Small-Angle Scattering Study of Water-Swollen Perfluorinated Ionomer Membranes

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ABSTRACT: A structural study using both small-angle X-ray and neutron scattering (respectively SAXS and SANS) of water-swollen perfluorosulfonated ionomer (PFSI) membranes is presented. The comparison between the SAXS and SANS spectra combined with the analysis of both the scattering invariant and the Porod behavior of the scattering curves confirms the phase separation between the water pools and the perfluorinated matrix. The experimental data obtained in absolute units were analyzed in terms of the different models proposed for ionomers, and the local order model appears as the best model for describing the structure of swollen PFSI membranes. The size of the water pools and the number of ionic groups per ionic aggregate deduced from the analysis of the asymptotic behavior of the scattering curve at large angles compare well with the values deduced from the local order model. The SAXS spectra of swollen PFSI membranes are presented for the first time over an extended angular range covering 3 decades of angles using an ultra-small-angle scattering camera. The study of the small-angle upturn in intensity at very low angles revealed the existence of large-scale fluctuations.

Introduction

The ionomers are polymers containing up to 15 mol % of ionic groups along the polymer chain.[1,2] The existence of a small-angle scattering maximum, called "ionomer peak", combined with the observation of dark spots on transmission electron microscopy pictures was attributed to the aggregation of the ionic groups in the low dielectric constant and hydrophobic polymer matrix.[3] The theoretical approaches gave an insight of the ion aggregation in multiplets and ionic aggregates,[4−6] but the shape, the size, and the distribution of these ionic aggregates deduced from the ionomer peak are still subject to controversy.

Among the numerous specific characteristics of the ionomers, their mechanical and ionic conductivity properties are the most important on an industrial point of view and have led to use of these polymers either as dry bulk materials or as swollen membranes.[2] Despite the advantages of studying swollen membranes, most of the structural models such as the "core−shell" model[7] were developed for dry bulk materials and were often directly applied to swollen membranes.[8,9] The presence of water leads to ionization of the ionic dipoles and swelling of the ionomer, modifying strongly the structure of the membrane. The water was shown to be localized in water pools,[10] and a reverse micellar structure was suggested (water droplets surrounded by the polymer matrix with the ionic groups at the polymer−solvent interface).[11]

The structural studies devoted to swollen membranes were mainly performed on perfluorosulfonated ionomer membranes (PFSI)[12] due to their industrial interest in chlor-alkali production and in H_2/O_2 fuel cells.[1,2,13] Fujimura et al.[8] proposed describing the structure of the swollen membranes using the core−shell model, while Gierke et al.[11] proposed a model based on space-filling arguments assuming a simple cubic lattice of spherical ionic aggregates. More recently, a model based on the existence of a local order between ionic aggregates was proposed.[14] This model was able to reproduce satisfactorily the small-angle neutron scattering (SANS) spectra of PFSI membranes by varying the water content from the dry membrane up to a swelling degree corresponding to 26% by volume of water.

The small-angle scattering spectra of ionomers are known to present an upturn in intensity at very low angles which was often neglected as arising from microvoids, impurities, or film preparation artifacts.[15] The contrast variation methods using either neutrons for swollen membranes[10] or X-rays for dry ionomers[16] indicated that the upturn was strongly related to the ionic aggregates. The use of an ultra-small-angle X-ray scattering (USAXS) camera allowed the investigation of the small-angle upturn for dry bulk sulfonated polystyrene ionomers. The origin of the upturn is now generally attributed to large-scale density fluctuations of the scatterers.[16,17]

All the SAXS and SANS spectra of PFSI membranes presented in the literature were recorded over a limited angular range focusing on the scattering maximum. In the present work, the small-angle scattering spectra of PFSI membranes have been recorded over an extended q range in order to analyze both the asymptotic behavior at large angles (Porod analysis) and the upturn in intensity scattered at low angles. The Porod analysis will allow extraction of the area of the water/polymer interface per polar head and the radius of the clusters independently of any model. The adjustment of the data on an absolute scale of intensity combined with the Porod analysis will allow for the first time discrimination between the different models proposed for the swollen membranes. The local order model will be improved in order to reduce significantly the number of adjusting parameters. In addition, the small-angle

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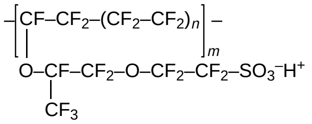
X-ray and neutron scattering (respectively SAXS and SANS) spectra will be compared and the effect of parameters such as the thickness of the membrane or the counterion on the structure will be studied. Such a reexamination of the small-angle scattering data and models appears necessary in order to progress in the understanding of the structure properties relationships.

