Thermodynamic Interactions in Double-Network Hydrogels

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Double-network hydrogels (DN-gels) prepared from the combination of a moderately cross-linked anionic polyelectrolyte (PE) and an uncross-linked linear polymer solution (NP) exhibit mechanical properties such as fracture toughness that are intriguingly superior to that of their individual constituents. The scheme of double-network preparation, however, is not equally successful for all polyelectrolyte/neutral polymer pairs. A successful example is the combination of poly(2-acrylamido-2-methyl-1-propane sulfonic acid) (PAMPS) cross-linked network and linear polyacrylamide (PAAm), which results in DN-gels with fracture strength under compression approaching that of articular cartilage ($\approx$20 MPa). Small-angle neutron scattering was used to determine the thermodynamic interaction parameters for PAMPS and PAAm in water as a first step to elucidate the molecular origin responsible for this superior property. Measurements on PAMPS/PAAm DN-gels and their solution blend counterparts indicate that the two polymers interact favorably with each other while in water. This favorable PAMPS/PAAm interaction given by the condition $\chi_{PE-NP} \ll \chi_{PE-water} < \chi_{NP-water}$, where χ is the Flory–Huggins interaction parameter, is consistent with some of the salient features of the DN structure revealed by SANS, and it may also contribute to the ultimate mechanical properties of DN-gels.

Introduction

Synthetic hydrogels have usually been mechanically inferior to natural soft tissues, such as Achilles tendon or articular cartilage, which can sustain large deformations in both tension and compression, despite their water content of about 90% by volume. Recent advances in synthesis have produced hydrogels with significantly improved mechanical properties, such as the nanocomposite gels, slide-ring gels, and double-network hydrogels.[1–3] Both slide-ring gels and nanocomposite hydrogels are highly extensible due to the presence of mobile junction points.[4–7] Double-network hydrogels (DN-gels), on the other hand, are prepared by polymerizing a linear polymer within a cross-linked polyelectrolyte that is highly swollen in water. In the absence of the linear polymer, the swollen polyelectrolyte network is stiff but extremely brittle. It is thus surprising that the DN-gel sustains orders-of-magnitude higher compressive stresses than that of the polyelectrolyte network due simply to the presence of a concentrated linear polymer solution.[8–11]

The mechanism responsible for the toughening of DN-gels is not clearly understood, despite several experimental and theoretical efforts.[12–16] Creton et al. have recently shown that the toughness of cross-linked hydrogels can be increased by introducing weakly associative hydrophobic interactions along the network backbone.[17] The improved strength in such systems was attributed to the additional energy required to dissociate the hydrophobic clusters that hinder crack propagation in highly strained regions. The formation of such clusters is improbable

in DN-gels since the network backbone comprises a strong polyelectrolyte with characteristic repulsive interactions. In a recent study of PAMPS/PAAm DN-gels using dynamic light scattering, Gong and co-workers have proposed that the two constituents may be entangled and the deformation energy is mainly dissipated in a region that is sufficiently softened under deformation.[18] However, a clear insight into the nature of entanglements within the DN-gels and a molecular level mechanism for sustaining large deformations are lacking.

Moreover, the scheme of double-network preparation is not equally successful for all the polymer pairs. For example, Table 1 in ref 3 shows that the fracture stress of the poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) single network increases to 3 MPa when 2 mol/L PAMPS is in situ polymerized to form a DN-gel, whereas it increases to 17 MPa when 2 mol/L polyacrylamide (PAAm) is polymerized as the second component. Clearly, the specific chemical nature of the constituents seems to be influencing the ultimate mechanical properties of DN-gels. Establishing the thermodynamics specific to this PAMPS/PAAm pair may thus be useful to unravel the synergistic mechanism due to which the materials sustain large deformations and high stress.

In a previous communication, we highlighted the difference between the structure of constituents within DN-gels and the structure of individual components in water using neutron scattering.[19] We noted that the observed changes in structure are consistent with enthalpically favorable interactions between the constituents. Here, we use small-angle neutron scattering (SANS) to measure the thermodynamic interactions between PAMPS and PAAm, which constitute the toughest DN-gels, as a first step to unravel the molecular mechanism responsible for their unusual toughness. The notion that a neutral polymer does

