Data Article

Small angle neutron scattering data of polymer electrolyte membranes partially swollen in water

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In this article, we show the small-angle neutron scattering (SANS) data obtained from the polymer electrolyte membranes (PEMs) equilibrated at a given relative humidity. We apply Hard-Sphere (HS) structure model with Percus–Yervick interference interactions to analyze the dataset. The molecular structure of these PEMs and the morphologies of the fully water-swollen membranes have been elucidated by Zhao et al. “Elucidation of the morphology of the hydrocarbon multi-block copolymer electrolyte membranes for proton exchange fuel cells” [1].

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Specifications Table

| Subject area       | Materials science  |
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| Type of data           | Table, figure                                                                 |
|-----------------------|-------------------------------------------------------------------------------|
| How data was acquired | Small angle neutron scattering instrument at KWS2, FRM2                      |
| Data format           | Analyzed                                                                      |
| Experimental factors  | The dry membranes with an average thickness of ~50 μm were prepared by       |
|                       | solution casting onto a flat glass plate from its dimethyl sulfoxide solution |
|                       | with a concentration of 5 wt%. Partially water swollen membranes were         |
|                       | prepared by putting the dry membranes into a humidity controller at 30%       |
|                       | relative humidity and 25 °C.                                                  |
| Experimental features | The incident neutron beam was monochromatized with a velocity selector to     |
|                       | have the average wavelength (λ) of 5 Å with a wavelength resolution of Δλ/λ  |
|                       | = 20%. All of the measurements were done at 25 ± 0.5 °C. The scattering       |
|                       | patterns were collected with a two-dimensional scintillation detector, and     |
|                       | circularly averaged to obtain scattering intensity profiles as a function of q,|
|                       | where q is the scattering vector, defined as q = (4π/λ)sin(θ/2) with θ being  |
|                       | the scattering angle. The scattering profiles were corrected for the instrument|
|                       | background, detector sensitivity, and scattering from empty cell, and finally  |
|                       | calibrated on the absolute scale (cm⁻¹) using a Plexiglas secondary standard. |
| Data source location  | SANS measurements were performed with KWS-2 at the neutron source Heinz      |
|                       | Maier-Leibnitz (FRM II reactor) in Garching, Germany.                         |
| Data accessibility    | Data is with this article                                                     |

Value of the data

- Hard-sphere structure model is introduced to elucidate the morphology of polymer electrolyte membranes.
- Data of partially swollen membranes together with that of fully swollen membranes leads to a thorough understanding of the morphology.
- The method and model analysis are worthy being applied to other types of membranes.

1. Data

Partially water swollen membranes were prepared by putting the dry PEMs into a humidity controller at 30% relative humidity and 25 °C. The SANS measurements were performed with KWS-2 at the neutron source Heinz Maier-Leibnitz (FRM II reactor) in Garching, Germany, and the scattering intensity profiles has been corrected and calibrated on the absolute scale (cm⁻¹).

Fig. 1a and b show the SANS intensity profiles of the two membranes, PSP₁₄-b-PAEK₁₄ and PSP₂₈-b-PAEK₁₄, as a function of scattering vector q, respectively. The profile of the corresponding fully D₂O-swollen membranes is plotted in the same figure as a reference. Hard-Sphere (HS) structure model with Percus–Yervick interference interactions was applied to analyze these scattering profiles [1,2]. The best fitting parameters are listed in Tables 1 and 2. Note that the profiles at high-q range (0.08 < q < 0.45 Å⁻¹) can be fitted well by Eq. (6) below, and the best fitted curve is summed up with the fitting curve in the middle-q range and shown in the figure.

