

Polymer Communication

# The molecular origin of enhanced toughness in double-network hydrogels: A neutron scattering study<sup>☆</sup>

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Received 3 August 2007; received in revised form 4 October 2007; accepted 5 October 2007

Available online 22 October 2007

## Abstract

Double-network hydrogels (DN-gels) are a new class of crosslinked polymer networks with extraordinary mechanical properties while containing 80–90 vol.% water. Small-angle neutron scattering (SANS) was applied to investigate the molecular origin of the mechanical properties observed in DN-gels. We present SANS results in both deformed and undeformed conditions for a tough DN-gel made of poly(2-acrylamido-2-methyl-1-propane sulfonic acid) (PAMPS) and polyacrylamide (PAAm). The SANS measurements indicate that deformation of DN-gels results in periodic and mesoscale ( $\sim 1.5 \mu\text{m}$ ) compositional fluctuations in both PAMPS and PAAm. In addition, SANS measurements also indicate that the DN-gel constituents interact favorably with each other while in water. This favorable interaction between PAMPS and PAAm is consistent with the rheological results on solution mixtures of these two polymers. The implications of the above observations to toughening mechanisms are discussed.

Published by Elsevier Ltd.

**Keywords:** Hydrogels; Small-angle neutron scattering; Solution blends

## 1. Introduction

Hydrogels are considered potential replacements for articular cartilage and other soft tissues as they can absorb water many times their volume, are biocompatible and have low surface friction. However, the fracture toughness of chemically crosslinked hydrogels is low, typically with fracture strength of a few hundred kPa. Many approaches, such as nanocomposite hydrogels [1] and slide-ring gels [2], have been taken to significantly improve the mechanical properties of hydrogels by rendering the network junction points mobile [3–6]. A new approach, incorporating a high relative molecular mass

neutral polymer (linear chains) within a swollen polyelectrolyte network, double-network hydrogels (DN-gels), was recently discovered and developed [7–10]. Surprisingly, DN-gels have the highest fracture toughness among crosslinked hydrogels [11]. The mechanical properties of DN-gels prepared from many different polymer pairs were shown to be much better than that of the individual components [7]. Among all the polymer pairs studied so far the one made of poly(2-acrylamido-2-methyl-1-propane sulfonic acid) (PAMPS) polyelectrolyte network and polyacrylamide (PAAm) linear polymer stands out with unusual properties, e.g. the compressive strength of this DN-gels approaches that of articular cartilage ( $\approx 20 \text{ MPa}$ ) at 2 mol/L initial AAm concentration [12]. The use of soft, viscoelastic polymer chains to reinforce the mechanical properties of a brittle polyelectrolyte network is counter-intuitive and not understood [13–15]. To identify the molecular mechanism responsible for the enhanced

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compression strength and fracture toughness in general and for the PAMPS/PAAm pair in specific, we perform small-angle neutron scattering (SANS) measurements with contrast variation to selectively probe the structure of each polymer component and the total network within DN-gels under both deformed and undeformed conditions. In the following paragraphs we will show that deformation of DN-gels results in a periodic and mesoscale ( $\sim 1.5 \mu\text{m}$ ) compositional fluctuations in both PAMPS and PAAm. The SANS results from undeformed samples indicate that the DN-gel constituents interact favorably with each other while in water. This favorable interaction between PAMPS and PAAm is further supported by the rheological results on solution mixtures of these two polymers. The implications of these observations on the toughening mechanism of DN-gels will be discussed.

Several models have been proposed to understand the remarkable increase in toughness of DN-gels [16–18]. So far, the proposed mechanisms are based on macro-scale mechanical tests and phenomenological observations without an appreciation for strain-induced changes in their component structure at small length scales. Neither do the models predict the formation of periodic compositional fluctuations as observed in this work. Albeit our quest for the molecular mechanism responsible for the supreme mechanical properties of DN-gels is still at its early stage and ongoing, a brief overview of the findings from neutron scattering measurements will likely facilitate a rapid progress on this topic.