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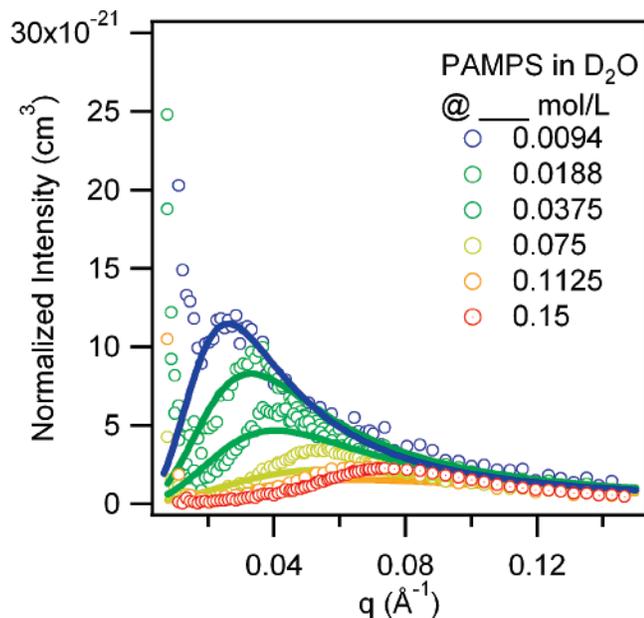
Figure 1. Changes in the static structure factor of aqueous PAMPS solutions measured as a function of polymer concentration. Symbols are experimental data, and lines correspond to model fits obtained from eq 8 by setting $\phi_{NP} = 0$.

TABLE 1: The Compositions (in Volume Fraction) of the Solution Blend Samples Used in SANS Study[a]

sample	φ_{PE}	φ_{NP}	φ_S
pure PE	0.0179	0	0.982
3:1 (PE/NP)	0.0134	0.0021	0.989
1:1	0.0089	0.0043	0.987
1:3	0.0045	0.0064	0.989
1:7	0.0022	0.0075	0.990
1:15	0.0011	0.0080	0.991

[a] Subscript PE stands for PAMPS, NP for PAAm, and S for water. The molar ratio of each sample is given in the first column.

not interact favorably with a charged polymer may not be valid in polar solvents such as water. Most water-soluble polymers are polarizable, and their dissolution is accompanied by an exothermic heat of mixing as a result of hydrogen bonding with the solvent. The polarizability of water-soluble polymers could also make them susceptible to weak electrostatic interactions with polyelectrolytes. We examine this hypothesis by measuring the changes in the static structure factor of linear PAMPS chains in its solution blends with linear polyacrylamide. The in situ structure of PAMPS and PAAm within solution blends and within DN-gels can be accurately measured by SANS using contrast variation methods.[19] Neutron-scattering results from mixtures of neutral and charged polymers, such as the case with DN-gels or their solution-phase counterparts, can be quantitatively modeled following the approach of Benmouna and coworkers elaborated in the theoretical section below.[20-22] The thermodynamic interaction parameters were first determined from the solution blends, and these results were used as a benchmark for comparison with those obtained from DN-gels.

Scattering Theory for Solution Blends of Charged and Neutral Polymers. For solution blends of two different polymers, the scattering intensity as a function of the wave vector can be derived following the random phase approximation (RPA) method[23] or a modified Ornstein–Zernicke (OZ) approach.[24] Both approaches result in an identical set of equations, which relate the observed scattering intensity to the intrachain form factors of individual polymers and the interaction param-
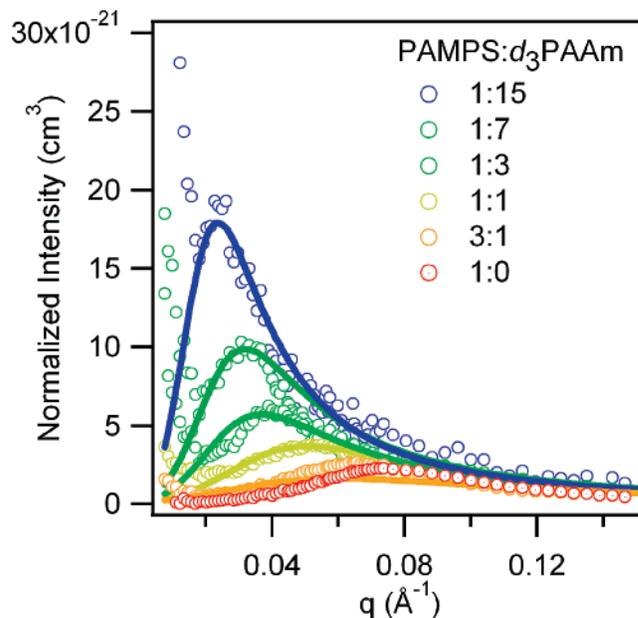
Figure 2. Changes in the static structure factor of 0.15 mol/L aqueous PAMPS solutions diluted by the addition of 0.15 mol/L aqueous PAAm-d_3 solution, measured as a function of blend composition. Legend represents molar ratios. Symbols are experimental results. Lines correspond to model fits obtained from eq 8 and the best fit parameters given in Table 3.

