Determination of the components of the hydrated regions.

To estimate b_{hydra}, we have to know the components of hydrated regions. We think about three possible cases for the hydrated region as illustrated in Figure S1: case 1) the entire graft chains (both imidazole and styrene segments are included) and water, as shown in the inset of Figure 6 as well; case 2) the imidazole segments on the graft chains (styrene segments are excluded) and water; and case 3) water. In these three cases, we plot $I(q_I)$ as a function of $(b_{cry\text{-}ETFE} - b_{amo})^2$ separately to see which case gives a linear relationship as shown in Figure 6, Figure S2 and S3.

Case 1. In this case, the hydrated regions are composed of the entire graft chains and water. Thus b_{hydra} is given by the averaged SLD of all the components in the region as

$$b_{hydra} = \frac{\phi_{im} b_{im} + \phi_{st} b_{st} + \phi_w b_w}{\phi_{graft} + \phi_w} \qquad \text{(S1)}$$

at m_1 (f_{D2O} = 55%), b_{hydra} is estimated to be 2.23×10^{10} cm^{-2} by eq. (S1). Thus b_{cry_ETFE} is determined to be 2.23×10^{10} cm^{-2}. $(b_{cry\text{-}ETFE} - b_{amo})^2$ in eq. (5) can be calculated in terms of eq. (6) as a function of f_{D2O}. We plot $I(q_I)$ vercus $(b_{cry\text{-}ETFE} - b_{amo})^2$ in Figure 6, and a good linear relationship is obtained, verifying not only the correctness of b_{cry_ETFE} but the components of the hydrated regions.

IV-1.2 Case 2. In this case, the hydrated regions are composed of the partial of the graft chains-imidazole segments, and water. Thus b_{hydra} is given by

$$b_{hydra} = \frac{\phi_{im} b_{im} + \phi_w b_w}{\phi_{im} + \phi_w} \qquad \text{(S2)}$$

at m_1, b_{hydra} is calculated to be 2.4×10^{10} cm^{-2} by eq. (S2). Consequently, b_{cry_ETFE} is

estimated to be 2.4 × 10^{10} cm^{-2}. $(b_{cry\text{-}ETFE} - b_{amo})^2$ in eq. (5) can be calculated in the same way as in case 1. Figure S2 shows the plot $I(q_1)$ versus $(b_{cry\text{-}ETFE} - b_{amo})^2$, and the datapoints are scattered, indicating the incorrect assumptions of b_{cry_ETFE} and the components of the hydrated regions.

IV-1.3 Case 3. In this case, the hydrated regions are only composed of water, which is the characteristic pattern in Nafion.[43,44] Thus b_{hydra} is simply given by

$$b_{hydra} = b_w \qquad \text{(S3)}$$

at m_1, b_{hydra} is estimated to be 3.235 × 10^{10} cm^{-2} by eq. (S3). Thus b_{cry_ETFE} ~ 3.235 × 10^{10} cm^{-2}. The plot between $I(q_1)$ versus $(b_{cry\text{-}ETFE} - b_{amo})^2$ on the base of case 3 is shown in Figure S3, and an even more scattered dataset is observed, revealing the assumption of case 3 is wrong.

According to the discussions above, we conclude that the hydrated regions are composed of the entire graft chains and water, and SLD of the crystalline ETFE domains (b_{cry_ETFE}) is 2.23 × 10^{10} cm^{-2}, the value of which is listed in Table 1.

Verification of contrast factors *A* and *B* in eq. (10). *A* is the contrast factor, proportional to the contrast square between crystalline region (b_{cry_ETFE}) and the entire amorphous region (b_{amo}), given by

$$A \sim (b_{cry\_ETFE} - b_{amo})^2 \qquad \text{(S4)}$$

where b_{cry_ETFE} is estimated to be 2.23× 10^{10} cm^{-2} in section IV-1 in the text. b_{amo} can be calculated by eq. (6) in the text. We plot *A* versus $(b_{cry\_ETFE} - b_{amo})^2$ for all the

profiles at f_{D2O} > 55% in Figure S4. A good linear relationship is clearly observed, evidencing the correctness of A.

B is the contrast factor, proportional to the contrast square between amorphous ETFE (b_{amo_ETFE}) and all the rest components in the sample (b_{rest}), given by

$$B \sim (b_{amo\_ETFE} - b_{rest})^2 \qquad \text{(S5)}$$

where b_{amo_ETFE} is ~ 2.0× 10^{10} cm^{-2}, which was listed in Table 1 in the text. b_{rest} can be calculated by eq. (S6) below

$$b_{rest} = \frac{\phi_{cry\_ETFE} b_{cry\_ETFE} + \phi_{im} b_{im} + \phi_{st} b_{st} + \phi_w b_w}{\phi_{cry\_ETFE} + \phi_{graft} + \phi_w} \qquad \text{(S6)}$$

where all parameters have been explained in the text and listed in Table 1. We plot B versus $(b_{amo\_ETFE} - b_{rest})^2$ for all the profiles at f_{D2O} > 55% in Figure S5. A good linear relationship is clearly observed, evidencing the correctness of B.

