali ions. For this and related supramolecular discoveries, Pedersen, Cram and Lehn were awarded the Nobel Prize in Chemistry in 1987.

Evidence was found in the early 1980’s to suggest the importance of polymer segmental motion in driving ion transport and making the amorphous phase more favourable than the crystalline for ion conduction [8,9]. Since the intrinsic conductivity of PEO-Li salts at room temperature is rather low (≈10⁻⁷ S/cm) due to their high degree of crystallinity, the main research effort has focussed on promoting the amorphous phase [10,11].

Several routes have been successful in this context: chain cross-linking, incorporating small plasticizing molecules [5] or inorganic nanoparticles [12] (see Fig. 1). Room temperature conductivity has been brought above 10⁻⁵ S/cm which is, nevertheless, still lower than what is considered a minimal requirement for battery applications: 10⁻³ S/cm. Moreover, ion-pairing and anionic transport further reduce the performance of polymer electrolytes. At this point, the research field needs to move in some new direction.

**Ordering in polymer electrolytes**

Paradoxically, the highest room-temperature Li-ion conductivities are seen in crystalline ceramics, like the perovskite Li₉.₃₄La₇.₅₁TiO₂.₉₄ [13] or Li-β-alumina [14], where it reaches 10⁻³ S/cm. This has been attributed to the high concentration of available sites and low migration barriers [15]. Rotator
phases exhibiting “paddle-wheel” type promotion of ion conduction have also been seen to give much higher ionic conductivities in inorganic materials, but only at greatly elevated temperatures [16]. This has inspired the research community to seek to design polymer structures that provide analogous low-energy pathways for Li-ions.

To this end, Wright et al. have synthesized and characterized two-dimensional smectic liquid crystals to overcome the underlying problems of amorphous polymer electrolytes. The molecules involved in these crystals comprise oligo-ethoxy fragments attached to alkyl chains. The latter order locally and confine the Li-ions to planes of compressed oligo-ethoxy loops, where conduction pathways are created. The relaxation of oligo-ethoxy fragments is inhibited and coordination to cations is weakened. Conductivities as high as $10^{-3}$ S/cm at 20 °C have been reported. [17-20].

In a similar fashion, Armand et al. have studied the Li-ion conductivity in PEO together with anions with attached aliphatic side-chains, and found an enhancement effect on conductivity [21]. Interestingly, conductivity increases by an order of magnitude have been reported for several PEO-salt complexes when mechanically stretched. This has been attributed to the alignment of crystallites in the partially crystalline material [22].

In known crystalline PEO/Li-salt complexes with EO:Li ratios from 1:1 to 4:1 [23], each cation is coordinated by only one helical PEO chain in such a way that there are no vacancies available into which Li-ions can migrate without forming ion-pairs. However, the discovery of new crystalline phases of LiXF₆·PEO₆ (for X = P, As or Sb) [24,25] with conductivities higher than their amorphous counterparts raised questions as to the basis of the conductivity mechanism in these materials [26,27]. Diffraction studies could show that the polymer forms hemi-helices, which arrange pair-wise to form cylindrical channels for the Li-ions, while the anions are situated outside these channels [24,25]; see Fig. 2.

Figure 2  The structure of crystalline LiPF₆·PEO₆ viewed a) along the polymer channel axis, showing Li ions inside the channels and PF₆⁻ ions outside, and b) along the unique monoclinic axis perpendicular to the channels, showing the anion and cation positions and chain configuration
NMR measurements suggest the ion conductivity to be dominated by cation transport; i.e., $t_+ \approx 1$ [26]. Conductivity is shown to be enhanced through doping with the larger isovalent anion $\text{N(SO}_2\text{CF}_3)_2^-$ [28] or with the aliovalent anion $\text{SiF}_6^{2-}$ [29] to give conductivities on a par with the very best amorphous PEO-Li electrolytes.

**Short-chain LiPF$_6\cdot$PEO$_6$ crystal structures**

The majority of experimental structure work and especially conductivity studies has been performed using fairly short methoxy end-capped polymer chains, typically with average $M_w$ in the range 1000–2000. These chain-lengths are below the entanglement limit of ca. 3200 for PEO, and introduce a significant concentration of chain-end defects into the structure. Nevertheless, powder XRD studies show that LiXF$_6\cdot$PEO$_6$ crystals prepared from high-$M_w$ PEO ($M_w=100000$) and from short-chain PEO were isostructural [25], with even higher crystallinity observed in the short-chain structures. This situation implies directional alignment of the short chains, as shown in Fig. 3.

![Figure 3](image)

*Figure 3*  Schematic representations of crystallites formed by (a) a long-chain polymer (chain-length $>>$ crystallite size), and (b) a short-chain polymer (chain-length $<<$ crystallite size).

An increase in ionic conductivity by two orders of magnitude on decreasing the molecular weight of PEO from 2000 to 1000 in crystalline phases of LiPF$_6\cdot$PEO$_6$ has also been reported. This phenomenon was attributed to the increase in crystallite size, thereby facilitating longer pathways for ion transport and lower grain-boundary resistance (shown in Fig. 3) [30]. However, the experimental evidence to support this increase in crystallite size (from 200 to 250 nm) on decreasing the $M_w$ of the PEO chains from 2000 to 1000 was based on peak-width analysis (using the Scherrer equation) of a single
XRD peak – the (0 2 1) reflection [30]. Since this reflection is insensitive to crystallite size along the \(a\)-axis, which is the direction of the PEO channels (see Fig. 2), all this tells us is that crystallite size increases slightly in directions perpendicular to the PEO channels. This situation can imply the possible existence of ion-conduction pathways perpendicular to PEO channel axis, as will be discussed below.

In a recent paper [31], Bruce et al. specifically address the question of chain-end ordering when interpreting XRD and impedance spectroscopy data for crystalline systems containing mono- and polydisperse methoxy-capped (M\(_w\) ~1000) PEO chains. They attribute the lower observed ionic conductivity in the monodisperse system to a more ordered distribution of end-groups [31]; such order is clearly unfeasible in polydisperse systems. It has therefore now become relevant to consider the effect of increasing the concentration of chain-end defects (see Fig. 4) as we go to short-chain PEO-salt systems.

![Figure 4 A schematic representation of a PEO channel fragment in infinite (a) and short-chain (b) systems; anions occupy the space between the polymer channels and Li-ions (circles) occupy the channels.](image)

Computer simulation of the crystalline polymer electrolytes

Developments in computational resources and software have made it possible to model the structure and dynamics of PEO-based polymer electrolytes at the atomic level; see [32-34] and references therein. This has helped to elucidate the mechanisms of ion transport [35,36] using Molecular Dynamics (MD) simulation methods. More demanding quantum mechanical
calculations have also been used to map the energy landscape of polymer conformations and polymer interaction with ions [37-41], and to design polymer-salt additives in a systematic manner [42]. Of these studies, few have addressed crystalline systems, such as PEO₃NaI [43]. This is partially due to lack of structural information for crystals that can be potentially good ion-conductors, but can also be a result of the unavailability of the relevant interatomic force-fields.

