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Molecular dynamics simulation of the structure of an ion-conducting PEO-based solid polymer electrolyte

Jaana Ennari*, Lars-Olof Pietilä[1], Ville Virkkunen, Franciska Sundholm

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

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Abstract

Proton-conducting solid polymer electrolyte containing poly(ethylene oxide) sulfonic acid anions (PEO) cations and 35 wt% of water is constructed by atomistic molecular modelling. The structure of the PEO sulfonic acid anions and PEO was studied by calculating the dihedral angle distributions, intramolecular pair correlation functions between the carbon atoms and ether oxygen atoms and by performing the conformational triads population analysis and dimension analysis. The results were compared with the results obtained for similar non-conducting systems and for the system containing only one PEO sulfonic acid anion in water. Some differences were found in the structures. However, the differences in the structures of the polymers were not able to explain the conductivity behaviour of the systems. Instantaneous coordination of cations was studied to get a detailed view of the local environment of the cations. The local environment of the cations shows many variations in the studied systems. Small microphase separation in the conducting system was found. © 2002 Published by Elsevier Science Ltd.

Keywords: Poly(ethylene oxide) sulfonic acid; Polyelectrolyte; Modelling

1. Introduction

Polymer-based conducting materials have stimulated considerable attention in the field of solid polyelectrolytes during the last two decades due to their potential applications in electrical vehicles, electronic equipments and medical devices [1–6]. The traditional attempts in developing polymer electrolytes are to dissolve salts in a polymer matrix like poly(ethylene oxide) PEO [7–11]. Recently a new group of materials, namely the proton conducting polymers, have been studied because they are potentially useful as solid electrolytes in low temperature fuel cells for zero emission vehicles and electrochemical devices [12–17]. Many experimental attempts have been made to develop polymer electrolytes, but the experimental work has been very slow. Molecular modelling offers a new way to accelerate the development of new materials. Molecular modelling is not yet widely used to study proton-conducting polymers. This is due to the lack of force fields containing parameters both for ions and polymers and also due to the complexity of the proton conduction phenomena [18]. However, a force field that is able to handle both ions and polymers and a model to simulate the hopping mechanism in a general way has been developed recently [19]. We have recently reported results of three different simulated materials containing different amounts of PEO sulfonic acid anion ($^{-}O_3SCH_2CH_2CH_2$-$O(CH_2CH_2O)_4CH_2CH_2CH_2SO_3^{-}$) cations, water and PEO [19–22]. The water contents of these materials were 0, 20 or 90 wt%. Only the material containing 90 wt% of water was found to be conducting [19]. The materials are amorphous since the conductivity in these kinds of materials is associated with the amorphous regions. In addition we have made a fourth material containing 35 wt% of water and this material is found to be conducting [23]. We now report the study of the structure of this material. The PEO-based materials have been experimentally studied [12]. Ionic conductivities up to 1.5×10^{-3} S/cm were reached and the studied PEO sulfonic acid ($\langle M_w \rangle = 436$ g/mol) was found to be amorphous according to the polarising microscope investigations [12]. The conductivity has been experimentally found to be very much dependent on the water content of the material.

The primary aim of this work is to study the structure of the ion conducting 35 wt% water-containing system and

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

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

[1] Present address: VTT Chemical Technology, P.O. Box 1401, FIN-02044 VTT, Finland.

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compare it to the structure of non-conducting materials. The main question is, has the large water content (35 wt%) changed the structure of the polymer matrix so that the structure can promote conductivity? Other possibility is, that higher conductivity in the 35 wt% water-containing system is mainly due to other factors, like the higher dielectric constant of the material having more water or forming of larger water clusters around the end groups in the more water containing system compared to the system having only 20 wt% of water. This question is very interesting also because the structure of the PEO backbone and a model molecule, its conformer fraction $CH_3OCH_2CH_2OCH_3$ (1,2-dimethoxyethane) has been extensively studied both experimentally (NMR, electron diffraction, ED, IR, SANS) and by molecular modelling and the structure has been reported to vary in different conditions [7,8,24–31]. The most interesting feature in the spatial configuration of the PEO (and DME) is, that the dihedral angle OCCO prefer the *gauche* conformation to the *trans* form (i.e. *gauche* effect).

2. Theory

To study the structure of the PEO sulfonic acid anion intramolecular pair correlation functions, i.e. radial distribution functions were calculated to get the relative density of atoms pairs separated by a certain distance.

The intermolecular pair correlation functions between individual cations and atoms are calculated to study the instantaneous coordinations of cations. The coordination numbers were calculated by the equation

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

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

The average values of the radius of gyration and end-to-end distance were calculated to study the dimensions of the PEO sulfonic acid anion. The characteristic ratio as a limit of C_n as $n \to \infty$ is defined [32]

$$C_n \equiv \langle r^2 \rangle / \sum_{i=1}^{n} l_i^2 \tag{2}$$

where $\langle r^2 \rangle$ is the mean square end-to-end distance of the chain, n is the number of bonds and l_i is the length of the bonds.

3. Computational details

The calculations were made on one Octane and two Silicon Graphics Indigo 2 workstations of the Laboratory of the Polymer Chemistry at the University of Helsinki and on the SGI Power Challenge computers of CSC (Centre for Scientific Computation Ltd, Espoo, Finland). The programs InsightII and Discover version 4.0.0P from Accelrys Inc. (former Molecular Simulations Inc. MSI) were used and in addition some codes were written to perform the conformational triad population analysis. The studied 3D system called cell4 consists of four PEO sulfonic acid anions ($^{-}O_3SCH_2CH_2CH_2O(CH_2CH_2O)_4CH_2CH_2CH_2SO_3^{-}$) eight cations, 150 water molecules and one PEO molecule with degree of polymerisation 60 (Fig. 1). All the cell4 samples were cubic and their volumes varied from 12,125.210 to 12,098.886 Å^3 and densities from 1.0274 to 1.0296 cm^3. We have previously reported results concerning the structures of systems (Figs. 2,3 and 4) containing one PEO sulfonic acid, one hydronium ion, one proton and 220 water molecules (cell1) of systems containing four PEO sulfonic acid anions, four hydronium ions, four protons, 74 water molecules and one PEO molecule with degree of polymerisation 60 (cell2) and of systems containing four PEO sulfonic acid anions, four hydronium ions, four protons and one PEO molecule with degree of polymerisation 60 (cell3) [20–22]. The water content of cell1 is 90 wt%, of cell4 is 35 wt%, of cell2 is 20 wt% and cell3 is water-free.

The PCFF force field [33–37] has been found to be suitable for modelling the PEO sulfonic acid [38]. Parameters for the ions were added to the PCFF force field and the new force field is called NJPCFF force field. The NJPCFF force field was used in all calculations. We have previously studied the dynamic behaviour of the ions in cell4 [23]. For that study the density of three similar systems were calculated and found to be about 1.0285 cm^3.

