Polymer 50 (2009) 5449–5455

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Design of high-toughness polyacrylamide hydrogels by hydrophobic modification

Suzan Abdurrahmanoglu [b], Volkan Can [a], Oguz Okay [a,*]

[a] *Istanbul Technical University, Department of Chemistry, 34469 Maslak, Istanbul, Turkey*
[b] *Marmara University, Department of Chemistry, Kadikoy, Istanbul, Turkey*

ARTICLE INFO

Article history:
Received 9 July 2009
Received in revised form
8 September 2009
Accepted 15 September 2009
Available online 20 September 2009

Keywords:
Hydrogels
Toughness
Elasticity

ABSTRACT

Polyacrylamide (PAAm) hydrogels possessing a very large extensibility at break have been prepared via micellar crosslinking copolymerization of acrylamide monomer and *N*,*N*′-methylenebis(acrylamide) crosslinker in the presence of hydrophobic comonomers. *N*-butyl-, *N*-hexyl-, *N*-octyl-, and *N*,*N*-dihexylacrylamides were used as the hydrophobes in the hydrogel preparation. Incorporation of hydrophobes with an alkyl chain length $x > 4$ results in an increase in the loss factor tan δ of hydrogels due to the formation of temporary junction zones inside the gel network. The number N_H of the hydrophobes per hydrophobic block together with the alkyl chain length x of the pendant hydrophobic group were used to tune the loss factor of the hydrogels over two orders of magnitude. Tensile mechanical measurements show that increasing N_H or x also increases the degree of toughness of PAAm hydrogels. Keeping constant the hydrophobe level (20 mol%) at an alkyl chain length $x = 6$, increasing N_H from 9 to 30 increased the elongation ratio at break from 125 to 250%. Hydrogels exhibiting a high toughness, i.e., about 300% elongation ratio at break were obtained by modification of PAAm network chains with 10 mol% *N*-octylacrylamide.

1. Introduction

Design of hydrogels with good mechanical properties such as a high toughness is crucially important in many application areas of soft materials. However, hydrogels that are highly swollen in a liquid are normally very brittle. This feature of hydrogels originates from their very low resistance to crack propagation due to the lack of an efficient energy dissipation mechanism in the gel network [1,2]. As schematically illustrated in Fig. 1A, the energy stored very close to the crack tip cannot be dissipated in conventional, chemically-crosslinked hydrogels, inducing the fracture of the whole material. 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 recently been proposed including the double network gels [3,4], topological gels [5], nanocomposite hydrogels [6], and cryogels [7].

Recently, it was shown that hydrophobic modification of polyelectrolyte hydrogels leads to a dramatic increase in the viscous modulus G'' while the elastic modulus G' remains almost unchanged [8]. The increase in G'' reflects creation of energy dissipation mechanisms due to the formation of hydrophobic associations, i.e., temporary junction zones inside the hydrogel network. The driving force for the formation of associations is the interaction between the hydrophobic groups that arises in order to minimize their exposure to water. According to several models [9–13], the activation energy for the disengagement of hydrophobes from the associations is in the order of the thermal energy *kT*, so that the free and bonded hydrophobes in such hydrogels are in a dynamic equilibrium. As a consequence, one may expect that hydrophobically modified hydrogels prepared under certain conditions should exhibit better mechanical performances compared to the conventional hydrogels. As illustrated in Fig. 1B, the crack energy may be dissipated by the reversible disengagements of the hydrophobes from the hydrophobic associations so that the growth of crack to a macroscopic level can be prevented.

Hydrophobically modified polyelectrolyte hydrogels mentioned above were prepared by a complicated three step procedure [8]: a) introduction of double bonds onto a poly(acrylic acid) (PAA) backbone, b) hydrophobic modification of PAA with dodecyl amine, and c) crosslinking of double bonds using a dithiol. However, a simple, straightforward alternative for the preparation of such materials is the micellar copolymerization technique. In this technique, a hydrophobic comonomer solubilized within the micelles is copolymerized with a hydrophilic monomer in aqueous solutions by free-radical mechanism [14,15]. Because of high local concentration of the hydrophobe within the micelles, the hydrophobic monomers are distributed as blocks randomly along the hydrophilic polymer backbone. It was shown that the number of hydrophobes per hydrophobic block (N_H) and the number of blocks

---

* Corresponding author. Tel.: +90 212 2853156; fax: +90 212 2856386.
E-mail address: okayo@itu.edu.tr (O. Okay).

0032-3861/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2009.09.042

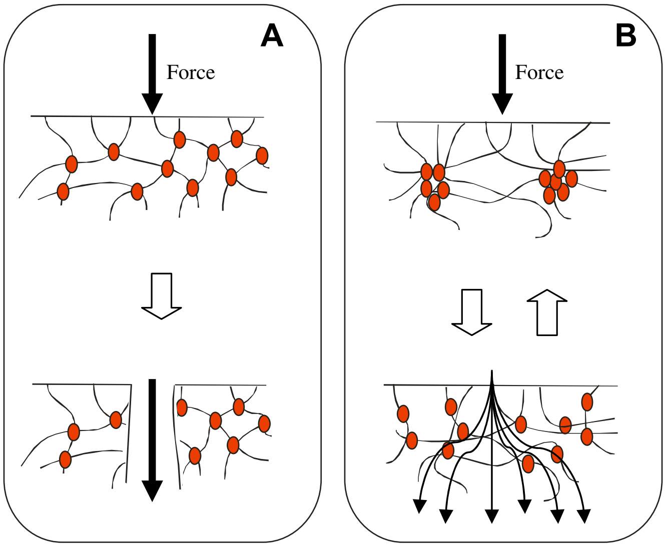


Fig. 1. Cartoon demonstrating crack of a chemically-crosslinked hydrogel due to the localization of the crack energy (A) and, dissipation of the crack energy in a hydrophobically modified hydrogel (B).

