



Highly stretchable self-healing poly(N,N-dimethylacrylamide) hydrogels



Melek Pamuk Algi¹, Oguz Okay^{*}

Istanbul Technical University, Department of Chemistry, 34469 Istanbul, Turkey

ARTICLE INFO

Article history:

Received 16 May 2014

Received in revised form 16 July 2014

Accepted 19 July 2014

Available online 30 July 2014

Keywords:

Hydrogels

Self-healing

Hydrophobic associations

Mechanical properties

ABSTRACT

Poly(N,N-dimethylacrylamide) (PDMA) is a very useful hydrophilic biocompatible polymer with associative properties. Although there is a growing interest in PDMA hydrogels, they generally exhibit rather low mechanical strength and very low stretchability due to the lack of an efficient energy dissipation mechanism in the chemically crosslinked gel network. Highly stretchable PDMA hydrogels with self-healing properties are of great interest in tissue engineering and for biomedical applications. A promising strategy to design synthetic hydrogels with self-heal ability is to substitute the covalently crosslinked polymer chains by supramolecular ones. Here, we describe preparation of self-healing PDMA hydrogels by micellar copolymerization of N,N-dimethylacrylamide with 2 mol% stearyl methacrylate in aqueous sodium dodecyl sulfate–NaCl solutions. The supramolecular PDMA hydrogels formed via hydrophobic interactions in micellar solutions can be compressed up to about 100% strain without any permanent failure, while during elongation, they rupture when stretched to 4200% strain. The hydrogels soften with increasing strain and exhibit liquid-like response ($\tan \delta > 1$) at high strains, while they turn back to the initial gel state, if the force is removed. Loading and unloading mechanical cycles show a significant hysteresis and perfect superposition of the successive loading curves demonstrating damage done during loading is recoverable in nature. Tensile testing experiments performed using virgin and healed gel samples show that a healing time of 20 min suffices to recover all the initial mechanical properties of PDMA hydrogels.

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1. Introduction

Poly(N,N-dimethylacrylamide) (PDMA) is a very useful hydrophilic biocompatible polymer with associative properties [1–3]. Linear polymers [4], hydrogels [5–7], interpenetrating polymer networks [8], and blends [9] based on PDMA find numerous applications in molecular biology [10], DNA sequencing [11–13], medical and pharmaceutical fields including contact lenses and in drug delivery

[4,14,15]. However, PDMA hydrogels generally exhibit rather low mechanical strength due to the lack of an efficient energy dissipation mechanism in the chemically crosslinked PDMA network. In the past decade, hybrid PDMA hydrogels with improved mechanical properties have been prepared using silica or clay nanoparticles acting as dynamic multifunctional crosslinkers [16–18]. Haraguchi et al. demonstrated self-healing behavior of hybrid PDMA hydrogels prepared using Laponite clay nanoparticles [19]. The hydrogels sustain up to about 1500% strain and the damage created in the gels could be healed at 50 °C within 10 h. Mechanically strong hydrogels based on PDMA and hyaluronic acid were also prepared by a two-step photo-crosslinking process [20]. Recently, Hao

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

¹ Present address: Aksaray University, Vocational School of Health Services, Aksaray, Turkey.

and Weiss prepared PDMA hydrogels by free-radical copolymerization of N,N-dimethylacrylamide (DMA) and 2-(N-ethylperfluorooctane sulfonamido) ethyl acrylate (FOSA) in dioxane with varying FOSA concentration [21]. The hydrogels formed via hydrophobic interactions between FOSA units exhibit a modulus of 130–190 kPa and elongation at break of 1000–1600%. Since the elastic modulus of these gels decreases with increasing temperature [21], it is likely that the gels have self-healing ability, which could be induced by heating. In contrast to these improvements, highly stretchable PDMA hydrogels with the ability to self-heal autonomously at room temperature have not been prepared before. Such hydrogels are of great interest in tissue engineering and for biomedical applications.

The unique properties of PDMA are mainly due to the existence of both hydrogen bonding and hydrophobic interactions in its aqueous solutions and hydrogels [22,23]. For instance, strong hydrogen bonding interactions exist between PDMA and silica nanoparticles in aqueous solutions leading to hydrogels with reinforced properties [16,17]. Different from PDMA, polyacrylamide (PAAm) shows weak interactions with these particles, since it is simultaneously hydrogen-bonding donor and acceptor [17]. PDMA hydrogels also exhibit reentrant phenomenon in aqueous solutions of acetone, dioxane, propanol or t-butanol, i.e., the hydrogels first collapse then reswell if a particular external parameter such as organic solvent concentration is continuously varied [24,25]. Since this phenomenon is not observable in PAAm hydrogels [25], hydrophobic interactions between the methyl groups of PDMA network and the organic solvent are responsible for the reentrant transition behavior of the hydrogels. Thus, we conclude that PDMA generates much stronger reversible molecular interactions as compared to PAAm, making it a good candidate for the preparation of supramolecular polymer gels.

