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Structural evolution of water swollen perfluorosulfonated ionomers from dry membrane to solution

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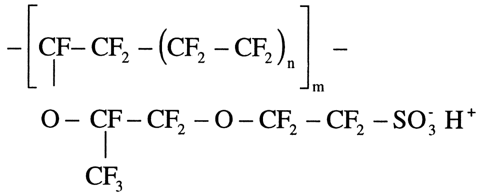
Abstract

The structural evolution of perfluorosulfonated ionomer (PFSI) membranes from dry materials to highly swollen membranes and solutions was investigated using mainly small-angle scattering techniques. The small-angle scattering maximum ("ionomer peak") is shown to be observable up to very large water content and shifts continuously toward small-angle as water content increases. A modification of the swelling process is observed for a water content larger than 50% by volume. This behavior is attributed to an inversion of the structure from a reverse micellar structure to a connected network of polymer rod-like particles. The swelling behavior of the membranes was determined in different solvents and was analyzed in terms of interfacial energy effects. The conductivity measurements indicate that the structure of the highly swollen membrane is close to the one observed for solutions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Perfluorinated ionomer; Small-angle X-ray scattering; Small-angle neutron scattering

1. Introduction

Perfluorosulfonated ionomer (PFSI) membranes are composed of a polytetrafluoroethylene backbone and perfluorinated pendant side chains terminated by a sulfonate ionic group [1,2]



$$\begin{array}{l} -\left[\mathrm{CF}-\mathrm{CF_2}-\left(\mathrm{CF_2}-\mathrm{CF_2}\right)_n\right]_m- \\ \quad | \\ \mathrm{O}-\mathrm{CF}-\mathrm{CF_2}-\mathrm{O}-\mathrm{CF_2}-\mathrm{CF_2}-\mathrm{SO_3^-}\ \mathrm{H^+} \\ \qquad | \\ \qquad \mathrm{CF_3} \end{array}$$

These polymers are commercialized as ion-exchange membranes by du Pont de Nemours & Co. under the trade name Nafion® to be used as electrolyte polymer separator in many electrochemical devices such as chlor-alkali electrolyzers or H_2/O_2 fuel cells.[3–5] PFSI membranes are characterized by a microphase separation between the hydrophobic matrix and hydrophilic ionic domains. In swollen membranes, the water was shown to be localized into water pools embedded in the perfluorinated matrix by neutron scattering experiments [6,7]. The water content increases continuously increasing temperature and large swelling degrees can be obtained using high temperatures in a pressure vessel [8]. PFSI membranes exhibit a swelling memory, namely, water uptakes obtained at high temperatures remain at room temperature due to a non-reversible deformation of the polymer matrix [8]. Owing to their industrial interest, the structure and the properties of these membranes have been extensively studied in the swollen state soaked in either neat water or electrolyte solutions [1,2]. However, the structural studies were only performed on low water content membranes (i.e. from 0 up to 0.2 w/w) [6,9,10]. PFSI small-angle neutron and X-ray scattering (SANS and SAXS, respectively) spectra exhibit a broad maximum in the medium angular range (the so-called "ionomer peak") and an upturn of the scattered intensity at very low angles [6,9–11]. As water content increases, SAXS and SANS spectra of PFSI membranes revealed an increase of the overall scattered intensity and a shift of the ionomer peak position toward small angles attributed to the swelling of the ionic aggregates. The membrane structure was shown to be well described by the "local order" model [10,11] which considers that each spherical ionic aggregate is surrounded by four neighbors at a well-defined distance and that the correlation between hydrated clusters is lost for the following aggregates. At higher swelling levels, a percolation model based on spherical ionic aggregates connected by small cylinders was proposed to interpret the excellent ionic conductivity and anion versus cation permselectivity of the membranes [12,13]. However the existence of

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connecting cylinders have never been directly evidenced by scattering techniques and electron microscopy.

On the contrary, PFSI solutions were studied by small-angle scattering [14,15] and magnetic resonance techniques [16,17]. A colloidal structure formed of polymer rod-like shaped particles with the ionic groups located at the polymer–solvent interface was evidenced. The value of the radius was shown to vary from 20 to 25 Å depending on the nature of the solvent and the length was estimated to be larger than 300 Å [15,18].

Swollen PFSI membranes are thus considered as presenting a “reverse micellar structure” formed of more or less connected spherical water pools embedded in the polymer matrix with the ionic groups located at the interface, while PFSI solutions were shown to present a “direct structure” formed of rod-like polymer aggregates. The aim of the present work is to study highly swollen membranes in terms of structure and properties in order to understand the structural evolution from membrane to solution during the dissolution process. The structure of the swollen membranes depending on the water content will be examined using SAXS and SANS techniques. The ionic conductivity and swelling properties of the highly swollen membranes depending on the nature of the solvent will be determined. The data will be compared to the results obtained for PFSI solutions.

2. Experimental

2.1. Materials

115 and 117 Nafion® PFSI membranes were purchased from du Pont de Nemours. The equivalent weight is 1100 g/eq. corresponding to $n \approx 6.5$ in the chemical formula. The dry 115 and 117 Nafion® membrane thicknesses are 125 and 175 μm, respectively. The membranes were first cleaned in boiling concentrated nitric acid and rinsed several times with pure water. Neutralized membranes were obtained by soaking the polymer in a 1 M LiCl solution overnight. The membranes were then dried out overnight at 110°C under vacuum in order to determine the dry weight and to avoid any effect of the membrane pretreatment.