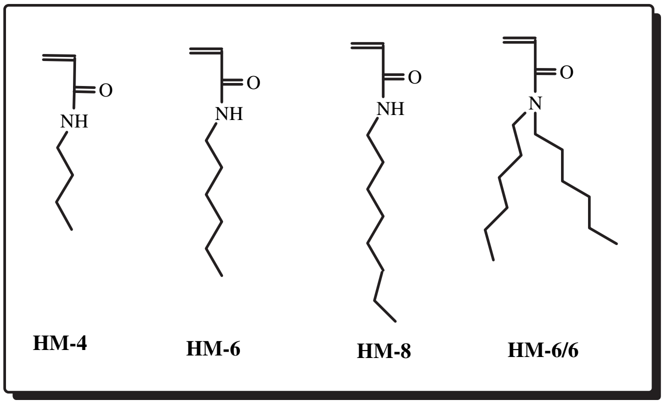
per chain (S) can be estimated from the concentration ratio of hydrophobic monomer (HM) to the surfactant (SDS) by

$$N_H = \frac{[\text{HM}]\, N_{\text{Agg}}}{[\text{SDS}] - CMC} \tag{1a}$$

$$S = \frac{f_{\text{HM}}\, N}{N_H} \tag{1b}$$

where N_{Agg} is the aggregation number of the surfactant, CMC is its critical micelle concentration, f_{HM} is the mole fraction of HM in the comonomer feed and N is the chain length of polymer [16]. Since incorporation of a small amount of hydrophobic group in a hydrophilic backbone results in systems with unique rheological characteristics in aqueous solutions, intensive work has been conducted in the past two decades on the preparation and solution properties of hydrophobically modified hydrophilic polymers [17,18]. Candau and co-workers investigated in detail the formation and rheological properties of polyacrylamides modified with various amounts of *N*-alkyl-, *N*,*N*-dialkylacrylamides of various alkyl chain length [14–17,19–21]. A strong enhancement of the zero-shear viscosity of semi-dilute solutions of such polymers was observed upon increasing the number N_H of hydrophobes per block or the number S of blocks attached to each chain [15,19,20]. Hydrophobically modified polyacrylamides attract great interest because of their possible applications in various industrial areas, including oil recovery, paints, pharmaceuticals, cosmetics, and food. However, chemically-crosslinked analogs of such polymers as well as their toughness vs hydrophobicity trends draw much less attention [8].

In the present work, a series of hydrophobically modified polyacrylamide (PAAm) hydrogels were prepared via micellar crosslinking copolymerization of acrylamide (AAm) monomer and *N*,*N*′-methylenebis(acrylamide) (BAAm) crosslinker in the presence of a hydrophobic comonomer. *N*-butyl-, *N*-hexyl-, *N*-octyl-, and *N*,*N*-dihexylacrylamides were used as the hydrophobic comonomer in the hydrogel preparation (Scheme 1). Our aim was to investigate whether the degree of toughness of such hydrogels could be tuned with the extent of viscous dissipation of energy during their deformation. To our knowledge, no such investigation has yet been conducted for this kind of materials. We first monitored the gelation reactions of AAm, BAAm and the hydrophobic comonomer in aqueous solutions by rheometry using oscillatory deformation tests. The gelation reactions were carried out in the presence of various amounts of the hydrophobic comonomer between 0 and 10 mol%. The complex shear modulus G^* measured can be resolved into its real and imaginary components, i.e.,



Scheme 1. Hydrophobic comonomers used in the preparation of PAAm hydrogels. HM-4: *N*-butylacrylamide. HM-6: *N*-hexylacrylamide. HM-8: *N*-octylacrylamide. HM-6/6: *N*,*N*-dihexylacrylamide.

$$G^* = G' + iG'' \tag{2}$$

where the elastic (or storage) modulus G' is a measure of the reversibly stored deformation energy, and the viscous (or loss) modulus G'' represents a measure of the irreversibly dissipated energy during one cycle. As will be seen below, after passing a critical length and concentration of the hydrophobic side group, the loss factor $\tan\,\delta = G''/G'$ was found to be much larger for the hydrophobically modified hydrogels in comparison with conventional polyacrylamide (PAAm) hydrogels. The increase in $\tan\,\delta$ depending on the size and the amount of the hydrophobe in PAAm hydrogels is well correlated with the degree of toughness, as determined by the tensile mechanical measurements.

2. Experimental section

2.1. Materials

Acrylamide (AAm, Merck), *N*, *N*′-methylenebis(acrylamide) (BAAm, Merck), sodium dodecylsulfate (SDS, Sigma), ammonium persulfate (APS, Fluka), and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED, Fluka) were used as received. Stock solutions of APS and TEMED were prepared by dissolving 0.080 g APS and 0.25 mL TEMED each in 10 mL of distilled water. Stock solution of BAAm was prepared by dissolving 0.123 g of BAAm in 10 mL of distilled water. The hydrophobic monomers *N*-butylacrylamide, *N*-hexylacrylamide, *N*,*N*-dihexylacrylamide, and *N*-octylacrylamide were prepared by the reaction of the corresponding *N*-alkyl- or *N*,*N*-dialkylamines with acryloyl chloride in methylene chloride in the presence of triethylamine as a catalyst, as described in the literature [22–24]. The purity of the monomers was checked by elemental analysis. In the following, the hydrophobic monomer (HM) used in the gel preparation was denoted by HM-*x*, where *x* denotes the alkyl chain length of the hydrophobic side group. Thus, the values of *x* varied were 4, 6, 8, and 6/6, where 6/6 denotes *N*,*N*-dihexyl group.

