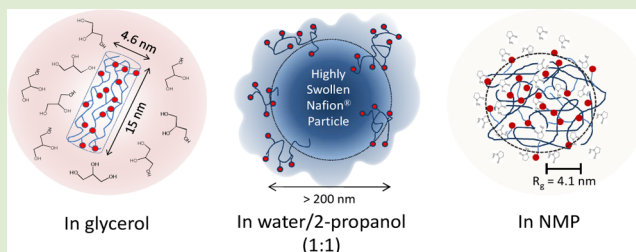


Nafion in Dilute Solvent Systems: Dispersion or Solution?

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Supporting Information

ABSTRACT: The morphology of Nafion (EW = 1000, Na⁺ form) in dilute solvents is investigated using small angle neutron scattering (SANS) and ¹⁹F NMR. SANS modeling indicates three types of particle morphology: (i) a well-defined cylindrical dispersion in glycerol and in ethylene glycol with different degrees of solvent penetration; (ii) a less-defined, highly solvated large particle (>200 nm) in water/isopropanol mixtures; and (iii) a random-coil conformation (true solution behavior) in *N*-methylpyrrolidone. These distinct morphological characteristics of Nafion are consistent with the main and side chain mobilities measured by ¹⁹F NMR.



Nafion polymers, produced by the E. I. DuPont Company, are the industrial standard perfluorosulfonic acid materials for polymer electrolyte fuel cells.¹ While the structures of dry and water-swollen Nafion membranes have been studied extensively,² the microstructure of Nafion dispersions in liquid media has not been thoroughly investigated. Structural analysis of Nafion dispersions via small angle scattering (SAS) techniques began in the mid-1980s, after procedures for dispersing Nafion in liquid media were established.³ Pioneering works by Aldebert and co-workers suggested that the H⁺ and Li⁺ forms of Nafion formed cylindrical particles in polar solvents such as water, ethanol, formamide, and *N*-methyl formamide (NMF) with a volume fraction of polymer ranging from 0.28 to 25%.⁴ Although the scattering curves were complicated by particle interactions, indicated by a maximum in the scattering intensity, the authors calculated cylinder radii that ranged from 18 to 31 Å, based on a Guinier analysis for cylindrical particles and from geometrical arguments for cylinders organized in a hexagonal array.⁴ Loppinet et al. expanded on these studies to examine the effects of counterion and added salt in a larger number of solvents to screen the electrostatic interactions between particles, thereby reducing the degree of local order.⁵ For all dispersions studied, including the dispersions with added salt, a cylindrical particle morphology was found. A Porod analysis, in addition to the Guinier and geometrical analyses, yielded fairly consistent cylinder radii in the range of 12–26 Å.

While the SAS data reported in the literature indicate a cylindrical colloidal structure of Nafion for all solvents studied so far, experimental analysis from viscosity, electron spin resonance (ESR), and NMR spectroscopies suggest somewhat different conclusions for the structure of Nafion in a liquid medium. Moore and Martin observed that the viscosity of the Na⁺ form of Nafion dispersed in a water/methanol (1:1)

mixture dramatically increased at low concentration, and they suggested a major morphological transition from colloidal dispersion to highly solvated extended state, probably due to an extensive polyelectrolyte effect.⁶ Later, Aldebert and co-workers also observed a significantly higher intrinsic viscosity for an aqueous Nafion dispersion compared to other solvent dispersions.⁷ Using ESR, Schlick and co-workers reported that large aggregated particles of Nafion were formed in water and formamide, while no indication of large aggregates was observed in ethanol and NMF.⁸ In spite of having a significantly different time scale than ESR, ¹⁹F NMR results also indicated that Nafion in ethanol forms a true solution (i.e., polymer solvated completely).⁹ Using size exclusive chromatography (SEC), Lousenberg observed that Nafion aggregates in water/alcohol/dimethylsulfoxide mixture disappeared when the dispersions were heated to high temperatures.¹⁰ Several investigators have reported that the level of Nafion aggregation in dilute dimethyl formamide and dimethyl acetamide is minimal,¹¹ thereby enabling the molecular weight measurement of Nafion using SEC with static light scattering.^{11a–c} These viscosity and spectroscopic analyses indicate that the particle morphology of Nafion in liquid media may be more diverse than that suggested from earlier SAS analyses, and the question of whether Nafion in a liquid medium is a dispersion or a true solution is still open.

