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Supramolecular Hydrophobic Aggregates in Hydrogels Partially Inhibit Ice Formation

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Supporting Information

ABSTRACT: Prevention of ice crystallization is a challenging problem with implications in diverse applications, as well as examining the fundamental low temperature physics of water. Here, we demonstrate a simple route, inspired by water confinement in antifreeze proteins, to inhibit crystallization and provide high water mobility of highly supercooled water using supramolecular hydrogels of copolymers of dimethylacrylamide (DMA) and 2-(*N*-ethylperfluorooctane sulfonamido)ethyl acrylate (FOSA). These hydrogels can suppress or inhibit freezing of their water, depending on the copolymer composition. Dynamic and static neutron scattering



Crosslink density ~ composition

Cool to <250 K

Low density of crosslinks Near complete freezing Segregation of polymer Loss of nanostructure



High density of crosslinks Limited freezing Structure intact

indicate that hydrogels using the copolymer with 22 mol % FOSA partially inhibit ice formation. This behavior is attributed to confinement (<2 nm) of water between the hydrophobic FOSA nanodomains that prevents 45% of the water within the hydrogel from freezing even at 205 K. Very fast dynamics of the amorphous water are observed at 220 K with an effective local diffusivity decreased by only a factor of 2 from that observed at 295 K within the hydrogel using the copolymer with 22 mol % FOSA. The spacing between the hydrophobic nanodomains, tuned through the copolymer composition, appears to modulate the water that can crystallize. These fully hydrated hydrogels (at equilibrium with liquid water at 295 K) can enable a significant fraction of highly supercooled water to be stable down to at least 205 K.

INTRODUCTION

Control of ice formation is a critical industrial challenge for numerous applications from renewable wind power¹ and preservation of biologics,² where inhibition of freezing is desired, to food products,³ where precise control of ice crystallization is desired. Decades of work involving fundamental investigations of water have identified numerous crystalline and amorphous ice structures.^{4–6} One key finding from these fundamental studies is that the confinement of water to dimensions less than 10 nm tends to inhibit water crystallization;^{7,8} typically this inhibition is a kinetic limitation. These confinement studies tend to be limited to hard materials where water concentrations are generally low and water is confined within the pores of the material.^{9–11}

Conversely, Nature has evolved unique methods for mitigating ice formation with soft materials in aqueous environments.¹² Typically these inhibition strategies involve adsorption of water-soluble macromolecules to the surface of nuclei that prevent the growth of ice crystals. Synthetic mimics of these proteins can inhibit ice growth in aqueous solutions,² but these strategies are limited to relatively low degrees of undercooling (<10 K). An alternative evolutionary strategy for proteins involves water confinement between hydrophobic residues to inhibit freezing.⁸ However, soft synthetic mimics that inhibit ice by hydrophobic confinement are, in general,

lacking and represent an unexplored route to enable the supercooling of water.

Hydrogels represent one of the most widely examined forms of water-rich soft matter, as they can mimic the mechanical properties and aqueous environment of biological tissue.¹³ However, the freezing of water is generally only modestly impacted by inclusion in a hydrogel, while the polymer network of the hydrogel is irreversibly damaged structurally by ice crystallization.^{2,14,15} Antifreeze proteins with hydrophobic residues can inhibit ice formation⁸ and thus provide inspiration toward the development synthetic analogues. Within this context, it is hypothesized that nanoscale confinement of water between hydrophobic moieties within hydrogels should also inhibit ice formation.

Herein, we describe the ability to tune water freezing within supramolecular hydrogels. The water is confined by hydrophobic nanodomain cross-links that are formed through the physical association of the hydrophobic constituent (FOSA) of a DMA–FOSA random copolymer hydrogel. Prior small-angle neutron scattering (SANS) measurements have demonstrated <10 nm hydrophilic regions between the FOSA nano-

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Figure 1. (A) Schematic of the hierarchical structure of the DMA–FOSA hydrogels showing core–shell morphology with FOSA core and waterdepleted DMA shell. The average center-to-center distance between the supramolecular cross-links (*d*), measured by SANS as a function of FOSA content of the copolymer: O, this work; \bullet , ref 17. (B) DSC heating and cooling thermograms at 2 K/min for DF5 hydrogel (80 wt % H₂O). (C) DSC heating and cooling thermograms at 2 K/min for DF22 hydrogel (45 wt % H₂O).

domains;¹⁷ here we confirm these SANS results and demonstrate the persistence of the hydrogel nanostructure, at sufficiently high FOSA content, deep into the supercooled state for water, while the scattering from the nanostructure was lost at low FOSA content during crystallization of the water in the hydrogel. The dynamics of water within the hydrogel examined by quasielastic neutron scattering (QENS) were significantly altered from that of bulk water and demonstrated that extremely mobile water with liquid-like diffusivity can persist to 205 K within these hydrogels. These characteristics appear to prevent damage to the hydrogel on thawing, similar to strategies in Nature for survival in cold climates. This demonstration of unexplored strategy for ice inhibition will enable the design of new materials for applications, such as the preservation of biologicals and anti-icing surfaces.

