Supporting Information

Microscopic Determination of the Local Hydration Number of Polymer Electrolyte Membranes Using SANS Partial Scattering Function Analysis

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S1. Preparation and characterization of Nafion and ETFE-g-PSSSA PEMs.

Nafion membrane (NR-212, mass density of 1.97 g/cm^3, and IEC of 1.0 mmol/g) was purchased from DuPont. Before the experiment, the membranes were sequentially immersed in 3 wt% hydrogen peroxide solution, deionized water, 1 M sulfuric acid, and then deionized water at 80 ℃ for 1 hr in each process as previously reported.[22] The ETFE base film with a thickness of 50 μm (mass density = 1.75 g/cm^3, crystallinity (X_c) = 0.32) were purchased from Asahi Glass Co. Ltd, Japan. ETFE-g-PSSA membrane with a grafting degree (GD) of 38% and an ion exchange capacity of 2.0 mmol/g was prepared according to our previous report.[23] The crystallinity of the dried ETFE-g-PSSA membrane is 22% determined by DSC measurement. The water uptake (WU) and swelling ratio (SR) of the fully hydrated membrane at room temperature were about 40% and 63.7%, respectively. Here, WU and SR are defined by the change of the membrane weight and volume between the dry and wet conditions, as $\mathrm{WU} = \frac{W_{wet}-W_{dry}}{W_{dry}} \times 100\%$, with W_{dry} and W_{wet} being the weight of the dry and wet membrane in water, respectively; and $\mathrm{SR} =$

$\frac{V_{wet}-V_{dry}}{V_{dry}} \times 100\%$, with V_{dry} and V_{wet} being the volume of the dry and wet membrane in water, respectively. The proton conductivity of the membrane was evaluated to be 0.104 S/cm at 60 °C in liquid water using electrochemical impedance spectroscopy. To ensure that the membranes were in the proton form, they were immersed in 1 M hydrochloric acid at room temperature for 1h and then washed with deionized water before the experiment. 1 M hydrochloric acid was supplied by Fujifilm Wako Pure Chemical Co. Deionized water was purified by a Millipore Milli-Q UV system to produce water with a resistance of 18.2 MΩ·cm and a total organic carbon content of <10 ppb. Sigma-Aldrich Co. Ltd. supplied the deuterated water (D_2O, 99.9 atom% D) used in the SANS experiments.

For CV-SANS measurements, PEMs were equilibrated in a water mixture with prescribed volume fractions (f_{D2O}) at room temperature for 24 h.[22, 23] The fully hydrated membranes were placed in SANS sample cells sealed by two quartz-plate windows with a silicon spacer in between to prevent evaporation. Then, they were put on the neutron beam. SANS measurements were performed on a KWS-2 SANS diffractometer operated by Juelich Centre for Neutron Science (JCNS) at the neutron source Heinz Maier–Leibnitz (FRM II reactor) in Garching, Germany.[29] The incident neutron beam at KWS-2 was monochromatized with a velocity selector to have an average wavelength (l) of 5 Å with a wavelength resolution of $\Delta l/l$ = 20%. All SANS measurements were performed at room temperature. The scattering patterns were collected using a two-dimensional (2D) scintillation detector and circularly averaged to obtain scattering intensity profiles as a function of q, where q is the scattering vector and defined as $q = (4\pi/l)\sin(\theta/2)$, where θ is the scattering angle. The operable q-range in this study covered $0.03 < q < 5$ nm^{-1}. The final intensity profiles obtained were corrected for the cell's background, the detector's

electronic noise, detector sensitivity, and incoherent scattering.