Swollen membranes were prepared varying the temperature from 25 to 190°C in a pressure vessel for 12 h using pure water as a swelling agent. For temperatures larger than 200°C, the swelling is no more homogeneous and macroscopic domains of solvent are detectable. At least three pieces of membrane were weighed on the dry state before and after the swelling process, and on the swollen state in order to determine both the swelling degree of the membrane and the quantity of polymer dissolved during the swelling procedure [8]. The water and polymer volume fractions, ϕ_w and ϕ_p, respectively, were calculated from the weight increase assuming a complete polymer–solvent phase separation and that the polymer matrix density is equal to 2.1 g/cm^3 as determined from density measurements with PFSI solutions [15]. The membrane volume was increased by a factor from 1.4 to 12 with respect to the dry volume depending on the swelling temperature corresponding to a variation of the water volume fraction from $\phi_w = 0.3$ to 0.93. The mechanical properties of the swollen membranes are reduced increasing the water content and the membranes containing more than 90% by volume of solvent are difficult to handle.

In order to determine the evolution of the solvent uptake depending on the nature of the solvent, the water swollen membranes were soaked in a large quantity of the new solvent at room temperature. The external solvent was renewed after one day equilibration and this procedure was repeated at least three times.

A 5% w/w 1:1 water/ethanol solution was obtained according to the standard procedure [19] and was then dialyzed with pure water. A series of solutions was prepared by either dilution or evaporation. Homogeneous PFSI aqueous solutions were prepared with concentrations up to a polymer volume fraction $\phi_p = 0.12$ [15]. Therefore, swollen membranes and aqueous solutions can be prepared corresponding to the same polymer volume fraction.

2.2. Techniques

The PFSI solution ionic conductivity was measured using Tacussel platinum platanized electrode with a Tacussel CD 7N type conductimeter at 1 kHz. The swollen membrane conductivity was determined by impedance spectroscopy using a mercury cell in order to reduce the effect of the electrode-membrane ohmic drops. The impedance measurements were performed using a Solartron Instrument SI1210 as frequency analyzer and a Paar 273 as potentiostat. The conductivity of the swollen membranes was determined when the imaginary part of the impedance is equal to zero.

Small-angle X-ray scattering (SAXS) experiments using synchrotron radiation were performed on the D22 spectrometer (LURE, laboratoire CEA-CNRS-MENRT, Orsay, France). The spectrometer provides a highly focused beam allowing the pinhole collimation assumption and is equipped with a one-dimensional position sensitive detector [20]. $\lambda = 1.4$ Å was chosen as incident wavelength and the sample to detector distance, D, was varied from 0.5 to 2 m. The explored q values varied from $q = 0.005$ to 0.35 Å^{-1} where q is the momentum transfer ($q = (4\pi \sin \theta/\lambda)$) and 2θ is the total scattering angle. Experiments were performed using 1 mm thick polytetrafluoroethylene cells with thin Kapton® windows.

Small-angle neutron scattering (SANS) experiments were performed on the PAXE spectrometer (Laboratoire CEA-CNRS Léon Brillouin, Orphée reactor, Saclay, France). The spectrometer is equipped with a BF_3 two-dimensional detector composed of 64×64 1 cm^2 cells. The beam size was fixed using a 7 mm diameter diaphragm in front of the

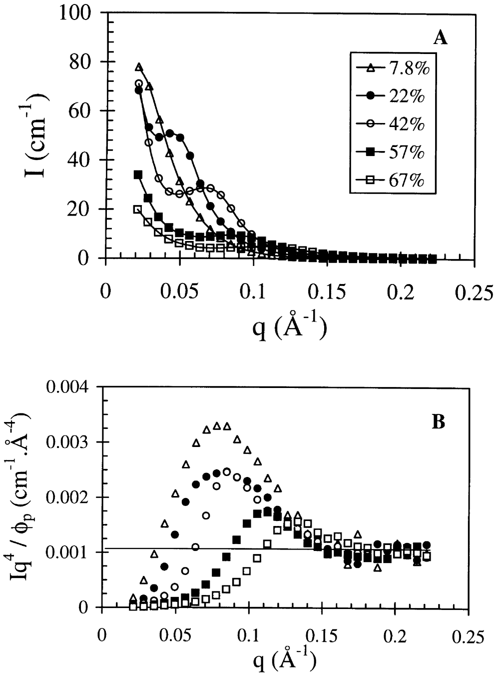

Fig. 1. (A) Evolution of Nafion 117 SANS spectra depending on water content, ϕ_p is the polymer volume fraction. (B) Porod plot of the same data.

