



Poly(ethylene oxide)–poly(butadiene) interpenetrated networks as electroactive polymers for actuators: A molecular dynamics study

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ARTICLE INFO

Article history:

Received 20 October 2008

Received in revised form 22 March 2009

Accepted 29 April 2009

Available online 6 May 2009

Keywords:

Interpenetrating polymer network

Molecular dynamics

Poly(ethylene oxide)

Lithium perchlorate

Ion transport

ABSTRACT

Molecular dynamics (MD) techniques have been used to study ionic transport and coordination stability in an interpenetrating polymer (IPN) network used as electrolyte for actuator devices. The system consisted of poly(ethylene oxide) (PEO) and poly(butadiene) (PB) in a 80/20% weight ratio at a total polymer of 32%, immersed into propylene carbonate (PC) solutions of LiClO₄. The system has been studied for five different concentrations of LiClO₄ in PC: 0.25, 0.5, 0.75, 1.0 and 1.25 M, and with applied external electric fields of 0, 1 and 5 MV/m. It is shown that the polymer matrix has little involvement in the movement of ions and solvent, but that the polymer arrangement is important for the solvent phase nano-structure, and thereby influences the mobility. The mobility of PC is higher than of the other species in the system, but the charged species display higher mobility under external field. The field threshold level for conductivity processes is between 1 and 5 MV/m. It is argued that ion pairing, phase separation and coordination stability are important for the overall dynamic properties.

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1. Introduction

Electroactive polymers (EAPs) are polymer materials that change their shape or size in response to electrical stimuli. This class of materials is therefore a good candidate for actuators in the field of medical devices, soft manipulators and biomimetics, since they mimic the behavior of biological muscles. EAPs which also inhibit properties similar to biological materials in terms of force, strain and speed are attractive for creating artificial muscles used in biologically inspired robots [1]. However, the most promising devices today in terms of operating voltage and high-strain output – the ionomeric polymer–metal composites (IPMCs) – are dependent on metallic surface layers, which are expensive, have low biocompatibility and have a tendency to crack upon actuator operation [2].

Recent years have shown some significant efforts to make an all-polymeric ionic EAP, by combining electronically (as electrodes) and ionically (as electrolyte) conductive polymer materials [3,4]. The architecture of such an all-polymeric EAP device can vary. The simplest mimics IPMCs, consisting of a solid polymer electrolyte (SPE) sandwiched between two layers of electronically conductive polymer (Fig. 1a). Unfortunately, these materials can undergo a delamination process, which limits the actuator's life time severely

[5]. However, this problem can be overcome [6,7] by designing the actuator as a three-component conducting interpenetrating polymer network (IPN), with the conducting polymer embedded in an elastic polymer electrolyte network (Fig. 1b).

A promising all-polymeric IPN actuator combination studied in recent years has been using poly(3,4-ethylenedioxythiophene) (PEDOT) as the electronically conductive polymer, and a network of poly(ethylene oxide) (PEO) and polybutadiene (PB) as the SPE [8,9]. The simultaneous synthesis of PEO and PB ensures an IPN formation of good mechanical strength and relatively high ion conductivity. PEO act as a solvent for salts (in the present study LiClO₄ dissolved in propylene carbonate (PC)), while PB is an elastomer. The actuation motion of the membrane is considered to be due to the ionic and solvent transport in the system.