S2. Incompressibility assumption for a ternary system

Assuming a ternary system with 3 different components, the scattering intensity can be split into partial scattering functions according to the scattering theory as follows:[S1, S2]

$$I(q) = \sum_{i=1}^{3} b_i^2 S_{ii}(q) + 2\sum_{i<j}^{3} S_{ij}(q) \qquad \text{(S1)}$$

S_{ii} is PSF self-term, defined as

$$S_{ii}(q) = \frac{1}{V} < \iint \delta\varphi_i(\vec{\mathrm{r}})\delta\varphi_i\left(\overrightarrow{\mathrm{r}'}\right) \exp\left[-i\vec{q}\left(\vec{\mathrm{r}} - \overrightarrow{\mathrm{r}'}\right)\right] d\vec{\mathrm{r}} d\overrightarrow{\mathrm{r}'} > \qquad \text{(S2)}$$

where V is the scattering volume and $\delta\varphi_i(\vec{\mathrm{r}})$ is the fluctuation part of the volume fraction of the *i* component at position $\vec{\mathrm{r}}$ ($\varphi_i(\vec{\mathrm{r}})$), which is expressed as

$$\delta\varphi_i(\vec{\mathrm{r}}) = \varphi_i(\vec{\mathrm{r}}) - \overline{\varphi}_i \qquad \text{(S3)}$$

where $\overline{\varphi}_i$ is the average volume fraction of the *i* component (*i.e.*, $\overline{\varphi}_i = \frac{1}{V}\int \varphi_i(\vec{\mathrm{r}}) d\vec{\mathrm{r}}$). The definition in Eq. (S2) indicates that $S_{ii}(q)$ is the Fourier transform of the correlation function $[\gamma_i(\vec{\mathrm{u}})]$ of $\delta\varphi_i(\vec{\mathrm{r}})$, given by

$$\gamma_i(\vec{\mathrm{u}}) = \int \delta\varphi_i(\vec{\mathrm{r}})\delta\varphi_i(\vec{\mathrm{r}} + \vec{\mathrm{u}}) d\vec{\mathrm{r}} \qquad \text{(S4)}$$

As $\gamma_i(\vec{\mathrm{u}})$ specifies how $\delta\varphi_i(\vec{\mathrm{r}})$ and $\delta\varphi_i\left(\overrightarrow{\mathrm{r}'}\right)$ in neighboring regions separated by $\vec{\mathrm{u}}$ correlate with each other in the real space, $S_{ii}(q)$ gives the structural information of the *i* component.

$S_{ij}(q)$ ($i \neq j$) is the PSF cross-term, defined by the following equation

$$S_{ij}(q) = \frac{1}{V} < \iint \delta\varphi_i(\vec{\mathrm{r}})\delta\varphi_j\left(\overrightarrow{\mathrm{r}'}\right) \exp\left[-i\vec{q}\left(\vec{\mathrm{r}} - \overrightarrow{\mathrm{r}'}\right)\right] d\vec{\mathrm{r}} d\overrightarrow{\mathrm{r}'} > \qquad \text{(S5)}$$

According to the incompressibility assumption, we have

$$\sum_{i=1}^{3} \delta\varphi_i(\vec{\mathrm{r}}) = 0 \qquad \text{(S6)}$$

Multiplying Eq. (S6) by $\delta\varphi_k\left(\vec{r'}\right)\exp\left[-i\vec{q}\left(\vec{r}-\vec{r'}\right)\right]$ and doing the integration over the scattering volume, we obtain

$$\sum_{i=1}^{3} S_{ki}(q) = 0 \qquad \text{(S7)}$$

where $1 \leq k \leq 3$. Eq. (S7) leads to

$$S_{kk}(q) = -\sum_{i\neq k}^{3} S_{ki}(q) = \sum_{i\neq k}^{3} S_{ii}(q) + 2\sum_{i,j\neq k, i<j}^{3} S_{ij}(q) \qquad \text{(S8)}$$

From Eq. (S8), we have

$$2S_{12} = S_{33} - S_{11} - S_{22} \qquad \text{(S9)}$$

$$2S_{13} = S_{22} - S_{11} - S_{33} \qquad \text{(S10)}$$

$$2S_{23} = S_{11} - S_{22} - S_{33} \qquad \text{(S11)}$$

Eqs. (S9) to (S11) mean that all the cross-terms can be substituted by the self-terms. Therefore, the scattering intensity can be described only by the self-terms, S_{ii}. Thus Eq. (S1) can be rewritten to

$$I(q) = (b_1 - b_2)(b_1 - b_3)S_{11}(q) + (b_2 - b_1)(b_2 - b_3)S_{22}(q) + (b_3 - b_1)(b_3 - b_2)S_{33}(q) \qquad \text{(S12)}$$

Which is Eq. (3) in the main text. On the basis of the incompressibility assumption, the number of partial scattering functions to express $I(q)$ is reduced from 6 in Eq. (S1) to 3 in Eq. (S12).