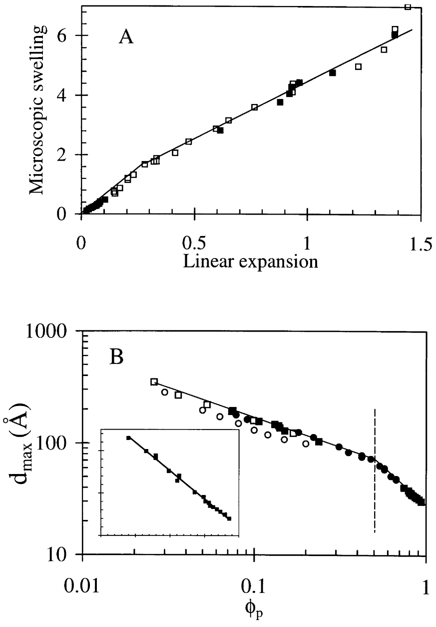

Fig. 2. (A) Microscopic swelling vs. macroscopic linear expansion for the H^+ (■) and Li^+ (□) water swollen membranes. (B) Ionomer peak position vs. polymer volume fraction for the H^+ (■) and Li^+ (●)water swollen membranes and for the H^+ (□) and Li^+ (○) aqueous solutions. The inset corresponds to a zoom of the low water content part of the curve.

sample. Several different configurations were used from $\lambda = 5$ Å, $D = 1.2$ m to $\lambda = 12$ Å, $D = 5$ m in order to access the largest q range available on the spectrometer ($0.005 < q(\text{Å}^{-1}) < 0.4$). Experiments were carried out using quartz cells with a 1 mm path length. Usual corrections [21] for background and incoherent scattering subtraction, transmission correction and for normalization were applied.

3. Results

A series of SANS spectra of a Nafion® 117 Li^+ membrane is presented in Fig. 1 varying the polymer volume fraction, ϕ_p, over a wide range (from 0.7 to 0.07). The scattering maximum, shifts toward smaller q values increasing the water content. Despite the presence of an intense small-angle upturn in intensity at low q values, the ionomer peak is still discernible up to an increase of the membrane volume by a factor 12 ($\phi_p = 7\%$). The complete set of data was obtained with both SAXS and SANS. The spectra obtained with these two techniques are exactly superimposable once normalized by the contrast term confirming that the swollen membranes can be considered as two-phase systems. A scattering curve is a combination of a form factor and of an interference term due, respectively, to the shape and the distribution of the scattering objects. The origin of the ionomer peak can be attributed to the existence of a maximum in one of these two components. The continuous evolution of the scattering maximum position from low to very large water contents thus confirms its attribution to a correlation peak. Despite the existence of Babinet's principle which says that it is not possible to differentiate from a SAXS curve alone if it originates from particles of A dispersed in a phase B or the opposite, [22] one can consider that the correlation is observed between swollen ionic aggregates embedded in the polymer matrix at low water contents and between polymer aggregates at large water contents with an inversion of the origin of the scattering at $\phi_p = 0.5$. The peak position, $q_{\max}$, can be related to a Bragg distance, $d_{\max}$, defined as $q_{\max} = 2\pi/d_{\max}$. The shift of the ionomer peak is very large since it is located at 0.13 Å^{-1} ($d_{\max} = 48$ Å) for a membrane soaked in water at room temperature, and at 0.03 Å^{-1} ($d_{\max} = 210$ Å) for a membrane containing 93% of water. The extrapolation of the peak position to zero water concentration leads to 27 Å as Bragg distance for the dry material. This distance is smaller than the one determined for sulfonated polystyrene or EPDM ionomers for which the radius of the dry clusters was estimated to be roughly 10 Å and larger than the value determined for carboxylated polyethylene based ionomers in which the dry cluster size was estimated to be 4–5 Å [23]. Therefore, the dry cluster diameter is roughly 15 Å which is significantly smaller than the inter-cluster distance and explains the very low value of the ionic conductivity observed at low water contents.

A microscopic degree of swelling can be defined as the increase of the Bragg distance normalized with respect to the Bragg distance extrapolated for the dry membrane. Fujimura et al. [9] first observed that the evolution of the microscopic degree of swelling against the macroscopic linear expansion ratio for PFSI membranes exhibited a linear trend with a slope equal to 6 for macroscopic expansions varying from 0 to 0.16. Fig. 2A presents the microscopic vs. macroscopic swelling obtained for highly swollen H^+ and Li^+ PFSI membranes over an extended water content range up to 1.5 as macroscopic expansion. For low water contents, the membrane was equilibrated with controlled water vapor pressures and the swelling degree was determined from sorption isotherms [10]. The results revealed no difference between the acidic and the Li^+ neutralized form and between the Nafion 115 and 117 membranes. Two different behaviors are observed for a macroscopic linear expansion lower and larger than 0.3 (Fig. 2a). A linear approximation provides a slope equal to 5.6 for low water content while a lower slope (4.2) is obtained for larger water contents. Such a transition indicates a modification of the swelling process. It can be noted that the behavior at low water content does not appear to be linear as stated by Fujimura et al but exhibits a significant curvature when plotted over a larger range of linear expansion.

