



Non-Gaussian elasticity of swollen poly(*N*-isopropylacrylamide) gels at high charge densities

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Abstract

Modulus of elasticity of highly charged *N*-isopropylacrylamide (NIPA) based hydrogels (PNIPA) are measured at various swelling degrees in water. The sodium salt of 2-acrylamido-2-methylpropane sulfonic acid (AMPS) was used as the ionic comonomer of NIPA in the hydrogel preparation. The mole fraction of AMPS in the comonomer feed was varied between 0 and 1, while the crosslinker ratio was fixed at 1/85. The elasticity data show that the equilibrium swollen PNIPA hydrogels are in the non-Gaussian regime. Equations were derived based on the inverse Langevin function for the swelling ratio and the modulus of highly charged PNIPA hydrogels and checked by experiments. Results of calculations show good agreement to the swelling and elasticity data of highly swollen PNIPA gels.

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1. Introduction

In recent years, hydrogels derived from *N*-isopropylacrylamide (NIPA) have received considerable attention for use in drug delivery systems, separation operations in biotechnology, processing of agricultural products, sensors, and actuators [1–4]. NIPA based hydrogels, denoted by PNIPA, are prepared mainly by free-radical crosslinking copolymerization of NIPA monomer with *N,N'*-methylenebis(acrylamide) (BAAm) crosslinker. In order to increase their swelling capacity, an ionic comonomer is also included in the monomer mixture. The experimental studies of PNIPA hydrogels reported in the past focused essentially on their swelling behavior. To interpret the swelling data of the hydrogels, a number of theories were used [2,5–8]. However, fitting the existing theories to the swelling data requires PNIPA network crosslink density as an adjustable pa-

rameter and does not allow definitive conclusions regarding the suitability of the theories. Such conclusions are more appropriately obtained from independent elasticity measurements.

Although much has been reported on the swelling behavior of PNIPA gels, only a few studies reported their mechanical properties [9–11]. Takigawa et al. observed that the elastic modulus of PNIPA gels in the collapsed state is much higher than in the swollen state due to the formation of physical crosslinks at high PNIPA network concentrations [12]. Muniz and Geuskens investigated the elastic modulus of semi-interpenetrated polymer networks of crosslinked polyacrylamide (PAAm) having linear NIPA homopolymer inside [13]. They observed a decrease in the swelling ratio and an increase in the modulus of the networks with an increasing NIPA concentration due to the less hydrophilic character of NIPA homopolymer. Recently, we reported that, even at low charge densities, PNIPA network chains in equilibrium swollen hydrogels exhibit non-Gaussian elasticity [14].

In the present work, we investigated the elastic behavior of PNIPA hydrogels over the entire range of

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charge densities. For this purpose, a series of hydrogels starting from the monomer NIPA and the ionic comonomer sodium salt of 2-acrylamido-2-methylpropane sulfonic acid (AMPS) was prepared. The mole fraction of AMPS in the comonomer feed was varied between 0 and 1, while the crosslinker ratio was fixed at 1/85. The mechanical properties of PNIPA gels were measured at various swelling states and the results were interpreted using the non-Gaussian form of the rubber elasticity theory.

2. Experimental

2.1. Materials

N-isopropylacrylamide (NIPA, Aldrich) *N,N'*-methylenebis(acrylamide) (BAAM, Merck), ammonium persulfate (APS, Merck), and *N,N,N',N'*-tetramethylethylenediamine (TEMED) were used as received. 2-Acrylamido-2-methylpropane sulfonic acid (AMPS-H⁺, Merck) was crystallized from boiling methanol. It was neutralized with NaOH and a stock solution was prepared containing 0.966 M AMPS.

