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Rheological characterization of a charged cationic hydrogel network across the gelation boundary

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Abstract

The in situ rheological behavior across the gelation threshold has been investigated for an affine network of a completely charged cationic monomer (3-acrylamidopropyl)-trimethylammonium chloride (APTMAC1) when it is crosslinked with a neutral crosslinker (N,N'-methylenebisacrylamide) to form a fully charged novel cationic hydrogel. The elastic moduli (G') near the gel point (during the crosslinking or 'curing' process) show a power law dependence of the form $G'(t)=\varepsilon^z$, where $\varepsilon=((t-t_c)/t_c)$ is the distance from the gel point (t_c). The critical exponent, z, for the hydrogel series investigated is estimated to be 1.5, slightly lower than the predictions based on percolation theory ($z\sim 1.7$–1.9). From the equilibrium (after the curing process) rheological measurements of a series of samples, it is inferred that there is a critical crosslinker mole percent (X_c) with respect to the monomer concentration, required to form a well-defined three-dimensional network with a solid-like behavior. The value of this X_c is found to be between 0.5 and 1%. The theoretically predicted value of X_c using the percolation theory (for the percolation of crosslinks, $G_0(X)\propto[|X-X_c|/X_c]^z$) and the exponent estimated from the in situ measurements ($z=1.5$), is $X_c\sim 0.6$, which is in good agreement with the experiments. The results may have applicability in translating from bulk systems to the nanoscale in hydrogel design.

Keywords: Rheological characterization; Charged hydrogel; Gelation

1. Introduction

Hydrogels are crosslinked hydrophilic polymer chains forming a three-dimensional network capable of absorbing large amounts of water. Due to their ability to change shape and volume in response to external stimuli, they have been studied intensively for a variety of applications [1–3]. Amongst hydrogel forming materials, polyelectrolytes with ionizable groups have a special significance, since they impart the network responsive properties. Many biological applications of polyelectrolytes are due to their ability to bind oppositely charged species to form complexes. Amongst them, cationic polymers are of interest in gene therapies, and the development of viral and non-viral vectors for DNA and oligonucleotide delivery [4–6].

The mechanical characterization of hydrogels obtained from polyelectrolytes is very important in determining their range of applications. Mechanical properties of the hydrogel network also provide an understanding of the underlying microstructure and give insight to the design of novel systems [7]. There is a significant literature on the mechanical and viscoelastic behavior of uncharged polymer networks such as elastomers [8], polyalkylsiloxanes [9], polyurethanes [10,11], and nylons (caprolactones) [12] etc. and several theories have been developed to elucidate the rheological response of the network near the gel point [13–16]. However, there are only a few reports on the rheological investigations of hydrogels in the literature; most of these studies are based on hydrogels with partial or non-ionizable groups [17,18]. Most of the studies conducted on charged networks focused on the partially charged networks obtained by: (1) adding a small fraction of an ionizable group containing monomer (such as –SO_3H) to a mixture of neutral monomers and crosslinkers [19–22], (2) using monomers with partially ionizable functional groups (such as –COOH) [23,24], and (3) using oppositely charged polyelectrolytes that couple to produce crosslinks [25,26].

The literature on the rheology of charged hydrogels is limited to the measurement of the swelling behavior and equilibrium elastic response [27–29]. There are a few reports on scaling of rheological properties of hydrogels from

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associating polymers [25,30]. In the present work, we report the in situ rheological response of a novel cationic hydrogel (degree of dissociation, $\alpha = 100\%$) during the formation of a three-dimensional network, and the characterization of its equilibrium elastic response.

2. Experimental section

2.1. Materials

(3-Acrylamidopropyl)-trimethylammonium chloride (APTMACl) (75 wt% solution in water), as monomer, *N*,*N*′-methylenebisacrylamide (bis) as a crosslinker, ammonium persulfate (APS) as redox initiator, and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) as an accelerator, were purchased from Aldrich Chemical Company, Inc. (Milwaukee, Wisconsin) as research grade chemicals and used as received.

2.2. Hydrogel preparation

Hydrogels of APTMACl with varying levels of crosslinker (defined as the mole percent, *X*, of crosslinker with respect to monomer) were synthesized according to general procedures and described as follows. Two stock solutions were prepared, one containing the required amounts of crosslinker, monomer, accelerator and water, and the other, an initiator solution. In a typical hydrogel synthesis: (1) 4.5 ml of monomer solution was mixed with 300 µl TEMED, and 3 ml water containing the desired amounts of the crosslinker (at *X* values 0, 0.25, 0.5, 1, 2, 3, 4, and 5%). (2) Three millilitres of the initiator-solution (1% w/w in water) was prepared and kept refrigerated before polymerization-crosslinking step. The amounts of all ingredients were determined by trial and error in order to simultaneously monitor the rheological changes during the polymerization-crosslinking reaction.