2. Experimental design, materials and methods

2.1. Materials

Two multiblock copolymer poly(sulfonate phenylene)-b-poly(arylene ether ketone) with different block ratios, designated as PSP₁₄-b-PAEK₁₄ and PSP₂₈-b-PAEK₁₄ for brevity, were synthesized.
by varying the stoichiometry of the sulfonated monomers and hydrophobic oligomers via the nickel-catalyzed polymerization [3,4]. The subscript 14 or 28 refers to the repeating unit number in each block. The molecular structure and characteristics of these two polymers can be found elsewhere [1,2]. The dry membranes with an average thickness of ~ 50 μm were prepared by solution casting onto a flat glass plate from its dimethyl sulfoxide solution with a concentration of 5 wt% [3].

**Table 1**
Parameters used to fit SANS data of PSP14-b-PAEK14 membranes equilibrated at RH = 30% and in D2O by Eqs. (1) and (6).

| PSP14-b-PAEK14 | Middle-q range (HS model) | High-q range (ionomer peak) |
|----------------|---------------------------|----------------------------|
|                | φ (°C) | R (Å) | σR/R | K | lm,ion (Å⁻¹) | qm,ion (Å⁻¹) | σq/qm,ion |
| Equilibrated at RH = 30% | 0.25  | 80   | 0.247 | 1.56 | 0.004 | 0.18 | 0.194 |
| Equilibrated in D2O     | 0.32  | 85   | 0.247 | 211.3 | 0.026 | 0.18 | 0.194 |

**Table 2**
Parameters used to fit SANS data of PSP28-b-PAEK14 membranes equilibrated at RH = 30% and in D2O by Eqs. (1) and (6).

| PSP28-b-PAEK14 | Middle-q range (HS model) | High-q range (ionomer peak) |
|----------------|---------------------------|----------------------------|
|                | φ (°C) | R (Å) | σR/R | K | lm,ion | qm,ion (Å⁻¹) | σq/qm,ion |
| Equilibrated at RH = 30% | 0.08  | 150  | 0.243 | 25.9 | 0.01  | 0.152 | 0.243 |
| Equilibrated in D2O     | 0.07  | 145  | 0.245 | 295.3 | 0.08  | 0.152 | 0.243 |

Fig. 1. Part (a) SANS profiles of PSP14-b-PAEK14 membranes equilibrated at RH = 30% (triangles) and fully D2O-swollen state (squares) at room temperature. The best-fitted theoretical curves ranging from the middle-q region based on HS model to the high-q region based on Eq. (6) for both membranes are also shown in the figure by red dashed and solid lines, respectively. Part (b) SANS profiles of PSP28-b-PAEK14 membranes equilibrated at RH = 30% (triangles) and fully D2O-swollen state (squares) at room temperature. The best-fitted theoretical curves ranging from the middle-q region based on HS model to the high-q region based on Eq. (6) for both membranes are also shown in the figure by red dashed and solid lines, respectively.
Partially water swollen membranes were prepared by putting the dry membranes into a humidity controller at 30% relative humidity and 25 °C.

2.2. Methods

SANS measurements were performed with KWS-2 at the neutron source Heinz Maier-Leibnitz (FRM II reactor) in Garching, Germany [5]. The incident neutron beam was monochromatized with a velocity selector to have the average wavelength (\( \lambda \)) of 5 Å with a wavelength resolution of \( \Delta \lambda/\lambda = 20\% \). All of the measurements were done at 25 ± 0.5 °C. The scattering patterns were collected with a two-dimensional scintillation detector, and circularly averaged to obtain scattering intensity profiles as a function of \( q \), where \( q \) is the scattering vector, defined as \( q = (4 \pi/\lambda) \sin(\theta/2) \) with \( \theta \) being the scattering angle. The scattering profiles were corrected for the instrument background, detector sensitivity, and scattering from empty cell, and finally calibrated on the absolute scale (cm\(^{-1}\)) using a Plexiglas secondary standard.