In this letter, we investigate the Nafion particle morphology in diluted liquid media using small angle neutron scattering (SANS) and ¹⁹F NMR techniques. While previous SANS studies examined the Nafion particle morphology by Guinier and geometrical analyses, we performed more precise structural

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modeling for describing the Nafion particle morphology; from such fits to the data, we can ascertain polymer/particle shape and size, as well as the percentage of solvent within the particle. The small-angle scattering intensity can be written in terms of the contrast ($\Delta\rho$) between scattering entities (for example, polymers or aggregates with bound solvent and free solvent), the form factor ($P(Q)$) that describes the shape and size of the particle, and the structure factor ($S(Q)$) that describes interparticle interactions, averaged ($\langle \rangle$) over orientation and polydispersity:

$$\frac{d\Sigma(Q)}{d\Omega} = N_0 \Delta\rho^2 \langle V^2 P(Q) S(Q) \rangle \quad (1)$$

where N_0 is the particle density and V is the volume.

For dilute dispersions or solutions in which no interparticle interactions occur, $S(Q) = 1$ and the scattering data can be fit to a form factor to gain information on the polymer/particle shape and size. ^{19}F NMR is used to measure the chain mobility in the various solvent systems. The chain mobility due to aggregation into higher order structures can then be correlated with the morphological features investigated by the SANS modeling analysis.

Figure 1 shows SANS data for Nafion dispersions in glycerol and ethylene glycol (EG). The data from both the glycerol and

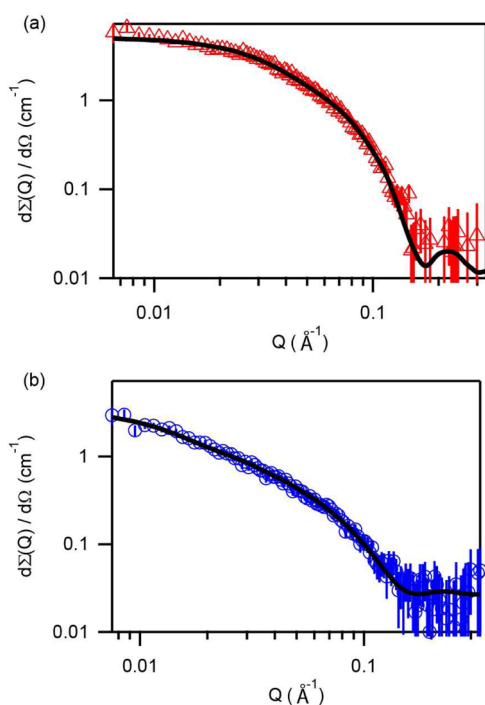


Figure 1. SANS data (symbols) and model fits (lines) for the 2.5 wt % (a) glycerol and (b) EG dispersions. Root mean squared uncertainties in intensity are indicated by the bar lines.

EG can be fit well to the form factor for cylindrical particles,¹² and these fits yield the cylinder radius (22 Å for both), cylinder length (150 Å and 370 Å, respectively), and cylinder scattering length density (SLD) ($4.0 \times 10^{-6} \text{ \AA}^{-2}$ and $2.5 \times 10^{-6} \text{ \AA}^{-2}$, respectively). Comparing the cylinder SLDs to those expected from Nafion 212 ($4.2 \times 10^{-6} \text{ \AA}^{-2}$) and the respective solvents, the volume fraction of solvent within the cylindrical particles can be calculated. For the glycerol dispersion, this volume fraction is quite small, ≈ 0.05 , indicating that very little glycerol

is present in the particle; a considerably higher volume of EG (≈ 0.42) resides in the Nafion particles for the EG dispersion. The Nafion particle dimensions in glycerol and EG obtained from form factor modeling are well matched with the values that we calculated from Guinier and Porod analyses. For example, the radius and cylinder length of Nafion in glycerol are 22.5 and 135 Å, respectively.

