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Polymer 46 (2005) 8430–8437
polymer
www.elsevier.com/locate/polymer

SAXS characterization of the Nafion membrane nanostructure modified by radiation cross-linkage

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Received 21 March 2005; received in revised form 24 May 2005; accepted 2 June 2005
Available online 21 July 2005

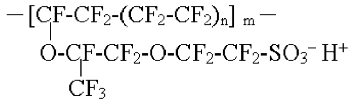
Abstract

The present study employs small-angle X-ray scattering (SAXS) to investigate the water-swollen structures of two types of Nafion membranes, commercial Nafion 117 membranes and the membranes synthesized from the Nafion precursor, subjected to gamma radiation. The membrane structure can be characterized by two-length scales, comprised the long-range order of lamellar crystalline domains in the matrix and the local order of ionic cluster domains. Both the long-range order lamella and local order cluster in the membranes are significantly affected by the radiation-induced cross-linking. We have extended a local order model to take into account the polydispersity effect, which can more satisfactorily reproduce the ionomer SAXS peak than other existing models. The structural parameters determined from the SAXS model analysis are self-consistent with those obtained from the model-independent Porod analysis. The modified membrane structure by the radiation cross-linking is very helpful for developing a high performance and low cost of direct methanol fuel cells.

Keywords: Small-angle X-ray scattering; Ionomer membrane; Gamma irradiation

1. Introduction

Nafion, a best-known perfluorosulfonated ionomer (PFSI) membrane, has been widely used as a proton-conducting electrolyte in electrochemical devices [1]. For instance, in the highly interested direct methanol fuel cells (DMFC), the Nafion membrane is a vital component serving as (1) a separator to prevent mixing of fuel and air, and (2) an electrolyte to transport protons from the anode to the cathode [2]. The Nafion ionomer can be simply characterized by a hydrophobic polyterafluoroethylene backbone with regularly spaced shorter side-chains, terminated by hydrophilic SO_3^- ionic groups. The molecule architecture of the studied Nafion 117 membrane from the DuPont company is



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

Dry Nafion membranes are composed of ionic clusters dispersed in a perfluorinated matrix. In the solvent-swollen Nafion membranes, the resulting cluster structure is formed of water pools with the ionic groups located at the polymer–solvent interface, which is embedded in the perfluorinated matrix. These solvent-swollen clusters are closely related to the ionic conductivity. For improving the electrochemical properties of Nafion membrane in DMFC, reducing the crossover effect [3] of fuel in the separator and remaining a good conductivity of electrolyte is required. The modification of proton exchange membrane (PEM) with the cross-linked structure induced by gamma irradiation [4,5] is shown recently as a novel way [6]. It needs to be investigated that the radiation cross-linked structure cannot only suppress the crossover effect of fuel in a separator but also change the spatial distribution and aggregate size of formed ionic clusters. However, no study on the structural characterization of the radiation-induced cross-linked PEM

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doi:10.1016/j.polymer.2005.06.010

has been reported. Small-angle X-ray and neutron scattering (SAXS and SANS) are the most efficient techniques to study accurately the nanostructure of the phase-separated polymer materials with the unique advantages of nondestructive way and free sample preparation [7–15]. Therefore, SAXS and SANS techniques are currently necessary tools to investigate the nanostructure of a swollen Nafion membrane which is closely related to its proton conductivity. In the present study, SAXS is employed to investigate quantitatively the solvent-swollen nanostructure of the radiation cross-linked Nafion membranes, which is very important for developing high-performance and lower-cost DMFC.

The SAXS intensity profiles collected for this work exhibit two scattering peaks, reflecting two characteristic length scales of the structure. The scattering peak located in the low-q region is attributed to the long period of the lamellar crystalline domains in the perfluorinated matrix [16–18]. Whereas the scattering peak located in the high-q region associates with the ionic cluster domains, and is termed as the ionomer peak. Despite numerous studies for the ionomer membrane structure, the structural properties are still not clearly understood [1,19–22]. The main origin is that several structural models proposed for the interpretation of the SAXS ionomer peak are still controversial. These structural models can be generally categorized into two types: (1) Two-phase model. The SAXS ionomer peak is mainly attributed to an inter-cluster interference, which can be described by the *para*-crystalline lattice model [16,23] and the liquid-like interference models [22]. (2) Core-shell model. The SAXS ionomer peak is herein attributed to the internal structure of ionic clusters that can be characterized by either a typical core-shell model (short-range order distance in the cluster) or a depleted zone core-shell model [17,24].