## 2. Materials and methods

### 2.1. Materials used

2-Acrylamido-2-methyl-1-propane sulfonic acid (AMPS) (monomer; TCI America) and 2-oxoglutaric acid (initiator, Polysciences, Inc.) were used as received. Acrylamide (AAM) (monomer) was recrystallized from chloroform. Deuterated acrylamide (monomer) ( $d_3$ -AAM; Cambridge Isotope Laboratories, Inc.) free of inhibitor was used as received.  $N,N'$ -methylene bisacrylamide (MBAA) (crosslinker) was recrystallized from ethanol. Deuterated water was used as received from Aldrich.

### 2.2. Synthesis of double-networks

The toughest DN-gels were prepared from AMPS and AAM at an initial molar ratio of 1:20, following the previously reported sequential two-step free radical polymerization [7]. Briefly, 4 mol% of MBAA and 0.1 mol% of 2-oxoglutaric acid were added to 1 mol/L AMPS aqueous solution (the molar percentages, 0.1 mol%, were determined with respect to the AMPS monomer). The mixture was degassed by bubbling with argon gas for 30 min. The crosslinked PAMPS network was then prepared by UV irradiation of the mixture in a glass mold separated by silicone spacer of desired thickness under an argon blanket. In the second step, the PAMPS gel was immersed into aqueous solution of AAM or  $d_3$ -AAM monomer containing 0.1 mol% of 2-oxoglutaric acid. After allowing

sufficient time for equilibrium swelling of the first network ( $>60$  h) polyacrylamide was subsequently polymerized in situ. The prepared DN-gels were washed thoroughly in an excess amount of water to remove unreacted monomers. Pure PAAm solutions were also prepared by the polymerization of AAM monomer in deuterated water by UV irradiation for comparison with the in situ PAAm structure within the DN-gels.

To measure the structure of the linear chains within the DN-gels, deuterated acrylamide was polymerized within a PAMPS network swollen in water. The scattering contribution from the PAMPS network structure swollen in water is negligible compared to that from  $d_3$ -PAAm. The structure factor of PAMPS was measured by matching the neutron contrast between  $d_3$ -PAAm and water using a mixture of light and heavy water at a 29:71 ratio by volume. For the overall network structure of the combination of PAMPS and PAAm chains 100% deuterated water was used while both PAAm and PAMPS were in their hydrogenated form. Therefore, each DN-gel was studied in triplicate to determine the structure of each component and the overall network in deformed and undeformed conditions.

### 2.3. Measurements

#### 2.3.1. Small-angle neutron scattering

Neutron scattering measurements were performed at the 30 m NG3 and NG7 beamlines at the NIST Center for Neutron Research, Gaithersburg, MD. Scattering data were acquired at different sample-to-detector distances 1 m, 4.5 m/5 m and 13.7 m/15.3 m using neutrons of wavelength,  $\lambda = 8.09 \text{ \AA}$  and a wavelength spread  $\Delta\lambda/\lambda = 0.11$ . The measured reciprocal wave vector space,  $q$  corresponds to  $10^{-3} \leq q (\text{\AA}^{-1}) \leq 0.15$ . Scattering data in the range  $5 \times 10^{-5} < q (\text{\AA}^{-1}) < 10^{-3}$  were measured using a Bonse–Hart type diffractometer for ultra-small-angle neutron scattering, beamline BT5, at the NIST Center for Neutron Research, Gaithersburg, MD. Structural information is thus probed over 5 orders of magnitude in  $q = 2\pi/\xi$ ; where  $\xi$  is real-space correlation length ranging from nanometers to micrometers [19,20].