eters between polymers and solvent. For the current ternary (polyelectrolyte-neutral polymer–water) system, there are three thermodynamic pair interaction parameters. The basic simplification used in the above-mentioned approaches is the linearization of the multichain interaction; that is, all the higher order interchain interactions are approximated as products of interchain pair interaction in Fourier space. As long as the interchain interaction is highly localized, such as the case of excluded volume interaction in good solvent, the RPA or OZ approaches are remarkably successful in fitting the scattering data at an arbitrary polymer concentration. For systems containing polyelectrolytes, the interchain interaction is no longer short ranged. Strictly speaking, the abovementioned RPA or OZ approaches are not applicable; however, they are still used in this work to model the SANS data, and the agreement between the theory and experimental results appears reasonable.

The static structure matrix in the RPA is given for a general multicomponent mixture by the classical Benoit's equation[25]

$$\mathbf{S}^{-1}(q) = \mathbf{S}_o^{-1}(q) + \mathbf{v} \tag{1}$$

where $\mathbf{S}_o(q)$ is the bare structure matrix, and the elements in the excluded volume interaction matrix, $\mathbf{v}$, are

$$v_{ij} = \frac{v_i v_j}{v_S}\left(\frac{1}{\varphi_S} - \chi_{iS} - \chi_{jS} + \chi_{ij}\right) \tag{2}$$

where v_i is the molar volume of the species i, χ_{ij} is the Flory–Huggins interaction parameter between i and j (subscript S denotes the solvent), and φ_s is the volume fraction of the solvent.

For the present case, PAMPS is highly charged, and the interchain interaction between charged chains is long ranged. The approach based on RPA or OZ is not strictly valid; however, as a first order of approximation, we still adopt the RPA type results by following the work of Benmouna et al.[20] The long-range electrostatic interaction is simply added to the excluded volume term. Explicitly, we have

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$$v_{PE-PE} = \frac{v_{PE}^2}{v_S}\left(\frac{1}{\varphi_S} - 2\chi_{PE-S}\right) + \frac{4\pi l_b}{q^2 + \kappa^2} \quad (3)$$

l_b is the Bjerrum length of water and is 0.7 nm, κ^{-1} is the Debye screening length, and the subscript PE denotes polyelectrolyte or PAMPS.

The excluded volume interactions between polyelectrolyte and neutral polymer are defined as

$$v_{PE-NP} = \frac{v_{PE}v_{NP}}{v_S}\left(\frac{1}{\varphi_S} - \chi_{PE-S} - \chi_{NP-S} + \chi_{PE-NP}\right) \quad (4)$$

where the subscript NP refers to the neutral polymer (for the present case, polyacrylamide). The partial static structure factor is defined as

$$S_{\alpha\alpha}(q) = \frac{1}{V}\langle \rho_\alpha(q)\, \rho_\alpha(q)^*\rangle \quad (5)$$

where V is the total volume of system and $\rho_\alpha(q)$ is the Fourier transform of all segment distribution of α-component. (The dimension of the structure factor is cm^{-3}.) The partial intensity can be written as

$$I_{\alpha\alpha} = \left(\frac{b_\alpha}{v_\alpha} - \frac{b_S}{v_S}\right)^2 v_\alpha^2 S_{\alpha\alpha} \quad (6)$$

where b_α denotes the scattering length of the α-component. From eq 1, the partial structure factor of PAMPS, i.e., S_{PE}, can be expressed as

$$\frac{1}{S_{PE}} = \frac{1}{S_{PE}^o} + v_{PE-PE} - \frac{v_{PE-NP}^2 S_{NP}^o}{(1 + v_{NP-NP}S_{NP}^o)} \quad (7)$$

S_{PE}^o is the bare structure factor of PAMPS and is simply the product of its number concentration (φ_{PE}/v_{PE}), its molecular weight relative to that of water ($N_{PE}\, v_{PE}/v_S$), and its normalized single chain form factor ($P_{PE}(q)$). Combining eq 3 and the definition of S_{PE}^o, the above equation can be rewritten as

$$\frac{1}{S_{PE}} = \frac{1}{\left(N_{PE}\frac{v_{PE}}{v_S}\right)\left(\frac{\varphi_{PE}}{v_{PE}}\right)P_{PE}(q)} + \frac{v_{PE}^2}{v_S}\left(\frac{1}{\varphi_S} - 2\chi_{PE-S}\right) +$$

$$\frac{4\pi l_b}{q^2 + \kappa^2} - \left(\frac{v_{PE}v_{PE}}{v_S}\left(\frac{1}{\varphi_S} - \chi_{PE-S} - \chi_{NP-S} + \chi_{PE-NP}\right)\right)^2 \times$$