Recent studies [18,20,21,25] by Gebel et al. on the swollen ionomer membranes showed that only the local order model could reproduce satisfactorily the shape and the absolute intensity of the SAXS ionomer peak measured, particularly the upturn intensity in the low-q region. The local order model [26] assumes that each ionic aggregate/cluster is spherical and surrounded by the nearest four clusters (tetrahedral coordination) at a well-defined distance while the other following ionic domains are considered to be randomly distributed. Nevertheless, the local order model used by Gebel et al. did not show a consistent result with those obtained from the model-independent Porod analysis [18].

In the present work, we improve the local order model by including the polydispersity effect in the ionic clusters. With the improved model, we analyze the SAXS data measured for the water-swollen membranes with the cross-linked structure induced by different gamma irradiation doses. The structural parameters obtained by this improved model are well consistent with those deduced form the model-independent Porod analysis. In addition, the improved model can fit the high-q intensity of SAXS ionomer peak better than the conventional monodisperse local order model used by Gebel et al. [20]. The yielded results demonstrate the excellent ability of the local order model on the structural study of Nafion ionomer membranes.

The radiation-modified Nafion membranes are the as-received DuPont Nafion 117 membrane and the membrane we synthesized from the pre-treatment transforming the precursor with SO_2F end groups into the hydrolyzed membrane in the acid form (with SO_3H end groups as ionic exchange sites). Because the Nafion structure and properties depend on the membrane pre-treatment, such as thermal history and/or drying process [16,21], the pre-treatment effect and the effect with the radiation modification on the membrane structure are also studied by SAXS in the present work.

2. Experimental

Commercial Nafion 117 membranes in the acid form in this experiment were purchased from DuPont de Nemours, with a dry thickness of 175 μm and an equivalent weight of EW = 1100 g/equiv corresponding to 13 CF_2 groups on average between two lateral chains. The precursor of Nafion 117 with side chains of SO_2F end groups was also purchased from the DuPont (as pellets, DuPont product name R1100). The precursor pellets were hot pressured into films of 175 μm in thickness. The Nafion 117 membranes and the precursor membranes were cross-linked by gamma irradiation using a Co-60 radioactive source at room temperature. For each of the two membrane types, four samples irradiated, respectively, with gamma doses of 0, 0. 1, 1, 10 Gy were prepared.

The final treatment is to yield the Nafion membranes R1100 from the precursor membranes. The side chain end group $-SO_2F$ of the precursor was transformed into $-SO_3H$ through the following procedures: (1) Rinsed in a mixed solution of KOH and DMSO at an elevated temperature, (2) rinsed in the de-ionized (DI) water, (3) acidification in HNO_3 solution at an elevated temperature, and (4) rinsed in the DI water.

Before the SAXS measurement, the specimens were dried at room temperature (designated as 'room-temperature dry') and were soaked in water for a few days (designated as 'soaked') [24] for a water-swollen state. The water uptake of the soaked specimens was determined by weighing. The water volume fraction of each specimen (listed in Table 1) in the swollen state was calculated assuming a polymer density of 2.1 g/cm^3.

SAXS experiments were performed on the 4-m SAXS instrument at the National Tsing-Hua University (NTHU), Taiwan, for obtaining the intensity profiles in the intermediate-to-high-q region ($0.03\ \text{Å}^{-1} < q < 0.4\ \text{Å}^{-1}$), where the scattering vector $q = 4\pi\lambda^{-1}\sin(\vartheta/2)$, with ϑ and λ for the scattering angle and the incident X-ray wavelength, respectively. For obtaining data in the lower-q region ($0.004\ \text{Å}^{-1} < q < 0.1\ \text{Å}^{-1}$), we performed SAXS with the