2.2. Synthesis of hydrogels

PNIPA gels were prepared by free-radical crosslinking copolymerization of NIPA and AMPS with a small amount of BAAM in aqueous solution at 5 °C. APS (3.51 mM) and TEMED (0.25 ml/100 ml reaction solution) were used as the redox initiator system. The initial concentration of the monomers C_0 was fixed at 0.70 M. The mole fraction of AMPS in the monomer mixture x_i was varied between 0 and 1, while the crosslinker ratio X (mole ratio of the crosslinker BAAM to the monomers NIPA + AMPS) was fixed at 1/85. The detail about the hydrogel preparation was described before [14]. The degree of dilution of PNIPA networks after their preparation was denoted by v_2^0 , the volume fraction of crosslinked PNIPA after the gel preparation. In order to determine v_2^0 , the hydrogels after preparation were first swollen in water to extract non-polymerizable or soluble components and then dried to constant mass. v_2^0 was then calculated as

$$v_2^0 = \left(1 + \frac{(q_F - 1)\rho}{d_1} \right)^{-1}, \quad (1)$$

where q_F is the weight swelling ratio of gels just after their preparation (mass of gel after preparation/mass of extracted, dry network), ρ the polymer density, and d_1 the solvent density (1.00 g/ml). For the calculations, we assumed a constant density of 1.35 g/cm³ for all the PNIPA networks. Assuming that the monomer conversion is complete after the crosslinking copolymerization,

v_2^0 can also be calculated from the initial molar concentration of the monomers C_0 (mol/L) as

$$v_2^0 = 10^{-3} C_0 \bar{V}_r, \quad (2)$$

where \bar{V}_r is the average molar volume of polymer repeat units (in ml/mol), which was calculated from the molar volumes of NIPA and AMPS repeat units as

$$\bar{V}_r = 83.7 + 85.9x_i. \quad (2a)$$

The theoretical values of v_2^0 calculated using Eqs. (2) and (2a) are shown in Fig. 1 as the solid curve together with the experimentally determined v_2^0 values (filled symbols). It is seen that, although the initial monomer concentration was fixed at 0.70 M, v_2^0 increases with increasing x_i due to the larger molar volume of AMPS units compared to that of NIPA units. Another point shown in Fig. 1 is that the experimental v_2^0 values are larger than the theoretical ones. This would indicate a monomer conversion higher than 100%, or, the presence of residual water in the dried polymers. Indeed, previous work reveals that the crosslinked NIPA-AMPS copolymers always contain about 10–20 wt% water, even after several months of drying under vacuum [15]. Therefore, in the following paragraphs, the theoretical v_2^0 values were used for further calculations.

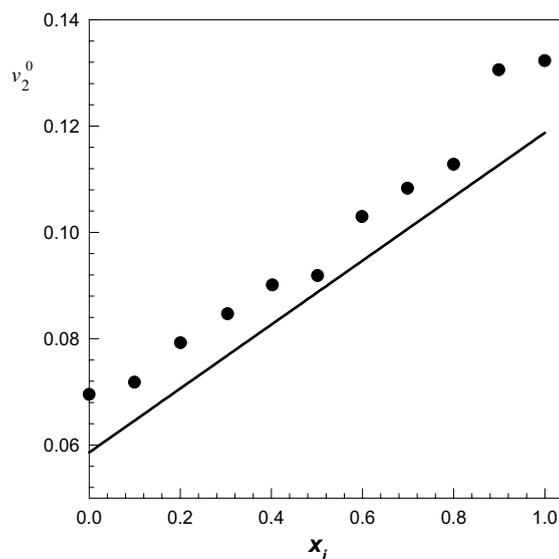


Fig. 1. Variation of the polymer network concentration after the gel preparation v_2^0 with the mole fraction of AMPS in the comonomer feed x_i . The filled symbols represent experimentally determined v_2^0 values while the solid curve was calculated using Eqs. (2) and (2a) with the assumption that the monomer conversion is complete after the crosslinking copolymerization.

2.3. Swelling measurements in water

The hydrogels in the form of rods of 4 mm in diameter were cut into samples of about 10 mm length. Then, each sample was placed in an excess of water at room temperature (24 ± 0.5 °C). In order to reach swelling equilibrium, the hydrogels were immersed in water for at least two weeks replacing the water every other day. The swelling equilibrium was tested by measuring the diameter of the gel samples. To achieve good precision, three measurements were carried out on samples of different length taken from the same gel. The normalized volume of the equilibrium swollen hydrogels V_{eq} (volume of equilibrium swollen gel/volume of the gel just after preparation) was determined by measuring the diameter of the hydrogel samples by a calibrated digital compass (Mitutoyo Digimatic Caliper, Series 500, resolution: 0.01 mm). V_{eq} was calculated as $V_{\text{eq}} = (D/D_0)^3$, where D and D_0 are the diameter of hydrogels after equilibrium swelling in water and after synthesis, respectively. The volume fraction of crosslinked polymer in the equilibrium swollen gel $v_{2,\text{eq}}$ was calculated as $v_{2,\text{eq}} = v_2^0/V_{\text{eq}}$.