$$\left(N_{NP}\frac{v_{NP}}{v_S}\right)\left(\frac{\varphi_{NP}}{v_{NP}}\right)P_{NP}(q) \Big/ \left(1 + \frac{v_{NP}^2}{v_S}\left(\frac{1}{\varphi_S} - 2\chi_{NP-S}\right)\left(N_{NP}\frac{v_{NP}}{v_S}\right) \times\right.$$

$$\left.\left(\frac{\varphi_{NP}}{v_{NP}}\right)P_{NP}(q)\right) \quad (8)$$

TABLE 2: Best Fit Model Parameters Used in Eq 8 to Describe the Polyelectrolyte Structure Factor Measured Using Neutron Scattering from Aqueous PAMPS Solutions as a Function of Polymer Concentration

PAMPS in D$_2$O (mol/L)	ξ (Å)	N_{PE}	κ^{-1}	χ_{PE-S}
0.15	33	7	50	0.3
0.1125	37	10	75	0.3
0.075	44	15	100	0.35
0.0375	59	28	200	0.35
0.0188	79	60	320	0.3
0.0094	103	80	470	0.3

Similarly, the partial structure factor of PAAm, i.e., S_{NP}, can be written as

$$\frac{1}{S_{NP}} = \frac{1}{\left(N_{NP}\frac{v_{NP}}{v_S}\right)\left(\frac{\varphi_{NP}}{v_{NP}}\right)P_{NP}(q)} + \frac{v_{NP}^2}{v_S}\left(\frac{1}{\varphi_S} - 2\chi_{NP-S}\right) -$$

$$\left(\frac{v_{NP}v_{NP}}{v_S}\left(\frac{1}{\varphi_S} - \chi_{PE-S} - \chi_{NP-S} + \chi_{PE-NP}\right)\right)^2 \times \left(N_{PE}\frac{v_{PE}}{v_S}\right) \times$$

$$\left(\frac{\varphi_{PE}}{v_{PE}}\right)P_{PE}(q) \Big/ \left(1 + \frac{v_{PE}^2}{v_S}\left(\frac{1}{\varphi_S} - 2\chi_{PE-S}\right) + \frac{4\pi l_b}{q^2 + \kappa^2}\right) \times$$

$$\left(N_{PE}\frac{v_{PE}}{v_S}\right)\left(\frac{\varphi_{PE}}{v_{PE}}\right)P_{PE}(q) \quad (9)$$

The molar volumes of the monomers (AMPS, 200 Å^3; AAm, 85 Å^3) and the solvent (30 Å^3) are estimated from their melt densities. As to the single chain form factor in eq 8, we use the well-known Debye function,

$$P(x) = \frac{2}{x^2}[\exp(-x) + x - 1] \quad (10)$$

where x is $\xi^2 q^2$, and ξ is the mesh size for PAAm and the electrostatic blob size for PAMPS. Following Odijk's scaling theory,[26] the blob size for PAMPS was estimated as follows:

$$\xi = \text{const}\left(l_p + \frac{1}{16\pi l_b Ac}\right)^{-1/4}(4\pi Ac)^{1/8}(Ac)^{-3/4} \quad (11)$$

where l_p is the bare persistence length ($l_p = [(C_o/2)a]/0.83^2$, C_o is the characteristic ratio (12 for PAMPS), and a is the bond length; hence, l_p is 13.4 Å), A is the contour distance for two adjacent charge groups along the polymer chain, c is the number concentration, and the numerical constant is 0.22.[27] The blob size for PAAm was similarly estimated following a scaling relationship, $\xi_{NP} = 2.09C^{-0.76}$, where C is the polymer concentration in g/mL.[28]

Experimental

Starting Materials. 2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPS) (monomer; TCI America) and 2-oxoglutaric acid (initiator, Polysciences, Inc.) were used as received. Acrylamide (AAm) (monomer) was recrystallized from chloroform. Deuterium-labeled acrylamide monomer (AAm-d_3) free of inhibitor was obtained from Cambridge Isotope Laboratories Inc. and was used as received. N,N′-Methylene bisacrylamide (MBAA) (cross-linker) was recrystallized from ethanol. Deuterated water was used as received from Aldrich Chemical Co.