Experimental Section

The PFSI membranes used in these experiments are commercialized under the trade name Nafion by du Pont de Nemours & Co. and correspond to the following chemical formula:



$$-[CF(-O-CF(CF_3)-CF_2-O-CF_2-CF_2-SO_3^-H^+)-CF_2-(CF_2-CF_2)_n]_m-$$

The Nafion 117 membrane is characterized by its equivalent weight, EW = 1100 g/equiv corresponding to 13 CF_2 groups on average between two lateral chains, and its dry membrane thickness, 175 μm. The Nafion 115 and 112 membranes present the same EW compared to the Nafion 117 membrane, but the membrane thicknesses are 125 and 50 μm, respectively.

The membranes were cleaned in boiling concentrated nitric acid for 1 h, rinsed several times with pure water, and dried overnight at 110 °C. Neutralized membranes were prepared by soaking the polymer for 3 h in a 1 M LiOH solution. The membrane were equilibrated at least 5 h in water at room temperature. The solvent uptake was determined by weighing. The solvent volume fraction, ϕ, was calculated assuming that the polymer density is 2.1 g/cm^3.[18] For the H^+- and Li^+-swollen membranes, the water volume fraction is $\phi_w = 29\%$.

The SANS experiments were carried out at Laboratoire Léon Brillouin (CEA/CNRS, Orphée reactor, Saclay, France) on the PAXE spectrometer. The overall angular range ($0.007 < q$ (Å^{-1}) < 0.3 with $q = 4\pi \sin(\theta/\lambda)$, where θ is the scattering angle) was accessed by varying the wavelength from $\lambda = 5$ to 15 Å and the sample to detector distance from 1.2 to 5 m. The samples were studied in quartz cells with 1 mm path length. The signal of the empty cell and the water incoherent scattering were subtracted. The data were normalized by the incident flux determined during the transmission measurements.[19]

The SAXS experiments were performed using the synchrotron radiation at LURE (CEA/CNRS/MENESR, Orsay, France) on the D22 spectrometer with a linear position-sensitive detector. The incident wavelength was 1.4 Å, and the sample to detector distance was varied from 0.7 to 1.7 m ($0.008 < q$ (Å^{-1}) < 0.4). The membranes were studied in polytetrafluoroethylene cells with Kapton windows.

The USAXS experiments were performed on a double crystal multiple reflection camera.[20,21] The X-ray beam, produced by a RU300 rotating anode from Rigaku at 18 kW with a Cu Kα target, coming out of the monochromator crosses the sample and is then analyzed by a scintillator rotating around the analyzer axis. The monochromator and the analyzer are identical multiple-reflection channel-cut crystals. The apparatus and the data desmearing method are described in detail in refs 20 and 21.

Small-Angle Scattering Background and the Models

The ionomer peak can be described as an oscillation of the form factor (intraparticle origin) associated with the ionic aggregates considered as noninteracting particles. The core−shell model considers that the water pools are surrounded by a first shell composed of polymer chains and by a second shell containing some ionic groups (Figure 1a).[22] The scattered intensity can be calculated from the scattering length density profile:[7,15]