To obtain hydrogels at various degrees of swelling, equilibrium swollen gels were placed in sealed 50-ml vials at room temperature to evaporate a desired amount of the gel water. This procedure ensured uniformity of the network concentration throughout the gel sample. After a given evaporation time (a few minutes up to a few months), the diameters of partially swollen gels were measured, from which their volumes and network concentrations (V and v_2 , respectively) were calculated.

2.4. Mechanical measurements

Uniaxial compression measurements were performed on gels at various degrees of swelling. All the mechanical measurements were conducted in a thermostated room of 24 ± 0.5 °C. The stress–strain isotherms were measured by using an apparatus previously described [15]. Briefly, a cylindrical gel sample of about 7 mm in length was placed on a digital balance (Sartorius BP221S, readability and reproducibility: 0.1 mg). A load was transmitted vertically to the gel through a rod fitted with a PTFE end-plate. The compressional force acting on the gel was calculated from the reading of the balance. The resulting deformation was measured after 20 s of relaxation by using a digital comparator (IDC type Digimatic Indicator 543-262, Mitutoyo Co.), which was sensitive to displacements of 10^{-3} mm. The measurements were conducted up to about 15% compression. Reversibility of the isotherms was tested by recording the force and the resulting deformation during both force–increasing and force–decreasing processes. The two processes yielded almost identical stress–strain re-

lations. From the repeated measurements, the standard deviations in the modulus value were less than 3%. The sample weight loss during the measurements due to water evaporation was found to be negligible. The elastic modulus G was determined from the slope of linear dependence:

$$F = G(\lambda - \lambda^{-2}), \quad (3)$$

where F is the force acting per unit cross-sectional area of the undeformed gel specimen, and λ is the deformation ratio (deformed length/initial length). Typical stress–strain data correlated according to Eq. (3) are shown in Fig. 2 for hydrogels with varying AMPS contents.

For a homogeneous network of Gaussian chains, the elastic modulus of gels G is related to the network crosslink density by [16,17]

$$G = A \frac{\rho}{\bar{M}_c} RT (v_2^0)^{2/3} (v_2)^{1/3}, \quad (4)$$

where \bar{M}_c is the molecular weight of the network chains. The front factor A equals to 1 for an affine network and $1 - 2/\phi$ for a phantom network, where ϕ is the functionality of the crosslinks. The number of segments between two successive crosslinks N is related to the molecular weight of the network chains \bar{M}_c by

$$N = \bar{M}_c / (\rho V_1), \quad (4a)$$

where V_1 is the molar volume of a segment, which is taken as the molar volume of water (18 ml/mol).

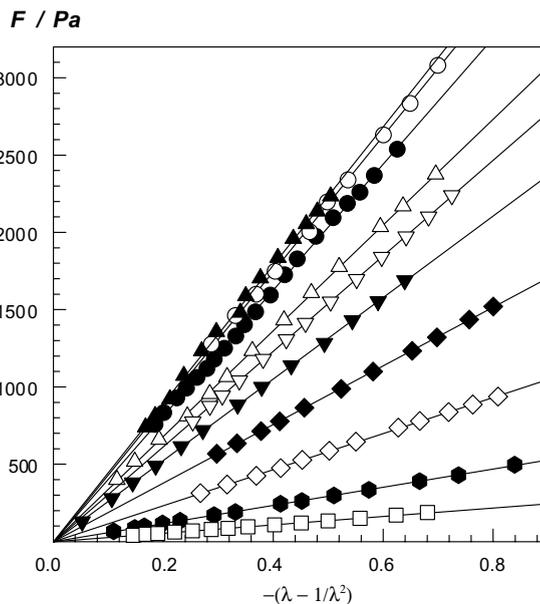


Fig. 2. Typical stress–strain data for PNIPA hydrogels just after their preparation. The mole fraction of AMPS x_i : (●), 0.20 (○), 0.30 (▲), 0.40 (△), 0.50 (▽), 0.60 (▼), 0.70 (◆), 0.80 (◇), 0.90 (●), and 1 (□).