A promising strategy to design synthetic hydrogels with self-heal ability is to substitute the covalently crosslinked polymer chains by supramolecular ones. In the past few years, different reversible molecular interactions have been used to generate self-healing hydrogels, including hydrogen bonding [19,26–29], electrostatic interactions [30–32], molecular recognition [33–35], metal coordination [36,37], π - π stacking [38], dynamic chemical bonds [39–42], and molecular diffusion [43,44]. Recently, we presented a simple strategy for the production of self-healing hydrogels via hydrophobic interactions in micellar solutions [45–50]. Large hydrophobes such as stearyl methacrylate (C18) could be copolymerized with the hydrophilic monomer acrylamide (AAm) in aqueous sodium dodecyl sulfate (SDS) solutions. This was achieved by the addition of salt (NaCl) into the reaction solution. Salt leads to micellar growth and hence, solubilization of large hydrophobes within the grown wormlike SDS micelles [45,46]. Incorporation of hydrophobic sequences within the hydrophilic PAAm chains via micellar polymerization generates dynamic hydrophobic associations between the hydrophobic domains of polymer chains and surfactant micelles acting as physical crosslinks of the resulting hydrogels.

We propose that a stronger self-healing and a better mechanical performance in such hydrogels could be

achieved by replacing PAAm with PDMA backbone that would mediate stronger hydrophobic associations and hydrogen bonding across a rupture in the hydrogel. Here, we prepared physical PDMA hydrogels by the micellar copolymerization of N,N-dimethylacrylamide (DMA) with the hydrophobic monomer C18 in aqueous SDS–NaCl solutions. The gels obtained in the presence of 2 mol % C18 exhibit very high stretchability (about 43 times its original length) and autonomous self-healing within 20 min, as evidenced by mechanical measurements.

2. Experimental

2.1. Materials

N,N-dimethylacrylamide (DMA, Sigma), sodium dodecylsulfate (SDS, Merck), ammonium persulfate (APS, Sigma), N,N,N',N'-tetramethylethylenediamine (TEMED, Sigma), and NaCl (Merck) were used as received. Commercially available stearyl methacrylate (C18, Sigma) consists of 65% n-octadecyl methacrylate and 35% n-hexadecyl methacrylate.

2.2. Hydrogel preparation

Hydrogels were prepared by the micellar copolymerization of DMA with 2 mol% C18 at 50 °C for 16 h in the presence of an APS (3.5 mM) – TEMED (0.25 v/v %) redox initiator system. SDS and NaCl concentrations were set to 7 w/v % (0.24 M) and 0.5 M, respectively. The aggregation number of SDS micelles in this solution is 200 nm [45], as compared to 60 for the minimum spherical SDS micelle. The growth of the micelles provides complete solubilization of the hydrophobe C18, [45,47] and thus permits its copolymerization with DMA in aqueous media. The total monomer concentration was varied while C18 content of the monomer mixture was fixed at 2 mol%. The gel preparation procedure was the same as in our previous studies [45]. Shortly, SDS (0.7 g) was dissolved in 8.14 mL aqueous solution of NaCl (0.2925 g) at 35 °C to obtain a transparent solution. Then, hydrophobic monomer C18 (0.0949 g) was dissolved in this SDS–NaCl solution under stirring for 2 h at 35 °C. After addition and dissolving DMA (1.46 mL) for 1 h, TEMED (25 μ L) was added into the solution. Finally, 0.1 mL of APS stock solution (0.8 g APS/10 mL distilled water) was added to initiate the reaction. A portion of this solution was transferred between the plates of the rheometer to follow the reaction by oscillatory small-strain shear measurements. For the determination of the gel fraction and for the mechanical measurements, the remaining part of the solution was transferred into several plastic syringes of 4.8 mm internal diameters and the polymerization was conducted for 16 h at 50 °C.

2.3. Gel fraction and swelling measurements

Cylindrical hydrogel samples (diameter 4.8 mm, length about 2 cm) were immersed in a large excess of water at 24 °C for at least 15 days by replacing water every second or third day to extract any soluble species. The mass m of

the gel samples was monitored as a function of swelling time by weighing the samples. The relative weight swelling ratio m_{rel} of gels was calculated as $m_{rel} = m/m_0$, where m_0 is the initial mass of the gel sample. Then, the equilibrium swollen gel samples were taken out of water and freeze dried. The gel fraction W_g (mass of water-insoluble polymer / initial mass of the monomer) was calculated from the masses of dry, extracted polymer network and from the comonomer feed.

2.4. Rheological experiments

Gelation reactions were carried out at 50 °C within the rheometer (Gemini 150 Rheometer system, Bohlin Instruments) equipped with a cone-and-plate geometry with a cone angle of 4° and a diameter of 40 mm. The instrument was equipped with a Peltier device for temperature control. During all rheological measurements, a solvent trap was used to minimize the evaporation. An angular frequency ω of 6.3 rad s⁻¹ and a deformation amplitude γ_0 of 0.01 were selected to ensure that the oscillatory deformation is within the linear regime. After a reaction time of 2 h, the dynamic moduli of the reaction solutions approached limiting values. Then, frequency-sweep tests at $\gamma_0 = 0.01$ were carried out at 25 °C over the frequency range 0.06 to 410 rad s⁻¹. The gels formed within the rheometer were also subjected to strain-sweep tests (both up and down) at $\omega = 6.3$ rad s⁻¹ for γ_0 ranging from 0.001 to 10.