The fact that both the ionomer peak shifts toward smaller q values and that its intensity increases as water content increases reveals a swelling of the ionic aggregates. However, the behavior observed at low water contents has to be understood not only as an effect of the swelling of the ionic aggregates but also as an evidence that a polymer reorganization occurs with swelling since a linear behavior with a slope close to 1 would be expected in Fig. 2a for an affine swelling of the membrane [9]. The swollen state corresponds energetically to an equilibrium between: (i) the osmotic pressure which leads to dilution of the ionic species; (ii) the elastic deformation of the polymer chains which increases in order to locate the ionic groups at the polymer–water interface; and (iii) the polymer–solvent interfacial energy. Several analyses of small-angle scattering data of perfluorinated ionomer membranes [10,11,24,25] suggested that the specific surface (area of polymer–water interface per polar head) is the more relevant parameter defining the structure of swollen membranes. The value of the specific surface can be deduced from the asymptotic behavior of the scattering curves at large angles. In the presence of a sharp polymer–solvent interface, the intensity has to scale as q^{-4} according to the Porod law [26]. The specific surface, σ, can be extracted from

$$\lim_{q\to\infty} Iq^4 = 2\pi\Delta\rho^2\phi_p\frac{\sigma}{v_0}$$

where $\Delta\rho$ is the polymer–solvent scattering length density difference ($\Delta\rho = 5.27\times10^{10}\ \mathrm{cm}^{-2}$ for neutrons) and v_0 is the average volume of polymer associated with an ionic group ($v_0 = 870\ \text{Å}^3$).

The spectra of swollen PFSI membranes presented on a Iq^4/ϕ_p versus q plot exhibit the same asymptotic behavior indicating that the specific surface is independent of the water content (Fig. 1B). The average value deduced from the Porod limit is $\sigma = 55\ \text{Å}^2$ confirming the previous experimental determination for low water contents [11] and the value deduced from the peak position using geometrical arguments and assuming the existence of spherical aggregates connected by small cylinders [24]. At low water content, the swelling of the ionic aggregates thus involves a continuous increase of the number of ionic groups per aggregate in order to keep constant the specific surface. In other words, a structural reorganization occurs inducing a decrease of the total number of water pools and an increase of the inter-cluster distance significantly larger than the observed linear macroscopic expansion. At large water content ($\phi_p > 0.5$), the membrane is composed of connected polymer particles. The conservation of the specific surface varying the water content can be achieved without major structural modification on a local scale and can then be depicted as a swelling of the network of polymer particles with a decrease of the connectivity.

The double logarithmic plot of the peak position against the polymer volume fraction appears as a more attractive way to represent the data (Fig. 2B). At low water contents, the behavior is linear with a slope equal to -1.33 (inset Fig. 2b) while, at large swelling degrees, a linear trend is also observed with a slope close to -0.5. A transition between two swelling processes was also observed studying the temperature dependence of the swelling properties [8]. It was observed that, for a temperature larger than 140°C, the water content increases much more rapidly as temperature increases. Since this temperature is usually attributed to the polymer matrix glass transition [16,27], the transition was tentatively attributed to the fact that the mechanical resistance of the polymer matrix is smaller at higher temperatures [8]. In Fig. 2B, it appears clearly that the transition between these two regimes appears for a polymer volume fraction equal to $\phi_p = 50\%$ which indicates that the modification of the swelling process is probably not only due to the cross-over of the glass transition but should also be attributed to an inversion from a water-in-polymer to polymer-in-water structure. In order to discriminate between these two possible causes, it would be interesting in the future to study the swelling behavior of PFSI membranes presenting various ionic contents since the swelling degree at a defined temperature is related to the equivalent weight while the glass temperature transition of the polymer matrix is expected to be independent of the ionic content.

Recently, Litt [28] reanalyzing previous SAXS data [6] plotted the evolution of the Bragg spacing calculated from the ionomer peak position against the water volume fraction and he found an almost linear behavior. He suggested that the proportionality between the peak position and the water could be interpreted as originating from a lamellar structure of the ionic aggregates imposed by the semi-crystalline character of the polymer. The fact that the slope found in the present work using a larger linear expansion range and a

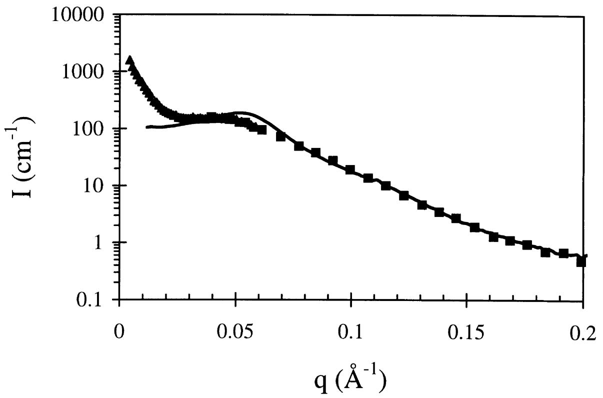

Fig. 3. SANS spectra of Nafion 117 H^+ swollen membrane (■) and solution (solid line) for $\phi_p = 0.05$.

double logarithmic plot of the peak position against the polymer volume fraction is significantly larger than -1 is not in agreement with such interpretation and should be interpreted as an effect of the polymer reorganization with swelling as discussed above. Moreover, such a model can hardly explain the fact that two different scattering maxima related to the crystallinity and the distribution of the ionic domains shift differently toward smaller angles as water content increases as shown recently for short pendant chain PFSI membranes [25].