Since $v_2 = v_2^0$ for the hydrogels just after preparation, the modulus G_0 after preparation becomes $G_0 = A \frac{\phi}{M_c} RT v_2^0$. From Eq. (4), the reduced modulus G_r defined as the ratio of the elastic modulus of the gel at a given degree of swelling to that of the same gel after its preparation is given for a network of Gaussian chains by

$$G_r = \frac{G}{G_0} = \left(\frac{v_2}{v_2^0} \right)^{1/3} = V^{-1/3}. \quad (5)$$

3. Results and discussion

The results from swelling and elasticity tests are plotted in Fig. 3. In Fig. 3A, the equilibrium swollen volumes V_{eq} of gels are shown as a function of the mole fraction of AMPS in the comonomer feed x_i . The filled circles are the results of measurements while the filled triangles are data points taken from the literature [14]. As expected, V_{eq} increases as the AMPS content of the hydrogel x_i increases. This is a consequence of the osmotic pressure exerted by the counterions of AMPS units in the network chains [18]. This osmotic pressure increases as the concentration of the counterions increases. However, contrary to the classical theory of swelling equilibrium [16], the gel volume is not a monotonically increasing function of the ionic group content of the hydrogels. The dependence of the gel swelling on x_i shows three stages. First, the volume of gel increases sharply with increasing ionic group content until a plateau is reached at about $x_i = 0.10$. Second, between $x_i = 0.10$ and 0.40, the gel volume does not change much with the ionic group content of the hy-

drogels. Third, further increase in the AMPS content beyond this value increases the gel volume continuously up to $x_i = 1$. In Fig. 3B, the elastic moduli of gels after preparation G_0 (filled symbols), and after equilibrium swelling in water G_{eq} (open symbols) are plotted as a function of x_i . G_0 does not change much with x_i up to $x_i = 0.6$ but then rapidly decreases at higher values of x_i . Another point shown in Fig. 3B is that, the modulus of equilibrium swollen ionic gels G_{eq} is larger than the modulus of gels measured after their preparation G_0 over the whole range of AMPS content. This behavior is an indication of the limited extensibility of the network chains and, suggests that the equilibrium swollen ionic PNIPA gels are in the non-Gaussian regime. Indeed, the equilibrium swelling ratios of the gels shown in Fig. 3A indicate that the network chains are about 6- to 16-fold extended conformation than those in dry state.

From the modulus data of gels after preparation G_0 and assuming phantom network behavior ($\phi = 4$), the number of segments between two successive crosslinks N of the hydrogels were calculated using Eqs. (4) and (4a). The results are shown in Fig. 3C plotted against the mole fraction of AMPS x_i . The dotted line in the figure represents the chemical crosslink density, N_{chem} , which would result if all the crosslinker (BAAm) molecules formed effective crosslinks in the hydrogel. N_{chem} was calculated from the crosslinker ratio X used in the gel preparation using the equation

$$N_{chem} = \frac{X^{-1} \bar{V}_r}{2 V_1}. \quad (6)$$

Although the crosslinker ratio X was fixed at 1/85 in the experiments, N_{chem} slightly increases with increasing