RESULTS AND DISCUSSION

Figure 1A shows the hierarchical structure of the supramolecular hydrogels. These hydrogels are physically crosslinked by FOSA nanodomains. Small-angle neutron scattering (SANS) showed that a water-depleted DMA shell is formed around the FOSA nanodomains.¹⁷ By adjusting the FOSA content of the copolymer from 5 mol % (DF5) to 22 mol % (DF22), the center-to-center spacing between the nanodomains was varied between 7.1 and 6.4 nm (inset in Figure 1A). From prior SANS measurements, the radius of the FOSA nanodomains is approximately 2 nm with a 1 nm water depleted shell of DMA¹⁶ and confirmed by the SANS measurements here with the shell thickness independent of FOSA content in the hydrogel. From geometry, the average hydrated distance between the FOSA nanodomains is 1-2 nm and is dependent on the FOSA content in the hydrogel. These length scales for confinement of water are similar to those where large changes in the freezing of water occur in carbon nanotubes,¹⁷ so the nanodomains may act to confine the water in a manner similar to that of hard porous matter. However, the

efficacy of these hydrogels in inhibiting freezing of water appears to be intimately tied to the composition of the copolymer. For the DF5 hydrogel (low cross-link density), water freezing was suppressed to 256 K for a hydrogel that was swollen to an equilibrium water concentration of ~80 wt % at 295 K (DSC thermogram in Figure 1B). This suppression in the freezing point is reminiscent of the influence of some electrolytes commonly observed in pharmaceuticals.^{18,19} However, all of the water within the hydrogel (Figure 1B) melts at approximately the normal melting point of water. This is in contrast to the influence of electrolytes where both the freezing and melting points are suppressed to a similar degree.²⁰ The lack of reversibility within the hydrogel is suggestive of a change in the local environment for water on freezing, which is not unexpected as freezing of water within hydrogels is known to degrade mechanical properties (directly correlated with the network structure of the hydrogel).² The normal freezing point provides evidence that the water phase separates from the copolymer on freezing. The exotherm and endotherm in these studies provide a direct route to estimate the fraction of water that has crystallized. Recently, a cubic form of ice with nearly the same normal melting point has been reported for water confined within alumina nanochannels,²¹ but the crystallization is not confined to nanoscopic dimensions in the hydrogel as will be discussed later. Thus, we assume that the ice within the hydrogel is I_h with the specific enthalpy of fusion of 334 J/g. With this assumption, we calculated that \sim 95 wt % of the water in the DF5 hydrogel was crystallized on cooling from the enthalpy of the melting endotherm of the hydrogels. This near complete freezing of water is expected for hydrogels.

A more complex freezing behavior is observed when the FOSA content in the hydrogel is increased to 22 mol % (DF22), which decreases the water content to ~45 wt %. The thermogram on cooling exhibited three exotherm peaks at 254, 244, and 227 K (Figure 1C). These transitions suggest three



Figure 2. Temperature-dependent SANS profiles for (A) DF22, (B) DF15, and (C) DF5 hydrogels equilibrated at 295 K with D_2O for maximum total scattering. Contrast variation provides the (D) interdomain spacing (using 27/73 v/v D_2O/H_2O) and (E) the effective volume fraction of the supramolecular aggregates separated by hydrated DMA (using 50/50 v/v D_2O/H_2O). Error bars represent one standard deviation; if not visible, error bars are smaller than the size of the symbol.

distinct local environments for water with the DF22 hydrogel; these different environments are not clearly observed when freezing water within the DF5 hydrogel despite the chemical similarities. Recent work by Floudas and co-workers demonstrated how slight modulation in the confinement could lead to significant variation in the freezing point of the supercooled water.^{21–23} However, both hydrogels (DF5 and DF22) exhibit a single peak in the heating endotherm near the normal melting point of ice. These endotherms suggest that the ice in both hydrogels is likely Ih, but cubic ice also melts at a similar temperature.²¹ For the DF22 hydrogel and again assuming the enthalpy of I_h, only 55 wt % of the water is frozen, based on the heating endotherms, in comparison to the near complete freezing (~95%) in DF5. One potential explanation is the difference in hydration between the samples as bound water to hydrophilic polymers can inhibit crystallization. However, normalizing mass of amorphous water by that of the dry copolymer in the hydrogel still has more amorphous water for DF22 (0.36 w:w) than for DF5 (0.2). Note that the DF22 copolymer contains less of the hydrophilic DMA, but the fraction of amorphous water increased in comparison to DF5. Thus, the change in the freezing behavior does not appear to be associated with favorable interactions between the water and the copolymer.

Moreover, the partial suppression of ice formation in the DF22 hydrogel does not appear to be a consequence of kinetic factors; using cooling rates that differed by nearly an order of magnitude and annealing the sample at low temperature do not significantly alter the exotherm or change the fractional freezing as determined from the heating endotherm (Figure S1). We hypothesize that this large fraction of amorphous water in the DF22 hydrogel is due to confinement of water between the FOSA nanodomains. However, the supramolecular structure of the hydrogel can rearrange when stressed,²⁴ e.g., from stresses associated with water expansion when it crystallizes, so understanding the nanostructure of these hydrogels at low temperature will provide insight into the mechanical vs

thermodynamic origins of confinement that appears to partially suppress ice formation.

