Available online at www.sciencedirect.com

ScienceDirect

Polymer 48 (2007) 1435–1440

polymer

www.elsevier.com/locate/polymer

Nanoscale modeling of the structure of perfluorosulfonated ionomer membranes at varying degrees of swelling

Yves Termonia

Central Research and Development, Building E304, Room C219, Experimental Station, E.I. DuPont de Nemours, Inc., Wilmington, DE 19880-0304, United States

Received 18 October 2006; received in revised form 3 January 2007; accepted 9 January 2007
Available online 13 January 2007

Abstract

We present a comprehensive model for the structure of swollen ionic membranes using a stochastic simulation process at the nanoscale level. In our model, the membrane is viewed as an entangled network of chains interacting at their backbone and ionic groups. Equilibration of the network is obtained through local moves of the groups according to the Boltzmann exponents of the corresponding changes in internal energy. The approach allows one to consider in detail the importance of equivalent weight, polymer molecular weight, length of pendant ionic groups as well as crosslinks and non-ionic polymer additives. At infinite dilution, our simulation results reveal that the ionic chains segregate into platelet-like structures with the ionic sites exposed on each surface and a core (∼2 nm thick) made of two layers of the hydrophobic polytetrafluoro-backbone units. As concentration is increased above the critical value for network formation, the platelets are stretched into narrow ribbons connected at entanglement points. Our description is in line with recent experimental evidence suggesting that ionic membranes can be considered as a connected network of rods. Finally, model predictions of X-ray scattering data are found to be in good agreement with experimental values obtained over a wide range of water content spanning two orders of magnitude.

Keywords: Model; Perfluorinated ionomer; Structure

1. Introduction

Perfluorosulfonated ionomer (PFSI) membranes have received significant attention over close to half a century. For recent updates on the vast amount of literature published on the subject, the reader is referred to the excellent reviews of Doyle and Rajendran [1] and Mauritz and Moore [2]. The interest in PFSI membranes stems from their excellent ionic conductivity due to a microphase separation between the hydrophobic fluorinated matrix and the hydrophilic ionic domains. Swelling by water leads to an increase in ionic conductivity and a deep knowledge of the intimate microstructure of the membrane is therefore crucial for arriving at a full control of its performance.

In spite of its importance, there is however very little understanding of the nanoscale morphology of PFSI membranes. X-ray and neutron scattering analyses provide limited information because the polymer yields only a single broad scattering maximum which has been commonly attributed to the characteristic dimensions of the ionic domains. Several models based on the scattering data have been proposed to describe the morphology of PFSI membranes. These include the interparticle cluster-network model proposed by Gierke [3], the intraparticle three-phase models of Yeager [4] and Fujimura [5], the local-order model of Dreyfus [6], the lamellar model of Litt [7], the sandwich-like model proposed by Haubold [8] and, more recently, the rod-like model of Rubatat [9] and Gebel [10]. All these studies present rather simple morphological models which are calibrated to experimental data and involve specific assumptions on structure. They also are not concerned with how the phase separated morphology can be assembled.

E-mail address: yves.termonia@usa.dupont.com

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.01.016

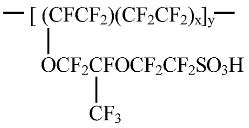
In view of these limitations, molecular simulation approaches have also been used. The percolation aspects of the ionic conductivity of PFSIs have been addressed by Hsu et al. [11] in a model which however neglects details of the connectivity and chemical composition of the molecular chains. *Ab initio* methods which do embrace chemical structure have been proposed by Paddison [12], Khalatur [13] and Jang [14]. In view of computer limitations, the studies were restricted to a small number of rather short polymer chains, with molecular weight values way below 10^5-10^6 Da typical of PFSIs. A dissipative particle dynamics study has been proposed by Yamamoto [15]. The approach however is again limited to short chains which also are not self-avoiding.