2.2. Polymerization

The hydrogels were prepared by free-radical micellar crosslinking copolymerization of AAm, HM-*x*, and BAAm in aqueous SDS solutions at 25 °C. The concentration of SDS in the reaction solution was 7 w/v%, which is much above its critical micelle concentration (0.25 w/v%) [25]. The initial concentration of the total monomer (AAm + HM-x) was set to 5 w/v% throughout the experiments while the HM-x content in the comonomer mixture was varied between 0 and 10 mol%. The crosslinker ratio X, that is the molar ratio of BAAm to the total monomer was also fixed at 1/80. APS (3.5 mM) and TEMED (0.25 mL/100 mL reaction solution) were used as the redox initiator system. To illustrate the synthetic procedure, we give details for the preparation of hydrogels with 10 mol% HM-8:

N-octylacrylamide (0.113 g) was added to the solution of SDS (0.7 g) in 7.05 mL of water and stirred for 30 min to obtain a transparent solution. After addition of AAm (0.388 g) and stock solutions of BAAm (0.95 mL) and TEMED (1 mL), the solution was purged with nitrogen gas for 10 min. Then, stock solution of APS (1 mL) was added to initiate the reactions. For the rheological experiments, portion of this solution was transferred between the parallel plates of the rheometer. For the swelling and mechanical measurements, the solution was transferred into several plastic syringes of 4 and 10 mm internal diameters and the polymerization was conducted for one day at 25 °C.

It should be noted that, due to the crosslinked structure, the hydrophobe content of the network chains cannot be determined directly. However, previous work shows that, in case of linear micellar copolymerization, hydrophobe content in the comonomer feed equals to that in the copolymer [26]. Further, incorporation of the hydrophobic comonomers into the network structure was checked by conducting gel fraction measurements as well as by the swelling tests in water at 21 °C. After polymerization in syringes, hydrogel samples were immersed in a large excess of water for three months to extract any soluble polymers, unreacted monomers and the initiator. Since the extraction time used was extremely long and the swelling ratio of gel samples after this time attained a limiting value (Fig. 2), we assume that SDS is completely extracted from the gel samples. In order to dry the equilibrium swollen gel samples, they were first immersed in methanol over night and then dried under vacuum. The conversion of monomers to the crosslinked polymer (mass of crosslinked polymer/initial mass of the monomer) was found to be complete in all the experiments. For the swelling tests, gel samples of initial mass m_o just after preparation were immersed into an excess of water and water was replaced every week. The masses m of the gel samples were monitored as a function of swelling time by weighing the samples.

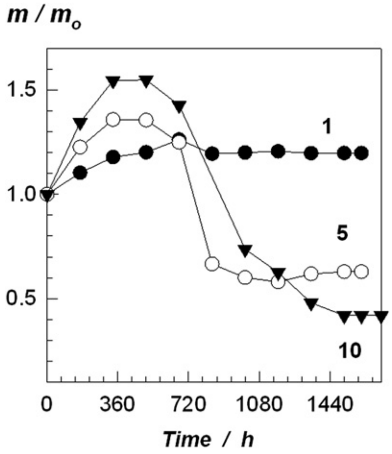


Fig. 2. Swelling ratio m/m_o of PAAm hydrogels with various amounts of HM-6 shown as a function of the swelling time. Swelling temperature = 21 °C. HM-6 mol% in the comonomer feed is indicated.

Fig. 2 shows typical swelling ratio m/m_o vs swelling time curves of hydrogels prepared with various amounts of HM-6 in the comonomer feed. It is seen that the gels after preparation first swell in water to attain a maximum value. This initial swelling period is due to the osmotic pressure of the counterions of SDS, convering the gels into polyelectrolyte gels. However, as the swelling time is increased, that is, as SDS moves from the gel to the solution phase, the swelling ratio decreases again until attaining an equilibrium value at long times. Equilibrium swelling ratio measurements showed that increasing amount of HM-x in the comonomer feed from 0 to 10 mol% decreases the equilibrium swelling ratio of the resulting hydrogels in water. This also indicates that the HM-x mol% of the comonomer feed is proportional to the HM-x content of the network chains.

2.3. Rheological experiments

Gelation reactions were carried out between the parallel plates of the rheometer (Gemini 150 Rheometer system, Bohlin Instruments) equipped with a Peltier device for temperature control. The upper plate (diameter 40 mm) was set at a distance of 500 μm before the onset of the reactions, i.e., during the induction period. During all rheological measurements, a solvent trap was used to minimize the evaporation. A frequency of $\omega = 1$ Hz and a deformation amplitude $\gamma^o = 0.01$ were selected to ensure that the oscillatory deformation is within the linear regime. The reactions were monitored in the rheometer at 25 °C up to a reaction time of about 2 h to avoid the effect of the solvent evaporation. After 2 h, frequency-sweep tests at $\gamma^o = 0.01$ were carried out at 25 °C over the frequency range 10^{-2} to 10^1 Hz both in up and down directions.

2.4. Tensile mechanical tests

Tensile mechanical measurements were performed on cylindrical hydrogel samples just after preparation of the same size (4 mm diameter × 50 mm length) using a Zwick Roell, 500 N test machine at 25 °C under the following conditions: Crosshead speed = 50 mm/min, sample length between jaws = 20 mm. The tensile strength (from the initial crosssection of 12.57 mm^2) and percentage elongation at break were recorded. For reproducibility, at least six samples were measured for each gel and the results were averaged. Standard deviations in the average values of the tensile strength and the elongation ratio at break for each gel were less than 15%.

