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Superabsorbent Hydrogels That Are Robust and Highly Stretchable

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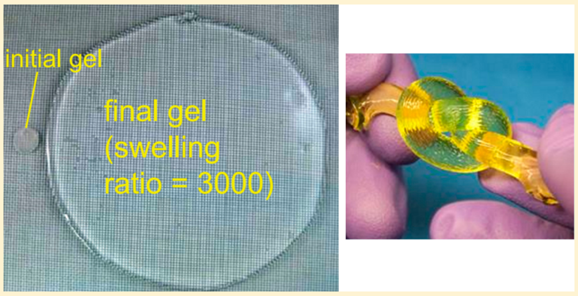
Supporting Information



ABSTRACT: Polymer hydrogels synthesized by chemical cross-linking of acrylate or acrylamide monomers can absorb more than 100 times their weight in water. However, such gels are usually fragile and rupture when stretched to moderate strains (∼50%). Many strategies have been developed to create tougher gels, including double-networking, incorporation of nanoparticles as cross-linkers, etc., but these strategies typically retard the water absorbency of the gel. Here, we present a new approach that gives rise to superabsorbent hydrogels having superior mechanical properties. The key to our approach is the self-cross-linking ability of *N,N*-dimethylacrylamide (DMAA). That is, we conduct a free-radical polymerization of DMAA (along with an ionic comonomer such as sodium acrylate) but without any multifunctional monomers. A hydrogel still forms due to interchain covalent bonds between the growing linear polymer chains. Gels formed by this route can be stretched up to 1350% strain in the unswollen state. The same gels are also superabsorbent and can imbibe up to 3000 times their weight in water (which is believed to be a record). Even in the swollen state, these gels can be stretched up to strains ∼400% before rupture, which substantially exceeds that of conventional superabsorbent gels. The superior properties of DMAA-based gels are attributed to a more uniform distribution of cross-links within their networks.

1. INTRODUCTION

Polymer hydrogels are three-dimensional (3-D) networks of polymer chains cross-linked by covalent or strong physical bonds and swollen in aqueous solution.[1−3] These materials are used in a variety of applications ranging from consumer products to tissue engineering.[4−6] Synthetic hydrogels can be engineered to exhibit significant swelling when placed in water.[7] The swelling ratio, defined as the mass ratio of swollen gel to dry network, can be on the order of 100−1000 for many gels. Such gels are termed superswelling or superabsorbent materials and are used in products such as disposable diapers.[6−9] The swelling ratio depends on the fraction of ionizable groups along the polymer backbone; i.e., ionic gels swell considerably more than nonionic gels.[7,9] Also, the swelling ratio depends on the density of cross-links within the gel—the lower the cross-link density, the higher the swelling.[7,9] However, gels with low cross-link densities tend to be soft and floppy. Thus, the synthesis of gels with an ideal combination of water absorbency and mechanical properties remains a challenge.

In terms of mechanical properties, synthetic hydrogels usually fall in one of two extremes, depending on cross-link density.[2,3] If the gels are weakly cross-linked, as mentioned above, they tend to be soft (low elastic modulus). Such gels may be difficult to handle as they may be slippery and difficult to grasp by hand or with a pair of tweezers or forceps. In contrast, gels that are highly cross-linked tend to be stiff (high elastic modulus), but they are also generally quite brittle. These gels are easy to handle but have low elongation at break and their tensile strength, toughness, and resiliency tend to be quite low. The low strength has been attributed to the nanostructure that typically exists in gels made by conventional free-radical polymerizations.[10,11] In particular, cross-links tend to be distributed inhomogeneously; i.e., there is a wide distribution in segment lengths (molecular weights) between adjacent cross-links, and there are many chain loops and dangling ends. When such a gel is deformed, some chain segments tend to get deformed much more than others, which creates zones of high stress in the gel. Consequently, the gel suffers irreversible rupture at low deformations.

In recent years, many researchers have recognized that the gels and soft materials found in nature (e.g., aquatic creatures like the jellyfish or various tissues in the body) are much tougher and more resilient than gels prepared in the laboratory.[10,11] This realization has led to intense research to improve the toughness and stretchability of highly cross-linked hydrogels,[12−21] as summarized in recent reviews.[10,11] For example, Tew et al.[21] created gels with a more uniform distribution of cross-links using special end-functionalized monomers, and they confirmed the higher toughness of these gels. Haraguchi et al.[13,14] showed that the use of nanoparticles as cross-linkers, in lieu of traditional multifunctional monomers, gave gels with high elongations at break (∼1200%). Gong et

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al.[12,15] pioneered the concept of interpenetrating or "double-network" gels as a route to improved properties. Their central idea was to create a first network, swell that in a second monomer, followed by a second polymerization to yield a "double-network" gel. Such gels have been shown to be very robust, tough, and fracture resistant. Variations of double networks can be created in which one network is based on covalent bonds and the other on physical bonds. For example, a gel based on coexisting networks of polyacrylamide (covalent) and alginate (ionic) has been reported to have elongations at break of over 2000%.[19] This gel is one of the toughest soft materials reported to date.

An important limitation of current methods to produce tough gels is that they are not tailored toward ensuring a high water absorbency at the same time. For example, double-network gels have a higher density of cross-links due to their coexisting networks, but the extra cross-links reduce the swelling extent of the gels.[12,19] Thus, the high toughness comes at the expense of water absorbency. In the case of nanoparticle-cross-linked gels, they typically have higher degrees of swelling compared to their conventional counterparts.[13,14] However, nanoparticles (such as clays or silica) usually have strong surface charges, and in the presence of ionic monomers, the particles frequently get destabilized before or during polymerization. Nanoparticle-cross-linking is thus not usually carried out with ionic monomers, which are necessary for high swelling ratios in water. On the whole, alternate methods are needed to devise hydrogels that swell greatly and remain reasonably tough even in the swollen state.

In this work, we report a class of hydrogels that offer a superior combination of high swelling (superabsorbency) as well as good mechanical properties (toughness and high extensibility). The gel is based on the monomer *N,N*-dimethylacrylamide (DMAA), which is an acrylamide derivative that has been used extensively in hydrogel synthesis.[13,17,18] Typically, DMAA gels are synthesized by free radical polymerization in the presence of a cross-linking monomer such as *N,N*′-methylene(bis)acrylamide (BIS) and/or in the presence of clay or silica nanoparticles. Here, we do not employ BIS or nanoparticles or any other extrinsic species as cross-linkers. Rather, we exploit the ability of DMAA to undergo a process called *self-cross-linking* in the presence of certain free-radical initiators like potassium persulfate (KPS). Although the self-cross-linking ability of DMAA has been known for more than 50 years,[22−24] it has thus far been regarded as a nuisance, and efforts are typically taken to eliminate it during gel synthesis. Here, we put this characteristic to use in our synthesis scheme. Along with DMAA, which is nonionic, we include the ionic comonomer sodium acrylate (SA) during polymerization. The resulting ionic gels swell significantly in water, with swelling ratios approaching 3000, which are among the highest reported to date.[7] At the same time, these gels exhibit mechanical properties that are substantially better than those of typical superabsorbent gels. Specifically, the gels are highly stretchable compared to conventional gels, both in the as-prepared and in the swollen states, with elongations at break of 1350% and 400%, respectively. This unique combination of properties is likely to enable new applications for these gels.