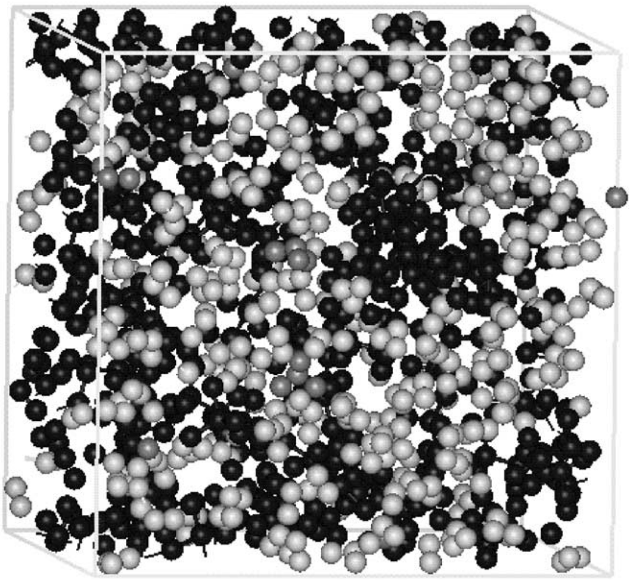

Fig. 1. A snapshot from the MD simulation of cell4. The polymers are marked with black, the water molecules are marked with white and the cations are marked with grey.

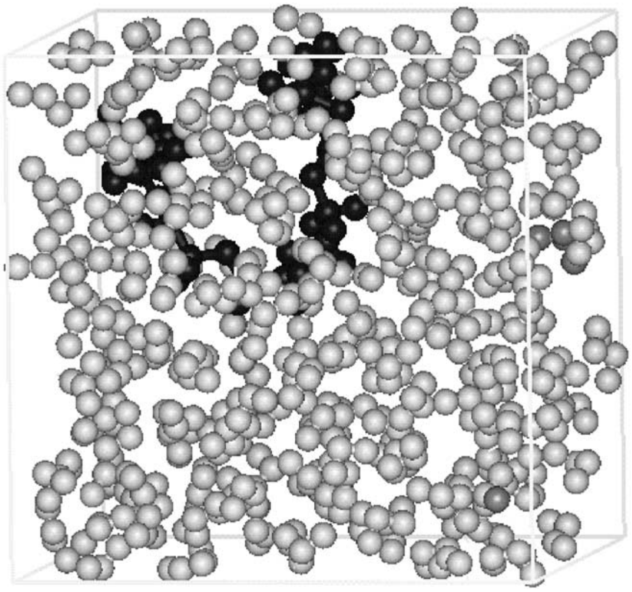

Fig. 2. A snapshot from the MD simulation of cell1. The polymers are marked with black, the water molecules are marked with white and the cations are marked with grey.

To get better statistics for the present study 10 new cells were constructed by the amorphous_cell builder by MSI using this density. The 10 cells were first minimised using molecular mechanics methods (Steepest descents and Conjugate gradients) until the maximum derivative reached the value 10 kcal/(mol Å). Then, a 100 ps long dynamics runs with the NVT ensemble at 298 K were made for each cell. For three cells having the lowest energy, an additional 500 ps long dynamics runs with the NVT ensemble at 298 K were made. The cell multipole method (CMM) was used in all NVT the calculations and the time step was 1 fs. The previously made two cells and three new cells were used to study all the calculated properties except the instantaneous coordination to get better statistics for the structure of the anion. This was done, because we have previously seen, that better statistics are obtained when many small trajectories from different starting structures are used instead of a long trajectory from one starting structure [21]. The final properties were calculated utilising only the 200 last ps from each trajectory.

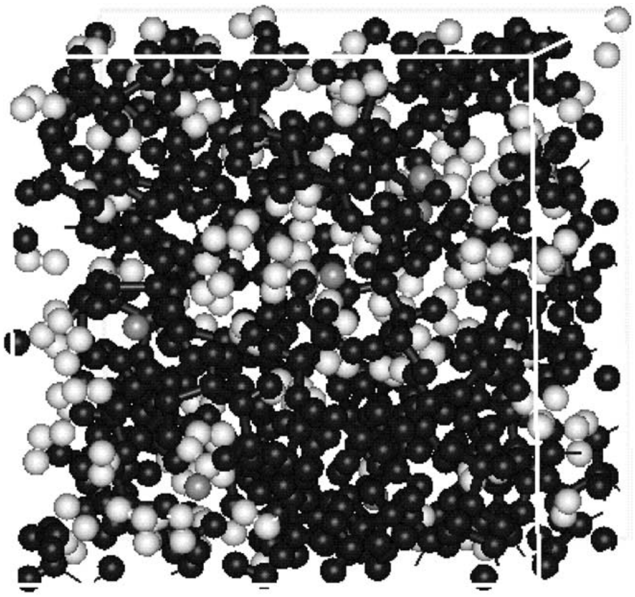

Fig. 3. A snapshot from the MD simulation of cell2. The polymers are marked with black, the water molecules are marked with white and the cations are marked with grey.

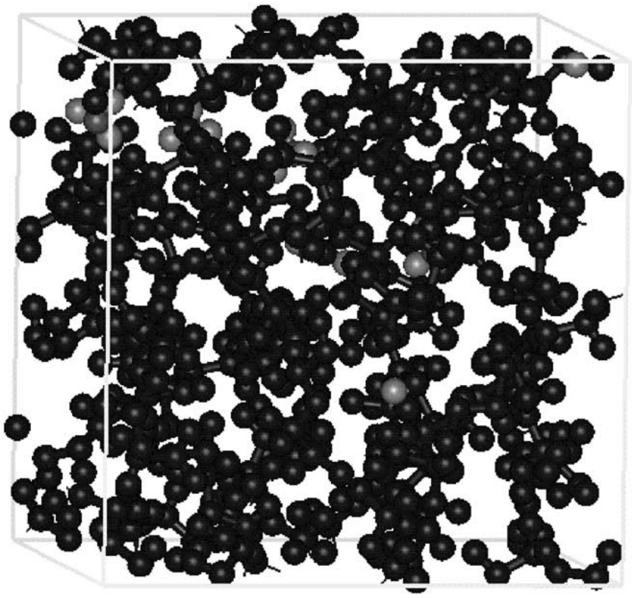

Fig. 4. A snapshot from the MD simulation of cell3. The polymers are marked with black, the water molecules are marked with white and the cations are marked with grey.

4. Results and discussion

4.1. Dihedral angle study

The structure of the PEO sulfonic acid anion and the PEO was studied by calculating the OSCC, SCCC, CCCO, CCOC and OCCO dihedral angle distributions. The mean values for the percentages of *trans* conformations are listed in Table 1. The *trans* conformation (T) is in the present work defined to cover the dihedral angles from −60 to 60°, while the *gauche* minus conformation (G^-) covers the dihedral angles from −180 to −60° and the *gauche* plus conformation (G^+) from 60 to 180°.

The average of the OSCC dihedral angle distribution calculated for the PEO sulfonic acid anion in cell4 is in Fig. 5a. Due to the symmetry in the sulfonic acid anion end group three maxima can be detected in Fig. 5a: the *gauche* plus conformation around −120°, the *trans* conformation around 0° and the *gauche* plus conformation around +120° with nearly similar probabilities. This applied also for the OSCC dihedral angles in PEO sulfonic acid anion in cell1, cell2 and cell3 [21,22]. The average of the SCCC dihedral

Table 1
Mean values of the percentage of *trans* states in the dihedral angle distribution of the PEO sulfonic acid anion (anion), the PEO sulfonic acid (acid) or of PEO

% of *trans* states in dihedral angle, *a*	Cell1[a]	Cell4[b]	Cell2[c]	Cell3[b]	Anion in vacuum	Acid in vacuum
a(OCCO) in anion	16	48	32, 39	34	88	
a(OCCO) in PEO		49	40, 36	43		
a(OCCO) in acid						35
a(CCOC) in anion	85	80	54, 57	69	82	
a(CCOC) in PEO		81	66, 66	79		
a(CCOC) in acid						65
a(OSCC) in anion	33	33	33, 33	33	33	
a(OSCC) in acid						33
a(SCCC) in anion	95	86	71, 55	77	55	
a(SCCC) in acid						61
a(CCCO) in anion	31	43	34, 24	28	53	
a(CCCO) in acid						12

[a] Calculated using the group-based summation method.
[b] Calculated using the CMM method.
[c] The first value is calculated using the CMM method and second using the Ewald summation method.