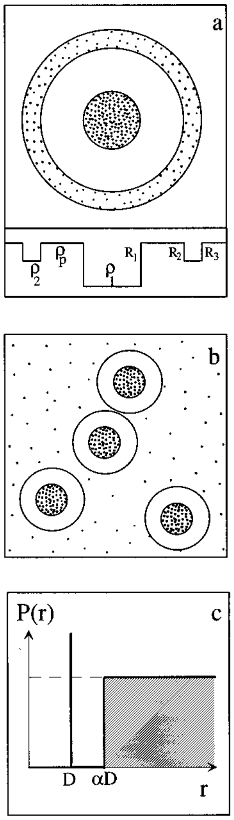


Figure 1. Different models proposed for PFSI membranes: (a) the core shell model; (b) the random distribution model; (c) the local order model. The corresponding scattering length density profile is also presented for the core−shell model.

$$I(q) = \frac{16\pi^2}{9V_p}[(\rho_p - \rho_1){R_1}^3\Phi(qR_1) + (\rho_p - \rho_2)({R_3}^3\Phi(qR_3) - {R_2}^3\Phi(qR_2))]^2 \quad (1)$$

where R_1 and ρ_1 are respectively the radius and the scattering length density of the ionic core, R_2 and R_3 are respectively the inner and the outer radii of the shell of scattering length density ρ_2, ρ_p is the polymer scattering length density, V_p is the average sample volume per aggregate, and

$$\Phi(x) = 3\frac{\sin(x) - x\cos(x)}{x^3} \quad (2)$$

The “depleted zone core−shell model” corresponds to a core−shell model in which R_3 is equal to infinity. The second ionic shell is thus replaced by the matrix containing a homogeneous distribution of the isolated ionic groups:

$$I(q) = \frac{16\pi^2}{9V_p}[(\rho_p - \rho_1){R_1}^3\Phi(qR_1) + (\rho_p - \rho_2){R_2}^3\Phi(qR_2)]^2 \quad (3)$$

The ionomer peak can originate from the spatial distribution of the ionic aggregates (interparticle origin). For scattering objects presenting a spherical symmetry, the scattered intensity can be written as the product of an interference term, $S(q)$, describing the spatial distribution of the scatterers and of a form factor, $F(q)$, related to the shape and the dimension of the particles:

$$I(q) = \frac{(\Delta\rho)^2}{V_p}(F(q))^2 S(q) \tag{4}$$

where $\Delta\rho = \rho_p - \rho_{H_2O}$ is the scattering length density difference between the perfluorinated matrix and the solvent. Assuming a random distribution (Figure 1b), an analytical form of the interference term was proposed, introducing a hard-sphere repulsion potential and a closest distance of approach, $2R_{CA}$, between the ionic aggregates.[15]

$$S(q) = \frac{1}{1 + (8V_{CA}/V_p)\epsilon\Phi(2qR_{CA})} \tag{5}$$

where $V_{CA} = 4\pi R_{CA}{}^3/3$ and ϵ is a constant very close to 1.

The water is supposed to be totally contained in the spherical ionic aggregates. Therefore, $V_p = 4\pi R^3/(3\phi_w)$ where ϕ_w is the water volume fraction and the form factor of homogeneous spheres of radius R is given by $F(q) = \phi_w V_p \Phi(qR)$.

The local order model is based on the existence of a short-range order and a long-range gas-like disorder. These hypotheses are taken into account in a simplified radial distribution function (Figure 1c) in which the four first neighbors of an ionic aggregate are located at a well-defined distance, D, while the following ionic aggregates located at a distance larger than αD are assumed to be randomly distributed. The scattered intensity can then be expressed as

$$I(q) = \frac{4\pi R^3\phi_w(\Delta\rho)^2}{3}\Phi(qR)^2\left(1 + 4\frac{\sin(qD)}{qD} - z\Phi(\alpha qD)\right) \tag{6}$$

where R is the radius of the ionic aggregates and z is the lack of ionic aggregates in the distribution function due to the existence of the correlation hole.