Table 1
The comparison of the structural parameters obtained from (1) the model-independent Porod analysis, (2) the polydisperse local order model fitting and (3) the estimation based on the cubic lattice model and the ionomer peak position

Parameters	117 (0 Gy)	117 (0.1 Gy)	1100 (0 Gy)	R1100 (0.1 Gy)
η, Water volume fraction	0.386	0.4	0.457	0.35
Σ (Å^{-1})^a	0.0474	0.0641	0.056	0.0576
σ_0 (Å^2)^a	67.1	93.0	89.7	77.1
R_Σ (Å)^a	24.4	18.7	24.5	18.2
R (Å)^b	24.4	19.5	20.7	19.1
R_S (Å)^c	29.6	22.1	24.03	20.7
$\Delta\rho$ ($\times 10^{-6}$ Å^{-2})^a	6.8	6.8	6.6	6.2
$\Delta\rho$ ($\times 10^{-6}$ Å^{-2})^b	7.2	7.0	7.1	6.2
$N_\Sigma{}^a$	111	47	84	54
$N_L{}^b$	98	46	43	63
D (Å)^b	46.8	37.0	37.5	37.8
σ, Polydispersity^b	0.25	0.17	0.21	0.19
α^b	1.16	1.14	1.12	1.17
z^b	4.71	4.66	4.56	4.33
$N_S{}^c$	189	75	78	75
d_{max} (Å)^c	62.8	46.5	48.7	45.2

[a] The parameters obtained from the model-independent Porod analysis.
[b] The parameters determined from the fitting of the polydisperse local order model.
[c] The calculated parameters based on the assumed cubic lattice model and the ionomer peak position.

SAXS instrument at the BL01B beam line of National Synchrotron Radiation Research Center (NSRRC), Taiwan [27]. The samples for SAXS were sealed, respectively, in an air-tight-cell with Kapton windows. The SAXS data collected were corrected for transmission and background, and averaged as a function of the scattering vector q. The intensity was then scaled to an absolute intensity (scattering cross section per unit sample volume, cm^{-1}).

3. Analysis methods

3.1. Local order model for polydisperse system

The local order model employed for the SAXS data of the Nafion membranes bases mainly on the following hypothesis [18,20,26]: The ionic aggregates are spherical. The first four neighbors of each aggregated cluster are located at a well-defined distance D. The ionic clusters at a larger distance αD are randomly distributed, namely, of no long-range order. The corresponding radial pair distribution function of this structural model manifests a correlation hole containing four particles in a Dirac peak at the distance D. The SAXS intensity distribution for a monodisperse system consisting of spherical clusters with a radius R can be expressed as [18,20,21]

$$\tilde{I}(q) = \eta(\Delta\rho)^2 \times \frac{4\pi R^3}{3} F(qR)^2 \left[1 + 4\frac{\sin(qD)}{qD} - zF(qD\alpha)\right] \quad (1)$$

where D is the distance between cluster domains, $\Delta\rho$ the scattering length density difference between the cluster and the polymer matrix, αD the size of the correlation hole defined in the pair distribution function, and z the number of ionic aggregates missing in the distribution function due to the existence of the correlation hole. The function $F(x)$, with $x = qR$, related to the form factor of a spherical cluster is defined as

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

Combining the space-filling argument with the tetrahedral coordination yields a relationship between the inter-aggregate distance D and their radius R,

$$D = \left(\frac{\sqrt{3}\pi}{2\eta}\right)^{1/3} R \quad (3)$$

In our non-linear least squares procedure of the model fitting using Eq. (1), the four fitting parameters are R, z, α, and $\Delta\rho$.