S3. Decomposition of scattering intensity profiles into partial scattering functions by contrast variation SANS.

When the SANS experiments are performed on the same sample with *m* different contrast by using H_2O/D_2O mixtures, the obtained $I(q)$s (as shown in Figure S4 with symbols) in CV-SANS experiments represent a group of linear equations as expressed in Eq. (3) in the main text and below

$$\begin{pmatrix} I_1(q) \\ \vdots \\ I_m(q) \end{pmatrix} = \boldsymbol{M} \cdot \begin{pmatrix} S_{11}(q) \\ S_{22}(q) \\ S_{33}(q) \end{pmatrix} \qquad \text{(S13)}$$

with each individual $I_i(q)$ being a linear equation in the ith measurement, described by the three PSF self-terms as shown in Eq. (3) in the main text.

$$I_i(q) = (b_1 - b_2)(b_1 - b_3)S_{11}(q) + (b_2 - b_1)(b_2 - b_3)S_{22}(q) + (b_3 - b_1)(b_3 - b_2)S_{33}(q) \qquad \text{(S14)}$$

$\boldsymbol{M}$ is the coefficient matrix of the difference in SLD, as expressed in Eq. (S15) below,

$$\boldsymbol{M} = \begin{pmatrix} {}^1\Delta_{12}\ {}^1\Delta_{13} & {}^1\Delta_{21}\ {}^1\Delta_{23} & {}^1\Delta_{31}\ {}^1\Delta_{32} \\ \vdots & \vdots & \vdots \\ {}^m\Delta_{12}\ {}^m\Delta_{13} & {}^m\Delta_{21}\ {}^m\Delta_{23} & {}^m\Delta_{31}\ {}^m\Delta_{32} \end{pmatrix} \qquad \text{(S15)}$$

where ${}^m\Delta_{ij} = {}^m(b_i - b_j)$ is the SLD difference between i and j in mth measurement.

In order to obtain three PSF self-terms in the right side of Eq. (S13), mathematically the inverse matrix $\boldsymbol{M}^{-1}$ for every three intensities profiles, *i.e.* $I_\alpha(q)$, $I_\beta(q)$ and $I_\gamma(q)$, can be found, then $S_{ii}(q)$ can be mathematically calculated as

$$\begin{pmatrix} S_{11}(q) \\ S_{22}(q) \\ S_{33}(q) \end{pmatrix} = \boldsymbol{M}^{-1} \cdot \begin{pmatrix} I_\alpha(q) \\ I_\beta(q) \\ I_\gamma(q) \end{pmatrix} \qquad \text{(S16)}$$

The best solution of $S_{ii}(q)$ is determined by evaluating the consistency between the reconstructed SANS $I(q)$ profiles and the experimental ones using Eq. (S13) via back-substitution. In this study, the best solution of $S_{ii}(q)$ for Model-I is shown below,

$$\begin{pmatrix} S_{BP-BP\_1}(q) \\ S_{GP-GP}(q) \\ S_{W-W}(q) \end{pmatrix} = \begin{pmatrix} -4.58E(-21) & 5.83E(-22) & 2.04E(-20) \\ 8.44E(-21) & -6.81E(-22) & 8.68E(-21) \\ -2.69E(-21) & 9.13E(-22) & 1.78E(-21) \end{pmatrix} \cdot \begin{pmatrix} I_{D60}(q) \\ I_{D100}(q) \\ I_{D40}(q) \end{pmatrix} \qquad \text{(S17)}$$