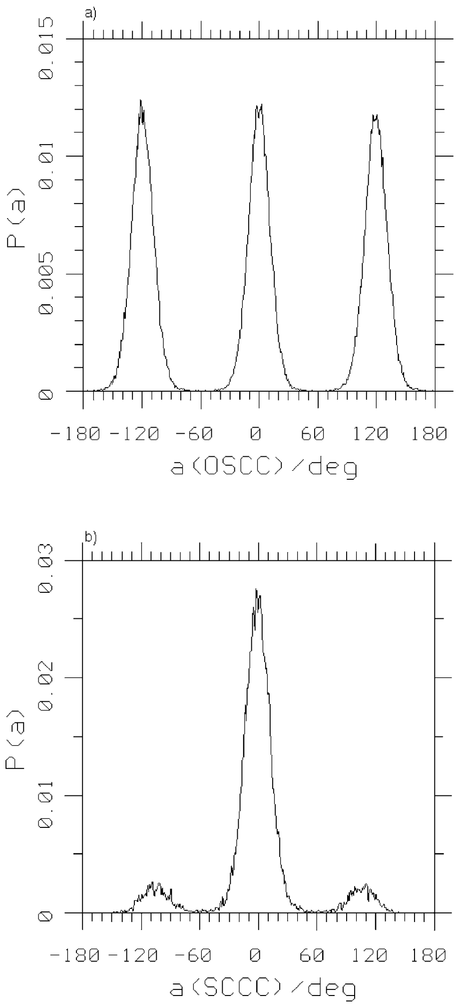

Fig. 5. (a) The average of the OSCC dihedral angle distribution, (b) the average of the SCCC dihedral angle distribution, calculated for the PEO sulfonic acid anion in cell4.

angle distribution calculated for the PEO sulfonic acid anion in cell4 was almost completely in *trans* conformation (Fig. 5b) which was also the case in cell1, cell2 and cell3 [21,22]. The maxima of the *gauche* conformations are found at the same places (about at −110 and 110°) in all cells studied both in SCCC and in CCCO dihedral angle distributions (Figs. 5b and 6). In the average of the CCCO dihedral angle distribution calculated for the PEO sulfonic acid anion in cell4 the *trans* conformation is slightly more populated (the percentage of *trans* conformation is 43) than the *gauche* conformations (Fig. 6). In cell1, cell2 and in cell3 the mean values for the percentages of *trans* conformations are about 30 [21,22]. However, because of the small amount of CCCO dihedral angles in the system studied, the deviation in the population of the *trans* states in cell4 and in other cells can be caused by the small statistics used in the calculations.

The average of the OCCO dihedral angle distribution in cell4 is similar for the PEO and the PEO sulfonic acid anions. The mean value of the *gauche* minus conformation is at −110°, of the *trans* conformation is at 0° and of the

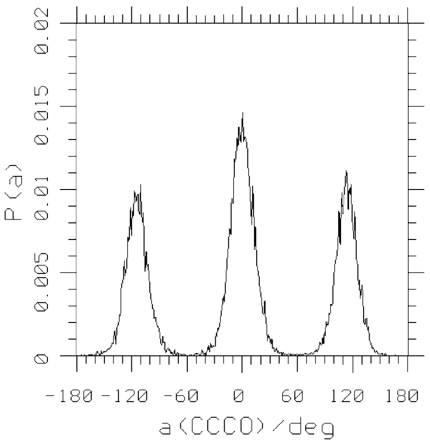

Fig. 6. The average of the CCCO dihedral angle distribution calculated for the PEO sulfonic acid anion in cell4.

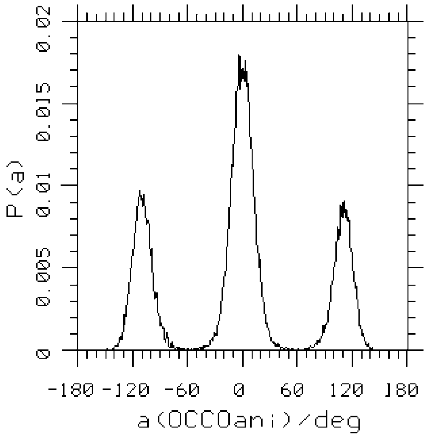

Fig. 7. The average of the OCCO dihedral angle distribution calculated for the PEO sulfonic acid anion in cell4.

gauche plus conformation is at 110° (Fig. 7). Similar shifts in mean values of the *gauche* states from the ± 120° was also seen in all other cells [21,22]. The probability of the *trans* conformation in the PEO sulfonic acid anion and PEO is about 48% in cell4, which is of the same order of magnitude as in cell2 and cell3 (32–43%) (Table 1). However, the probability of the *trans* conformation of the OCCO dihedral angle distribution of the PEO sulfonic acid anion in the system containing 90 wt% of water is about 16% indicating the so-called *gauche* effect, which is well known for the PEO in water [8]. The *gauche* effect is the origin of the helix structure of the crystalline PEO [39], but it is also detected in the amorphous PEO [40]. It is known that, e.g. the temperature [41], the polarity [42], dielectric constant and the hydrogen bonding character of the surrounding media have a strong effect on the conformations of the PEO [30,43]. In the systems studied the polymer matrix moderates the *gauche* effect in cell4, which is conducting, as much as in cell2, which was not conducting, and thus the *gauche* effect cannot cause the ion conductivity in cell4. Also the mechanism where the cations would move inside the PEO helix was not significant in cell4, because no remarkable coordination between the ether oxygen in PEO chain and the cations was found [23]. For the CCOC dihedral angle the probability of *trans* conformation was 80% for the PEO sulfonic acid anion and 81% for the PEO (Fig. 8 and Table 1). The probability of the *trans* conformation is dominating as also in all other cells studied [21,22]. A shift in the *gauche* conformation is found, the centre of the gauche peaks are at ± 100°, a similar shift was also found in other cells studied [21,22].

Thus, no clear effect was found in the dihedral angle study of the backbone to explain why cell4 is conducting and cell3 not. Some more *trans* conformations were found in cell4 compared to cell3 in OCCO, CCOC and SCCC dihedral angle distributions but the difference is not significant when the error of the calculation (about 15%) is taken into account.

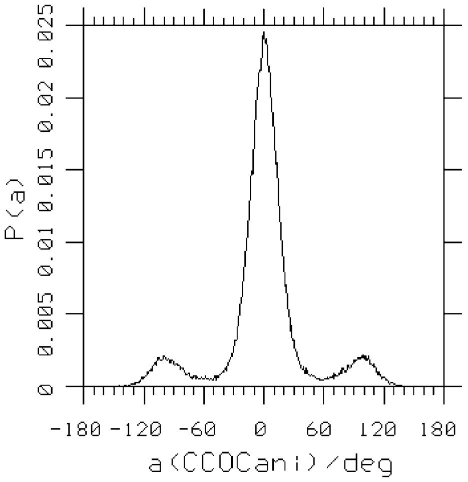

Fig. 8. The average of the CCOC dihedral angle distribution calculated for the PEO sulfonic acid anion in cell4.