The crystal structure determinations of LiXF₆-PEO₆ (for X = P, As or Sb) [24, 25] facilitate the computation of activation energies [44], and the simulation of structural and dynamical properties for LiPF₆-PEO₆ [45]. This present thesis focuses on fundamental questions relating to the structural and dynamical properties of the crystalline phases of these LiXF₆-PEO₆ crystals, involving short-chain PEO (M₆≈1000) polymers. Chain-ordering and the effect of aliovalent doping with SiF₆²⁻ are both addressed at the atomic level by MD methods. Identification of charge-carriers and of likely pathways for ion migration are also discussed. The content of the four papers summarized in this thesis is as follows:

**Paper I**: Force-field development for potential Li-ion donor dopant Li₂SiF₆, for use in crystalline polymer electrolytes. The ability of the force-field to predict the crystal structure for Li₂SiF₆ on the basis of available experimental information on isostructural Na₂SiF₆ was tested.

**Paper II**: Smectic and nematic arrangements of a short-chain (n=22, methoxy-terminated) LiPF₆-PEO₅.₇₅ system are compared with the long-chain system studied earlier. These systems show ca. 50% ion-pairing, increased dynamics and disorder, resulting in the loss of crystallographic periodicity but maintained PEO/Li channel structure, although the channel-ends misalign near the smectic interface.

**Paper III**: The stoichiometric short-chain (n=23) LiPF₆-PEO₆ structure was studied in 5 different possible arrangements to assess the most likely situations in a real material. All 5 models resemble more the infinite structures than the n=22 systems of Paper II. An important factor emerges: Li-ion coordination in the chain-defect regions determines local order and dynamics; short PEO channels of smectically aligned PEO chains are quasi-continuous in the presence of cross-linking Li-ions.

**Paper IV**: Ion conduction in the three most realistic models taken from Paper III was studied under an applied external electric field. The systems ranked in order of ion conductivity are: nematic-R > nematic-B > smectic-B; ordering of the chain-ends in these systems follows the reverse order, with nematic-R the most disordered. Conductivity within the smectic plane is lower than along the channels and is hindered by ion-pairing.
Methodology

Molecular dynamics simulations

The Molecular Dynamics (MD) simulation technique involves the routine integration of Newton’s classical equations of motion for a many-atom system. If this is done sequentially at sufficiently short time-intervals, the procedure should result in a complete history of atomic trajectories over a limited time period. The interatomic forces are described by simple analytical functions (the force-field) involving parameters evaluated empirically or from quantum mechanical calculations (see the next section). MD simulations of an infinite solid system use periodic boundary conditions and an Ewald summation routine to treat long-range electrostatic forces [46].

Specific details of the performed simulations are as follows: the short-range cut-off used is 16 Å and the Verlet sphere used in the construction of the Verlet neighbour-list has a 0.5 Å radius. A NVT Nose-Hoover thermostat is used with a temperature relaxation time of 0.1ps. Longer relaxation times were tested but led to increased temperature fluctuations. Additionally, to allow the MD-box size to vary, simulations were run with a constant anisotropic pressure (N\_\_\_\_VT Nose-Hoover) thermostat with a corresponding relaxation time of 0.3ps (Paper III); the short-range cut-off was then reduced to 15 Å. A multiple time-step technique was used, with a longer time-step of 0.5 fs at longer distances and a shorter time-step of 0.1 fs inside a sphere of radius 6 Å.

The simulation temperature was 293K, except for the external electric field studies in Paper IV, where the temperature was set to 328K (to match the experimental temperature used in [29]). A constant volume ensemble (NVT) was used for 1 ns, followed by a constant anisotropic pressure (N\_\_\_\_VT) simulation for 1ns. Trajectory data were sampled at 0.1ps intervals for subsequent analysis. A parallelized simulation program DL_POLY: Version 2.14 was used [47]. Applications of this program are reviewed in [48] for a variety of problem types.
Force field

The potential functions involved in the applied force-fields are listed in the **Appendix**. All inter- and intramolecular force-field parameters for PEO were taken from Neyertz *et al.* [49], except for the bond-stretching and methyl-group rotation potentials; these are taken from Jaffe *et al.* [50] and Borodin *et al.* [51], respectively. The set of PEO potentials was developed originally by Gejji *et al.* [38] from MP2/6-311++G**//HF/3-21G energy minimisation of the diglyme system and was validated for crystalline PEO [49], NaI-PEO [43], a PEO surface [52-54], and for various amorphous polymer electrolytes [55-63].

The parameters for the interaction of PEO, Li$^+$ and PF$_6^-$ are taken from [39,64], while those involving an aliovalent dopant SiF$_6^{2-}$ have been developed in Paper I and are given in Table A-I of the **Appendix**. In these potentials, an averaged polarisation contribution to the total energy has been taken into account by introducing a polarization term (with parameter D). These potentials were also tested in the simulation of the crystal structure of Li$_2$SiF$_6$ (see Paper I). Standard Lorentz-Berthelot combination rules were used to obtain force-field parameters for the interactions of PEO with the dopant [65].

Starting structures

The starting structures in the MD simulation boxes comprise 4 × 2 × 4 unit cells of crystalline LiPF$_6$-PEO$_6$ [25] (see Fig. 1), with dimensions: $a = 46.928$ Å, $b = 34.750$ Å, $c = 34.768$ Å, $\beta = 107.8^\circ$, involving 32 PEO hemihelices of CH$_3$-(OCH$_2$CH$_2$)$_n$-OCH$_3$, along with 128 LiPF$_6$ units.

The starting structures used in Paper II (n=22) and in Papers III and IV (n=23) were generated from the asymmetric unit resulting from the neutron diffraction study [25], with no internal symmetry conditions imposed within the periodic simulation box. Terminal methyl groups were incorporated either by removing one EO unit (Paper II) or breaking a C-C bond (Papers III and IV) in the chain and attaching an extra hydrogen atoms to each end-carbon, with the H-C-H angles constrained to 109.45$^\circ$ and C-H distances to 1.1 Å. Both CH$_3$-groups were constrained to preserve (C$_{3v}$) symmetry, and rotated about the C-O and O-C$_{meth}$ bonds using a Monte-Carlo procedure to arrive at an orientation free from steric hindrance. In Paper II, the removal of ether oxygens using this method resulted in an effective formula
LiPF$_6$-PEO$_{5.75}$ and a lowering of the density by 2.5%. This was chosen as a compromise to provide space for the end-groups to redistribute, and corresponds to the average molecular weight of PEO used in the experimental studies [30,31]. Two models were generated with $n$=22, representing ordered and disordered extremes in the spatial distributions of the methoxy end-groups:

- In the smectic model (Fig. 5, left), all end-groups were initially situated in a single plane perpendicular to the polymer-chain direction.
- In the nematic arrangement (Fig. 5, right), one of each pair of hemi-helices in the smectic model was shifted by one crystallographic asymmetric unit (6 EO-units) in the positive or negative helical direction with respect to its hemi-helical partner, thus creating a system without chain-end pairs.

![Figure 5 Schematic representation of the smectic and nematic models for short-chain monodisperse PEO.](image)

A model with the exact formulation LiPF$_6$-PEO$_{6}$, containing 23 EO monomers ($n$=23) facilitates the study of the situation in which the end-groups are packed more tightly, and is more compatible with the size of the experimentally determined unit cell [25]. Also, to learn more about the structural conditions which relate to ion mobility, it was necessary to create a range of models to represent different structural situations one might reasonably expect to encounter in this type of system. In Paper III, five models were simulated: two smectic and three nematic; see models 1-5 in Fig. 6:

- **Smectic-A** (1 in Fig. 6): the chain-ends are here all arranged in planes to form a common interface, with the Li-ions all 6-fold coordinated to ether oxygens within the same PEO double hemi-helix (three from each); see also the upper figures in Fig. 6.