The proposed models do not take into account the upturn in intensity at low angles. It was then suggested that the small-angle upturn originates from large-scale fluctuations which could be described by the Debye–Bueche model. This model assumed an exponential damping of the spatial correlations characterized by a correlation length, ξ, leading in the reciprocal space to the following expression of the scattered intensity:

$$I(q) = \frac{A\xi^3}{(q^2\xi^2 + 1)^2} \tag{7}$$

where A is a scaling constant. For ξ values larger than the explored q values (≈100 nm), the scattered intensity appears to scale as q^{-4} in the explored q range.[23]

The scattered intensities can be divided by the scattering invariant in order to normalize the intensities, to avoid any hypothesis on the contrast term such as the quantity of ion pairs embedded in the perfluorinated matrix, and to compare directly SAXS and SANS data. The scattering invariant for a two-phase system is defined as[24]

$$\mathrm{INV} = \int_0^\infty q^2 I(q)\,\mathrm{d}q = (\Delta\rho)^2\phi_w(1 - \phi_w) \times 2\pi^2 \tag{8}$$

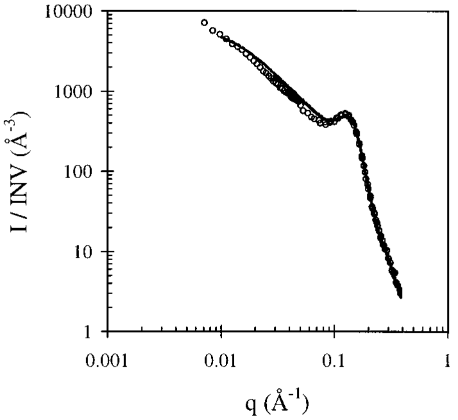


Figure 2. SAXS (solid line) and SANS (○) spectra normalized by the scattering invariant of the water-swollen Li^+ PFSI membrane.

At large angles, the effect of the interference term on the scattering curve can be considered as negligible. Assuming a sharp polymer–solvent interface, the asymptotic behavior of the scattering curves was shown to be related to the quantity of interface through the relation:[24]

$$\lim_{q\to\infty} q^4 I(q) = 2\pi(\Delta\rho)^2\Sigma = \frac{\Sigma\mathrm{INV}}{\pi\phi_w(1 - \phi_w)} \tag{9}$$

where Σ is the surface over total volume ratio. It is worth noting that the Σ determination is not model dependent and that the size of the scattering particles can be extracted from the Σ value assuming a geometry (i.e., spherical aggregates).

Results

The SANS and SAXS spectra of the Nafion 117 Li^+ membrane equilibrated with neat water are presented over an extended q range in Figure 2. The spectra have been normalized by the scattering invariant in order to compare directly the SANS and SAXS data. The two spectra are superimposable over the entire angular range, indicating that the swollen membranes can be analyzed as two-phase systems. The contrast mainly arises from the scattering length density difference between the water and the perfluorinated matrix. The calculated contrast terms for water-swollen PFSI membranes, assuming 2.1 g/cm^3 as the density of the perfluorinated matrix, are very close for neutrons and X-rays ($\Delta\rho_{\mathrm{neutron}} = 5.27 \times 10^{10}$ cm^{-2} and $\Delta\rho_{\mathrm{X-rays}} = 5.64 \times 10^{10}$ cm^{-2}). These contrast terms were calculated without taking into account the contribution of the ionic groups, but it can be shown that this contribution is negligible compared to the contrast between the perfluorinated matrix and water.

The SANS spectrum obtained in absolute units allows determination of the experimental scattering invariant by the q-integration of the scattering curve according to eq 8 and deduction of the experimental contrast term ($\Delta\rho_{\mathrm{exp}} = 4.86 \times 10^{10}$ cm^{-2}). The good agreement between the experimental and the calculated values indicates that the number of hydrated ionic groups dispersed in the polymer matrix is lower than 10%; namely, the ionic groups and the solvent molecules are located in water pools as previously shown by the SANS contrast variation method.[10] The swelling agent acts as a plasticizer as shown by ^{19}F NMR[25] releasing most of the conformational constraints resulting from cluster-

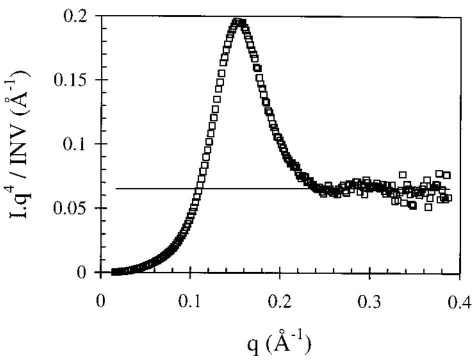


Figure 3. Porod representation of the SAXS curve presented on Figure 2.

