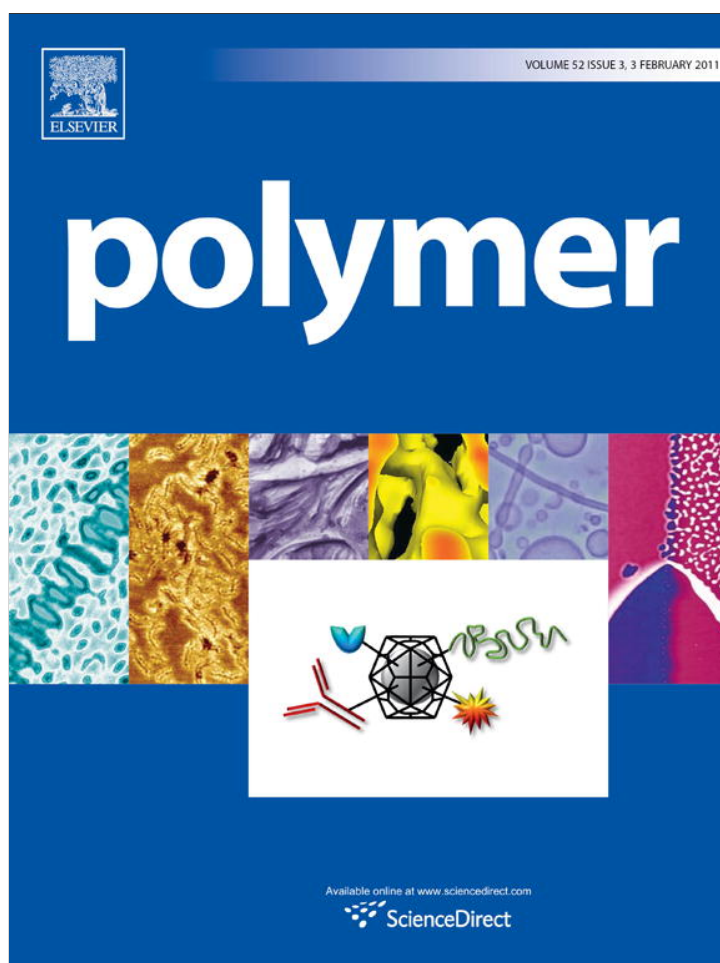


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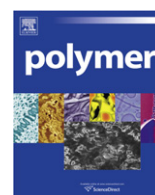


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# Dodecyl methacrylate as a crosslinker in the preparation of tough polyacrylamide hydrogels

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## ABSTRACT

Copolymerization of acrylamide with dodecyl methacrylate (C12) solubilized in aqueous micelles of sodium dodecyl sulfate produces tough hydrogels exhibiting moduli of elasticity around 1 kPa. Swelling and gel fraction measurements show that the hydrophobic associations acting as temporary crosslinks are too strong to be destroyed in water during the expansion of the gel network. An order of magnitude larger value of loss factor  $\tan \delta$  of the hydrogels formed using the hydrophobe C12 as compared to the conventional hydrogels indicates the dynamic nature of their crosslink zones. The hydrogels are more homogeneous than the corresponding gels prepared by a chemical crosslinker, as determined by the static light scattering measurements. Mechanical tests indicate that, in addition to the dodecyl domains, permanent crosslinks are also needed to obtain hydrogels that are mechanically stable up to 250% elongation ratios.

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## 1. Introduction

Although synthetic hydrogels resemble natural biological soft materials, their mechanical properties greatly differ from those of biological gels [1]. For example, conventional hydrogels formed by free-radical crosslinking copolymerization are normally very brittle when handled in the swollen state, which limits their technological applications. This feature originates from the very low resistance of chemical hydrogels to crack propagation due to the lack of an efficient energy dissipation mechanism in the gel network [2–4]. To obtain a hydrogel with a high degree of toughness, one has to increase the overall viscoelastic dissipation along the gel sample by introducing dissipative mechanisms at the molecular level. A number of techniques for toughening of gels have been proposed including the double network gels [5–7], topological gels [8], nanocomposite hydrogels [9], and cryogels [10]. Hydrogels with improved mechanical properties were also prepared using gamma-ray induced polymerization of micellar solutions containing a surfmer and *N*-isopropylacrylamide (NIPAAm) [11]. The blocks of polymerized surfmer form micellar aggregates acting as physical crosslinks while slightly crosslinked blocks of poly(NIPAAm) connect the individual micelles.