Polymer Synthesis. Pure PAMPS and PAAm-d_3 solutions were prepared by free-radical UV-initiated polymerization of

TABLE 3: Best Fit Model Parameters Used in eq 8 to Describe the Polyelectrolyte Structure Factor in Blends of 0.15 mol/L Aqueous PAMPS and PAAm-d_3 Solutions Measured as a Function of Composition Using Neutron Scattering

PE/NP molar ratio	ξ_{PE} (Å)	ξ_{NP} (Å)	N_{PE}	N_{NP}	κ^{-1}	χ_{PE-S}	χ_{NP-S}	χ_{PE-NP}
1:0	33		7		50	0.3		
3:1	37	187	10	1500	75	0.3	0.45	0.05
1:1	44	111	15	580	110	0.35	0.45	0.05
1:3	59	81	28	330	200	0.35	0.45	0.05
1:7	79	72	55	260	300	0.3	0.45	0.05
1:15	103	69	80	235	570	0.3	0.45	0.05

TABLE 4: Best Fit Parameters That Describe the Structure Factors of Polyelectrolyte and Neutral Polymer in PAMPS/PAAm DN-gels[a]

DN-gel with [PAAm] mol/L	ξ_{NP} (Å)	N_{PE}	N_{NP}	κ^{-1}	χ_{PE-S}	χ_{NP-S}	χ_{PE-NP}
0		7		150	0.3		
0.5	26	18	40	300	0.3	0.45	0.015
1	16	18	20	350	0.3	0.45	0.015
2	9	18	15	450	0.3	0.45	0.015

[a] ξ_{PE} is kept constant at 33 Å, since the same PAMPS network at 0.1 mol/L concentration was used to prepare all the DN-gels.

their monomers in deuterated water at 1.8 vol % codissolved with 0.1 and 0.01 mol % of 2-oxoglutaric acid, respectively. Solution-phase blends were prepared by mixing linear polymer solutions of PAMPS and PAAm-d_3 at various volume ratios, as shown in Table 1. The mixtures were homogenized by continuous stirring for 2–4 days prior to the SANS measurements.

Double-network hydrogels were prepared from AMPS and AAm following a sequential two-step free-radical polymerization.[3] Briefly, 4 mol % of MBAA and 0.1 mol % of 2-oxoglutaricacid were added to 1 mol/L AMPS aqueous solution (the mole percent, 0.1 mol %, was determined with respect to the AMPS monomer). The mixture was degassed by bubbling with argon gas for 30 min. The cross-linked PAMPS network was then prepared by UV irradiation of the mixture in a glass mold separated by a silicone spacer of the desired thickness under an argon blanket. In the second step, the as-prepared PAMPS gel immersed into an aqueous solution of AAm or AAm-d_3 monomer. After allowing sufficient time for equilibrium swelling of the first network (>60 h), acrylamide was subsequently polymerized in situ. The nominal PAMPS concentration in the DN-gels is 0.1 mol/L since the swelling degree is about ten times by volume. The prepared DN-gels were washed thoroughly in excess water to remove unreacted monomers.

Sample Preparation. The samples for determining the structure of linear chains within DN-gels were prepared by in situ polymerizing AAm-d_3 within a PAMPS network swollen in water. The scattering contribution from the PAMPS network structure swollen in water is negligible as compared to that from PAAm-d_3. The structure factor of PAMPS was measured by matching the neutron contrast of PAAm-d_3 using a mixture of light and heavy water at a 29:71 ratio by volume.[19] For the overall polymer structure determination, both PAMPS and PAAm are hydrogenated, and pure D_2O was used as the solvent. Therefore, each sample was prepared in triplicate to determine the structure of each component and that of the overall DN-gel.

Small-angle Neutron Scattering Measurements. Neutron scattering measurements were performed using the 30 m NG3 and NG7 beamlines at the NIST Center for Neutron Research (NCNR).[29] Scattering data were acquired at sample-to-detector distances of 1, 4.5 (5 m), and 13.7 m (15.3 m) with a neutron wavelength of $\lambda = 8.09$ Å and a wavelength spread, $\Delta\lambda/\lambda = 0.11$. This provides a q range of $10^{-3} \leq q$ (Å^{-1}) ≤ 0.15. Scattering data in the range $5 \times 10^{-5} < q$ (Å^{-1}) $< 10^{-3}$ were collected using a Bonse Hart type diffractometer (the ultrasmall-angle neutron scattering, USANS, beamline BT5), also at NCNR.[30]

SANS and USANS data were reduced into absolute intensity units by subtracting contributions from the instrument background and incoherent scattering from the sample and correcting for variations in the detector sensitivity.[31] Scattering intensity

in absolute units was further normalized by the neutron contrast factor, $(b_{PE} - b_S)$,[2] and the volume fraction factor, $\varphi_{PE} (1 - \varphi_{PE})$, as described previously.[19] Specific volumes of PAMPS and PAAm are taken as $v_{PAMPS} = 0.575 \pm 0.1$ cm^3/g [32] and $v_{PAAm} = 0.696 \pm 0.1$ cm^3/g.[27]

