ELSEVIER

Polymer 42 (2001) 8043–8050

polymer

www.elsevier.nl/locate/polymer

Estimation of the ion conductivity of a PEO-based polyelectrolyte system by molecular modeling

Jaana Ennari*, Igor Neelov, Franciska Sundholm

Laboratory of Polymer Chemistry, University of Helsinki, PB 55, FIN-00014 Helsinki, Finland

Received 14 December 2000; received in revised form 10 April 2001; accepted 1 May 2001

Abstract

Atomistic molecular modeling has been used to construct amorphous 35.0 wt% water-containing polymer electrolyte materials consisting of two polymers: poly(ethylene oxide) (PEO) and poly(ethylene oxide) with sulfonic acid anion end groups (PEO sulfonic acid anion). The cations in the system are the hydronium ion, which simulates the classical diffusion of the hydronium ion and a particle called proton, which simulates the proton hopping mechanism. The possibility of the ions to move together with the polymers in the matrix is also discussed. The coordination between the ions were calculated and compared with the results for similar systems having different amounts of water. The diffusion coefficients for the ions and the conductivity of the system were calculated. The system was found to be conducting, which agrees with the experimental work. In the simulation, both the hopping and the diffusion mechanism were important in the studied system, while in the simulated system, which contains only one PEO sulfonic acid anion in water, the hopping mechanism dominated. The good correlation between the experimental and simulated results shows that the used model is able to estimate whether the material is conducting or non-conducting. The model can also offer interesting information concerning the possible mechanisms of proton conductivity in polymer electrolyte materials. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyelectrolyte; Modeling; Conductivity

1. Introduction

Polymer-based conducting materials have stimulated remarkable interest in the field of solid polyelectrolytes during the last two decades due to their potential applications in different types of electronic equipment and electrical vehicles [1–5]. Traditionally, ion-conducting polymers are developed by dissolving salts into a polymer matrix like poly(ethylene oxide) (PEO) [6–8]. Recently, proton-conducting polymers have become an interesting area of study due to the possible use of these materials in low temperature fuel cells for zero emission vehicles and electrochemical devices [9,10]. However, experimental attempts to develop these new materials have turned out to be very slow. In addition, the experimental and the theoretical investigations have not been able to solve the conduction mechanisms. Molecular modeling, which shows the structure of the polymer matrix in detail as a function of time, can offer an efficient method to get information about the conduction mechanisms in polyelectrolytes and to estimate the conductivity of a new material. Molecular modeling has not yet been utilized widely to study polyelectrolytes [11]. This is due to some difficulties related to MD simulations of polymer electrolytes, such as lack of force fields and models, which could treat both polymers and ions, especially protons, and long simulations times. However, new force fields and models, which can simulate polymers and ions at the same time, have been developed recently [12] and with the capacity and effectivity of the new computers, the simulations long enough to study the conductivity can be made even in a month or two.

We have previously reported the synthesis and the testing of a proton-conducting membrane containing high molar mass PEO, sulfonated PEO (PEO sulfonic acid), and water [13]. Recently, we have also reported the results of molecular modeling of three amorphous systems based on this experimental material. The modeled systems contained different concentrations of the PEO sulfonic acid anions, ($M_w = 436$), PEO and water [12,14–17]. The main results of these systems were that a system called cell1, which contained only one PEO sulfonic acid anion in water, was conducting while the systems also containing PEO, called cell2 and cell3, were non-conducting. This was assumed to be due to the small amount of water in the PEO-containing

---

* Corresponding author. Tel.: +358-9-1914-0333; fax: +358-9-1914-0330.

E-mail address: ennari@csc.fi (J. Ennari).

PII: S0032-3861(01)00311-1

systems (cell2 was containing 20 wt% water, and cell3 was water-free). However, the experimental system was proton-conducting, but its content of water was unknown. In this work, a system containing PEO and 35 wt% water was constructed and found to be conducting.

Three different mechanisms, the proton hopping mechanism, the classical diffusion mechanism and the possibility of the ions to move along the polymer matrix, are discussed in this work [6,9,18–20]. Two different cations were used in the simulations to be able to study two different mechanisms of the conductivity: the classical diffusion and the proton transfer from one water molecule to another, i.e. the proton hopping mechanism or Grotthus chain mechanism [9,18–20]. The hydronium ion was parametrized to study the classical diffusion of the hydronium ion. The hopping mechanism was studied by a particle called proton, which has been described in detail previously [12]. The proton in the simulation can interact with the water molecules and jump from one water molecule to another. The model is not perfect since, e.g. no chemical bonds can be created or broken during the simulation. However, the results obtained using the model are in agreement with the experimental work. All the calculated parameters for the ions are included into a force field called the NJPCFF force field, which we have described previously in detail [12,17]. The NJPCFF force field was used in all calculations.

The aim of this work is to show that the molecular modeling can be used to estimate ion conductivity of a polymer system and to get information of the mechanisms occurring in the conducting systems. Thus, it is probable that in future, molecular modeling can increasingly be used to help the development of new polyelectrolyte materials by experimentalists.