2.5. Mechanical tests

The measurements were performed in a thermostated room at 24 °C on cylindrical hydrogel samples of 4.8 mm diameter. The uniaxial compression measurements were performed on a Zwick Roell test machine using a 500 N load cell. The hydrogel sample of 5.3 ± 0.7 mm length was placed between the plates of the instrument. Before the test, an initial compressive contact to 0.004 ± 0.003 N was applied to ensure a complete contact between the gel and the plates. The tests were conducted at a nominal strain rate of 0.0156 s⁻¹ (5 mm/min). Load and displacement data were collected during the experiment. Compressive stress was presented by its nominal σ_{nom} and true values σ_{true} ($=\lambda \sigma_{nom}$), which are the forces per cross-sectional area of the undeformed and deformed gel specimen, respectively, while the strain is given by λ , the deformation ratio (deformed length/initial length). Compressive modulus was calculated from the slope of stress–strain curves between 5% and 15% compressions. Cyclic compression tests were conducted at a constant crosshead speed of 5 mm/min to a maximum compression ratio, followed by retraction to zero force and awaiting time of 7 min, until the next cycle of compression. For reproducibility, at least five samples were measured for each gel and the results were averaged.

The uniaxial elongation measurements were performed on a Zwick Roell test machine using a 10 N load cell under the following conditions: Nominal strain rate = 0.0833 s⁻¹ (50 mm/min), sample length between jaws = 10 ± 0.5 mm. The tensile modulus was calculated from the slope of

stress–strain curves between elongations of 5% and 15%. Samples were held on the test machine between clamps altered with anti-slip tape (Tesa, 25 × 15 mm) together with wood strips to better grip the slippery gel samples. Cyclic elongation tests were conducted at a constant crosshead speed of 50 mm min⁻¹ to a maximum elongation ratio, followed by retraction to zero force and a waiting time of 7 min, until the next cycle of elongation. For reproducibility, at least five samples were measured for each gel and the results were averaged.

The self-healing efficiency of the gel samples was determined by tensile testing experiments performed using virgin and healed cylindrical gel samples of 5 mm in diameter and 6 cm in length. The samples were cut in the middle and then, the two halves were merged together within a plastic syringe (of the same diameter as the gel sample) at 24 °C by slightly pressing the piston plunger. The healing time was varied from 2 to 30 min, and each experiment was carried out starting from a virgin sample. The tensile modulus E , the fracture stress σ_f , and the elongation ratio at break λ_f of the healed gel samples were recorded.

3. Results and discussion

PDMA hydrogels were prepared by the micellar copolymerization of DMA with 2 mol% C18 at 50 °C in aqueous SDS–NaCl solutions. Since the hydrogels formed at or below 10 w/v % DMA were too weak, the hydrogel prepared at 15 w/v % DMA will be presented and used for discussion. We first conducted the micellar polymerization of DMA with and without the hydrophobic comonomer C18 by real-time rheological measurements. In Fig. 1A, the elastic modulus G' , viscous modulus G'' , and the loss factor $\tan \delta$ ($=G''/G'$) of the reaction solutions at 50 °C are shown as a function of the reaction time t . With or without C18, the general trend is a rapid increase of the dynamic moduli followed by a plateau regime where the moduli slightly increase. The addition of the hydrophobe C18 into the polymerization system increases both the elastic and viscous, energy dissipating properties of the resulting physical gel system.

Fig. 1B and C show frequency dependencies of G' , G'' , and $\tan \delta$ after a reaction time of 2 h for the systems without and with 2 mol % C18, respectively. PDMA solution formed in the absence of C18 exhibits a liquid-like response typical for a semi-dilute polymer solution, i.e., G'' exceeds G' at low frequencies while there is a crossover between G' and G'' at $\omega = 0.5$ s⁻¹. Incorporation of 2 mol% C18 into the PDMA backbone shifts the crossover frequency outside of the experimental window indicating formation of hydrophobic associations between the blocks of stearyl groups in the semi-dilute PDMA solution. Since the hydrodynamic correlation length of SDS micelles containing C18 is about 3 nm in the gelation solution [45], the physical gel system can be considered as a network of PDMA chains formed by reversible nanoparticles (mixed micelles) occupying an unswollen volume fraction of about 0.08.

To determine the mechanical performance of the physical gels formed via hydrophobic interactions, cylindrical