In the present work, we develop a comprehensive model for the self-assembly of ionic membranes using a simulation procedure "from the ground up" [16]. In that procedure, individual PFSI chains are first generated on a cubic lattice with unit spacing of the order of the statistical segment length for the polymer ($\sim$1 nm). Empty lattice sites are occupied by water. At the start of the simulations, local interactions are imposed between sites occupied by different moieties (polymer segments, ionic groups, water) and the phase separated morphology is then assembled through free energy minimization techniques. These techniques involve local motions of the chains (kink jumps, crankshaft rotations) which are weighted by Boltzmann exponents of the corresponding changes in internal energy. During these motions, topological constraints such as excluded volume and chain entanglements are explicitly taken into account. The approach as described is very flexible and allows one to consider in detail the importance of EW (equivalent weight), overall polymer molecular weight, length of pendant ionic groups as well as crosslinks and non-ionic polymer additives. Note also that details of the chemical composition of a segment are lumped into its interaction parameter, which is easily extracted from solubility data.

In view of recent X-ray and neutron scattering studies [9,10,17] indicating a continuum in structural evolution from dry membrane to solution, the present work focuses on a schematic representation of the PFSI membrane in terms of a regular network of entangled chains which continuously expands with an increase in water content.

2. Model

Perfluorosulfonate ionomers are composed of a polytetrafluoro-backbone with a pendant side branch terminated by a sulfonate ionic group [1].



$$\begin{array}{l} -[(\mathrm{CFCF_2})(\mathrm{CF_2CF_2})_x]_y- \\ \quad | \\ \quad \mathrm{OCF_2CFOCF_2CF_2SO_3H} \\ \qquad\quad | \\ \qquad\quad \mathrm{CF_3} \end{array}$$

The variable x determines the equivalent weight (EW) defined as the number of grams of dry PFSI per mole of sulfonic group, $\mathrm{EW} = 100x + 446$. Values of x range from 6 to 13 leading to $\mathrm{EW} = 1046-1746$.

In our approach, the PFSI chains are modeled as a string of freely rotating bonds of length equal to that of a statistical segment for the backbone. Assuming same chain flexibility as in polyethylene and polytetrafluoroethylene [18], the statistical segment length is set at $\ell \approx 1$ nm [19] with a molecular weight m of about $10\mathrm{CF_2}$ units, *i.e.* $m = 498$ Da. (For simplicity, the length of the pendant ionic chain is given the same $\ell \approx 1$ nm). In view of the typically high molecular weight values of PFSI ionomers (10^5-10^6 Da), the number of backbone segments is set at 700. In the present work, we also take two statistical segments between pendant groups. This corresponds to $x = 9$, *i.e.* $\mathrm{EW} = 1346$.

Throughout our approach, we assume that the ionic chains are in thermodynamic equilibrium. This is motivated by the fact that, in typical neutron scattering studies [9,10,17], the swollen membranes are prepared by varying the temperature from 25 to 190 °C in a pressure vessel for 12 h using pure water as a swelling agent. Under such conditions, it is unlikely that the membrane structure would be partially "frozen" by the crystalline phase. According to Starkweather [20] the crystallites are made of only two layers of perfluorinated chains with the ionizable side groups extending on either side. Thus, since the swelling experiments are performed in the 25–190 °C range with a T_g for the polymer around 100 °C and water acting as a plasticizer, such thin crystallites can probably not resist the swelling pressures which are of the order of several atmospheres [21].

The chain segments are arranged on a simple cubic lattice where they link backbone and pendant ionic sites, henceforth labeled as "A" and "B", respectively. Sites which remain unconnected are filled-in with water and labeled "W". In order to account for their widely different miscibilities in water, we impose repulsive interactions between A and W sites ($\varepsilon_{AW}/k_BT > 0$) and attractive values ($\varepsilon_{BW}/k_BT < 0$) between B and W sites. Following the mixing energies determinations in Ref. [15], we took $\varepsilon_{AW}/k_BT = 1$, $\varepsilon_{BW}/k_BT = -0.5$ and $\varepsilon_{AB}/k_BT = 0.5$.