3. Results and discussion

We discuss the results of our experiments in 2 subsections. In the first subsection, characteristic features of the gelation reactions and the rheological behavior of the hydrophobically modified hydrogels are discussed. In the second subsection, the results of the tensile mechanical measurements are discussed and experimental observations are interpreted.

3.1. Formation conditions of tough hydrogels

By all the free-radical crosslinking micellar copolymerizations, a certain induction period was observed, i.e., an initial reaction period during which the moduli are below the detection level. The duration of the induction period was found to vary between 30 and 60 min, much longer than that observed in usual crosslinking copolymerizations [27–29]. However, repeated measurements showed that the results are unaffected from these variations. In the following, the reaction time t is defined as the total time elapsed minus the time needed for the induction period. Fig. 3 shows

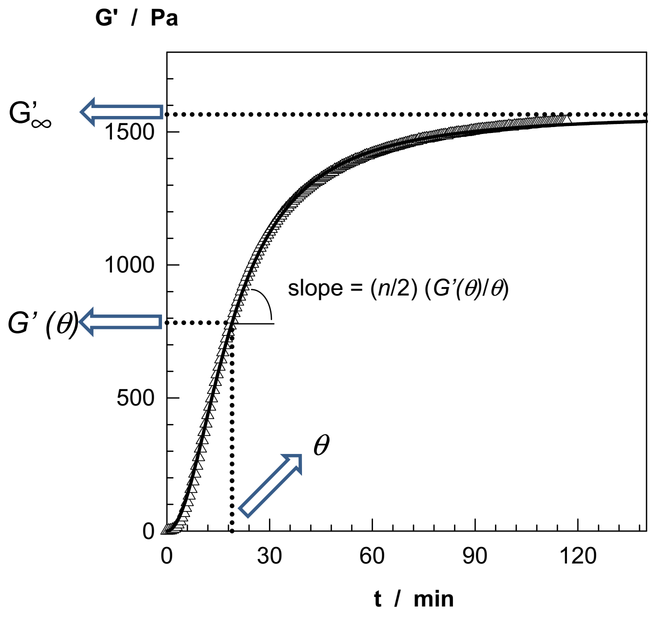


Fig. 3. Elastic modulus G' during the free-radical crosslinking micellar copolymerization of AAm, BAAm, and HM-6 shown as a function of the reaction time t. HM-6 = 10 mol%. $X = 1/80$. SDS = 7 w/v%. The curve was calculated using Eq. (3). $\omega = 1$ Hz. $\gamma^o = 0.01$.

a typical elastic modulus G' vs reaction time t plot during the free-radical crosslinking micellar copolymerization of AAm and BAAm in the presence of 10 mol% HM-6. G' increases rapidly with increasing reaction time and then approaches a plateau value after about 90 min. To estimate the final elastic modulus G'_∞ of the hydrogel, the experimental time-dependent modulus data were fitted to the equation

$$G'(t) \quad = \quad G'_\infty \frac{t^n}{t^n \; + \; \theta^n} \tag{3}$$

where θ is the half-gelation time for which $G'(\theta) = 0.5G'_\infty$, and the exponent n relates to the asymptotic slope at the half-gelation time by $(n/2)(G'(\theta)/\theta)$ (Fig. 3) [27–31]. The fitting result using Eq. (3) is also shown in the figure by the solid curve, which yields $G'_\infty = 1.57$ kPa, $\theta = 19$ min, and $n = 2.04$. Similar plots were also obtained for other HM-x comonomers with amounts between 0 and 10 mol% (Fig. S1). In Fig. 4, the final elastic modulus G'_∞, the half-gelation time θ, and the exponent n extracted from the fits are shown as a function of the alkyl chain length x of HM-x. Each data point in Fig. 4 is the average of the values obtained between 0 and 10% HM-x. General trend is that G'_∞ is a slightly increasing function of the amount of HM-x or, of the alkyl chain length x of the hydrophobe. The increase in G'_∞ with HM-x mol% becomes significant for alkyl chain length $x > 6$. As will be seen later, this increase is due to the simultaneous increase of the viscous modulus of hydrogels. Further, $\theta = 28 \pm 7$ min and $n = 2.2 \pm 0.3$ for all hydrogels, indicating that $dG'(t)/dt \cong G'(t)/t$ up to $t = \theta$, i.e., the crosslinking occurs randomly up to the half-gelation time. Thus, the gelation kinetics and the elastic properties of hydrogels are not much affected by the presence of HM-x in the comonomer mixture.

However, the viscous modulus G'' of hydrogels is strongly affected by the comonomer composition. Fig. 5A shows the loss factor tan δ plotted as a function of the reaction time t during the crosslinking micellar copolymerization of AAm, BAAm, and HM-6. tan δ decreases with time and approaches a limiting value at longer times. The quantity tan δ represents the ratio of dissipated energy to stored energy during one deformation cycle. For the reaction system without HM-6, the limiting value of tan δ is less than 0.01, indicating formation of a strong gel with negligible viscous properties. With the addition of HM-6 in the comonomer feed, the limiting tan δ increases and this increase is significant between 1 and 5 mol% HM-6; at 10 mol%, tan δ becomes larger than 0.1, which is a typical feature of a so-called weak gel [32,33]. Similar tan δ vs time plots were also obtained for other hydrophobic comonomers (Fig. S1).