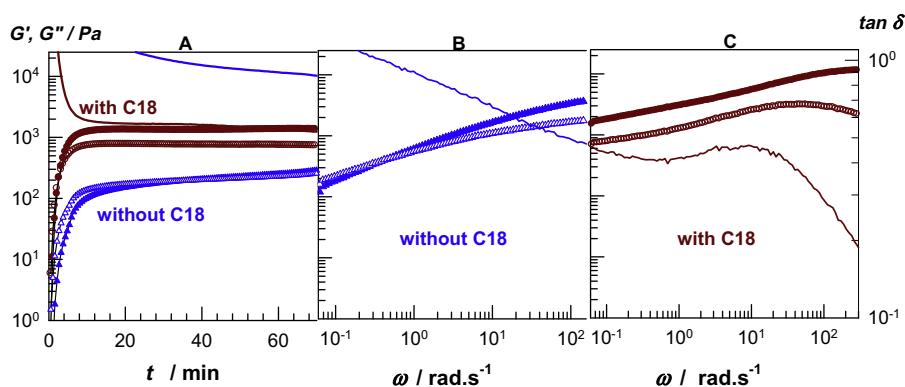


Fig. 1. (A): Elastic moduli G' (filled symbols), the viscous moduli G'' (open symbols), and the loss factor $\tan \delta$ (lines) during the DMA polymerization at 50 °C without and with 2 mol% C18 shown as a function of the reaction time t . $\omega = 6.3 \text{ rad s}^{-1}$ (B and C): G' (filled symbols), G'' (open symbols) and $\tan \delta$ (lines) of the reaction system at 25 °C without (B) and with 2 mol% C18 (C) shown as a function of angular frequency ω . Reaction time = 2 h. $\gamma_0 = 0.01$.

gel samples after a reaction time of 16 h were subjected to uniaxial compression and tensile tests. The Young's modulus of the hydrogel was found to be $11 \pm 2 \text{ kPa}$ both during compression and elongation. The compressive stress–strain curves of 15 gel samples are shown in Fig. 2A, where the nominal σ_{nom} and true $\sigma_{true} (= \lambda \sigma_{nom})$ stresses are plotted against the deformation ratio λ . The gel samples did not break even at a strain of about 100% compression and therefore, the nominal stress σ_{nom} increases continuously with increasing strain. However, the corresponding $\sigma_{true} - \lambda$ plots pass through maxima indicating the onset of failure in the gel specimen (gray curves in the figure). The fracture nominal stress and stretch λ_f at failure, calculated from the maxima in $\sigma_{true} - \lambda$ plots, were $2.4 \pm 0.2 \text{ MPa}$ and 0.04 (96% compression), respectively. However, successive compression tests conducted on the same gel sample shows that this failure is recoverable in nature. This is illustrated in the inset to Fig. 2A where two successive test results are given. A good superposition of the curves indicates that the damage in the gel is

self-healed upon unloading. The results thus reveal that the gel can be compressed up to about 100% strain without any permanent failure. Fig. 2B shows tensile stress–strain data of PDMA hydrogel. The gel ruptures when stretched to 43 ± 4 times its original length ($4200 \pm 400\%$ elongation). We have to mention that PAAm hydrogels formed under identical conditions exhibit elongation at break of about 2000% [45,47]. This suggests that the hydrogen bonding and hydrophobic interactions between the DMA units of the network chains additionally contribute to the mechanical properties of gels.

The large strain properties of the hydrogels were investigated by uniaxial cyclic mechanical tests. Successive loading – unloading cyclic compression ($\lambda < 1$) and tensile cycles ($\lambda > 1$) of the gels are shown in Fig. 3A. The tests were carried out with increasing maximum strain and with a waiting time of 7 min between cycles. For clarity, loading and unloading curves of successive cycles are presented with different colors (dark red and blue) and line types (solid and dashed). In all cases, the loading curve of the

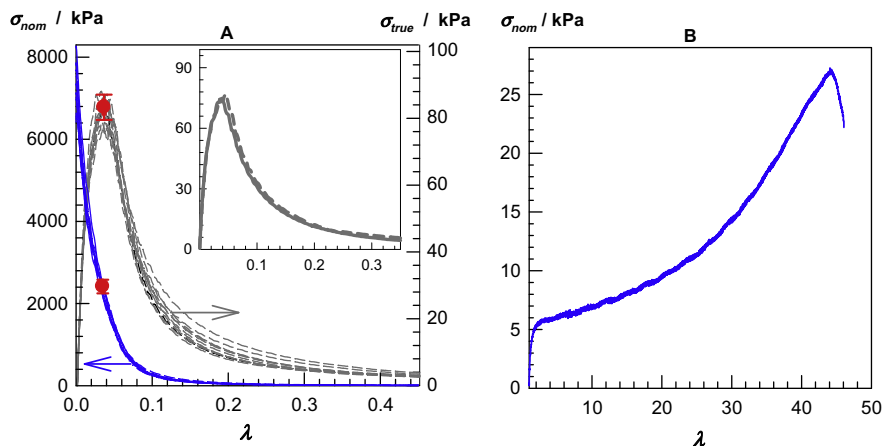


Fig. 2. (A): Typical stress–strain curves of PDMA hydrogel under compression as the dependences of nominal σ_{nom} (blue solid curves) and true stresses σ_{true} (gray dashed curves) on the deformation ratio λ . Results of 15 separate tests are shown in the figure. Red circles represent the points of failure in the gel samples. The inset shows $\sigma_{true} - \lambda$ curves of 2 successive tests conducted on the same gel sample up to 99.99% compression. (B): Stress–strain curve of PDMA hydrogel under elongation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