2. Theory

Intermolecular pair correlations are utilized in the simulations to give the probabilities of finding a pair of particles at distance r apart relative to the probabilities expected for a completely random distribution at the same density [21]. Eq. (1) was used to calculate the coordination numbers in the present study:

$$n_{x\cdots z}(r) = 4\pi \frac{N_z}{\langle V \rangle} \int_0^r g_{x\cdots z}(s) s^2 \, \mathrm{d}s \tag{1}$$

where $n_{x\cdots z}(r)$ is the number of x particles coordinated to particle z within a radius r, $\langle V \rangle$, the volume of the cell, N_z, the total number of the particles z in the system and $g_{x\cdots z}(s)$, the radial distribution function between x and z.

The following equation was used in the simulations to calculate the diffusion coefficients:

$$D_\alpha = \frac{1}{6N_\alpha} \lim_{t\to\infty} \frac{\mathrm{d}}{\mathrm{d}t} \sum_{i=1}^{N_\alpha} \langle [\mathbf{R}_i(t) - \mathbf{R}_i(0)]^2 \rangle \tag{2}$$

where D_α is the diffusion coefficient for the particle α, N_α, the number of diffusing particles, t, the time and $\mathbf{R}_i(t)$, the position vector of particle α at time event t. In Eq. (2), the sum term on the right-hand side divided by N_α is called the mean square displacement (MSD). Eq. (2) is valid only when the motion of the diffusing particle follows a random walk, i.e. the Einstein diffusion is reached by the diffusing particle. The region in which Eq. (2) is valid was tested by plotting log(MSD) against log(t). In the case of Einstein diffusion, the slope of the curve is one, and the calculation of the diffusion coefficient can be made by using Eq. (2).

The ionic conductivity, σ, can be determined using the Einstein equation [11]:

$$\sigma = \frac{e^2}{6tVkT} \left(\sum_i z_i^2 \langle [\mathbf{R}_i(t) - \mathbf{R}_i(0)]^2 \rangle + 2 \sum_{j>i} z_i z_j \langle [\mathbf{R}_i(t) - \mathbf{R}_i(0)][\mathbf{R}_j(t) - \mathbf{R}_j(0)] \rangle \right) \tag{3}$$

where t is the time, V, the volume of the cell, k, Boltzmann's constant, T, the temperature and $\mathbf{R}$, the position vector of the diffusing ion. The first term on the right-hand side of Eq. (3) is the sum over individual MSDs weighted with the charges, and the second is the sum of correlation of displacements of ions describing the interactions between different ions.

3. Computational details

The computational results were calculated on two Silicon Graphics Indigo 2 and one Octane workstations of the Laboratory of Polymer Chemistry at the University of Helsinki and the SGI Power Challenge computers of CSC (Center for Scientific Computation Ltd, Espoo, Finland). An own code was made to calculate the conductivity; otherwise, the software programs INSIGHTII and DISCOVER version 4.0.0P from Molecular Simulations Inc. (MSI) were used in the calculations [22]. Ten 3D amorphous cells were constructed with periodic boundary conditions. The polymer components in each cell were four PEO sulfonic acid anions ($^{-}O_3SCH_2CH_2CH_2O(CH_2CH_2O)_4CH_2CH_2CH_2SO_3^{-}$) and one PEO molecule with degree of polymerization 60. In addition, each cell contained four hydronium ions, four protons, four small gas molecules (O_2, H_2, and CO_2) and 150 water molecules corresponding to 35.0 wt%. This system is called cell4 in this paper since we have previously reported results for systems containing different amounts of PEO and water and those cells are called cell1, cell2 and cell3 (see Table 1) [12,14–17].

We have previously shown that the PCFF force field [23–27] is suitable for modeling the PEO sulfonic acid [28]. All calculations are made using the NJPCFF force field, which consists of the PCFF force field and of the added parameters for the ions, which lacked the PCFF force field [12]. The proton in the simulation is a particle, which has the mass and the charge of a proton, but its van der Waals radius is

Table 1
Description of the different simulated systems, e.g. cells

Cell	Number of					wt% of water
	PEO[a]	Anion[b]	Proton	Hydronium ion	Water	
Cell4	1	4	4	4	150	35
Cell3	1	4	4	4	0	0
Cell2	1	4	4	4	74	20
Cell1	0	1	1	1	220	90

[a] The degree of the polymerization is 60.

[b] Anion means PEO sulfonic acid anion.

derived from condensed phase properties of molecules containing highly polarized hydrogen [12]. Thus, it is possible to study the proton hopping mechanism in a general way since the charge and the rather large size of the proton gives it the possibility to interact constantly with surrounding molecules by a strong electrostatic interaction and jump from one water molecule to another. The classical diffusion mechanism is modeled by the hydronium ion.

The cells were first minimized using molecular mechanics methods (Steepest descents and Conjugate gradients) until the maximum derivative reached the value 0.1 kcal/(mol Å). Then, 200 ps long dynamics runs with the NVT ensemble at 298.00 K were performed for each cell.