#### 2.3.2. Data reduction

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 following established procedures [21]. Scattering intensity in absolute units was then normalized with respect to the neutron contrast factor and the term  $\phi(1 - \phi)$  where  $\phi$  is the volume fraction of scatterers. For example, the neutron scattering intensity from  $d_3$ -PAAm labeled DN-gels swollen in light water is normalized with respect to the volume fraction of  $d_3$ -PAAm in the system and the effective neutron scattering contrast between  $d_3$ -PAAm and the PAMPS network swollen in light water. The volume fraction of PAAm in DN-gels is calculated from the difference in weight between a freeze-dried PAMPS network and the corresponding DN-gel determined during

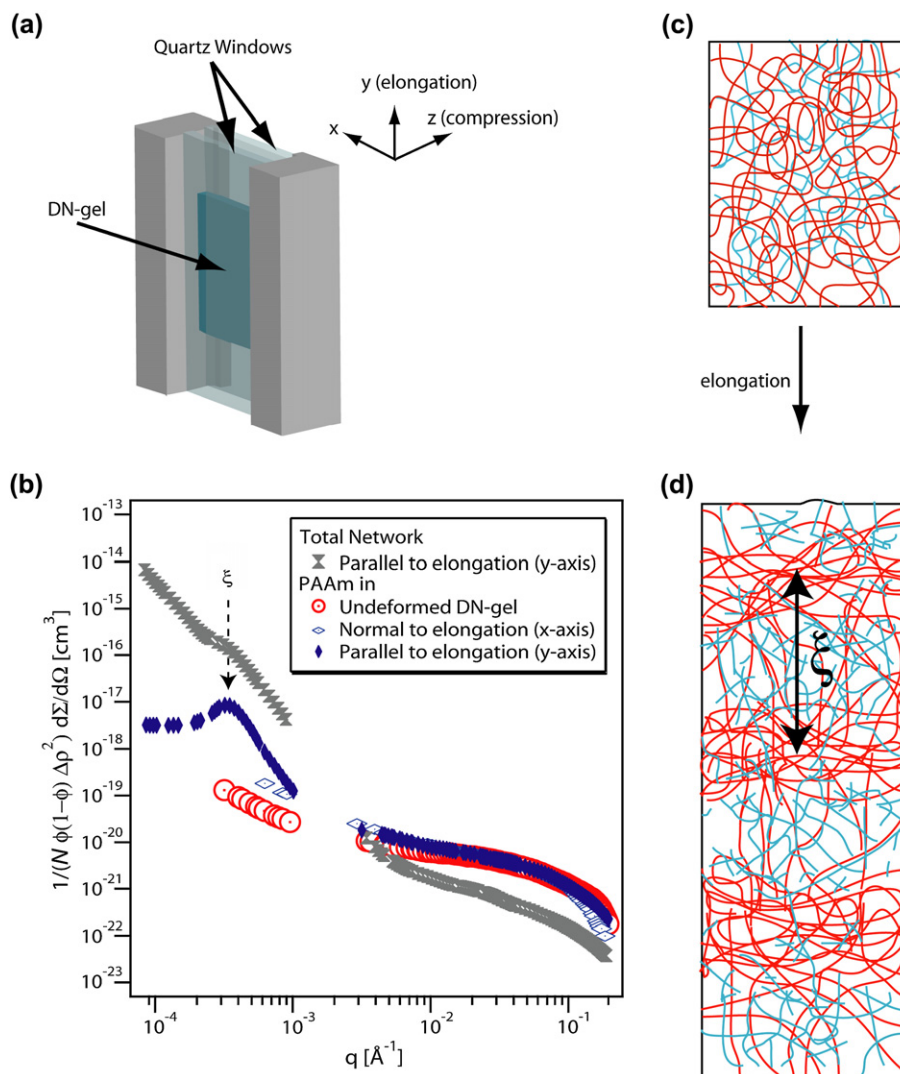


Fig. 1. (a) Schematic of the sample cell used for in situ SANS measurements of DN-gels under pure shear deformation. (b) SANS from DN-gels measured in undeformed state and in pure shear deformation mode. Scattering data parallel and normal to the tensile deformation plane at ultra-low  $q$  are collected using a Bonse–Hart diffractometer. Uncertainty in measured neutron scattering intensity is smaller than the size of the markers used. Schematics represent the (c) static structure of DN-gel and (d) the change it undergoes when subjected to a 50% extension using the sample cell shown in (a). PAMPS and PAAm are represented in the schematics by line colors blue and red, respectively. The correlation length,  $\xi$ , corresponding to the peak position in SANS from deformed DN-gel is from the concentration fluctuations in the component structure of PAAm at  $\approx 1.5 \mu\text{m}$ .

swelling degree measurements. Specific volumes of PAMPS [22] and PAAm [23] are taken as  $v_{\text{PAMPS}} = 0.575 \pm 0.1 \text{ cc/g}$  and  $v_{\text{PAAm}} = 0.696 \pm 0.1 \text{ cc/g}$ .