In situ freezing studies using SANS experiments illustrate differences in the nanostructure of the hydrogels and how these nanostructures evolve through the freezing transition(s). Figure 2 demonstrates the influence of the FOSA content in the hydrogel on the temperature dependence of the scattering profiles. As shown in Figure 2A, the absolute scattering intensity for the DF22 hydrogel swollen with D₂O shows that the peak position associated with the correlation of the FOSA domains (analogous to *d*-spacing) was nearly invariant; thus, the nanostructure persists to 205 K although the scattering intensity decreased on cooling. However, there is an increase in low Q scattering at temperatures below 260 K; this is associated with the generation of macroscopic heterogenities in the hydrogel (likely small D_2O ice crystals within the hydrogel). For the DF15 and DF5 hydrogels (Figures 2B and 2C), the correlation peak associated with the FOSA domains was no longer well resolved at temperatures below 260 K. This behavior is attributed to the exclusion of the copolymer when the water crystallized. This effectively decreases the concentration of D₂O within the DMA phase upon freezing to decrease the spacing between FOSA nanodomains and the scattering contrast associated with the nanodomains and the matrix of DMA/D₂O. For these hydrogels, the scattering was essentially unchanged at lower temperatures (<260 K), which is consistent with the DSC data (Figure 1B and Figure S3), indicating that >90% of the water crystalllized when the DF5 and DF15 hydrogels were cooled to 260 K.

To explain this evolution in the nanostructure of these hydrogels, the impact of ice formation must be considered. For more conventional covalently cross-linked hydrogels, stresses that develop due to the expansion of water upon ice crystallization break covalent bonds.²⁵ However, for the supramolecular hydrogels examined herein, the physical cross-links can rearrange to accommodate the water expansion that accompanies ice formation. This rearrangement will distort the nanodomain structure and decrease the correlation peak in the

SANS profile. As the water crystallizes, it phase separates to exclude the copolymer from the ice. This will impact the scattering through a significant decrease in contrast by the loss of D_2O between the FOSA nanodomains. Also the increase of local FOSA volume fraction, which is discussed later in the paper, shifts the structure factor peak to a higher Q value resulting the further decrease of the correlation peak.

To better understand the structural changes in these hydrogel during cooling, contrast variation SANS was performed using mixtures of H_2O and D_2O to match the contrast of the DMA or FOSA phase of the hydrogel. SANS experiments using 27/73 (v/v) D_2O/H_2O mixtures to contrast match the neutron scattering length density (NSLD) of the DMA phase quantify the changes in the FOSA nanostructure (Figure S4) induced by freezing water. These scattering profiles were fit with a Broad Peak Model^{26,27} (representative fit shown in Figure S5):

$$I(Q) = \frac{A}{Q^{n}} + \frac{C}{1 + (|Q - Q_{0}|\xi)^{m}} + B$$
(1)

where A and C are scaling factors, B is the background, ξ is the Lorentzian screening length, n is the Porod exponent, and m is the Lorentzian exponent. These fits determine the temperature dependence of the interdomain FOSA spacing, $d = 2\pi/Q_0$, and a Porod term that describes the fractal dimensions of the aggregates responsible for the low Q upturn in scattering.

Figure 2D summarizes the evolution of the interdomain spacing (d) on cooling for the DFx hydrogels. For DF5 and DF15, d decreased abruptly between 270 and 260 K and remained almost constant on cooling to 210 K. The large decrease in d was attributed to the water phase separating from the copolymer during ice crystallization. In contrast, the gradual decrease in the d-spacing upon cooling the DF22 hydrogel (nearly exponential between 270 and 242 K) was a consequence of the suppression of ice crystallization in that system. This evolution in the structure on cooling for DF22 is consistent with the large amorphous water fraction calculated from DSC.

Similarly, matching the NSLD of the FOSA with 50/50 (v/v) D_2O/H_2O mixture enabled direct interogation of the DMA structure (Figure S6). These scattering profiles (representative fit shown in Figure S7) were fit with a core–shell model with a Schulz distribution of radii and hard sphere interaction.²⁸ This model provides the thickness of the dehydrated shell surrounding the FOSA core and a Porod term that describes the composition fluctuations within the hydrogel

$$I(Q) = \frac{A}{Q^n} + cF^2(Q)S(Q) + B$$
⁽²⁾

where A is the scale factor for the Porod fit at low Q with exponent n, B is the background scattering, F(Q) is the form factor from a core-shell structure with a Schulz probability density distribution, and S(Q) is the structure factor for a coreshell system²⁹ using the Percus-Yevick³⁰ closure for a polydisperse hard sphere structure. The small scattering contribution of the DMA chains between the nanodomains was lumped into the background as this scattering was nearly invariant for the Q range examined (Figure S8). From these fits, the effective volume fraction of FOSA nanodomains (separated by DMA/water) was determined for these DFx hydrogels (Figure 2E). For DF15, a sharp increase in the effective volume fraction was found on cooling from 270 to 260 K. This behavior was attributed to the deswelling of the DMA phase when ice was formed. In contrast, the nanodomain volume fraction only modestly decreases for the DF22 hydrogel between 275 and 240 K, and the volume fraction was invariant on cooling further below 240 K. That result is consistent with the suppression of ice formation in DF22 (limited deswelling of DMA phase).