The best solution of $S_{ii}(q)$ for Model-II with $\lambda_{local} = 11$ is given as,

$$\begin{pmatrix} S_{BP-BP\_2}(q) \\ S_{PS-PS}(q) \\ S_{HI-HI}(q) \end{pmatrix} = \begin{pmatrix} -8.65E(-21) & 1.31E(-21) & 1.58E(-20) \\ 4.24E(-21) & -3.46E(-22) & 4.52E(-21) \\ -3.91E(-21) & 1.33E(-21) & 2.58E(-21) \end{pmatrix} \cdot \begin{pmatrix} I_{D60}(q) \\ I_{D100}(q) \\ I_{D40}(q) \end{pmatrix}$$

(S18)

where I_{D60} (q), I_{D100} (q) and I_{D40} (q) are experimental SANS intensity profiles at f_{D2O} = 60%, 100% and 40%, respectively.

Using S_{ii} (q) given by Eqs. (S17) and (S18), the reconstructed $I(q)$ profiles (solid lines) are well matched to the experimental profiles (symbols), as shown in Figure S3 and Figure S6 in this supporting information, respectively, indicating the correctness of S_{ii} (q).

References:

S1) G. E. Bacon, *Neutron Diffraction*, Clarendon, Oxford, 1975.

S2) J. S. Higgins and H. C. Benoit, *Polymers and Neutron Scattering*, Clarendon, Oxford, 1994.

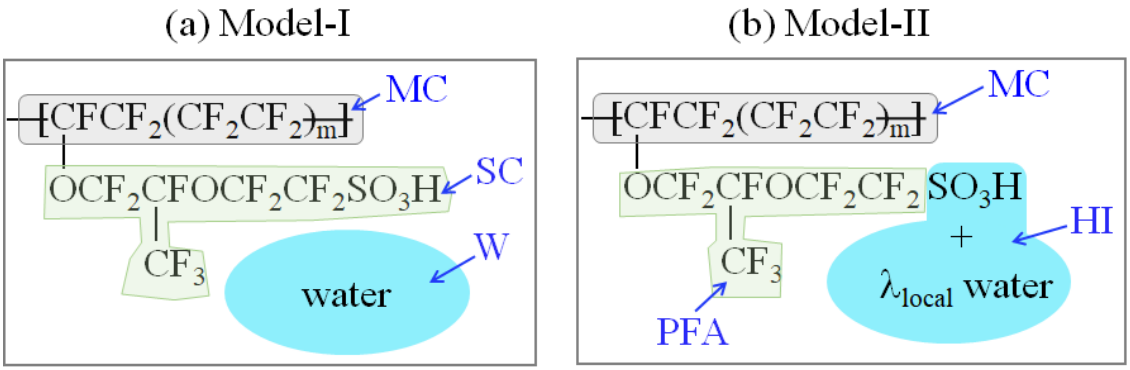

Figure S1 Three-component system illustration of the fully hydrated Nafion composed of (a) Model-I: main chain (MC), side chain (SC), and water (W) (Adapted from Macromolecules 2021, 54, 4128-4135. Copyright [2021] American Chemical Society.); (b) Model-II: MC, perfluoroalkyl ether (PFA), and HI.