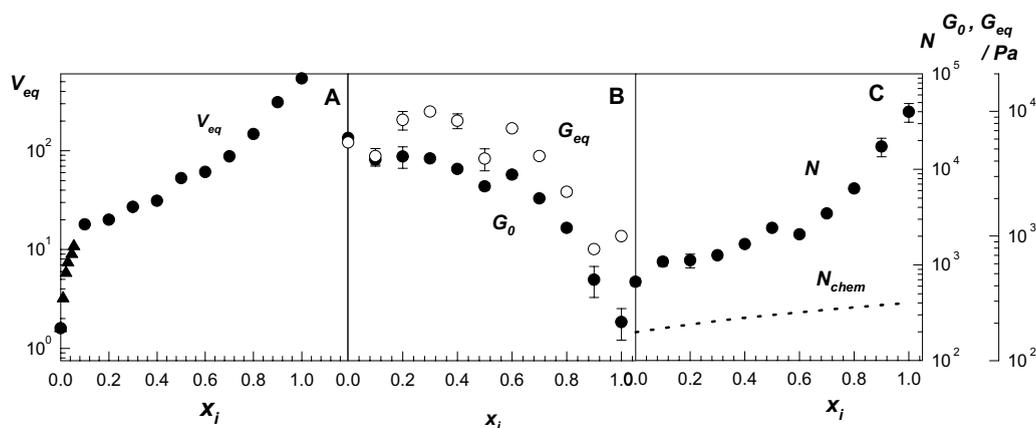


Fig. 3. (A) The equilibrium volume of the hydrogels normalized with respect to the after preparation state V_{eq} shown as a function of the mole fraction of AMPS in the comonomer feed x_i . The circles are results of measurements. The triangles are data points taken from Ref. [14]. (B) The elastic moduli of gels after preparation G_0 (filled symbols) and after equilibrium swelling in water G_{eq} (open symbols) shown as a function of x_i . (C) The effective crosslink densities of PNIPA gels in terms of N (number of segments between crosslinks) calculated from the elastic moduli G_0 of the hydrogels shown as a function of x_i . The symbols are calculation results for phantom ($\phi = 4$) network model. The dotted line was calculated using Eq. (6).

x_i due to the larger molar volume of AMPS compared to that of NIPA units (Figs. 1 and 3C). Moreover, the effective value of N is much larger than its chemical value N_{chem} and, the difference between N and N_{chem} further increases at high charge densities. The difference between the effective and chemical crosslink densities of PNIPA hydrogels indicates that a significant fraction of the crosslinker BAAM is wasted during the crosslinking copolymerization, probably due to the cyclization and multiple crosslinking reactions. The high degree of dilution during the gel preparation as well as the higher crosslinker reactivity compared to the monomer reactivity are mainly responsible for these reactions [19,20].

Swelling data of the hydrogels collected in Fig. 3A show that ionic PNIPA gels are highly swollen in water. For such highly swollen hydrogels, an appreciable proportion of the network chains becomes highly extended so that deviation from the Gaussian statistics may appear due to the finite extensibility of the network chains [21]. Elasticity data given in Fig. 3B also suggest this behavior. In the following paragraphs, we will use the well-known treatment based on the inverse Langevin function, L^{-1} , to derive a formula for the change of elastic free energy ΔG_{el} of gels due to swelling [17,21]:

$$\Delta G_{\text{el}} \approx N^{-1} \alpha n^{1/2} L^{-1}(\alpha n^{-1/2}), \quad (7)$$

where α is the linear deformation ratio, i.e., $\alpha = (D/D_0) = V^{1/3}$, n the number of flexible units between crosslinks, which includes the non-Gaussian properties of the network. The value of n depends on the stiffness of the polymer backbone and on the molar mass of the network chains. Note that the relative end-to-end distance of the network chains (r/nl) was replaced in Eq. (7) by $\alpha n^{-1/2}$. It was shown that the inverse Langevin function can be accurately approximated by a Pade equation [22,23], i.e.,

$$L^{-1}(x) = x(3 - x^2)/(1 - x^2). \quad (8)$$

When Eq. (8) is substituted in Eq. (7), one obtains

$$\Delta G_{\text{el}} \approx N^{-1} \alpha^2 \left(1 + \frac{2}{1 - \alpha^2/n} \right). \quad (9)$$

Serial expansion of the second term of Eq. (9) and truncating at α^4 yield the following equation for the elastic free energy of non-Gaussian chains:

$$\Delta G_{\text{el}} \approx N^{-1} \alpha^2 (3 + 2\alpha^2/n + 2\alpha^4/n^2). \quad (10)$$

According to Eq. (10), when n approaches infinity, the equation reduces to the Gaussian description, i.e., ΔG_{el} scales with the second power of the deformation ratio. For finite values of n , i.e., as the network chains deviate from the Gaussian statistics, elastic free energy ΔG_{el} will increase with a higher power of α .

