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Data Article

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



Yue Zhao^a, Miru Yoshida^b, Tatsuya Oshima^b, Satoshi Koizumi^c,
Masahiro Rikukawa^b, Noemi Szekely^d, Aurel Radulescu^d,
Dieter Richter^e

^a Quantum Beam Science Center (QuBS), Japan Atomic Energy Agency (JAEA), Watanuki-machi 1233, Takasaki, Gunma 370-1292, Japan

^b Department of Material Science, Sophia University, Tokyo 102-0094, Japan

^c Department of Engineering, Ibaraki University, Hitachi 615-8510, Japan

^d Forschungszentrum Jülich GmbH, Jülich Centre for Neutron Science @ MLZ, Lichtenbergstraße 1, D-85747 Garching, Germany

^e Jülich Centre for Neutron Science & Institute for Complex Systems, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

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ABSTRACT

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–Yevick 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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E-mail address: zhao.yue@jaea.go.jp (Y. Zhao).

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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 $\sim 50\text{ }\mu\text{m}$ 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 $\Delta\lambda/\lambda = 20\%$. All of the measurements were done at $25 \pm 0.5\text{ }^\circ\text{C}$. 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 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 ($0.08 < q < 0.45\text{ }\text{\AA}^{-1}$) 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

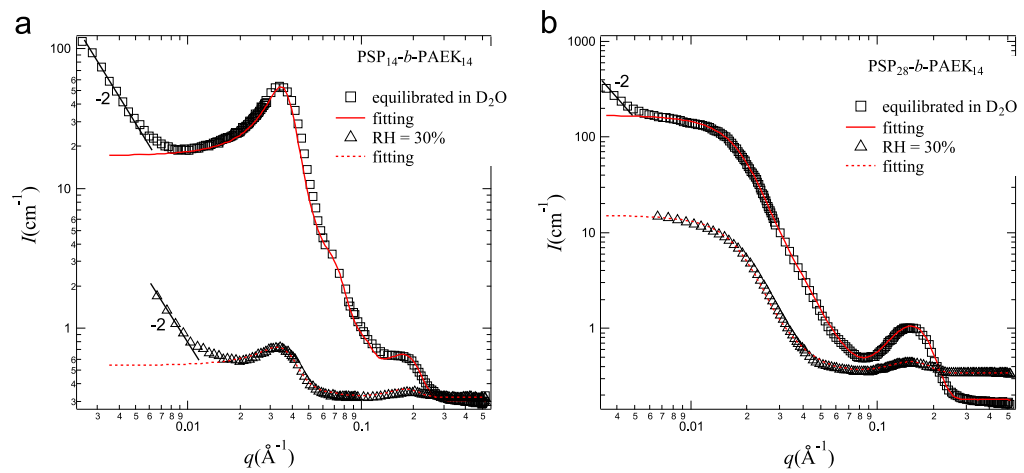


Fig. 1. Part (a) SANS profiles of PSP₁₄-b-PAEK₁₄ membranes equilibrated at RH=30% (triangles) and fully D₂O-swollen state (squares) at room temperature. The best-fitted theoretical curves ranging from the middle-*q* region based on HS model to the high-*q* region based on Eq. (6) for both membranes are 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.

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).

PSP ₁₄ -b-PAEK ₁₄	Middle- <i>q</i> range (HS model)				High- <i>q</i> range (ionomer peak)		
	ϕ	R (Å)	σ_R/R	K	$I_{m,ion}$	$q_{m,ion}$ (Å ⁻¹)	$\sigma_q/q_{m,ion}$
Equilibrated at RH=30%	0.25	80	0.247	1.56	0.004	0.18	0.194
Equilibrated in D ₂ O	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).

PSP ₁₄ -b-PAEK ₁₄	Middle- <i>q</i> range (HS model)				High- <i>q</i> range (ionomer peak)		
	ϕ	R (Å)	σ_R/R	K	$I_{m,ion}$	$q_{m,ion}$ (Å ⁻¹)	$\sigma_q/q_{m,ion}$
Equilibrated at RH=30%	0.08	150	0.243	25.9	0.01	0.152	0.243
Equilibrated in D ₂ O	0.07	145	0.245	295.3	0.08	0.152	0.243

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 $\sim 50\ \mu\text{m}$ were prepared by solution casting onto a flat glass plate from its dimethyl sulfoxide solution with a concentration of 5 wt% [3].