4.2. Pair correlation study

The structure of the polymers is also studied by plotting the intramolecular pair correlation function between the carbon atoms, the ether oxygen atoms and between the carbon and oxygen atoms in the PEO and PEO sulfonic acid anion in cell4 (Figs. 9–11).

From Fig. 9 it can be seen, that the intramolecular pair correlation function between the carbon atoms in the PEO sulfonic acid anion (marked with a solid line) and in the PEO (marked with boxes) are very similar. There is one very high peak at 1.55 Å corresponding to the average bond length between the carbon atoms in the polymers. The calculated average bond length between carbon atoms is 1.54 Å for PEO sulfonic acid anion and 1.56 Å for the PEO in the system studied. The peak at 2.45 Å corresponds to the

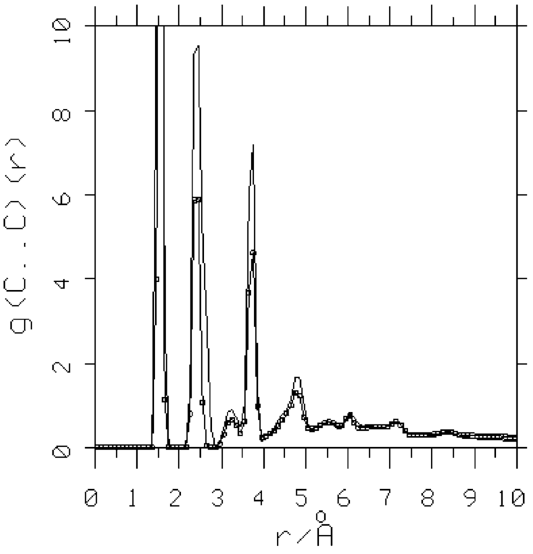

Fig. 9. The intramolecular pair correlation function between the carbon atoms in the PEO sulfonic acid anion (marked with a solid line) and in the PEO (marked with boxes).

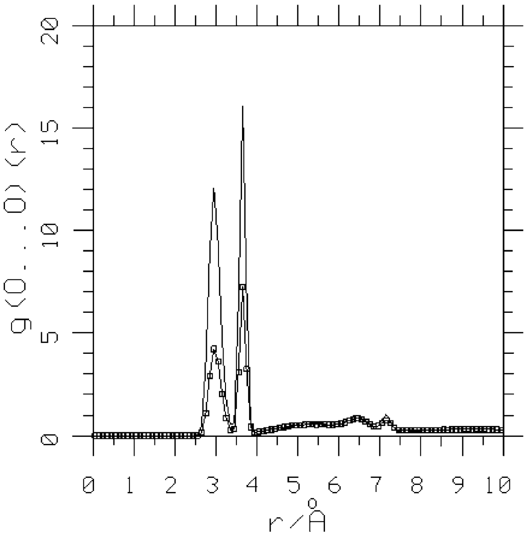

Fig. 10. The intramolecular pair correlation function between the ether oxygen atoms in the PEO sulfonic acid anion (marked with a solid line) and in PEO (marked with boxes).

distance 2.3 Å between two carbon atoms, which are both bonded to the same ether oxygen. In the case of the PEO sulfonic acid anion (solid line in Fig. 9) this peak is broader than for the PEO. This is due to the distance of two carbon atoms bonded to a carbon in the ends of the anion before the sulfonic acid anion group (2.6 Å) which is larger than the distance between two carbon atoms bonded to same ether oxygen (2.3 Å). The small peak at 3.25 Å corresponds to the distance of the carbon atoms in the *gauche* conformation of the COCC dihedral angle. At 3.75 Å a peak is seen corresponding to the distance of the carbon atoms in the *trans* conformation of the COCC dihedral angle. The peak at 3.75 Å is much larger than the peak at 3.25 Å indicating that the *trans* conformation is more populated in the PEO sulfonic acid anion and in the PEO in the system studied than the *gauche* states, this was also seen from the dihedral angle analysis (Table 1). The most intensive peak after 4 Å is at 4.8 Å. This peak corresponds to distance of the first and last carbon atoms (C1 and C4) in two *trans* conformation in succession, TT along the C1–C–O–C–C4 sequence (calculated average is 4.9 Å). In the used force field peaks indicating the distance between carbons C1 and C4 along the C1–O–C–C4 sequence in TG^{+} or TG^{-} is at about 4.5 Å, in G^{+}G^{+} or G^{-}G^{-} is at about 4.3 Å and for G^{+}G^{-} is at about 3.28 Å (in the calculations the dihedral angle *gauche* state is ± 110° for OCCO and ± 100° for COCC and *trans* states 0°). Some population is seen at these distances indicating the possibilities of these states, but because the dihedral angles can vary a lot and different conformations can cause correlation or peaks at the same places, to get definitive conclusions concerning conformations in succession a triad population analysis must be made.

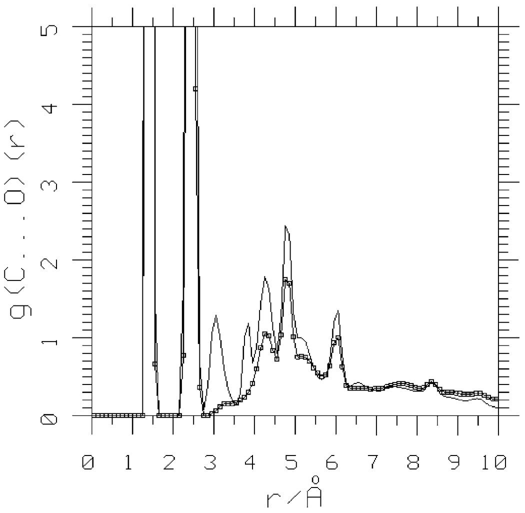

Fig. 11. The intramolecular pair correlation function between the carbon atoms and ether oxygen atoms in the PEO sulfonic acid anion (marked with a solid line) and in PEO (marked with boxes).

The patterns of the plots in the intramolecular pair correlation function between the ether oxygen atoms in the PEO sulfonic acid anion and in PEO are similar (Fig. 10). Two main peaks are seen. The peak at 3.00 Å corresponds to the distance of the oxygen atoms in the *gauche* conformation of the OCCO dihedral angle and the distance of oxygen atoms O1 and O3 in the O1–C–C–O2–C–C–O3 sequence in the two *gauche* plus states and two *gauche* minus states (e.g. G^{-}G^{+}G^{+}G^{-} at about 3.09 Å). The peak at 3.70 Å corresponds to the distance of the ether oxygen atoms in the *trans* conformation of the OCCO dihedral angle. The peak at 6.45 Å corresponds to the distance O1 and O3 along the O1–C–C–O2–C–C–O3 sequence having three *trans* states and one *gauche* conformation in succession (e.g. G^{+}TTT at about 6.40 Å). The peak at 7.46 Å corresponds to the distance between the O1 and O3 having four *trans* conformations in succession along the O1–C–C–O–C–C–O3 sequence (TTTT at about 7.30 Å). The above-mentioned states seem to dominate. However, also other states in succession occur, since a broad line is seen in Fig. 10 at 5.25 Å corresponding to the distance between O1 and O3 along the O1–C–C–O2–C–C–O3 sequence having other combinations, e.g. two *trans* and two *gauche* conformations in succession (e.g. G^{+}TTG^{+} or G^{-}TTG^{-} at about 5.70 Å) or two *trans* and one *gauche* plus and one *gauche* minus states (e.g. G^{-}TTG^{+} at about 4.8 Å) or four *gauche* states (e.g. G^{+}G^{+}G^{+}G^{+} at about 5.92 Å) or three *gauche* plus and one *gauche* minus state (e.g. G^{+}G^{+}G^{-}G^{+} at about 4.79 Å or TG^{+}G^{+}G^{-} at about 4.42 Å).