For three cells having the lowest energy, an NPT run for 300 ps was made using the Ewald summation method [29] at 298 K to calculate the real density of the system. The initial density was 0.9796 g/cm^3 for each cell and the final densities varied from 1.0274 to 1.0296 g/cm^3 corresponding to volumes 12125.210–12098.886 Å^3.

After the final density was reached for two cells, 2 ns long NVT molecular dynamics simulations were made to study the diffusion of the ions in the systems at 298 K. We have previously reported that for cell2 and cell3 (see Table 1), results obtained using the Ewald summation method [29] and the cell multiple method (CMM) [30] did not differ remarkably [31]. Since the CMM is much faster than the Ewald summation method, the CMM was used in the present study to model the non-bonding interactions during the NVT runs.

4. Results and discussion

4.1. Coordination study

The coordination was studied by plotting the pair correlation functions $g(r)$ as a function of the separation distance r and by calculating the coordination numbers in the first coordination shell $n(r)$. The curves for cell4 are marked with x in all pair correlation plots (Figs. 1–3). The coordination numbers are collected in Table 2.

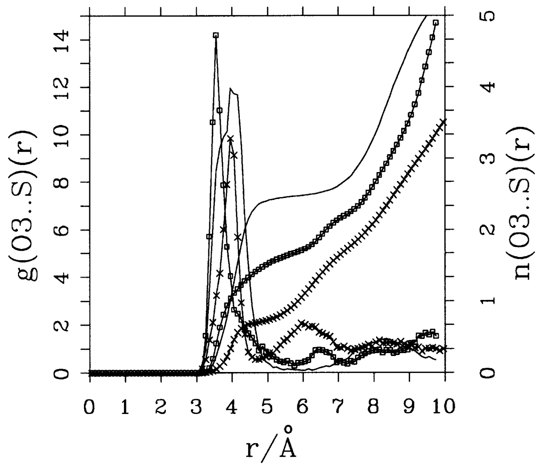

Fig. 1. The pair correlation function between the oxygen atom in the hydronium ion and the sulfur atom in the PEO sulfonic acid anion in cell4 marked with crosses, in cell2 marked with boxes and in cell3 marked with a solid line.

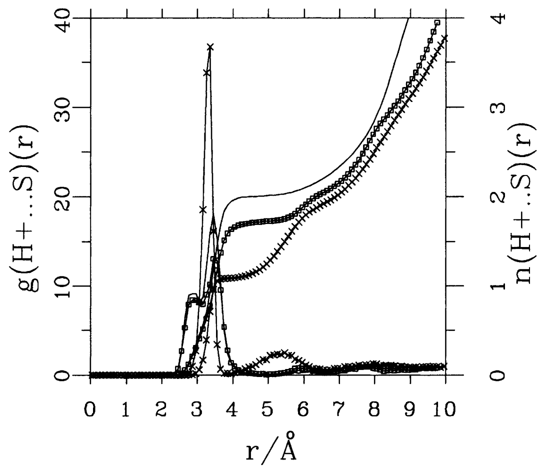

Fig. 2. The pair correlation function between the proton and the sulfur atom in the PEO sulfonic acid anion in cell4 marked with crosses, in cell2 marked with boxes and in cell3 marked with a solid line.

The pair correlation function between the oxygen atom in the hydronium ion and the sulfur atom in the PEO sulfonic acid anion is shown in Fig. 1. There is a strong peak at 4.0 Å due to the first coordination shell and a weaker peak at 6.0 Å indicating the second coordination shell. The curves of the pair correlation function for cell1, cell2 and cell3 are rather similar to the curve for cell4 concerning the first coordination shell, but a clear second coordination shell is observed only in cell1 and cell4. The coordination number in the first coordination shell is 0.7 in cell4, while it was 0.3 in cell1, 1.3 in cell2 and 2.4 in cell3 [12,15,17,31]. It has to be kept in mind that the number of the cations and sulfur atoms is the same in cell2, cell3 and in cell4 (see Table 1). Thus, the coordination number between the oxygen atom in the hydronium ion and the sulfur atom in the PEO sulfonic acid anion decreases as the amount of water increases in the system. The pair correlation function between the proton and the sulfur atom in the PEO sulfonic acid anion is shown in Fig. 2. The maximum peak is found at 3.5 Å and the second coordination shell is found at 5.4 Å. The coordination number in the first coordination shell is 1.1 in cell4, while

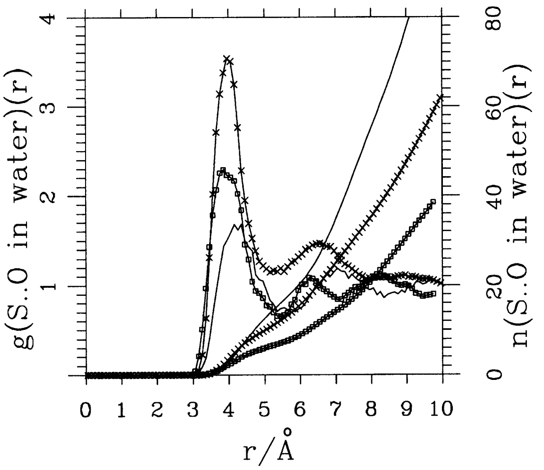

Fig. 3. The pair correlation function between the sulfur atom in the PEO sulfonic acid anion and the oxygen atom in the water molecule in cell4 marked with crosses, in cell2 marked with boxes and in cell3 marked with a solid line.