SANS profiles for grafted-ETFE membranes and the corresponding AEMs with different GDs. SANS profiles for grafted-ETFE membranes with GD of 30, 46 and 120% and the corresponding AEMs with *IEC*s of 0.95, 1.26 and 2.15 mmol/g are shown in Figure S6. To avoid overlapping, the profiles were vertically shifted.

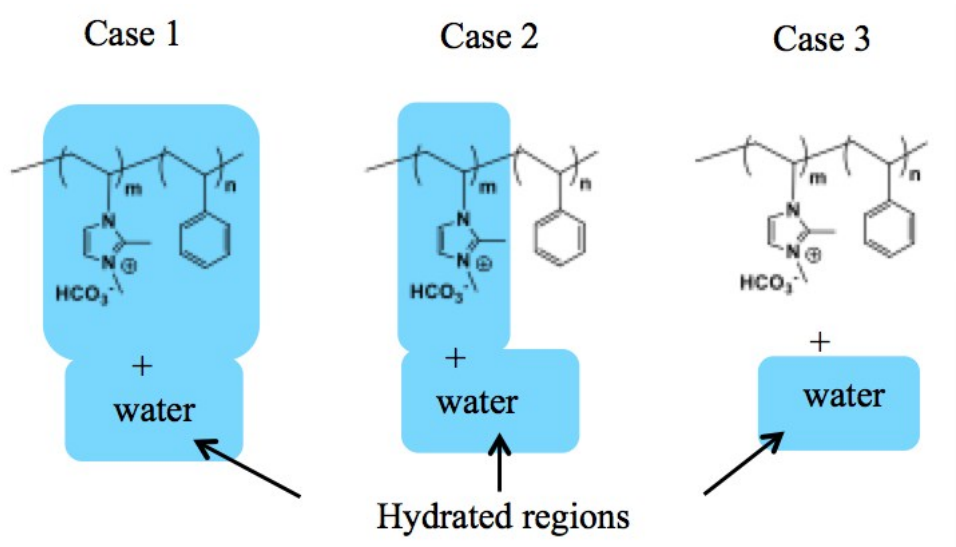

Figure S1

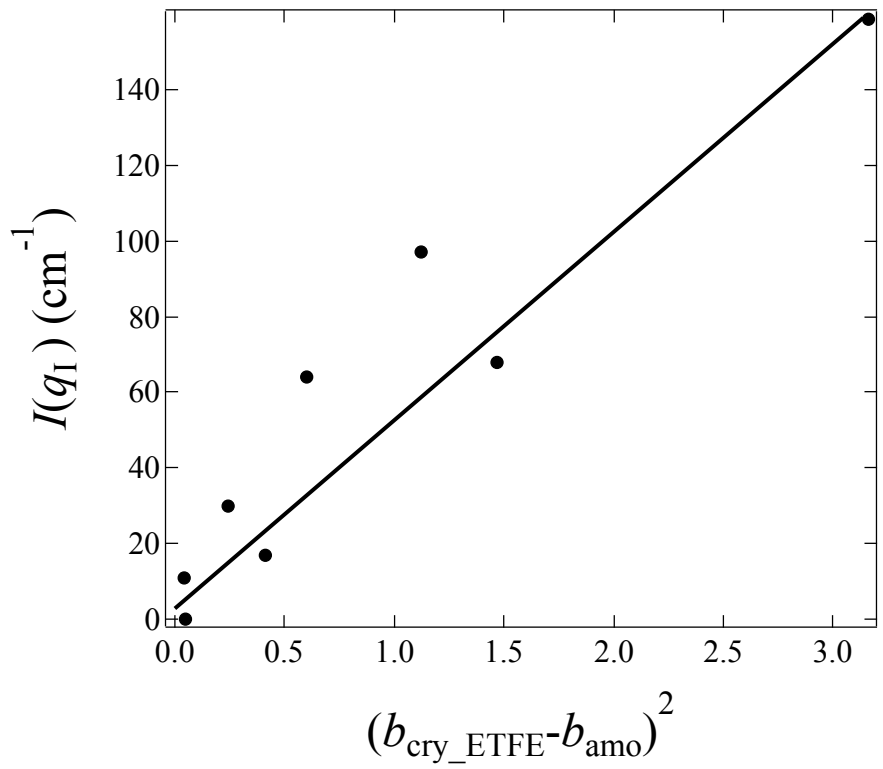

Figure S2

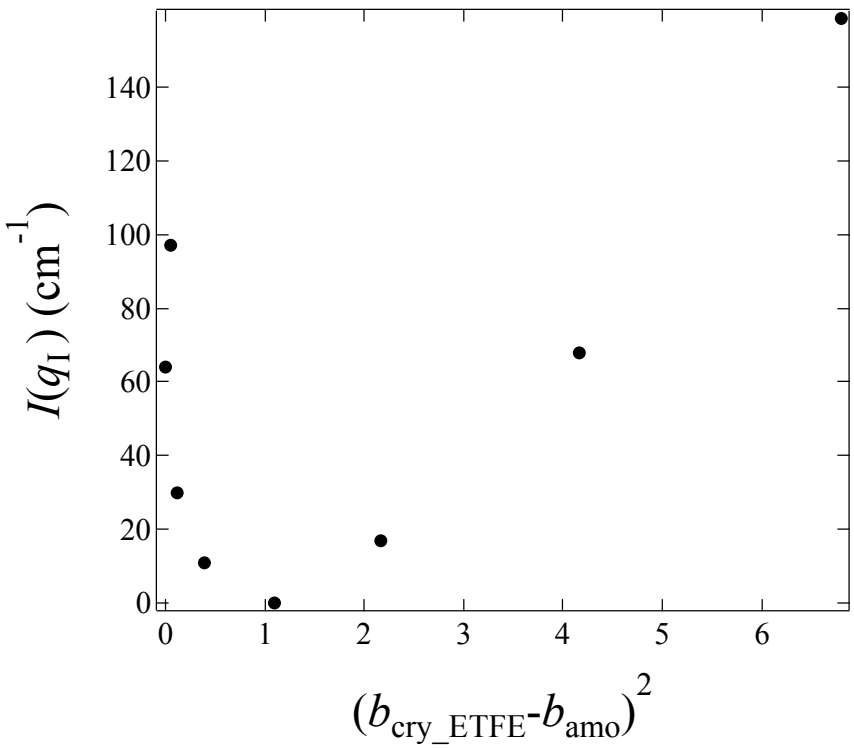

Figure S3

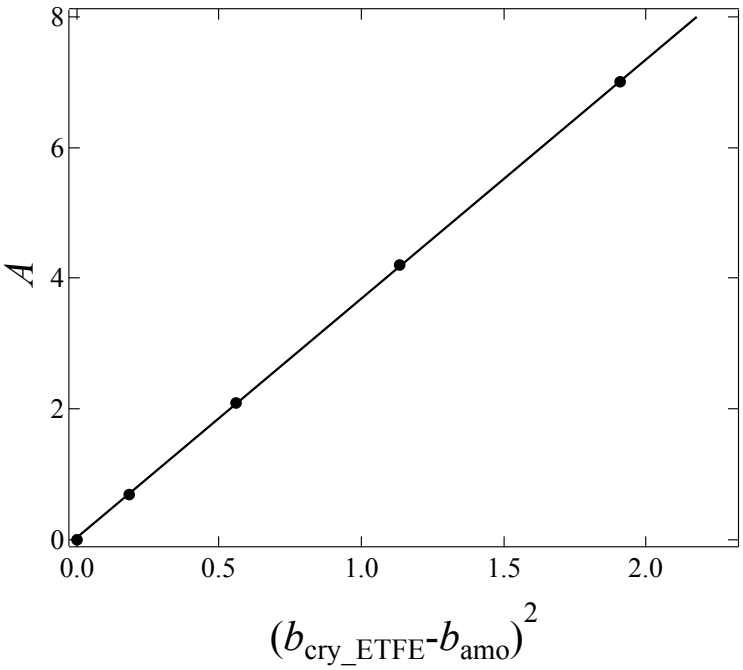

Figure S4