2. EXPERIMENTAL SECTION

Materials. The monomers DMAA, SA, acrylamide (AAm), and BIS, the initiator KPS, and the accelerator *N,N,N*′*,N*′-tetramethylethylenediamine (TEMED) were purchased from Sigma-Aldrich. All materials were used as received. All the gels were prepared in deionized (DI) water.

Hydrogel Preparation. Self-cross-linked gels were prepared by combining DMAA and KPS in deionized water at DMAA concentrations between 5 and 50 wt %. To exemplify the process, a 33 wt % DMAA and 1 mol % KPS gel was prepared as follows. First, 3.3 g of DMAA was added to 6.7 g of DI water. Nitrogen (N_2) gas was bubbled into this solution for 45 min to displace dissolved oxygen. Then, 0.089 g of KPS was added, corresponding to 1 mol % relative to DMAA in solution. N_2 gas continued to be bubbled through this solution for an additional 15 min, and then 40 μL of TEMED was added. The resulting pregel solution was then sandwiched between two glass plates (∼10 × 10 cm), with the thickness between the plates and hence the gel thickness being either 0.54 or 1.5 mm. The samples were left to polymerize for at least 24 h at room temperature (∼23 °C). Gels were also prepared with higher or lower levels of KPS (0.07−1.85 mol %), as indicated in the text.

The above procedure yielded gels of DMAA alone, which are nonionic. To create high-swelling gels, SA was copolymerized with DMAA. The total monomer fraction in solution was fixed at 33 wt %, and the SA fraction was varied between 5 and 20 mol % relative to the total. The molar ratio of KPS relative to total monomer was fixed at 0.4 mol %. For comparison, conventional cross-linked gels were also made by copolymerizing AAm with SA. Here, the monomers SA (5−100 mol %) and AAm (95−0 mol %) were dissolved in 10 g of water at a total concentration of 1 M (∼7 wt %), along with the cross-linker BIS at a concentration of 3 mol % relative to the total monomer content. Nitrogen gas was bubbled through the solution for a period of 1 h followed by the addition of 0.015 g of KPS and 12 μL of TEMED. This solution was sandwiched between plates and polymerized to form gels with the dimensions indicated above.

Rheological Studies. Dynamic rheological experiments were performed on an RDA III strain-controlled rheometer (TA Instruments). Samples were run at 25 °C on a parallel plate geometry (25 mm diameter). Dynamic frequency spectra were obtained in the linear viscoelastic regime of each sample as determined by dynamic strain-sweep experiments.

Swelling Measurements. The 0.54 mm thick gels were used to determine the swelling ratio of the gels. Disks of ∼1.5 cm diameter were punched out from the gel film using a round die punch. The disks were then immersed in DI water and allowed to swell for 24 h at room temperature. After this time, the disks were patted dry and weighed. The same gel disks were then dried in an oven. The swelling ratio was calculated as follows:

$$Q = \frac{\text{mass of swollen gel}}{\text{mass of dry network}} \qquad (1)$$

Tensile Measurements. The 1.5 mm thick gels were used for the tensile tests on the as-prepared and swollen gels. An Instron Tensile Tester 3345 was used for these tests. Rectangular samples (24.5 mm wide) were cut out from the gels with a sharp razor. While the thickness of the as-prepared gel samples was 1.5 mm, the thickness of the swollen samples was determined individually using a set of calipers. The ends of the gel were covered by square strips of acrylic film, and the gel was then loaded between the rubber-coated clamps of the Instron. The length of gel between clamps was measured, and the strain was defined with respect to this initial length. The rate of stretching during the experiments was 1 min^{-1} (i.e., samples were stretched by 1 original length per min). The test yielded a plot of tensile stress vs strain, with the data extending until the point of sample break. Tests were run in triplicate. The relative standard deviation in the modulus (measured from the initial slope of the plot) was 23%, whereas the relative standard deviation for the elongation at break was 5%.

3. RESULTS AND DISCUSSION

Characterization of DMAA Gels. As described above, we prepared DMAA hydrogels without the addition of a multifunctional cross-linker such as BIS. The reaction mixture consisted of the DMMA monomer, KPS initiator, and TEMED accelerant. Photographs of typical DMAA gels are shown in Figure 1. Despite the lack of a cross-linker, the materials visually exhibit all the hallmarks of a gel (solid) rather than that of a viscous or viscoelastic material. For example, the gel can be placed on a table in the absence of a holding container, and it will retain its shape and dimensions for long times (Figure 1a). (In contrast, note that a viscoelastic material will tend to sag or creep with time.[25]) The gel can also be held between one's fingers and easily stretched like an elastomer (Figure 1c), and for moderate extents of stretching, the gel reverts to its original dimensions when the stretching is ceased, which again reveals its elastic character. What is more, the gel is so strong and extensible that it can be stretched and tied into a knot without any visible cracks or breaks along the material (Figure 1b).

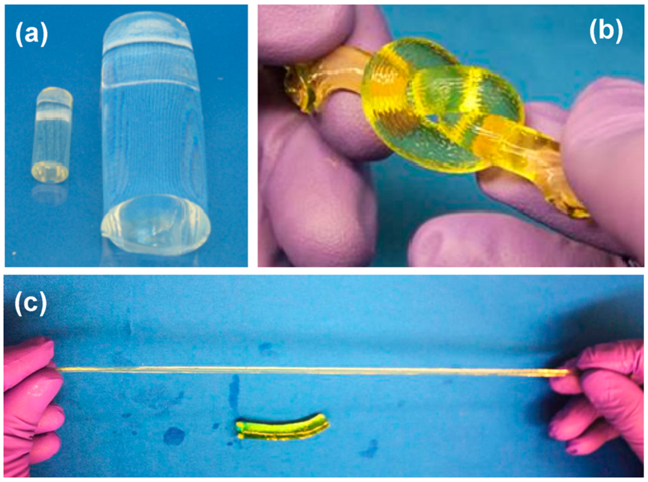


Figure 1. Photographs of self-cross-linked DMAA gels. All gels shown here correspond to 33 wt % DMAA and 0.4 mol % KPS. In (a), two such gels are placed on the tabletop in the absence of a holding container. The gel on the left is as-prepared (unswollen) whereas the gel on the right is swollen with water (swelling ratio of 70). In both cases, the gels retain their shape and dimensions (no creep or sagging), indicating their solidlike character. In (b), the unswollen DMAA gel is stretched and tied into a knot using one's fingers. The ability to manipulate the gel in this manner shows its strength and extensibility. In (c), the extensibiilty is further shown by stretching the unswollen DMAA gel to more than 5 times its original length (i.e., strain of 500%). An identical strip of unstretched gel is shown below the stretched one for comparison.