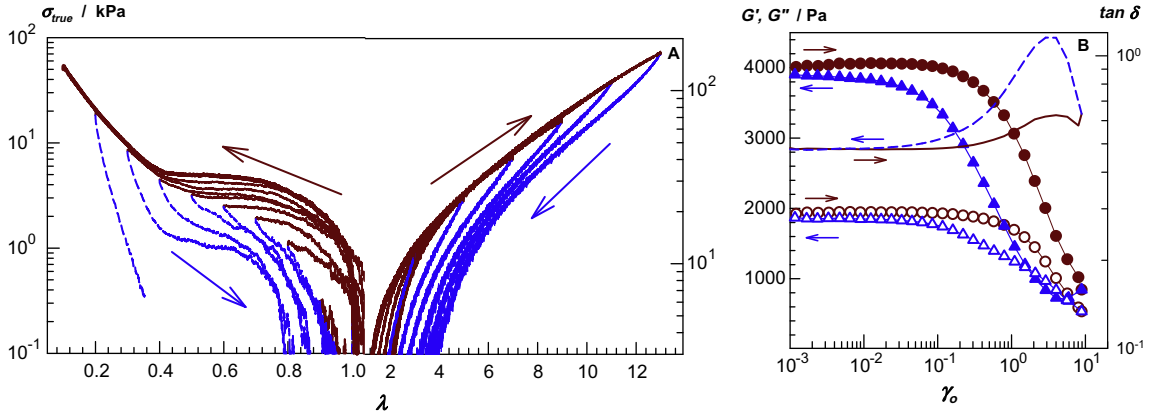


Fig. 3. (A): True stress σ_{true} vs deformation ratio λ curves of PDMA hydrogel from cyclic compression ($\lambda < 1$) and elongation tests ($\lambda > 1$). The tests were conducted with increasing strain with a waiting time of 7 min between cycles. (B): G' (filled symbols), G'' (open symbols), and $\tan \delta$ (curves) of PDMA hydrogel shown as a function of the strain γ_0 at $\omega = 6.3 \text{ rad s}^{-1}$. Sweep tests were conducted in up (dark red circles) and down directions (blue triangles), as also indicated by the arrows. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

compressive or tensile cycle is different from the unloading curve indicating damage in the gel samples and dissipation of energy during the cycle. The perfect superposition of the successive loading curves demonstrates that the damage done to the gel samples during the loading cycle is recoverable in nature. Thus, the behavior of the virgin gel sample can be recovered after a waiting time of 7 min without stress.

The recoverability of the damage in the gel samples was further demonstrated by the rheological measurements. Strain-sweep tests were conducted at a frequency $\omega = 6.3 \text{ rad s}^{-1}$ for strain amplitudes γ_0 ranging from 0.001 to 10 (0.1% to 1000% deformations). Fig. 3B shows up and down strain sweep experiments, where G' , G'' and $\tan \delta$ are plotted against γ_0 . The upward curves show a linear viscoelastic region at low strains ($\gamma_0 < 0.1$) beyond which the dynamic moduli decrease while the loss factor increases. Comparison of the up and down curves indicates that the gel exhibits an almost reversible strain sweep spectrum; the breakdown of the microstructure caused by the strain is recovered at low strain amplitudes. Thus, PDMA hydrogel softens with increasing deformation and exhibits liquid-like response ($\tan \delta > 1$) at high strains, but reversibly, if the force is removed, the solution turns back to the same gel state.

Cyclic mechanical tests also show the appearance of a significant hysteresis that increases with increasing degree of deformation of the gel samples (Fig. 3A). The reversibility of the mechanical cycles indicates that the energy associated with the hysteresis is due to the hydrophobic associations that break and reform dynamically preventing the fracture of PDMA backbone. The energy U_{hys} dissipated during the compression and tensile cycles was calculated from the area between the loading and unloading curves. Since uniaxial compression is equivalent to biaxial stretching [51], we converted the maximum strain λ_{max} during compression to maximum biaxial extension ratio $\lambda_{biax,max}$ by $\lambda_{biax,max} = \lambda_{max}^{-0.5}$. In Fig. 4A, the hysteresis energies U_{hys} calculated during compression and tensile cycles are plotted against the maximum strain in terms of uniaxial λ_{max}

and biaxial extension ratios $\lambda_{biax,max}$. It is seen that all U_{hys} data fall into a single curve, i.e., the hysteresis energy only depends on the maximum extension of the polymer chains.

U_{hys} can be interpreted as the sum of the dissociation energies of hydrophobic associations broken down reversibly during the cyclic tests [51,52], i.e.,

$$U_{hys} = U_{xl}n \quad (1a)$$

where U_{xl} is the average dissociation energy of a single association and n is the total number of reversibly breakable associations, which can be estimated as:

$$n = v_e f_v \quad (1b)$$

where v_e is the crosslink density of the gel, i.e., the concentration of elastically effective hydrophobic associations, and f_v is the fraction of associations broken during the loading. We assume that the energy U_{xl} required for the detachment of the hydrophobe C18 from associations is of the order of 10^2 kJ/mol [53,54]. To estimate the crosslink density v_e , the plateau modulus G_0 of PDMA gel was obtained from the constant value of G' at high frequencies (Fig. 1C). Since G_0 corresponds to the shear modulus G , v_e was calculated using the equation [55,56],

$$G = v_e RT \quad (1c)$$

where R is gas constant and T is the absolute temperature (K). Eq. (1c) assumes affine deformation of the network chains, which is a reasonable assumption for the physical gels formed by hydrophobic associations [46]. Using $G' = 11 \text{ kPa}$ at $\omega = 130\text{--}410 \text{ rad s}^{-1}$, the concentration of elastically effective associations v_e in PDMA hydrogel was calculated as 4.4 mol/m^3 . The values U_{hys} , U_{xl} , and v_e together with Eqs. (1a) and (1b), we calculated the fraction f_v of physical crosslinks reversibly broken during the mechanical cycles. In Fig. 4B, f_v is plotted against the maximum strain (λ_{max} or $\lambda_{biax,max}$) achieved during the tensile and compression cycles. Like the hysteresis energy, f_v only depends on the maximum strain indicating that the maximum extension ratio of the chains is the only parameter controlling the fraction of physical crosslinks broken