At large water contents, the linear behavior with a slope equal to -0.5 observed in Fig. 2B suggests a dilution of rod-like polymer aggregates. This deduction is corroborated by the fact that the structure of PFSI solutions was shown to be well described by the existence of cylindrical polymer particles [15]. While, at fixed concentrations, the same peak position is observed comparing acidic swollen membranes and solutions and Li^+ neutralized swollen membranes, a significant shift of the peak position is observed for the PFSI solutions in Li^+ form (Fig. 2B). However, the comparison of the small-angle spectra obtained for Li^+ neutralized solutions and swollen membranes reveals a very different behavior at low angles and an almost perfect match of the scattering curves at large angles which suggests that the local structure on the scale of few nanometers is identical (Fig. 3). The similarities between highly swollen membranes and solutions suggests that the membranes can be considered as a connected network of rod-like polymer particles. The presence of nodes in the network structure induces a poorer spatial arrangement of the polymer particles compared to solutions and the existence of large scales heterogeneities. They are respectively responsible for a lower intensity of the scattering maximum and for the presence of an intense upturn in intensity at low angles whose combined effect induces the apparent shift of the ionomer peak toward small angles in swollen membrane SAXS and SANS spectra. A similar apparent shift of the peak position was evidenced for PFSI solutions in the presence of added salt and was also attributed to a poorer spatial arrangement due in this case to the screening of the electrostatic repulsions between charged polymeric particles [15]. The highly water swollen membranes equilibrated in a 5 M LiCl aqueous solution exhibit the same water content than in pure water which indicates that the driving force defining the structure in highly swollen membranes is rather the polymer–solvent interfacial energy than the electrostatic repulsions between the charged polymeric particles.

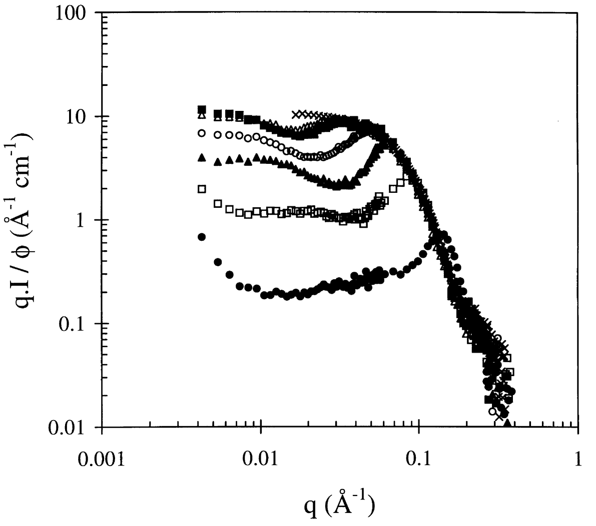

Fig. 4. qI vs.q representation of the SANS spectra of Nafion 115 Li^+ swollen membranes depending on the water content; $\phi_p = 0.66$ (●), $\phi_p = 0.43$ (□), $\phi_p = 0.25$ (▲), $\phi_p = 0.13$ (▲), $\phi_p = 0.075$ (■), $\phi_p = 0.069$ (△). The SANS spectrum obtained for a PFSI solution ($\phi_p = 0.01$) is presented for comparison (×).

The Nafion 115 Li^+ membrane spectra are presented on a double logarithmic qI/ϕ_p vs. q plot in Fig. 4 for a polymer volume fraction ranging from 0.7 to 0.1 and compared to the spectrum obtained for a dilute PFSI Li^+ solution ($\phi_p = 0.012$). Since the intensity scattered at low q values roughly scales as q^{-1}, such a plot provides information about the details of the small-angle upturn. The swollen membrane spectra tend to resemble the dilute solution spectrum as water content increases, namely, the plateau observed at low q values increases in intensity and the scattering maximum vanishes. The existence of a plateau in such a plot suggests a rod-like structure and its level in intensity is related to the osmotic compressibility which increases as polymer concentration decreases. The structure becomes looser increasing the water content and the effect of the interference term decreases. At very large water content, the experimental curve corresponds to the form factor of cylindrical particles with $R = 25$ Å as radius for both the shape and the level of scattered intensity. This result confirms that the highly swollen membranes can be depicted as a connected network of rod-like particles. The contribution of the nodes to the scattering intensity becomes negligible as water content increases but their existence is necessary to explain the existence of mechanical properties. The most striking feature is the existence of a second very

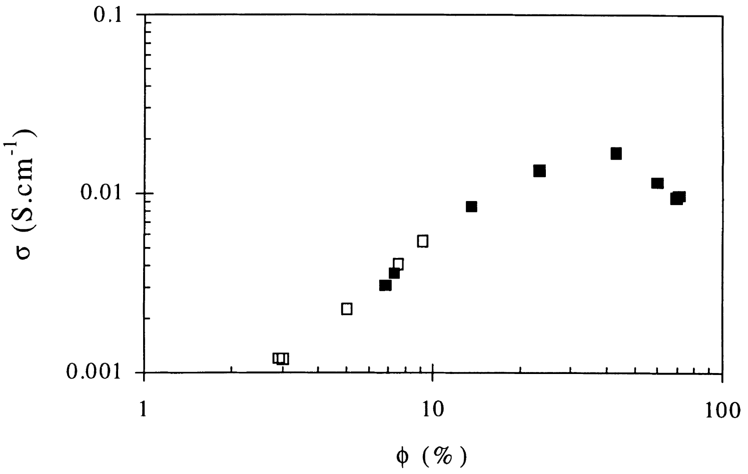

Fig. 5. Conductivity of aqueous PFSI solutions (□) and of swollen membranes (■) depending on the polymer volume fraction.