- **Smectic-B** (2 in Fig. 6): same as smectic-A except that Li-ions now bridge the interface and are coordinated to PEO chains on both sides
of the smectic plane. In this way, we introduce a disorder feature into the Li-ion coordination at the interface. Again, see the upper figures in Fig. 6.

- **Nematic-A** and **nematic-B** (3 and 4 in Fig. 6): these models derive from their corresponding smectic counterparts through random displacement of neighbouring hemi-helical PEO pairs along the channel direction. These types of configuration were suggested by Bruce *et al.* to best represent the crystal structure for monodisperse systems [31].

- **Nematic-R** (5 in Fig. 6): this is the most disordered of the models simulated, in which all chain-breaks occur randomly throughout the structure. This model corresponds to that proposed in [31] as the most rational structure for polydisperse systems.

Within this smectic/nematic classification of starting structures for n=23, we also distinguish two types of chain-end coordination around the Li-ions: *ideal* coordination, in which chain termination does not disrupt either of the polymer chains involved in the 6-fold coordination sphere of a Li-ion, and *broken* coordination, where this is not the case.

As shown in Fig. 6, smectic-A, and nematic-A involve *ideal* coordination, while smectic-B and nematic-B contain *broken* coordination. Nematic-R involves both types of coordination, but where the majority are broken. This issue of order/disorder in Li-ion coordination has largely been overlooked earlier because the crystalline oligoether-salt complexes studied have involved either very short monodisperse PEO oligomers [66-69], where the coordination in stoichiometric complexes is well defined, or much longer polydisperse chains, where the lower concentration of chain-ends renders them of minor significance. However, a study of single crystals of PEO₃(Mₜ=500).LiCF₅SO₃ has revealed a high selectivity to polymer chain-lengths on crystal formation [70].

Chain ordering is therefore analysed in terms of two distinct structural features: (i) ordering in neighbouring chain-ends; and (ii) the coordination (*ideal* or *broken*) of Li-ions to the polymer chain.
Non-equilibrium molecular dynamics

When an external perturbation like an electric field is imposed on the simulation box (as in Paper IV), the system response, in this case ion migration, can be investigated by MD. The major challenge in such a study is to choose an appropriate strength for the external electric field. As we see below, too high field strength can induce unwanted structural transformations, while the effect of too low a field strength remains unnoticed throughout the duration of the simulation. In Paper IV, a series of static electric fields (ranging from $3 \times 10^6$ V/m to $6 \times 10^6$ V/m) were applied parallel to the hemi-helical axes of models smectic-B, nematic-B and nematic-R, and simulated for a further 300 ps.
The same range of fields was also applied in the \( c \)-direction parallel to the end-plane of the smectic-B system. Some tests were also made to apply the fields in the \( b \)-direction within the smectic plane; these gave qualitatively identical results. The smectic-A model was also simulated under the conditions shown in Table 1 for the smectic-B system, to assess the effect of complete vs. broken coordination.

**Ion transport**

Rather than calculating ionic conductivity values from diffusion coefficients derived from mean-square displacements of different ion-types (an unreliable procedure in view of the poor statistics from short simulation times), comparative values are derived for the different systems by counting **ion-jumps** in the direction of the imposed field.

Ion conductivity (\( \sigma \)) in electric field \( E \) can be derived from the frequency of ion jumps (\( n \)) for the 1-D case using the expression:

\[
\sigma = \frac{j}{E} = \frac{\Delta q}{\Delta t \cdot s \cdot E} = n \cdot \frac{r \cdot e}{a} \cdot \frac{1}{\Delta t \cdot b \cdot c \cdot \sin \beta \cdot E} \approx 5 \cdot 10^3 \frac{n}{E \cdot \text{cm}} \approx \frac{S}{\text{cm}}
\]

where we use the MD-box geometry (\( a, b, c, \sin \beta \)), the characteristic Li jump-length (\( r = 2 \text{Å} \)) and \( E = 10^8 \text{ V/m} \) (an estimate of the thermal excitation at the temperature of the simulation: 328K); the value of \( r \) corresponds to a Li-ion propagation distance of one O-\( \text{O} \) distance. This gives an estimated jump frequency (\( n \)) of 0.05 jumps/ns for an experimentally observed conductivity (\( \sigma \)) of \( 10^{-6} \text{ S.cm}^{-1} \). Under these circumstances, it is quite unrealistic to hope to quantify conductivity values on the basis of observed jump frequency, but rather to establish the most likely pathways for ion transport, as evidenced by observed ion migration modes under the electric field. However, local conductivity measurements in amorphous polymer electrolytes using microelectrodes suggest that conductivities along the most conducting pathways can be \( 10^3 \) times higher than the macroscopically measured average conductivity [71].

It was established from several test simulations that a very narrow window of electric field strength exists within which ion migration can be observed without structural instability. Ion conductivities have therefore been quantified for the different short-chain systems modelled at the electric field-strength threshold values where ion jumps clearly begin to occur. Additionally, an in-depth analysis of typical ion-jump events is carried out by looking at related local coordination situations and attempting to relate these to differences in the models.
Simulation of XRD profiles

An effective diffraction pattern was calculated by accumulating the scattering contributions from 500 MD-generated “snapshots” of the positions of all the atoms in the MD box. This is done using an adapted version of the DISCUS program [72]. No symmetry constraints are applied to the system during this calculation – the program treats the entire MD box as a primitive unit-cell. Only Bragg reflections are sampled; peak-widths are all constrained to $0.16^\circ$ (in $2\theta$) to roughly match experimental values.
Results

As in our earlier study (Paper III), the general form of the “infinite-chain” structure is retained throughout the various simulations of the n=23 system, despite the high concentration of end-group “defects”. Isotropic atomic displacement factors (ADF’s) averaged over all 32 PEO chains in the MD-box have been extracted for the backbone ether-oxygen atoms along the chain (see Fig. 7). Higher displacements at the chain-ends are clearly reproduced, and are seen to agree quite well with the overall experimental value for salt-free PEO (ca. 0.11 Å²).

![Figure 7](image_url)

Figure 7  The atomic displacement factors (ADF’s) for the backbone oxygens along the chain (n=23); the lines show our MD values for Li-ions and the experimental value for long-chain crystalline PEO.

Structural stability

Visual inspection of the sampled snapshots could readily confirm that all the simulated systems maintain the general characteristics of their start structures – with cylindrical double hemi-helical PEO channels still separating the Li-ions within the channels from the PF₆⁻ anions outside the channels.

In the n=23 systems, all structural disruption occurs only in the vicinity of the end-groups, and ion-pairing is noted only in systems involving broken Li-ion coordination in the defect regions. However, in the n=22 systems
distortions are significantly larger, and many more ion-pairs form in defect-free regions, with the PEO channels tilting as shown in Fig 8.

Another observation is that the shape and size of all MD boxes for \( n=23 \) are generally retained for all models, when their geometry is released on going from NVT to N\(_{\text{VT}}\) ensemble simulation. All boxes tend to shift in the same general way: the \( a\)-axes (the polymer-chain direction) all expand (on average by 2.5\%), while the \( b\)- and \( c\)-axes both contract by roughly the same amounts.