### 2.3.3. Viscosity measurements

An Advanced Rheometric Expansion System (ARES-LS; TA Instruments) was used to measure the viscosity of solution-phase mixtures of PAMPS and PAAm. PAMPS and PAAm solutions were prepared separately using photopolymerization without a crosslinker. Samples were prepared by mixing the individual solutions at an appropriate volume ratio. The viscosity was measured in a steady shear sweep mode. Data points at a certain shear rate were given as an average over 1 min. The figure in this paper was derived by extrapolating the data in the range of  $10^0$ – $10^{-3} \text{ s}^{-1}$  to zero-shear rate.

## 3. Results

### 3.1. Deformation induced structure changes in DN-gels

We performed SANS measurements of the structure of each component and the total network of the DN-gel under a pure shear deformation. A sample cell with quartz windows (Fig. 1a) was designed to deform the DN-gel and to keep it in deformed state during SANS measurements. The specimen was elongated along the  $y$ -axis by compressing quartz windows along the  $z$ -axis while maintaining a constant width ( $x$ -axis). This design minimizes the potential for crack or micro-void formation, features that would also scatter neutrons because there is no tensile stress exerted on the specimen. For these measurements, the imposed strain was 50% in extension along  $y$ -axis. Fig. 1b shows the SANS data taken in situ on the