We have recently shown that hydrophobically modified chemically crosslinked polyacrylamide (PAAm) hydrogels prepared by

micellar polymerization technique exhibit a high degree of toughness, i.e., a very large extensibility at break [12]. Incorporation of hydrophobes with an alkyl chain length  $x > 4$  into hydrophilic PAAm network chains results in an increase in the viscous modulus of hydrogels due to the formation of associations inside the gel network. However, in addition to the hydrophobic comonomer with alkyl chain lengths between 4 and 8 carbons, a chemical crosslinker was also used in the gel preparation to prevent the solubility of the resulting hydrogels [12]. Here, we used dodecyl methacrylate (C12) as the hydrophobic comonomer in the micellar copolymerization of acrylamide in the absence of a crosslinker. As will be seen below, the presence of a small amount of C12 in the comonomer feed leads to the formation of hydrogels with a gel fraction above 0.80. This highlights a new route for the preparation of high-toughness hydrogels without using a chemical crosslinker.

## 2. Experimental section

### 2.1. Materials

Acrylamide (AAm, Merck), dodecyl methacrylate (C12, Fluka), *N,N'*-methylenebis(acrylamide) (BAAm, Merck), sodium dodecyl sulfate (SDS, Sigma), ammonium persulfate (APS, Fluka), and *N,N,N',N'*-tetramethylethylenediamine (TEMED, Fluka) were used as received. The hydrogels were prepared by free-radical micellar copolymerization of AAm and the hydrophobic comonomer C12 in aqueous SDS solutions at 25 °C. For comparison, polymerization

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reactions were also carried out in the presence of the chemical crosslinker BAAm. The concentration of SDS in the reaction solution was 7 w/v % which is much above its critical micelle concentration (0.25 w/v %) [13]. The initial concentration of the total monomer was set to 5 w/v % throughout the experiments while the hydrophobe content in the comonomer mixture was varied between 0 and 10 mol %. APS (3.5 mM) and TEMED (0.25 mL/100 mL reaction solution) were used as the redox initiator system. Polymerization reactions were carried out in plastic syringes of 4 and 10 mm internal diameters as well as between the parallel plates of the rheometer (Gemini 150 Rheometer system, Bohlin Instruments) equipped with a Peltier device for temperature control. The synthetic procedure was similar to that given in our previous publication [12] (see Supplementary data for details).

## 2.2. Characterization

The hydrogels formed within the rheometer were subjected to frequency-sweep tests at a deformation amplitude  $\gamma_0 = 0.01$  over the frequency ( $\omega$ ) range  $10^{-2}$  to  $10^1$  rad/s both in up and down directions. They were also subjected to stress–relaxation experiments at 25 °C. An abrupt shear deformation of controlled strain amplitude  $\gamma_0$  was applied to the gel samples and the resulting stress  $\sigma(t, \gamma_0)$  was monitored as a function of time. The time  $t$  after application of step deformation represents a time scale that describes the motion of the PAAm strands in the network and is equivalent to the inverse of the frequency  $\omega$  in an oscillatory test [14]. Here, we report the relaxation modulus  $G(t, \gamma_0)$  as functions of the relaxation time  $t$  and strain amplitude  $\gamma_0$ . The experiments were conducted with increasing strain amplitudes  $\gamma_0$  from 0.01 to 10. For each gel, stress–relaxation experiments at various  $\gamma_0$  were conducted starting from a value of the relaxation modulus deviating less than 10% from the modulus measured at  $\gamma_0 = 0.01$ .