it was 0.1 in cell1, 1.7 in cell2 and 2.0 in cell3 [12,15,17,31]. Thus, the coordination between the proton and the sulfur atom in the PEO sulfonic acid anion decreases as the amount of water in the system increases. A strong coordination between the cation and the anion decreases the conductivity. The experimental studies are in accordance with the simulated studies because in the Raman spectroscopic studies of the dried but hygroscopic material, only few or no uncoordinated SO_3^- end groups were found [13].

The pair correlation function between the sulfur atom in the PEO sulfonic acid anion and the oxygen atom in the water molecule is seen in Fig. 3. The first coordination shell is found at 4.0 Å and the second at 6.5 Å. The coordination number is 19 in cell1, 11 in cell4 and 7 in cell2 in the first coordination shell [12,15,17,31]. Thus, the coordination between the sulfur atom and the oxygen atom in the water molecule increases as the amount of water increases in the system and at the same time also the conductivity increases. Experimental work has shown that the number of water molecules per sulfonic acid groups in a Nafion membrane containing 20% of the water is 12.9 [32]. This is in accordance with the simulated results for the PEO membrane in this work. It has been experimentally shown that more than 10 water molecules per sulfonic acid end group are needed in the material to gain a significant proton conductivity [33]. As there were 11 water molecules per sulfonic acid end group in cell4, it should be conducting, which was also found by calculating the conductivity.

In cell4, the pair correlation function between the oxygen atom in the hydronium ion and the ether oxygen atoms in the PEO sulfonic acid anion or PEO shows very weak coordination, the maximum value of the $g(r)$ is 0.48 corresponding to coordination number 0.3 at 3.3 Å, where the first coordination shell is seen, e.g. in cell3 [17]. The coordination number in the range 2.5–4.0 Å is 0.3 in cell1, 0.6 in cell2 and 2.4 in cell3 [12,15,17,31]. There was no coordination between the proton and the ether oxygen atoms in the polymers in cell4. This was also the situation in cell1 and in cell2, while in the water-free cell3, the coordination number between the proton and the ether oxygen atoms in the polymer chains was 2.0 at 2.5 Å [12,15,17,31]. Thus, the coordination between the cation and the ether oxygen is very weak or does not exist in the systems containing water. Also, in experimental Raman spectroscopic measurements on systems containing PEO and PEO sulfonic acid, no coordination between the cation and the ether oxygen was found [13]. Thus, a conduction mechanism, where the cation is moving inside the polymer chain from one ether oxygen to another is very unlikely for the studied amorphous PEO systems containing over 20 wt% of water. In the amorphous and water-free cell3, there was coordination between the cation and the ether oxygen, but the system was non-conducting. However, in non-aqueous PEO systems, the coordination between metal cations and the ether oxygen of the PEO chain has been found in several investigations and the transport mechanism inside the PEO chain is found to be possible [6,34].

The pair correlation between the oxygen atom in the water molecules and the ether oxygen in the polymers shows a small peak, ($g(r)$ is 0.5), at 3.6 Å, where the first coordination shell is found, e.g. for cell2. The coordination is 0.5 for cell4, 1.0 for cell1 and 1.2 for cell2 [12,15,17,31]. In the literature, the coordination number between the ether oxygen in the PEO in water is usually reported to be 1 [35]. Both cations are coordinated to water in all cells containing water. The coordination number between the oxygen atom in the hydronium ion and the oxygen atom in the water is 10 in cell1, 6.0 in cell4 and 5.5 in cell2 in the first coordination shell. The coordination number between the proton and the oxygen atom in the water in the first coordination shell is 7.0 in cell1, 3.0 in cell4 and 2.6 in cell2 [12,15,17,31]. Also, the coordination between the oxygen atoms in the water molecules was studied. The main peak was found at 3.1 Å and the coordination number is 12 in cell1, 8.0 in cell4 and 3.6 in cell2 [12,15,17,31].

4.2. *Diffusion coefficients*

The calculated diffusion coefficients of the proton, the hydronium ion, the water, the oxygen anion in the sulfonic acid anion end group and of the ether oxygen of the polymer chains in cell4 and cell1 are listed in Table 3. In cell4, Einstein diffusion was reached in all particles. The diffusion coefficient for the proton is $(0.36 \pm 0.03) \times 10^{-9}\ m^2/s$ in cell4 and $(12 \pm 2) \times 10^{-9}\ m^2/s$ in cell1 [12]. The diffusion coefficient for the hydronium ion is $(0.55 \pm 0.05) \times 10^{-9}\ m^2/s$ in cell4 and $(1.9 \pm 0.4) \times 10^{-9}\ m^2/s$ in cell1 [12]. Thus, the diffusion coefficient of the proton is about 33 times higher in cell1 than in cell4, while the diffusion coefficient of the hydronium ion is only about three times higher in cell1 than in cell4. This is illustrated in Fig. 4, which shows 900 ps long trajectories of the proton (gray) and the hydronium ion