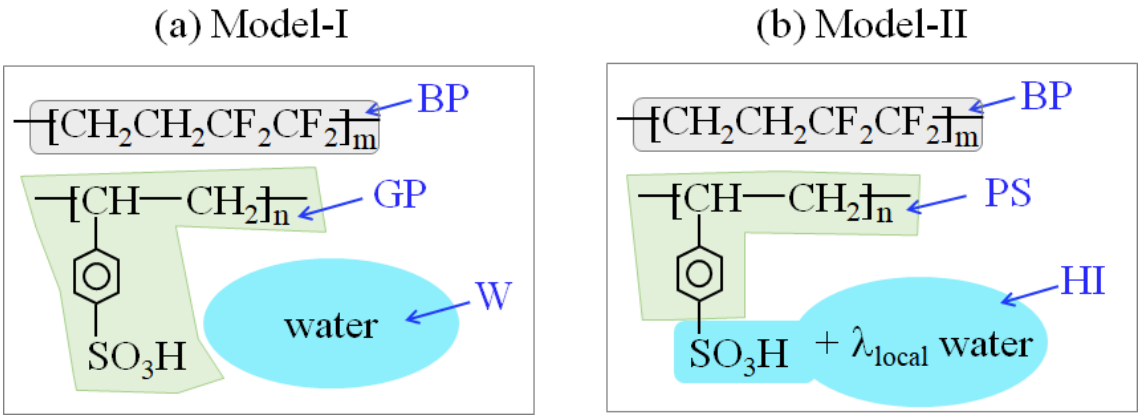

Figure S2 Three-component system illustration of the fully hydrated ETFE-g-PSSA PEMs composed of (a) Model-I: ETFE base polymer (BP), PSSA graft polymer (GP), and water (W) (Adapted from Macromolecules, 2022, 55, 16, 7100-7109. Copyright [2022] American Chemical Society.); (b) Model-II: BP, polystyrene (PS), and HI.

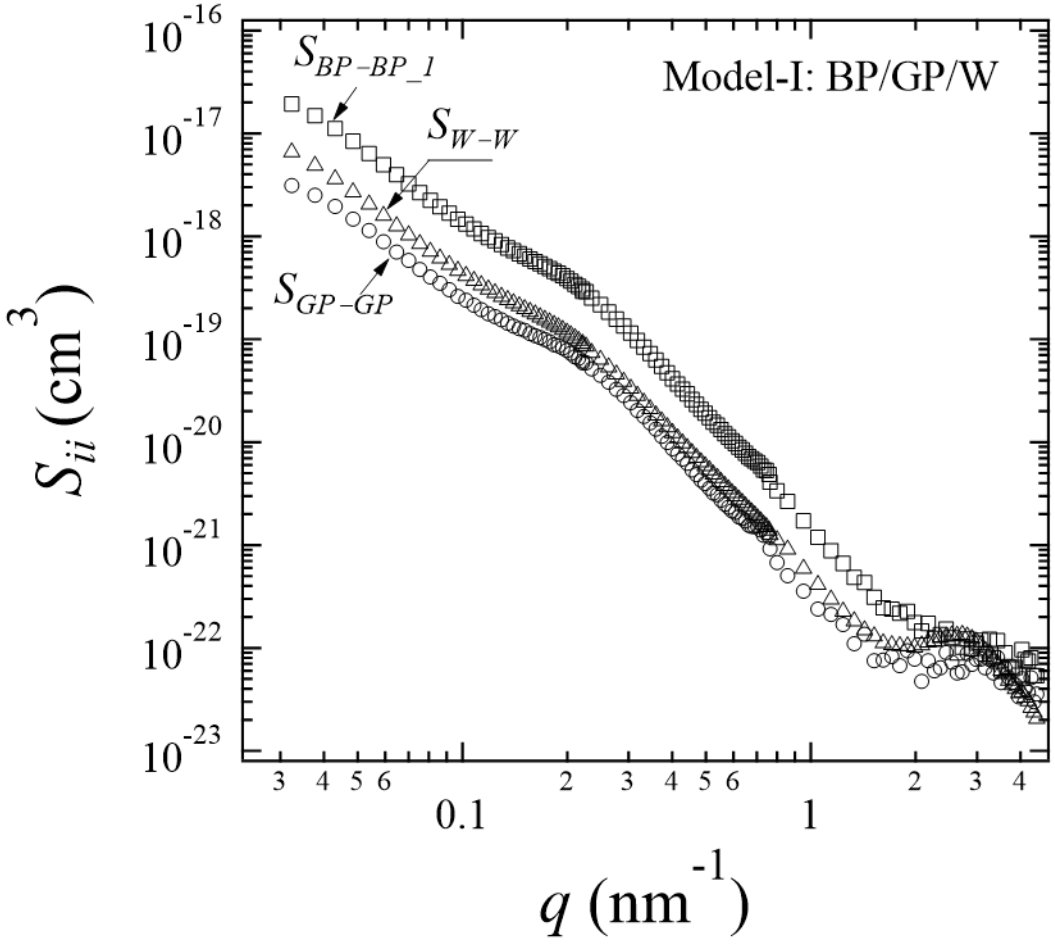

Figure S3 Three PSF self-terms of the fully hydrated ETFE-g-PSSA PEMs in Model-I. Adapted from Macromolecules, 2022, 55, 16, 7100-7109. Copyright [2022] American Chemical Society.