broad maximum located at very low *q* values which shifts continuously toward small angles as water content increases. This broad maximum is not an artifact due to poor data correction since all the presented data were recorded during the same run and were corrected using the same reference spectra. The existence of a second maximum at low *q* values was already observed for dry and was attributed to a long period between lamellar crystallites because its intensity varies depending on the membrane equivalent weight and on the thermal annealing treatment for solution-cast membranes [6,25,29,30]. This maximum was expected to disappear as the swelling degree increases due to the "melting" of the crystallites resulting from the structural evolution of the membrane upon swelling. Up to now we cannot explain that this maximum is still observable at very large water contents. It would be interesting to study larger equivalent weight PFSI membranes which present a more intense scattering maximum at low *q* values due to a higher level of crystallinity index. Unfortunately such polymers are not commercially available. A recent study [25] of short pendant chain PFSI membranes (***EW*** = 800 g/eq.) has evidenced the presence of a relatively intense well-defined scattering maximum located at small angles and that this maximum is still clearly observed for swollen membranes containing a large amount of water ($\phi_p = 57\%$). However, its attribution to a crystalline component has still to be verified since the wide-angle X-ray scattering spectra do not exhibit a large amount of crystallinity.

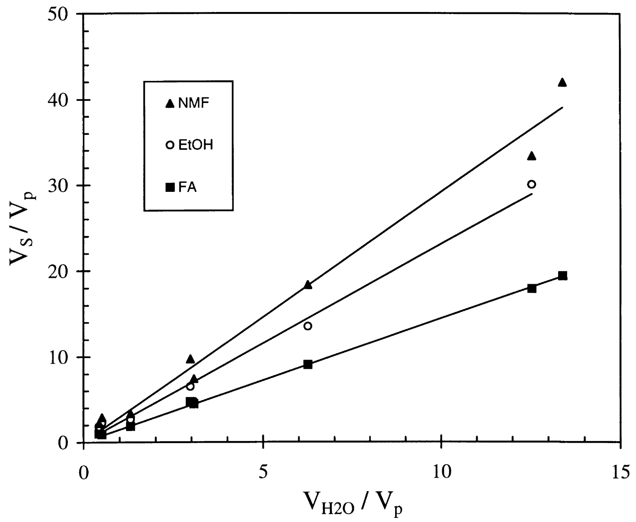

Fig. 6. Swelling degree for different solvents (*N*-methyl formamide, ethanol and formamide) depending on the swelling degree in water. V_S is the volume of solvent and V_p is the dry polymer volume.

The values of the ionic conductivity obtained for swollen membranes and solutions are presented in Fig. 5 depending on polymer concentration. The conductivity data also indicate a modification of the behavior for a solvent content around 0.5. The ionic conductivity is related to both the ion mobility and concentration. At low water content, the increase of the ionic conductivity as water content increases can be attributed to a decrease of the tortuosity of the cluster network, in other words the overall connectivity between clusters increases and the path length from one side of the membrane to the other decreases. At large water content the ionic conductivity of swollen membranes decreases due to the dilution of the ionic groups since the counterion mobility should not be affected anymore by the swelling of the rod-like polymer network. The evolution of the conductivity is identical for the swollen membranes and the solutions at low polymer concentrations confirming the similarity of the structure at least on a local scale since the swollen membrane conductivity was measured by impedancemetry at relatively high frequencies (>10 kHz). Another interesting result deduced from these conductivity measurements is the fact that a maximum in the ionic conductivity is observed for a water content close to $\phi_p = 0.4$. Such a water content can be achieved by soaking the membrane in water at 120°C in a pressure vessel for few hours. This maximum corresponds to an increase of the ionic conductivity by a factor 2 compared to the membrane soaked in