2.3. Rheological experiments

The redox polymerization and simultaneous crosslinking reactions were carried out between the parallel plates of a rheometer. All the rheological data were collected by placing a 2 ml mixture of hydrogel precursors obtained from by mixing 2.5 ml of stock solution (1) with 1 ml of the stock solution (2). The only variation in the system compositions used in rheological experiments was the crosslinker level. Each experiment was repeated 3 times for a given crosslinker/-APTMACl ratio (*X*). The results are highly reproducible with less than 5% error.

Rheological tests were conducted on a TA instruments AR-2000 constant stress rheometer (controlled-strain and controlled-rate is achieved through an extremely sensitive feed back loop) with built-in temperature and gap calibration. Parallel plate geometry (diameter 40 mm), with a crosshatched upper plate was used. This is to avoid slip at the hydrogel-plate interface, and allows accurate measurements of the storage (G') and loss moduli (G''). As soon as the sample was placed between the parallel plates, the data were collected. All experiments were conducted in the dynamic (oscillatory) mode. The oscillation stress was kept constant such that the maximum strain amplitude (γ_0) was less than 1% for all the experiments, except for the stress relaxation experiment where a 10% strain (γ_0) was applied in 0.01 s ($\gamma_0 = 10^3\ \mathrm{s}^{-1}$). The temperature was kept constant at 25 °C for all experiments, except for the temperature sweep experiments where the temperature was varied from 25 to 50 °C. For the time sweep and temperature sweep experiments, the frequency (ω) was held at 1 rad/s. For the frequency sweep experiments, the frequency was varied from 0.1 to 500 rad/s. The duration of a typical experiment was approximately 3 h. A vendor supplied solvent trap was used in order to mitigate solvent (water) loss during the experiments. The Weissenberg–Rabinowitsch correction [31] in the TA analysis software was used to account for the non-uniformity of shear rate in the parallel plate geometry.

3. Result and discussion

The most commonly employed methods for polymerization and crosslinking for hydrogel synthesis are based on UV irradiation and redox [32–34]. The hydrogels in the present study have been synthesized using redox free radical polymerization/crosslinking reaction as indicated in Section 2. Fig. 1 depicts the in situ polymerization and crosslinking reaction mechanism between the monomers and the crosslinkers. The rheological response of the incipient hydrogel network is monitored as a function of time, immediately after the introduction of the hydrogel precursor solution. Fig. 2(a) shows a typical transient rheological response of a developing

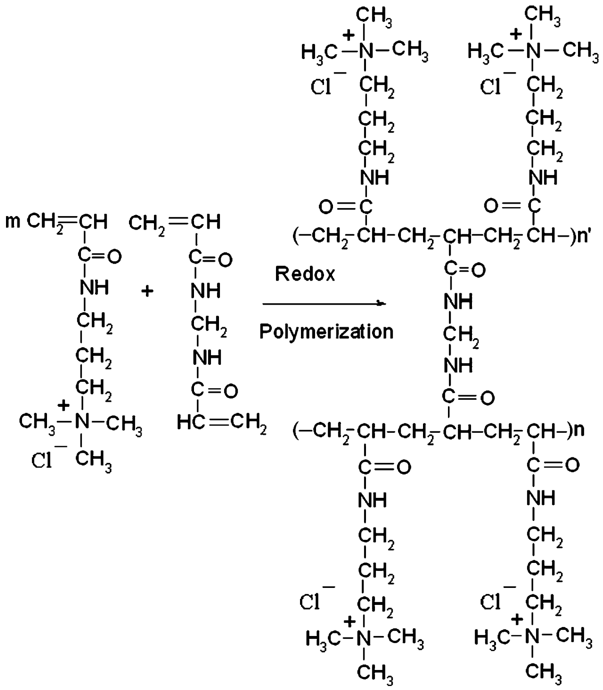

Fig. 1. Schematic of the polymerization/crosslinking reaction for the synthesis of the cationic hydrogel.