These structural characteristics from SANS provide indirect evidence to crystallization/supercooling of water within these hydrogels that depends on the FOSA content. In order to more directly examine the potential supercooling, quasielastic neutron scattering (QENS) was used to provide a direct measure of the water dynamics in the hydrogels Figure 3



Figure 3. QENS measurements of proton dynamics at Q = 1.25 Å⁻¹ for DCS at (A) 295 K and (B) 260 K for DF22 (red), DF15 (blue), and DF5 (green). All hydrogels were equilibrated at 295 K with H₂O prior to measurements. Error bars represent one standard deviation.

illustrates the QENS spectra at 295 and 260 K for the three DFx hydrogels obtained using the disk chopper spectrometer (DCS) at the NIST Center for Neutron Research (Gaithersburg, MD).³¹ The DCS has an accessible measurable range of relaxation times, τ , from 2.1 to 75 ps with slower protons contributing to the elastic peak in the spectra. The mobility of the protons is directly related to the breadth of the peak. Within the measurable range, shorter relaxation time for the proton will lead to more energy being transferred and a broader peak in the spectrum. In these hydrogels, the protons are primarily from H₂O. At 295 K, the spectrum for DF5 is broader than that for DF22 (Figure 3A), which suggests a decrease in the water mobility in the DF22 hydrogel. This decreased mobility is likely a consequence of the FOSA-contentdependent water fraction in the hydrogels (Figure 2E) and the length scale of confinement between FOSA domains (Figure 2D).

On decreasing the temperature to 260 K, the QENS spectra narrowed significantly (i.e., decreased dynamics of the protons) as was expected as shown in Figure 3B. The compositional dependence of the hydrogel (FOSA content) on the resolvable proton dynamics by DCS is inverted at 260 K relative to that at 295 K. At 260 K, the narrowest spectrum is for the DF5 hydrogel (low mobility) and broadest spectrum is for the DF22 hydrogel (higher mobility). This narrowing is likely partially due to an increase in the intensity of the elastic peak as the dynamics of ice are below the resolution of the instrument as has been reported previously.³²

In order to quantify the diffusive motions within these hydrogels, the QENS data were fit by a single Lorentzian that is convoluted with the energy-independent background and an elastic delta function that is smeared by the instrumental resolution as shown in Figure 4. Figure 4A shows the fit of the DCS spectrum for the DF22 hydrogel at 295 K. The Lorentzian describes the broadening of the spectrum and provides a more quantitative measure of the proton dynamics that are within the



Figure 4. Representative fits for the DF22 hydrogel swollen with H_2O at (A) 295 K and (B) 220 K. The full data fit is shown as the solid line with contributions from the elastic peak associated with instrumental resolution (slower motions is shown with the dotted line), the background is the horizontal dashed line, and the dashed Lorentzian associated with the relaxation processes (data of interest). Error bars represent one standard deviation.

energy resolution of the DCS (0.055 meV) through the width of the Lorentizian. Comparing this peak to the Lorentizian for the DF22 hydrogel at 220 K (Figure 4B) shows that the peak slightly narrows on cooling to 220 K. This result demonstrates that motions of some protons in the DF22 hydrogel remained within the energy window for the DCS QENS measurements at 220 K. These relatively fast motions at 220 K within this hydrogel are noteworthy as protons motions in supercooled water confined in mesoporous silica are not resolvable at temperatures below 250 K.³³ This difference suggests that the amorphous water within the DF22 hydrogel is significantly more mobile than supercooled water confined within nanopores of inorganic materials.

To enable comparison of the water dynamics in these hydrogels to other systems, the apparent self-diffusion constant of water was calculated from the Q-dependent full width at half maximum (fwhm) (2Γ) obtained from the Lorentzian fits of the QENS data. At 270 K, 2Γ increased linearly with Q^2 at high Q with a plateau at low Q as shown in Figure 5A. The plateau is indicative of water confinement and modeled as a caged Fickian process³⁸

$$\Gamma(Q) = D_w Q^2 + C \tag{3}$$

where 2Γ is fwhm, D_w is Fickian diffusion constant, and C is a constant. A cage radius³⁸ can then be calculated

$$\Gamma_0 = 4.33296 D_w / A^2 \tag{4}$$

where $2\Gamma_0$ is the plateau fwhm and A is the cage radius. As shown in the Supporting Information, the estimated cage radius is around 6 Å. The prefactor constant results from the intermediate scattering function Fourier integral approximation of the elastic line width in the low Q regime (associated with the plateau in DQ^2).³⁹ Experimentally, this linear relationship between 2Γ and Q^2 was found for all temperatures examined for the DF22 hydrogel. As shown in Figure 5B, these motions were weakly dependent on temperature below 260 K from the Q-dependent fwhm. These motions can be quantified in terms of an effective diffusivity (based on eq 3) for the three hydrogel systems examined. Figure 5C illustrates that the water diffusivity within DF5 and DF15 decreased rapidly on cooling below 270 K. For these two hydrogels, the motions became too slow to resolve at temperatures below 260 K. We attribute this behavior to water crystallization. For DF15 and DF5 hydrogels, a small compositional dependence can be resolved with the diffusivity slightly greater in DF15 than DF5 at 260 K (see Figure 5C).