The intramolecular pair correlation function between the carbon atoms and ether oxygen atoms in the PEO sulfonic acid anion and in PEO is shown in Fig. 11. The strongest peak is at 1.5 Å corresponding the average bond length between the carbon and the ether oxygen atoms. The peak at 2.5 Å corresponds to the distance between the carbon atoms and the ether oxygen atoms, which are separated by a carbon in the PEO chain. The third peak at 3.1 Å corresponds to the distance of the carbon and oxygen atoms in the *gauche* conformations of CCCO dihedral angle in the end of the anion and to the distance between the C1 and O2 atoms along the C1–O–C–C–O2 sequence in the G^{+}G^{-} or G^{-}G^{+} states (e.g. G^{+}G^{-} at about 3.2 Å) in the polymer backbone. The fourth peak at 3.8 Å corresponds to the distance of the carbon and oxygen atoms in the *trans* conformation of CCCO dihedral angle in the end of the anion and to the distance between the C1 and O2 atoms along the C1–O–C–C–O2 sequence in G^{+}G^{+} or G^{-}G^{-} states (at about 3.8 Å). The peak at 4.3 Å corresponds to the distance between the C1 atom and O2 atom along the C1–O–C–C–O2 sequence in one *trans* and one *gauche* minus or plus state (e.g. TG^{+}, G^{+}T, TG^{-} or G^{-}T at about 4.3 Å). The peak at 5.1 Å corresponds to the distance between the C1 atom and O2 atom along the C1–O–C–C–O2 sequence in two *trans* conformations in succession (TT at about 5.0 Å). The peak at 6.0 Å corresponds to the distance the C2 atom and O2 atoms along the C2–C–O–C–C–O2 in three *trans* states (TTT 6.0 Å). The peak at 4.75 Å corresponds to the distance the C2 and O2 atoms along the C2–C–O–C–C–O2 in other than three *trans* states in succession (e.g. TTG^{-} at about 4.6 Å or TG^{+}G^{+} at about 4.7 Å). Thus several different conformations in succession are seen.

4.3. Conformational triads population analysis

To study the local structure of the polymers a conformational triads population analysis was made along the C–C–O–C–C–O sequence and along the C–O–C–C–O–C sequence for the PEO sulfonic acid anion and for the PEO, respectively, in all cells. The results are collected in Table 2.

The population analysis of conformational triads along the C–C–O–C–C–O sequence shows a large variation of the states. However, some states are dominating. The results agree with the results obtained from the intramolecular pair correlations. The most significant conformations in cell1, cell3 and cell4 are the TTT, TTG^{+} and TTG^{-} conformations. In cell2 the TTG^{+} and TTG^{-} conformations are also dominating, but the TTT states are dominating only for PEO. In the PEO sulfonic acid anion in cell2 the G^{+}TG^{+} and G^{-}TG^{-} states are more populated than the TTT state. This deviation is not found in all but several studied frames. The origin of the G^{+}TG^{+} and G^{-}TG^{-} states is probably in the coordinations where the both ends of the anion are coordinated to the same cation. In this case an increase is found also in the *gauche* states for CCOC dihedral angle. However, when the instantaneous coordinations

Table 2
The percentages of populations of conformational triads along C–C–O–C–C–O and C–O–C–C–O–C sequences for cell1, cell2, cell3 and cell4 in PEO and PEO sulfonic acid anion (anion)

		C–C–O–C–C–O sequence				C–O–C–C–O–C sequence			
Triads	Subset	Cell1	Cell4	Cell2	Cell3	Cell1	Cell4	Cell2	Cell3
TTT	Anion	17.5	37.6	6.3	17.1	16.7	18.8	8.3	18.8
TTT	PEO		35.3	17.5	25.2		38.2	18.7	27.0
TTG^{+} or TTG^{-}	Anion	62.5	30.1	31.2	26.6	0.0	8.7	6.3	6.3
TTG^{+} or TTG^{-}	PEO		28.9	28.0	36.3		6.5	6.8	7.4
TG^{+}T or TG^{-}T	Anion	2.5	11.8	6.25	7.8	66.7	31.9	27.1	29.2
TG^{+}T or TG^{-}T	PEO		8.2	7.3	6.0		27.8	27.3	34.5
TG^{+}G^{+} or TG^{-}G^{-}	Anion	7.5	1.1	4.7	10.9	0.0	3.0	18.7	4.2
TG^{+}G^{+} or TG^{-}G^{-}	PEO		4.7	9.3	5.4		4.2	8.9	7.1
TG^{+}G^{-} or TG^{-}G^{+}	Anion	5.0	5.4	7.8	10.9	0.0	1.4	14.6	8.3
TG^{+}G^{-} or TG^{-}G^{+}	PEO		4.4	5.6	3.7		3.2	6.2	4.4
G^{+}TT or G^{-}TT	Anion	0.0	5.4	3.1	7.8	3.3	11.6	2.1	8.3
G^{+}TT or G^{-}TT	PEO		9.0	9.3	9.3		8.3	7.9	6.5
G^{+}TG^{+} or G^{-}TG^{-}	Anion	0.0	2.1	21.9	3.1	0.0	1.4	6.3	0.0
G^{+}TG^{+} or G^{-}TG^{-}	PEO		4.0	8.0	7.4		1.0	2.7	0.9
G^{+}TG^{-} or G^{-}TG^{+}	Anion	5.0	3.2	9.4	7.8	0.0	3.0	2.1	0.0
G^{+}TG^{-} or G^{-}TG^{+}	PEO		2.3	6.6	2.5		0.9	1.5	1.3
G^{+}G^{+}T or G^{-}G^{-}T	Anion	0.0	2.1	4.7	1.6	6.7	1.4	2.1	6.3
G^{+}G^{+}T or G^{-}G^{-}T	PEO		1.4	3.8	1.4		3.4	9.3	4.2
G^{+}G^{-}T or G^{-}G^{+}T	Anion	0.0	1.1	0.0	3.1	0.0	7.3	4.2	6.3
G^{+}G^{-}T or G^{-}G^{+}T	PEO		0.6	1.0	0.5		3.4	3.7	3.5
G^{+}G^{+}G^{+} or G^{-}G^{-}G^{-}	Anion	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.3
G^{+}G^{+}G^{+} or G^{-}G^{-}G^{-}	PEO		0.6	2.4	1.1		1.0	1.0	1.2
G^{+}G^{+}G^{-} or G^{-}G^{-}G^{+}	Anion	0.0	0.0	6.3	1.5	0.0	0.0	2.1	0.0
G^{+}G^{+}G^{-} or G^{-}G^{-}G^{+}	PEO		0.4	1.1	0.5		0.8	2.0	1.2
G^{+}G^{-}G^{+} or G^{-}G^{+}G^{-}	Anion	0.0	0.0	3.1	1.5	0.0	0.0	0.0	0.0
G^{+}G^{-}G^{+} or G^{-}G^{+}G^{-}	PEO		0.2	0.8	0.1		0.2	1.3	0.2
G^{+}G^{-}G^{-} or G^{-}G^{+}G^{+}	Anion	0.0	0.0	1.6	1.5	0.0	0.0	6.3	6.2
G^{+}G^{-}G^{-} or G^{-}G^{+}G^{+}	PEO		0.2	1.2	0.6		1.0	2.5	6.2