In Fig. 5B, the limiting values of the loss factor tan δ of all hydrogels are shown as a function of HM-x content in the feed. Hydrophobic comonomer with an alkyl chain length of $x = 4$ does not induce an increase in tan δ over the whole range of the hydrophobe contents. On the contrary, the comonomers with $x > 4$ result in an increase in tan δ beyond a critical concentration of the hydrophobe. This critical concentration decreases and tan δ reaches to larger values as x is increased. The marked increase in tan δ with HM-x % or with x is due to the increasing number of carbon atoms in associations creating stronger hydrophobic interactions [10]. Further, since the association energy is about x times of the thermal energy kT [10,12,13], the results suggest that a critical length of $x = 6$ is required to detect the associations within the experimental time scales. As a result, the viscous properties of hydrogels are raised strongly while their elastic properties remain almost unchanged by incorporation of HM-6, HM-8, or HM-6/6 units into the network chains. Fig. 5B also shows that, as compared to the monohexyl groups, the use of dihexyl groups leads to increased associativity in the gel network due to the higher density of the hydrophobic domains, which is in accord with the viscosity results of the dilute solutions of the corresponding copolymers [26].

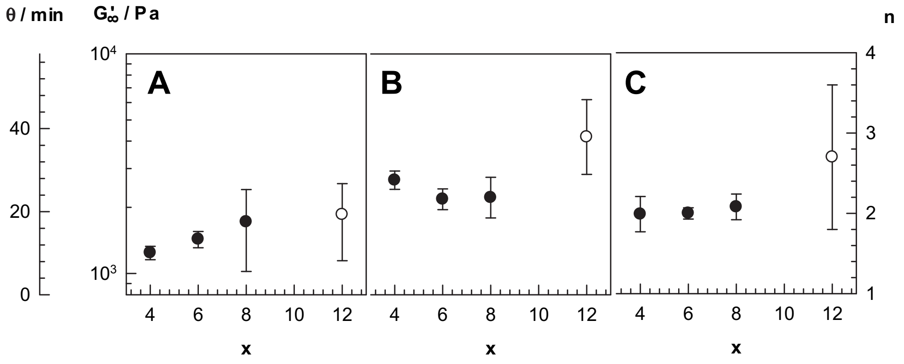


Fig. 4. The final modulus of the hydrogels G'_∞ (A), the half-gelation time θ (B), and the coefficient n (C) extracted from the fits of G' vs t plots to Eq. (3) shown as a function of the chain length x of HM-x. Open symbols represent data obtained using HM-6/6. $X = 1/80$. SDS = 7 w/v%. $\omega = 1$ Hz. $\gamma^o = 0.01$.

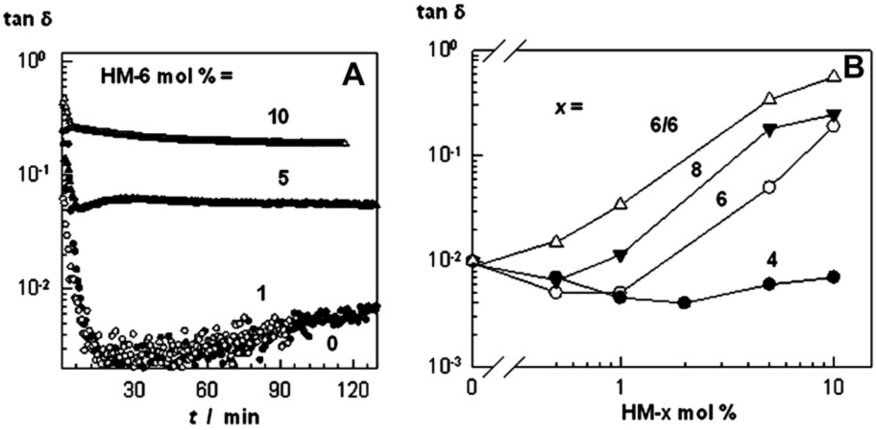


Fig. 5. (A): The loss factor tan δ shown as a function of the reaction time t during the free-radical crosslinking micellar copolymerization of AAm, BAAm, and HM-6. $\omega = 1$ Hz. $\gamma^o = 0.01$. $X = 1/80$. SDS = 7 w/v%. HM-6 mol% indicated. (B): tan δ shown as a function of HM-x mol% in the comonomer feed. $x = 4$ (●), 6 (○), 8 (▼), and 6/6 (△). $X = 1/80$. SDS = 7 w/v%. The solid curves are guide to the eye.

To correlate the experimental observations with the two characteristic numbers of hydrophobically modified hydrogels, namely with the values of N_H and S given by Eqs. (1a) and (1b), respectively, the aggregation number of SDS was assumed to be 62 [25]. Solution of Eq. (1b) also requires the effective chain length N of the network chains. Assuming that G' at $\omega = 1$ Hz equals to the equilibrium shear modulus G, one may estimate the effective length N of the network chains. For a phantom tetrafunctional network, G at the state of gel preparation is given by

$$G = 0.5 \left(\frac{\rho}{\overline{M}_c}\right) RT\,\nu_2^0 \tag{4a}$$

$$N = \overline{M}_c / \overline{M}_r \tag{4b}$$

where ρ is the polymer density $\overline{M}_c$ is the molecular weight of the network chains, $\overline{M}_r$ is the average molecular weight of the repeat units, ν_2^0 is the volume fraction of crosslinked polymer in the gel, R and T are in their usual meanings [34,35]. Since $\rho\,\nu_2^0$ equals to 50 kg/m^3, from the elastic moduli of hydrogels together with Eqs. (1b), (4a), and (4b), the number S of hydrophobic blocks per network chain was calculated. The results show that as HM-x mol% is increased from 0 to 10, the number N_H of the hydrophobes per hydrophobic block increases up to 17 while the number S of blocks between two elastically active junctions remains between 3 and 4. Thus, the length of the hydrophobic blocks together with the alkyl chain length of the hydrophobes can be used to tune the loss factor of PAAm hydrogels over two orders of magnitude.