To verify that the material synthesized is indeed a gel and not a viscoelastic polymer solution, we turn to dynamic rheology. In Figure 2, we compare frequency sweeps for three materials: a DMAA gel, a concentrated solution of linear polyacrylamide (PAAm), and an AAm-BIS gel. In all cases, the data shown are for the elastic (G') and viscous (G'') moduli as functions of angular frequency ω. The DMAA gel corresponds to 33 wt % DMAA and an initiator concentration of 1 mol % KPS. We see that this gel shows a predominantly elastic response (Figure 2a), with the elastic modulus G' exceeding the viscous modulus G'' by a factor of 5 over the entire frequency range, down to $\omega \sim 0.01$ rad/s. Note also that G' is nearly independent of frequency. Taken together, these two features in dynamic rheology indicate gel-like behavior of the DMAA sample.[25]

For comparison, we studied a 25 wt % PAAm solution. This was prepared by free-radical polymerization of AAm monomer in the absence of cross-linkers. We chose this concentration as it results in a similar molar concentration of monomers as in 33 wt % DMAA, thus allowing a meaningful comparison of the rheological data. Figure 2b shows that the PAAm solution exhibits viscoelastic behavior, as expected. That is, G' is much larger than G'' at high frequencies, but the two are nearly equal at lower frequencies. Both moduli thus show strong frequency dependence, as expected for viscoelastic materials.[25] As a second comparison, we studied an AAm-BIS gel made with 25 wt % AAm and 0.1% BIS. This material is a conventional, lightly cross-linked hydrogel, and its rheological response is indeed gel-like (Figure 2c). Here, G' is frequency-independent and exceeds G'' by a factor of about 50 at high frequencies and more than 500 at lower frequencies. Note that the data for G' is very smooth whereas that for G'' is erratic; this is typical for strongly elastic materials.[25]

Comparing Figures 2a−c, we can conclude that the response of the DMAA gel is closer to that of the AAm-BIS gel than to the PAAm solution. This is consistent with the physical nature of the samples. The PAAm solution does not have dimensional stability; i.e., it cannot be placed on the tabletop and retain its shape. In contrast, both the DMAA and AAm-BIS gels are dimensionally stable. With regard to the ratio of the moduli, we can quantify this in terms of the loss tangent $\tan\delta = G'/G''$, which is a standard measure of the extent of viscous dissipation in the material.[25] From the data in Figure 2, plots of $\tan\delta$ vs ω

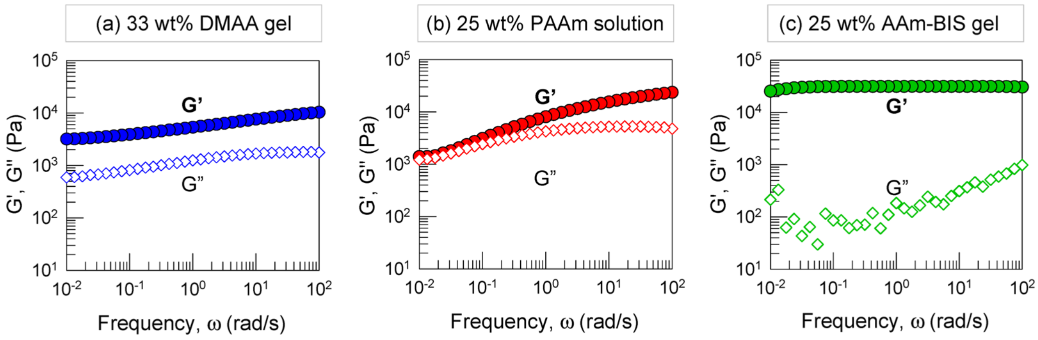
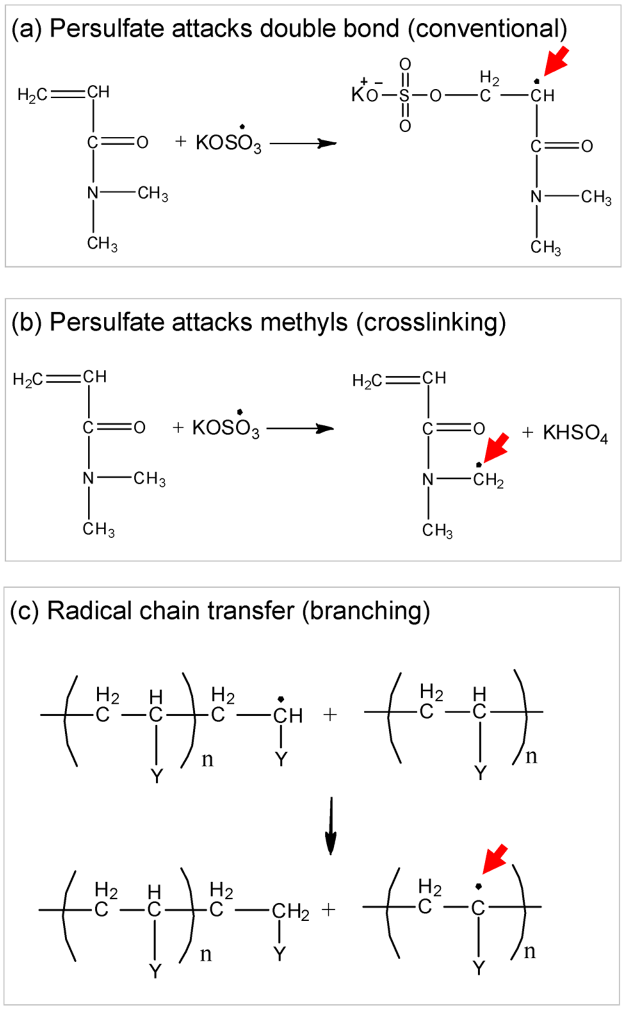


Figure 2. Dynamic rheology of DMAA gels compared with that of PAAm solutions and gels. Data are shown for the elastic modulus G' (filled circles) and the viscous modulus G'' (unfilled diamonds) as functions of the frequency ω. (a) 33 wt % DMAA, self-cross-linked into a gel using 1 mol % KPS initiator. The rheology confirms the gel-like character, with G' exceelding G'' by a factor of 5. (b) 25 wt % AAm polymerized without cross-linker, which yields a solution of linear polymer. Here, the rheology shows a viscoelastic response. (c) 25 wt % AAm cross-linked with 0.1% BIS to yield a conventional gel. The rheology reveals a highly elastic, gel-like response, with G' exceeding G'' by a factor >50.

for the three samples are plotted in Figure S1 (Supporting Information). We note that for the DMAA gel tan δ is about 0.2 and nearly constant across the frequency range. On the other hand, for the AAm-BIS gel, tan δ is about 0.02 at the higher frequencies and much smaller (~0.002) at lower frequencies (because G'' is erratic, so is tan δ). Thus, tan δ for the DMAA gel is at least an order of magnitude higher than for conventional hydrogels. This suggests that the DMAA gel has some viscous character, and we believe this could be important in explaining the high extensibility and robustness of the gel.