Cylindrical hydrogel samples prepared within the syringes were subjected to tensile mechanical tests as well as to swelling measurements, as described before [12]. During the swelling period of the hydrogels, the concentration of SDS extracted from the gel phase was estimated using the methylene blue (MB) method [15]. The optical absorbance of the chloroform phase was measured at 650 nm with a T80 UV–vis spectrophotometer. The conversion of monomers to the crosslinked polymer (mass of crosslinked

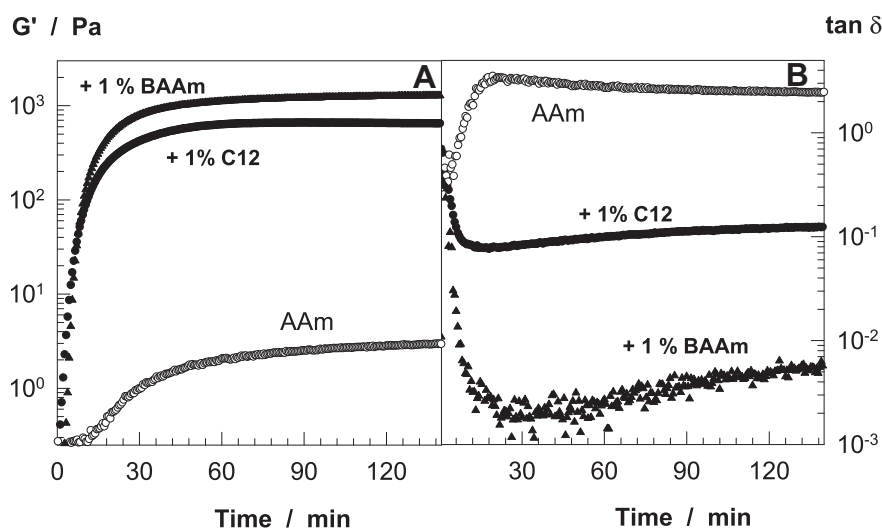
polymer/initial mass of the monomer) was calculated from the masses of dry, extracted polymer network and from the comonomer feed.

The light scattering measurements were carried out at 24 °C using a commercial multi-angle light scattering DAWN EOS (Wyatt Technologies Corporation) equipped with a vertically polarized 30 mW Gallium–arsenide laser operating at  $\lambda = 690$  nm and 18 simultaneously detected scattering angles. The light scattering system was calibrated against a toluene standard. The scattered light intensities from gels were recorded from  $42.8^\circ$  to  $142.5^\circ$ , which correspond to the scattering vector  $q$  range  $8.8 \times 10^{-4}$ – $2.3 \times 10^{-3}$  Å<sup>-1</sup>, where  $q = (4\pi n/\lambda)\sin(\theta/2)$ ,  $\theta$  the scattering angle,  $\lambda$  the wavelength of the incident light in vacuum,  $n$  the refractive index of the medium. The gels subjected to the measurements were prepared in the light scattering cuvettes. The reaction solutions were filtered through membrane filters (pore size = 0.2  $\mu\text{m}$ ) directly into the cuvettes. For calculation of excess scattering from gels, all the micellar polymerizations were repeated under the same experimental conditions except that the hydrophobe C12 was not used. Excess scattering intensities from gels  $R_{\text{ex}}(q)$  were calculated as  $R_{\text{ex}}(q) = R_{\text{gel}}(q) - R_{\text{sol}}(q)$ , where  $R_{\text{gel}}(q)$  and  $R_{\text{sol}}(q)$  are the Rayleigh ratios for gel and polymer solution, respectively.

## 3. Results and discussion

### 3.1. Hydrophobic associations instead of permanent crosslinks

We first monitored the micellar polymerization of acrylamide (AAm) with and without the hydrophobe C12 by real-time rheological measurements. Fig. 1A and B show the elastic modulus  $G'$  and the loss factor  $\tan \delta$  during the micellar polymerization of AAm alone and with 1 mol % C12. For comparison,  $G'$  and  $\tan \delta$  during the micellar polymerization of AAm in the presence of 1 mol % chemical crosslinker BAAm are also shown in the figures. In the absence of the hydrophobe (open symbols), AAm polymerization leads to the formation of a polymer solution with an elastic modulus of a few Pascal's and a loss factor larger than unity. Addition of 1 mol % C12 into the comonomer feed drastically changes the reaction profile (filled circles); the elastic modulus  $G'$  rapidly increases with the onset of the reactions and, a viscoelastic gel with  $G'$  in the order of  $10^3$  Pa and with a loss factor around 0.1 was obtained. This indicates



**Fig. 1.** Elastic modulus  $G'$  (A) and the loss factor  $\tan \delta$  (B) during the micellar polymerization of AAm alone (open symbols), with 1 mol % C12 (filled circles), and 1 mol % BAAm (filled triangles).  $\omega = 6.28$  rad/s.  $\gamma_0 = 0.01$ .