After a reaction time of 2 h, frequency-sweep tests at $\gamma^o = 0.01$ were carried out over the frequency range 0.01–40 Hz. Fig. 6A shows frequency-dependence of G' (filled symbols) and G'' (open symbols) for the hydrogels with 0–10% HM-6. The hydrogel without any hydrophobe shows a solid-like response, i.e., G' shows a plateau over the whole frequency range while G'' remains on a low level about 2 orders of magnitude smaller than G'. This situation changes drastically for the hydrophobically modified hydrogels; G'' increases significantly with the frequency and this increase starts at lower frequencies as the amount of HM-6 is increased, indicating decreasing disengagement rate of the hydrophobes from associations leading to longer relaxation times. Moreover, at high-frequency range, the elastic modulus G' also increases with frequency because the viscous modulus increases, so that the width

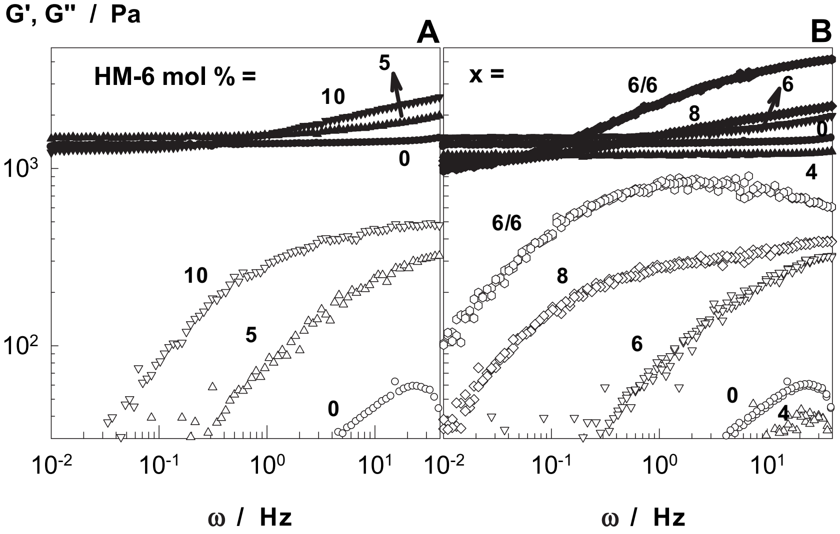


Fig. 6. Elastic moduli G' (filled symbols) and viscous moduli G'' of hydrogels (open symbols) shown as a function of the frequency ω. $\gamma^o = 0.01$. $X = 1/80$. SDS = 7 w/v%. (A): HM-6 = 0 (●, ○), 5 (▲, △), and 10 mol% (▼, ▽). (B): HM-x = 5 mol%. The values of x are indicated.

of the plateau of G' becomes shorter as the HM-6 content is increased. At $x = 8$, the plateau of G' disappears for hydrophobe contents above 5 mol% (Fig. S2). Fig. 6B compares the mechanical spectra of all hydrophobically modified hydrogels containing 5 mol% HM-*x*. For $x > 4$, increasing alkyl chain length *x* of the hydrophobe significantly increases the viscous modulus, which is also reflected in the increase of elastic modulus G' and its frequency-dependence. At $x = 6/6$, G'' vs ω plot shows a shallow maximum at about 1 Hz followed by a final slow decrease at the highest frequencies.

3.2. Mechanical properties of hydrogels

The hydrogels at various levels of HM-*x* were subjected to tensile mechanical measurements just after their preparation. Pure PAAm hydrogels or hydrogels modified with HM-4 were too weak to carry out the measurements; they always broke before obtaining precise mechanical data. On the contrary, it was observed that the hydrogels containing larger hydrophobic side groups exhibited very large extensibility before fracture. For example, at 5 mol% HM-*x*, although the hydrogels with $x = 6$ were still too fragile, those with $x > 6$ withstand very large elongation ratios. The curves in Fig. 7A and B represent tensile stress–strain data of hydrogels containing 5 and 10 mol% HM-*x* with different alkyl chain length *x*, respectively. Compared to HM-6, HM-6/6 produces a gel exhibiting a high elongation ratio at break (214–265%) and ultimate tensile strength (40–51 kPa). This is due to the increased associativity in the gel network containing dihexyl groups (Fig. 6B) so that more energy is dissipated under deformation at large strains. Further, both the elongation ratio at break and the strength remarkable increase as the alkyl chain length *x* is increased above 6; At $x = 8$, 150% elongation ratio at 30 kPa were measured before the fracture of the hydrogel samples containing 5 mol% hydrophobes. Increasing HM-*x* content from 5 to 10 mol% further improved the tensile mechanical properties of all hydrophobically modified hydrogels. Thus, the general trend is that increasing the size and the amount of hydrophobic side chain improves the mechanical performance of the hydrogels. Modification of PAAm hydrogels with 10 mol% *N*-octylacrylamide (HM-8) produced hydrogels of extremely high toughness (313% elongation ratio at 71 kPa). Fig. 7C showing the pictures of a hydrogel sample with 10 mol% HM-8 indicates that the gel is able to withstand not only high level of deformation, but also knotting, such as the nanocomposite hydrogels made by Laponite crosslinkers [6].

The results thus show that both the length N_H of the hydrophobic block and the alkyl chain length *x* are the main parameters determining the toughness of PAAm hydrogels. To highlight the effect of N_H, experiments were conducted using hydrogels prepared at a crosslinker ratio $X = 1/80$ with 20 mol% HM-6 in the comonomer feed. Two different surfactant concentrations were used during the hydrogel preparation to obtain hydrophobic blocks of length $N_H = 9$ and 30. Fig. 8A and B show the mechanical spectra and the stress–strain curves of these hydrogels, respectively. As expected, the viscous modulus starts to increase at a lower frequency while the elastic modulus remains almost unchanged by increasing N_H from 9 to 30 (Fig. 8A). Simultaneously, an increase in the elongation ratio at break from 125 to 250% was observed, demonstrating the important role of the number N_H of hydrophobes per block in the toughening of PAAm hydrogels (Fig. 8B).