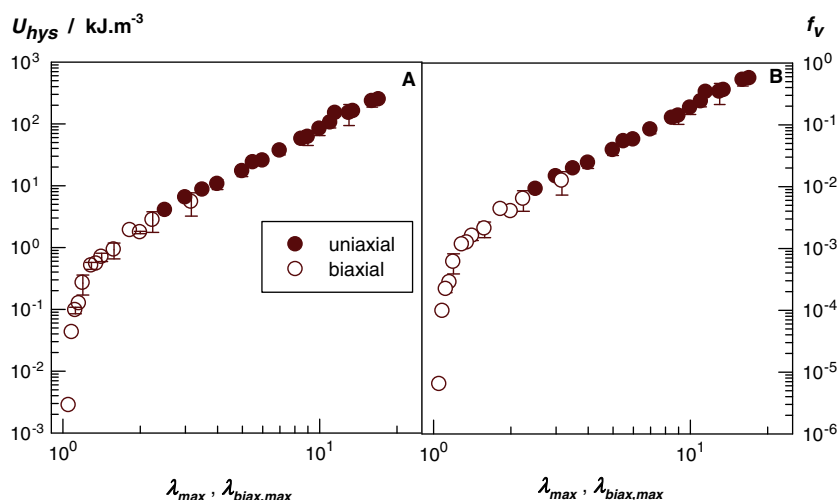


Fig. 4. Hysteresis energy U_{hys} (A) and the fraction f_v of dissociated crosslinks (B) during the loading/unloading compression (open symbols) and elongation cycles (filled symbols) of PDMA hydrogel shown as a function of the maximum strain λ_{max} or $\lambda_{biax,max}$.

during the loading. Thus, both compression and elongation have the same effect on the physical crosslinks of the present hydrogels. However, when f_v is plotted against the maximum value of the first strain invariant $J_{1,max}$, which represents a general strain state of gels, the data do not fall into a single curve (Fig. S1). This behavior is similar to that of double network hydrogels during their first compression and tensile cycles, as reported by Webber et al. [51]. Fig. 4B also shows that f_v varies between 10^{-6} and 10^0 indicating that up to all of the physical crosslinks dissociate under force, but reversibly, if the force is removed they reform again.

The results reveal reversible disengagements of the hydrophobic units from the associations under an external force and thus point out the ability of PDMA hydrogel to self-heal upon damage. This was indeed observed experimentally. The images in Fig. 5A were taken from a gel sample before and after elongation up to $\lambda = 10$. After a waiting

time of 10 min, the gel returns to its initial length indicating the recovery of the original shape. Moreover, when the fracture surfaces of a ruptured PDMA gel sample are pressed together, the two pieces merge into a single piece (Fig. 5B). The joint reformed withstands very large extension ratios before its fracture.

To quantify the healing efficiency, tensile testing experiments were performed using virgin and healed cylindrical gel samples. The samples were cut in the middle and then, the two halves were merged together at 24 °C for various healing times. In Fig. 6A, stress–strain curves of the virgin and healed gel samples are shown for different healing times. In Fig. 6B, the tensile modulus E , the fracture stress σ_f , and the elongation ratio at break λ_f of the healed gel samples are plotted against the healing time. The horizontal solid lines represent the characteristics of the virgin gel with standard deviations indicated by the dashed lines. The modulus E is recovered within 2 min indicating the

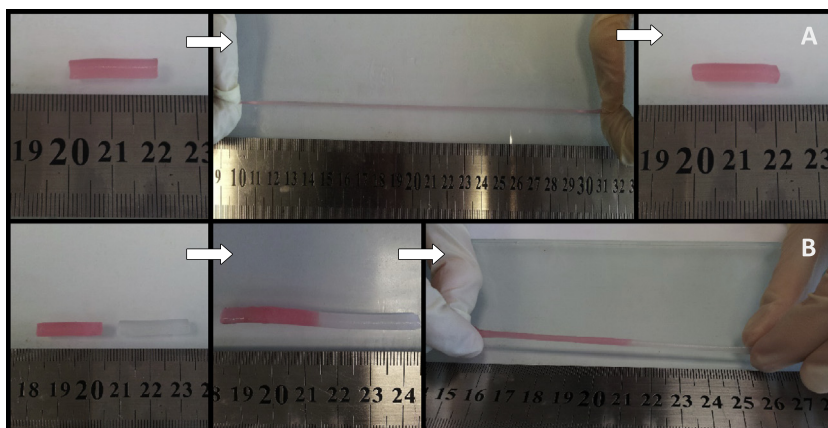


Fig. 5. (A): Photographs of a gel sample before and after stretching to an elongation ratio of 10. After a waiting time of 10 min, it recovers its original length. (B): Photographs of two gel samples. One of the samples was colored with a dye for clarity. After cutting into two pieces and pressing the fractured surfaces together for 10 min, they merge into a single piece. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