In developing a local order model for polydisperse systems, we adopt the ‘local monodisperse approximation’ [28] to correlate the particle form factor with the inter-particle structure factor. The ‘local monodisperse approximation’ assumes that clusters in a nearby region are of the same size and can be considered as a local monodisperse system. The numerical algorithm of SAXS model based on the ‘local monodisperse approximation’ has been extensively applied to the alloys [29,30] and polymers [31,32] systems. In the present study, SAXS intensity for a polydisperse system is expressed as

$$I(q)=\int_0^\infty p(R)\tilde{I}(q,R)\mathrm{d}R$$
$$=\eta(\Delta\rho)^2\int_0^\infty p(R)$$
$$\times\frac{4\pi R^3}{3}F(qR)^2\left[1+4\frac{\sin(qD)}{qD}-zF(qD\alpha)\right]\mathrm{d}R \tag{4}$$

where $p(R)$ is the normalized size distribution in terms of radius R. A square size distribution ranging from $R_0(1-\sigma)$ to $R_0(1+\sigma)$ is assumed for $p(R)$. The polydispersity of this system σ is defined as the ratio of the half width of square size distribution to the mean radius R_0. The value of σ can be determined from the model fitting using Eq. (4).

The number of ionic groups per cluster can be deduced from the structural parameters determined from the SAXS data fitting with the local order model. Because z ionic aggregates are 'missing' in a sphere of a radius αD, the number of ionic groups per aggregated cluster is equal to

$$N_\mathrm{L}=\frac{2\sqrt{3}\pi^2\alpha^3R^3(1-\eta)}{3\eta z v_0} \tag{5}$$

where v_0, 870 Å^3 calculated from the equivalent weight, is the average volume of polymer associated with one ionic group.

3.2. Model-independent Porod analysis

For clusters with sharp polymer–water interfaces, SAXS manifests an asymptotic scattering behavior in the high-q region, where $I(q)\propto q^{-4}$. The power-law scattering characteristic allows a model-independent determination of the total interface area through the Porod's law

$$\lim_{q\to\infty}q^4I(q)=2\pi(\Delta\rho)^2\Sigma=\frac{\Sigma Q_0}{\pi\eta(1-\eta)} \tag{6}$$

where Σ is the surface-to-volume ratio, and Q_0 is the scattering invariant defined as

$$Q_0=\int_0^\infty q^2I(q)\mathrm{d}q=2\pi^2(\Delta\rho)^2\eta(1-\eta) \tag{7}$$

The scattering invariant Q_0 can be obtained from the integration of the SAXS profile measured, which Q_0 is a useful quantity to banish an unrealistic scattering contrast obtained from the model-dependent fitting. Using the Porod law (Eq. (6)) together with the experimentally determined Q_0 value, the surface-to-volume ratio Σ can be thus calculated. With the Σ value and the volume fraction, the radius of the scattering particles (here the ionic clusters) can be model-independently extracted from the simple relation

$$R_\Sigma=\frac{3\eta}{\Sigma} \tag{8}$$

Assuming that all the ionic groups are located at the poly-solvent interface, the area per polar head, σ_0, can be calculated from the known Σ value and the v_0 value:

$$\sigma_0=\frac{v_0\Sigma}{1-\eta} \tag{9}$$

The number of ionic groups per aggregated cluster, N_Σ, is then easily determined from the surface area and the specific surface σ_0:

$$N_\Sigma=\frac{4\pi R_\Sigma^2}{\sigma_0} \tag{10}$$

3.3. Simple cubic lattice model

The ionomer peak position q_max in the measured SAXS profile corresponds to an average distance between cluster domains d_max according to the Bragg's law ($d_\mathrm{max}=2\pi/q_\mathrm{max}$). Gierke et al. proposed a classical analysis [16, 20] of a space-filling argument on the basis of a simple cubic lattice. In the model,

$$R_\mathrm{S}=\left[\frac{3}{4\pi}\left(\eta+\frac{v_{\mathrm{SO_3}}(1-\eta)}{(v_0-v_{\mathrm{SO_3}})}\right)\right]^{1/3}d_\mathrm{max} \tag{11}$$

$$N_\mathrm{S}=\frac{d_\mathrm{max}^3(1-\eta)}{(v_0-v_{\mathrm{SO_3}})} \tag{12}$$

where $v_{\mathrm{SO_3}}$ is the volume of one ionic group (=68 Å^3) [20], and N_S and R_S are the number of ionic groups and the radius of the cluster aggregate, respectively.