The rheological data confirm that DMAA can be converted to a gel in the absence of chemical cross-linkers. But how does this occur? As mentioned, the self-cross-linking ability of DMAA in the presence of persulfate initiators like KPS has been known[24] since 1965, and the likely mechanisms that have been proposed for this are indicated in Figures 3b,c.[23,26] First, as shown in Figure 3b, persulfate radicals from KPS may abstract a hydrogen from one or both of the dimethyls on DMAA, which would result in a methylene radical. The latter can connect to another growing polymer chain either through the double bond or at the methylene position.[23,24] The polymer chains thus become branched and cross-linked to each other, which explains the gel formation. Effectively, this mechanism implies that DMAA is transformed into a multifunctional monomer by KPS. Other polymer branching mechanisms are also possible, as shown in Figure 3c. A radical terminated chain may attack another chain and abstract an α-hydrogen (relative to the carbonyl) resulting in transfer of the radical to the polymer.[26]


(a) Persulfate attacks double bond (conventional)

(b) Persulfate attacks methyls (crosslinking)

(c) Radical chain transfer (branching)

Figure 3. Possible reactions that can occur during KPS-initiated polymerization of DMAA. (a) The conventional case, where persulfate radicals attack the double bond and thus facilitate the formation of linear polymer chains. (b) The main self-cross-linking scenario, where persulfate radicals attack the methyl groups and abstract a hydrogen. In this case, the growing chain can connect to another chain, leading to a cross-linked network. (c) Chain transfer from one chain to another, resulting in the formation of branches or junctions between linar chain segments. Arrows indicate the radical on the growing polymer chain.

To further understand the mechanism, we conducted FTIR spectroscopy on the self-cross-linked DMAA gel and compared it to reference data[27] available for DMAA monomer (see Supporting Information, Figure S2). We find that (a) an absorption peak at 1000 cm^{-1} for the DMAA monomer is absent in the case of the DMAA gel and (b) a peak at 3400 cm^{-1} for the DMAA gel is absent in the case of the DMAA monomer. The peak at 1000 cm^{-1} corresponds to the stretching of a vinyl hydrogen; the absence of this peak in the gel indicates that no unreacted DMAA is present in the gel. The peak at 3400 cm^{-1} reflects the stretching of a hydrogen on a primary amine; the presence of this peak in the DMAA gel indicates that DMAA is being dealkylated.[23,24] The dealkylation of DMAA by attack of persulfate radicals is known to be preceded by the formation of methylene radicals. The latter can either lead to dealkylated DMAA or to self-cross-linking. The FTIR data thus indirectly support the mechanism in Figure 3b for DMAA self-cross-linking.

We proceeded to examine the range of monomer and initiator concentrations required to form self-cross-linked DMAA gels. Samples were prepared for DMAA monomer concentrations between 5 and 50 wt % and KPS between 0.07 and 1 mol % relative to monomer. Gel formation was detected by the vial inversion test; i.e., samples that did not flow upon vial inversion were classified as being in the gel state.[28] We found that gels could be formed with as low as 5 wt % DMAA if KPS was above 0.4 mol %. At 10 wt % DMAA, gels were formed for KPS > 0.22 mol %. At all higher DMAA contents, gels were obtained even for the lowest KPS concentration tested, which was 0.07 mol %. Thus, self-cross-linked gel formation requires both a minimum DMAA and a minimum KPS concentration. This finding is consistent with the mechanism for gel formation shown by Figure 3b in which persulfate ions from KPS play an active role in the cross-linking of DMAA chains. Note that by this mechanism, higher levels of KPS at a constant DMAA imply higher cross-link densities in the gel.[23,24]

We then characterized the mechanical properties under tension of the self-cross-linked DMAA gels. These studies were done for gels over a range of KPS (0.4, 0.7, and 1.8 mol %) while keeping a constant DMAA concentration of 33 wt %. The tensile properties of the three gels are shown as plots of stress vs strain in Figure 4a. Each curve shows an initial linear region with a high slope (elastic region) followed by a reduction in slope and a subsequent elongration region up to the point of fracture. For the 0.4 and 0.7% KPS samples, the elongation region is substantial (many times the original sample length). This shape of the stress−strain curve is typical of elastomeric materials.[25] The initial slope of the plot yields the elastic modulus, which is plotted in Figure 4b. We note that the modulus doubles from ~2.5 to 5 kPa as the KPS is increased from 0.4 to 1.8 mol %. On the other hand, the elongation at

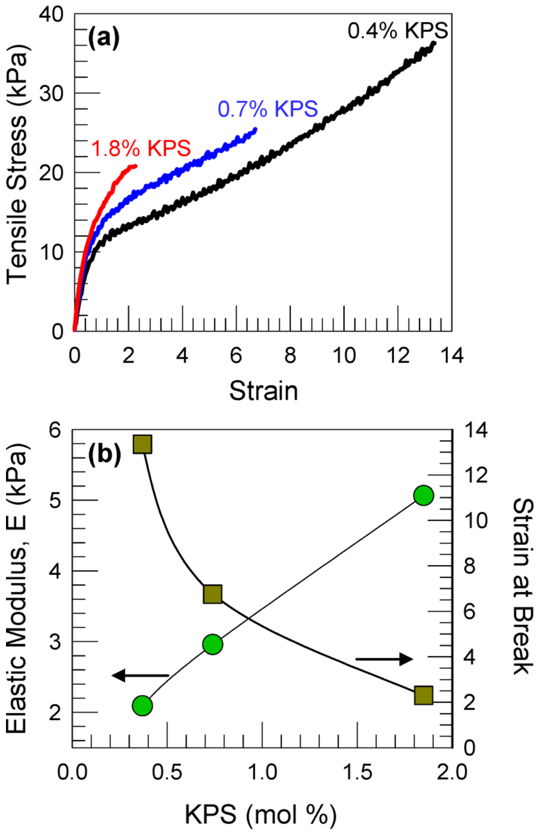


Figure 4. Tensile tests on unswollen DMAA gels. (a) The tensile stress is plotted as a function of tensile strain for three gels with a constant DMAA content of 33 wt % and varying KPS concentrations, as indicated in the plot. Each curve ends at the point where the sample breaks. The gels at low KPS show significant extensibility before break. (b) Properties extracted from the above curves are plotted against the KPS concentration. From the linear region of each curve, the elastic modulus is calculated, and from the break point, the elongation (strain) at break is obtained. At low KPS, the gels have low modulus and high extensibility.

break (Figure 4b) decreases from 1350% to 200% over the same range of KPS. The increase in modulus reflects the increase in cross-link density with KPS concentration. It is significant that the elongation at break exceeds 1000% at low KPS levels, which shows the high extensibility of these gels. This is also revealed by the photograph in Figure 1c.