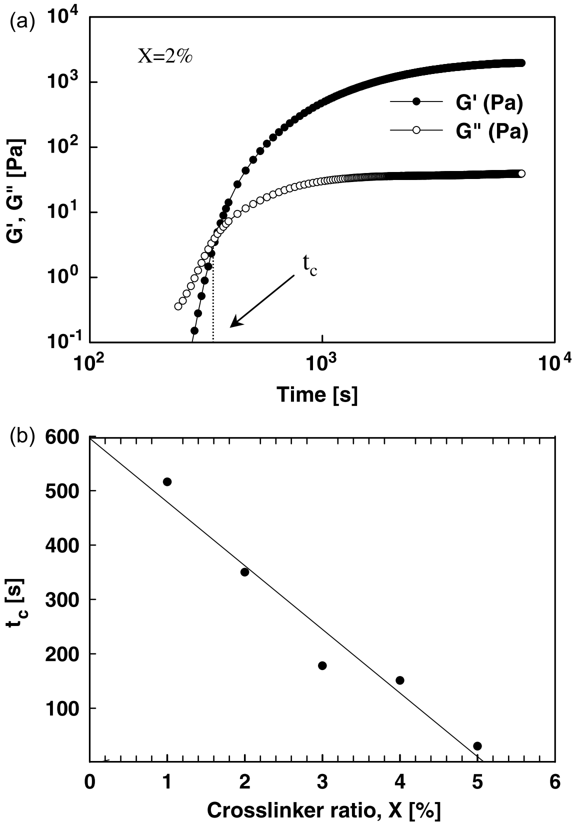

Fig. 2. (a) Time sweep (strain = 1%, $\omega = 1$ rad/s, $T = 25$ °C) experiments during the polymerization/crosslinking of the hydrogel precursor solution at $X = 2$. The dashed line indicates the gel point (t_c). (b) Variation of the gel point (t_c) with the crosslinker/monomer ratio used in the synthesis of the hydrogels.

three-dimensional hydrogel network. The elastic (G') and loss (G'') moduli start from very small values corresponding to the precursor sol. The moduli build rapidly (the build-up rate depends on the crosslinker/monomer ratio) as the reaction progresses. The rate of increase of the elastic modulus (G') is typically higher than that of the loss modulus (G''). This difference in the rates leads to a G'/G'' crossover. This crossover is a well-known phenomenon in curing/crosslinking reactions [35], described by the gel point (t_c), and the critical crossover value ($G' = G'' = G_c$). This gel point represents the transition from the liquid-like (G'') behavior to the solid-like behavior, and marks the percolation threshold for the precursor sol. This rheologically determined gel point coincides with the analytically determined value, which is the maximum degree of cure/crosslinking at which the partially crosslinked system still dissolves completely in a good solvent [36]. The moduli (G', G'') reach equilibrium values as the polymerization/crosslinking reaction reaches completion (Fig. 2(a)). In this paper, these equilibrium values of the elastic moduli are denoted by G_∞ (or $G'_\infty = G_0$). The gel point for a hydrogel precursor (sol) depends on the rate of polymerization (monomer) and crosslinking (crosslinker). In the series of hydrogels investigated here, the monomer concentration is held constant for all samples. This implies that the gel point for this series should be a function of the X alone, under identical reaction conditions for all samples. In Fig. 2(b) the gel points for the hydrogel series have been plotted against the corresponding ratio of X. The plot (Fig. 2(b)) shows an almost linear decrease in the gel point with the crosslinker ratio. The gel point occurs at an early stage in the polymerization/crosslinking reaction and the observation can be understood in terms of the rate of crosslinking, which directly depends on the initial crosslinker concentration. This point is further elucidated in the discussion of Fig. 4(a).

Near the gel point a three-dimensional network does not fully develop, and dangling ends, loops and stray chains that are elastically ineffective, are common [37]. It is well known [25] that the elastic modulus near the gel point typically follows a power law, or,

$$G' = \varepsilon^z \tag{1}$$

where ε is a measure of the distance from the gelation threshold, and can be defined in terms of the gel point as,

$$\varepsilon = \frac{(t - t_c)}{t_c} \tag{2}$$

and z is a positive constant. The theoretical predictions for the value of the exponent, z, from percolation theory depend on whether one uses Rouse–Zimm (R–Z) theory [38] ($z = 2.7$) or an analogy between elasticity and the growth of conductivity in a random electrical network ($z = 1.7$–1.9) [39,40]. Adolf and coworkers [8] have demonstrated a very good agreement of the exponent ($z = 2.7$) with percolation model using R–Z theory for a system of partially cured epoxides. Fig. 3 shows the exponential dependence of the reduced elastic moduli (G'/G_0) with ε near the gel point. The value of z in for the hydrogel system under the present study is 1.5, slightly lower than the percolation theory predictions based on the analogy between the hydrogel network and a random electrical network (EN). The free energy of the network, F_{net} can be expressed as, $F_{\text{net}} = F_{\text{el}} + F_{\text{int}} - TS_{\text{couterion}} + F_{\text{(el/int)}}$ where, F_{el} and F_{int} are the elastic and interaction part of the free energy, $-TS_{\text{couterion}}$ is the entropic contribution due the counter ion mobility, and $F_{\text{(el/int)}}$ is a free energy dependence arising from the cross term