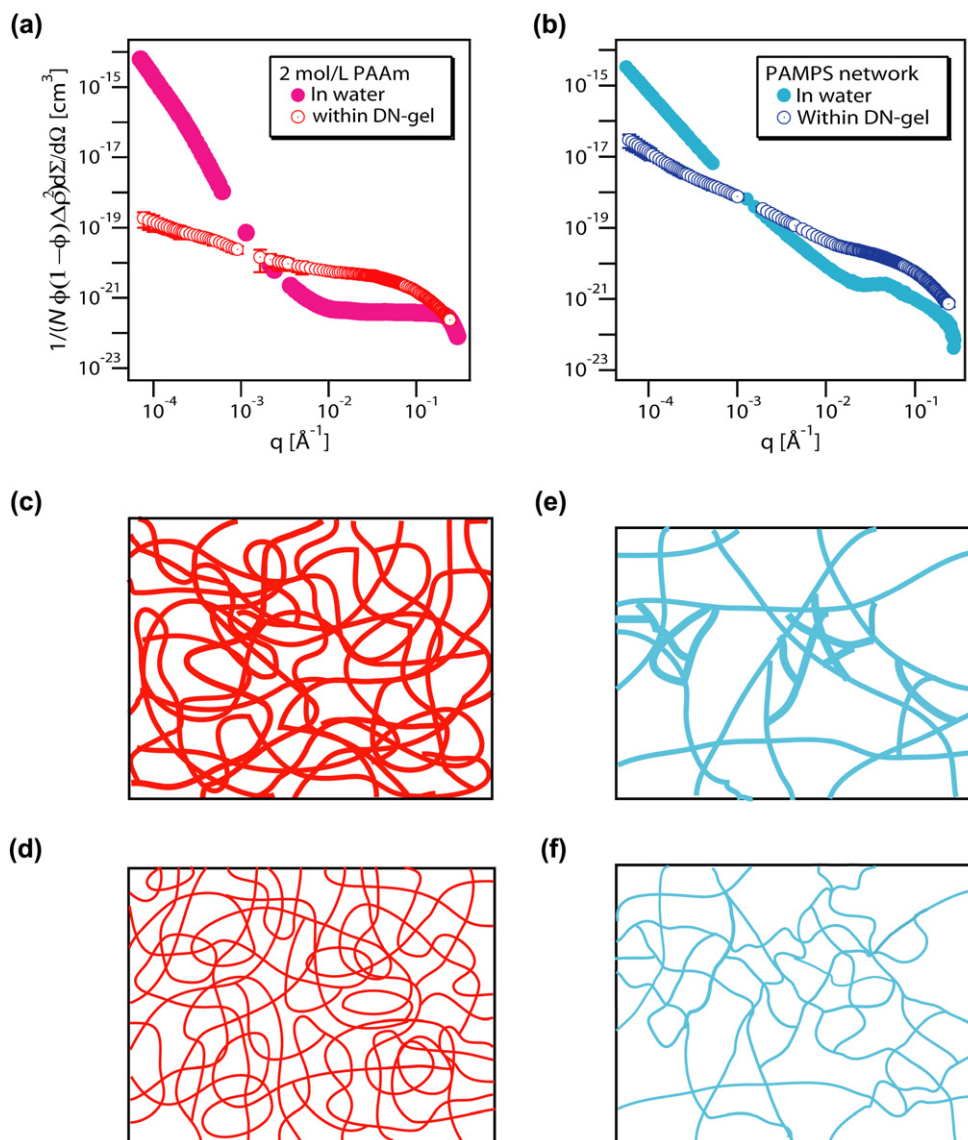


Fig. 2. SANS from (a) PAAm linear chains and (b) PAMPS network within the DN-gels prepared at 2 M PAAm concentration and in pure water. The neutron scattering intensity in absolute units is normalized with respect to the contrast factor and volume fraction of scatterers. Uncertainty in measured intensity is smaller than the size of markers used. Data show that the dense, inhomogeneous structure of PAAm and PAMPS (schematics c and e, respectively) polymerized in water gets homogenized when polymerized in the presence of each other (schematics d and f, respectively).

deformed DN-gel at two contrast conditions that reveal the PAAm structure and the total network structure. Neutron scattering in the small-angle region ( $10^{-3} \text{ \AA}^{-1} < q < 1 \text{ \AA}^{-1}$ ) did not exhibit anisotropic “butterfly” patterns that are commonly found in deformed polymer networks. In the ultra-small-angle regime ( $5 \times 10^{-5} \text{ \AA}^{-1} < q < 10^{-3} \text{ \AA}^{-1}$ ), the scattering intensity is anisotropic as seen from the difference in the scattering curves between the data averaged parallel and perpendicular to the elongation direction. The most striking feature in the data is a pronounced scattering maximum at a  $q$  value corresponding to  $\sim 1.5 \text{ \mu m}$  periodicity along the elongation axis. This feature is grossly different from the conventional “butterfly” patterns where the scattering intensity monotonically decays with  $q$ . This feature is also present in the deformed structure of samples prepared with contrast conditions to reveal the PAMPS structure, but to a less extent. Scattering intensity from the total

network is also anisotropic in the ultra-small-angle region but exhibited only a barely discernible scattering maximum in the direction parallel to the elongation axis (Fig. 1b). The lack of a pronounced scattering maximum from the total network under deformation indicates that the compositional fluctuations of the components are mostly out-of-phase. These results clearly show the occurrence of compositional fluctuations from both linear PAAm chains and the PAMPS network when DN-gels are deformed (Fig. 1d).

The length scale of this deformation induced feature is noteworthy; compositional fluctuations with a periodicity at micrometer length scale can occur only if the deformation process is self-regulating in nature. A self-regulating process can lead to the observed increase in fracture toughness of DN-gels because the development of a regularly repeating structure offers an energy dissipating mechanism throughout

the entire sample volume instead of being concentrated at the crack tip, which results in run-away fracture. A well-known example is the stress-induced crystallization in deformed natural rubber, where the deformed molecular network is stabilized by the formation of crystallites albeit at relatively much smaller repeating length scales. As a first step to unravel the molecular mechanism for this self-regulating and cooperative nature of deformation, we study the interaction between PAMPS and PAAm via SANS and viscosity measurements. Having favorable enthalpic interactions between these two components will compel large energy dissipation in the deformation process depicted in Fig. 1c, d. However, it will not necessarily result in a self-regulating mechanism that would suppress crack propagation.