We start by describing our process for simulating the equilibrium conformation of a *single* PFSI chain on the lattice. The state of the chain is first generated at infinite temperature and taking fully into account excluded volume conditions. Phase segregation of the polymer is then initiated by lowering the temperature in small increments. This slow annealing process is crucial for preventing the freezing of aggregates into metastable states and in order to conform as close as possible to the experimental swelling conditions which involve equilibration over several days. For each temperature decrement, the entire state of the polymer solution is re-equilibrated using a combination of segment moves of two types [16,20], see Fig. 1. The first involves local moves such as end-flip, two-segment kink jump and three-segment crankshaft motion. The second incorporates nonlocal reptation modes which involve cutting a short sequence of segments (one repetition unit long) at one end of a chain and rebuilding it at the other end. Each move is chosen at random with the condition that it does not violate the excluded volume (non-overlapping) condition and its probability of acceptance

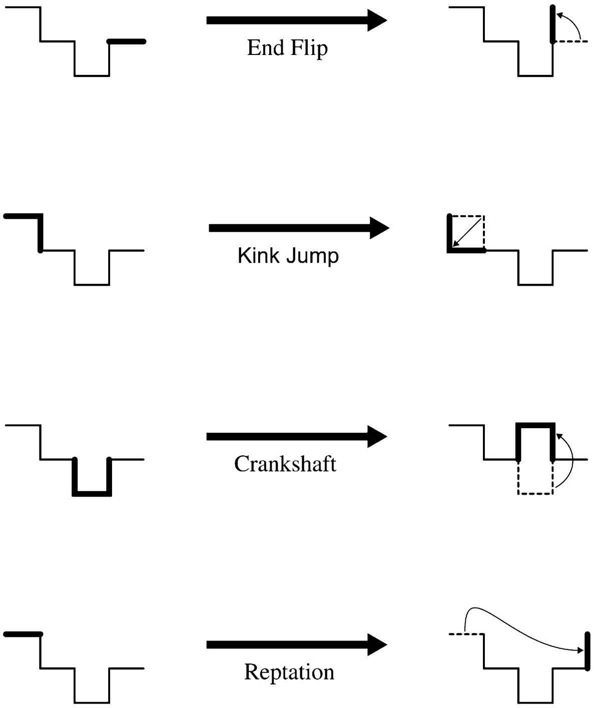


Fig. 1. Segment moves used in our chain equilibration algorithms.

is calculated according to the standard Metropolis algorithm [16,22]

$$P = \min\{1,\ \exp[-\Delta E(\varepsilon_{AW},\ \varepsilon_{BW},\ \varepsilon_{AB})/k_B T]\} \quad (1)$$

In Eq. (1), $\Delta E(\varepsilon_{AW}, \varepsilon_{BW}, \varepsilon_{AB})$ is the difference in energy between the trial and old configurations, whereas k_B is Boltzmann's constant and T is the temperature.

In the present work, we choose not to apply the algorithms described above to a brute force simulation of the equilibrium structure of an ensemble of the typically long ($n = 700$) PFSI chains. Our reasons are two-fold. First, such a calculation would require prohibitively large computer times which typically scale as the third power of the chain length n. Second, the approach would provide little information on the arrangement of the ionic clusters deep inside the membrane. For this reason, we turn to a schematic representation of the membrane which allows for a better insight into the details of its properties and intimate structure at varying water contents.

In our approach, we hypothesize that a PFSI membrane can be viewed as an entangled network of flexible chains. Since, in all swelling experiments, the membrane structure is allowed to develop over long periods of time over the order of several days, it is reasonable to assume that the network of entanglements is at equilibrium. Therefore, the number of statistical segments between entanglements, n_e, along the backbone can be estimated from

$$n_e = n_u/\phi \quad (2)$$

in which n_u is the corresponding number for the undiluted system and ϕ is the polymer volume fraction. Eq. (2) was derived empirically by Graessley [23] from viscosity data of flexible polymers at various concentrations. The equation is also at the basis of the gel spinning technique developed by Smith et al. [24] for flexible polymers. At $\phi = 0.02$, experiments [10] on PFSI membranes reveal that true solutions are formed, *i.e.* disentanglement is complete so that $n_e = n$ and, using Eq. (2),

$$n_u = n \times 0.02 = 14 \quad (3)$$

It is reassuring to find that the latter value $n_u = 14$ is the same as that reported for the number of statistical segments between entanglements in a poly(tetrafluoroethylene) melt [18]. That quantitative agreement however is fortuitous as the actual number for PFSI chains should be slightly higher because of the presence of side groups.