Recently, it was shown that hydrophobic modification of polyelectrolyte hydrogels mentioned in the introduction section only leads to a moderate toughening in the gels [36]. This finding is reasonable because the polyelectrolyte hydrogels contain randomly distributed single hydrophobic units ($N_H \cong 1$) instead of blocks of hydrophobes. We should also note that, for comparison purposes, the stress–strain tests were also conducted using nanocomposite hydrogels prepared by in situ polymerization of *N*,*N*-dimethylacrylamide and *N*-isopropylacrylamide monomers in aqueous Laponite dispersions [6,37]. The initial concentration of the monomers was the same (5 w/v%) as that used in the preparation of the hydrophobically modified hydrogels. The stress–strain curves of these hydrogels containing 6 w/v% Laponite showed that their elongation ratios at break were between 600 and 700%, i.e., much larger than the present hydrogels. The action of Laponite as a multifunctional crosslinker as well as the absence of a chemical crosslinker in nanocomposite hydrogels seem to be responsible for their better mechanical properties compared to those of the hydrophobically modified PAAm hydrogels.

We should note that all the mechanical spectra of hydrogels were taken from their after-preparation states so that they contain surfactant (SDS) molecules at concentrations much above CMC. Since the presence of SDS reduces the contacts of the hydrophobes with water and consequently lowers the energy of the system, the lifetime of hydrophobes in associations is expected to be longer than that in systems containing no SDS. Moreover, a major problem of micellar polymerization technique is the compositional heterogeneity observed for copolymers with monosubstituted acrylamide hydrophobes, which increases strongly with increasing number N_H of hydrophobes per micelle [26]. Therefore the values N_H reported

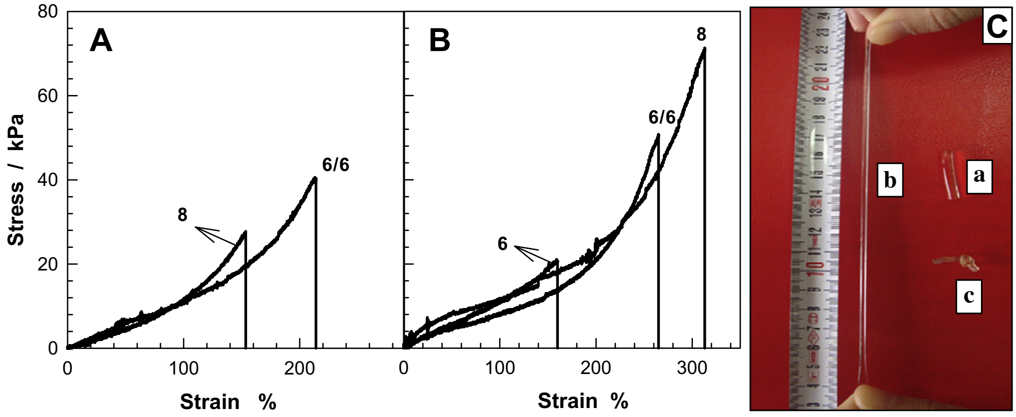


Fig. 7. (A,B): Stress–strain curves of hydrophobically modified PAAm hydrogels with 5 (A) and 10 mol% HM-*x* (B). The alkyl chain length *x* indicated. $X = 1/80$. SDS = 7w/v%. (C): Pictures of PAAm hydrogels with 10 mol% HM-8 before (a) and after elongation (b), and after knotting (c).

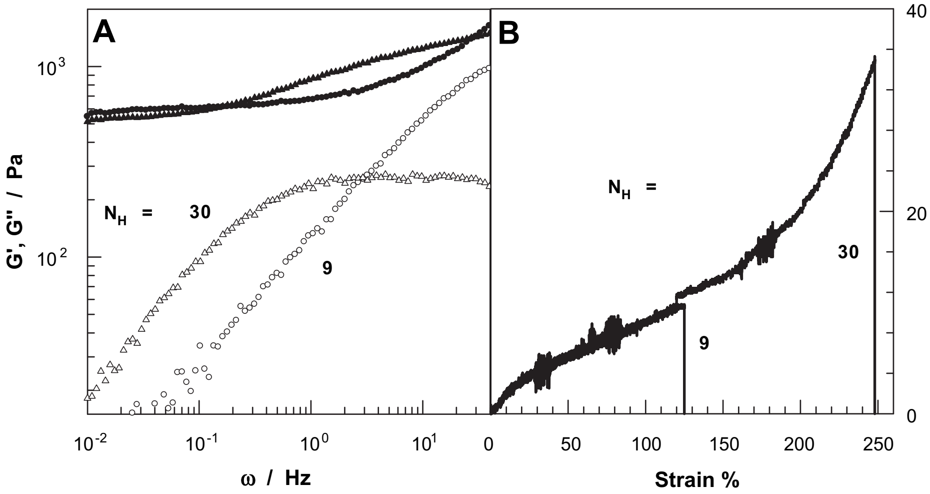


Fig. 8. (A): G' (filled symbols) and G'' (open symbols) of hydrogels modified with 20 mol% HM-6 shown as a function of the frequency ω. $\gamma^o = 0.01$. $X = 1/80$. SDS = 7 (▲, △) and 23.4 w/v% (●, ○) corresponding to $N_H = 30$ and 9, respectively. (B): Stress–strain curves of the hydrogels with 20 mol% HM-6 mentioned in Fig. 7A. The values N_H are indicated.

in this work are only illustrative and they actually represent the number of hydrophobic comonomers per micelle during the initial stage of the gelation reactions.