formation of hydrophobic associations in the solution acting as crosslink zones between the polymer chains. Fig. 1 also shows that the effect of the chemical crosslinker BAAM is similar to that of the hydrophobe C12, except that  $\tan \delta$  obtained using BAAM is about one order of magnitude smaller than that obtained using C12. For the present system containing hydrophobic associations,  $\tan \delta$  may be considered as the ratio of crosslinks being broken down and reconstituted during dynamic strains to those remaining intact and unchanged. An order of magnitude larger value of  $\tan \delta$  of hydrogels formed by hydrophobic associations thus indicates dynamic nature of their crosslink zones.

Fig. 2A shows the mechanical spectra of solutions of PAAm with 0, 1 and 5 mol % C12 prepared under the same experimental conditions. PAAm solution prepared in the absence of C12 exhibits a liquid-like response typical for a semi-dilute polymer solution, i.e.,  $G''$  exceeds  $G'$  at low frequency while there is a crossover between  $G'$  and  $G''$  at a high frequency. Incorporation of 1 mol % dodecyl groups into the PAAm backbone shifts the crossover frequency from  $10^2$  to  $10^{-2}$  rad/s indicating formation of strong and long lived associations between the blocks of dodecyl groups in the semi-dilute solution. Recent light scattering results of Ivanova et al indeed show formation of strong associations in solutions of PAAm's with 2–5 mol % C12 [16]. Moreover, increasing C12 content from 1 to 5 mol % increases both  $G'$  and  $G''$  and the crossover frequency shifts outside of the experimental window. The solid curve in Fig. 2A shows  $G'$  versus frequency plot of the chemically crosslinked gel with 1 mol % BAAM;  $G'$  of the chemical gel is independent of frequency while  $G''$  remains on a low level less than three orders of magnitude smaller than  $G'$  (not shown in the figure). Comparison of the results obtained using C12 and BAAM indicates that the gels behave similar at short experimental time scales while deviations appear at frequencies below 0.8 rad/s corresponding to time scales longer than 1.2 s.

Swelling tests showed that the gels were insoluble in water if C12 concentration in the comonomer feed was 3 mol % or above. As seen in Fig. 2B where the relative swelling ratio  $m_{rel}$  (swollen gel mass/mass of gel after preparation) is plotted against the swelling time of the hydrogels,  $m_{rel}$  rapidly increases and, after attaining a maximum, it decreases again until it reaches a limiting value after about 17d. It was found that, during the initial swelling period, namely up to 100 h of swelling time, SDS exists in the external

solution whose concentration rapidly decreases below the detection limit (0.20 mg/L) after 200 h. Thus, large swelling ratios at short times and the appearance of maxima in the swelling curves are due to the osmotic pressure of the counterions of SDS, converting the gels into polyelectrolyte ones. However, as the swelling time is increased, SDS moves from the gel to the solution phase so that the swelling ratio decreases again until attaining an equilibrium value at long times. Equilibrium swelling ratio measurements showed that  $m_{rel}$  is equal to  $0.6 \pm 0.1$  for C12 contents between 4 and 8% while gel fraction was above 0.80. The results indicate that the hydrophobic associations are too strong to be destroyed in water during the expansion of the gel network and hydrogels could be obtained without a chemical crosslinker.

A characteristic feature of the conventional gels prepared by a chemical crosslinker is the inhomogeneous distribution of the crosslink density, known as the spatial gel inhomogeneity [17,18]. Since the incorporation of mobile crosslink zones into the gel network may reduce the spatial gel inhomogeneity [19,20], the microstructure of the hydrogels formed by the hydrophobe C12 was investigated by static light scattering technique. Fig. 3A shows the excess scattering  $R_{ex}(q)$  for gels prepared with 3–5 mol % C12 plotted as a function of the scattering vector  $q$ . For comparison, Fig. 3B shows  $R_{ex}(q)$  vs.  $q$  plots reported for chemically crosslinked PAAm hydrogels of comparable moduli of elasticity prepared at three different BAAM concentrations [21,22]. The chemical gels were prepared at the same monomer concentration as the present gels. We see that, both covalently and non-covalently crosslinked hydrogels exhibit excess scattering  $R_{ex}(q)$  in the range of  $10^{-4} \text{ cm}^{-1}$ . The scattering curves of chemical gels are rather flat, while those of physical gels show a considerable  $q$ -dependence, indicating the presence of correlations on a much larger length scale than observed in the former gels. Further, for the chemical gels, increasing BAAM content increases both the elastic modulus and the excess scattering. This is expected due to the fact that the spatial fluctuations of polymer concentration are amplified with increasing crosslink density [17,18]. In contrast, however, although the excess scattering increases with increasing C12 content from 3 to 5% and the gels became opaque above 5% C12, the elastic modulus does not change much. This means that the presence of 3 mol % C12 suffices to obtain a hydrogel with an elastic modulus between 1 and 2 kPa, while additional amounts of C12 enhance the