Table 2
Collected data of coordination study between particles X and Y in cell1, cell4, cell2 and cell3 (the simulated placements and coordination numbers at the first coordination shell $n(1)$ and experimental coordination numbers are shown. The cells are in the order of decreasing amount of water)

$X\cdots Y$	Simulated			Experimental
	System studied	First coordination shell (Å)	$n(1)$	$n(1)$
Proton···ether oxygen	Cell1	–	–	–[a]
	Cell4	–	–	–[a]
	Cell2	–	–	–[a]
	Cell3	2.5	2.0	2–5[b]
Oxygen in hydronium ion···ether oxygen in polymer	Cell1	3.5	0.3	–[a]
	Cell4	3.4	0.3	–[a]
	Cell2	3.3	0.6	–[a]
	Cell3	3.3	2.4	2–5[b]
Ether oxygen···oxygen in water	Cell1	3.5	1.0	1[c]
	Cell4	3.5	0.5	1[c]
	Cell2	3.2	1.2	1–4[c]
Proton···sulfur in PEO sulfonic acid anion	Cell1	3.5	0.1	Yes[d]
	Cell4	3.5	1.1	Yes[d]
	Cell2	3.5	1.7	Yes[d]
	Cell3	3.5	2.0	
Oxygen in hydronium ion···sulfur in PEO sulfonic acid anion	Cell1	4.2	0.3	Yes[d]
	Cell4	4.1	0.7	Yes[d]
	Cell2	3.5	1.3	Yes[d]
	Cell3	4.0	2.4	
Sulfur in PEO sulfonic acid anion···oxygen in water	Cell1	4.0	19	22[e]
	Cell4	4.0	11	12[f]
	Cell2	3.8	7.0	8.5[g]
Proton···oxygen in water	Cell1	2.3	7.0	
	Cell4	2.4	3.0	
	Cell2	2.3	2.6	
Oxygen in hydronium ion···oxygen in water	Cell1	3.1	10	
	Cell4	3.1	6.0	
	Cell2	3.1	5.5	
Oxygen in water···oxygen in water	Cell1	3.1	12	
	Cell4	3.1	8.0	
	Cell2	3.1	3.6	

[a] Experimental for PEO and PEO sulfonic acid-containing material [13].
[b] Simulated for Na^+ in crystal PEO without water [6].
[c] Measured for PEO in water [35].
[d] Coordination is found in experimental work, but the coordination number is not reported [13].
[e] Measured for Nafion boiled for 1 h in water [32].
[f] Measured for Nafion containing 19.4 wt% of water [32].
[g] Measured for Nafion containing 12.9 wt% of water [32].

(black) in cell1, cell2 and cell4. A dramatic difference in the movement of the ions as a function of the concentration of water and PEO is seen. In cell1 and cell4, the cations reach the Einstein diffusion, while in cell2, the diffusion of the cations is anomalous and cell2 is non-conducting. The movement of the cations in cell2 and in cell3 is similar. In cell4, the proton and the hydronium ion are moving nearly with same speed.

The diffusion coefficient of the water molecule is $(1.11 \pm 0.09) \times 10^{-9}$ m^2/s in cell4 and $(2.13 \pm 0.04) \times 10^{-9}$ m^2/s in cell1 [12]. Thus, the diffusion coefficient of the water in cell4 was larger than the diffusion coefficients of the cations. This is probably due to interaction between the cations and the anions in the system, which decreases the speed of the movement of the cations. In cell4, the effective diffusion coefficient of the oxygen anion in the end of the PEO sulfonic acid anion is $(0.09 \pm 0.02) \times 10^{-9}$ m^2/s and of the ether oxygen in the PEO sulfonic acid anion and in the PEO is $(0.07 \pm 0.03) \times 10^{-9}$ m^2/s. These values are less than one-fifth of the diffusion coefficients of the cations. Thus, it is unlikely that the cations would move only together with the polymers in the matrix. However, the values of the diffusion coefficients of the cations are significantly smaller in cell4 compared to the values in cell1, and this shows the

Table 3
The average values for the calculated diffusion coefficients of hydronium ion (H_3O), proton (H^+), water (H_2O), the oxygen anion in the PEO sulfonic acid anion (O −), and the ether oxygen in the PEO and in the PEO sulfonic acid anion (OC), in cell1 and cell4 [12]

Penetrant	Cell	Total simulation time (ps)	Diffusion coefficient (10^{-9} m^2/s)	Literature values in pure water (10^{-9} m^2/s)
H^+	Cell1	1000	12±2	9.31
	Cell4	2000	0.36±0.03	
H_3O	Cell1	1000	1.9±0.4	9.31
	Cell4	2000	0.55±0.05	
H_2O	Cell1	1000	2.13±0.04	2.26
	Cell4	2000	1.11±0.09	
O^-	Cell1	1000	0.6±0.1	
	Cell4	2000	0.09±0.02	
OC	Cell1	1000	0.26±0.03	
	Cell4	2000	0.07±0.03	

hindering effect of the polymer matrix to the movement of the cations.