4. Conclusions

Polymer hydrogels that are highly swollen in water are known to be very brittle, which limits their application areas. In this work, we demonstrated that PAAm hydrogels possessing a very large extensibility at break can be prepared via micellar crosslinking copolymerization of acrylamide monomer and *N*,*N*′-methylenebis(acrylamide) crosslinker in the presence of a hydrophobic comonomer. Hydrophobic side groups of an alkyl chain length $x > 4$ result in an increase in the loss factor tan δ of hydrogels after passing a critical amount of the hydrophobe. The number N_H of the hydrophobes per hydrophobic block together with the alkyl chain length x of the hydrophobic side group were used to tune the loss factor of PAAm hydrogels over two orders of magnitude. Tensile mechanical measurements show that increasing N_H or x also increases the degree of toughness of PAAm hydrogels. At an alkyl chain length $x = 6$, increasing N_H from 9 to 30 increased the elongation ratio at break from 125 to 250%. Hydrogels exhibiting a high toughness, i.e., about 300% elongation ratio at break were obtained by modification of PAAm backbone with 10 mol% *N*-octylacrylamide. Comparison of the results of the rheological and mechanical tests thus show that temporary associations of hydrophobic blocks within the hydrogel network lead to the formation of tough hydrogels withstanding high levels of deformations. Since the lifetime of the associations can be tuned by varying the size and the concentration of the hydrophobic comonomers, the required degree of toughness in hydrogels could be achieved by adjusting the composition of the gelation system.

Acknowledgments

Work was supported by the Scientific and Technical Research Council of Turkey (TUBITAK). O. O. thanks Turkish Academy of Sciences (TUBA) for financial support.

Appendix. Supplementary data

Supplementary data associated with this article can be found in online version, at doi:10.1016/j.polymer.2009.09.042.

References

[1] Ahagon A, Gent AN. J Polym Sci Polym Phys Ed 1975;13:1903–11.
[2] Brown HR. Macromolecules 2007;40:3815–8.
[3] Gong JP, Katsuyama Y, Kurokawa T, Osada Y. Adv Mater 2003;15:1155–8.
[4] Tanaka Y, Gong JP, Osada Y. Prog Polym Sci 2005;30:1–9.
[5] Okumura Y, Ito K. Adv Mater 2001;13:485–7.
[6] Haraguchi K, Takehisa T. Adv Mater 2002;14:1120–4.
[7] Ceylan D, Okay O. Macromolecules 2007;40:8742–9.
[8] Miquelard-Garnier G, Demoures S, Creton C, Hourdet D. Macromolecules 2006;39:8128–39.
[9] Tanaka F, Edwards SF. Macromolecules 1992;25:1516–23.
[10] Annable T, Buscall R, Ettelaie R, Whittlestone D. J Rheol 1993;37:695–726.
[11] Bell GI. Science 1978;178:618.
[12] Pham QT, Russel WB, Thibeault JC, Lau W. Macromolecules 1999;32:5139–46.
[13] Tripathi A, Tam KC, McKinley GH. Macromolecules 2006;39:1981–99.
[14] Hill A, Candau F, Selb J. Macromolecules 1993;26:4521–32.
[15] Volpert E, Selb J, Francoise C. Polymer 1998;39:1025–33.
[16] Regalado EJ, Selb J, Candau F. Macromolecules 1999;32:8580–8.
[17] Candau F, Selb J. Adv Colloid Interface Sci 1999;79:149–72.
[18] Gao B, Guo H, Wang J, Zhang Y. Macromolecules 2008;41:2890–7.
[19] Candau F, Regalado EJ, Selb J. Macromolecules 1998;31:5550–2.
[20] Kujawa P, Audibert-Hayet A, Selb J, Candau F. J Polym Sci Part B Polym Phys 2004;42:1640–55.
[21] Kujawa P, Audibert-Hayet A, Selb J, Candau F. Macromolecules 2006;39:384–92.
[22] Chiesl TN, Shi W, Barron AE. Anal Chem 2005;77:772–9.
[23] McCormick CL, Nonaka T, Johnson CB. Polymer 1988;29:731–9.
[24] Yu H, Grainger DW. Macromolecules 1994;27:4554–60.
[25] Turro NJ, Yekta A. J Am Chem Soc 1978;100:5951–2.
[26] Volpert E, Selb J, Candau F. Macromolecules 1996;29:1452–63.
[27] Calvet D, Wong JY, Giasson S. Macromolecules 2004;37:7762–71.
[28] Okay O, Oppermann W. Macromolecules 2007;40:8742–9.
[29] Abdurrahmanoglu S, Okay O. Macromolecules 2008;41:7759–61.
[30] Giraldo J, Vivas NM, Vila E, Badia A. Pharmacol Ther 2002;95:21–45.
[31] Hill AV. Biochem J 1913;7:471–80.
[32] Ross-Murphy SB, Morris VJ, Morris ER. Faraday Symp Chem Soc 1983;18:115–29.
[33] Ross-Murphy SB. J Rheol 1995;39:1451–63.
[34] Flory PJ. Principles of polymer chemistry. Ithaca, NY: Cornell University Press; 1953.
[35] Treloar LRG. The physics of rubber elasticity. Oxford: University Press; 1975.
[36] Miquelard-Garnier G, Hourdet D, Creton C. Polymer 2009;50:481–90.
[37] Haraguchi K, Farnworth R, Ohbayashi A, Takehisa T. Macromolecules 2003;36:5732–41.