Figure 2a shows SANS profiles for Nafion dispersions in water/2-propanol mixtures of various volume ratios that range

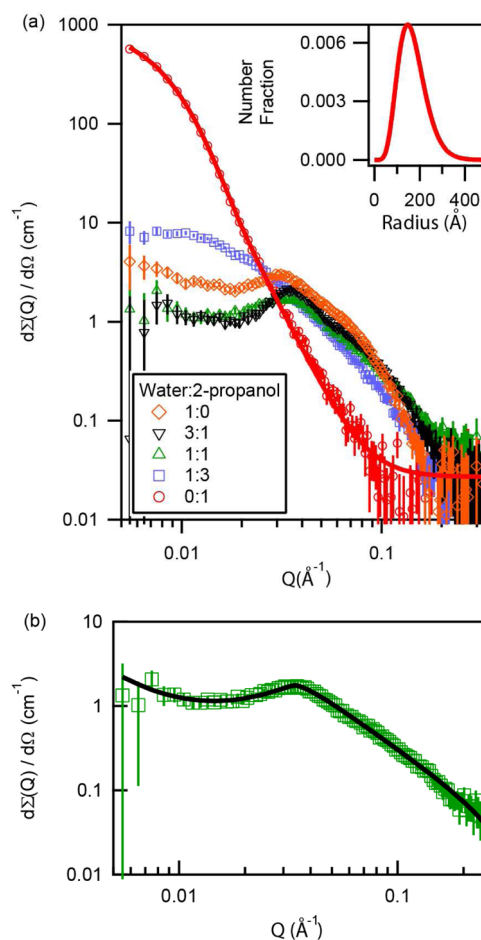


Figure 2. (a) SANS data (symbols) for the 2.5 wt % water/2-propanol dispersions as a function of water to 2-propanol ratio; red line indicates the fit to the 0:1 dispersion data, and the inset is the distribution of particle sizes obtained from the fit (b) SANS data (symbols) and model fit (line) for the 1:1 water/2-propanol dispersion.

from 1:0 (pure water) to 0:1 (pure 2-propanol). More complicated Nafion morphology appeared with this mixed solvent system. In pure 2-propanol, the large upturn in scattering intensity at low Q suggests large particles or aggregates; furthermore, the scattering intensity exhibits a Q^{-4} dependence at high Q , which is indicative of a smooth particle/solvent interface. The best fit to this data was obtained from the form factor for a polydisperse population of spherical particles, in which the polydispersity in radius is described by a Schulz distribution.¹³ This fit yields an average radius of 170 Å and a particle SLD of $3.6 \times 10^{-6} \text{ \AA}^{-2}$, which suggests a relatively low volume fraction of 2-propanol within the spherical particles (≈ 0.14). The polydispersity (defined as $p = \sigma/R$, where σ^2 is the variance of the distribution and R is the mean particle

radius) is 0.36 and results in the distribution of radii shown in the inset of Figure 2a. Interestingly, the data for the 2-propanol dispersion can also be fit fairly well to a cylindrical form factor when polydispersity in the cylinder radius is included. The length of the cylinder is 350 Å and its mean radius is 155 Å, with a polydispersity of 0.48. These dimensions are quite similar to those obtained from the fit to the spherical form factor. In addition, the particle SLDs from the two fits are identical. These results show that, in 2-propanol, Nafion forms a polydisperse population of large, roughly spherical particles that incorporate a low volume fraction of solvent (≈ 0.14) and have a mean radius in the range of 155–170 Å.

As the 2-propanol concentration is lowered in the 1:3 and 1:1 dispersions, the scattering at low Q decreases and a peak appears. In addition, the magnitude of the slope at high Q decreases, indicating greater solvent penetration into the Nafion particles. As the 2-propanol concentration is further lowered to 0 (i.e., pure water dispersion), a new low- Q upturn becomes evident, the peak grows in intensity and shifts to lower Q , and the magnitude of the high- Q slope increases again. Taken together, these data show that the Nafion particle morphology is strongly affected by changes in the water/2-propanol ratio. Even without performing any precise model fits similar to those of Figure 1a, the changes in scattering observed between these samples suggest that the large particles formed in pure 2-propanol become more solvated with the addition of water up to the 1:1 water/2-propanol mixture and then perhaps less solvated as the water content is further increased. Unlike the dispersions in glycerol and EG, the dispersions in water/2-propanol mixtures that are dominated by a peak at $Q \approx 0.03 \text{ \AA}^{-1}$ cannot be fit to any discrete particle form factors. One possible model for Nafion in these mixed solvent dispersions is a large swollen cluster or network model. An ansatz for such a model was developed by Hammouda et al.¹⁴

$$\frac{d\Sigma(Q)}{d\Omega} = \frac{A}{Q^n} + \frac{C}{\{1 + (|Q - Q_0|L)^m\}} + B \quad (2)$$

where the first term captures scattering due to the large length-scale structure (evidenced by upturn at low Q), the second describes local polymer–solvent interactions, and the third is for incoherent background scattering.