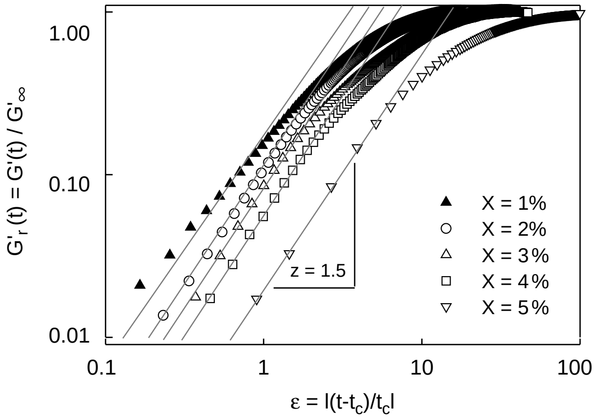

Fig. 3. The variation of the elastic moduli (G') with the distance from the gelation threshold, ε, indicating a power law behavior of the hydrogel samples near the gel point.

between the elastic and interaction contributions [43]. Hence, a lower value of the exponent z indicates that the non-elastic contributions to the free energy ($F_{\text{int}} - TS_{\text{couterion}} + F_{(\text{el/int})}$) in this case are negative, but do not affect the scaling behavior greatly. We would also like to point out that this exponent is much smaller than the prediction from the classical theory of rubber elasticity ($z = 3$), and thus the tree approximation for the network growth is not correct for the present study [41]. The percolation model provides a better explanation of the dynamic phenomenon involved in the random polymerization/crosslinking reaction in the present study, indicating the importance of connectivity in the network elasticity.

Fig. 4(a), shows the build-up of the elastic moduli as a function of the reaction time, with increasing X ratio. In a free radical polymerization/crosslinking reaction, the extent of crosslinking between the propagating polymer chains increases monotonically with time. For an elemental reaction of the form $\mathrm{P} + \mathrm{X} + \mathrm{P}' \Rightarrow \mathrm{P}-\mathrm{X}-\mathrm{P}'$ (P and P′ are two representative polymer chains crosslinked by the crosslinker, X), the rate of reaction can written as rate, $r = -(rx) = k[\mathrm{P}][\mathrm{X}][\mathrm{P}'] = k'[\mathrm{X}]$ (k and k' are kinetic constants), as the monomer concentration is held constant for the entire series. At the beginning of the reaction, the rate can be assumed constant, depending on the initial concentration of the crosslinker, or rate $= k'[X]$. Since, the crosslinking of polymer chains in an incipient three-dimensional network leads to an increase in the elastic properties of the network, the transient elastic modulus, $G'(t)$, also increases monotonically with the reaction time for all the samples. Thus, the rate of increase of $G'(t)$ also reflects the rate of the reaction. The initial growth rate of $G'(t)$, ($\mathrm{d}G'(t)/\mathrm{d}t$) is constant (Fig. 4(a)), as expected from a constant initial rate of polymerization/crosslinking. The elastic moduli reach an equilibrium value (G_0) upon the completion of the reaction. The elastic response of a neutral crosslinked network depends on the extent of crosslinking and the system temperature [42]. For a neutral Gaussian network, the classical theory of rubber elasticity predicts that the elastic modulus (G_0) for an uncharged, isotropic network is [42]

$$G_0 \propto Nk_{\mathrm{B}}T \tag{3}$$

where N is the number of elastic chains in the network, k_B is the Boltzmann constant, and T is the absolute temperature. There have been a few attempts to understand the elastic properties of polyelectrolyte gels. Rubenstein and coworkers [29] have reported a scaling theory for the elastic modulus for polyelectrolyte gels and presented a scaling law very similar to Eq. (3), except they also find a dependence on monomer concentration, c:

$$G_0 \propto Nk_{\mathrm{B}}Tc^{5/6} \tag{4}$$

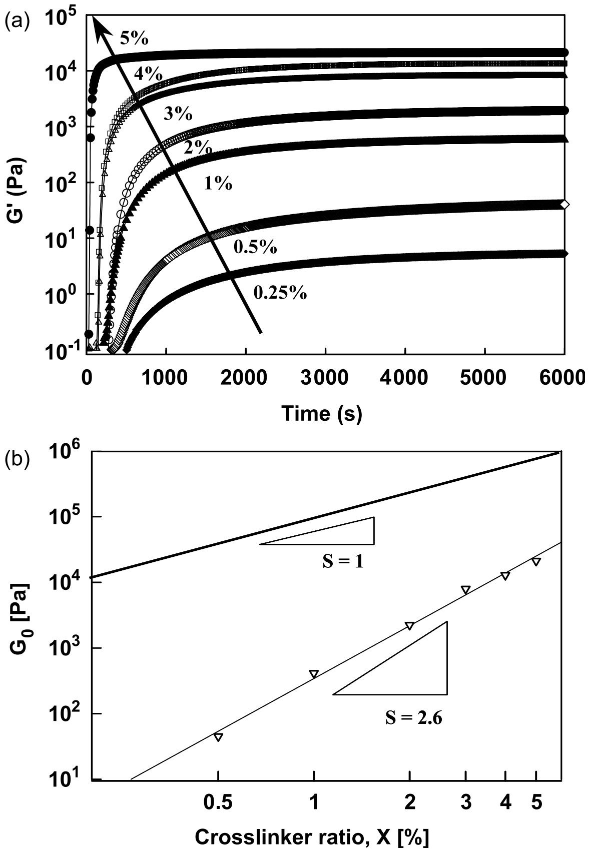

Fig. 4. (a) Gelation kinetics of hydrogel samples for various crosslinking ratios as indicated by time sweep (strain = 1%, $\omega = 1$ rad/s, $T = 25$ °C) experiments. (b) Equilibrium elastic moduli (G'_∞) as a function of crosslinker (X) ratio (the slopes, $s = 1$ and $s = 2.6$ correspond to theoretical and experimental values, respectively).

In the present study, the monomer concentration is held constant for the entire series, hence Eq. (4) is very similar to Eq. (3) for the present analysis. Candau and coworkers [28] have studied ionized poly(acrylic acid) gels at low salt additions (implying lower screening of the electrostatic interactions, as opposed to earlier studies [17–24] with high sail concentration with a high degree of electrostatic screening) and indicated that the electrostatic interactions lower the elastic moduli significantly except at high crosslinking where the entropic contributions (of the polymer chains) to the free energy dominate. Candau and coworkers, based on the osmotic pressure considerations, propose that the elastic modulus (G_0) for a polyelectrolyte gel at the swelling equilibrium (simple affine deformation [18]) can be expressed as:

$$G_0 \propto N^2k_{\mathrm{B}}T \tag{5}$$

Wilder and coworkers [43] argue that the assumption that the elastic and solvent parts of the free energy are additive is not precise, and some cross terms must be included. Through a non-trivial analysis Wilder and coworkers show that the modulus of the partially charged ($\alpha < 100\%$) polyelectrolyte has two parts:

$$1/G_0 \propto (1/G_{\mathrm{N}} + G_{\mathrm{I}}) \tag{6}$$

the first part G_{N}($G_{\mathrm{N}} \propto Nk_{\mathrm{B}}T$) is the term corresponding to the classical rubber elasticity (Eq. (3)), and the second term G_{I}($G_{\mathrm{I}} \propto N^2k_{\mathrm{B}}T^{3/2}$) stems purely from interactions. Assuming every crosslinker molecule leads to a crosslink formation; N, the number of elastic chains in the network, is directly proportional to the ratio of crosslinker to the monomer. Or

$$N \propto X \tag{7}$$

In a typical free radical polymerization/crosslinking reaction, some of the crosslinker is wasted through cyclization and multiple crosslinking reaction and/or ineffective radical formation [21,44]. Dangling ends also lead to a smaller value of the elastic moduli [45]. Hence, only a fraction, *f*, of the crosslinker molecules initially present in the reaction mixture results in an effective crosslink formation or,

$$N \propto fX \tag{8}$$

The hydrogels investigated in the present work contain water that is present in the reaction mixture at the time of the synthesis, corresponding to a swelling ratio/degree ((Weight$_{\text{swollengel}}$/Weight$_{\text{drygel}}$)100) of less than 300, which is within 10–15% of their equilibrium swelling ratios depending on the used crosslinker amount ($\sim$2000–3000). Also, the hydrogel network is exposed to very small strain ($<1\%$). Therefore, the limited extensibility [18,28] of the network chains is not very crucial to this study, and all the models that apply to polyelectrolyte gels below equilibrium swelling can used to compare the experimental results. The equilibrium elastic moduli (G_0 or G'_∞ values found experimentally are plotted in Fig. 4(b). The theoretical predictions based on the classical theory of rubber elasticity indicated by straight line with a slope of 1). The experimental values of the elastic moduli (G_0) show an exponential dependence on the stoichiometric X ratio. The exponent obtained from the regression of the experimental data ($s=2.6$). This dependence indicates:

$$G_0 \propto (X)^{2.6} \quad \text{or} \quad G_0 \propto (fN)^{2.6} \tag{9}$$

Since, the functionality of *f* is unknown, it is very difficult to compare the experimental correlation with any proposed models (Eqs. (3)–(6)). Since, the percolation theory (EN) seems to explain the scaling behavior during the polymerization/crosslinking process (Fig. 3), we can try to understand this exponential dependence ($s=2.6$) in terms of the percolation of the crosslinks in a three-dimensional network. The hydrogel series investigated here is conceptually analogous to a single polymerization/crosslinking process where the amount of the crosslinker is well above the level required to reach a percolation threshold, where the series represent the crosslinking process quenched at different time intervals. This analogy yields the scaling law near the gelation threshold, X_c:

$$G_0 \propto \varepsilon^z \tag{10}$$

where

$$\varepsilon = \left| \frac{(X - X_c)}{X_c} \right| \tag{11}$$

The value of the exponent, z, found in the discussion of Fig. 3 is 1.5. If we use this value of z, in Eqs. (10) and (11), we get $X_c \sim 0.6$. Hence, this exponential dependence can be explained in terms of the percolation of crosslinks in a three-dimensional network, if the percolation threshold is given by $X_c \sim 0.6$. Indeed, as we will demonstrate in the next section, the threshold crosslinker/monomer concentration, X_c, found experimentally is between 0.5 and 1.