All types of double hemi-helices modelled undergo breakdown within the 300 ps simulation sampling time beyond the structural instability threshold value. This value was lowest for the \( n=22 \) systems. Among the systems with \( n=23 \), the smectic-B model is the most stable, while the nematic-R model is the least stable. Also, the crystalline structure is less stable when the electric field is applied in the direction of the PEO channel compared to perpendicular to the channel. Notably, no significant differences in stability could be detected between the doped and undoped systems. The breakdown process when the system becomes amorphous can be correlated to the extraction of Li-ions from inside the double hemi-helices. Since Li-ions can more easily leave the PEO channels near the chain-ends and methoxy end-groups tend to retain their coordination to the Li-ions, they are dragged away from their normal locations into the anion channel. Given the more uniform distribution of chain-ends in the nematic-R arrangement, chain breakdown is initiated simultaneously at a number of sites throughout the structure, thus explaining the lower stability of this system. Generally, when two adjacent Li-ions leave a channel, this region of the polymer loses its original conformation, and the individual chains straighten out and separate from one another; see the dashed region in Fig. 9. It was also pointed out earlier by Henderson et al. [68] that the cylindrical two-chain configuration is unlikely to be preserved if ether oxygen atoms do not coordinate Li-ions.
Li-O coordination and ion-pairing

Chain-shortening as in the n=22 systems leads to a redistribution of Li-ion coordination compared to infinite systems: CN(Li-O) decreases to 5 while CN(Li-P) increases to 0.5, *i.e.*, 50% of the Li-ions form contact pairs with anions both in defect and defect-free regions.

More detailed analysis has been undertaken for the n=23 systems. The models involving ideal 6-fold Li-O coordination all maintain this coordination number throughout the simulations, even in defect regions (see Fig. 10; smectic-A and nematic-A), while CN(Li-O) is seen to vary from 4 to 7 in the remainder of the systems simulated. Such variations in broken-coordination situations occur mainly in defect regions involving 2-3 Li-ions.

The 7-fold Li-O coordination (the dashed line in Fig. 11) is unstable, with the 7th coordinating oxygen spending typically < 5 ps at a Li-O distance less than 3Å.
Figure 10  Distribution of Li coordination numbers CN(Li-O) for the five simulated LiPF$_6$·PEO$_6$ systems (see Fig. 6).

Figure 11  Li-O radial distribution functions RDF(Li-O) and coordination numbers CN(Li-O) for the nematic-B LiPF$_6$·PEO$_6$ model with defect-free and defect regions plotted separately.

A typical smectic-B broken-coordination situation is demonstrated in Fig. 12: in the left-hand channel, the Li-ion on the lower side of the defect region remains coordinated by one end-group oxygen belonging to the next polymer chain (A), whereas another oxygen has migrated to coordinate to the Li-ion on the upper side of the defect (B). In the right-hand channel, however, both chain-ends from the polymer channel at the upper end of the defect have left the coordination sphere of the Li-ion on the lower side of the defect, resulting in two uncoordinated methoxy-groups in the defect region (C). This deficit in coordinating oxygens around the Li-ion on the lower side of the gap causes the end-region of this channel to contract, allowing ion-pair formation (D). The persistence of the “Li-bridging” coordination (A) shown in Fig. 12 can have an important impact on the overall stability of the structure.
Ion-pairing thus occurs predominantly in coordination situations which involve exclusively Li-ions with low CN(Li-O); see Fig. 12. Through competition with the coordinating ether oxygens, Li-F coordination is always 1-fold, unless the Li-ion has migrated outside the PEO channel. Since defect regions contain uncoordinated methoxy groups (Fig. 12C), ion-pairs occasionally dissociate, thereby restoring the bridging configuration A shown in Fig. 12. These ion association-dissociation events occur on a nanosecond time-scale and correlate with changes in CN(Li-O); pair formation leads to a decrease in CN(Li-O) and vice versa.

The proportion of Li ions with 4-fold coordination decreases in the systems simulated in the order: smectic-B > nematic-B > nematic-R, which correlates well with the observed decrease in ion-pair concentration. The nematic-R system incorporates predominantly situations in which only one of the PEO hemi-helices in any Li-O coordination sphere is broken; as illustrated in Fig. 6. This reduces the possibilities for lower Li-O coordination, and thus leads to a higher incidence of 5-fold coordinated Li (Fig. 10). In the nematic-R system, almost 50% of the ion pairs form outside the defect region, which corresponds well with the more dispersed nature of the imposed isolated defect distribution.

Considering the specific role of terminal groups in promoting ion-pair formation, we see that the further the methyl-group pairs move away from their positions along the channel walls (Fig. 13b), the more they avoid one another and thereby provide more space for ion-pair formation. From Figs. 13a-c, we see that the methyl end-group separation correlates well with the incidence of ion-pair formation.
Figure 13 (a) Percentage of Li-ions participating in ion-pairing for the five simulated models for LiPF$_6$-PEO$_6$, as described in Fig. 6; (b) chain-end methyl carbon (C$_{meth}$) displacements from the PEO channel axes compared to the displacements in defect-free PEO; and (c) corresponding C$_{meth}$-C$_{meth}$ separations across the chain-break regions.

It is possible that comparative vibrational spectroscopy data for mono- and polydisperse systems could distinguish ion-pairing and Li-O coordination for the different models simulated. All broken Li-O coordination regions should involve a detectable number of ion-pairs. Several spectroscopic studies have already addressed structural issues regarding LiPF$_6$-PEO$_6$ and its isostructural crystal forms [73-75]; there is some evidence to suggest “spectroscopically free” anions in these materials.

The channel structure

Let us first consider how the channel structures differ in the smectic and nematic models depending on the nature of the chain-break defect (A, B or R) (Fig. 6). The Li-Li distances are found to reflect well the different structural situations for the Li ions, especially in the chain-break regions. In the smectic-A and nematic-A systems, the average distance from a Li-ion in a defect region to its nearest Li neighbour is closely similar to that in a defect-free region (5.8 Å compared to 5.9 Å), while the Li-Li distance across the defect region is ca. 7.5 Å. This appears as an extra peak in the RDF(Li-Li) plot for the nematic-A case; Fig. 14a. This peak is also present for the smectic-A case (not shown). In this model, a slight lateral displacement was noted in successive PEO channels in adjacent blocks. Interestingly, these displacements were larger in the n = 22 PEO system.
Li-ions in channel-end defect regions for CN(Li-O) < 6 (i.e., B-type systems) tend to move closer to the Li ions in the end-regions of successive PEO channels; with Li-Li distances ca. 5.2 Å compared to 5.9 Å in defect-free regions (Fig. 14b). The Li-Li distances across the defect region vary over a broad range (6-8 Å) compared to this distance in A-type systems (Fig. 14), with the shorter ca. 6 Å Li-Li distance corresponding to the “chain-bridging” configuration shown in Fig. 12. This type of local structural arrangement provides regular continuity in the Li-ion sequence across a channel break, and could therefore facilitate the experimentally observed enhanced Li-ion transport [30]. On the basis of such structural considerations, the B-type defect would therefore seem the more reasonable.