ing. The existence of isolated ion pairs embedded in the polymer matrix usually taken into account in the models for dry ionomers[15] is thus highly questionable for swollen membranes, which is confirmed by the ESR study of the location of polar spin probes in swollen membranes.[26]

At large q values, the scattered intensities of swollen PFSI membranes (Figure 1) scale as q^{-4}, indicating that the polymer−solvent interface is sharp and confirming the phase separation in the swollen membranes. The q^{-4} behavior at large q allows one to extract independently the dimension of the water pools from the surface over volume ratio. In Figure 3, the SAXS spectrum is presented on a Porod representation. A constant background defined from a $I(q)$ versus q^{-4} plot was subtracted.[27] The Iq^4 vs q plot exhibits a well-defined plateau at large q values which allows an easy determination of the Porod limit. The surface over total volume ratio, determined using eq 9, is $\Sigma = 0.0439$ Å^2/Å^3. Assuming spherical particles, a value of the radius can be extracted from the relation $\Sigma = 3\phi_w/R$. This value of the radius, $R = 19.8$ Å, will be either compared to the fit values deduced from the models or introduced in the fitting procedure in order to reduce the number of free parameters.

The agreement between the experimental contrast term deduced from the scattering invariant and the one calculated from the chemical formula, associated with the Porod behavior of the scattering curves and energetic arguments, allows one to assume that all the ionic groups are located at the polymer−solvent interface. The area per polar head, σ, can then be calculated from the surface over volume ratio by introducing the average volume of polymer associated to one ionic group calculated from the equivalent weight ($v_0 = 870$ Å^3).

$$\sigma = \frac{v_0\Sigma}{1 - \phi_w} \tag{10}$$

The value of σ is 54 Å^2 and is in good agreement with the value calculated by Dreyfus[28] from the position of the SAXS peak using space-filling arguments and considering that the spherical ionic aggregates are connected by small cylinders according to Gierke's model.[29]

The number of ionic groups per aggregate, N, is easily determined by dividing the surface of one cluster ($4\pi R^2$) by the specific surface ($\sigma = 54$ Å^2):

$$N_S = \frac{4\pi R^2}{\sigma} = \frac{36\pi\phi_w^{\,2}(1 - \phi_w)}{\Sigma^3 v_0} \tag{11}$$

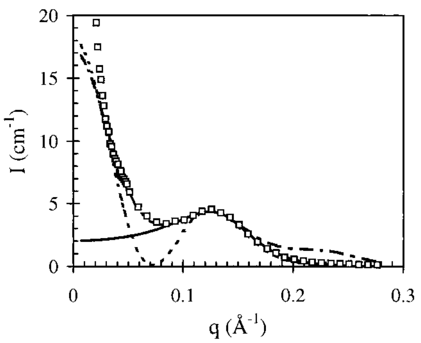


Figure 4. SANS data (□) fitted with the original (−•−) and depleted zone (- - -) core−shell model and with the random distribution model (—).

The number of ionic groups per aggregate is found to be $N_S = 90$. The same result can be obtained from the volume of one ionic aggregate ($4\pi R^3/3$) by taking into account the volume of the water molecule (30 Å^3) and the number of water molecules per cluster calculated from the water volume fraction.

In the intermediate q range, the spectra present a well-defined scattering maximum corresponding to the so-called ionomer peak. The ionomer peak obtained in absolute units allows comparison of the experimental data to the calculated curves obtained from the different models proposed for ionomers.