Frequency sweep experiments were performed on the hydrogel samples after the completion of the polymerization/crosslinking reaction. Fig. 5(a) shows the dynamic response of this hydrogel series. During the 'curing' process all hydrogel samples except $X=0.25$ and 0.5% show the G' and G'' crossover, indicating a switch from a liquid to solid-like behavior (data shown only for $X=2\%$ in Fig. 2(a)). These samples correspond to a pregel state [37]. For $X=1\%$ and above, the hydrogel samples exhibit frequency independent elastic moduli. This transition to a frequency independent regime marks the formation of a highly crosslinked three-dimensional rubbery network dependent only on temperature and crosslink density (Eq. (3)) [12]. The dynamic moduli (G', G'') for the $X=0.5\%$ sample exhibits a power law behavior, typical of gel networks near the gel point [10–12]. Fig. 5(b) shows the power law ($G'(\omega) \sim \omega^n \sim G''(\omega)$, $\omega > 0$) behavior observed in the dynamic response of the $X=0.5\%$ hydrogel sample. The exponent n in this case is 0.55, which is in very good agreement with the Kramers–Kronig relation for a gel network close to a sol–gel transition [46]. The power law behavior over the entire range of the oscillation frequency scanned, and the congruence of $G'(\omega)$ and $G''(\omega)$ suggest that the equilibrium gel at $X=0.5\%$ is very close to the gel point.

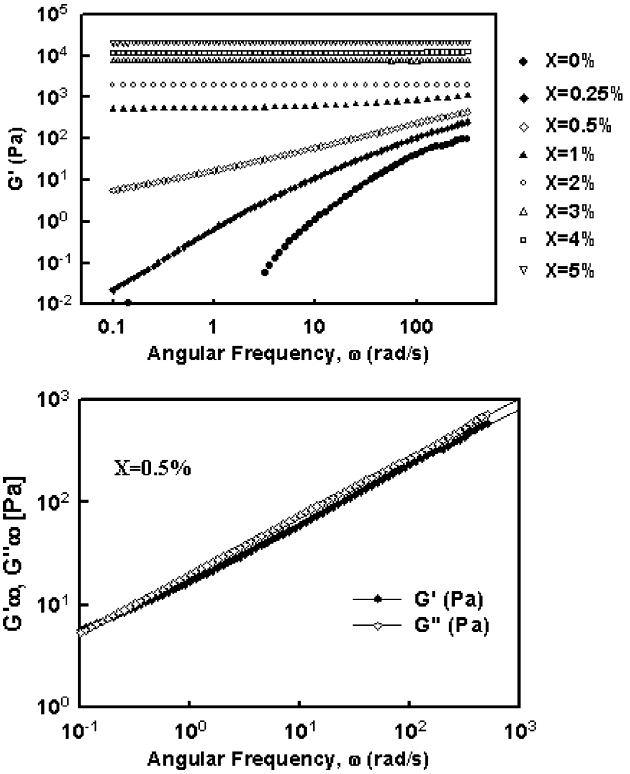

Fig. 5. (a) Frequency sweep (strain < 1%, $T=25$ °C) experiments for the hydrogel series after the completion of the polymerization/crosslinking reaction showing variation of the elastic moduli (G') with frequency. (b) Frequency sweep (strain < 1%, $T=25$ °C) test for $X=0.5$ hydrogel, showing the variation of dynamic moduli ($G'(\omega)$, $G''(\omega)$) with frequency.

Also, at $X = 0.25\%$ the hydrogel is predominantly a sol with long polymer chains in water with very few cross-links. Indeed, the gel samples corresponding to $X = 0.5\%$ or less dissolve in excess water. These results indicate that the samples corresponding to $X \leq 0.5\%$ have not reached the gel point. Hydrogel samples with $X = 1\%$ and above remain stable in excess water.