Chain defects in the nematic-R model situation rarely involve both hemi-helices around a given Li-ion. This appears to cause Li-Li distances in these defect regions to vary less than in the smectic-B and nematic-B models; typically 2 Å vs. 3Å. This is also evident from RDF(Li-Li) plots (Figs. 14a-c).

In A-type models involving 6-fold coordinated Li ions, the methyl-groups also remain somewhat closer to the PEO channel axis compared to the B- and R-type situations (Fig. 13b). The shorter distance of methoxy-composed to ethoxy-carbons from the central channel-axis indicates that the Li ions in the defect regions are tightly bound to the surrounding polymers, and may well be immobilised by high activation-energy barriers to Li transport. Interestingly, even if the Li-Li distances across the gap in the A-type
models (as discussed above) are larger than in B-type systems, the distance between the methyl-groups across the defect are consistently shorter (Fig. 13c). This is because ca. 50% of the methoxy-groups in B-type systems are not coordinated to Li ions and are therefore free to migrate away from their normal positions near the PEO channel walls into the space outside the channels (see Fig. 12).

The smectic surface

One of the prime goals of this study has been to endeavour to set up what could best be described as a smectic interface model. This has been done by creating an MD box in which registry has been established between an array of parallel monodisperse short-chain (n=23) PEO double hemi-helices, thereby creating an extended plane of methyl chain-ends at either end of “nano-crystalline blocks”. The periodic symmetry relating the blocks generates the required smectic interface; see Fig. 15.

Figure 15  MD snapshots for (a) smectic-A and (b) smectic-B models of short-chain LiPF$_6$:PEO$_6$.

As described earlier, two types of smectic model (A and B) are studied, differing only in the position of the chain-breaks with respect to the Li-ions. The behaviour of the two models is found to be quite different: in the smectic-B model (Fig. 15b), the PEO-tunnels link together via “bridging” methoxy groups, and the defect region involves disordered Li-ions, which could
favour ion transport. In contrast, the smectic-A system (Fig. 15a) exhibits neither bridging groups nor disordered Li-ions. Furthermore, the double hemi-helical PEO channels in the smectic-A system show small (~ 0.5 Å) lateral displacements which slightly perturb the translational symmetry of the crystallite; see Fig. 15.

Simulated XRD profiles

The calculated XRD profiles are shown in Fig. 16. These can be compared with the experimental XRD profile (Fig. 16, bottom) [76]. In this context, however, it is most important that we first consider the basis for the appearance of particularly the experimental profile. Since experimental XRD intensities (to a good approximation) only contain information regarding translational features in the unit-cell structure, these will therefore not contain any direct information relating to surface or chain-end features present in the material. Two interesting possibilities thus arise:

- The experimental XRD data will lack information on such “defect regions” lying at the surfaces of the effective diffracting mosaic blocks in the real material, and refinement of the data will therefore only reflect the structure of the defect-free regions inside these blocks. This is the situation for a smectic arrangement; or
- When the “defect regions” are more or less randomly distributed throughout the real structure (as is the case for the various nematic models simulated), the XRD data will actually contain partial information on these defects, and refinement of the resulting XRD data will include an “averaged-in” weighted component of the defect regions superposed on the defect-free structure. In other words, the resulting refined model will fit less well to the data – but will, in this case, include the averaged-in effect of the defect distribution.
We are left therefore with the paradoxical situation that a better fit to experimental data could imply a smectic situation but would actually tell us little about the end-chain defects in the system, whereas a poorer fit could imply a nematic-type structure, since the effect of defects is now present in the experimental data but not in the refined model.

In practise, we see no significant differences in agreement with experiment for the smectic and nematic models. There are, however, added complications, e.g., there is no direct correspondence between MD-box dimensions and the size of the scattering “mosaic blocks”; nor have we considered the coherence length of the diffraction process in relation to the size of the MD-box or the “mosaic blocks”. In short, XRD is an inappropriately crude and uncertain technique for distinguishing between possible short-chain ordering models.
Effect of ordering on ion transport in PEO channels

A detailed analysis of ion migration events has been undertaken for the $n=23$ systems smectic-$B$, nematic-$B$ and nematic-$R$, containing mobile and “bridging” methoxy groups in the defect regions. Two types of ion-jump can be distinguished in the direction of the PEO channels: longer jumps corresponding to typical Li-Li distances in the material (~6 Å), and shorter jumps of around 2-3 Å (see Fig. 17). These short jumps correspond to Li migration within the PEO channel involving only a few (up to 4) ether oxygen atoms. From Table 1, it is clear that shorter jumps are more common for Li-ions, whereas anions tend to undergo longer jumps (also ~6 Å). These occur cooperatively, involving the chain-sequence of neighbouring anions.

Figure 17. The x-coordinates (along the polymer-chain direction) for the Li-ions along a PEO channel plotted over 300 ps for the short-chain LiPF$_6$PEO$_6$ ($n=23$) system at $E=4.5 \times 10^6$ V/m.

The differences compared to the infinite systems are: 1) the increase in the number of Li-ion jumps with respect to number of anion jumps, and 2) the large variations in anion jump-rates from system to system. In most of the models simulated here, Li-ions undergo fewer longer jumps than the PF$_6^-$ ions, since longer jumps require a collective sequence of participating sites, which is inhibited by the strong local Li-O$_{et}$ interactions. Predominantly short Li-ion jumps were also seen in the infinite-chain system [77], but in the short-chain situations simulated here, they clearly dominate, even over short anion jumps. This raises the question as to whether it would be possible to observe only short jumps at lower electric fields if longer simulation times were feasible. Indeed, only short jumps occurred in the undoped nematic-$R$ simulation (Table 1), which would appear to support the notion of the dominance of Li-ion transport, as suggested by Bruce et al. on the basis of NMR measurements [26]. It is certainly clear that the transport number for Li-ions
is here considerably higher than in the infinite-chain systems, where it was only 0-0.1 [77], but where poor statistics disallowed any attempt at further quantification.

<table>
<thead>
<tr>
<th>System</th>
<th>Field/10^6 V/m</th>
<th>Li^+ jumps &lt; 4.5 Å</th>
<th>Li^+ jumps &gt; 4.5 Å</th>
<th>PF6- jumps &lt; 4.5 Å</th>
<th>PF6- jumps &gt; 4.5 Å</th>
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<tr>
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<tr>
<td></td>
<td>\perp 6</td>
<td>12</td>
<td>0</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>SiF_6^-</td>
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<td></td>
<td>4.75</td>
<td>18</td>
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<tr>
<td>-doped</td>
<td>\perp 6</td>
<td>11</td>
<td>3</td>
<td>11</td>
<td>6</td>
</tr>
<tr>
<td>Nematic-B</td>
<td></td>
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</tr>
<tr>
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<td>18</td>
<td>3</td>
<td>6</td>
<td>48</td>
</tr>
<tr>
<td>SiF_6^-</td>
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<td>18</td>
<td>7</td>
<td>0</td>
<td>4</td>
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<tr>
<td>-doped</td>
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<tr>
<td>Nematic-R</td>
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</table>

**Li-ion conduction mechanisms**

A basic requirement for Li-ion migration inside the PEO channels seems to be the availability of a low-CN to ether oxygen atoms. In Paper III, we found generally that more ion-pairs and uncoordinated ether oxygens are found near the chain-ends. In the smectic-B system, these ether oxygens are therefore confined to the smectic interface, separated by highly ordered regions; while they are more uniformly distributed throughout the nematic systems. The concentration of 5-fold coordinated Li-ions (Fig. 10) is found to be highest in the nematic-R (18%) and lowest in the smectic-B case (10%). Unlike in the smectic-B case, however, a substantial number of Li-ions with CN(Li-O)<6 are found in defect-free regions of the nematic systems. Li-ion coordination would appear to be more stable in the ordered regions of the smectic-B system. This would all suggested that Li-ion conductivity within the PEO channels is lower in the smectic-B than in the nematic-B and nematic-R systems, which is consistent with the higher electric field needed to trigger Li-ion migration in the smectic-B system.
Figure 18 An anion-mediated Li-ion conduction mechanism inside a PEO channel: (a) ion-pair formation followed by (b) ion-pair migration and simultaneous Li-occupation of the vacancy site left as a result of the pair formation; and finally (c) ion-pair breaking and Li-occupation of an available vacancy site.

