Thermodynamic Interactions in Double-Network Hydrogels

Taiki Tominaga,†§ Vijay R. Tirumala,†§ Sanghun Lee,† Eric K. Lin,† Jian Ping Gong,‡ and Wen-li Wu*,†

Polymers Division, National Institute of Standards and Technology, Gaithersburg Maryland, Graduate School of Sciences, Hokkaido University, Sapporo Japan, and Polymer Science and Engineering, University of Massachusetts, Amherst Massachusetts

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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 (≈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 \( \chi \) 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.4–7 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 orderns-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...
24 Both approaches result in an identical set of equations, 

\[ \text{eq 8} \]

and experimental results. Lines correspond to model fits obtained from eq 8 and the best fit parameters given in Table 3.

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

<table>
<thead>
<tr>
<th>sample</th>
<th>(v_{\text{NP}})</th>
<th>(v_{\text{NP}})</th>
<th>(v_{\text{S}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure PE</td>
<td>0.0179</td>
<td>0</td>
<td>0.982</td>
</tr>
<tr>
<td>3:1 (PE/NP)</td>
<td>0.0134</td>
<td>0.0021</td>
<td>0.989</td>
</tr>
<tr>
<td>1:1</td>
<td>0.0089</td>
<td>0.0043</td>
<td>0.987</td>
</tr>
<tr>
<td>1:3</td>
<td>0.0045</td>
<td>0.0064</td>
<td>0.989</td>
</tr>
<tr>
<td>1:7</td>
<td>0.0022</td>
<td>0.0075</td>
<td>0.990</td>
</tr>
<tr>
<td>1:15</td>
<td>0.0011</td>
<td>0.0080</td>
<td>0.991</td>
</tr>
</tbody>
</table>

* 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 within DN-gels can be accurately measured by SANS using 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 within DN-gels or their solution-phase counterparts, can be quantitatively modeled following the approach of Benmouna and co-workers elaborated in the theoretical section below.20 The approach based on RPA or OZ is not strictly valid; 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 Benoît’s equation:

\[ S^{-1}(q) = S_0^{-1}(q) + v \]  

where \(S_0(q)\) is the bare structure matrix, and the elements in the excluded volume interaction matrix, \(v\), are

\[ v_{ij} = \frac{v_{ij}}{v_S} \left( \frac{1}{q_{ij}} - \chi_{ij} \right) \]  

where \(v_{ij}\) is the molar volume of the species \(i\), \(\chi_{ij}\) is the Flory–Huggins interaction parameter between \(i\) and \(j\) (subscript \(S\) denotes the solvent), and \(q_{ij}\) 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

**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 \(q_{ij} = 0\).

**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.
Flory-Huggins parameters of Double-Network Hydrogels

\[
v_{\text{PE-PE}} = \frac{v_{\text{PE}}^2}{v_S} \left( \frac{1}{q_S} - 2\chi_{\text{PE-PE}} \right) + \frac{4\pi l_b}{q^2 + \kappa^2} \tag{3}\]

\(l_b\) is the Bjerrum length of water and is 0.7 nm, \(\kappa^{-1}\) 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

\[
v_{\text{PE-NP}} = \frac{v_{\text{PE}NP}}{v_S} \left( \frac{1}{q_S} - \chi_{\text{PE-NP}} - \chi_{\text{NP-NP}} + \chi_{\text{PE-NP}} \right) \tag{4}\]

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

\[S_\alpha(q) = \frac{1}{V} \langle \rho_\alpha(q) \rho_\alpha(q)^* \rangle \tag{5}\]

where \(V\) is the total volume of system and \(\rho_\alpha(q)\) is the Fourier transform of all segment distribution of \(\alpha\)-component. (The dimension of the structure factor is \(\text{cm}^{-1}\).) The partial intensity can be written as

\[I_\alpha = \left( b_\alpha - b_\beta \right)^2 v_\alpha^2 S_\alpha \tag{6}\]

where \(b_\alpha\) denotes the scattering length of the \(\alpha\)-component. From eq 1, the partial structure factor of PAMPS, i.e., \(S_{\text{PE}}\), can be expressed as

\[\frac{1}{S_{\text{PE}}} = \frac{1}{2} + v_{\text{PE-NP}} - \frac{v_{\text{PE-NP}}^2 S_{\text{NP}}^0}{1 + v_{\text{NP-NP}} S_{\text{NP}}^0} \tag{7}\]