Results

Aqueous PAMPS Solutions. The thermodynamic parameters for polyelectrolyte in water were first obtained by modeling the SANS data from aqueous PAMPS solutions at various concentrations. The effect of dilution on the polyelectrolyte structure factor in aqueous solutions is well-established.[33−35] Therefore, the fitting parameters, Debye screening length (κ^{-1}) and the number of monomers in a mesh of polyelectrolyte (N_{PE}), should further satisfy the scaling relationships for polyelectrolyte systems given by $\kappa^{-1} \propto c^{-0.5}$ and $N_{PE} \propto \xi^2$ ($\xi \approx b \sqrt{N}$, where b is the bond length).[34,36] Figure 1 shows the normalized SANS data from aqueous PAMPS solutions and the corresponding fits obtained from eq 8 by letting ϕ_{NP} equal to zero. The three model parameters, κ^{-1}, N_{PE} of PAMPS, and χ_{PE-S}, obtained by fitting the SANS data are shown in Table 2. The exponents for scaling of κ^{-1} and N_{PE}, with c and ξ, respectively, are −0.43 and 2.2. The value of 0.3 for χ_{PE-S} is unexpected and is rather high, since water is a good solvent for strongly charged polyelectrolytes, such as PAMPS. In the present scheme of extracting χ_{PE-S}, however, the ionic contribution to solvation was separated from χ_{PE-S}, and this high value may reflect the hydrophobic nature of the PAMPS chain without the sulfonic acid group.

PAMPS/PAAm Solution Blends. The structure of PAMPS in the presence of PAAm-d_3 was measured using SANS in contrast-matched water. The composition of solution blends was chosen such that the PAMPS concentration in solution blends is analogous to that in aqueous solutions discussed in the previous section. Thus, the thermodynamic parameters obtained from aqueous PAMPS solutions can be used as starting points to fit the SANS data from solution blends. Figure 2 shows the normalized SANS data and the corresponding fits obtained by modeling the scattering profiles using eq 8. It is rather surprising that eq 8 adequately describes the data for all PAMPS/PAAm ratios, with the exception of the upturn in scattering intensities as q approaches zero. A sharp increase in SANS intensity at low q is a common occurrence in concentrated polymer solutions, gels, and polyelectrolytes.[37−41] Concentration fluctuations at large length scales are believed to be the reason for the observed excess scattering intensities. A more quantitative description of the underlying physics for the large scale heterogeneity is not the focus of this work.

The scattering data from samples with various PAMPS/PAAm volume ratios were simultaneously fit to eq 8 by allowing the number of monomers in a blob of neutral polymer (N_{NP}), and the two Flory−Huggins parameters, χ_{NP-S} and χ_{PE-NP}, as floating variables. The parameters for polyelectrolyte, such as

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the κ^{-1}, N_{PE}, and χ_{PE-S}, obtained from aqueous solutions (Table 2) are taken as initial estimates to fit the SANS data from solution mixtures. The best fit model parameters obtained by fitting the SANS data are given in Table 3. It is worth noting that the fitted value of χ_{PE-NP} of 0.05 is smaller than both χ_{NP-S} and χ_{PE-S} with their fitted values of 0.45 and 0.35, respectively. The value of 0.45 for χ_{NP-S} indicates that water is a marginal solvent for PAAm and is close to that reported earlier by Prausnitz and co-workers.[42] Additional SANS results from pure PAAm aqueous solutions also support this notion of a marginal solvent; the scattering has a huge forward intensity but drops to a flat background level at $q \geq 0.01$ Å^{-1}.[19] This clearly indicates excessive agglomeration of PAAm segments in semidilute aqueous solution. The Debye screening length in solution blends is larger than that in aqueous solutions at the lowest PAMPS concentration due probably to effective charge compensation by PAAm in solution blends. The small mutual interaction parameter, χ_{PE-NP}, implies numerous AMPS-AAm contacts in aqueous solutions.

PAMPS-PAAm Double-Network Gels. The thermodynamic parameters in DN-gels were determined following the procedure used for solution blends. The normalized SANS data that corresponds to the polyelectrolyte structure factor or S_{PE} in DN-gels is given as a function of in situ polymerized acrylamide concentration in Figure 3a. The excess scattering intensity from cross-linked PAMPS gels as q approaches zero is indicative of concentration fluctuations at large length scales due to inhomogeneous distribution of cross-links.[43] A power-law function was employed to subtract the contribution of excess forward scattering intensity without affecting the data at high q. The polyelectrolyte structure factor data obtained after subtracting the excess forward scattering intensity (Figure 3b) is modeled using eq 8 (Figure 3c), and the best fit parameters are given in Table 4. The value of ξ is set at 33 Å for PAMPS, a value taken from the result of solution blend ξ at the identical PAMPS concentration. Note that the PAMPS networks used to prepare all the DN-gels are identical in their concentration. Hence, the value for ξ used in all cases was the same.