The depleted zone core−shell model proposed by Fujimura *et al.*[8] does not reproduce satisfactorily the shape of the scattering curve (Figure 4). The values of the parameters obtained from the fitting procedure are $R_1 = 15$ Å, $R_2 = 43$ Å, $\rho_2 = 0.56 \times 10^{10}$ cm^{-2}, and $V_p = 8.12 \times 10^4$ Å^3. The ρ_2 value can be understood as the fact that 11% of the water molecules are dispersed in the matrix, which is in agreement with the starting hypothesis of the model and with the analysis of the scattering invariant. Nevertheless, V_p is only equal to R_2^3, while the volume of sample associated with an ionic aggregate, V_p, should be significantly larger than the volume of the aggregate ($4\pi R_2^3/3$) in order to be able to consider the ionic aggregates as isolated particles. Moreover, there are no ionic groups between R_1 and R_2. Thus, the volume of the ionic core divided by the volume of the polymer shell should be larger than the water volume fraction ($\phi_w = 29\%$) and the values of the parameters deduced from the fitting procedure lead only to $(R_1/R_2)^3 = 4.2\%$.

The original core−shell model leads to a better agreement with the data except the excess of intensity scattered at large angles (Figure 4). The values of the five parameters were found to be $R_1 = 11.8$ Å, $R_2 = 54$ Å, $R_3 = 62$ Å, $\rho_2 = 0.08 \times 10^{10}$cm^{-2}, and $V_p = 2.315 \times 10^4$ Å^3. As observed for the depleted zone core−shell model, unphysical values of the parameters are obtained; namely, the difference between R_1 and R_2 is too large and V_p is too small. Moreover, the contrast of the shell compared to the matrix is only 1.5% of the contrast of the core.

The peak position is $q_{\max} = 0.125$ Å^{-1} which corresponds to $d_{\max} = 50.25$ Å as Bragg distance. The classical analysis is to consider the space-filling argument based on a simple cubic lattice as proposed by Gierke *et al.*[11] The number of ionic groups per aggregate and its radius can be obtained according to the relations

$$N = \frac{d_{\max}{}^{3}(1 - \phi_w)}{(v_0 - v_{SO_3})} \qquad (12)$$

$$R = \left(\frac{3}{4\pi}\left(\phi_w + \frac{v_{SO_3}(1 - \phi_w)}{(v_0 - v_{SO_3})}\right)\right)^{1/3} d_{\max} \qquad (13)$$

where v_{SO_3} is the volume of one ionic group (=68 Å^3).[11] The calculated number of ionic groups per cluster and the radius are respectively $N = 112$ and $R = 22$ Å. These two values are significantly larger than the ones determined from the Porod analysis ($R = 19.8$ Å and $N = 90$). A better agreement was obtained considering that the ionic groups do not participate to the aggregate volume ($N = 104$ and R=22). This rough model leads to relatively good results within only 10% of errors.

The scattering curve calculated from the model based on a random distribution of spherical water pools does not fit the data for both the peak position and the level of the scattered intensity when the value of the radius is chosen as $R = 19.8$ Å. Nevertheless, the scattering curve can be reproduced with an excellent agreement for q values larger than 0.09 Å^{-1} (Figure 4) considering the radius as a parameter and introducing a scaling factor, K, in order to take into account the effect of the existence of isolated ionic groups on the contrast term. The values of the parameters are then $R = 16.5$ Å, $R_{CA} = 19.2$ Å, and $K = 0.6$. The radius of the ionic aggregates and the scaling factor are found to be rather small compared to the values determined from the Porod analysis and from the analysis of the scattering invariant, respectively.

The ionic groups are attached on the polymer chains, and the formation of ionic aggregates is energetically favored. Therefore, the existence of an ionic aggregate increases the probability of finding other aggregates in its close vicinity. The three basic hypotheses of the local order model are the existence of a short-range order, a long-range gas-like disorder, and a fixed number of first neighbors.[14] According to the local order model, the scattering maximum is due to the presence of four neighbors at a well-defined distance, D, in order to agree with the percolation threshold at low water content.[28] Such a distribution is similar to that of a diamond-like structure, and space-filling arguments can be used on the basis of a diamond lattice to calculate the distance between first neighbors using only the water volume fraction and the dimension of the particles determined from the Porod analysis.

$$D = \left(\frac{\sqrt{3}\pi}{2\phi_w}\right)^{1/3} R \qquad (14)$$

For spherical particles of radius $R = 19.8$ Å, the calculated distance between ionic aggregates is $D = 42.24$ Å. The parameters are then z and α. The agreement between the experimental and the calculated curves is excellent for both the shape of the scattering curve and its intensity using $z = 4.45 \pm 0.05$ and $\alpha = 1.155 \pm 0.005$ (Figure 5).