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 (λ) 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 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.

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 Δb be the contrast of the particle density with respect to the matrix density and ν be the of average volume of a single particle, then the observed scattering intensity, $I(q)$, is [6]

$$I(q) = (\Delta b)^2 n \nu^2 P(q) S(q) = KP(q) S(q) \quad (1)$$

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 Δb , n and ν . 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, Δb 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 $b = \sum_i b_i \frac{dN_A}{M_w}$ 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:

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

with R being the average radius, and σ_R being its standard deviation. Thus $\nu = \frac{4\pi R^3}{3}$. 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:

$$S(q, R, \phi) = \frac{1}{1 + 24\phi \left(\frac{F(A)}{A} \right)} \quad (3)$$

here $A=2qR$ and ϕ is the hard sphere volume fraction. $F(A)$ is a trigonometric function of A and ϕ given by

$$F(A) = \frac{\alpha}{A^2}(\sin A - A \cos A) + \frac{\beta}{A^3}(2A \sin A + (2 - A^2) \cos A - 2) + \frac{\gamma}{A^5}(-A^4 \cos A + 4[(3A^2 - 6) \cos A + (A^3 - 6A) \sin A + 6]) \quad (4)$$

$$\begin{aligned} \alpha &= (1 + 2\phi)^2 / (1 - \phi)^4 \\ \beta &= -6\phi(1 + \frac{\phi}{2})^2 / (1 - \phi)^4 \\ \gamma &= \frac{1}{2\phi}(1 + 2\phi)^2 / (1 - \phi)^4 \end{aligned} \quad (5)$$

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 $0.08 \text{ \AA}^{-1} < q < 0.45 \text{ \AA}^{-1}$, $I_{\text{ion}}(q)$, can be expressed by

$$I_{\text{ion}}(q) = I_{m,\text{ion}}G(q) + I_{\text{inc}} \quad (6)$$

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 $G(q) = \frac{1}{(2\pi)^{1/2}\sigma_q} \exp[-(q - q_{m,\text{ion}})^2 / (2\sigma_q^2)]$, with σ_q being the standard deviation of $q_{m,\text{ion}}$, and I_{inc} is the incoherent scattering intensity, which can be determined by the average intensity of the flat part of the profile at $q > 0.4 \text{ \AA}^{-1}$ 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>.

References

- [1] Y. Zhao, M. Yoshida, T. Oshima, S. Koizumi, M. Rikukawa, N. Szekeely, A. Radulescu, D. Richter, Elucidation of the morphology of the hydrocarbon multi-block copolymer electrolyte membranes for proton exchange fuel cells, *Polymer* 86 (2016) 157–167.
- [2] J.K. Percus, G.J. Yevich, Analysis of classical statistical mechanics by means of collective coordinates, *Phys. Rev.* 110 (1958) 1–13.
- [3] M. Yoshida, Y. Zhao, M. Yoshizawa-Fujita, A. Ohira, Y. Takeoka, S. Koizumi, M. Rikukawa, PFG-NMR and SANS studies in cation exchange membranes based on sulfonated polyphenylene multiblock copolymers, *ECS Trans.* 50 (2013) 1045–1053.
- [4] I. Tonozuka, M. Yoshida, K. Kaneko, Y. Takeoka, M. Rikukawa, Considerations of polymerization method and molecular weight for proton-conducting poly(p-phenylene) derivatives, *Polymer* 52 (2011) 6020–6028.
- [5] A. Radulescu, V. Pipich, H. Frielinghaus, M.S. Appavou, KWS-2, the high intensity/wide Q-range small-angle neutron diffractometer for soft-matter and biology at FRM II, *J. Phys.: Conf. Ser.* 351 (2012) 012026.
- [6] R.J. Roe, *Methods of X-ray and Neutron Scattering in Polymer Science*, Oxford University Press, New York, 2000.
- [7] D.J. Kinning, E.L. Thomas, Hard-sphere interactions between spherical domains in diblock copolymers, *Macromolecules* 17 (1984) 1712–1718.