At the swelling equilibrium of highly swollen ionic hydrogels, the gel rubberlike elasticity given by Eq. (10)

is balanced by the ionic free energy due to the mixing entropy of the counterions. The ionic contribution to the free energy ΔG_i may be written as follows [16]:

$$\Delta G_i \approx f \ln(f v_2^0 / \alpha^3), \quad (11)$$

where f is the effective charge density of the network, i.e., the fraction of segments bearing ionic groups. Note that Eq. (11) assumes an equivalent size for both the solvent molecules and the network segments. Because of the different molar volumes of the monomer units and solvent in real systems, x_i does not correspond to f . f values of the hydrogels are related to x_i through the equation

$$f = x_i V_1 / \bar{V}_r. \quad (12)$$

Balancing the two opposite free energy contributions represented by ΔG_{el} (Eq. (10)) and ΔG_i (Eq. (11)) by minimizing their sum with respect to α and, since $\alpha = V_{\text{eq}}^{1/3}$ at the swelling equilibrium, one obtains

$$6V_{\text{eq}}^{2/3} + 8 \frac{V_{\text{eq}}^{4/3}}{n} + 12 \frac{V_{\text{eq}}^2}{n^2} \approx fN. \quad (13)$$

For the Gaussian chains, that is, when n approaches infinity, Eq. (13) reduces to

$$V_{\text{eq}} \approx (fN)^{3/2} \quad (13a)$$

which indicates a scaling parameter of 1.5 between the equilibrium swollen volume V_{eq} of the hydrogels and the number of charges per network chain fN . The scaling parameter predicted by Eq. (13) decreases below 1.5 as the number of flexible units between crosslinks represented by n decreases, i.e., as the network chains deviate from Gaussian behavior.

Fig. 4 shows a semi-logarithmic plot of the equilibrium gel volume V_{eq} versus the number of charges per network chains fN . Experimental data are shown by symbols. The solid curve in the figure is the best fitting curve to the experimental swelling data of the hydrogels, which gives a scaling relation $V_{\text{eq}} \approx (fN)^{0.68}$. The scaling parameter 0.68, thus found, is much smaller than the predicted value of 1.5 for Gaussian chains (Eq. (13a)). Moreover, the scaling parameter 0.68 is also smaller than the exponent 0.75 found for PNIPA hydrogels with x_i below 0.5 [14]. An exponent between 0.6 and 0.8 has been reported before for both weak- and strong-polyelectrolyte hydrogels equilibrium swollen in water [18,24–26]. The dashed curves in Fig. 4 represent the prediction of Eq. (13) for various values of n . Fitting of Eq. (13) to the experimental data by the method of least squares gives the number of flexible units between crosslinks $n = 34.9 \pm 0.1$. The corresponding theoretical curve is also shown in the figure. It is seen that Eq. (13) with $n = 34.9$ well reproduces our experimental results.

The elastic moduli of the hydrogels were measured for hydrogel samples of various charge densities

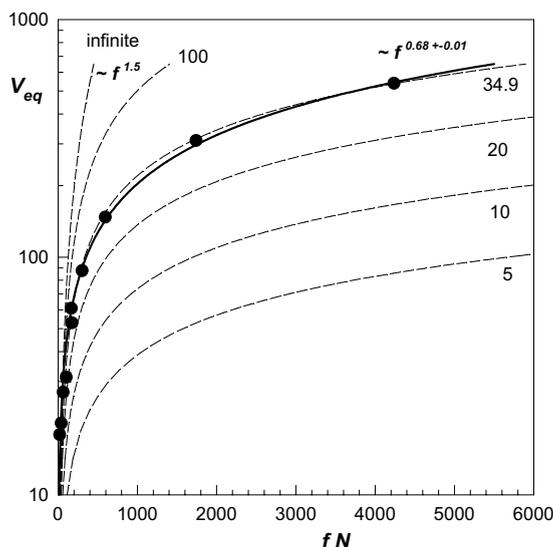


Fig. 4. The equilibrium volume of the hydrogels normalized with respect to the after preparation state V_{eq} shown as a function of the number of charges per network chain fN . The dotted curves represent the prediction of Eq. (13) for n values indicated in the figure. The solid curve is the best fitting curve to the experimental data.