Characterization of DMAA-SA Superabsorbent Gels. Next, we turned our attention to creating ionic gels containing DMAA. In these cases, the reaction mixture comprises the DMMA and SA monomers, KPS initiator, and TEMED accelerant. Once again, no multifunctional monomers are used, and so the gels are formed by the self-cross-linking mechanism discussed earlier. We fixed the total polymer content at 33 wt %, with DMAA as the major component (80−95 mol %) and SA as the minor component (5−20 mol %). KPS was used at a relatively low level of 0.4 mol %. Figure 5a illustrates the superabsorbent nature of these gels. The photograph here is for a 80/20 mole ratio of DMAA/SA. The initial unswollen network is the small (~15 mm diameter) disk. When placed into deionized water at ambient temperature, the gel swells substantially and the diameter increases by a factor of about 10. The swelling ratio Q (eq 1) for this gel is 3000. To our knowledge, this is the highest swelling ratio for any hydrogel that has been reported so far. Swelling ratios reported for other gels are at least a factor of 2 lower.[6−9]

Figure 6 plots the equilibrium swelling ratio Q of DMAA/SA gels as a function of the SA content (0−20 mol %) (other variables as above, i.e., overall polymer at 33 wt %, KPS at 0.4 mol %). In each case, gels were placed in water and left to swell until there was no further change in gel volume. When no ionic monomer is present, we have the nonionic DMAA gel, which exhibits a Q of about 48. It is only when SA is included along with the DMAA that the gels become superabsorbent. For 10 mol % SA Q exceeds 1000, and for 20 mol % SA Q is 3000. Note that these gels take a long time (~24 h) to reach swelling equilibrium.

Next we discuss the mechanical properties of the DMAA-SA superabsorbent gels. The gels are still quite robust, even when swollen, in contrast to conventional gels. For example, Figure 5b shows that a swollen DMAA-SA gel (swelling ratio ~150) can still be grasped in two hands. Note that this is quite remarkable because the material being held is >99% water and <1% polymer. Typical ionic gels such as those based on AAm and SA tend to be very fragile in their swollen state, making them difficult to handle (or if they are highly cross-linked to improve their mechanical properties, they do not swell as much).

We attempted to quantify the differences in tensile properties in the swollen state between a self-cross-linked DMAA-based gel and a conventional AAm-based chemically cross-linked gel. These measurements are difficult to perform because swollen gels cannot be easily gripped by the fixtures of the Instron instrument. To obtain a fair basis for comparison, we prepared two such gels with the *same degree of swelling*: a 33 wt % DMAA gel self-cross-linked with 0.4 mol % KPS and an AAm-SA-BIS gel with 92 mol % AAm, 5 mol % SA, and 3 mol % BIS cross-linker (total monomer content of 1 M or ~7 wt %). Both gels display a swelling ratio Q ~ 70 in water at ambient pH. (The selection of these compositions was done using the data in Figures S3 and S4.) Note that, while the gels have different polymer concentrations initially, the polymer content is about the same in both cases when the gels are completely swollen.

Figures 7a and 7b compare the tensile properties of the two gels in the unswollen and swollen states, respectively. The unswollen DMAA gel is highly stretchable and exhibits the stress−strain profile shown earlier in Figure 4. It has an elastic modulus around 2.5 kPa and an elongation at break of 13.5 strain units or 1350%. In comparison, the unswollen AAm-SA-BIS gel has a 10-fold higher modulus (around 25 kPa), but it ruptures at a strain of 100%. These results for the AAm-SA-BIS gel are consistent with those reported in the literature for such conventional chemically croslinked gels. Next, the same gels are compared in their swollen states (Q ~ 70). In this case, the tensile curves have a jagged appearance due to the difficulty in clamping these gels to the instrument while testing. However, the same trend is seen to persist. In this case, the swollen DMAA gel is extensible up to a strain of nearly 400% before breaking, whereas the swollen AAm-SA-BIS gel ruptures at a strain of just 50%. In the swollen states, the moduli of the gels are reduced relative to their unswollen values (~18 kPa for the AAm-SA-BIS gel and ~1 kPa for the DMAA gel). Note also that the stress−strain curve of the DMAA gel is almost linear, which suggests that the tensile response is elastic over the range of deformations. That is, the gel retracts to about its original length when the strain is removed. Lastly, we should point out the differences in tensile toughness (area under the stress−