In view of the above considerations, PFSI membranes can be viewed as an array of *short* chain strands connected at entanglement points. A schematic of our model representation of the repetition unit in the membrane is given in Fig. 2. The elementary cube contains 16 chain strands (wiggling lines) connected at entanglement points (grey spheres) arranged in a diamond-like pattern. The elementary volume has side length

$$a = (16 \times n_e \times (3/2)/\phi)^{1/3} \quad (4)$$

in which $n_e \times (3/2)$ represents the total number of segments (backbone + ionic groups) for a single strand. These strands are equilibrated *individually* using the moves described in Fig. 1. During that process, the reptation algorithm is used

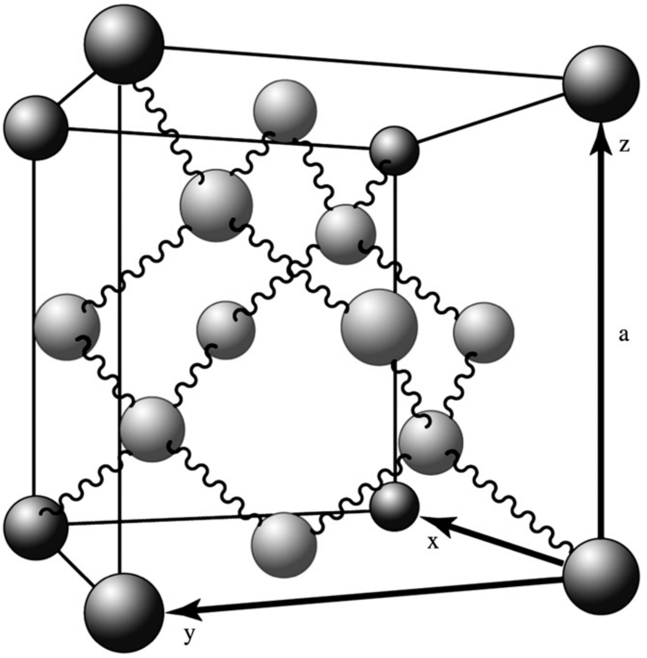


Fig. 2. Schematic model representation of the repetition unit in a PFSI membrane. The elementary cube of side a (Eq. (4)) contains 16 chain strands (wiggling lines) connected at entanglement points (grey spheres).

to ensure that the chain ends remain in close proximity of their connections at entanglement points.

All our simulations are done on a simple cubic lattice of a^3 lattice sites (see Fig. 2) with periodic boundary conditions. In order to ensure that the extent of phase segregation of individual chain strands does not depend on their length, we choose $k_BT = n_e/700$ [25]. Equilibration is done in small increments $1/k_BT = 0.002$ with up to 2000 moves per polymer site after each increment.

3. Results and discussion

Figs. 3–5 show our model predictions for the structure of PFSI chains at various polymer concentrations ϕ. Fig. 3 is for a single chain of $n = 702$ backbone segments at infinite dilution. Backbone and ionic sites are denoted by blue and red spheres, respectively. Our results reveal the formation of a platelet-like structure with the ionic sites exposed on each surface and a core (~2 nm thick) made of two layers of the hydrophobic polytetrafluoro-backbone units. Note that our predicted morphology is very similar to that proposed by Starkweather [20]. The case of finite dilution is studied in Fig. 4 which depicts an elementary volume of 16 chains at $\phi = 0.03$ ($a = 71$ nm). Also represented in the figure are the positions of the entanglement loci (grey spheres). A careful examination of the figure reveals the presence of narrow ribbons (see block arrows) with same cross-section as the platelet-like morphology in Fig. 3. Our observations are in agreement with the recent work of Perrin et al. [26] on the study of water relaxation by NMR and the previous theoretical work of Tovbin and Vasyatkin [27]. Note however that the ribbons in Fig. 4 appear deeply contorted probably because of our use of a simple cubic lattice which does not readily allow for the formation of rods/ribbons along chain vectors at 60° with