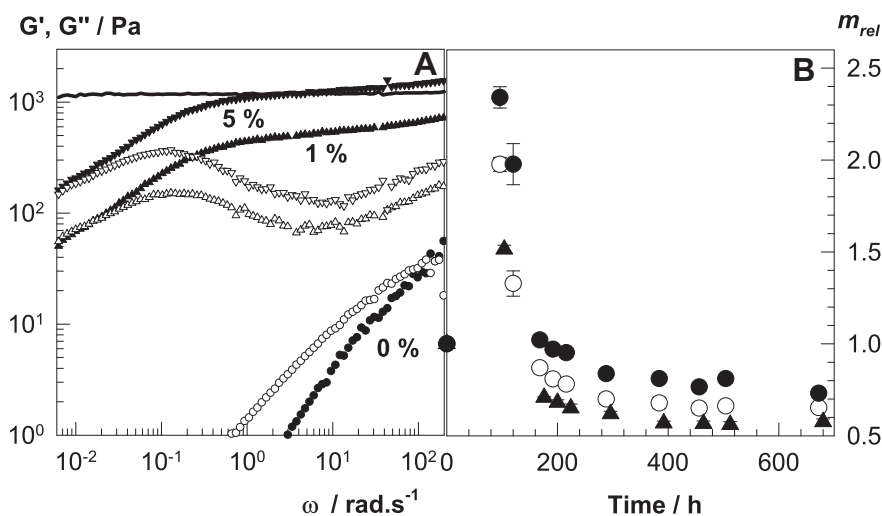
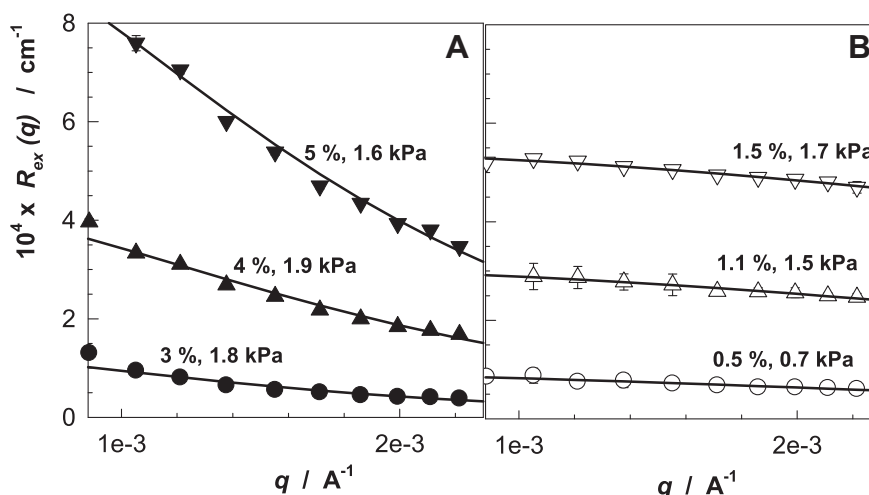


Fig. 2. (A):  $G'$  (filled symbols) and  $G''$  (open symbols) of PAAm solutions with 0 (circles), 1 (triangles up) and 5 mol % C12 (triangles down) shown as a function of the frequency  $\omega$ . For comparison,  $G'$  versus  $\omega$  plot of PAAm gel formed using 1 mol % BAAM is also shown by the solid curve.  $\gamma_0 = 0.01$ . (B): Relative weight swelling ratio  $m_{rel}$  of hydrogels shown as a function of the swelling time. C12 = 4 (○), 6 (●), and 7 mol % (▲).