It is difficult to obtain detailed experimental information in such a complex material on all the molecular processes and interactions which are involved in the actuation motion. The studies have mostly been limited to morphological and mechanical investigations. Therefore, atomic level simulations can give valuable insights. For Nafion-based IPMCs for example, such studies have helped to gain insights on several scales for both size and time [10–13]. In an earlier study [14], we used molecular dynamics (MD) simulations to examine some basic structural and morphological properties of the SPE phase of the IPN material (*i.e.*, with the PEDOT content omitted) – to our knowledge, the very first MD simulation of an IPN material for actuator applications. We were then able to reproduce the experimental picture of a phase-separated system between PEO

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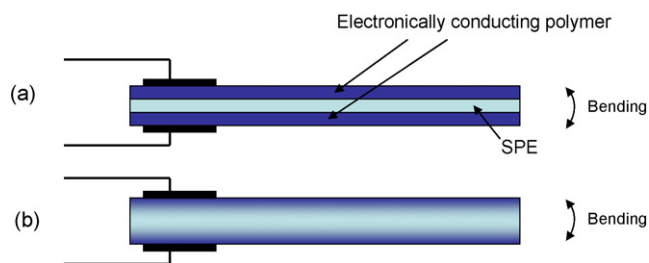


Fig. 1. All-polymeric actuator designs. A three-layer device (a) and a “gradient” IPN actuator (b).

and PB, with the PC solvent forming a homogenous phase with PB and most of the ions, but also found that the degree of phase separation was dependent on the salt concentration. In the present study, we are making an in-depth analysis of the dynamical properties of the system.

2. The molecular dynamics simulations

In an MD simulation, atomic motion in a chemical system is modelled in classical mechanics terms by solving Newton's equations of motion simultaneously and repeatedly for all particles in an appropriately chosen periodic simulation box. This set of equations is solved by a computational algorithm and depends implicitly on the description of the forces acting between the particles, *i.e.*, the force field. The result can be pictured as a “movie” of the material on the atomic scale; conventionally some nanoseconds long for some thousands of atoms.

Simulation details such as force field, box generation, equilibration procedure, software, *etc.*, have been given in [14]. Our $40\text{ Å} \times 40\text{ Å} \times 40\text{ Å}$ simulation box consisted of one single chain of a short chain methyl end-capped PEO homologue (260 monomers, *i.e.*, $\text{CH}_3-(\text{OCH}_2\text{CH}_2)_{259}-\text{OCH}_3$, a poly(ethylene glycol)dimethyl ether); one 55 units long chain of PB 55 ($\text{CH}_3-(\text{CHCHCH}_2\text{CH}_2)-\text{CHCHCH}_3$; all $\text{CH}=\text{CH}$ bonds initially in their *trans* configuration), 271 PC molecules and LiClO_4 salt to the concentrations of 0.25, 0.5, 0.75, 1.0 or 1.25 M (corresponding to 6, 12, 17, 23 or 29 ion pairs). The systems thus contain 32 wt% polymer, of which 80% is PEO and 20% PB, and rest of the 68 wt% consist of LiClO_4 and PC, in order to resemble the experimentally investigated systems [8]. The PEO chain has $-\text{CH}_3$ instead of $-\text{OH}$ terminal groups in order to prevent hydrogen-bonding interactions. The sampling period of the simulations was 2 ns at constant pressure (NPT simulation). Afterwards, external electric fields of size $1 \times 10^6\text{ V/m}$ and $5 \times 10^6\text{ V/m}$ were applied for another 2 ns for each field strength. The applied field is a non-equilibrium model, simulating the behavior under the potential drop close to the electrode surface upon actuation. A picture of the simulated system can be seen in Fig. 2, where the two polymer strands have been “unfolded” from the actual simulation box to better illustrate their size and shape.

3. Results and discussion

It is useful to investigate the Radial distribution functions (RDF) and coordination number (CN) functions resulting from an MD simulation in order to study local structures of materials. The RDFs show that the species with the most stable and well-defined coordination spheres in the systems are the Li^+ ions, which have a total coordination number of 4 with the nearest neighbors at 1.8 Å distance, and are coordinating to either the carbonyl oxygen atoms of the PC molecule, perchlorate oxygen atoms or – but to a much lesser extent, especially at higher concentrations – PEO ether oxygens. There is no coordination of Li^+ to the other oxygens on PC. RDFs and CN functions for lithium towards ClO_4^- (monodentate