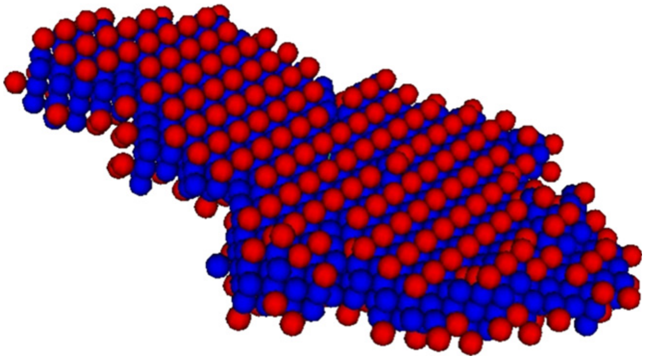


Fig. 3. Single PFSI chain of $n = 702$ backbone segments ($M = 350{,}000$) at infinite dilution, $\phi \rightarrow 0$. Backbone ("A") and ionic ("B") sites are denoted by blue and red spheres, respectively.

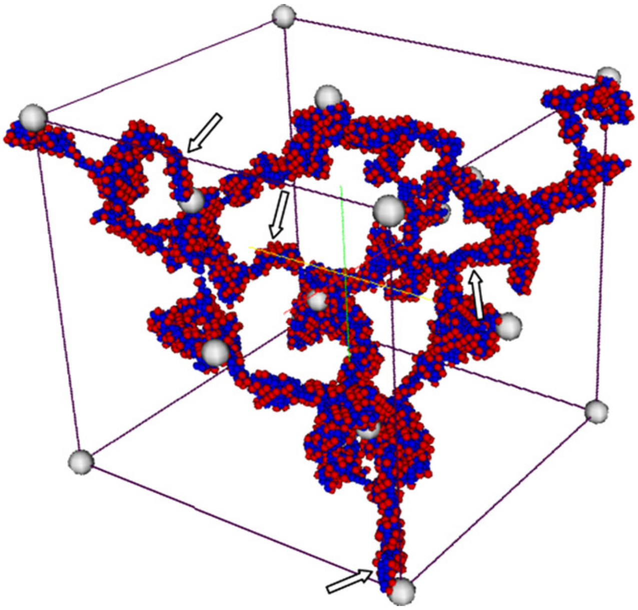


Fig. 4. Unit cube of 16 chain strands at a polymer volume fraction $\phi = 0.03$. Backbone and ionic sites are denoted by blue and red spheres, respectively. For easy visualization, the entanglement locations have been represented by grey spheres, see also Fig. 2. The block arrows point to ribbon-like elements with same cross-section as in Fig. 3. The unit cube has side length $a = 71$ nm.