and swelling degrees. Results of the measurements are collected in Fig. 5 as the dependences of the elastic modulus G and the reduced elastic modulus G_r on the normalized gel volume V . The ionic group contents of the hydrogels are indicated in the figure. The symbols at the upper right end of each series of gels are the data obtained from the equilibrium swollen hydrogels. Data points for $x_i < 0.10$ were taken from the literature [14]. Note that the hydrogels prepared at $x_i = 0.90$ and 1 were too weak to withstand repeated mechanical measurements at various swelling ratios. Therefore, they were only measured in equilibrium swollen and after preparation states. Several interesting features can be seen from Fig. 5. First, for the gel volumes V of less than 0.4, the modulus of gels increases sharply with decreasing gel volume due to the glassy-to-rubbery transition of PNIPA gels. In the range of V between 0.4 and 3.5, modulus decreases with increasing V with a slope -0.32 , close to the theoretical value of $-1/3$ (Eq. (5)). Thus, PNIPA hydrogels in this regime behave as Gaussian. For larger gel volumes, striking departures from Gaussian behavior appear with large upturns in the modulus data. The larger the gel volume, the steeper is the increase of the modulus with the gel volume. The slope of the data points obtained in this region increases from 1.0 to 1.6 ($\approx 5/3$) with increasing x_i from 0.5 to 0.8 (Fig. 5B). This implies that the Gaussian theory becomes increasingly inadequate as the gel volume increases.

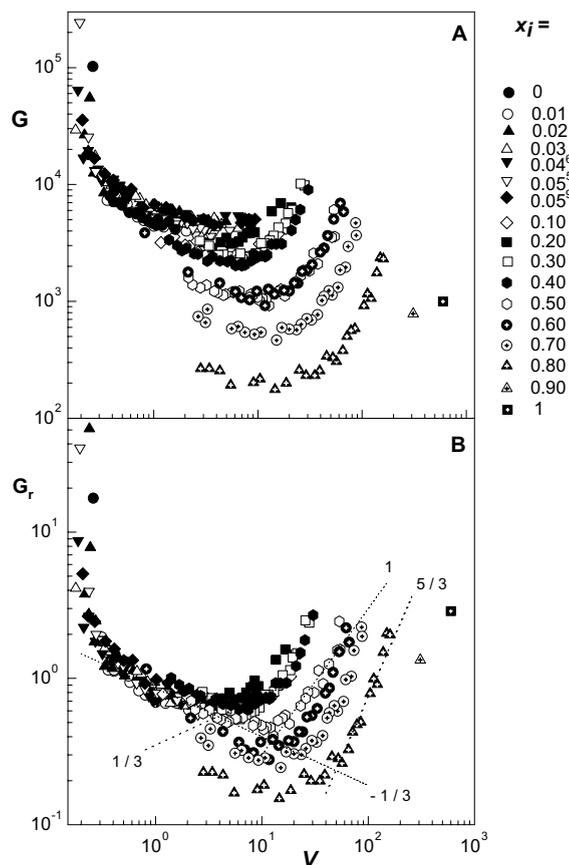


Fig. 5. The elastic modulus G (A) and the reduced modulus G_r (B) of the hydrogels shown as a function of the normalized gel volume V . The mole fraction of AMPS x_i is indicated in the figure. The data for $x_i < 0.10$ were taken from Ref. [14]. The dotted lines in Fig. 5B represent the theoretical slopes predicted by Eq. (17) for different gel regimes.