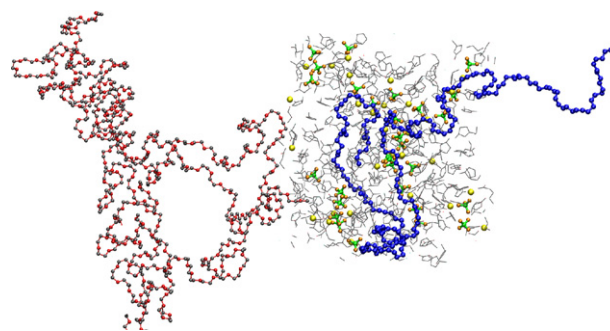


Fig. 2. The MD simulation box for the 1.25 M concentration with PEO (grey and red spheres) and PB (blue) unfolded out of the box for clarity. Li^+ are yellow spheres, ClO_4^- green and gold, and PC molecules are depicted as grey wires.

or polydentate coordinations are not distinguished) and PC can be seen in Fig. 3. The most prevalent coordination of lithium is to the PC molecules, to which it has a CN of ~ 3 . There is a tendency to tendency to ion pairing and clustering (Fig. 3b), which naturally increases with increasing concentration, but also is prevalent at the very lowest concentration – around 20–25% of the ions are then in pairs. The only noticeable exception from the expected trends is that the 0.5 and 0.75 M systems come in opposite order to each other, which can be explained from the very profound phase separation at 0.5 M [14]. As the $\text{Li}^+ \cdots \text{ClO}_4^-$ coordination increases with concentration, the $\text{Li}-\text{O}_{\text{carbonyl}}$ coordination decreases with the same amount.

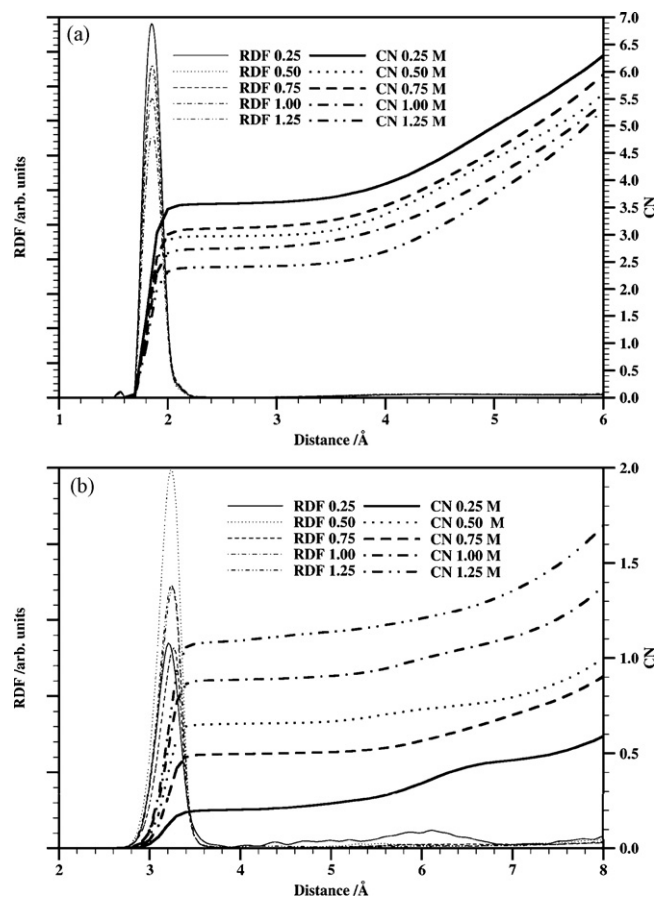


Fig. 3. $\text{Li}^+-\text{O}_{\text{carbonyl}}$ (a) and Li^+-Cl (b) radial distribution functions and coordination numbers for different concentrations. External field applied: (a) 0 and (b) 5 MV/m , respectively.

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