Fig. 6(a) shows the reduced elastic moduli $[G'(T)/G'(T = 298\ \text{K})]$ as a function of the reduced temperature [T(K)/298 K]. An isotropic, perfectly elastic solid shows a linear dependence of the elastic modulus ($G'(T)$) on temperature, given by Eq. (3). When the linear viscoelastic response of the hydrogel samples is studied as a function of temperature at a constant frequency ($\omega = 1$ rad/s), an interesting transition from a viscoelastic network to a perfectly isotropic rubbery solid is observed above a threshold cross-liker/monomer ratio (Fig. 6(a)). The hydrogel samples with a low crosslinker/monomer ratio ($<1\%$) deviate from this linear trend. Again, this emphasizes the fact that an elastic, solid-like response is seen only $X \geq 1\%$. At higher crosslinker/monomer ratios the linearity is evident. This result is in good agreement with most of the models for polyelectrolyte gels reported in the literature (Eqs. (3)–(5)). However, the non-linear dependence on temperature arising from the electrostatic interactions, pointed by Wilder and coworkers (Eq. (6)) [43], is not observed. This emphasizes the failure of the basic assumption of this model that there is only partial charge dissociation ($\alpha < 100\%$). However, the data are in qualitative agreement with the dynamic behavior of crosslinked networks when the elastic moduli (G') are monitored as a function of the angular frequency (ω), at constant T. The higher crosslinker/monomer ratio films display an elastic behavior that is almost independent of the oscillation frequency over a wide range (Fig. 5(a)).

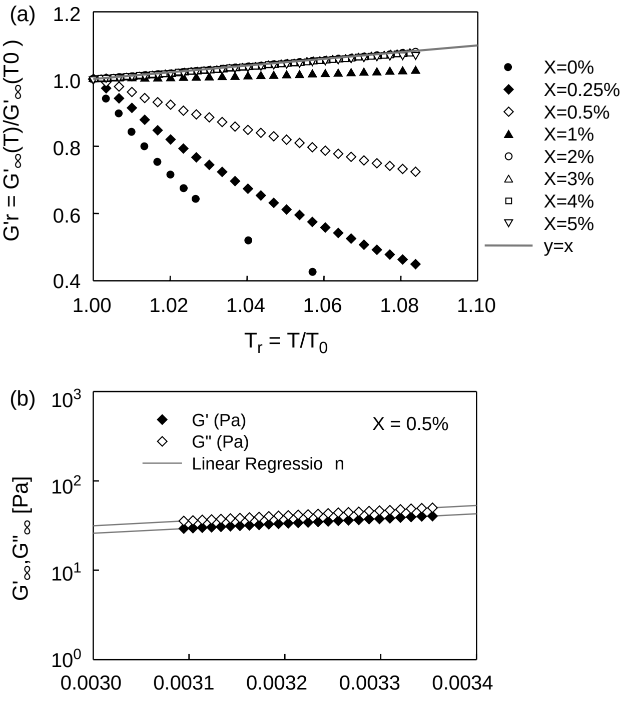

Fig. 6. (a) Temperature sweep (strain < 1%, $\omega = 1$ rad/s) experiments for the hydrogel series after the completion of the polymerization/crosslinking reaction showing the variation of the elastic moduli (G') with temperature. (b) Temperature sweep (strain = 1%, $\omega = 1$ rad/s) experiments for the $X = 0.5$ hydrogel after the completion of the polymerization/crosslinking reaction showing variation of the dynamic moduli ($G'(\omega)$, $G''(\omega)$) with temperature.

Fig. 6(b) also indicates the near-gel point behavior for the $X = 0.5\%$ hydrogel sample. Winter and coworkers [46] have investigated the temperature response of the dynamic moduli near the gel point, and shown the dynamic moduli (G', G'') follow,

$$G'(T,\omega) \sim G''(T,\omega) \sim \omega^n \left(\frac{T}{T_0}\right) \exp\left\{\frac{E}{2R}\left[\frac{1}{T} - \frac{1}{T_0}\right]\right\} \qquad (12)$$

Where, T_0 is a reference temperature ($T_0 = 298$ K, in Fig. 6), and C_0 is a constant of proportionality. For, the temperature sweep experiments in Fig. 6(b), the frequency is held constant. Hence,

$$\ln[G'(T)] \sim \ln[G''(T)] \sim \frac{E}{2RT} + \ln\left[\frac{T}{T_0}\right] \qquad (13)$$

an Arrhenius type dependence is predicted. The temperature range scanned in Fig. 6(b) is 298–323 K. Hence, the term $\ln[T/T_0]$ is close to zero, and the linear relationship between $\ln[G', G'']$ and $1/T$ is apparent. The activation energy calculated from the slope in Fig. 6(b) is approximately 9.05 kJ/mol.