The qualitative agreement between the experimental and modeling results is especially satisfactory, since the excess forward scattering intensity smeared out SANS data over a wide q range. Nonetheless, the thermodynamic interaction parameters and the changes in κ^{-1} as a function of PAAm concentration in DN-gels are consistent with those obtained from solution blends. The best fit parameters in Table 4 can also be used to predict the structure factor of the neutral polymer within DN-gels. The model predicts a gradual decrease in the normalized scattering intensity at zero-angle, with an increase in PAAm concentration within DN-gels. This is in good qualitative agreement with the observed trends in measured PAAm structure factor at high q in the range, $q > 0.01$ Å^{-1} (Figure 4).

We now focus on the low q part of the SANS data from individual components within DN-gels. The normalized low q scattering intensity from linear PAAm in DN-gels decreases with an increase in PAAm concentration and is several orders of magnitude lower than that from corresponding aqueous PAAm solutions. The decrease in scattering intensity with an increase in polymer concentration is unexpected for neutral polymer solutions but is in line with the model predictions (Figure 4b). Note also that the PAMPS network used in all the DN-gels is polymerized under identical conditions, and no systematic deviations in network morphology are expected with the addition of linear PAAm. However, the excess scattering intensity at low-q from PAMPS network in DN-gels decreases with the
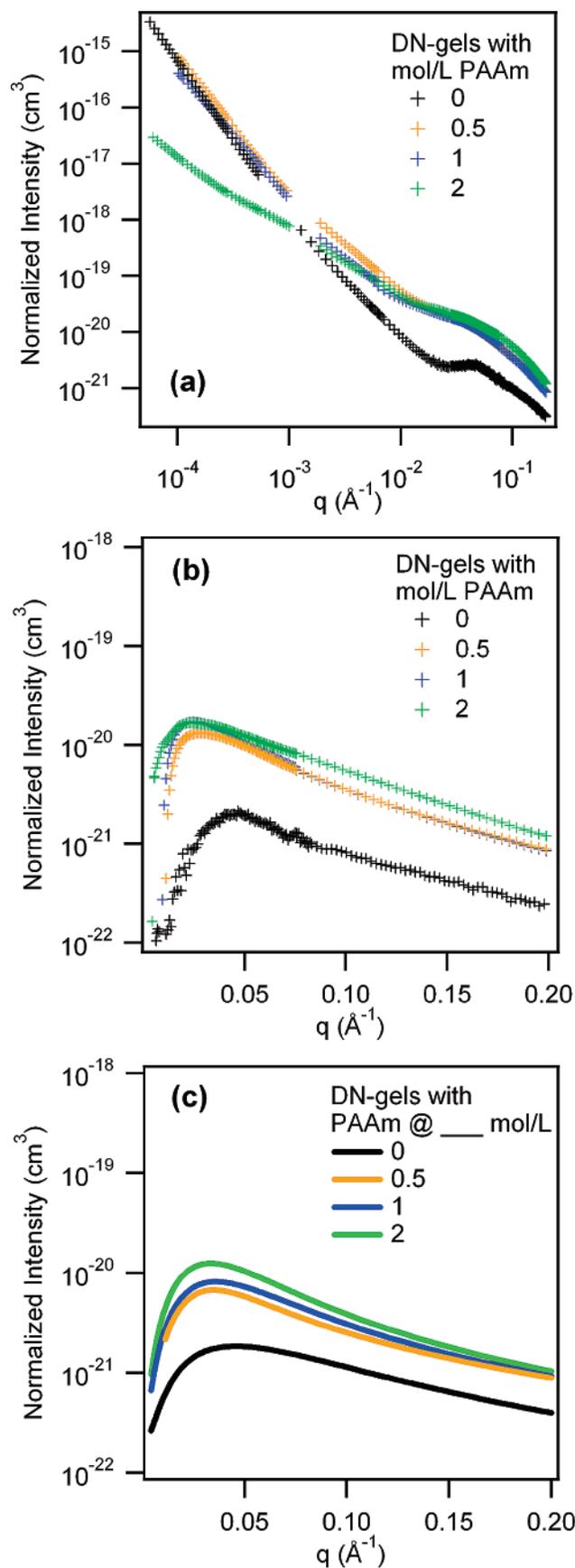
Figure 3. (a) Static structure factor of PAMPS network within DN-gels as a function of PAAm concentration, (b) scattering data after subtracting the excess forward scattering intensity at low q, and (c) model fits to experimental data obtained from eq 8 and the best fit parameters given in Table 4.