4. Results and discussion

Fig. 1 shows the variation of SAXS profiles for the swollen Nafion 117 and R1100 membranes, irradiated with various gamma doses. These SAXS profiles, covering a wide q range, exhibit two scattering peaks. The scattering peaks in the low-q region are attributed to the large crystalline domains of a lamellar structure in the matrix (crystalline layers + amorphous layers) [16–18]. Such a lamellar structure also appeared in the short pendant chain (SPC) PFSI membrane [18] and the solution-cast PFSI with long pendant chain (LPC) [33]. Basically, the crystalline structure still exists in the swollen membranes, as revealed from the SAXS data. The SAXS profile in the low-q region for the swollen 117 membrane without irradiation in Fig. 1(a) shows only a shoulder superimposing on a monotonic upturn intensity, which is consistent with those obtained in other studies [19,20]. This SAXS pattern indicates that the crystallinity index is low [20]. In contrast, a broad peak in the low-q region of SAXS profile of the swollen R1100 membrane without any irradiation is observable (Fig. 1(b)), indicating that water swelling containing 45 vol% water relatively does not disrupt the crystalline domains. The difference between these two

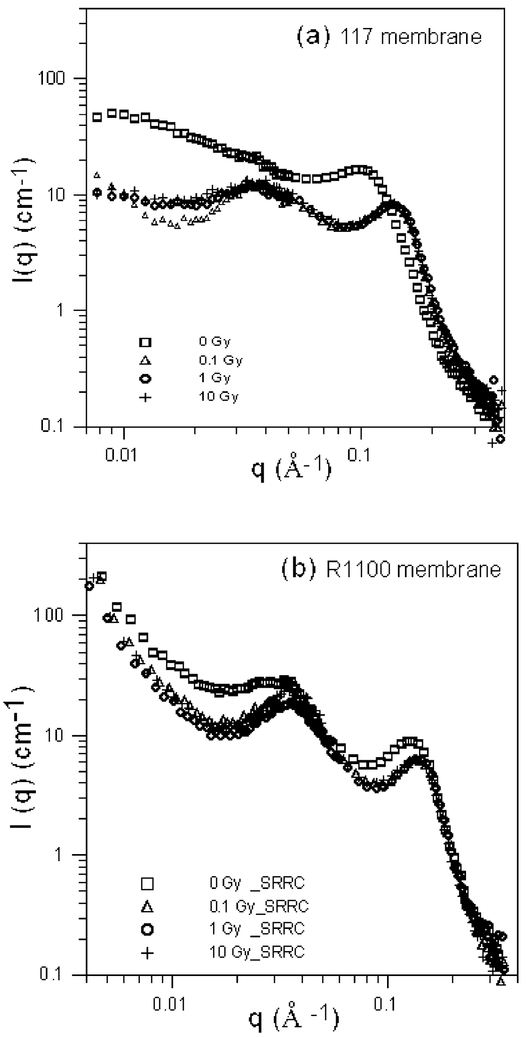

Fig. 1. The variation of measured SAXS profiles for the swollen (a) Nafion 117 and (b) R1100 membranes with various irradiation gamma doses. The SAXS curves are composed of two scattering maximums, which are related to the larger lamellar crystalline component with long period in the matrix and the ionic cluster domains, respectively.

SAXS patterns in the low-q region is the existence of well-defined lamellar structure (or crystalline domains). We attribute the difference between Nafion 117 and R1100 membranes in the lamellar structure to the different membrane pre-treatments (transforming the precursor into the acid form). It was pointed out that the properties and structure of the Nafion membrane, such as water uptake, crystalline component in matrix and ionic cluster domain, depend on the membrane pre-treatment like thermal history, used solvent and drying process etc. [16,21,33]. On the other hand, in the q region of 0.08–0.4 Å^{-1}, we have also observed clear differences in both the intensity and peak position of the ionomer peaks between the Nafion 117 and R1100 membranes.