\(S_{\text{PE}}^0\) is the bare structure factor of PAMPS and is simply the product of its number concentration \((q_{\text{NP}} v_{\text{PE}})\), its molecular weight relative to that of water \((N_{\text{NP}} v_{\text{PE}} / v_S)\), and its normalized single chain form factor \((P_{\text{NP}}(q))\). Combining eq 3 and the definition of \(S_{\text{PE}}^0\), the above equation can be rewritten as

\[\frac{1}{S_{\text{PE}}} = \frac{1}{N_{\text{NP}} v_{\text{PE}} / v_S} \left( \frac{q_{\text{NP}} v_{\text{PE}}}{v_{\text{PE}}} \right) P_{\text{NP}}(q) \left( + \frac{v_{\text{NP}}^2}{v_S} \left( \frac{1}{q_S} - 2\chi_{\text{PE-P}}} \right) \right) + \frac{4\pi l_b}{q^2 + \kappa^2} \times \left( \frac{v_{\text{NP}} v_{\text{PE}}}{v_S} \left( \frac{1}{q_S} - \chi_{\text{PE-NP}} - \chi_{\text{NP-NP}} + \chi_{\text{PE-NP}} \right) \right)^2 \times \left( N_{\text{NP}} v_{\text{NP}} / v_S \left( 1 + v_{\text{NP}}^2 \left( \frac{1}{q_S} - 2\chi_{\text{NP-NP}} \right) \right) \right) \tag{8}\]

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

\[\frac{1}{S_{\text{NP}}} = \frac{1}{N_{\text{NP}} v_{\text{NP}} / v_S} \left( \frac{q_{\text{NP}} v_{\text{NP}}}{v_{\text{NP}}} \right) P_{\text{NP}}(q) \left( \frac{v_{\text{NP}}^2}{v_S} \left( \frac{1}{q_S} - 2\chi_{\text{NP-NP}} \right) + \frac{4\pi l_b}{q^2 + \kappa^2} \right) \times \left( N_{\text{NP}} v_{\text{NP}} / v_S \left( 1 + v_{\text{NP}}^2 \left( \frac{1}{q_S} - 2\chi_{\text{NP-NP}} \right) \right) \right) \tag{9}\]

The molar volumes of the monomers (AMPS, 200 Å³; AAm, 85 Å³) and the solvent (30 Å³) are estimated from their melt densities. As to the single chain form factor in eq 8, we use the well-known Debye function,

\[P(x) = \frac{2}{x^2} \left[ \exp(-x) + x - 1 \right] \tag{10}\]

where \(x\) is \(\xi^2 q^2\), and \(\xi\) is the mesh size for PAAm and the electrostatic blob size for PAMPS. Following Ojlicher’s scaling theory, the blob size for PAMPS was estimated as follows:

\[\xi = \text{const} \left( l_p + \frac{1}{16.7 l_p A} \right)^{-1/4} (4\pi a c)^{1/8} A^{-3/4} \tag{11}\]

where \(l_p\) is the bare persistence length \([l_p = [(C_0/2)a]0.83^2, C_0\) is the characteristic ratio (12 for PAMPS), and \(a\) is the bond length; hence, \(l_p = 13.4\ Å\), \(A\) 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. The blob size for PAAm was similarly estimated following a scaling relationship, \(\xi_{\text{NP}} = 2.09 C^{-0.76}\), where \(C\) is the polymer concentration in g/mL.

**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-d3) 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-d3 solutions were prepared by free-radical UV-initiated polymerization of
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-d3 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. Briefly, 4 mol % of MBAA and 0.1 mol % of 2-oxoglutaric acid 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 immersed into an aqueous solution of AAm or AAm-d3 monomer. After allowing sufficient time for equilibrium swelling of the first network (about 60 h), acrylamide was subsequently codissolved in water to remove unreacted monomers. Therefore, each sample was prepared in triplicate to determine thermodynamic parameters such as PAMPS. In the present scheme of extracting thermodynamic parameters 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 from aqueous PAMPS solutions and the corresponding fits obtained from eq 8 by letting \( \phi_{\text{PAMPS}} \) equal to zero. The three model parameters, \( \kappa^{-1}, \phi_{\text{PAMPS}}, \) and \( \chi_{\text{PAMPS}} \), obtained by fitting the SANS data are shown in Table 2. The exponents for scaling of \( \kappa^{-1} \) and \( \phi_{\text{PAMPS}} \) are \( \frac{1}{2} \) and \( \frac{2}{3} \), respectively, as expected and is rather high, since water is a good solvent for strongly charged polyelectrolytes, such as PAMPS. In the present scheme of extracting \( \chi_{\text{PAMPS}} \), however, the ionic contribution to solvation was separated from \( \chi_{\text{PAMPS}} \), and this high value may reflect the hydrophobic nature of the PAMPS chain without the sulfonic acid group.