A new, anion-mediated Li-ion transport mode appears in the short-chain systems which was not seen in the earlier infinite-chain model simulations. Li-ions move along the PEO channel in the steps illustrated in Fig. 18 for the nematic-B model. Li-ion displacement to create an ion-pair leaves behind it a vacancy and an uncoordinated O$_{el}$ atom (Fig. 18a). This vacancy is subsequently occupied by a Li-ion (Fig. 18b), and the ion-pair finally breaks (Fig. 18c). In this way, a sequence of Li-ions has moved along the channel. The important difference compared to the Li-ion conduction mechanism described for the infinite system is that longer jumps occur here, as seen in Table 1.

Figure 19 Li-ion dynamics (without external electric field) in the defect region; P and Q are snapshots of two Li positions before (P) and after (Q) jumps across the defect gap. The lower figure exemplifies the times spent in these two types of site.
Poor statistics in the Li-ion jump-count makes it difficult to compare the barriers for Li-ion migration across the two types of defect gap (Fig. 6; nematic-B and nematic-R). This barrier can be low in nematic-B systems, where local hopping (Fig. 19; P→Q) occurs across the gap during 300ps under zero applied external field. Generally, Li-ion migration is observed for 3-6 available (uncoordinated) ether oxygens in the jump-target region (Fig. 20b). With less available ether oxygens, ion-pair formation is more likely (see Fig. 20a). When a vacancy extends over more than one Li site, i.e., when we have > 6 uncoordinated ether oxygen atoms, Li-ion migration is suppressed, since the PEO double hemi-helical channels break down; as shown in Fig. 9.

![Figure 20](image)

**Figure 20** Li-ion migration mechanisms across the defect gap under an imposed electric field along the chains: (a) when mediated by ion-pair formation, and (b) direct migration into an available vacancy site.

### Anion conduction mechanisms

In the infinite system, the longer anion jumps always occurred sequentially for a row of PF₆⁻ ions along the inter-helical channels. This mechanism was shown to be related to ion displacements perpendicular to the polymer chains (the yz-direction), whereby one anion is paired with a Li-ion still within the double hemi-helix. Such yz-displacements of the anions are often precursors to motion in the channel-direction, thereby creating a vacancy into which a neighbouring anion can move.
Figure 21  Ion-clustering in the smectic interface, which suppresses anion migration along the channel. The dashed region marks the boundary of a +1-charged ion-cluster region involving 5 Li-ions and 4 anions.

Long PF₆⁻ jumps still occur predominately between different anion sites, but the sequential movement is always interrupted somewhere along the anion column. In the smectic-B case, this often occurs at the interface region in conjunction with ion-pair formation. As shown earlier (Fig. 20a), an ion-pair formed at the interface can dissociate and reopen the channel for subsequent ion motion, but high carrier concentration at the smectic interface promotes aggregation of ionic species, and ion-clusters so formed block migration in the corresponding anion channel (Fig. 21). This explains the large difference in the number of long anion jumps between undoped (48 jumps) and SiF₆²⁻-doped (4 jumps) nematic-B and smectic-B systems (see Table 1) for the same field strength.

In the short-chain systems, in addition to long correlated anion jumps, shorter uncorrelated jumps occur in isolation or sequentially in pairs. This process has two origins: (i) the more mobile methoxy groups create space near the chain defects for anions close to the PEO channel; and (ii) ion-pairs are formed near the chain defects with longer lifetimes than in the infinite system; these influence the available positions for the neighbouring anions. A typical anion transport sequence is shown in Fig. 22, as taken from the nematic-B simulation; non-coordinating methoxy groups move deep into the anion channel, but do not block it. Instead, space is provided into which anions can migrate, leaving behind vacancy.
Figure 22. Typical events in the anion and Li/PEO channels (shown as excluded volumes) in the nematic-B model: (a) an uncoordinated methoxy group (P) moves into the anion channel; (b) a mobile chain-end provides space which becomes occupied by an anion (Q) and leaves behind a vacancy; (c) this vacancy-site (R) is not occupied immediately if there is structural blockage; (d) the vacancy-site is then occupied by an anion, but the anion channel is blocked as a result of structural chain rearrangement.

Ion transport within the smectic interface

Two types of jump occur within the smectic plane: shorter jumps of up to 4.5 Å, and long jumps of ~8 Å (Table 1). These distances correspond to the half and full distance between neighbouring channels (anion or cation), with longer jumps occurring considerably more infrequently. Longer anion jumps are also correlated, but the higher degree of disorder in the smectic plane means that this correlation and also the types of site occupied are less well defined than within the more ordered channels. Clearly, ion conduction is less in the smectic plane than along the PEO channels, as indicated by the
higher electric field needed to induce it (see Table 1). This is not unexpected, since there is no structural continuity (typically in the form of ion channels) perpendicular to the PEO channel direction, especially for Li ions which have to cross the gap between two approximately aligned PEO channels. The limiting factor for this to occur is ion-pairing in the interchannel space.

**Li-ion conduction mechanism**

The migration of Li-ions within the smectic plane is governed by two mechanisms: (i) direct migration, where PEO chain-ends move far enough into the anion channel to come into contact with one another - allowing Li-ions to use this as a bridge (see Fig. 15b); and (ii) indirect migration involving ion-pair formation as an intermediate step. Direct Li-ion migration is a fast process, while Li-ions are immobilised in the anion channel for the full duration of the simulation in the course of indirect migration. The first process is much less frequent, from which we can conclude that Li-ion conduction is very low. The reason for this is that the mobile methoxy groups within the smectic plane, which assist Li-ion transfer by coordinating it to both sides of the gap, provide only 2-3 fold Li-O coordination. Such an interaction is too weak to compete with ion-pairing.

**Anion conduction mechanism**

Anions appear to migrate more easily within the smectic interface than Li-ions (Table 1). The process involves two steps: migration into the gap between the two PEO chain-ends and transient pairing with Li-ions, followed by breaking the ion-pair and migrating into the neighbouring anion channel (see also Fig. 23). This process appears to involve local correlation – a vacant site is needed nearby to which the anion can migrate.