are studied it is found that these kinds of coordinations occur also in other cells. In crystal PEO the left- and right-handed helix are formed so that half of the chains have a $(TTG^{-}TTG^{-}TTG^{+})_2$ and the other half a $(TTG^{+}TTG^{+}TTG^{-})_2$ sequence [7]. In the amorphous state this *gauche* effect is also reported. The $G^{+}G^{-}G^{+}$ and $G^{-}G^{+}G^{-}$ states have the smallest probability in all cells. This is due to the $CH_2\cdots CH_2$ $1\cdots5$ pentane effect, which makes this state less favourable, while the $O\cdots CH_2$ $1\cdots6$ interactions stabilises the state so that it can exist [7].

The population analysis of conformational triads along the C–O–C–C–O–C sequence for the PEO sulfonic acid anion and for the PEO shows that the most populated triads are TTT, $TG^{+}T$ and $TG^{-}T$ in cell1, cell3, cell4 for PEO and PEO sulfonic acid anion and in cell2 for PEO. In cell2 the $TG^{+}T$, $TG^{-}T$, $TG^{+}G^{+}$, $TG^{-}G^{-}$, $TG^{+}G^{-}$ and $TG^{-}G^{+}$ states dominate for the PEO sulfonic acid anion. These results qualitatively agree with the results in the literature calculated for the PEO under different conditions (e.g. PEO melts, or PEO/LiI melts) [9,11,24].

4.4. Dimensional analysis

The average values of the root mean square radius of gyrations and end-to-end distances for PEO sulfonic acid anion in all cells and in vacuum and for the PEO sulfonic acid in vacuum are seen in Table 3. For the PEO sulfonic acid anion the radius of gyration is (5.7 ± 0.9) Å in cell4, in cell3 (5.78 ± 0.18) Å, in cell2 (5.38 ± 0.08) Å calculated using the CMM method and (5.22 ± 0.08) Å calculated using the Ewald summation method and in cell1 (5.6 ± 0.7) Å. These results are very close to each other. In vacuum the PEO sulfonic acid anion is in a more extended shape and the radius of gyration is (8.4 ± 0.4) Å.

The average of the end-to-end distance of the PEO sulfonic acid anion is (13 ± 4) Å in cell4, in cell3 (12 ± 4) Å, in cell2 (11 ± 3) Å and in cell1 (12 ± 3) Å. While the values for the end-to-end distance of the PEO sulfonic acid anion in the cells are rather similar, in vacuum the value is clearly larger (22 ± 2) Å. The characteristic ratio of the PEO sulfonic acid anion is 3.4 in cell4, in cell3 3.1, in cell2 2.5, in cell1 3.1 and in vacuum 9.4. The characteristic ratio of the PEO is reported to be 3.9 in pure water [44]. The simulated values are in accordance with this reported experimental value.

Table 3
The radius of gyration $g(r)$ and the end-to-end distance (S) for PEO sulfonic acid anion (anion) and for PEO sulfonic acid (acid)

System	Anion $g(r)$ (Å)	Acid $g(r)$ (Å)	Anion S (Å)	Acid S (Å)
Cell3, CMM	5.78 ± 0.18		12 ± 4	
Cell2, CMM	5.38 ± 0.08		11 ± 2	
Cell2, Ewald	5.22 ± 0.08		11 ± 3	
Cell4, CMM	5.7 ± 0.9		13 ± 4	
Cell1	5.6 ± 0.7		12 ± 3	
Anion in vacuum	8.4 ± 0.4		22 ± 2	
Acid in vacuum		4.8 ± 0.8		9.0 ± 4

CMM means calculations made by using the CMM and Ewald means calculations made by using the Ewald summation method.

Four important factors can be found to explain the average values of the end-to-end distance and radius of gyration: the repulsive interaction between the negative charges at the end groups of the PEO sulfonic acid anion, the dielectric constant of the system, the coordinations between the cations and the PEO sulfonic acid anion and the *gauche* effect. The first mentioned contribution favours the *trans* conformations in the chain, because they give the maximum distance between the end groups. The dielectric constant of the system is important because a high dielectric constant has a remarkable screening effect on the value of the coulombic potential of the charge. The influence of the coordination between cations and the PEO sulfonic acid anion is significant to the dimensions of the anion. The instantaneous coordinations between the cations and sulfonic acid anion group show many variations. Cases having the opposite effect to the shape of the anion are found; the same cation is coordinated to both sulfonic acid end groups of the same PEO sulfonic acid anion or many cations are coordinated to the chain and to the other end of the PEO sulfonic acid anion but no cation is coordinated to both ends of the same anion. The structure of the anion in the former case is more coiled than in the latter case [21]. The former case seems to be less common than the latter, but its effect to decrease the end-to-end distance and radius of gyration is large. The deviation of the end-to-end distances and radius of gyrations of the single chains between the former and the latter case in the same cell is larger than the deviations between the values in the different cells. The *gauche* effect favours the OCCO *gauche* conformations in some environments e.g. the polar solvent (like water) favours the polar conformations (OCCO *gauche*) and the less polar environment favours the non-polar conformations (OCCO *trans*) [43].

The contribution of the repulsive factor caused by the charged end groups is most significant for the PEO sulfonic acid anion in vacuum, because vacuum has a low dielectric constant and there is no coordination between the cations and the anion. Thus the largest end-to-end distance and radius of gyration is detected for the PEO sulfonic acid anion in vacuum. In the cells the dimensions of the anions are nearly the same, but they are partly caused by different factors. In cell1 the dielectric constant is very large (78.35) which decreases the influence of the repulsive force between the negative end groups. However, in cell1 the coordination between the cations and the anion is rather small [19]. In cell2 and cell3 the dielectric constant is small (about 3) compared to cell1, but coordination between cations and anions is strong. In cell4 the dielectric constant is small compared to the dielectric constant of cell1 and coordination between cations and anions are weaker than in cell2 and cell3. Particularly in cell4 large deviations are found in the dimension of different anions in different frames (e.g. between the end-to-end distances variations from 5.0 to 18.5 Å are found). A little more *trans* conformations are found in cell4 than in cell2 and cell3. This can be caused by the smaller amount of coordinations, and especially coordinations where cation is coordinated to both ends of the same anion, in cell4 than in cell2 and cell3. Since the cation is found to be outside the PEO sulfonic acid anion chain when it is coordinated to both end groups of the same anion, the coordination favours the *gauche* conformations both for OCCO and for CCOC dihedral angles. More water is located around the PEO chains in cell2 than in cell4 [23] and this can increase the *gauche* conformations in OCCO dihedral angles in cell2, since the gauche conformations are reported to increase as the amount of water increases [8,43]. Cell3 is water-free and the coordinations between cations and anions are strongest in this cell. The radius of gyration and the end-to-end distance of the PEO sulfonic acid in vacuum is only slightly smaller that these values for the PEO sulfonic acid anions in the cells. This indicates the strong influence of the dielectric constant and the coordinations to the dimensions of the molecules. Of course also other effects caused by the calculations e.g. the packing effect or the method chosen to model the non-bonding interactions can be present in the systems studied.