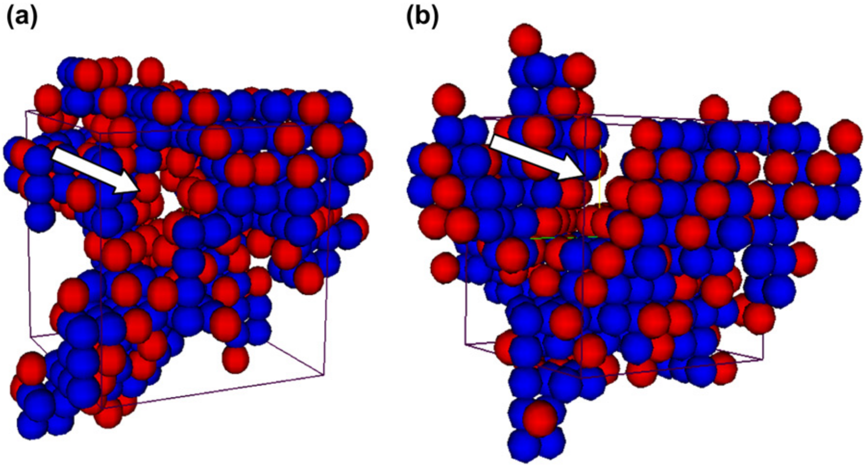


Fig. 5. Unit cubes of 16 chain strands at polymer volume fractions $\phi = 0.61$ (a) and $\phi = 0.78$ (b). Backbone and ionic sites are denoted by blue and red spheres, respectively. The block arrows point to water channels inside the unit cubes. The units have side lengths $a = 8$ nm (a) and $a = 7$ nm (b).

respect to the principal x-, y- and z-axes. Membrane structures at lower water contents are illustrated in Fig. 5a and b for $\phi = 0.61$ (a) and $\phi = 0.78$ (b). The unit cubes have side lengths $a = 8$ nm and $a = 7$ nm, respectively. The block arrows point to water channels inside the unit cubes. Note that the water clusters do not appear to be spherical but have a rather planar structure, see Fig. 5b.

We now turn to our model predictions of the X-ray scattering patterns of the hydrated PFSI membranes of Figs. 4 and 5. These patterns are easily obtained from the Fourier transform of the pair correlation function. The latter is obtained from

$$g(r) = \sum_{i=1}^{N} \sum_{j=i}^{N} \delta\left(\left|r_i - r_j\right| - r\right) / \Xi \tag{5}$$

in which N is the number of sites ("A", "B" or "W") and Ξ is a suitable normalization function. We choose to calculate Ξ from the same double summation as in Eq. (5) but, taken from a simulation at infinite temperature. Estimations of $g(r)$ in which Ξ is for a random distribution of sites, *i.e.*

$$\Xi = \left(N^2/a^3\right)(4/3)\pi\left(r^3 - (r - \delta r)^3\right) \tag{6}$$

lead to similar results. Our model predictions for the scattering patterns at various degrees of dilution are presented in Fig. 6. The results were obtained from simulations over large simple cubic lattices of side lengths equal to up to $9a$ in which "a" is the side of the elementary volume, see Fig. 2. The scattering patterns were calculated by adding the Fourier transforms of $g(r)$ for the "A", "B" and "W" sites, weighted by their corresponding volume fractions. Results (not reproduced) indicate that, at high dilution, the scattering contributions of the "A" and "B" sites dominate whereas at lower dilutions, scattering from the "W" sites is the most intense. For each ϕ value, the figure reveals the presence of a well defined maximum that can be attributed to a local ordering of the sites. Our results are in good qualitative agreement with experimental X-ray scattering data [9]. These experimental data further reveal (see Ref. [9]) that the average intensity on each side of the peak at small and large angle decays with power laws close to q^{-1} and q^{-4}, respectively. The latter is indicative of a dispersion of rod-like structures. Comparing to our model predictions in Fig. 6, we find that the decay at large angles is slower and rather closer to a q^{-3} powerlaw. As discussed above, that discrepancy may be due to our use of a simple cubic lattice which does not readily allow for the formation of rods/ribbons along the entanglement vectors.

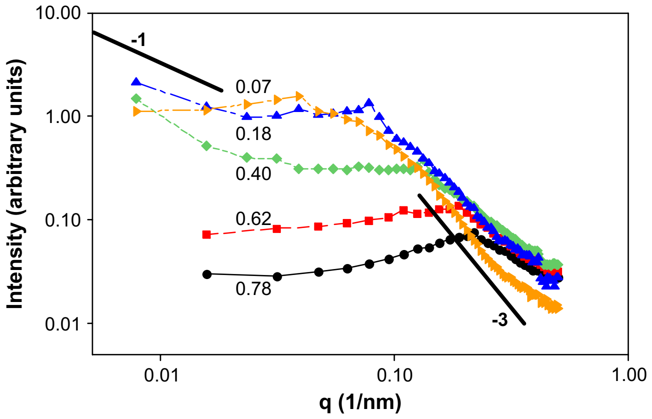


Fig. 6. Calculated small-angle X-ray scattering patterns at various polymer volume fractions. The values were obtained from the Fourier transforms of $g(r)$, see Eq. (5). The straight lines indicate various scaling regimes.