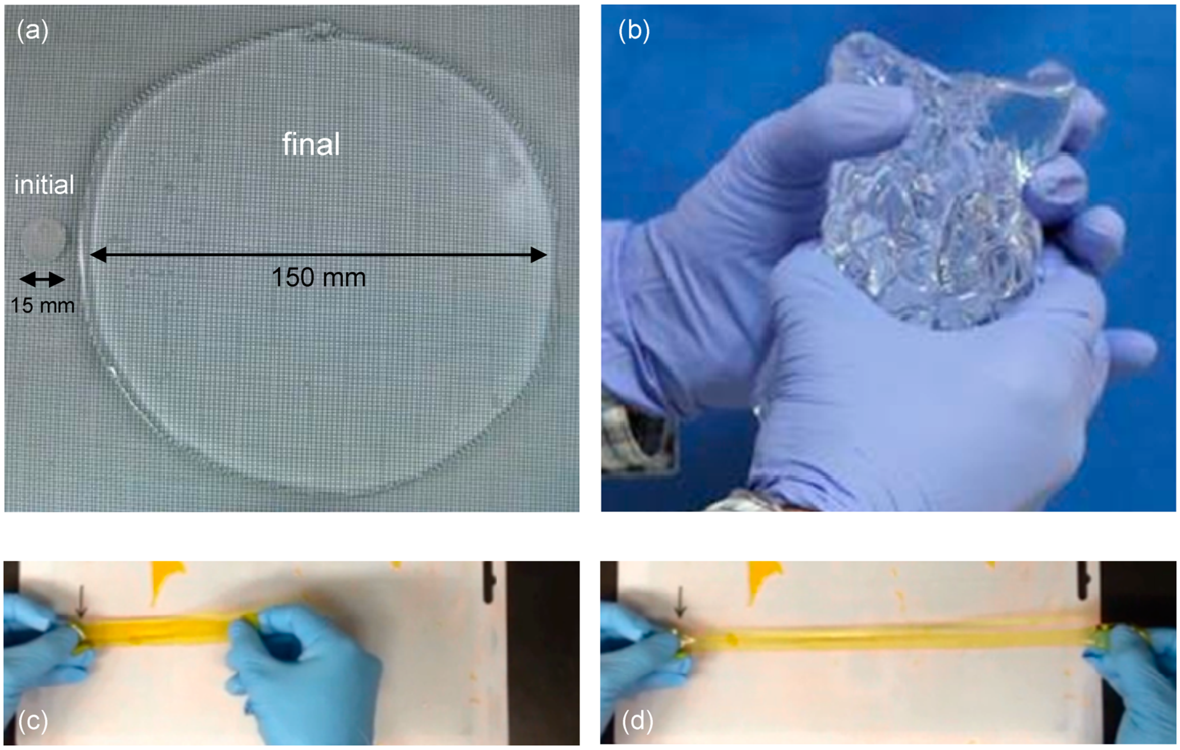


Figure 5. Photographs demonstrating the properties of swollen DMAA-SA gels. (a) An 80/20 DMAA/SA gel self-cross-linked with 0.4 mol % KPS is shown to be superabsorbent. The initial as-prepared gel is a disk of 15 mm diameter, and it swells to about 10 times its size when placed in water. The swelling ratio (mass of swollen gel/mass of dry network) is 3000 for this case. (b) A 99/1 DMAA/SA gel swollen in water is robust enough that it can be held in one's hands. This gel has a swelling ratio of about 150, implying that it is >99% water and <1% polymer. (c, d) A swollen strip of DMAA gel (swelling ratio 70) is stretched manually by hand (these are still images from Movie 1). As shown in (d), the gel can be stretched substantially (the movie reveals that the stretching can be done up to >300% strain). Also, the movie shows that the gel retracts to its original length when released.

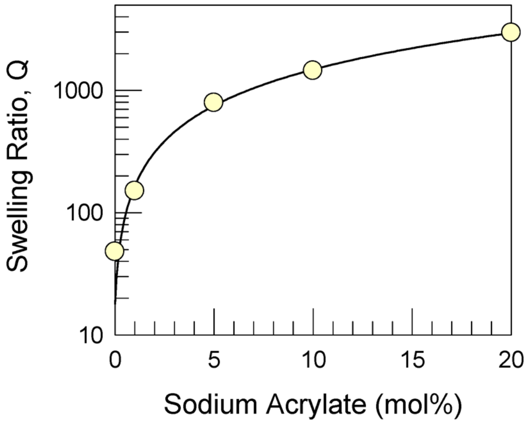


Figure 6. Swelling ratio of DMAA-SA gels as a function of the mol % SA in the mixture. The overall monomer content is 33 wt %, and the gels are self-cross-linked using 0.4 mol % KPS. The swelling ratio (mass of swollen gel/mass of dry gel) exceeds 1000 for SA above 10 mol %, indicating superabsorbency. The line through the data is drawn to guide the eye.

strain curve) for the two above gels. The DMAA gel has a toughness of about 320 kJ/m^3 in its unswollen state, which is about 30 times higher than that of the AAm-SA-BIS gel. In the swollen state, the toughness of the DMAA gel is about 8 kJ/m^3, which is about 4 times that of the AAm-SA-BIS gel.

We have further confirmed the differences in tensile properties between the above two swollen gels in a manual stretching experiment, shown in Movie 1 (Supporting Information). In this experiment, each gel is held by hand at its ends and stretched in one direction until it breaks. The movie confirms that the swollen AAm-SA-BIS gel breaks at a low deformation, whereas the swollen DMAA gel is able to be stretched up to 4 times its original length before breaking. These findings are consistent with the data in Figure 7b. Snapshots of the DMAA gel from this movie (before and during stretching) are shown in Figures 5c and 5d. The movie also shows that when the DMAA gel breaks, the main piece retracts to its original size, indicating near-elastic behavior. This observation is again consistent with the linearity of the data for the DMAA gel in Figure 7b.

Finally, we discuss the reasons behind the unusual mechanical properties of self-cross-linked DMAA and DMAA-SA gels when compared with conventional gels that employ multifunctional monomers (i.e., AAm-BIS and AAm-SA-BIS). We believe these differences reflect the *distribution of cross-links* in the two types of networks.[10,11] In AAm-BIS gels, there are likely to be differences in reactivity ratio beteween the bifunctional (AAm) and multifunctional (BIS) monomers.[8] This will lead to an inhomogeneous distribution of cross-links, with a wide range of chain segment lengths between adjacent cross-links.[21] As noted in the Introduction, when such gels are deformed, zones of high stress will be created that will ultimately lead to rupture of the gel at low deformations. In the case of self-cross-linked DMAA gels, however, there is no separate multifunctional monomer with a different reactivity ratio. Cross-linking occurs due to reactive radicals introduced by the initiator KPS, and the bonds are formed between

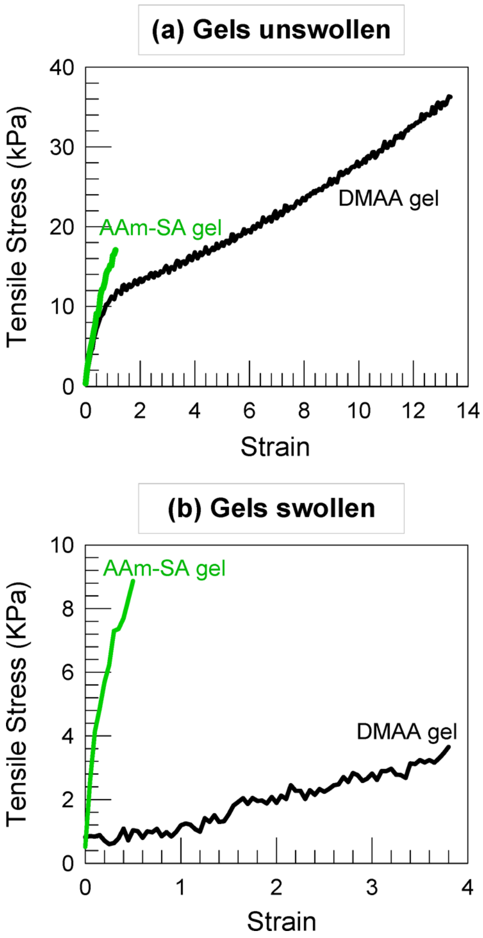


Figure 7. Tensile tests on DMAA and AAm-SA-BIS gels in the unswollen and swollen states. Two gels are compared: one a gel of 33 wt % DMAA self-cross-linked with 0.4 mol % KPS and the other an AAm-SA-BIS gel with 92 mol % AAm, 5 mol % SA, and 3 mol % BIS (total monomers ~7 wt %). The gels have the same swelling ratio of ~70. The tensile stress is plotted as a function of tensile strain for the two gels in (a) the unswollen and (b) the swollen state. Each curve ends at the point where the sample breaks. In both cases, the DMAA gel is seen to be much more extensible than the AAm-SA-BIS gel.

growing DMAA chains.[23,24] We therefore expect the cross-linking to be incorporated more homogeneously throughout the DMAA network. In turn, when a DMAA gel is deformed, stress will be distributed more uniformly across the material, and there will be fewer weak zones created by high local stress. This could explain why a DMAA gel is more robust and able to withstand high deformations without rupturing.