To derive a general relation between the reduced modulus and the gel volume, we consider the deformation of swollen network based on non-Gaussian chain statistics. The force F acting per unit cross-sectional area of the undeformed gel is given by [17,21]

$$F = \frac{1}{3} \frac{\rho}{M_c} RTn^{1/2} v_2^0 \alpha^{-2} \times \left\{ L^{-1}(\lambda \alpha n^{-1/2}) - \lambda^{-3/2} L^{-1}(\alpha(n\lambda)^{-1/2}) \right\}. \quad (14)$$

Replacing the inverse Langevin function by its Pade approximant (Eq. (8)), Eq. (14) simplifies to

$$f = G' \left(\lambda - \frac{1}{\lambda^2} \right) \quad (15)$$

where G' is the elastic modulus of non-Gaussian network, which is given by

$$G' = G \left(1 + \frac{2}{3} \sum_{i=1}^{\infty} \alpha^{2i} (n\lambda)^{-i} \left(1 + \sum_{j=1}^i \lambda^{3j} \right) \right). \quad (16)$$

The reduced moduli of the networks follow from Eqs. (4) and (16) as

$$G_r = V^{-1/3} + \frac{2}{3} \frac{(1 + \lambda^3)}{n\lambda} V^{1/3} + \frac{2}{3} \frac{(1 + \lambda^3 + \lambda^6)}{(n\lambda)^2} V + \frac{2}{3} \frac{(1 + \lambda^3 + \lambda^6 + \lambda^9)}{(n\lambda)^3} V^{5/3} + \dots \quad (17)$$

According to Eq. (17), an infinite number of statistical segments per network chain ($n = \infty$) yield a straight line with a slope of $-1/3$, which is the result for the Gaussian approach (Eq. (5)). For finite values of n , the exponent deviates from $-1/3$ and G_r increases with increasing gel volume. The dotted lines in Fig. 5B represent the theoretical slopes $-1/3$, $1/3$, 1 , and $5/3$, predicted by Eq. (17) for various gel volumes. It is seen that the dotted lines agree well with the experimental behavior of gels.

Fig. 5 also shows that, as the AMPS mole fraction x_i is increased, the upturn in the modulus starts at larger gel volumes. This is a consequence of decreasing crosslink density, i.e., increasing network chain length N with increasing x_i (Fig. 3C). Since the maximum extension of a chain is proportional to its length N , the longer the chain, the higher its maximum extension so that the deviation from the Gaussian behavior starts to appear later, i.e., at larger gel volumes. In Fig. 6, the critical gel volume V_{cr} at which the upturn in modulus occurs is

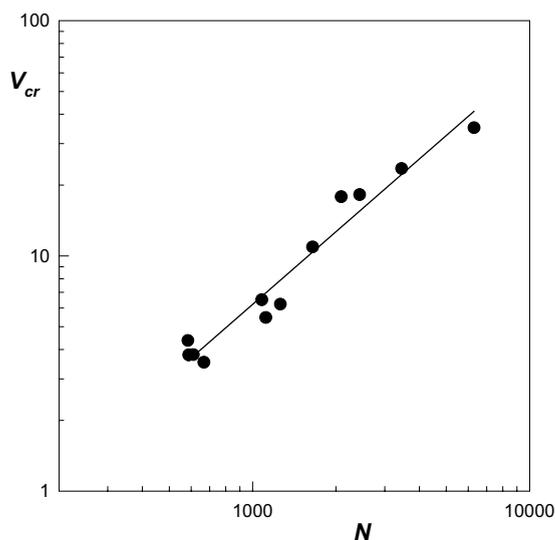


Fig. 6. The critical gel volume V_{cr} at which the upturn in modulus occurs shown as a function of the number of segments between crosslinks N . The solid curve is the best fitting curve to the experimental data with a slope 1.0.

plotted against the network chain length N . The best fitting curve to the data gives a relation $V_{cr} \propto N^{1.0}$, indicating that the critical gel volume at which the limited chain extensibility becomes apparent is linear in N .

4. Conclusions

A series of strong polyelectrolyte PNIPA hydrogels was prepared at a fixed crosslinker ratio and monomer concentration but at various charge densities. AMPS was used as the ionic monomer in the hydrogel preparation. The elastic moduli of the hydrogels were measured at various swelling degrees in water. The elasticity data show that the equilibrium swollen PNIPA hydrogels are in the non-Gaussian regime. Equations were derived based on the inverse Langevin function for the swelling ratio and the modulus of highly charged PNIPA hydrogels. In these equations, the inverse Langevin function was replaced with its Pade approximant. The results of calculations show good agreement to our experimental observations.

Acknowledgements

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