**Fig. 3.** Excess scattering intensities  $R_{\text{ex}}(q)$  shown as a function of the scattering vector  $q$  for PAAm gels formed by the hydrophobe C12 (A) and the crosslinker BAAM (B). The gels are at the state just after their preparation. C12 = 3 (●), 4 (▲), and 5 mol % (▼). BAAM = 0.54 (○), 1.1 (△), and 1.5 mol % (▽). The elastic moduli of gels are indicated. The data of the chemical PAAm gels were taken from Refs. [21,22]. The solid curves are calculation results using eq.(1).

gel inhomogeneities. As a consequence,  $R_{\text{ex}}(q)$  of gels formed at 3% C12 is much smaller than that of the chemical gels of the same crosslink density.

To interpret the excess scattering data of gels, Debye–Bueche (DB) equation was used [23–25]:

$$R_{\text{ex}}(q) = \frac{4\pi K \xi^3 \langle \eta^2 \rangle}{(1 + q^2 \xi^2)^2} \quad (1)$$

where  $K$  being the optical constant,  $K = \pi^2 n^2 \lambda^{-4}$ ,  $\xi$  is the correlation length of the scatterers, and  $\langle \eta^2 \rangle$  is the mean square fluctuation of the refractive index. According to eq. (1), the slope and the intercept of  $R_{\text{ex}}(q)^{-1/2}$  vs.  $q^2$  plot (DB plot) give  $\xi$  and  $\langle \eta^2 \rangle$  of a gel sample (see Fig. S1 and related text for details). Calculations showed that the correlation length  $\xi$  of the scatterers is  $38 \pm 3$  nm for gels made by C12, which is about two-fold larger than that calculated for the chemical gels ( $17 \pm 5$  nm). This larger value of  $\xi$  can be attributed to the larger size of the clusters formed due to the hydrophobic associations. The mean square fluctuations  $\langle \eta^2 \rangle$  of the refractive index is  $(1.1 \pm 0.9) \times 10^{-7}$ , while for the chemical gels, they are one order of magnitude larger,  $\langle \eta^2 \rangle = (22.2 \pm 2) \times 10^{-6}$ . With the refractive index increment of PAAm in water at 21 °C,  $dn/dc = 0.163$  mL/g [26], this converts to static concentration fluctuations  $\sqrt{\langle \delta c^2 \rangle} = 2.0 \times 10^{-3}$  and  $9.1 \times 10^{-3}$  for gels made by C12 and BAAM, respectively. Thus, since the mean polymer concentration in both gels is 5%, the average relative static concentration fluctuations on a length scale of a few tens of nm reduces from 18 to 4% by replacing the chemical crosslinks with mobile crosslink zones. This means that the dynamic nature of the crosslinks in the present hydrogels reduces the spatial gel inhomogeneities, as also observed before in topological gels [19,20].