2.3. Analysis

We assume that the topology of the swollen membranes can be described by an almost random distribution of \( n \) particles in a homogeneous matrix. Let \( \Delta b \) be the contrast of the particle density with respect to the matrix density and \( v \) be the of average volume of a single particle, then the observed scattering intensity, \( I(q) \), is [6]

\[
I(q) = (\Delta b)^2 n v P(q) S(q) = K P(q) S(q)
\]

where \( P(q) \) is the form factor of the particles, \( S(q) \) is an approximate interference factor and \( K \) is a constant in terms of \( \Delta b \), \( n \) and \( v \). We assume that the number of the particles per volume is high that \( S(q) \) must be considered despite the random arrangement of the particles. The contrast \( \Delta b = b_p - b_m \) is defined by the difference between the scattering length density (SLD) of the particle phase, \( b_p \), and that of the matrix phase, \( b_m \). Thus, \( \Delta b \) is computable as long as the shape and composition of the particle phase and the matrix phase are well determined, and their SLDs are theoretically estimated below.

SLD of a molecule of \( i \) atoms is related to its molecular structure and may be readily calculated from the simple expression given by \( b = \sum_i b_i \frac{d}{M_w} \) where \( b_i \) is the scattering length of \( i \)th atom, \( d \) is the mass density of the scattering body, \( M_w \) is the molecular weight, and \( N_A \) is the Avogadro constant [6].

Let us consider an ensemble of spheres with varying sizes that can be described by a Gaussian size distribution:

\[
P(q) = \int_0^\infty \frac{3}{(qr)^3} \left[ \sin (qr) - qr \cos(qr) \right]^2 \frac{1}{(2\pi)^{1/2} \sigma_R} \exp \left[ \frac{-(r-R)^2}{2\sigma_R^2} \right] dr
\]

with \( R \) being the average radius, and \( \sigma_R \) being its standard deviation. Thus \( v = \frac{4\pi R^3}{3} \). We consider Percus–Yevick expression to account for interparticle interference [2,7], then \( S(q) \) is the interference factor, described for a random arrangement of spheres by the following expression:

\[
S(q, R, \phi) = \frac{1}{1 + 24\phi \left( \frac{f(A)}{\pi} \right)}
\]
here $A = 2qR$ and $\phi$ is the hard sphere volume fraction. $F(A)$ is a trigonometric function of $A$ and $\phi$ given by

$$F(A) = \frac{\alpha}{A^2}(\sin A - \cos A) + \frac{\beta}{A^3} \left( 2A \sin A + \left( 2 - A^2 \right) \cos A - 2 \right)$$

$$+ \frac{\gamma}{A^5} \left( -A^4 \cos A + 4 \left[ 3A^2 - 6 \right] \cos A + \left( A^3 - 6A \right) \sin A + 6 \right)$$

(4)

$$\alpha = (1 + 2\phi)^2 / (1 - \phi)^4$$

$$\beta = -6\phi (1 + \frac{1}{2})^2 / (1 - \phi)^4$$

$$\gamma = \frac{1}{2\phi} (1 + 2\phi)^2 / (1 - \phi)^4$$

(5)

The distribution of the ionic clusters at high-$q$ range can be fitted well by Gaussian distribution function, where the scattering intensity around the ionomer peak at $0.08 \, \text{Å}^{-1} < q < 0.45 \, \text{Å}^{-1}$, $I_{\text{ion}}(q)$, can be expressed by

$$I_{\text{ion}}(q) = I_{m,\text{ion}} G(q) + I_{\text{inc}}$$

(6)

where $I_{m,\text{ion}}$ is the ionomer peak height, $G(q)$ is Gaussian distribution function about the ionomer peak at $q_{m,\text{ion}}$, given by $G(q) = \frac{1}{(2\pi)^{1/2}\sigma_q} \exp \left[ - (q - q_{m,\text{ion}})^2 / (2\sigma_q^2) \right]$, with $\sigma_q$ being the standard deviation of $q_{m,\text{ion}}$, and $I_{\text{inc}}$ is the incoherent scattering intensity, which can be determined by the average intensity of the flat part of the profile at $q > 0.4 \, \text{Å}^{-1}$ in the high-$q$ region. Eq. (6) is used to fit profiles in Fig. 1a and b and the fitting parameters are listed in Tables 1 and 2.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.dib.2016.03.011.

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