Figure 5. Influence of interaction parameter, χ_{PE-NP}, on the polyelectrolyte structure factor S_{PE} in solution blends. Markers are experimental data presented in Figure 2 for the PAMPS:PAAm-d_3 solution blend of 1:7 volume ratio, and lines are estimates obtained by using the corresponding best fit parameters from Table 3 for different χ_{PE-NP} values.

Figure 4. Static structure factor of linear PAAm solutions within the DN-gels (a) predicted using eq 8 and the best fit parameters given in Table 4 and (b) that measured using SANS as a function of PAAm concentration.

addition of PAAm (Figure 3a). The mutual association between the two components given by the condition $\chi_{PE-NP} \ll \chi_{PE-S} < \chi_{NP-S}$ is likely to be responsible for the macroscopic homogenization of cross-linking and entanglement heterogeneities that contribute to excess scattering intensity from PAMPS network and linear PAAm solutions, respectively.

Discussion and Conclusions

Our analysis of scattering data is clearly a first-order approximation for the current system involving charged polymers. For example, we assume that the structure of PAMPS network can be approximated with a collection of polyelectrolyte blobs. The critical parameters that describe the structure factor of PAMPS in solution blends and DN-gels are the three interaction parameters (χ_{PE-S}, χ_{NP-S}, χ_{PE-NP}) and Debye length (κ^{-1}) of the polyelectrolyte. Nevertheless, the best fit parameters can be uniquely obtained due to their dissimilar influence on the polyelectrolyte structure factor, S_{PE}. The intensity of the

polyelectrolyte peak is especially sensitive to the mutual interaction parameter, χ_{PE-NP}. Figure 5 shows the effect of χ_{PE-NP} on the modeled scattering data from a 1:7 (PAMPS: PAAm-d_3) solution blend. The best fit values for χ_{PE-NP} are clearly within -0.1 and 0.1, a range that is well below the polymer−solvent interaction parameters for PAMPS and PAAm with water. It is also to our surprise how well the model describes the experimental data in both the single component PAMPS solutions and the solution blends of PAMPS and PAAm, especially at very low polyelectrolyte concentrations. The presence of the neutral polymer seems to improve the fit between the SANS data and the theory by comparing the results between Figures 1 and 2.

The association between PAMPS and PAAm is driven probably by weak electrostatic interactions between sulfonic acid and carbonyl groups. Such weak interactions are perhaps necessary to minimize the formation of irreversible complexes that are obtained typically from mixtures of oppositely charged polymers.[44] Although our study is specific to PAMPS/PAAm system, the results are consistent with the behavior of charged polymer/neutral polymer blends in which PAAm is a constituent. For example, polymerizing acrylamide in the presence of anionic components, such as sodium dodecyl sulfate or poly(sodium *p*-phenylene sulfonate) results in a relatively homogenized network morphology as compared to that prepared in pure water.[45,46] Similarly, Durmaz and Okay reported that the swelling degree of copolymerized poly(AMPS-*co*-AAm) hydrogels unexpectedly attains a plateau region in the composition range 10 mol % PAMPS.[47−49] The observed results were attributed to the existence of counterions that do not contribute to Donnan osmotic pressure. The association between PAAm and the anionic polyelectrolyte in water may provide a physical explanation for the existence of "osmotically hidden" counterions.[50] Most of the polymer pairs used in ref 3 for the preparation of DN-gels may similarly associate via hydrogen bonding between the carboxylic acid or sulfonic acid group of the polyelectrolyte and the amide group on the "neutral" polymer. The association between the pair of poly(acrylic acid)/ poly(ethylene glycol) used recently by Frank and co-workers[51]

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in the preparation of artificial cornea was also well-established previously by Tanaka and co-workers.[52]

We establish, for the first time, the weak (and possibly reversible) thermodynamic interactions between the constituents of DN-gels in water using small-angle neutron scattering measurements. Such interactions may account for the highly "entangled state" of PAMPS/PAAm DN-gels reported recently.[18] Unlike topological chain entanglements, however, enthalpically favorable interactions between PAMPS and PAAm in DN-gels offer an energy dissipation mechanism that may account for their improved mechanical properties. The deformation models presented in the literature thus far do not consider energetic interactions within DN-gels and instead rely on mechanistic concepts pertinent to filled rubbers and semi-interpenetrating networks. Relating the contribution of thermodynamic interactions to energy dissipation and the resulting changes in constituent structure during deformation of DN-gels is beyond the scope of this paper but will be discussed elsewhere.

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(53) Certain equipment, instruments or materials are identified in this paper in order to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology nor does it imply the materials are necessarily the best available for the purpose.

(54) The error in measurement of neutron scattering is less than the size of the markers used unless explicitly shown using error bars.