Figure 5. Analysis of DCS data provides insight into the water dynamics. (A) The fwhm at 270 K for H₂O hydrogels of (\bigcirc) DF5, (\blacksquare) DF15 and (\blacktriangle) DF22 illustrates water motion is locally caged Fickian diffusion due to invariant fwhm at low Q. (B) The fwhm for DF22 hydrogels is only slightly impacted by temperature: (\bigstar) 260, (\blacklozenge) 250, (\blacksquare) 240, and (+) 220 K. The horizontal dashed line provides the slowest motions resolvable with DCS. (C) Calculated effective self-diffusion constant of H₂O within the hydrogels (\diamondsuit) DF5, (\blacksquare) DF15, and (\bigstar) DF22 with comparison to bulk water (\diamondsuit) as measured by NMR³⁶ and QENS³² and predicted by simulations (\diamondsuit).³⁷ Below 260 K, no motions in DF5 or DF15 hydrogel were resolvable, while water remained mobile down to 220 K in the DF22 hydrogel. (D) The fit of the EISF provides the fraction of protons, n(T), in the sample that can be resolved by DCS. The line is a guide to the reader's eyes. Error bars represent one standard deviation.

In contrast to DF5 and DF15 hydrogels, the self-diffusion coefficient for the mobile water within the DF22 hydrogel was only modestly impacted on cooling from 295 to 220 K. Over this entire temperature range, the effective diffusivity decreases by less than a factor of 2. Even at 270 K, the self-diffusion coefficient is greater for the DF22 hydrogel than the other hydrogels examined. When comparing to neat supercooled water (in 300 μ m capillary tubes) in Figure 5C, the selfdiffusion coefficient for the water in the DF22 hydrogel near the normal melting point is nearly an order of magnitude less than found for supercooled water.^{32,36} However, the selfdiffusion of the supercooled water within the capillary decreases significantly on cooling.^{32,36} At approximately 235 K, the selfdiffusion of water within the DF22 hydrogel nearly matches that of the supercooled water (Figure 5C). At the lowest temperatures examined for the hydrogels, the self-diffusion of the supercooled water is almost an order of magnitude slower than the mobile water within the DF22 hydrogel.³⁷ This behavior suggests that either the DMA segments or confinement between glassy FOSA domains leads to enhanced dynamics in H₂O at these low temperatures in comparison to neat supercooled water. Typically, confinement suppresses the dynamics except when it inhibits crystallization and the comparison is between different states.^{22,33} However, there are cases where the mobility of small molecules is enhanced by confinement, such as for the flow of liquid water through carbon nanotubes.⁴⁰

The compositional dependence of the freezing behavior of water within these DFx hydrogels suggests that the FOSA nanodomains act to confine water. The effective length scale for confinement of the water was estimated from the elastic incoherent structure factor (EISF) obtained from the QENS data. The water in the DFx hydrogels was assumed to be confined between neighboring FOSA nanodomains, and the EISF was fit by a simple diffusion equation for water confined between two parallel surfaces⁴¹ (see Figure S10)

$$F_{\text{EISF}}(T, Q) = n(T)[A_0(Q) - 1] + 1$$
(5)

$$A_0(Q) = j_0^{-2}(QL/2) \tag{6}$$

where n(T) is the fraction of protons participating in the measurable diffusive motions, A_0 describes the cage size relative to the EISF ratio,⁴² L is the length of confinement, and j_0 is a Bessel function of the first kind and zero order. The confinement length scale, L, decreased on cooling, and the changes in L were greatest for DF5 and least for DF22, which are consistent with the results of the SANS analyses for the changes in the nanostructure of these hydrogels on cooling. For DF22, the calculated cage size at 270 and 295 K was 3.2 and 4.2 Å, respectively. However, these cage sizes are significantly smaller than the average hydrated interstitial space between the hydrophobic FOSA domains calculated from SANS (~10–30 Å at 270 K).^{43,44} Cage sizes calculated from EISF and fwhm assuming Fickian diffusion are shown in Figure S11.

In addition to understanding the caging effect of the FOSA nanodomains, the EISF also provides quantification of the fraction of protons in the hydrogel with motions in the measurable dynamic window of the spectrometer (n(T)). Figure 5D shows how n(T) changed on cooling. At 295 K (above the normal melting point of ice), most of the protons in the system were measurable by the QENS experiments. Protons with mobility slower than the resolution energy scatter elastically and act to decrease n(T). As n(T) includes the protons on the copolymer, it is instructive to compare this calculation to how the protons are distributed within the hydrogel. Table 1 summarizes this comparison for the three

Table 1. Comparison of the Mobile Fraction of ProtonsCalculated from the EISF with the Proton-BasedComposition of the Hydrogels

		mole fraction of H in hydrogel		
	n(T) at 295 K	H ₂ O	DMA	FOSA
DF5	0.79 ± 0.02	0.86	0.13	0.009
DF15	0.78 ± 0.02	0.80	0.16	0.039
DF22	0.53 ± 0.02	0.67	0.24	0.090

hydrogels at 295 K. The fraction of resolvable protons, n(T), correlates qualitatively with the mole fraction of protons in H_2O for the hydrogels. However, n(T) is consistently less than the fraction of H_2O in the system. This disagreement may be associated with the oversimplification of the geometry (particle between two parallel plates) for calculation of the mobile fraction of the scattering from the EISF as well as H_2O coupled to the DMA segments (where the DMA segmental motions are slow to be effectively elastic for the energy window examined). Nonetheless, the reasonable correlation of n(T) with the protons on water is consistent with the assumption that mobile protons in the QENS spectra are dominated by H_2O .