As the samples are irradiated, several common consequent effects for the Nafion 117 and R1100 membranes can be observed: The long period between the lamellar crystalline domains (inter-lamellar spacing) decreases and their internal order improves (a long-range order develops), as indicated by the formation of well-defined low-q peaks (Fig. 1) and the shift of the low-q peaks toward a high-q value. Moreover, for gamma dose larger than 0.1 Gy, the SAXS profiles measured for each swollen membrane are nearly the same, as shown in the well-overlapped curves. The dose-independence of the radiation-enhanced lamellar structure in matrix signifies that the cross-linked structure fully developed upon the 0.1 Gy dose level in these water-swollen membranes. Interestingly, we found that all the radiation cross-linked Nafion 117 and R1100 membranes have peaks, centered at a common position of $\sim 0.035\ \text{Å}^{-1}$, regardless the differences in the lamellar structure and crystallinity pre-existed in the membranes before irradiation. The result demonstrates that the enhancement of the lamellar structure by cross-linking upon gamma irradiation is not limited by the membrane pre-treatment. From the wide-angle X-ray diffraction result on the PFSI membrane [16], the crystalline component in the matrix was attributed to the consequences of the ‘chain folding’.

For a closer observation in the R1100 membrane, the shift of the low-q peak from 0.025 to 0.035 Å^{-1} due to the irradiation is proportional to the decrease of the water volume fraction from $\eta = 0.457$ to $\eta = 0.35$. Such result follows the expected behavior for the swelling of a lamellar structure. The long period of the lamellar crystallites L deduced from the low-q peak position for the un-irradiated and irradiated R1100 membranes are 250 and 180 Å, respectively, which is consistent with those for the water-swollen EW = 800 SPC PFSI membrane ($L \approx 250$ Å) [18] and the thermal-annealed solution-cast EW = 1100 LPC PFSI membrane ($L \approx 150$ Å) [33]. Since the cross-linking takes place mainly in the amorphous region and the interface between the amorphous and crystalline phases [34], therefore, the radiation cross-linking introduced to the network structure, can restrict the membrane swelling and decrease the inter-lamella distance, as evidenced by the SAXS result. The better long-range order observed for the irradiated membranes can be explained by a larger resistance of the lamellar structure to the water swelling due to the cross-linked network. Our other experiment [35] shows that the crossover effect can be suppressed in the radiation cross-linked Nafion membrane for a better performance of DMFC. The suppression of the crossover effect maybe attributed to the radiation-enhanced lamellar structure.

Since the SAXS profiles measured for 117 and R1100 membranes are nearly the same for irradiation dose ≥ 0.1 Gy, we selectively mode-fit the SAXS ionomer peaks of zero and 0.1 Gy irradiation membranes in deducing the structural changes of the ionic cluster domains upon irradiation. Using the local order model for polydisperse system formulated in Eq. (4), we can well reproduce the measured SAXS profiles, as shown in Fig. 2, using the best fitted values of R, z, α, $\Delta\rho$ and σ (listed in Table 1) with the

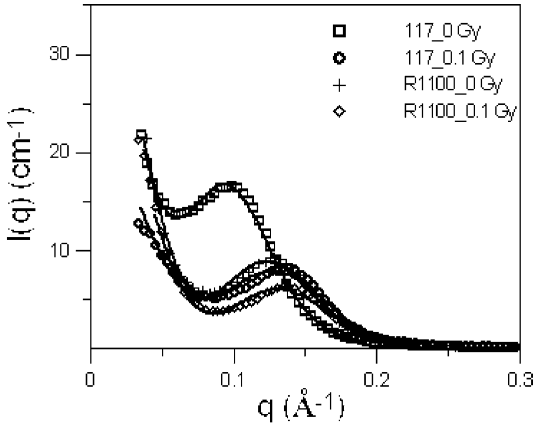

Fig. 2. The SAXS profiles associated with the ionomer peak for the swollen 117 and R1100 membranes with 0 and 0.1 Gy. The solid lines represent the SAXS intensities calculated by the polydisperse local order model.

fixed water volume fraction η and the inter-cluster distance D that relates to R through Eq. (3). The determined z and α values are very close to those found for PFSI membranes of long pendent chains ($z=4.45$ and $\alpha=1.155$) [20] and PFSI membranes of short pendent chains ($z=4.5$ or 4.1, and $\alpha=1.15$–1.19) [18]. The values for the number of ionic groups per aggregated cluster N_L deduced from Eq. (5) are also presented in Table 1.