4.3. Conductivity and interactions between ions

Fig. 5 shows the total correlation function of ions displacement including the MSD of ions and the correlations between different ions for two separate samples of cell4. The values of the conductivity calculated from the slopes of these curves using formula (3) are 2.6×10^{-2} and 2.5×10^{-2} S/cm with an error of about 0.1×10^{-2} S/cm. In the experimental work, the conductivity of the PEO

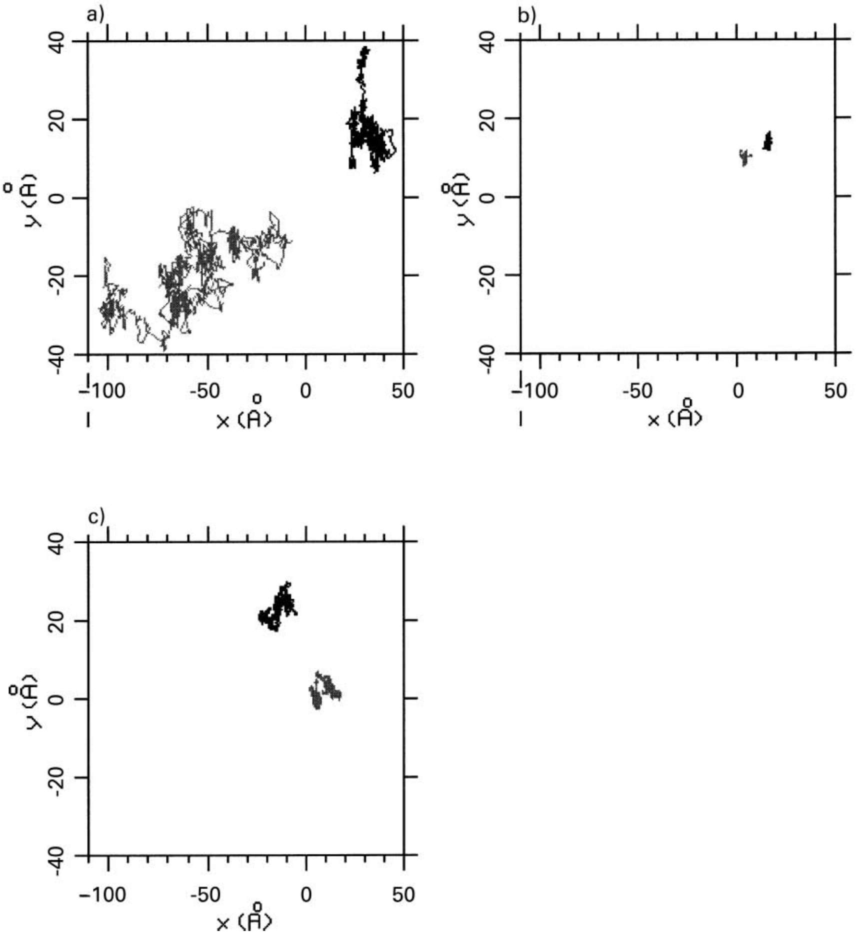

Fig. 4. The 900 ps long trajectories of one proton (marked with gray line) and of one hydronium ion (marked with black line): (a) in cell1, (b) in cell2 and (c) in cell4.

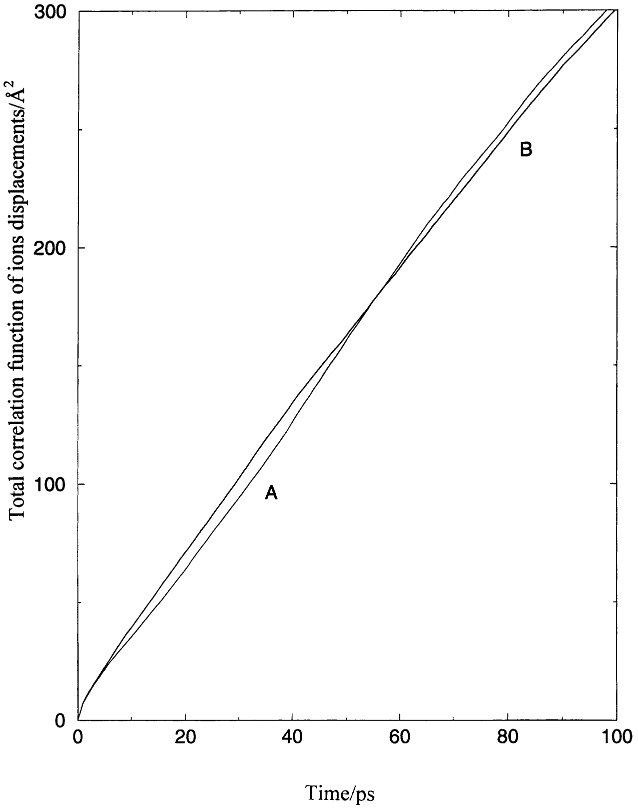

Fig. 5. The total correlation function of ions displacement including the MSD of the ions and the correlations between different ions for two different cells of cell4 (marked A and B).