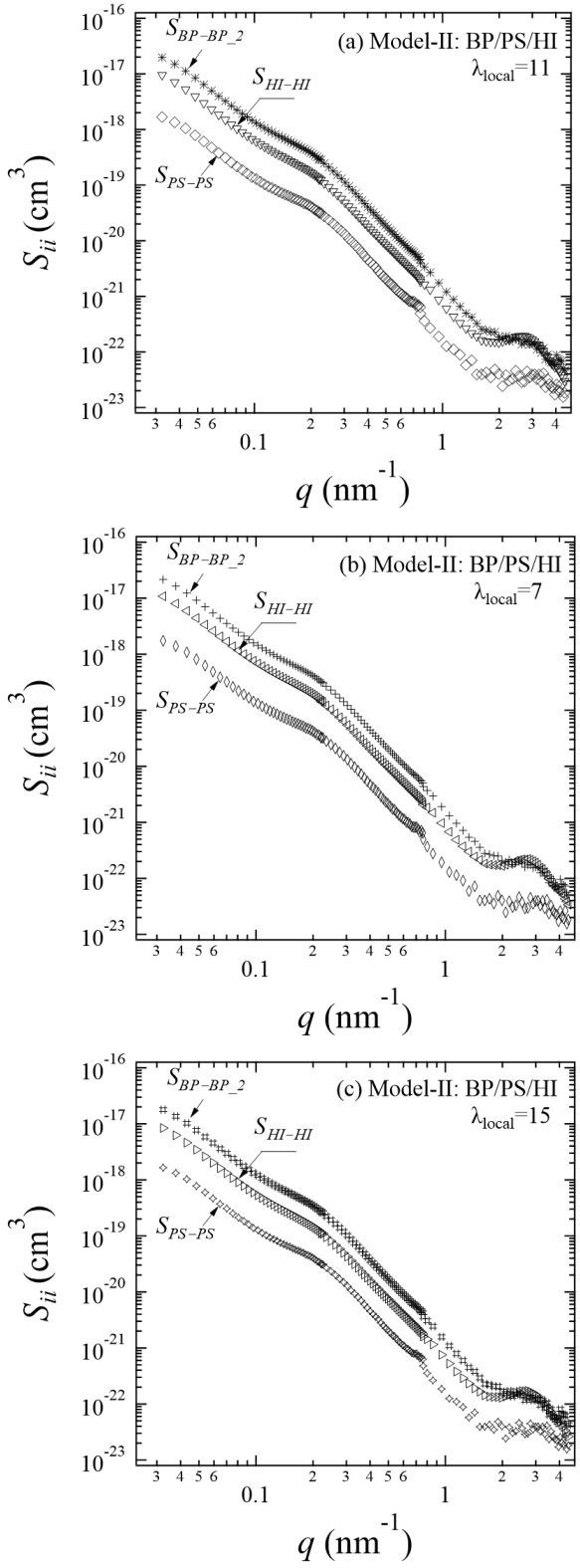

Figure S4 Three PSF self-terms of the fully hydrated ETFE-g-PSSA PEMs in Model-II for (a) λ_{local} = 11; (b) λ_{local} = 7; and (c) λ_{local} = 15.