In Fig. 3, we compare the fitting results for the same set of SAXS data of the un-irradiated Nafion 117 membrane, using the three different models mentioned previously. With the conventional local order model in Eq. (1), assuming a monodisperse system, the best-fitted SAXS profile deviates significantly from the data after $q \geq 0.18$ Å^{-1}. Similar mismatch also occurred in a study of Gebel's using the local order model (Fig. 5 in Ref. [11]). On the other hand, the polydisperse local order model adopted here can fit well the data over an extended q range (including the up-turn intensity in the low-q region). Presumably, the polydispersity is a natural characteristic of the Nafion ionic clusters. Nevertheless, the parameters determined from the monodisperse model deviate only a marginal 5% from those obtained using the polydisperse model of a polydispersity of 25%.

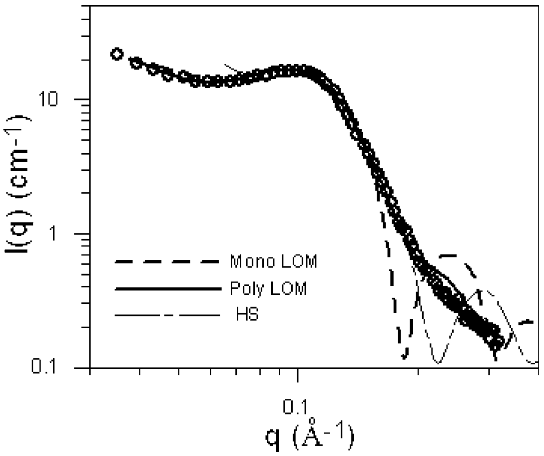

Fig. 3. The comparison of the SAXS intensities calculated by the monodisperse local order model (LOM), the polydisperse LOM and the HS model, together with the measured SAXS profile (for the swollen 117 membrane with 0 Gy).

In another branch of model fitting basing the liquid-like ordering, in contrast to the solid-like ordering of the local order model, Yarusso et al. [22] showed that a modified hard-sphere (HS) model could be more suitable than both the original and depleted-zone core-shell models [17,24], in interpreting the SAXS result of their PFSI membranes. The model proposed by Yarusso et al. assumes a hard sphere (HS) liquid-like interference for the ionic clusters, having a closest distance $2R_{CA}$, where R_{CA} is the radius of a hard sphere surrounding a cluster. The concept of the modified HS model with the Percus–Yevic approximation [28] for the inter-cluster interference has been generally accepted in other applications [28–32]. In Fig. 3, we also show the fitting result using the modified HS model with the Percus–Yevic approximation. As shown in Fig. 3, the HS model cannot take into account the feature of the up-turn intensity in the low-q region although the model can describe well the ionomer peak. In the fitting procedure, we have used a fixed value $\eta=0.386$ (measured by weighing). The radius of the cluster domain and the corresponding R_{CA} determined from the model analysis are 20.1 and 50.6 Å, respectively. However, it should be pointed out that the calculated HS volume fraction ($=\eta R_{CA}^3/R^3$) is larger than 1.0. This inconsistency in the measured and deduced values for the HS and the cluster volume fractions also appeared in the Yarusso's result.

As shown in Fig. 4 of the Porod representation (Iq^4 vs. q), the SAXS profiles of the Nafion 117 and R1100 membranes of zero and 0.1 Gy gamma irradiation (corresponding to Fig. 2) display a constant plateau behavior in the high q region, indicating the existence of sharp water–polymer interfaces, according to the Porod analysis described previously. Using the measured asymptotic value and the calculated scattering invariant Q_0, we can deduce the surface-to-volume ratio Σ, the area per polar head σ_0, R_Σ

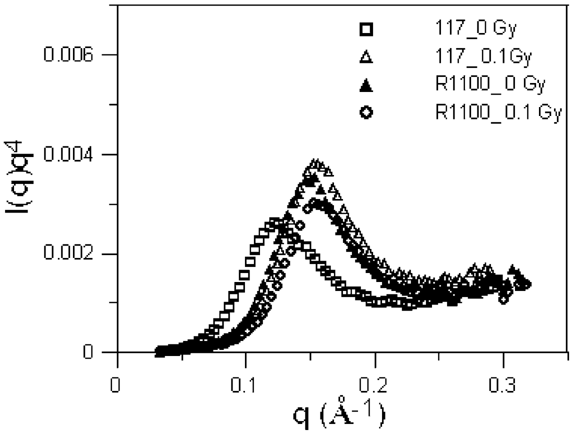

Fig. 4. Porod plot (Iq^4 vs. q) of the SAXS profiles presented on Fig. 2.