As an example, we consider the 1:1 water/2-propanol dispersion in Figure 2b; fitting the dispersion data to this model yields a Porod exponent $n \approx 2$, suggesting that the large-scale clusters (>200 nm) are solvent-swollen and have a fuzzy interface. The same fit gives a correlation length $L = 4 \text{ nm}$ and the exponent $m \approx 1.4$. These results are consistent with the highly viscous, fuzzy gel-like particles observed by Moore and Martin.⁶

Figure 3 shows the SANS profile for Nafion in NMP. The data show a clear absence of a peak, which is similar to those of glycerol and EG. However, the SANS data for Nafion in NMP neither fits well to the form factor for a cylindrical particle, nor does it fit to form factors for any other simple shape (e.g., sphere, ellipsoid, etc.). Instead, the best fit to this scattering curve is the Debye form factor, which describes a linear polymer chain in a theta solvent, a random coil.¹⁵ This fit yields a radius of gyration (R_g) of 41 Å, which agrees well with our Guinier analysis for this data. We also obtained equally good fits to the form factor for polymer chains with excluded volume.¹⁶ As with the Debye fit, the R_g is 41 Å; in addition, this fit yields the scaling exponent $\nu = 0.44$, suggesting that the

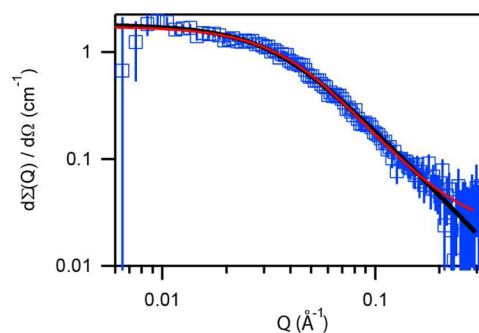


Figure 3. SANS data (symbols) and model fits (lines) for the 2.5 wt % NMP dispersion. Black line = Debye model fit;¹⁵ red line = fit to polymer with excluded volume model.¹⁶

polymer is in a slightly poor solvent condition. This analysis provides further evidence that Nafion polymer chains may, in fact, exist as single molecules in solution rather than within aggregates. It also supports the idea that the absolute molecular weight of Nafion can be measured using SEC with static light scattering.^{11a–c}

Figure 4a shows ^{19}F NMR spectra for the Nafion in glycerol, EG, and NMP. The chemical shifts for Nafion in a liquid medium were assigned from previous reports.¹⁷ The peaks at