The number of ionic groups per cluster can be obtained from the parameters of the local order model. Considering that z ionic aggregates are "missing" in a sphere of radius αD, it can easily been shown that the number of ionic groups per aggregate is equal to

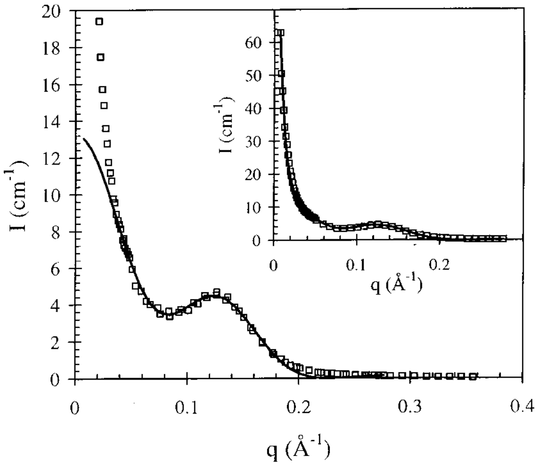


Figure 5. SANS data (□) fitted with the local order model (solid line). The inset presents the same result with a Debye–Bueche component ($\xi = 80$Å).

$$N_z = \frac{2\sqrt{3}\pi^2\alpha^3 R^3(1 - \phi_w)}{3\phi z v_0} \qquad (15)$$

The calculated value, $N_z = 86$, is in excellent agreement with the value determined from the Porod analysis. Comparing eqs 11 and 15, a relation between α and z is obtained:

$$\alpha^3 = \frac{2z}{\sqrt{3}\pi} \qquad (16)$$

Nevertheless, it was not possible to satisfactorily reproduce the experimental data by introducing this relation in the fitting procedure. For $z = 4.45$, the value of α deduced from the fit ($\alpha = 1.155$) is significantly lower than the one calculated using eq 16 ($\alpha = 1.178$) which suggests that the density of ionic aggregates in the vicinity of a reference one is larger than the average density of ionic aggregates in the sample. This result is in agreement with the starting hypothesis of the local order model and can be attributed to the presence of crystallinity.

The best agreement between the calculated and the experimental scattering curves was obtained with the local order model for both the shape of the scattering curve and its intensity between 0.03 and 0.2 Å^{-1}. At larger q values, the discrepancy observed on a logarithmic scale can be attributed to the fact that the model considers homogeneous and monodisperse ionic domains. A better agreement could be obtained by introducing an aggregate radius polydispersity and considering the existence of an ionic shell at the water–polymer interface, but at the expense of at least two parameters. At low q values, the small-angle upturn in intensity cannot be entirely reproduced by the model. The spectra display a small-angle upturn of the scattering intensity which roughly scales as q^{-1} (Figure 1), while the small-angle upturn observed for dry ionomers[16,17,23] usually scales as q^{-4}. The small-angle upturn can be satisfactorily reproduced (inset Figure 5) by considering the existence of large-scale fluctuations of the density of ionic domains and using the Debye–Bueche model with a correlation length equal to 80 Å. This value appears very small for large-scale fluctuations but surprisingly corresponds to the dimension of the correlation hole of the local order model. The existence of density fluctuations is in agreement with the results obtained with the local order model; namely,