and N_Σ from the model-independent Porod analysis for the swollen 117 and R1100 membranes, as presented in Table 1. The model-independently determined Σ, σ_0 and N_Σ values for the un-irradiated 117 membrane are close to those ($\Sigma = 0.044$ Å^{-1}, $\sigma_0 = 54$ Å^2 and $N_\Sigma = 90$) reported previously for the 'standard-swollen' 117 membrane [20].

From Table 1, except for the un-irradiated R1100 membrane, the values for $\Delta\rho$, R_Σ, and N_Σ, obtained from the Porod analysis are better consistent with the local order model fitting than the other models. The consistency between the two results validates the local order model. The determined scattering contrast here is $\sim 7 \times 10^{-6}$ Å^{-2}, in contrast to the 5.64×10^{-6} Å^{-2} calculated without taking into account the contribution of the ionic groups on the interface by Gebel et al. [20]. Including the contribution from the ionic groups on the interface can effectively increase the contrast to a larger value in this SAXS model fitting. In fact, it was shown that clusters containing different ionic groups can influence differently the ionomer peak intensity [16,17].

One interesting feature in the SAXS fitting result is that the radius of the cluster domains formed in the swollen state of the irradiated membranes is relatively reduced due to the constraint from the crosslinked network structure. After 0.1 Gy, the structure of the formed cluster domains is inert to the additional irradiation dose, as shown in Fig. 1. We have also examined the self-consistence of our fitting parameters. First, the D value obtained from the model analysis follows the proportional relationship $D = 3d_{\max}/4$ based on the diamond-like structure [16,18], where $d_{\max}$ is the Bragg distance deduced from the ionomer peak position (Table 1). In contrast, the evolution of D observed by Gebel et al. [18] did not follow the linear proportional relationship between D and $d_{\max}$. Also, the present study demonstrates a good consistence between R and R_Σ, whereas there exists a significant discrepancy between these two values in the study of Gebel et al. [18].

From Table 1, the area per polar head σ_0 changes upon the irradiation, indicating that the cross-linked structure has a significant influence in the formation of the water-swollen ionic clusters. The variations of the measured water intake with the irradiation for Nafion 117 and R1100 membrane are different due likely to the difference in the pre-treatments. Nevertheless, the structural parameters of the irradiated Nafion 117 and R1100 membranes become closer after irradiation. It is found that the evolutions of the Bragg distance $d_{\max}$ with the irradiation are the same for Nafion 117 and R1100 membranes, reflecting that the reduction in $d_{\max}$ by irradiation is independent of the water intake and pre-treatment. This behavior can also be explained by a general constraint from the radiation-induced crosslinked structure. The structural parameters listed in Table 1 vary slightly among different models used. However, they are still useful in serving as a cross check. It seems that the number of ionic groups per aggregate obtained using the cubic lattice model, N_S, deviates considerably from other models.

5. Conclusions

The two-length scales (i.e. the long-range order of lamellar domains in the matrix and the local order of the ionic cluster domains) of the commercial Nafion 117 membrane and the R1100 membranes synthesized from Nafion precursor are more quantitatively and precisely investigated using SAXS with the polydisperse local order model. The model fitting result is consistent with that obtained from the model-independent Porod analysis. The cross-linking induced by gamma irradiation enhances the long-range ordering of the lamellar structure and reduces the inter-lamellar distance between the crystalline domains in both the Nafion 117 and R1100 membranes, of a similar swollen state. The radiation-induced cross-linked structure also reduces the ionic cluster domain size and inter-ionic-cluster distance in both membranes. The structures of the two types of Nafion membranes are not sensitive to the irradiation after 0.1 Gy dose.

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