### 3.2. Static structure of components in DN-gels

In Fig. 2a, we show the SANS data from 2 mol/L PAAm linear chains in water and in DN-gel. This figure shows that the scattering results of PAAm in water and within the DN-gel, hence in the presence of PAMPS, are very different; particularly in the low  $q$  region there is a 4 orders of magnitude drop in the scattering intensity (Fig. 2a). In pure water, PAAm chains in the semi-dilute and concentrated regimes form aggregated clusters resulting in higher intensities at lower  $q$ . Since the PAAm concentration was kept constant, the decreased scattering intensity in the DN-gel shows that PAAm chains are better dispersed in the presence of PAMPS than in pure water.

Fig. 2b shows the SANS data for the PAMPS network structure in water and within the DN-gel. We again observe a lower scattering intensity in low  $q$  region for PAMPS in the DN-gel. In addition, the scattering peak located near  $0.04 \text{ \AA}^{-1}$  from PAMPS is also suppressed in the presence of PAAm in the DN-gel. The scattering peak from pure PAMPS gel represents inter-chain correlations due to the repulsive interactions between the sulfonic acid groups; the suppression in the polyelectrolyte peak provides an indication of the association between PAMPS and PAAm. Macromolecular complexation between oppositely charged weak polyelectrolytes in aqueous media via hydrogen bonding between proton-rich (e.g. carboxylic acid;  $-\text{COOH}$ ) and electron-rich (e.g. amide;  $-\text{CONH}_2$ ) groups is well established [24]. Similar association between the strongly charged sulfonic acid group with weakly charged amide group ( $-\text{SO}_3\text{H}$  and  $-\text{CONH}_2$ ) in DN-gels is therefore likely. We conducted some preliminary Density Functional Theory calculations and the result indicates the existence of hydrogen bonding between the sulfonic acid from AMPS and multiple amide groups from AAm [25]. Results from the literature show that the polymerization of acrylamide gel in an aqueous dispersion of poly(sodium phenylenesulfonate) also results in a relatively homogenized network compared to that polymerized in pure water [26].

### 3.3. Viscosity of PAMPS/PAAm solution mixtures

Molecular-level association between the constituents of DN-gels should also exhibit anomalous rheological behavior in solution. Therefore, we performed viscosity measurements

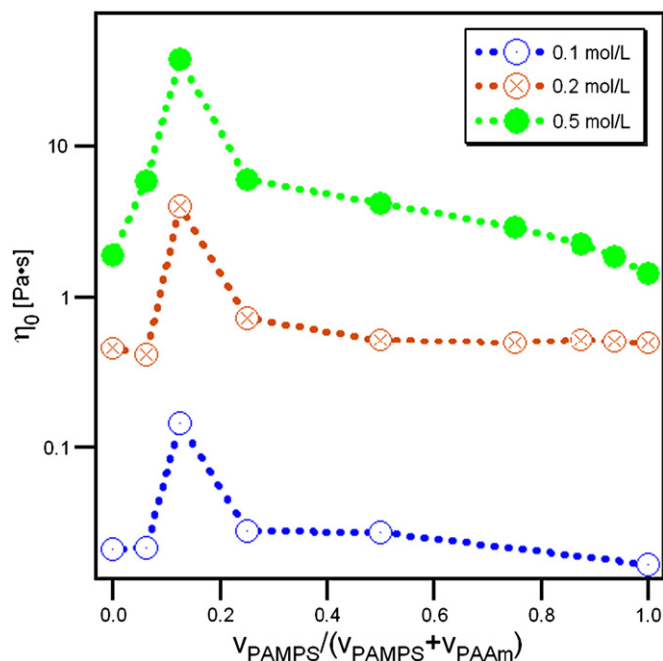


Fig. 3. Zero-shear viscosity of the PAMPS/PAAm solution mixtures as a function of PAMPS volume fraction, at three different total polymer concentrations. Uncertainty in the measured viscosity is smaller than the size of the markers used. Lines are drawn as a guide to the eye. The maximum in zero-shear viscosity within a narrow concentration range suggests strong association between PAMPS and PAAm, mediated probably by hydrogen bonding.