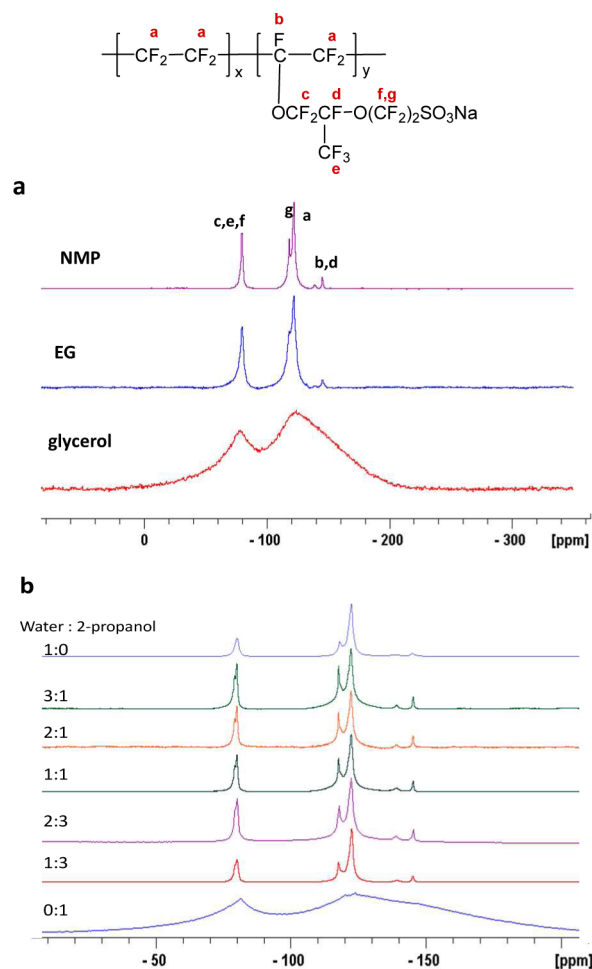


Figure 4. ^{19}F NMR spectra obtained for (a) glycerol, EG, and NMP and (b) water/2-propanol mixture dispersions (water to 2-propanol ratio varied from 1:0 to 0:1).

80, 117, 138.5, and 144.5 ppm are due to fluorine molecules in the side chain, whereas the peak at ~ 122 ppm is due to CF_2 groups in the backbone. The broadness of all the peaks for Nafion in the glycerol dispersion indicates that both main and side chains have low chain mobility. One may speculate that the low chain mobility is due to the high viscosity of glycerol ($\eta = 1.5$ Pa s). However, this can only account for a small fraction of the peak broadening, as we observed sharp peaks for a highly viscous polymer gel in NMP. Therefore, the low mobility of Nafion is primarily due to the motional constraints introduced by polymer–polymer interactions or ion clustering within the Nafion particle¹⁸ aggregate rather than polymer–solvent interaction. This is in good agreement with SANS data that show glycerol apparently does not penetrate well into either part of the polymer. Nafion in the EG and NMP dispersions shows much sharper peaks for both main and side chains. Comparing the ^{19}F NMR spectra of Nafion in EG and NMP, both have similar side chain mobility, as determined by the reciprocal value of line width at 80 and 117 ppm. However, when the ratio of main chain peak (at 122 ppm) to side chain peaks (at 80 and 117 ppm) is compared, the NMP dispersion has more than 50% greater value than that of the EG dispersion, indicating that the main chains of Nafion in NMP are better solvated and have greater mobility. Although these ^{19}F NMR data cannot conclusively determine whether the Nafion in NMP and EG is completely solubilized or not, these results are in good agreement with the above SANS analyses, which showed a solubilized random walk conformation in NMP and significant solvent penetration in EG.

Figure 4b shows ^{19}F NMR spectra for the Nafion in water/2-propanol mixtures as a function of water to 2-propanol ratio. The relatively sharp peaks observed for both main and side chains for each water/2-propanol mixture indicate that the solvent penetration within the Nafion particles is significant. For the pure water dispersion, the sharpness of the side chain peaks noticeably decreased. The suppression of side chain mobility in the pure water dispersion is probably due to the fact that side chain mobility is restricted by strong polar interaction between water and the sodium sulfonate group. For the pure 2-propanol dispersion, much broader peaks for both main and side chains are observed, probably due to the relatively low volume fraction of 2-propanol within the spherical Nafion particles, as indicated by the SANS results. The ^{19}F NMR results indicate that the Nafion particles in water/2-propanol mixtures are relatively well solvated, while Nafion in pure water is less solvated (indicated by the reduced side chain mobility) and Nafion in pure 2-propanol is much less solvated (indicated by the reduced side and main chain mobility). These results are in good agreement with the above SANS results.

In summary, SANS studies revealed three types of Nafion particle morphology in dilute liquid media (ca. 2.5 wt %). In glycerol and EG, Nafion formed cylindrical particles, which have similar radii (i.e., 22 Å) but noticeably different cylinder lengths (150 and 370 Å for glycerol and EG, respectively). The morphological features and particle dimensions are in good agreement with our Guinier and Porod analyses. While the cylindrical particle structure of Nafion in glycerol and EG is consistent with the particle morphology suggested by Aldebert and co-workers,⁴ our SANS results revealed additional radically different Nafion morphologies in water/2-propanol mixtures and aprotic NMP solvent. In water/2-propanol mixtures, we observed less-defined, highly solvated large particles (>200 nm), probably due to a strong polyelectrolyte effect between

sulfonated side chains that are solvated by water. The highly solvated side chains and large particle morphology supports the abnormally high viscosity observed in previous measurements.^{6,7} The scattering curve of Nafion in NMP was best fit with the Debye form factor, which describes a linear polymer chain in a theta solvent with $R_g = 41$ Å. The morphological features of Nafion in NMP support previous ESR and NMR results,^{8,9} which indicate solution behavior rather than a dispersion. The ability to disrupt all aggregates and completely solubilize Nafion provides a mechanism for measuring its molecular weight, which has been accomplished via SEC with light scattering in recent years.¹¹ Further evidence on the solution like behavior of Nafion in aprotic solvent systems, and the impact on mechanical properties of solution cast membranes will be reported in subsequent papers.