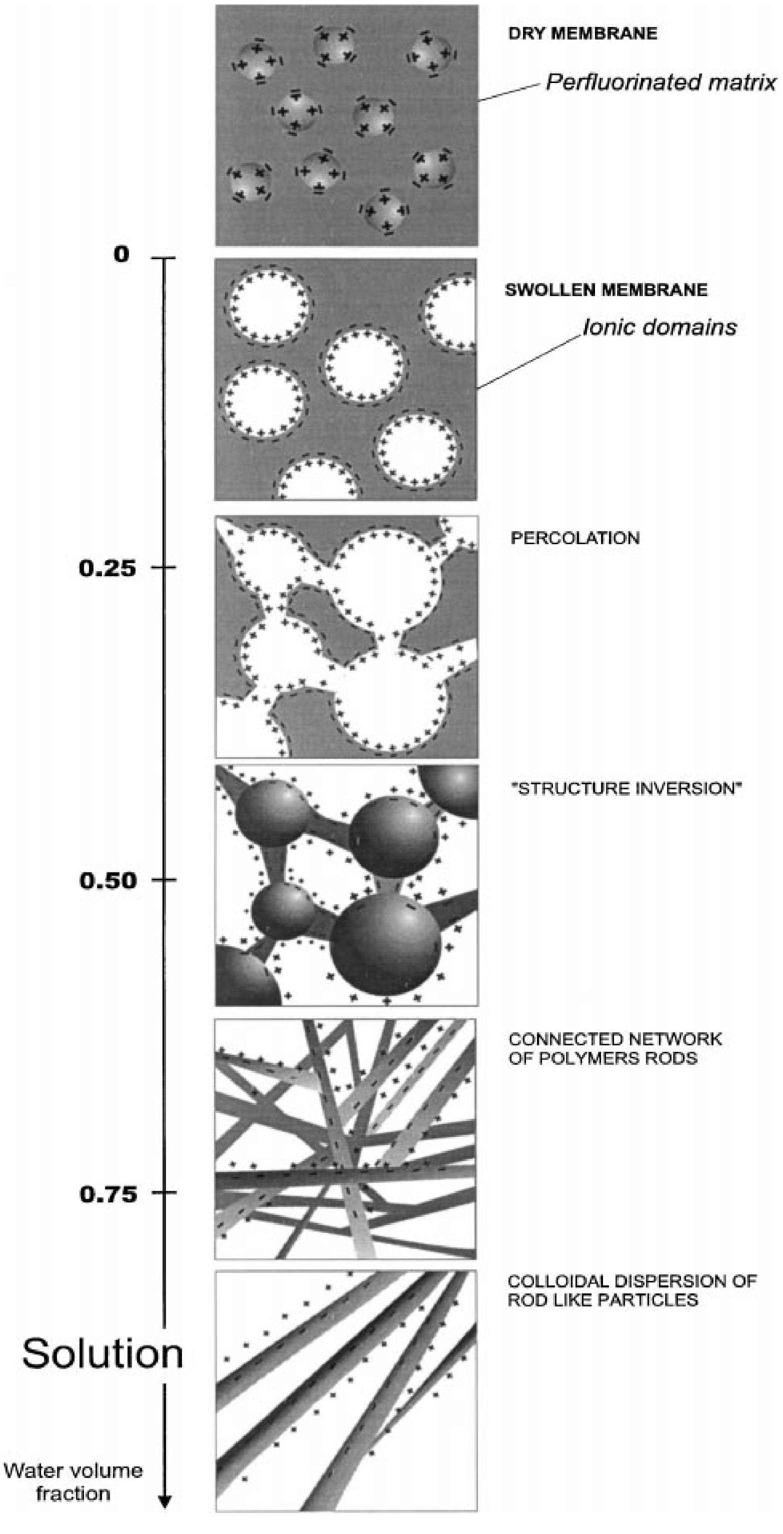

Fig. 7. Schematic representation of the structural evolution depending of the water content.

boiling water. Such a membrane pretreatment increasing the ionic conductivity can be very interesting from an application point of view for instance in H_2/O_2 fuel cells.

A very large increase of the solvent content is observed when a water swollen membrane is soaked in other polar solvents. The experiments were conducted with three different solvents: ethanol, formamide and *N*-methylformamide, respectively, characterized by $\varepsilon = 26$, 111 and 182 as dielectric constant. The results of the swelling measurements versus the initial water content are presented in Fig. 6. A linear trend is observed for the three solvents. The fact that the solvent increase is lower for formamide compared to ethanol and NMF indicates that the driving force is not the dielectric constant of the solvent. The study of PFSI solutions using small-angle scattering techniques revealed that the radius of the polymer rod-like particles was related to the polymer–solvent interfacial energy, for example the radius decreases from 25 Å in water to 20 Å in NMF and ethanol and an intermediate value were found in formamide [14,15]. On the basis of the similarity of small-angle scattering spectra between swollen membranes and solutions, the effect of the nature of the solvent on the local structure is expected to be identical for PFSI membranes and solutions. It is worth noting that these membranes soaked in water exhaust some solvent back to the initial swelling degree indicating that the variation of the solvent content depending on the nature of the solvent is reversible. Moreover the very large increase of solvent content due to an exchange of solvent observed at room temperature (the membrane volume can be multiplied by a factor 2) is not accompanied by any polymer dissolution while a partial dissolution proportional to the swelling degree was observed for a temperature-induced swelling [8]. The swelling increase varying the nature of the solvent thus results from a variation of the specific surface without modification of the connectivity of the rod-like network. Assuming that the structure of the membranes in the highly swollen state is a connected network of rods, it can easily been shown that the conservation of the polymer volume involves that the length between two nodes increases as the square of the radius decreases and that the total volume of the swollen network varies as the power 3 of the distance between nodes. Consequently the volume of swollen membranes should vary as the power 6 of the radius ratio. The linear behavior observed in Fig. 6 indicates that the volume variation changing the nature of the solvent does not depend on the initial water content. The slopes are 2.91, 2.30 and 1.44 for *N*-methylformamide, ethanol and formamide, respectively. Assuming that the value of the radius is 25 Å for water, the radii deduced from the volume variation are 20.9, 21.8 and 23.5 Å for *N*-methylformamide, ethanol and formamide, respectively. These values are in good agreement within the experimental uncertainties with the values determined studying PFSI solutions using the small-angle scattering technique [15].