Finally, the stress relaxation characteristics of the hydrogel network also reflect the transition from a viscoelastic network to a perfectly isotropic rubbery solid when the crosslinker/monomer ratio is increased from $X = 0.5$–5% (Fig. 7), as observed through temperature and frequency sweep experiments. The relaxation behavior of crosslinked polymers has been studied extensively in the literature [8,38]. The relaxation modulus, $G(t)$, depends on the extent of crosslinking in the polymer network. The relaxation behavior shows a marked change before and after the gelation threshold. Martin and coworkers [38] have suggested that the relaxation behavior in pre- and

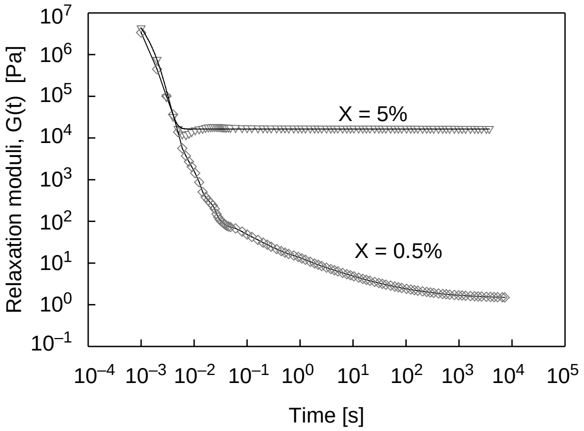

Fig. 7. Stress relaxation behavior of two hydrogel samples (10% strain (γ_0) was applied in .01 s, corresponding to a shear rate (γ_0) of 10 s^{-1}).

Table 1
Elastic moduli (G_{i}) and the relaxation times (τ_{i}) for the Maxwell elements (based on Eq. (15)) for the stress–relaxation data corresponding to $X=0.5\%$ hydrogel sample

τ_{i} (s)	G_{i} (Pa)
23,020	1.854
54.28	3.025
2.26	13.35
0.1241	75.04
5.35×10^{-03}	8796
7.13×10^{-04}	9.22×10^{6}

post-gelation states can be described by the following equations:

$$G(t)\sim\sum_{i=0}^{n}G_i\exp\left\{\frac{-t}{\tau_i}\right\}\quad\text{(before the gel point)}\tag{14}$$

where, G_i and τ_i are the elastic moduli and the relaxation times for the Maxwell elements.

$$G(t)\sim G'_{\infty}\left[1+\exp\left\{\frac{-t}{\tau}\right\}\right]\quad\text{(after the gel point)}\tag{15}$$

Model prediction associated with the relaxation times, τ_i (Eq. (14)) for the stress–relaxation data for $X=0.5\%$ hydrogel sample has been shown in Fig. 7 (solid line). Multiple relaxation times for this sample (Table 1) indicate a network composed of clusters of varying molecular weight, dangling segments, straight chains of oligomers and monomers [45]. This deduction is again in very good agreement with Figs. 5 and 6, that show the near-gel point behavior of the $X=0.5\%$ hydrogel sample. The relaxation from the $X=5\%$ hydrogel sample exhibits an expected single relaxation-time response for well-defined three-dimensional network structures, and relaxation to the equilibrium elastic modulus, G_0, (10^4 Pa for the $X=5\%$ hydrogel, in agreement with the data of Figs. 4(a) and 5(a)).

4. Conclusions

The build up of the elastic moduli during the process of polymerization and crosslinking is dictated by the crosslinker/monomer ratio. We have reported the rheological behavior of a completely charged network across the gelation threshold. The elastic moduli (G') near the gel point show the expected power law dependence of the form $G'=\varepsilon^{z}$, where ε is the distance from the gel point. The power law exponent, ($z\sim1.5$), is slightly lower than the predictions from the percolation theory based on the electrical network analogy. After the hydrogel formation the equilibrium elastic moduli (G_0) show an exponential dependence on the crosslinker/monomer ratio. This exponential dependence can be explained in terms of the percolation of crosslinks in a three-dimensional network. From the rheological response of a series of samples, we can deduce that there is a critical crosslinker/monomer ratio required to form a truly isotropic network. Below this threshold, the hydrogel matrix has not completely emerged into a three-dimensional network and can be regarded as a solution of clusters of varying molecular weights with few inter-crosslinks (branching). The percolation theory prediction for this critical crosslinker/monomer ratio (X_{c}) is ~0.6. This result is supported by frequency sweep and temperature sweep oscillatory tests, and swelling experiments. Stress–relaxation experiments performed on the hydrogel films not only support this assertion, but also provides important information about the modes of relaxation involved in the relaxation of different types of chains.

These observations and rheological characterizations of bulk hydrogels have application relevance. As a specific example, cationic polymers are used to condense DNA for gene delivery, and this field has been of tremendous research interest [4–6]. But it is only very recently that cationic nanohydrogels have been studied for the same purpose. The use of cationic nanohydrogels to adsorb and condense DNA has an additional advantage, in that the hydrogel can also be loaded with other drug species or with fluorescent or magnetic tags (magnetic or semiconductor nanoparticles). In other words, cationic nanohydrogels can have multiple functionalities. However, if one desires to prepare a cationic hydrogel on nanoscale dimensions, it is difficult to design and characterize the crosslinking required to create an open structure. Carrying out the crosslinking experiments with bulk gels will certainly give information about the crosslinker levels necessary to create hydrogels with varying degrees of 'openness'.

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