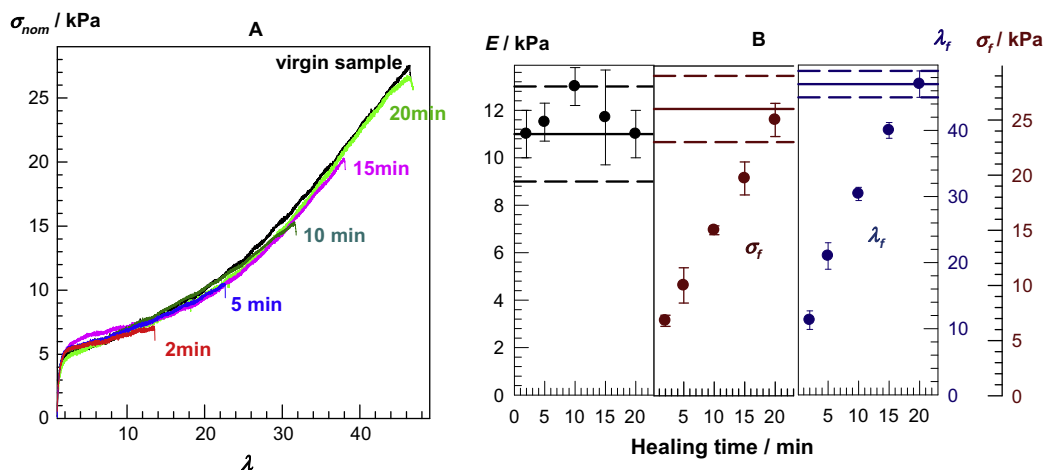


Fig. 6. (A): Stress–strain curves of virgin and healed gel samples. Healing times are indicated. Temperature = 24 °C. (B): Tensile modulus E , tensile fracture stress σ_f , and elongation ratio λ_f at break of healed gels shown as a function of the healing time. The solid lines represent the behavior of virgin gel sample and the dashed lines are the standard deviations.

occurrence of a very rapid and autonomous self-healing process in PDMA hydrogel. After 10 min, the fracture stress of the healed gel is 15 kPa which is 60% of the fracture stress of the virgin sample. A healing time of 20 min suffices to recover all the initial mechanical properties of the physical hydrogel.

Experiments were also carried out to optimize the formation conditions of PDMA hydrogels. Decreasing the initial DMA concentration C_0 in the feed from 15% to 10% produced weak hydrogels which were not suitable for the mechanical tests. Increasing C_0 from 15% to 20% increased the fracture stress to 70 ± 5 kPa while the elongation ratio at break decreased to 34 ± 2 (Fig. S2). Simultaneously, the self-healing efficiency drastically decreased. For instance, after a healing time of 1 h, the fracture stress of the healed gel was 10 kPa, which is 14% of the virgin sample (Fig. S2). Moreover, increasing SDS concentration at the gel preparation from 7% to 8.5% did not improve the healing ability of the gels formed at $C_0 = 20\%$ (Fig. S3). Thus, $C_0 = 15\%$ and SDS = 7% was found to be the optimum synthesis condition of PDMA hydrogel with a very high stretchability and complete self-healing at room temperature.

We have to mention that, all the features of PDMA hydrogels described above are related to their states just after their preparation, i.e., those containing surfactant micelles. The solubility tests showed that the hydrogels are insoluble in water with a gel fraction W_g equals to unity. This reveals that the monomers in the feed are completely converted into a water insoluble, physically cross-linked polymer network. The swelling kinetics of PDMA hydrogel formed at $C_0 = 15\%$ exhibited typical behavior of gels containing surfactants [45–47]. The gel immersed in water initially behaves like an ionic gel due to the presence of SDS counterions inside the gel network and thus exhibits a large swelling ratio m_{rel} (Fig. 7A). However, as SDS is progressively extracted, this osmotic effect disappears and the gel gradually converts into a nonionic gel having an equilibrium swelling ratio m_{rel} of 4.1 ± 0.2 in water.

Indeed, SDS concentration in the external solutions rapidly dropped below the detection limit of the methylene blue method (0.20 mg/L) after 10 d [45,57].

The internal dynamics of PDMA hydrogels significantly changed after equilibrium swelling in water, i.e., after extraction of surfactant micelles. Fig. 7B compares the mechanical spectra of the hydrogels before and after swelling in water. The swollen gel exhibits nearly time-independent elastic modulus and a loss factor below 0.1 corresponding solid-like behavior. It is obvious that this weak-to-strong gel transformation of PDMA hydrogel upon swelling is responsible for its insolubility in water. Since the extraction of SDS from the gel network increases the lifetime of hydrophobic associations (Fig. 7B), the gel without SDS remains stable in water. Indeed, immersion of the hydrogels in 7% SDS solution instead of water resulted in their solubilization due to the weakening of the hydrophobic interactions and disruption of the associations [3]. The gels were also soluble in aqueous DMA solutions containing more than 50% DMA. Since DMA is a good solvent for C18 due to its hydrophobicity, it solubilizes C18 units of the network chains and thus, enables dissociation of the physical crosslinks of PDMA hydrogels.