on simple mixtures of aqueous PAMPS and PAAm homopolymer solutions. The viscosity was measured using an Advanced Rheometric Expansion System (ARES-LS; TA Instruments) in a parallel plate geometry with shear rate sweep from  $10^{-3}$  to  $10^0 \text{ s}^{-1}$  at room temperature. The zero-shear viscosity data of samples prepared by mixing 0.1 mol/L, 0.2 mol/L and 0.5 mol/L homopolymer solutions are given in Fig. 3 as a function of PAMPS composition. A maximum in viscosity was observed when the volume ratio of solutions (PAMPS:PAAm) is between 1:15 and 1:3. This ratio is independent of solution concentration and, interestingly, is within a similar molar ratio range over which the maximum in mechanical properties is observed in DN-gels [27]. The anomalous increase in viscosity is neither due to an increase in polymer concentration nor is it found in diluted solutions of pure PAMPS or PAAm. A similar increase in viscosity driven by complex formation between the components was previously observed in mixtures of simple associating liquids such as pyridine/acetic acid, ethanol/water, or thiocarbimides/secondary amines [28].

## 4. Discussion and conclusions

It is interesting to note that both the maximum in solution viscosity and fracture toughness occur in a composition range dominated by PAAm. The physical origin of this particular ratio remains the topic of our ongoing research. There appears to be a correlation between the increase in viscosity of solutions and the increase in fracture toughness of crosslinked gels. Of course, association between the components alone is not

sufficient to explain the observed deformation induced structure at  $\sim 1.5 \mu\text{m}$  length scale. We do, however, observe shear thickening in samples that exhibit viscosity enhancement (data not shown here). From a simple mechanical property point of view it is possible that shear thickening could play a role in toughening DN-gels.

The experimental results from SANS and viscosity measurements indicate the existence of a molecular association between PAMPS and PAAm. SANS results from PAMPS and PAAm linear chain solution blends have also been obtained, and the general trend is rather similar to aforementioned results from DN-gels. Quantitative analysis of the solution blend data using the theory by Benmouna et al. [29] confirms the notion of favorable interaction between these two polymers in aqueous solution. A detailed analysis of the SANS results or a more comprehensive toughening mechanism in DN-gels is beyond the scope of this communication and will be presented in a forthcoming article.

With these findings we now revisit the fracture toughness data of other DN-gels included in Ref. [7]. It is interesting to note that the increase in fracture toughness of DN-gels prepared from two polymers with a favorable intermolecular association (PAMPS/PAAm, PAA/PAAm, PAMPS/TFEA, etc.) is always larger than those without favorable interactions (PAMPS/PAMPS, PAA/PAA or PAAm/PAAm). This observation suggests that the attractive enthalpic interactions between two components may play a role in the toughening of DN-gels. In the simplest picture, the deformation process depicted in Fig. 1c, d calls for a large scale dissociation between PAMPS and PAAm and the amount of energy dissipation during deformation can be related to the strength of inter-species association. Work is ongoing to develop a toughening mechanism of DN-gels to encompass all the SANS results as well as the mechanical test results by others.

## Acknowledgments

We are grateful to Dr. Paul Butler for his assistance during the neutron measurements. We acknowledge the support of National Institute of Standards and Technology, U.S. Department of Commerce, in providing the neutron research facilities used in this work. This work utilized facilities supported in part by the National Science Foundation under Agreement No. DMR-0454672. Y.O. acknowledges Grant-in-Aid for the Creative Scientific Research A and J.P.G. acknowledges Grant-in-Aid for the Specially Promoted Research from the Ministry of Education, Science, Sports and Culture of Japan.

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