A further intriguing aspect is the extent of viscous dissipation within the two types of gels. As shown by Figure 2 and Figure S1, tan δ is an order or magnitude higher for a DMAA gel than for an AAm-BIS gel (even though the elastic moduli are comparable). This implies that there is a mode of viscous dissipation in DMAA gels that is absent in conventional gels. We suggest that this mode could arise because the chain segments between adjacent cross-link points in a DMAA network are relatively long and uniform. In such a case, small deformations (within the linear viscoelastic regime) may get transmitted through the gel partially through the straightening or uncoiling of chain segments, which is expected to be a dissipative (viscous) process.[21] The elasticity still arises due to the connectivity of all the segments in the network. In contrast, we speculate that stress in an AAm-BIS gel is transmitted via relatively shorter (and hence more taut or rigid) chain segments, which will tend to store rather than dissipate the stress.[21] (That is, when there is a wide distribution of segment lengths, the shorter segments may disproportionately carry much of the load.) Taking the above reasoning further, *we can speculate that robust and highly extensible gels will tend to have a more viscous nature*, as measured by tan δ. For example, tan δ may be $O(0.1)$ for robust gels whereas it may be much lower, e.g., $O(0.01)$, for brittle gels. This hypothesis can be easily tested in the future for different classes of robust gels.

4. CONCLUSIONS

In this work, we have reported the formation of DMAA hydrogels in the absence of added multifunctional cross-linkers. Compared to conventional gels prepared by chemical cross-linking (such as AAm-BIS), we find that DMAA gels are much more robust and extensible. DMAA gels can also be formulated in the presence of ionic comonomers such as SA and the resulting hydrogels exhibit remarkable swelling ability in water (swelling ratios up to 3000). Moreover, a comparison of DMAA-SA and AAm-SA-BIS gels shows that the DMAA-based gels have better mechanical properties even in the swollen state. We propose that self-cross-linking in DMAA gels creates a more homogeneous distribution of cross-linking points and that this underlies their improved mechanical properties. Homogeneous cross-linking ensures that there will be no "weak spots" created by high local stress when the gel is deformed. Additionally, we have found that DMAA gels show a moderate extent of viscous dissipation, as measured by the loss tangent tan δ. This dissipative mode is largely absent in conventional AAm-BIS gels. In turn, we speculate that a moderate tan δ, possibly $O(0.1)$, may be a hallmark of various types of robust gels.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional data on the gels, as described in the paper, and Movie 1 showing the stretching of a swollen gel. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Tanaka, T. Gels. *Sci. Am.* **1981**, *244*, 124−138.

(2) Osada, Y.; Gong, J. P.; Tanaka, Y. Polymer gels. *J. Macromol. Sci., Polym. Rev.* **2004**, *C44*, 87−112.

(3) Laftah, W. A.; Hashim, S.; Ibrahim, A. N. Polymer hydrogels: A review. *Polym.-Plast. Technol. Eng.* **2011**, *50*, 1475−1486.

(4) Lee, K. Y.; Mooney, D. J. Hydrogels for tissue engineering. *Chem. Rev.* **2001**, *101*, 1869−1879.

(5) Peppas, N. A.; Hilt, J. Z.; Khademhosseini, A.; Langer, R. Hydrogels in biology and medicine: From molecular principles to bionanotechnology. *Adv. Mater.* **2006**, *18*, 1345−1360.

(6) Zohuriaan-Mehr, M. J.; Omidian, H.; Doroudiani, S.; Kabiri, K. Advances in non-hygienic applications of superabsorbent hydrogel materials. *J. Mater. Sci.* **2010**, *45*, 5711−5735.

(7) Zohuriaan-Mehr, M. J.; Kabiri, K. Superabsorbent polymer materials: A review. *Iran Polym. J.* **2008**, *17*, 451−477.

(8) Buchholz, F. L. Preparation methods of superabsorbent polyacrylates. In *Superabsorbent Polymers: Science and Technology*; Buchholz, F. L., Peppas, N. A., Eds.; American Chemical Society: Washington, DC, 1994; Vol. *573*; pp 27−38.

(9) Lee, W. F.; Wu, R. J. Superabsorbent polymeric materials. 1. Swelling behaviors of crosslinked poly(sodium acrylate-co-hydroxyethyl methacrylate) in aqueous salt solution. *J. Appl. Polym. Sci.* **1996**, *62*, 1099−1114.

(10) Peak, C. W.; Wilker, J. J.; Schmidt, G. A review on tough and sticky hydrogels. *Colloid Polym. Sci.* **2013**, *291*, 2031−2047.

(11) Zhao, X. H. Multi-scale multi-mechanism design of tough hydrogels: building dissipation into stretchy networks. *Soft Matter* **2014**, *10*, 672−687.

(12) Gong, J. P.; Katsuyama, Y.; Kurokawa, T.; Osada, Y. Double-network hydrogels with extremely high mechanical strength. *Adv. Mater.* **2003**, *15*, 1155−1160.

(13) Haraguchi, K.; Farnworth, R.; Ohbayashi, A.; Takehisa, T. Compositional effects on mechanical properties of nanocomposite hydrogels composed of poly(N,N-dimethylacrylamide) and clay. *Macromolecules* **2003**, *36*, 5732−5741.

(14) Haraguchi, K.; Li, H. J. Mechanical properties and structure of polymer-clay nanocomposite gels with high clay content. *Macromolecules* **2006**, *39*, 1898−1905.

(15) Yang, W.; Furukawa, H.; Gong, J. P. Highly extensible double-network gels with self-assembling anisotropic structure. *Adv. Mater.* **2008**, *20*, 4499−4503.

(16) Xiao, L. X.; Liu, C.; Zhu, J. H.; Pochan, D. J.; Jia, X. Q. Hybrid, elastomeric hydrogels crosslinked by multifunctional block copolymer micelles. *Soft Matter* **2010**, *6*, 5293−5297.

(17) Lin, W. C.; Fan, W.; Marcellan, A.; Hourdet, D.; Creton, C. Large strain and fracture properties of poly(dimethylacrylamide)/silica hybrid hydrogels. *Macromolecules* **2010**, *43*, 2554−2563.

(18) Hao, J. K.; Weiss, R. A. Viscoelastic and mechanical behavior of hydrophobically modified hydrogels. *Macromolecules* **2011**, *44*, 9390−9398.

(19) Sun, J. Y.; Zhao, X. H.; Illeperuma, W. R. K.; Chaudhuri, O.; Oh, K. H.; Mooney, D. J.; Vlassak, J. J.; Suo, Z. G. Highly stretchable and tough hydrogels. *Nature* **2012**, *489*, 133−136.