### 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. Therefore, the fitting parameters, Debye screening length (\( \kappa^{-1} \)) and the number of monomers in a mesh of polyelectrolyte (\( N_{\text{PE}} \)), should further satisfy the scaling relationships for polyelectrolyte systems given by eq 8 and \( \phi_{\text{PAMPS}} \). The three model parameters, \( \kappa^{-1}, \phi_{\text{PAMPS}}, \) and \( \chi_{\text{PAMPS}} \), obtained by fitting the SANS data are shown in Table 2. The exponents for scaling of \( \kappa^{-1} \) and \( \phi_{\text{PAMPS}} \) were obtained 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. 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 (\( N_{\text{NP}} \)), and the two Flory–Huggins parameters, \( \chi_{\text{NP}} \) and \( \chi_{\text{PE-NP}} \), as floating variables. The parameters for polyelectrolyte, such as

<table>
<thead>
<tr>
<th>PE/NP molar ratio</th>
<th>( \xi_{\text{PE}} ) (Å)</th>
<th>( \xi_{\text{NP}} ) (Å)</th>
<th>( N_{\text{PE}} )</th>
<th>( N_{\text{NP}} )</th>
<th>( \kappa^{-1} )</th>
<th>( \chi_{\text{PE-NP}} )</th>
<th>( \chi_{\text{NP}} )</th>
</tr>
</thead>
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<tr>
<td>1:0</td>
<td>33</td>
<td>7</td>
<td>50</td>
<td>0.3</td>
<td>0.45</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>3:1</td>
<td>37</td>
<td>187</td>
<td>1050</td>
<td>75</td>
<td>0.3</td>
<td>0.45</td>
<td>0.05</td>
</tr>
<tr>
<td>1:1</td>
<td>44</td>
<td>111</td>
<td>580</td>
<td>110</td>
<td>0.35</td>
<td>0.45</td>
<td>0.05</td>
</tr>
<tr>
<td>1:3</td>
<td>59</td>
<td>81</td>
<td>330</td>
<td>200</td>
<td>0.35</td>
<td>0.45</td>
<td>0.05</td>
</tr>
<tr>
<td>1:7</td>
<td>79</td>
<td>72</td>
<td>260</td>
<td>300</td>
<td>0.3</td>
<td>0.45</td>
<td>0.05</td>
</tr>
<tr>
<td>1:15</td>
<td>103</td>
<td>69</td>
<td>235</td>
<td>570</td>
<td>0.3</td>
<td>0.45</td>
<td>0.05</td>
</tr>
</tbody>
</table>

in absolute units was further normalized by the neutron contrast factor, \( b_{\text{PE}} - b_{\text{NP}} \), and the volume fraction factor, \( q_{\text{PE}} (1 - q_{\text{PE}}) \), as described previously. Specific volumes of PAMPS and PAAm are taken as \( V_{\text{PAMPS}} = 0.575 \pm 0.1 \text{ cm}^3/\text{g} \) and \( V_{\text{PAAm}} = 0.696 \pm 0.1 \text{ cm}^3/\text{g} \).
the $\kappa^{-1}$, $\eta_{NP}$, and $\eta_{PE-S}$, 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 $\eta_{PE-NP}$ of 0.05 is smaller than both $\eta_{NP-S}$ and $\eta_{PE-S}$ with their fitted values of 0.45 and 0.35, respectively. The value of 0.45 for $\eta_{NP-S}$ 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 $q \geq 0.01 \, \text{Å}^{-1}$.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, $\eta_{PE-NP}$, 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 $S_{NP}$ 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 $\xi$ is set at 33 Å for PAMPS, a value taken from the result of solution blend $\xi$ 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 $\xi$ 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 $\kappa^{-1}$ 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, $q > 0.01 \, \text{Å}^{-1}$ (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](image-url)  
*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.
addition of PAAm (Figure 3a). The mutual association between
the two components given by the condition $\chi_{\text{PE-NP}}$ is likely to be responsible for the macroscopic homog-
enization 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 poly-
mers. 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 ($\chi_{\text{PE-S}}, \chi_{\text{NP-S}}, \chi_{\text{PE-NP}}$) and Debye length
($\kappa^{-1}$) of the polyelectrolyte. Nevertheless, the best fit parameters

polyelectrolyte peak is especially sensitive to the mutual
interaction parameter, $\chi_{\text{PE-NP}}$. Figure 5 shows the effect of
$\chi_{\text{PE-NP}}$ on the modeled scattering data from a 1:7 (PAMPS:
PAAm-$d_3$) solution blend. The best fit values for $\chi_{\text{PE-NP}}$ 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
copolymers. Although our study is specific to PAMPS/PAAm
system, the results are consistent with the behavior of charged
copolymer/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
$\rho$-phenylene sulfonate) results in a relatively homogenized
network morphology as compared to that prepared in pure
water. Similarly, Durmaz and Okay reported that the
swelling degree of copolymerized poly(AMPS-co-AAm) hy-
drogels unexpectedly attains a plateau region in the composition
range 10 mol% PAMPS. 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” counte-

rions. 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
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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**References and Notes**