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## Data Article

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



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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
More specific sub- ject area	Soft matter

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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 ( $\lambda$ ) of 5 Å with a wavelength resolution of $\Delta\lambda/\lambda = 20\%$ . All of the measurements were done at $25 \pm 0.5$ °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 ( $\text{cm}^{-1}$ ) 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

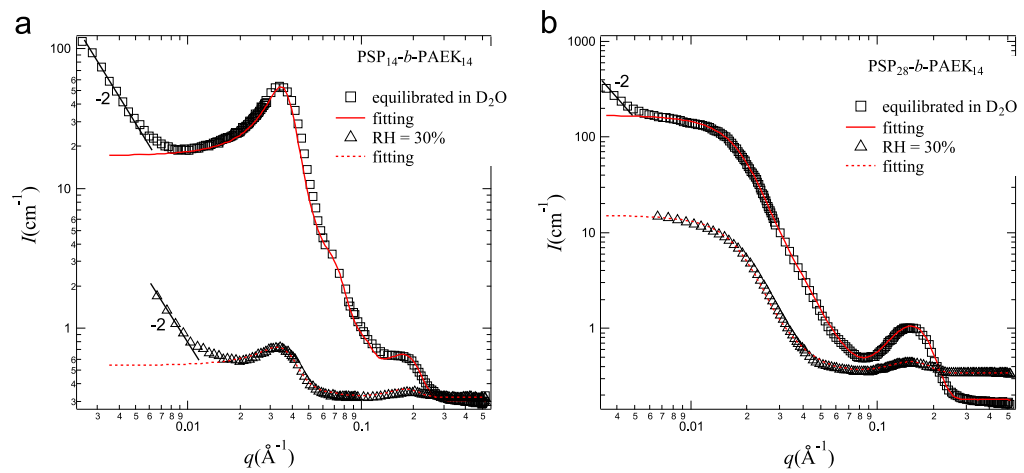
Partially water swollen membranes were prepared by putting the dry PEMs into a humidity controller at 30% relative humidity and 25 °C. The SANS measurements were performed with KWS-2 at the neutron source Heinz Maier-Leibnitz (FRM II reactor) in Garching, Germany, and the scattering intensity profiles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

Fig. 1a and b show the SANS intensity profiles of the two membranes, PSP<sub>14</sub>-b-PAEK<sub>14</sub> and PSP<sub>28</sub>-b-PAEK<sub>14</sub>, as a function of scattering vector  $q$ , respectively. The profile of the corresponding fully D<sub>2</sub>O-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 ( $0.08 < q < 0.45 \text{ Å}^{-1}$ ) 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 PSP<sub>14</sub>-b-PAEK<sub>14</sub> and PSP<sub>28</sub>-b-PAEK<sub>14</sub> for brevity, were synthesized



**Fig. 1.** Part (a) SANS profiles of PSP<sub>14</sub>-*b*-PAEK<sub>14</sub> membranes equilibrated at RH=30% (triangles) and fully D<sub>2</sub>O-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 PSP<sub>28</sub>-*b*-PAEK<sub>14</sub> membranes equilibrated at RH=30% (triangles) and fully D<sub>2</sub>O-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 PSP<sub>14</sub>-*b*-PAEK<sub>14</sub> membranes equilibrated at RH=30% and in D<sub>2</sub>O by Eqs. (1) and (6).

PSP <sub>14</sub> - <i>b</i> -PAEK <sub>14</sub>	Middle- <i>q</i> range (HS model)				High- <i>q</i> range (ionomer peak)		
	$\phi$	$R$ (Å)	$\sigma_R/R$	$K$	$I_{m,ion}$	$q_{m,ion}$ (Å <sup>-1</sup> )	$\sigma_q/q_{m,ion}$
Equilibrated at RH=30%	0.25	80	0.247	1.56	0.004	0.18	0.194
Equilibrated in D <sub>2</sub> O	0.32	85	0.247	211.3	0.026	0.18	0.194

**Table 2**  
Parameters used to fit SANS data of PSP<sub>28</sub>-*b*-PAEK<sub>14</sub> membranes equilibrated at RH=30% and in D<sub>2</sub>O by Eqs. (1) and (6).

PSP <sub>14</sub> - <i>b</i> -PAEK <sub>14</sub>	Middle- <i>q</i> range (HS model)				High- <i>q</i> range (ionomer peak)		
	$\phi$	$R$ (Å)	$\sigma_R/R$	$K$	$I_{m,ion}$	$q_{m,ion}$ (Å <sup>-1</sup> )	$\sigma_q/q_{m,ion}$
Equilibrated at RH=30%	0.08	150	0.243	25.9	0.01	0.152	0.243
Equilibrated in D <sub>2</sub> 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 ~ 50 μm 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 ( $\lambda$ ) of 5 Å with a wavelength resolution of  $\Delta\lambda/\lambda = 20\%$ . All of the measurements were done at  $25 \pm 0.5$  °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 ( $\text{cm}^{-1}$ ) 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  $\nu$  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  $\Delta b$ ,  $n$  and  $\nu$ . 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  $b = \sum_i b_i \frac{dN_A}{M_w}$  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  $\sigma_R$  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  $\phi$  is the hard sphere volume fraction.  $F(A)$  is a trigonometric function of  $A$  and  $\phi$  given by

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

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

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  $G(q) = \frac{1}{(2\pi)^{1/2} \sigma_q} \exp \left[ - (q - q_{m,\text{ion}})^2 / (2\sigma_q^2) \right]$ , 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  $q > 0.4 \text{ \AA}^{-1}$  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>.

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