4.5. Instantaneous coordination of cations

We have previously reported an average coordination study of the cells [19,20,23]. In this paper some instantaneous coordinations in the first coordination shell are studied in all cells in order to detect which kind of coordination occurs in different cells and to get detailed information on coordinations. This study is made on a limited number of cases and it does not, due to small statistics, necessarily include all possible different variations of coordination. However, it offers an interesting detailed view of the instantaneous local environment of the proton and the hydronium ion in the cells, which is an important factor in the conductivity. This study is based on the calculation of the pair correlation functions and coordination numbers in the first coordinations shell between each cation and each oxygen atom in each PEO sulfonic acid anion or PEO molecule or water molecules in 10 frames of cell1 and in two frames of cell2, cell3 and cell4. Examples of the instantaneous coordination in the first coordination shell in five frames in cell1 and in one frame in other cells are collected in Table 4. The first coordination shell of the proton ends at 3.5 Å and of the hydronium ion ends at 4.5 Å. The coordinations of the cations vary considerably. The total coordination numbers for protons varies from 4 to 7 in all cells and for the hydronium ions from 6 to 9 in cell2 and cell3 and from 9 to 14 in cell1 and in cell4. Coordination between two cations was found only once (in cell4 coordination was found between a hydronium ion and a proton. These cations were not coordinated to same anion).

In cell1 the protons and the hydronium ions in all frames studied are coordinated to water and in some frames cations are coordinated to the sulfonic acid end group of the PEO sulfonic acid anion (Table 4). The hydronium ion is seldom coordinated to the ether oxygen of anion and sometimes but not always coordinated to the sulfonic acid end group of this anion. The most interesting result was that the PEO sulfonic acid anion in cell1 in some frames is totally uncoordinated to both cations in first coordination shell. Cell1 has the largest conductivity of the systems studied and the hopping mechanism caused by the proton is dominating in this cell. In cell1 many cations uncoordinated to any anion were found and the protons are less coordinated to the anion than the hydronium ions.

Cell4 is conducting and both the hopping mechanism and the diffusion of the hydronium ions are important in this cell. In cell4 the coordinations between cations and anions are rather similar for protons and hydronium ions. All hydronium ions and protons are coordinated to water in cell4 as also in cell1 and cell2. The coordination number in cell4 between hydronium ions and water molecules varies a lot (from 5 to 12) and it is in the largest cases same as in cell1 (from 9 to 13) while in cell2 it is less (from 1 to 7). Due to the smaller size compared to the hydronium ion, the proton is coordinated to less water molecules in all cells (in cell4 about to 4, in cell2 about to 2 and in cell1 about to 6 water molecules). Thus the coordination between the cations and water increases as the amount of water increases in the systems.

From Table 4 it can be seen that more coordinations between the cations and the oxygen anions in the end groups of the PEO sulfonic acid anion are found in cell2 and cell3 than in cell4: in cell2 and in cell3 all the cations are coordinated to one or more oxygen anions, while in cell4 some cations are uncoordinated. A cation coordinated to the PEO sulfonic acid anion is in all the cells studied typically coordinated to two oxygen anions in the same sulfonic acid anion end group in the same PEO sulfonic acid anion. In some cases also an oxygen anion from different PEO sulfonic acid anion or in rare cases from the same PEO sulfonic acid anion molecule (from the different end group) is coordinated to the cation. Thus the basic way of coordination is rather similar in all cells. However, some deviations are found. Only in cell3 coordinations to all three oxygen anions of the same sulfonic acid end group are seen. In cell2 and cell3 the coordination between cation and oxygen anions in the sulfonic acid anion of three different anions was seldom detected, while in cell4 no such coordination was found. The coordination between the cation and the end groups has a significant influence on the conductivity and on the shape of the molecule.

The number of oxygen anions that are uncoordinated in the first coordination shell is about 14 in cell4, in cell2 about five and in cell1 about one (the total number of oxygen

Table 4

Examples of the individual coordinations between the cation (p = the proton and h = the hydronium ion) and the oxygen anions (*XYZ*, where *X* is the number of the PEO sulfonic acid anion, Y is a letter (G or I) indicating in which end of PEO sulfonic acid anion the oxygen anion is and *Z* is the number of the oxygen anion in the end group) and between the cation and ether oxygen in the PEO sulfonic acid anion (*X*oc, where *X* is the number of the PEO sulfonic acid anion)

Cation	Frame	Coordinated oxygen anion in the sulfonic acid anion end group[a]	Ether oxygen of the anion × N[a]	N with ether oxygens in PEO[a]	N with water[a]	Coordinated cations
1p	800	–	–		7	–
1h	800	I2	2		9	–
1p	750	–	–		7	–
1h	750	I2	–		9	–
1p	700	I2, I3	–		5	–
1h	700	–	–		12	–
1p	600	–	–		6	–
1h	600	–	–		13	–
1p	500	I4	–		5	–
1h	500	–	1		9	–
4p1	1420	1G2, 3G2	–	–	4	–
4p2	1420	3I4, 3G2, 4G2	–	–	3	–
4p3	1420	–	–	–	5	–
4p4	1420	2I4, 2G2	–	–	3	–
4h1	1420	–	–	2	6	4h4
4h2	1420	3I2, 3I3, 3G4	–	–	7	–
4h3	1420	3G2, 3G3	–	–	7	–
4h4	1420	–	–	–	10	4h1
2p1	970	3G4, 3I2, 3I3	–	–	3	–
2p2	970	4I2, 4I4, 3I4	1oc × 1	–	1	–
2p3	970	4G3, 1I2, 1I3	–	1	2	–
2p4	970	3G3	3oc × 1	1	4	–
2h1	970	2I2, 2I4	2oc × 2	2	4	–
2h2	970	2G2, 2G4, 1I3, 1I4	2oc × 1	1	2	–
2h3	970	2G3, 1G3, 1G4	–	2	6	–
2h4	970	4G4, 1G4	–	–	7	–
3p1	800	4G2, 4G3, 4G4	–	3		–
3p2	800	3I2, 3I3, 1G3, 1G4	–	2		–
3p3	800	3G4, 3I3, 3I4, 2I3, 2I4	–	1		–
3p4	800	1I2, 1I3, 1I4, 3G2	–	1		–
3h1	800	3I3, 2I2, 2I4	–	4		–
3h2	800	1G4, 2G2	(1oc) × 4	2		–
3h3	800	2G2, 2G3, 1G2, 1G3, 4I3, 4I4	(2oc) × 2	–		–
3h4	800	2G3, 2G4, 4G2, 4G4, 4I2, 4I4	–	2		–

The coordination numbers, *N*, between the cation and ether oxygen in the PEO and between the cation and the water are included. The number before the cation sign indicates the number of the cell and after the letter is the number of the cation (e.g. 2p1 is proton number 1 in cell2). The data concerning cell1 is collected from five frames to get better statistics.