As the temperature decreased, n(T) decreased sharply at 260 K for the DF5 and DF15 hydrogels due to freezing of a significant fraction of the water. Water motions within ice are below the resolution of DCS. At 240 K, only about 5% of the protons in DF5 were still mobile in DF5 and DF15. As 86% of

the protons in the hydrogel are from H₂O, n(T) at 240 K corresponds well with the fraction of unfrozen water (5–6%) estimated from the enthalpy of fusion data in Figure 1B.

The behavior of water within DF22 was markedly different in that the decrease in n(T) with decreasing temperature is less pronounced (Figure 5D). At 220 K, n(T) was ~15% compared with ~53% at 295 K. Note that the dynamic window examined here was significantly faster than typically used to examine the dynamics of water in confinement at low temperatures.^{33,45} For slower motions, HFBS measurements (as discussed in the following paragraph) using H₂O and D₂O swollen hydrogels (Figure S12) indicated coupling of the dynamics of the copolymer and water at low temperature. In this case, 15% of the protons in H₂O were active in the energy window associated with HFBS for the DF22 hydrogel (Figure S13); these motions are in addition to the fast motions probed by DCS (Figure 5D). The combination of the QENS and HFBS data indicated that a significant fraction of the protons within DF22 remain mobile at 220 K, which is consistent with the high fraction of unfrozen water elucidated from DSC measurements.

The QENS measurements with DCS provided information about only relatively fast motions ($\tau < 75$ ps) in the hydrogels. An instrument with a better energy resolution, the high flux backscattering spectrometer (HFBS) at the NIST Center for Neutron Research (Gaithersburg, MD)³⁴ with an energy window of ±0.000 85 meV (hwhm at Q = 1.01 Å⁻¹), corresponding to 0.14 ns < $\tau < 3.8$ ns, was used to probe the slower dynamics of the copolymer and the water in the hydrogels at low temperature. Figure 6 shows the mean-square



Figure 6. Slower dynamics in the system were probed using HFBS with the mean-squared displacement for DF22 and DF5 swollen in D_2O , H_2O , or dry (no water) during cooling at 2 K/min. Error bars represent one standard deviation.

displacement (MSD) calculated from measuring the elastic intensity change as a function of temperature within the fixed energy window (± 0.00085 meV) for DF5 and DF22 hydrogels. The MSD was calculated based on the elastic intensity using a Gaussian approximation and the intensity I_0 at the lowest temperature measured of 4 K to provide the approximate intrinsic scattering in the hydrogel. In this case, the larger the MSD, the faster are the dynamics. For the nonhydrated DF5 copolymer, the MSD is less than 1 Å² over the entire temperature range examined, which is consistent with motions in a glassy polymer (Figure 6).³⁵ DFx hydrogels swollen with D_2O enable the copolymer dynamics to be probed as protons on the copolymer dominate the QENS signal.

At T > 266 K, the MSD for the D₂O swollen DF5 was greater than that for the D₂O swollen DF22. Thus, the polymer is more mobile in the more hydrated hydrogel as the higher water content provides additional degrees of freedom for the motion of the copolymer segments. Here, D₂O plasticizes the



Figure 7. Reversibility of both the dynamics and mechanical properties are shown for the DF22 gel swollen with H_2O . (A) and (B) show the DCS signal at 1.1 Å⁻¹ as measured at 250 K and 270–275 K on cooling (orange) and heating (purple), respectively. The slightly different temperatures for 270–275 K is explained in the text. (C) shows the frequency behavior of the dynamic (G') and loss (G") shear moduli measured at room temperature from a pristine sample of DF22 (orange) and the thawed state (purple) after cooling the sample in liquid nitrogen for 20 min. (D) shows an image of the DF5 and DF22 gels prefreezing and postfreezing. Red dashed lines outline the hydrogel sample for clarity. Scale bar is 1 cm.

system, and the dynamics of the copolymers are intimately tied to their hydration and local environment. However, upon cooling the DF5 hydrogel to 260 K, the MSD decreased to nearly the same value as that of the dry glassy copolymer. This infers that the D₂O is no longer plasticizing the copolymer and is consistent with ice formation that extracts the liquid D₂O from the copolymer as suggested by the SANS data. The sharp decrease in MSD at ~265 K for the DF5 hydrogel swollen with D_2O in Figure 6 corresponds well with the freezing peak for the DF5 hydrogel from DSC. Consistent with the inhibition of ice formation, the MSD for the DF22 hydrogel did not abruptly decrease like observed the DF5 hydrogel, but rather the MSD of the D₂O swollen DF22 copolymer gradually decreases. The D₂O plasticizes the DF22 copolymer to produce a greater MSD in comparison to the dry copolymer (DF5 and DF22 are similar) down to 220 K.