We can note a clear difference in ordering within the smectic interface: the coordination of Li-ions in the interface region is broken in the smectic-B system studied in Paper III. This leads to ion-clustering, which involves typically three or more anions and cations (see Fig. 21), since the electric field forces them more easily out of their normal positions. The ion-exchange rate between these clusters and the solvating polymer appears to be a limiting factor for ion transport. This behaviour can be compared with that in the more ordered smectic interface of the smectic-A model (Fig. 6) under the same in-plane electric field; much longer anion jumps were observed and no ion-clustering, since the Li-ions could not leave their sites (Fig. 23).
Figure 23 The two significant steps in the anion migration mechanism within the smectic plane: (a) anions move into the gap between the chain-ends to form ion-pairs (this can be accompanied by a change in CN(Li-O) and chain-end movement into the space of the anion channel); (b) these ion-pairs break and the anions move into the next anion channel.

Doping effects

Doping LiPF$_6$-PEO$_6$ with $\sim$1% SiF$_6^{2-}$ ions has been shown experimentally to enhance its ionic conductivity [30,78]. This is seen in MD simulations of the infinite system as a lowering of the threshold field needed for ion motion [77]. The effect is less clear for the short-chain case (Table 1), with all systems exhibiting ion mobility irrespective of doping. The only significantly higher conductivity is seen for the nematic-B model, where a sequence of Li-ion jumps occurs in the channel containing the compensating Li-ion (see Fig. 11 in Paper IV). The mechanism is of the "anion-mediated" type discussed earlier. The SiF$_6^{2-}$ dopant ion itself does not actively participate in the
conduction process, but remains immobile or diffuses to defect regions throughout the simulations. It remains uncoordinated if is far away from a structural defect, i.e., away from chain-ends. However, Li-ions which have migrated to a metastable site in the PEO channel form ion-pairs in defect-free regions. Otherwise, SiF$_6^{2-}$ ions either forms ion-pairs with one Li-ion in an energetically favourable $C_{3v}$ conformation ([79]) or clusters (involving two Li$^+$ ions, one in $C_{3v}$, another in $C_{2v}$ conformation; see Fig. 24). Li ions are pulled out from the channel when CN(Li-O)<6, but continue to coordinate to ether oxygens, which distort to point outward from the channel. This configuration appears to suppress nearest-neighbour Li-ion migration, since there are no ether oxygens available for coordination.

Figure 24  A typical ion-pairing situation for the SiF$_6^{2-}$ dopant near the defect region, shown for the nematic-R system.
Conclusions and future work

Liquid crystal type ordering of short PEO chains (M_w~1000) in smectic (chain-ends confined to a two-dimensional plane) and nematic arrangements have been studied using Molecular Dynamics (MD) simulation. Highly ordered crystalline LiPF_6·PEO_6 systems have provided an ideal model structure to probe such features, where the chains represent an immediate situation between high-M_w PEO complexes with negligible effect of chain-ends and the complexes involving short PEO (“glyme”) molecules. While these molecules can readily find their most efficient packing, this is more complicated for longer oligomers, due to both slower kinetics and polydispersity. On this intermediate scale, the nature of chain-ordering defects plays a crucial rôle in determining its macroscopic behaviour - including ion conductivity.

XRD and MD simulation analyses both constrain the true structure into models: a crystallographic unit-cell and a quasi-periodic MD box, respectively. While MD simulation can provide unique information about local defects, it is still inadequate in describing long-range order; the opposite is true of the diffraction experiment. It is therefore challenging to find a common meeting ground for the two approaches where we can endeavour to construct a clearer picture of reality.

The poor statistics obtained for Li-ion mobility in the simulations means that, rather than attempting here to identify the “correct” local structure, it is more realistic to draw upon the somewhat fragmentary evidence available from the simulation of the multiple models investigated, and try to piece together some picture of the nature of the disorder in the material. Indeed, it is most unlikely that any genuinely “correct” structure actually exists, but rather a superposition of many metastable local structures. Nevertheless, some important findings can be highlighted:

- Slight non-stoichiometry (imposed by the removal of EO-groups from chain-defect regions in LiPF_6·PEO_{5.75}) leads to a significant disruption of crystallinity.
- Three models (nematic-R, nematic-B and smectic-B), containing chain-breaks in the Li-ion coordination sphere (“bridging” arrangement), all provide a structural basis for the continuous transport of Li-ions along discontinuous short-chain PEO molecules.
The transfer of Li-ions compared to anions is significantly increased in the short-chain systems compared to the long PEO-chain systems studied earlier. This can be explained by the increase in the proportion of Li-ions with lower coordination numbers (CN(Li-O)<6) and by the effect of the temporary formation of ion-pairs.

The more disordered nematic phases require a lower threshold field to promote ion conduction than the smectic phases. This can be related to the spatially more uniform distribution of chain-end defects in the nematic systems.

Likewise, the field threshold for ion conduction within the smectic interface is higher than that along the PEO channels.

The interstitial Li-ions in the PEO channel, introduced through doping with Li₂SiF₆, enhance Li-ion conduction.

Simulated XRD peak intensities for models with “bridging” arrangements (nematic-R, nematic-B, and smectic-B) agree reasonably well with experimental data. However, it is difficult to assess the stability of these “bridging” arrangements on a macroscopic scale using MD techniques.

In a broader sense, however, it must be admitted that this work has hardly brought us much closer to making any significant breakthroughs in polymer electrolyte design; the critical structural factors which will make this possible remain as yet undiscovered.

In future work, it would be interesting to look into the possibility of growing such nano-crystalline structures on nano-architected electrode materials [80,81], with potential applications in 3D micro- and nano-batteries, e.g., [82], where the one-dimensional character of the ion conduction can be a great asset. Simulation could then also help improve our understanding of local structure and dynamics at such interfaces. Modelling of this kind of interface requires much larger systems than studied in this thesis, but numerous simulation studies of interfaces between amorphous polymers and inorganic nanoparticles have demonstrated the feasibility of such studies (see, for example [83,84]).

Ion transport in low-dimensional channels is also highly relevant to bio-systems, since this is a vital function of living-cell membranes. It would also be tempting to speculate on the possibility of designing a highly ordered polymer structures to support higher temperature anhydrous proton transport, without the need for a mediator molecule, e.g., the rôle of water in the Nafion® fuel-cell membrane. To my knowledge, only amorphous systems have shown usable proton conductivity in anhydrous polymer materials (see [85]).
Populärvetenskaplig sammanfattning

Betydelsen av ordning i polymerelektrolyter

Ett envist problem
Elektrisk energi är en högst användbar form av energi, då den lätt kan konverteras till andra energiformer. Idag representerar elektrisk energi ca 6% av världens totala energikonsumtion, och distribueras främst genom globala och lokala elnät. Men elektriciteten kan också komma från andra små elektrochemiska enheter, som batterier och bränsleceller.


Fyrtio år senare, 1839, togs ytterligare ett avgörande steg i batteriutvecklingen när Michael Faraday upptäckte elektrolyter i fast fas, istället för de tidigare flytande. Detta har varit av stor betydelse under senare år, då säker-

**Polymerelektrolyter**


Efter Armands upptäckt tog forskningen om polymerelektrolyter fart på allvar. Snart kom man till slutsatsen att polymerernas rörelse var av stor betydelse för jontransporten genom dem, och därmed att jonledningen ägde rum i polymerenes amorfa, oordnade fas, och inte i dess kristallina, ordnade fas. Forskningen därefter syftade därför mycket till att försöka öka de amorfa delarna på de kristallina delarnas bekostnad. På det sättet lyckades man höja jonkonduktiviteten, men fortfarande inte tillräckligt för de flesta batterier.