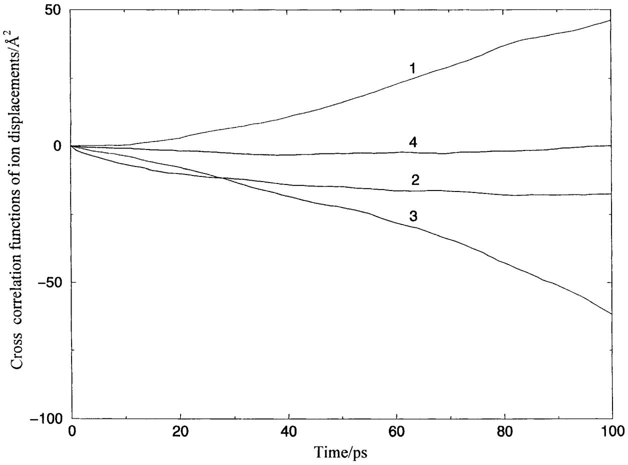

Fig. 6. Interactions between the ions in cell4. The interaction between the proton and the hydronium ion is marked with 1, between the proton and the oxygen atom in the sulfonic acid anion group is marked with 2, between the hydronium ion and the oxygen atom in the sulfonic acid anion group is marked with 3 and between the oxygen atoms in the sulfonic acid anion group is marked with 4.

sulfonic acid anion and PEO containing membrane measured by impedance measurements was 1.5×10^{-3} S/cm at relative humidity (RH) 75.3% and 1.5×10^{-5} S/cm at RH 38.2% [13]. Thus, the increase in the humidity from 38.2 to 75.3% increased the measured conductivity by a factor of 100. The water content of the real membrane was not measured, and thus, it is impossible to compare the exact values of the measured and simulated conductivity. For Nafion boiled for 1 h, the water content is found to be about 30% [32]. Thus, it is possible that the simulated cell4 contains more water than the measured sample at RH 73.5%, and thus, it is reasonable that the conductivity of cell4 is larger than the conductivity of the measured sample. Also, the fact that in the used model, the proton can move from one water molecule to another without creating and breaking bonds, can lead to a higher simulated value of the conductivity compared to the measured value. However, the simulated value predicts that the material is conducting as also found in the measurements. As expected, in cell1, which contained one PEO sulfonic acid in water, the value of the conductivity (12 S/m) is remarkably higher than that in cell4 [12]. A very interesting observation is that in cell1, the conductivity was mainly due to the diffusion of the proton, while in cell4, the diffusion coefficients of the proton and the hydronium ion were of the same order of magnitude. Thus, in cell1, the hopping mechanism seems to dominate, while in the cell4, both the hopping and the classical diffusion mechanisms are important.

Interactions between ions in cell4 are seen in Fig. 6. The interactions are relatively small, less than 20% of the total correlation function of ions displacement in the range (less than 100 ps) used for the calculation of the conductivity. In cell4, the correlations between the negatively charged anions were the smallest interactions as also in cell1 [12].

5. Conclusions

Amorphous systems called cell4 consisting of PEO sulfonic acid anions, PEO, cations and 35 wt% water were studied by molecular modeling. The results were compared with that obtained by the experimental work for similar materials and by molecular modeling for previously studied similar systems containing different amounts of water and polymers [12–17]. To study the mechanisms of the proton conductivity in the system, two cations were used. The hydronium ion was used to study the classical diffusion of the hydronium ion and a particle called proton was used to study the proton hopping mechanisms. The coordinations between the cations and the anions were studied by calculating the pair correlation functions and coordination numbers. The coordinations found were in accordance with the experimental and simulated results obtained for similar systems. The coordination between the sulfonic acid end group in the PEO sulfonic acid anion and cations decreased as the amount of water increased in the system. In the simulations, the coordination number between the sulfonic acid end group in the PEO sulfonic acid anion and the oxygen atom in the water molecules was more than 10 for systems containing 35 wt% or more water.

These systems, cell1 and cell4, were found to be conducting while systems containing only 20 wt% water or less were found to be non-conducting (cell2 and cell3). Experimentally, it has been found that to gain significant proton conductivity, there should be at least 10 water molecules per sulfonic acid end groups. Thus, the simulated and experimental results are in good agreement. The coordination between the cations and the ether oxygen in the PEO and the PEO sulfonic acid was remarkable only in the water-free system (cell3), which was non-conducting. Thus, the conduction mechanism, where the cations would move inside the PEO chain from one ether oxygen atom to another cannot be significant in the systems studied. The diffusion coefficients for the proton, the hydronium ion, the water molecules, the oxygen anion in the end group of the PEO sulfonic acid anion and for the ether oxygen in the PEO sulfonic acid anion and the PEO were calculated. All these particles reached the Einstein diffusion in the studied system containing 35 wt% water. From the diffusion coefficient, it could be concluded that in the system containing 90 wt% water (cell1), the hopping mechanism dominated, while in the system containing 35 wt% water, both the hopping and the classical diffusion mechanisms were important. In the systems containing less than 20 wt% water (cell2 and cell3), the movements of the cations were very closely associated with the dynamical relaxation modes of the polymer chain and the systems were not proton-conducting. The polymer matrix was found to prevent the movement of the cations also in the system containing 35 wt% water (cell4), but the effect was smaller than in systems containing less water (cell2 and cell3). The conductivity was calculated for cell4. The simulated value of the conductivity was a little larger than the experimental, which can be explained by the facts, that the amount of water in the experimental system was not known, and thus, the systems cannot be compared directly, and the used model does not account for the breaking and the creating of bonds between the proton and oxygen atom in the water molecule. However, the model can be used to estimate whether a material is conducting or non-conducting. The model also gives an interesting possibility to study the mechanisms of the proton conductivity on the molecular level.