To further understand the dynamics in the DF22 hydrogel, H_2O dynamics for the DF22 hydrogel were examined in the same energy window by replacing the D_2O with H_2O as shown in Figure 6. In this case, the MSD of the protons that include the H_2O is greater than the MSD associated with only the DF22 copolymer segments in the hydrogel (swollen with D_2O) for T > 235 K. Upon further cooling to T < 230 K, the water and the copolymer dynamics at the time scales probed by HFBS were strongly coupled. These characteristics are consistent with the persistence of water capable of plasticizing the DMA segments in the DF22 hydrogel down to low temperatures.

These fast dynamics in the DF22 hydrogel are reversible in the supercooled state. Figure 7A shows that the dynamics of the hydrogels were the same at 250 K for DF22 when cooled from 295 to 220 K and when heated from 220 to 250 K. The reversibility of the water dynamics at 250 K upon cooling and heating indicates the thermodynamic origin of the inhibition of ice formation described herein. The decrease in the water dynamics upon cooling DF22 from 250 to 220 K (see the data in Figure 5C) is not due to additional ice formation. Additionally, the EISF at 250 K was indistinguishable between the cooling and heating experiments. Figure 7B demonstrates the reversibility of the dynamics of liquid water upon reheating the DF22 hydrogel from the "frozen state". Different temperatures (270 K for cooling and 275 K for heating, Figure 7B) were used for the comparison to avoid artifacts from the hysteresis on melting (Figure 1C). The nanostructure appears to impact the H_2O dynamics with higher self-diffusion coefficients for water in the lower FOSA content hydrogels (Figure 5C), so this reversibility in dynamics on melting suggests that the water is in a similar environment.

To further demonstrate the reversibility, the dynamic mechanical (DM) properties, using oscillatory shear, of DF22 hydrogels (Figure 7C) show that the impact of a freeze-thaw cycle on the structure of the viscoelastic behavior, and presumably the microstructure, of the hydrogel was small. The dynamic (G') and loss (G'') shear moduli of the pristine DF22 sample decrease with decreasing frequency due to the viscoelastic nature of the supramolecular hydrogel.²⁴ The hydrogel was frozen and annealed in liquid N₂ for 60 min. The DM properties were then remeasured after heating to room temperature. The viscoelastic nature of the hydrogel was retained, though G' and G'' decreased by <30%. The catastrophic fracture behavior usually observed during freezing of a conventional, covalently cross-linked hydrogel was prevented by the ability of the DF22 network to rearrange and relax under the stress from ice formation and the low fraction of water that freezes in DF22. Visually the DF22 sample progressed from transparent to translucent and retained its shape with no crack formation after undergoing the freezethaw cycle (Figure 7D). In contrast, the DF5 hydrogel became opaque (snow white) and brittle during a freeze-thaw experiment (Figure 7D). Both behaviors are consistent with the generation of large scale heterogeneities from ice crystallization indicated by the low Q scattering from SANS of the DF5 hydrogel at low temperature.

CONCLUSIONS

A supramolecular DMA-FOSA copolymer hydrogel with high FOSA content was shown to partially inhibit significant ice formation through the confinement of water between hydrophobic nanodomains. At low FOSA content, the hydrogel microstructure was significantly altered as a consequence of the copolymer being excluded from the water crystals on freezing. However, at a sufficiently high FOSA concentration (22 mol %), the nanodomain microstructure persisted with only 55% of the water freezing upon cooling the hydrogel to 205 K. Dynamics representative of liquid-like water persisted in the DF22 hydrogel with less than a factor of 2 decrease in the effective self-diffusion coefficient of water on cooling from 295 to 220 K. Confinement of water between ~6 nm diameter hydrophobic supramolecular aggregates with <2 nm hydrated interstitial separation inhibits ice formation in this hydrogel. Ice suppression in a soft hydrogel is demonstrated using confinement by hydrophobic aggregates and may have biomedical applications, where freeze-thaw cycles may occur, as well as other applications where ice prevention is desirable, e.g., deicing surfaces.

EXPERIMENTAL SECTION

Materials. Statistical copolymers of *N*,*N*-dimethylacrylamide and 2-(*N*-ethylperfluorooctane sulfonamido)ethyl acrylate were synthesized by free radical polymerization as described previously in the literature.^{46,47} The comonomer feed composition was used to effectively tune the composition of the resulting copolymer. For H₂O, Milli-Q water (18.2 M Ω resistance) was used in all studies. For select neutron experiments, D₂O (99.9%, Cambridge Isotope Laboratories, Inc.) was used in place of H₂O. Hydrogels were formed simply by immersing compression molded sheets of the copolymer in an excess of Milli-Q water.

Differential Scanning Calorimetry (DSC). Copolymer pieces were soaked in H₂O for 3 days to form equilibrated hydrogels. Small pieces (3-6 mg) of the hydrogel were cut from the sample and blotted with lint free wipes to remove excess water. We found no dependence of the thermal transitions on mass loading. The hydrogel was placed into an aluminum DSC pan (TA) and hermetically sealed. Calorimetric measurements (TA DSC 8500) were performed between 293 and 205 K at cooling rates of 0.5, 2, and 5 K/min. The sample was isothermally held at 205 K for 10 min prior to reheating to 293 K at the same rate. This cool-heat cycle was repeated to check for reproducibility and any history dependence on the freezing/melting behavior. Additionally, the DSC pans were weighed before and after measurement to ensure that no water was lost during the measurement that could impact the analysis. No statistically significant change in mass was observed during the course of the measurement.