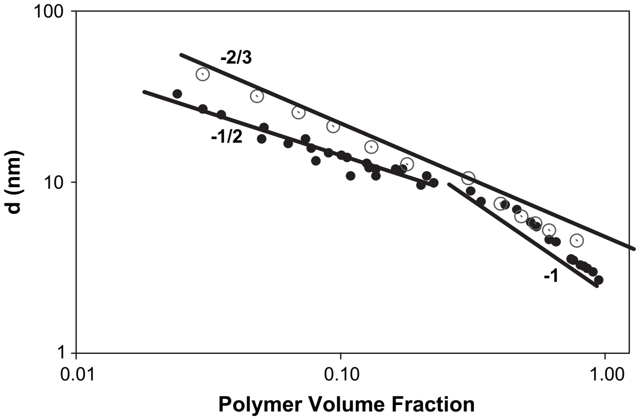


Fig. 7. Calculated values (symbol ⊙) of the inverse of the peak positions in Fig. 6 as a function of the polymer volume fraction. Symbol ● denotes experimental data for 115 and 117 Nafion® PFSI membranes (EW = 1100) [10]. The straight lines indicate various scaling regimes.

Fig. 7 shows our calculated values (symbol ⊙) for the inverse of the peak positions in Fig. 6 as a function of the polymer volume fraction. Also reproduced in the figure are experimental data reported by Gebel [10] for water swollen membranes ($0.075 < \phi < 1$) and aqueous solutions ($0.025 < \phi < 0.2$). The experimental values reveal that the peak positions follow two different regimes with a transition around $\phi = 0.5$ [9,10]. The first regime at high dilution exhibits a slope close to -0.5, which is indicative of an array of rod-like polymer aggregates. At low dilution, a slope of -1 is found which would be typical of a lamellar structure. Inspection of Fig. 7 reveals a reasonable agreement between model and experiment. Our model predictions however do not reproduce the two different regimes observed experimentally and they can be fitted to a single line with slope $-2/3$ (see Fig. 7). The latter corresponds to the scaling law for the size "a" of the elementary volume $a \sim \phi^{-2/3}$, see Eqs. (2) and (4). Again, it could be argued that the inability of the model to clearly reproduce the two scaling regimes found experimentally is due to our use of a simple cubic lattice.

4. Conclusions

In summary, we have presented a comprehensive model for the structure of swollen ionic membranes using a Monte-Carlo simulation process at the nanoscale level. In our model, the membrane is viewed as an entangled network of chains interacting at their backbone and ionic groups. Equilibration of the network is obtained through local moves of the groups according to the Boltzmann exponents of the corresponding changes in internal energy. The approach allows one to consider in detail the importance of equivalent weight, polymer molecular weight, length of pendant ionic groups as well as crosslinks and non-ionic polymer additives.

At infinite dilution, our simulation results reveal that PFSI chains segregate into platelet-like structures with the ionic sites exposed on each surface and a core (~2 nm thick) made of two layers of the hydrophobic polytetrafluoro-backbone units. That morphology is very similar to that proposed by Starkweather [20]. As concentration is increased above the critical value for network formation, the platelets are stretched into narrow ribbons connected at entanglement points. The thickness of these ribbons appears to be constant (~2 nm), independent of the degree of dilution. Our model results therefore indicate that the specific surface (area of polymer–water interface per polar head) is independent of water content, in agreement with experimental observation [10].

Our proposed structure for a PFSI membrane at the nanometer scale is fully consistent with Gierke's description [3] in terms of water clusters connected by channels. However, on a larger length scale, we further predict a supramolecular organization of the chains into an entangled network, which has to be taken into account to analyze the mechanical and conductivity properties. Our description is also in line with recent experimental evidence [9,10,17] suggesting that ionic membranes can be considered as a connected network of rods.