Fig. 7C compares tensile stress–strain data of PDMA hydrogel before and after swelling in water. Highly stretchable PDMA gel becomes a brittle one after swelling in water and ruptures at a stretch of $\lambda_f = 5 \pm 0.1$. Cyclic mechanical tests conducted on swollen hydrogels revealed appearance of irreversibility cycles and a significant decrease in the hysteresis (Fig. S4), indicating decreasing number of reversibly breakable associations. Indeed, no self-healing was observed in swollen gel samples. Thus, the hydrophobic interaction without micelles is too strong to reversibly associate. Surfactant micelles within the supramolecular network are needed to create self-healing in PDMA hydrogels. The weakening of hydrophobic interactions due to the presence of surfactant molecules increases the mobility of the hydrophobic associations inside the physical network so that self-healing of the

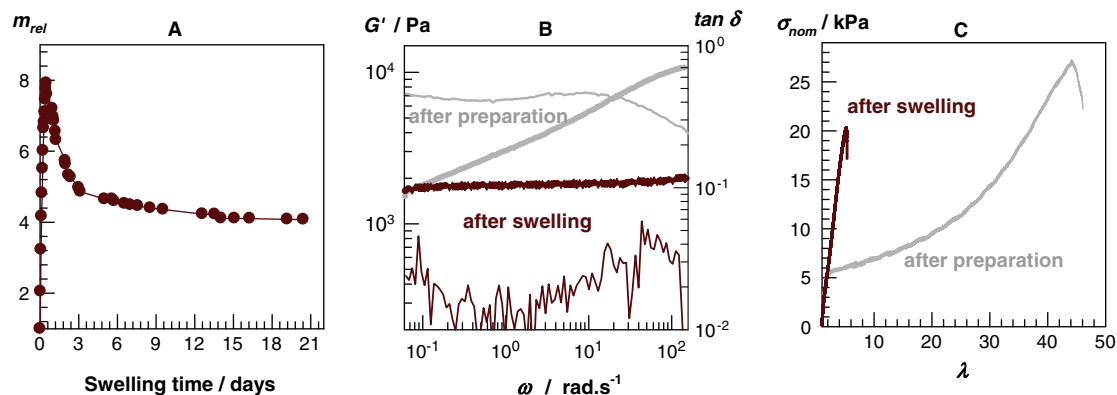


Fig. 7. (A): Relative weight swelling ratio m_{rel} of PDMA gels plotted against the swelling time in water. $C_0 = 15\%$. (B): G' (symbols) and $\tan \delta$ (lines) of PDMA gels after preparation (gray) and after equilibrium swelling in water (black) shown as a function of angular frequency ω . Temperature = 25 °C. $\gamma_o = 0.01$. (C): Stress–strain curves of the hydrogels under elongation.

damaged gel samples occurs within a short period of time. We have to mention that, in our previous study, we investigated the effect of SDS concentration on the self-healing characteristics of physical gels based on hydrophobically modified PAAm [47]. The highest self-healing efficiency was observed at the preparation state of the hydrogels containing 7% SDS while it gradually decreased as the SDS content is decreased. Thus, the unique properties of PDMA hydrogels such as very high stretchability and autonomic self-healing only exist if the hydrogels contain surfactant micelles. Without surfactant, they exhibit low stretchability and lose their ability to self-heal due to the increased lifetime of hydrophobic associations. Further work is in progress using hydrophobically modified polyelectrolytes with oppositely charged surfactants to stabilize the self-healing properties of hydrogels in aqueous environment.

4. Conclusions

PDMA hydrogels formed via hydrophobic interactions in SDS solution exhibit very high stretchability (about 4200% elongation) and autonomous self-healing at room temperature. They are also able to sustain large compressions without any permanent failure. The extraordinary mechanical properties of the present hydrogels as compared to the self-healing PAAm hydrogels formed under identical conditions suggest that the DMA units of the network chains additionally contribute to their mechanical properties. Loading–unloading compression and tensile cycles show perfect superposition of the successive loading curves demonstrating that the damage done to the gel samples during the loading cycle is recoverable in nature. The recoverability of the damage in the gel samples was also demonstrated by the rheological measurements. PDMA hydrogel softens with increasing deformation and exhibits liquid-like response ($\tan \delta > 1$) at high strains, while the solution turns back to the same gel state if the force is removed. The hysteresis energies calculated from the mechanical cycles indicate that up to all of the physical crosslinks dissociate under force, but reversibly, if the force is removed they reform again. Self-healing tests show that

a healing time of 20 min suffices to recover all the initial mechanical properties of PDMA hydrogels. The results also show that the hydrophobic interaction without micelles is too strong to reversibly associate and, the key factor leading to the self-healing behavior of PDMA hydrogels is the weakening of strong hydrophobic interactions due to the presence of surfactant molecules.

Acknowledgments

MPA acknowledges the financial support from the Scientific and Technical Research Council of Turkey (TUBITAK) for a postdoctoral scholarship. This work was supported by TUBITAK, TBAG–109T646. OO thanks the Turkish Academy of Sciences (TUBA) for the partial support.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.eurpolymj.2014.07.022>.

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