Small-Angle Neutron Scattering (SANS). All measurements were performed using NGB30 m SANS (NCNR NIST, Gaithersburg, MD) with a beam wavelength of 6 Å, a spread of 14%, and a beam size of 1.5 cm. Three sample-to-detector distances were used, 133, 350, and 1250 cm, to provide Q ranges of 0.020–0.31, 0.0085–0.083, and 0.0036–0.026 Å⁻¹, respectively. For 133 and 350 cm distances, four neutron guides were used before the sample. For 1250 cm, one neutron guide

was used. The scattering at each distance and temperature was collected for 5 min. The sample was cooled with a CCR at 2 K/ min to 2 K above the desired temperature and then slowly stepped to the set point to avoid overshoot in cooling. A similar procedure was followed on reheating to check the reversibility of structural changes induced on cooling. For each hydrogel (DF5, DF15, DF22), three contrasts were measured: pure D₂O (maximum contrast and minimal background), 50/50 v/v D₂O/H₂O (contrast match FOSA), and 27/73 v/v D₂O/H₂O (DMA contrast match). The scattering data were corrected to absolute intensity using the sensitivity of the detector, sample transmission, and an empty cell background. SANS results were reduced and analyzed using the NIST SANS tool package.²⁷

Disk Chopper Spectrometer (DCS). All DCS measurements performed on NG4 DCS (NCNR NIST, Gaithersburg, MD) using a wavelength of 6 Å. The hydrogel samples were prepared to have a final thickness after swelling in H₂O of 0.1 mm. For samples swollen in D₂O, the film was prepared with the dry sample having a thickness of 0.1 mm. These were compression molded in an aluminum pouch, then swollen and placed in an aluminum cell for the measurement purged with He and sealed with indium (see Supporting Information for additional details). The neutron beam on the sample was masked to 7 cm \times 1.5 cm by cadmium. The sample was cooled with a low temperature closed cycle refrigerator (CCR) with a temperature range of 325 to 4 K based on the Gifford-McMahon refrigeration scheme with helium as the coolant. An effective cooling rate of ≤ 2 K/min was used for all measurements. The sample was equilibrated at the measurement temperature (295, 270, 260, 250, 240, and 220 K) for 15 min prior to beginning the measurement. The scattering at each temperature was measured for 5 h to obtain good statistics. The reversibility was examined by reheating the samples from 220 K to 250 and 275 K at 2 K/min ramp. The background was determined using the empty can and dark count measurements for 1 h each at room temperature. The resolution was calibrated using a vanadium cell with statistics based on 4 h of scattering.

High Flux Backscattering Spectrometer (HFBS). All HFBS measurements performed on a NG2 HFBS (NCNR NIST, Gaithersburg, MD). The neutron beam wavelength was 6.27 Å. For these measurements, the full energy window configuration was limited to the DF22 sample as this was the most intriguing hydrogel. A standard top loading CCR with a temperature range of 4-700 K was used for measurements with temperature accuracy of 0.1 K. The mean-squared displacement (MSD) was calculated using a standard Gaussian approximation based on the elastic intensity. The intensity I_0 was calculated at the lowest temperature measured of 4 K for the samples. A cooling rate of 0.8 K/min was used from 345 to 4 K for these measurements. The MSD was averaged and recorded every minute. For these scans, hydrogels were fabricated with both D₂O and H₂O to examine the dynamics primarily associated with the copolymer and water, respectively. Additionally as a control, the scattering of a dry copolymer was also measured with HFBS. To elucidate the energies associated with the local motions, the hydrogels were measured using an energy window of $\pm 16 \ \mu eV$. The scattering of the DF22 hydrogel was measured at 295, 270, 260, 250, 240, and 220 K. Each temperature was measured for 6 h, and a cooling rate of 1 K/min was used to minimize overshoot between set temperatures. The sample was equilibrated for 10 min prior to each measurement.

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QENS Data Analysis. Data reduction and analysis were performed using DAVE software provided by NIST.48 The analysis used a delta function for the elastic peak as measured by a vanadium sample during measurement. For the 295 and 270 K on DCS only, the sample resolution was modeled as a Lorentzian. There was a process nearly the same as the resolution width of the instrument. To reduce fitting parameters, this process was incorporated as part of the delta resolution. And as this process is within the standard resolution of the instrument, it cannot be identified with confidence. A flat background was used to account for motions much faster than the instrument capability and for general background noise. Finally, a Lorentzian curve was used to fit the broadened quasielastic signal that represents the dynamic motions measured for the sample in both HFBS and DCS data; this method provided fits with a reduced χ^2 of less than 2 on average across all data curves. The standard deviation of all fits has been included in the final represented results in both the text and the Supporting Information.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.6b02863.

Expanded experimental details on sample preparation; DSC thermograms; additional SANS contrasts and representative model fits with tables of fit parameters; DCS spectra; representative fits of EISF and cage sizes; comparison of DCS and HFBS dynamics; and representative fits to calculate the Fickian diffusion coefficient (PDF)

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Notes

The authors declare no competing financial interest.

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