### 3.2. Hydrophobic associations together with permanent crosslinks

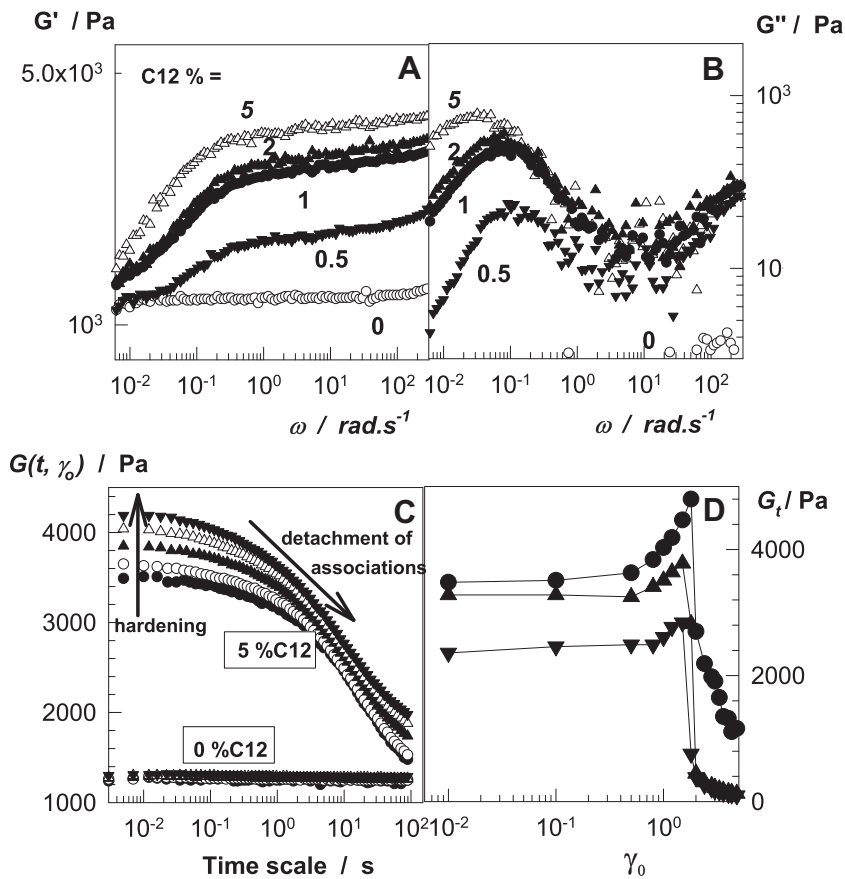
In this section, the chemical crosslinker BAAM was included into the micellar copolymerization system of AAm and C12 to obtain both permanent and temporary crosslink zones in the hydrogels. As expected, the elastic modulus  $G'$  increased and the plateau became broader as the crosslinker ratio  $X$  (molar ratio of BAAM to the monomers AAm + C12) is increased, i.e., as the number of permanent crosslinks is increased (Fig. S2). Fig. 4A and B show the

effect of the amount of the hydrophobe in the comonomer feed on the mechanical spectra of PAAm gels formed at a crosslinker ratio  $X = 1/80$ . Addition of the hydrophobe increases  $G'$  at high frequencies indicating that the hydrophobic associations inside the gel network are detected as permanent crosslinks at short experimental time scales. The larger the amount of the hydrophobe in the comonomer feed, the larger  $G'$  at high frequencies. Further, the maximum in viscous modulus  $G''$  shifts to slightly lower frequencies and its magnitude increases with increasing C12% due to the increase in the amount of the dissipated energy. Calculations indicate that, as the amount of C12 is increased from 0.5 to 5 mol %, the number of hydrophobes in each hydrophobic block also increases from 1 to 8 (see Supplementary data). As a consequence, more energy is dissipated because increasing hydrophobe length minimizes the exposure of the hydrophobic moieties to the aqueous environment.

To elucidate dynamics of the crosslink points in hydrophobically modified hydrogels further, stress-relaxation experiments were conducted. Fig. 4C shows typical relaxation profiles of hydrogels without and with 5% C12, where the relaxation modulus  $G(t, \gamma_0)$  is shown as a function of time scale  $t$  for various strain amplitudes  $\gamma_0$ .  $G(t, \gamma_0)$  of the hydrogel containing hydrophobic blocks decreases with increasing time and approaches to that of the conventional hydrogel at long times, in accord with the short frequency range of the mechanical spectra (Fig. 4A). Another result is that the modulus of hydrophobically modified hydrogel increases at a given time scale (strain hardening) while the conventional gel does not show this behavior. In Fig. 4D, the relaxation moduli  $G_t$  at a given time scale  $t$  are plotted as a function of the strain amplitude  $\gamma_0$  for the hydrogel with 5% C12. Hydrogel is in the linear regime for strain  $\gamma_0$  below 80%, while they exhibit strain hardening for  $\gamma_0$  between 80 and 150%, before softening at higher strains. The shorter the time scale, the larger the degree of strain hardening, the larger the yield strain  $\gamma_c$ , i.e., the strain at which the modulus starts decreasing. Since strain hardening behavior only appears after hydrophobic modification, the results suggest that applied strain contributes the organization degree of the dodecyl blocks inside the gel network so that the modulus increases.