(20) Tuncaboylu, D. C.; Sahin, M.; Argun, A.; Oppermann, W.; Okay, O. Dynamics and large strain behavior of self-healing hydrogels with and without surfactants. *Macromolecules* **2012**, *45*, 1991−2000.

(21) Cui, J.; Lackey, M. A.; Madkour, A. E.; Saffer, E. M.; Griffin, D. M.; Bhatia, S. R.; Crosby, A. J.; Tew, G. N. Synthetically simple, highly resilient hydrogels. *Biomacromolecules* **2012**, *13*, 584−588.

(22) Kamogawa, H.; Sekiya, T. Crosslinking of copolymers of N-methylolacrylamide and ethyl acrylate induced by heat treatment. *J. Polym. Sci.* **1961**, *50*, 211−225.

(23) Needles, H. L.; Whitfield, R. E. Free-radical chemistry of peptide bonds. I. Dealkylation of substituted amides. *J. Org. Chem.* **1964**, *29*, 3632−&.

(24) Needles, H. L.; Whitfiel, Re. Crosslinking of copolymers containing N,N-dimethylacrylamide. *J. Polym. Sci., Part A: Gen. Pap.* **1965**, *3*, 3543−3548.

(25) Larson, R. G. *The Structure and Rheology of Complex Fluids*; Oxford University Press: Oxford, 1999.

(26) Krishnan, S.; Klein, A.; El-Aasser, M. S.; Sudol, E. D. Influence of chain transfer agent on the cross-linking of poly(n-butyl methaerylate-co-N-methylol acrylamide) latex particles and films. *Macromolecules* **2003**, *36*, 3511−3518.

(27) Ilangovan, V. Vibrational Spectra, Assignments and Analysis of Some Amino Compounds. Pondicherry University, 1993.

(28) Raghavan, S. R.; Cipriano, B. H. Gel formation: Phase diagrams using tabletop rheology and calorimetry. In *Molecular Gels*; Weiss, R. G., Terech, P., Eds.; Springer: Dordrecht, 2005; pp 233−244.

Supporting Information for

Superabsorbent Hydrogels that are Robust and Highly Stretchable

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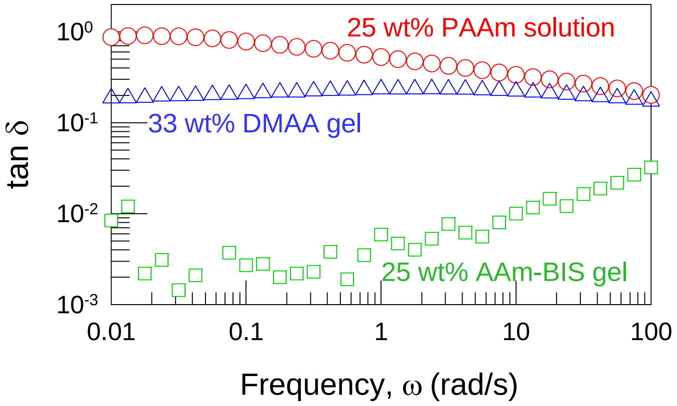

Figure S1. Loss tangent tan δ vs. frequency for (a) solution of 25 wt% AAm polymerized without crosslinker. (b) 33 wt% DMAA, self-crosslinked into a gel using 1 mol% KPS initiator; and (c) 25 wt% AAm crosslinked with 0.1% BIS to yield a conventional gel. The data correspond to the plots shown in Figure 2.

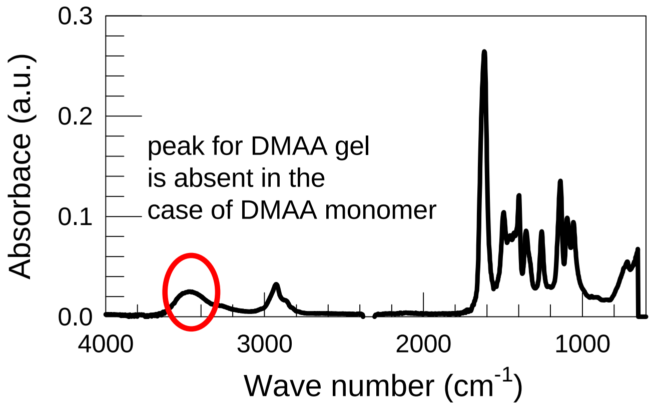

Figure S2. Data from Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy for a DMAA gel of thickness 1 mm that was air-dried overnight and scanned using a Thermo Nicolet NEXUS 670 instrument. The presence of a peak at 3400 cm^{-1} is indicative of self-crosslinking. See text for details.

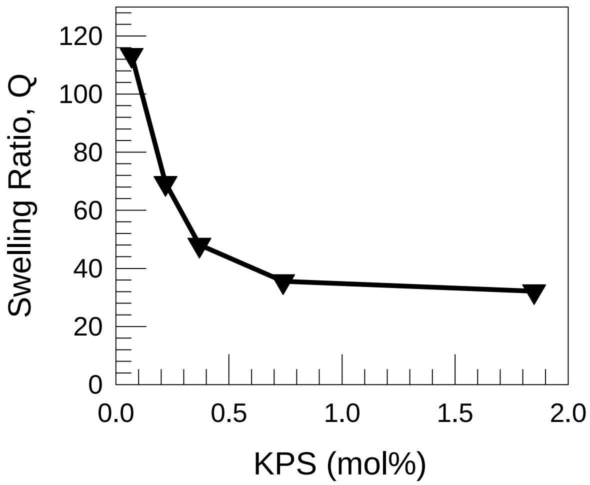

Figure S3. Swelling ratio vs. KPS initiator concentration for 33 wt% DMAA gels (with no ionic comonomer). Higher swelling ratios are observed at lower KPS concentrations, which correspond to lower crosslink densities.

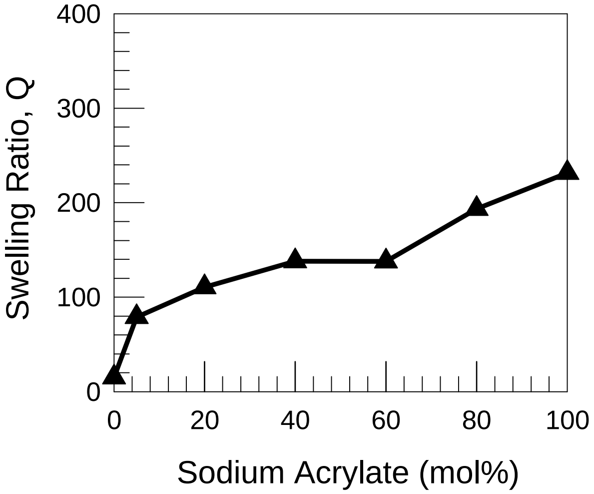

Figure S4. Swelling ratio of AAm-SA-BIS gels containing various levels of sodium acrylate. The total monomer concentration was fixed at 1 M and the mol% of BIS was maintained constant at 3 mol% relative to total monomer.