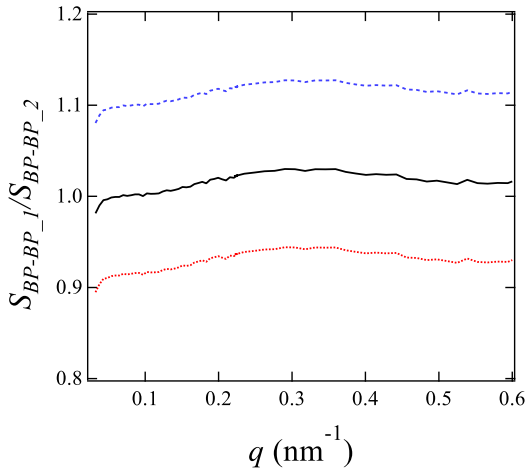

Figure S5 The plot of $S_{\text{BP-BP\_1}}/S_{\text{BP-BP\_2}}$ as a function of q in the low-q range with $\lambda_{\text{local}} = 7$ (the dotted red line), 11 (the solid black line) and 15 (the dashed blue line).

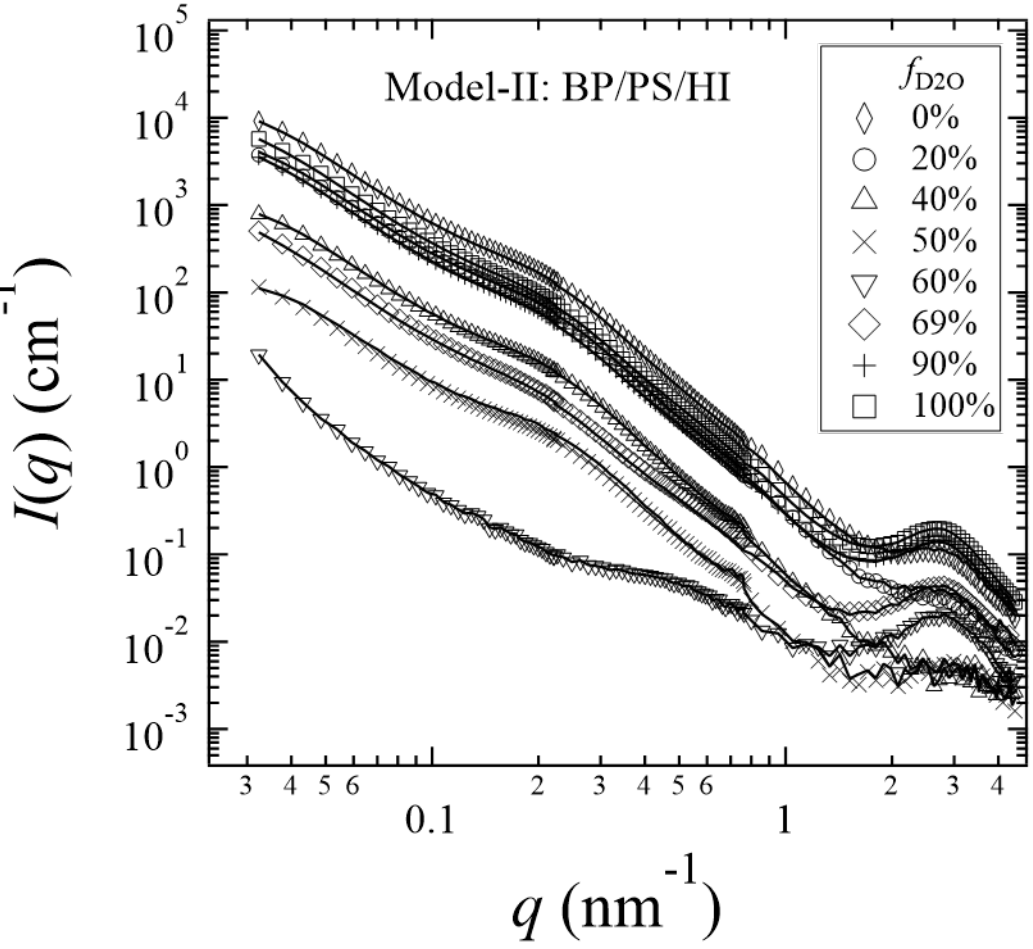

Figure S6 Experimental scattering intensity profiles (symbols) and the reconstructed intensity profiles (solid lines) of the fully hydrated ETFE-g-PSSA PEMs equilibrated in water mixtures of D_2O and H_2O with different ratios in Model-II with $\lambda_{local} = 11$. The error bar of the data is within the symbols.