■ EXPERIMENTAL SECTION

Glycerol-based Nafion dispersion was prepared by the Los Alamos National Laboratory-developed direct dispersing technique.¹⁹ Acid (H^+) form Nafion NR-212 (EW = 1100) membranes from DuPont were put in a boiling 1% solution of NaOH for 90 min and subsequently immersed in boiling deionized water for 90 min to remove any residual NaOH. After drying the Na^+ -form Nafion membrane at 60 °C in vacuo for 2 h, 0.5 g of the membrane was cut into small pieces and placed in a 60 mL vial with 20 g of glycerol; solid content was 2.5 wt %. The vial was heated in a convection oven at 210 °C for 3 h. A clear brown colored liquid solution was obtained without residual solid polymer. ^1H NMR of the glycerol dispersion indicates that no side reactions or degradation occurs during the dispersion process (Figure S1 in the Supporting Information). EG- and NMP-based liquid dispersions were prepared in the same way as the glycerol-based dispersion,¹⁸ except for the processing temperature and duration. The temperature/duration for EG and NMP-based liquid dispersions are 180 °C/1 h and 100 °C/1 h, respectively. Nafion dispersions in water/2-propanol mixtures were prepared by the conventional dispersing technique in a closed vessel.^{3a} For example, the preparation of the 1:1 water/2-propanol dispersion is as follows: 89.5 g of water, 70.5 g of 2-propanol, and 4.1 g of Na^+ -form Nafion 212 membrane were placed in a 200 mL Parr pressure reactor; the solid content was 2.5 wt %. The vessel was heated in a heating mantle at 210 °C for 3 h. The internal vessel pressure was ~ 500 psi. A transparent and clear liquid dispersion was obtained without residual solid polymer. Nafion dispersions in pure water or in pure 2-propanol were prepared by the solvent exchange method. For pure water dispersion, a 3:1 water/2-propanol dispersion (prepared via the conventional method) was heated to 80 °C. Deionized water (5 times the original volume) was added dropwise to the dispersion mixture while the solvent was evaporated. For pure 2-propanol dispersion, the 1:3 water/2-propanol dispersion was heated to 60 °C, and 2-propanol (~ 20 times the original volume) was slowly added during the evaporation process. ^1H NMR confirmed the completion of these solvent exchange processes. While the pure water dispersion was clear, the pure 2-propanol dispersion was hazy and viscous, indicating that the dispersion state was poor.

SANS measurements were performed on the time-of-flight, low- Q diffractometer, LQD, at the Manuel Lujan Jr. Scattering Center at Los Alamos National Laboratory and on the NG-3 beamline at the NIST Center for Neutron Research. Samples were placed in 1 mm path length fused silica cells. Data were

reduced by conventional methods to an absolute scale, differential scattering cross section per unit volume ($d\Sigma(Q)/(d\Omega)$ (cm^{-1})), as a function of momentum transfer, $Q = 4\pi/\lambda \sin \theta$, where 2θ is the scattering angle and λ is the incident neutron wavelength. Reduced solvent background was subtracted from each sample data set. Form factor fitting of the data was performed with the SANS and USANS Data Reduction and Analysis software (Igor Macros), provided by the NIST Center for Neutron Research.²⁰

¹⁹F NMR spectra were obtained using a Bruker Avance 300 spectrometer operating at 282.4 MHz. The pulse length was 2.5 μs , and 10s delay time was used with a 4 mm fluorine free probe. Number of scans varied between 512 and 1024; chemical shifts were referenced to external CFCl_3 at 0 ppm.

■ ASSOCIATED CONTENT

Supporting Information

Details of the SANS form factor model fits and ¹H NMR data of the Nafion dispersion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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