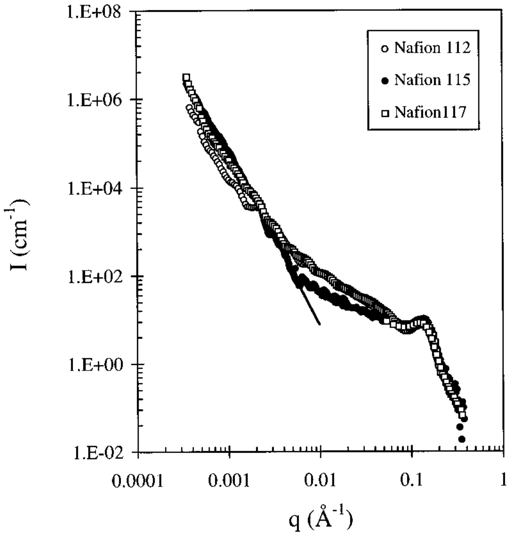


Figure 6. USAXS data obtained for the Nafion 117 (□), 112 (○), and 115 (●) membranes. The solid line was calculated using the Debye-Bueche model ($\xi = 3500$Å).

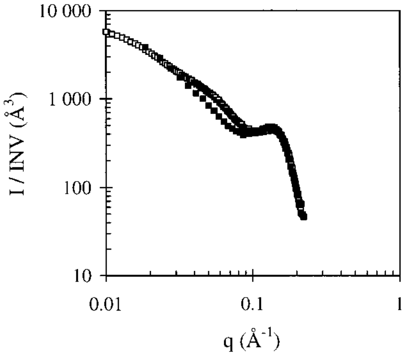


Figure 7. SAXS data obtained for the Nafion 117 H$^+$ (□) and Li$^+$ (■) membranes.

the density of ionic domains around one ionic aggregate is larger than the average density.

In order to study the small-angle upturn, the spectra of swollen Nafion 112, 115, and 117 membranes have been recorded over an extended q range using a USAXS camera (Figure 6). The USAXS spectra present a q^{-4} behavior at very low q values ($q < 5\ 10^{-3}$ Å^{-1}). This upturn can be analyzed as arising from large-scale density fluctuations, and the correlation length, extracted from a $I^{-1/2}$ vs q^2 plot,[30] is then $\xi \approx 3500$ Å. The effect of the membrane thickness is only sensitive in the intermediate q range where the intensity roughly scales as q^{-1}. The spectra obtained for the Nafion 117 and 112 membranes are almost identical, while a significant difference in the small-angle upturn is observed for the Nafion 115 membrane. This result suggests that the small-angle upturn can be strongly influenced by the membrane preparation method as previously proposed.[31] Both the scattering maximum and the Porod behavior are identical for the three membranes, indicating that the local structure is governed by the interfacial energy between the solvent and the perfluorinated matrix.

The water uptake of PFSI membranes strongly depends on the counterion, but the swelling degree is almost identical for the acid and lithium forms.[32] The SAXS spectra of the H$^+$ and the Li$^+$ membranes are presented on Figure 7. The spectra are identical at large q values, but an excess of intensity is observed in the small-angle upturn for the acid membrane. This difference can be attributed to the crystallinity of the polymer which is larger for the acid form compared to the neutralized one (respectively 12% and 8%).[8] The long period between crystallites was shown to induce a scattering maximum at low q values.[8,11] The crystalline component is rather small for the Nafion 117 membrane due to the low crystallinity index and appears only as a shoulder superimposed on the small-angle upturn as revealed by the study of quenched samples[33] or of annealed solution-cast membranes.[34] The modification of the upturn depending on the counterion indicates that the crystallites still exist in the swollen membrane as previously suggested.[35] The existence of a poorly defined crystalline component in the spectra does not allow properly study of this part of the scattering curve.

Conclusions

The SAXS and SANS spectra of water-swollen PFSI membranes were recorded over an extended q range which allow analysis of both the Porod behavior of the scattering curves and the small-angle upturn. The asymptotic behavior of the scattering curves allows one to determine the surface over volume ratio and the radius of the ionic aggregate supposed to be spherical. The spectra were compared to the models, and the local order model is the only one able to reproduce satisfactorily the shape and the intensity of the scattering curves. Moreover, the values of the parameters are in agreement with the existence of the percolation threshold and with the number of ionic groups per aggregate. The study of the small-angle upturn using a USAXS camera allowed evidence of the existence of large-scale fluctuations with a correlation length larger than 3000 Å.

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