[a] The first coordination shell ends at 3.5 Å in coordination concerning the proton and at 4.5 Å for the coordination concerning the hydronium ion.

anions is 24 in each system). In spite of the uncoordinated oxygen anions, some oxygen anions are coordinated to two or three different cations in the first coordination shell in all cells.

When the coordination between the oxygen atoms in water molecules and the ether oxygen in cell4 and cell2 are compared, it is found that the water molecules in cell4 are less coordinated to ether oxygen atoms (average coordination number is 0.5) than in cell2 (average coordination number is 1.2) [23]. In cell4 the average coordination number between water molecules and ether oxygen atoms in water molecules calculated separately for PEO and for PEO sulfonic acid anion shows, that the coordination is stronger between the water molecules and the ether oxygen atoms in the PEO sulfonic acid anion than between the water molecules and ether oxygen atoms of the neutral PEO. Thus the water molecules are more located around the PEO chain in cell2 than in cell4. The increase in the coordination numbers between water molecules and the sulphur atom in the end group of the PEO sulfonic acid anion shows, as the amount of the water increased in the systems, that the number of the water molecules increased around the end groups. The average coordination number between oxygen atoms in water is 8 in cell4 and 3.6 in cell2 [23]. The small microphase separation in cell4 can promote the ion conductivity. The cations seem to prefer water molecules to ether oxygen atoms and thus in cell4 the cations are located in the water clusters near the negatively charged end groups of the PEO sulfonic acid anion. In conducting Nafion systems the possibility of water clusters is discussed in the literature [45]. The size of the clusters in conducting Nafion system are reported to be over 20 nm^3, which is beyond our simulations due to the nanometer size-scale of the cells. However, the longer size-scale in simulations would increase the simulation time remarkably. The possibility of a phase separation between water and PEO is reported also in the literature at temperatures above 100 °C [43, 46–48].

The coordination between the cations and the ether oxygen atoms in PEO and between the cations and the ether oxygen atoms in the PEO sulfonic acid anion increases as the amount of water decreases in the cells and as the conductivity of the system decreases [23]. In cell4 and in cell1 no significant coordination between the cation and ether oxygen is found. In cell2 the coordination between the cations and the ether oxygen in the anion is weak and it is usually between an ether oxygen of an anion, in which the sulfonic acid end group is also coordinated to the same cation (Table 4). However, when the cation is coordinated to both end groups of the same PEO sulfonic acid anion, it is not coordinated to the ether oxygen atoms of this anion. This indicates that conduction mechanisms involving the cation moving inside from one ether oxygen to another, is not important in the systems, but the conductivity is more related to the amount of the water. While the coordinations between cations and the ether oxygen atoms in the PEO were occasional in cell2, in cell3 nearly all the cations were coordinated to the ether oxygen atoms of the PEO (coordination numbers varied from one to four). The coordination between the hydronium ions and the ether oxygen in the PEO sulfonic acid anions was not as strong as the coordination between cations and ether oxygen atoms in PEO (see also Table 4). However, coordination numbers up to four were found between the hydronium ions and ether oxygen atoms in the same anions in cell3. In cell3 no coordination was found between protons and the ether oxygen atoms of any PEO sulfonic acid anion. Thus the increase in the average coordination number between the cation and the ether oxygen in cell3 compared to cell2 was due to the increase of the coordination between the cation and the ether oxygen in the PEO.

5. Conclusions

The structure of the amorphous system called cell4 consisting of four PEO sulfonic acid anions, one PEO molecule, four hydronium ions, four protons and 35 wt% of water has been studied by molecular modelling. The dihedral angles study, intramolecular pair correlation functions and conformational triads analysis were made to examine the local structure of the PEO sulfonic acid anion and PEO in the systems. In addition molecular dimensions were determined and instantaneous coordinations of cations were studied. The results are compared to the results of three other simulated systems containing one PEO sulfonic acid anion, one hydronium ion, one proton and 90 wt% of water (cell1) or four PEO sulfonic acid anions, one PEO molecule, four hydronium ions, four protons and 20 wt% of water (cell2) or four PEO sulfonic acid anions, one PEO molecule, four hydronium ions, four protons and no water (cell3) [17]. Cell1 and cell4 are conducting, while cell2 and water-free cell3 are not conducting [23]. The aim of this paper is to elucidate the structure of the conducting solid polyelectrolyte (cell4) and seek to explain why cell4 is conducting and cell2 is not conducting from the structure of the cells.

The dihedral angle study showed, that a little more *trans* conformations are found in the OCCO, CCOC, CCCO average dihedral angle distributions in cell4 than in other cells. However, the difference is not large and cannot explain why cell4 is conducting and cell2 is non-conducting. The larger amount of *trans* conformations is probably caused by the smaller amount of coordinations between cations and anions, and especially by the smaller amount of coordinations where the cation would be coordinated to the both end groups of the same anion (these coordinations favour the *trans* conformations both for OCCO and CCOC dihedral angles). Another factor favouring the *trans* states in OCCO dihedral angles is the smaller amount of water in the first coordination shell of the ether oxygen in cell4 compared to cell2 or cell1.

The conformational triads population analysis along the C–C–O–C–C–O sequence and along the C–O–C–C–O–C sequence showed a large variation of the states in all cells. The most populated states in the triads analysis along the C–O–C–C–O–C sequence are TTT, TG^+T and TG^-T conformations in cell1, cell3, cell4 for PEO and PEO sulfonic acid anion and in cell2 for PEO and TG^+T, TG^-T, TG^+G^+, TG^-G^-, TG^+G^- and TG^-G^+ states in cell2 only for the PEO sulfonic acid anion. The results are in agreement with the results in the literature obtained for PEO or 1,2-dimethoxyethane [9,11,24]. The intramolecular pair correlations functions between the carbon atoms and oxygen atoms in the PEO chain in the PEO sulfonic acid anion and in PEO agrees with the results obtained by the dihedral angle study and the conformational triads analysis.

The average dimensional analysis shows that the PEO sulfonic acid anions have on average similar sizes and coiled shapes in all cells. However, rather large deviations in the dimensions between the different anions in the same cell are found in all cells, thus different factors can determine the dimensions of the anions in different cells. The influence of four main factors to the shape and size of the PEO sulfonic acid anion in the cells is discussed. These factors are the repulsive interaction between the negative charges at the end groups of the PEO sulfonic acid anion, the dielectric constant of the system, the coordinations between the cations and the PEO sulfonic acid anion and the *gauche* effect.

No significant reason why cell4 is conducting and cell2 is not conducting was found, when the structure of the matrix molecules, PEO and PEO sulfonic acid anion only is conceived. To study further the reason to the conductivity of cell4, instantaneous coordinations of the cations were studied. The main differences between the instantaneous coordination in non-conducting cell2 and in conducting cell4 are the coordination between cations and water and the coordination between cations and ether oxygen atoms. The coordination numbers between cations and end groups of the anions are much higher in cell4 than in cell2. The coordination between the ether oxygen atoms in PEO and the cations or between the ether oxygen atoms in the anion and the cations is much stronger in cell2 than in cell4. The water molecules are more coordinated to ether oxygen in cell2 than in cell4. In actual fact, a small microphase separation is found in cell4, where the water molecules are more coordinated to each other and to the end groups of the anions and less to the PEO chain than in cell4 than in cell2. This small microphase separation can promote the conductivity in cell4 compared to cell2.

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