Acknowledgements

We would like to thank the Center for Scientific Computation Ltd, Espoo, Finland for the calculation capacity and Dr David Rigby, Fiona Case and Dr Huai Sun from MSI for discussions. This work was supported by The Academy of Finland (MATRA).

References

[1] Armand M, Chabagno JM, Duclot M. In: Second International Meeting on Solid Electrolytes, 1978 September 20–22; St. Andrews, UK.
[2] Cowie JMG. Polym Int 1998;47:20.
[3] Scrosati B. Polym Int 1998;47:50.
[4] Hashmi SA, Latham RJ, Linford RG, Schlindwein WS. Polym Int 1998;47:28.
[5] Allcock HR, Sunderland NJ, Ravikiran R, Nelson JM. Macromolecules 1998;31:8026.
[6] Neyertz S. Computer simulation of PEO-based polymer electrolytes. Uppsala (Sweden): Acta Universitatis Upsaliensis; 1995.
[7] Borodin O, Smith GD. Macromolecules 1998;31:8396.
[8] Londono JD, Annis BK, Habenschuss A, Borodin O, Smith GD, Turner JZ, Soper AK. Macromolecules 1998;31:8026.
[9] Kreuer KD. Chem Mater 1996;8:610.
[10] Gottesfeld S, Zawodzinski TA. In: Alkire RC, Gerischer H, Kolb DM, Tobias CW, editors. Advances in electrochemical science and engineering, 5. New York/Weinheim: Wiley/VCH, 1997. p. 197.
[11] Müller-Plathé F. Acta Polym 1994;45:259.
[12] Ennari J, Elomaa M, Sundholm F. Polymer 1999;40:5035.
[13] Herranen J, Kinnunen J, Mattsson B, Rinne H, Sundholm F, Torell L. Solid State Ion 1995;80:201.
[14] Ennari J, Neelov I, Sundholm F. Comput Theor Polym Sci 2000;10:403.
[15] Ennari J, Neelov I, Sundholm F. Polymer 2000;41:4057.
[16] Ennari J, Elomaa M, Neelov I, Sundholm F. Polymer 2000;41:985.
[17] Ennari J. Atomistic molecular modeling of PEO sulfonic acid anion based polymer electrolytes. University of Helsinki; 2000 (http://ethesis.helsinki.fi/julkaisut/mat/kemia/vk/ennari/).
[18] Agmon N. Chem Phys Lett 1995;244:456.
[19] Trunkerman M, Laasonen K, Sprik M, Parrinello M. J Chem Phys 1995;103(1):150.
[20] Eikerling M, Kornyshev AA, Stimming U. J Phys Chem B 1997;101(50):10807.
[21] Allen MP, Tildesley DJ. Computer simulation of liquids. Oxford, UK: Clarendon Press, 1987.
[22] INSIGHT II. User guide. San Diego: MSI; 1995.
[23] Sun H. J Comp Chem 1994;15:752.
[24] Sun H. Macromolecules 1995;28:701.
[25] Hill J-R, Sauer J. J Phys Chem 1994;98:1238.
[26] Maple JA, Hwang MJ, Stockfisch TP, Dinur U, Waldman M, Ewig CS, Hagler AT. J Comp Chem 1994;15:162.
[27] Sun H, Mumby SJ, Maple JR, Hagler AT. J Am Chem Soc 1994;116:2978.
[28] Ennari J, Hamara J, Sundholm F. Polymer 1997;38:3733.
[29] Tosi MP. Solid State Phys 1964;16:107.
[30] Ding HQ, Karasawa N, Goddard WA. J Chem Phys 1992;97:4309.
[31] Ennari J, Neelov I, Sundholm F. Polymer 2000;41:2149.
[32] Sondheimer SJ, Bruce NJ, Fyte CA. J Macromol Sci, Rev Macromol Chem Phys 1986;C26(3):361.
[33] Hietala S, Homberg S, Näsman J, Ostrovskii D, Paronen M, Serimaa R, Sundholm F, Torell L, Torkkeli M. Angew Makromol Chem 1997;253:151.
[34] Catlow CRA, Mills GE. Electrochim Acta 1995;40:2057.
[35] Lüsse S, Arnold K. Macromolecules 1996;29:4251.