**Ordning**

Med denna kunskap om polymerelektrolyter kan det tyckas paradoxalt att de högsta jonkonduktiviteterna för fasta elektrolyter har upptäckts för kristallina material. Perovskiten Li_{0.34}La_{0.51}TiO_{2.94}, eller Li-β-alumina, är ett exempel på en sådan kristallin jonledare. Att dessa uppvisar hög jonkonduktivitet anses bero på att det finns gott om lämpliga plaster för jonerna att hoppa till när de vandrar genom materialet, och att det inte krävs så mycket energi för att hoppa mellan dessa platser. I andra kristallina material har man upptäckt hur vissa delar utgör små molekylära ”vattenhjul” som effektivt slussar jonerna genom materialet.

Dessa ordnade, kristallina fasta elektrolyter har varit en inspirationskälla när forskarna försökt förbättra sina polymerelektrolyter, och skapa motsvarande transportvägar i polymerer. Ett sådant exempel är den grupp polymerer som kartlades av Peter Bruce och hans medarbetare åren kring millennieskiftet: LiXF_6·PEO_6 (där X = P, As eller Sb). I dessa material så bildar polymeren (PEO) långa tunnlar för de positivt laddade Li-jonerna (Li⁺), samtidigt som de negativt laddade hexafluoridjonerna (XF_6⁻) ligger för sig själva utanför tunnlarna. Det visade sig att denna kristallina elektrolyt förvisso inte hade anmärkningsvärt hög jonkonduktivitet, men väl högre än den amorfa formen av samma material. Vissa forskare menar därför att förståelsen av detta system kan erbjuda en nyckel till hur man upptäcker polymerelektrolyter med högre jonkonduktivitet. Det är därför den här avhandlingen fokuserar på detta material.
Korta kedjor
Polymerer är som sagt långa molekylkedjor, men de kedjor som använts i fallet med LiXF₆·PEO₆ kan sägas vara anmärkningsvärt korta i flera fall då materialet studerats. Att de är korta har gjort att materialen är fulla med brott på polymerkedjkan, och där brotten finns så sitter det också en speciell slutgrupp på polymeren. Dessa brott och slutgrupper kan i sin tur också vara ordnade enligt olika mönster i materialet. Emellertid är detta något som det inte tagits någon större hänsyn till hittills i forskningen, och det är dessa effekter som står i centrum i den här avhandlingen.

Molekyldynamikstudier
Den fantastiska förbättringen av datorer och datorprogram har gjort det möjligt att modellera hur material ser ut och beter sig på den atomära nivån. Inte minst har Molekyldynamik (MD) varit ett hjälpmedel för att studera hur joner rör sig i olika material. Molekyldynamik använder klassisk mekanik för att teckna en kort ”film” av ett material bestående av några tusentals atomer; man simulerar alltså materialet dynamiskt. Det är den metodik som använts i det här arbetet, vilket består av följande fyra vetenskapliga artiklar:

Artikel I: Här har kvantmekaniska studier gjorts för att kartlägga interaktionerna mellan partiklarna i materialet Li₂SiF₆. En god beskrivning av dessa interaktioner behövs nämligen för att kunna möjliggöra en senare MD-simulering, och interatomära interaktionerna mellan jonerna Li⁺ och SiF₆²⁻ behövdes för vår studie av LiXF₆·PEO₆ med små mängder SiF₆²⁻ (så kallad dopning) skulle studeras.

Artikel II: Den här artikeln behandlar en jämförelse mellan de situationer som uppstår när polymerernas brott och slutgrupper samlas i ett vidsträckt plan (denna struktur kallas smectic) eller när de är slumpvis utspridda (denna kallas nematic).

Artikel III: Denna studie går in i djupare detalj på hur de olika brottsituationerna ser ut – i vissa ligger en litiumjon mitt i själva brotten, i andra inte.

Artikel IV: Denna artikel beskriver hur jonkonduktiviteten i de ovan beskrivna systemen har studerats. En avgörande slutsats är att jonkonduktiviteten är som högst, där ordningen mellan slutgrupperna är som minst. En annan är att konduktiviteten blir mindre i det plan som bildas i smectic struktur beroende på att positiva och negativa joner möts där och fastnar i varandra – så kallade jonpar bildas.
Acknowledgements

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I am also very thankful to my other supervisor Dr Daniel Brandell for being very patient and pragmatic in all our scientific discussions. And Daniel, what great discussions we have had on Politics and History!

Professor Alvo Aabloo - my advisor in Tartu University - thank you for introducing me to MD and for help in getting me started.

I am grateful to all the people at the Department of Materials Chemistry for creating such a pleasant research and social environment. ("No one mentioned, ..... ")

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I am very thankful to my parents and brother in Estonia for everything they have done for me and given to me.

Katrin! Your love and support have given me the strength to continue. Suur aitäh!

(Signed)

Antti Liivat

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References


Appendix

Interatomic interactions are described by the sum:

\[ U = \sum_{i,j} U_{bond}(r_{ij}) + \sum_{i,j,k} U_{bond}(\theta_{ijk}) + \sum_{i,j,k,n} U_{tors}(\phi_{ijkn}) + \sum_{i,j} U_{non-bond}(r_{ij}), \]

where bond-stretching:
\[ U_{bond}(r_{ij}) = \frac{k_{ij}}{2} (r_{ij} - r_{0ij})^2, \]
valence-angle bending:
\[ U_{bond}(\theta_{ijk}) = \frac{k_{ijk}}{2} (\theta_{ijk} - \theta_{0ijk})^2 \]
and torsional rotation potentials (different for methyl-group hydrogens):
\[ U_{tors}(\phi_{ijkn}) = \sum_{x=1}^{6} a_{x,ijkn} (-1)^x \cos^x(\phi_{ijkn}), \]
\[ U_{meth}^{tors}(\phi_{ijkn}) = \frac{k_{meth}}{2} [1 - \cos(3\phi_{ijkn})] \]
are imposed on bonded atoms with indices i,j,k,n. For interactions between non-bonded atoms, the following forms apply:

\[ U_{non-bond}(r_{ij}) = A_{ij}^{\beta} \exp(-B_{ij}^{\beta} r_{ij}) - \frac{C_{ij}^{\beta}}{r_{ij}^6} - \frac{D_{ij}^{\beta}}{r_{ij}^{12}} + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \]
\[ U_{non-bond}(r_{ij}) = A_{ij}^{LJ} \left( \frac{C_{ij}^{LJ}}{r_{ij}^{12}} - \frac{D_{ij}^{LJ}}{r_{ij}^6} \right) + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \]

where \( k_{ij}, k_{ijk}, r_{0ij}, \theta_{0ijk}, a_{x,ijkn}, A_{ij}^\beta, B_{ij}^\beta, C_{ij}^\beta, D_{ij}^\beta, A_{ij}, C_{ij}^{LJ}, q_i, q_j \) are constants depending on atom-types.
Table A-I. Force-field parameters for SiF₆²⁻/LiPF₆-PEO₆. Energy in unit of kcal/mol; Fᵣ and Fₛ refer to fluorine atoms in PF₆⁻ and SiF₆²⁻ respectively.

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