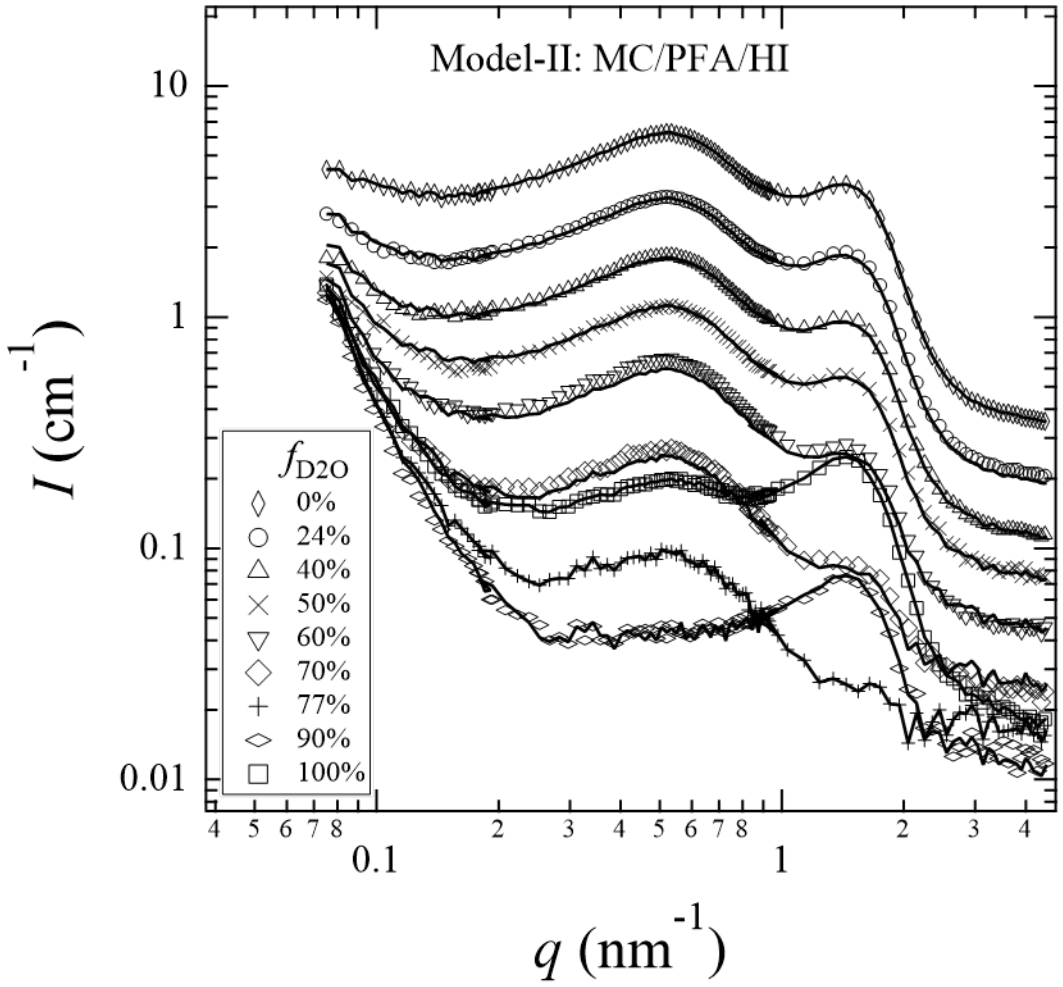

Figure S7 Experimental scattering intensity profiles (symbols) and the reconstructed intensity profiles (solid lines) of the fully hydrated Nafion membrane equilibrated in water mixtures of D_2O and H_2O with different ratios in Model-II with $\lambda_{local} = 21$. The error bar of the data is within the symbols.