Model predictions of X-ray scattering data are found to be in good agreement with experimental values obtained over a wide range of water content. Our results however do not fully validate the contention in Refs. [9,10] that PFSI membranes at high dilutions can be represented by an array of rod-like structures. That lack of validation may be due to our use of a simple cubic lattice which does not readily allow for the formation of rods/ribbons along chain vectors at 60° with respect to the principal x-, y- and z-axes.

It is important to note that our approach assumes that the ionic chains are in full thermodynamic equilibrium. This is motivated by the fact that, in typical neutron scattering studies, the membranes are swollen at high temperatures in a pressure vessel for 12 h using pure water as a swelling agent. Our assumption however may not be valid in cases where swelling is performed at low temperatures well below T_g.

Finally, the results of the present work are limited to one ionomer structure and a particular set of values for the mixing energies. Further investigation indicates that our model findings are rather insensitive to structural details but strongly dependent on the interaction energies ε. An in-depth study of the effects of these model parameters will be relegated to a future publication.

References

[1] Doyle M, Rajendran G. Handbook of fuel cells – fundamentals, technology and applications, vol. 3. Chichester, UK: John Wiley & Sons; 2003. Part 3, p. 351–95 [chapter 30].
[2] Mauritz KA, Moore RB. Chem Rev 2004;104:4535–85.
[3] Gierke TD, Hsu WY. In: Eisenberg A, Yeager HL, editors. Perfluorinated membranes. ACS symposium series no 180. Washington, DC: American Chemical Society; 1982. p. 283 [chapter 13].
[4] Yeager HL, Steck A. J Electrochem Soc 1981;128:1880–4.
[5] Fujimura M, Hashimoto T, Kawai H. Macromolecules 1981;14:1309.
[6] Dreyfus B, Gebel G, Aldebert P, Pineri M, Escoubes M, Thomas M. J Phys (Paris) 1990;51:1341.
[7] Litt MH. Polym Prepr 1997;38:80.
[8] Haubold H-G, Vad T, Jungbluth H, Hiller P. Electrochim Acta 2001;46: 1559–63.
[9] Rubatat L, Rollet A-L, Gebel G, Diat O. Macromolecules 2002;35: 4050–5.
[10] Gebel G. Polymer 2000;41:5829–38.
[11] Hsu WY, Barkley JR, Meakin P. Macromolecules 1980;13:198–200.
[12] Paddison SJ, Zawodzinski TA. Solid State Ionics 1998;333:113–5.
[13] Khalatur PG, Talitskikh SK, Khokhlov AR. Macromol Theory Simul 2002;11:566–86.
[14] Jang SS, Molinero V, Cagin T, Goddart WA. J Phys Chem B 2004;108: 3149–57.
[15] Yamamoto S, Hyodo S-A. Polym J 2003;35:519–27.
[16] Termonia Y. J Polym Sci Part B Polym Phys 2002;40:890–5.
[17] Rubatat L, Gebel G, Diat O. Macromolecules 2004;37:7772–83.
[18] Smith P, Matheson RR, Irvine PA. Polym Commun 1984;25:294–7.
[19] Termonia Y, Smith P. Macromolecules 1988;21:2184–9.
[20] Starkweather Jr HW. Macromolecules 1982;15:320–3.
[21] Gebel G, Aldebert P, Pineri M. Polymer 1993;34:333–9.
[22] Binder K, Muller M, Baschnagel J. In: Kotelyanskii M, Theodorou DN, editors. Simulation methods for polymers. New York: Marcel Dekker, Inc; 2004. p. 125 [chapter 4].
[23] Graessley WW. Adv Polym Sci 1974;16:58.
[24] Smith P, Lemstra PJ, Booij HC. J Polym Sci 1981;19:877–88.
[25] Groot RD, Madden TJ. J Chem Phys 1998;108:8713–24.
[26] Perrin J-C, Lyonnard S, Guillermo A, Levitz P. J Phys Chem B 2006; 110:5439–44.
[27] Tovbin YK, Vasyatkin NF. Colloids Surf A Physicochem Eng Asp 1999; 158:385–97.