### 3.3. Mechanical properties

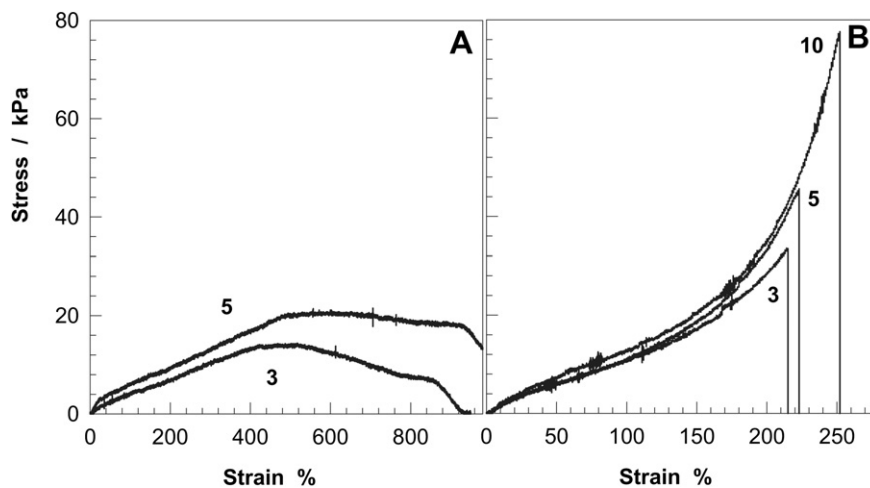
Fig. 5A and B represent tensile stress–strain data of the hydrogels prepared at various levels of C12 with and without the chemical



**Fig. 4.** (A, B):  $G'$  (A) and  $G''$  (B) of PAAm hydrogels containing dodecyl groups shown as a function of the frequency  $\omega$  measured after 2 h of reaction time.  $\gamma_0 = 0.01$ .  $X = 1/80$ . SDS = 7%. C12 = 0 ( $\circ$ ), 0.5 ( $\blacktriangledown$ ), 1 ( $\bullet$ ), 2 ( $\blacktriangle$ ), and 5 mol % ( $\triangle$ ). (C): The relaxation modulus  $G(t, \gamma_0)$  of PAAm hydrogels with 0 and 5 mol % C12 as a function of time scale  $t$  for various strain amplitudes  $\gamma_0$ .  $X = 1/80$ .  $\gamma_0 = 0.10$  ( $\bullet$ ), 0.50 ( $\circ$ ), 0.80 ( $\blacktriangle$ ), 1.00 ( $\triangle$ ), and 1.20 ( $\blacktriangledown$ ). Figure D was derived from C for hydrogels with 5% C12 and shows the relaxation modulus  $G_t$  at given time scale  $t$  as a function of  $\gamma_0$ .  $t = 0.01$  ( $\bullet$ ), 1 ( $\blacktriangle$ ), and 10 s ( $\blacktriangledown$ ).

crosslinker BAAM, respectively. C12 contents are indicated in the figures. In the absence of C12 (not shown in the figures), PAAm solutions formed under the experimental conditions flowed under gravity, while PAAm gels prepared using BAAM always broke before obtaining precise mechanical data. Addition of C12 into the comonomer feed leads to the formation of gels withstanding very large extension ratios. In the absence of the chemical crosslinker BAAM,

the gels start flowing above 450% elongation ratios (Fig. 5A), while the presence of both permanent and temporary crosslinks produces both tough and elastic hydrogels (Fig. 5B). The hydrogels with 10 mol % C12 exhibit more than 250% elongation ratio at break and ultimate tensile strength of about 80 kPa. The results demonstrate that both permanent and temporary crosslinks are required to obtain tough and elastic hydrogels.



**Fig. 5.** Stress–strain curves of hydrophobically modified PAAm hydrogels with various C12 mol % indicated.  $X = 0$  (A) and  $1/80$  (B).

#### 4. Conclusions

Incorporation of dodecyl blocks into the hydrophilic PAAm chains leads to the formation of strong and long lived intermolecular hydrophobic associations. The three-dimensional network structure formed due to the dodecyl domains preserves its integrity in the presence of excess water, indicating that the approach presented here allows preparation of tough hydrogels without the use of a chemical crosslinker. Compared to the chemical gels, the mobility of the crosslink zones in the present hydrogels reduces the degree of spatial gel inhomogeneity. Mechanical tests also show that, in addition to the dodecyl domains, permanent crosslinks are also needed to obtain hydrogels that are mechanically stable up to 250% elongation ratios. The hydrogels exhibit strain hardening behavior due to the organization of dodecyl blocks under the applied strain.

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#### Appendix. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.polymer.2010.12.044.

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