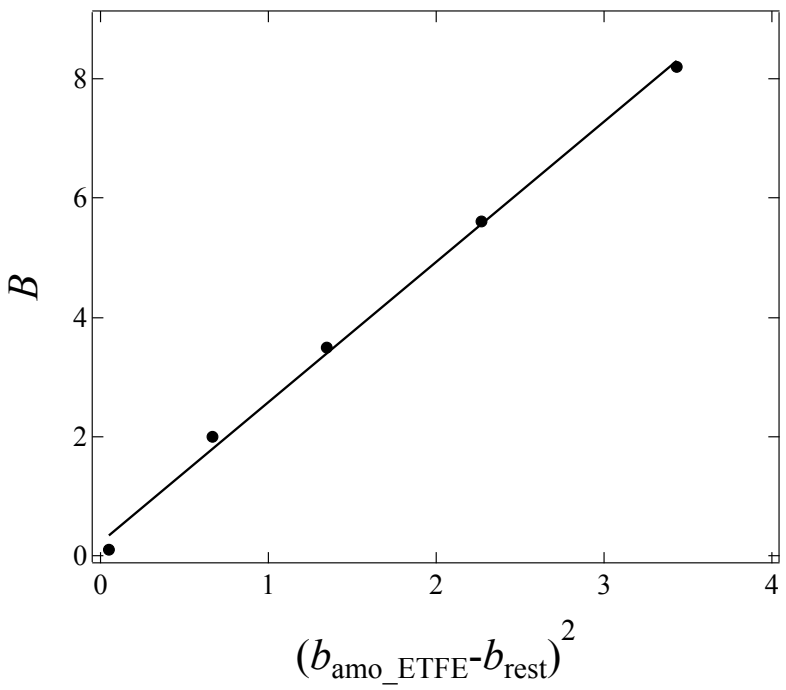

Figure S5

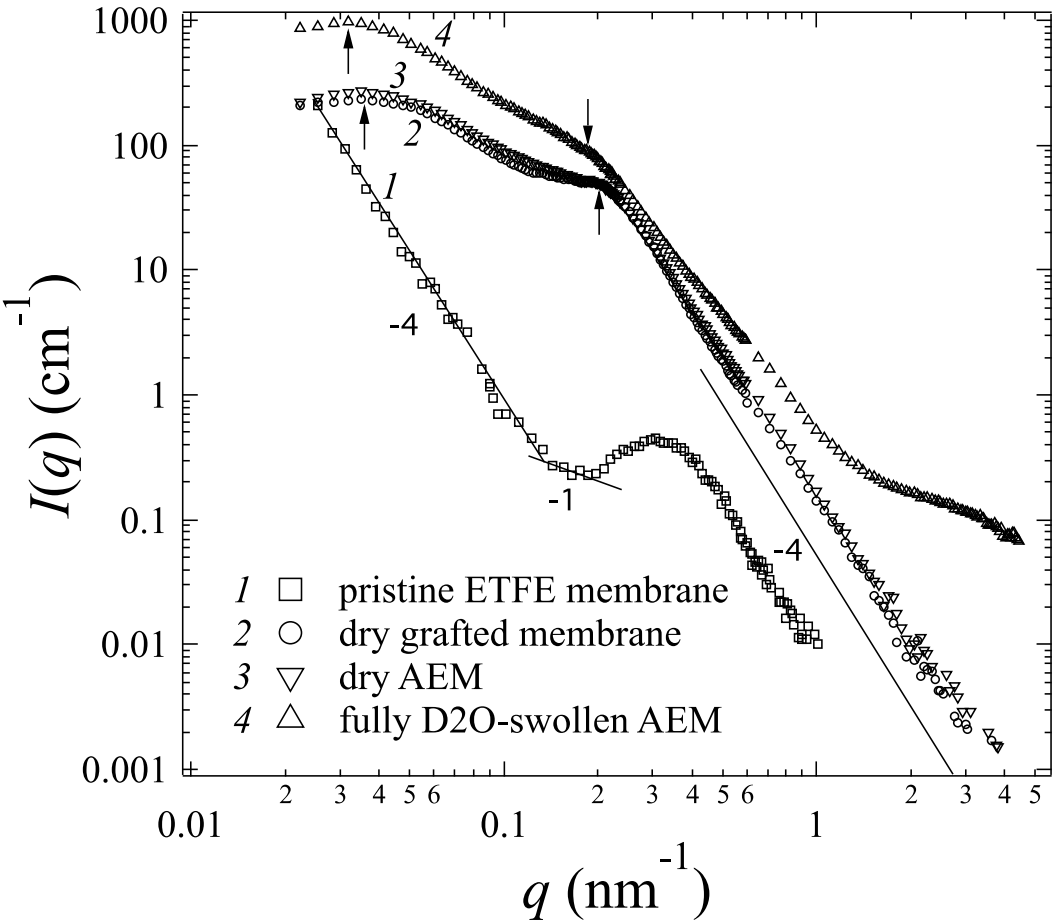
1000
100
10
1
0.1
0.01
0.001
I(q) (cm-1)
0.01
0.1
1
q (nm-1)
1
2
3
4
-4
-1
-4
1 pristine ETFE membrane
2 dry grafted membrane
3 dry AEM
4 fully D2O-swollen AEM

Figure S6