Based on the present results combined with energetic considerations, a schematic description of the dissolution process can be proposed as depicted in Fig. 7. The dry membrane is characterized by the presence of isolated spherical ionic clusters with a diameter close to 15 Å and an inter-cluster distance close to 27 Å. The swelling induces a modification of the cluster structure which become spherical water pools with the ionic groups at the polymer water interface in order to minimize the interfacial energy. The water pool diameter is close to 20 Å while the inter-aggregate distance is roughly 30 Å indicating that they are still isolated as revealed by the extremely low value of the ionic conductivity and since at low water content, the swollen cluster spatial distribution is well-described by the local order model considering a short range order limited to the four first neighbors (tetrahedral coordination). By increasing the water content, the clusters swell, the cluster diameter increases from 20 to 40 Å while the inter-cluster distance increase is relatively smaller leading to percolation and the number of ionic groups per cluster increases in order to keep constant the specific surface ($\sigma = 55$ Å^2) and consequently the total number of clusters decreases. This reorganization is favored by the presence of water which acts as a plasticizer. For a water volume fraction larger than $\phi_w = 0.2$, the large increase of the ionic conductivity indicates a percolation of the ionic aggregates. The percolation is not due to a modification of the swelling process corresponding to a first order transition since a continuous evolution of the SAXS and SANS spectra is observed. Its origin has to be interpreted as a combination of the effect of the interfacial energy and of the limitation of the swelling due to the polymer chain elastic energy. The increase of the aggregate volume induces an increase of the polymer inter-aggregate volume, which is limited by the maximum distance between two ionic groups along the polymer chain. These geometrical constraints are rather severe and govern the structural evolution. If this condition had not been fulfilled, some isolated groups would be embedded in the polymer matrix which would be strongly energetically unfavorable.

Between $\phi_w = 0.3$ and $\phi_w = 0.5$, the structure is formed of spherical ionic domains connected with cylinders of water dispersed in the polymer matrix. The ionic domain diameter increases from 40 to 50 Å. The connectivity, the length and the diameters of the connecting channels are not known but the increase of the ionic conductivity as water content increases suggests that both the connectivity and the diameter increase. The polymer reorganization is facilitated above the percolation threshold since an ionic group has to overcome a lower energy barrier to migrate from one aggregate to another. The structure is still well described by the local order model probably due to the fact that the volume of the connecting channels is not large enough to give a significant contribution to the scattered intensity in the observed q range. However the percolation threshold can be deduced from the analysis using the local order model since the inter-aggregate distance becomes very close and in some experiments smaller than the aggregate diameter. Since the structural evolution is dominated by interfacial phenomena, the next step of the analysis should be to apply some of the models which have been developed successfully for bicontinuous microemulsions such as the disorder open connected model [31]. However, these models based on geometrical constraints have to be modified in order to take into account the polymeric nature of the hydrophobic phase, which limits the maximum distance between two hydrophobic domains.

At ϕ_w values larger than 0.5, an inversion of the structure occurs and the membranes correspond to a connected network of rod-like polymer aggregates. The mechanical properties of the two phases are significantly different, namely the hydrophobic phase is composed of entangled polymer chains while the hydrophobic phase composed of water and ions is fluid which explains that the structure is always dominated by the possibility of reorganization of the hydrophobic phase. Despite the fact that a spherical shape would be energetically favorable for the polymeric domains in order to minimize the interfacial energy, it is not possible to obtain such a structure at ϕ_{w} values larger than 0.5 because the polymer volume associated with each ionic group is too large compared to the average distance between ionic groups along the polymer chain. The best compromise between the minimization of the interfacial energy and the packing constraints thus leads to the formation of connected cylindrical particles. Between $\phi_{\mathrm{w}} = 0.5$ and $\phi_{\mathrm{w}} = 0.9$, this connected rod-like network swells. The radius of the rods ($R = 25$ Å) is imposed by the interfacial energy and is not modified by increasing the swelling at large temperatures in the same solvent. The swelling is then due to an increase of the distance between nodes and thus to a decrease of the overall number of nodes which explains the fact that a partial dissolution occurs. This partial dissolution which increases linearly as water content increases [8] explains that very large objects are observed in solution by dynamic light scattering experiments [32]. The structure of highly swollen membranes is then very close to the one encountered with PFSI solutions.

Changing the nature of the solvent (e.g. the polymer–solvent interfacial energy) involves a variation of the particles radius and consequently a large increase of the swollen membrane volume without modification of the nodes density in the network as shown by the complete reversibility. Despite the macroscopically observable effect on the membrane volume, the modification of the nature of the solvent induces only a local polymer reorganization through a modification of the area of interface per polar head. At the opposite, the structural evolution from dry to highly swollen membrane requires a large amount of thermal energy to permit the necessary important polymer reorganization. It follows that this evolution induced at a large temperature is not reversible at room temperature. However, the structure and the properties of the membranes can be restored by a thermal annealing of the dry membrane at an elevated temperature (>150°C) [30]. The existence of this swelling memory explains the different values of the water uptake and of the ionic conductivity observed by several authors consecutive to a different membrane pretreatment.

4. Conclusion

The small-angle scattering analysis of highly swollen membranes combined with swelling and conductivity measurements allows us to evidence a structure inversion at 50%. The structure, at low water contents, corresponds to more or less connected spherical domains of water embedded in the polymer matrix while the structure for higher water content is a connected network of polymer rods. The structural evolution over the entire concentration range is determined by the polymer–water interfacial energy which imposes the conservation of the specific surface ($\sigma = 55$ Å^2).

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