Swelling and Elasticity of Poly (*N*-isopropylacrylamide-*co*-4-Vinyl Benzene Sulfonic Acid Sodium Salt) Hydrogels

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Abstract: The mechanical properties and the swelling behavior of hydrogels based on *N*-isopropylacrylamide (NIPA) and 4-vinylbenzenesulfonic acid sodium salt (styrene sulfonate, SSA) monomers were investigated. The mole fraction of SSA in the comonomer feed varied between 0 and 1, whereas the crosslinker ratio was fixed at 1/85. Both the swelling and the elasticity data of the hydrogels swollen in water show that they are in the non-Gaussian regime. The exponents found for the charge density dependence of the equilibrium swelling ratio as well as for the volume dependence of the gel elastic modulus are in good agreement with the predicted course of the non-Gaussian elasticity of swollen hydrogels. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 135–141, 2004

Key words: hydrogels; swelling; mechanical properties; modulus

INTRODUCTION

In recent years, hydrogels derived from *N*-isopropylacrylamide (NIPA) have received considerable attention for use in drug delivery systems, separation operations in biotechnology, and processing of agricultural products, sensors, and actuators.[1–4] NIPA-based hydrogels (PNIPA) are prepared mainly by free-radical crosslinking copolymerization of NIPA monomer with *N*,*N*′-methylenebis(acrylamide) (BAAm) crosslinker. To increase their swelling capacity, an ionic comonomer is also included in the monomer mixture. Although much has been reported on the swelling behavior of PNIPA gels, only a few studies reported their mechanical properties.[5–9] Recently, we investigated the elasticity of a series of PNIPA hydrogels with varying amounts of charged units derived from the sodium salt of 2-acrylamido-2-methylpropane sulfonic acid (AMPS).[10,11] It was shown that, even at low charge densities, the increase of the equilibrium gel volume with the gel charge density is considerably weaker than expected assuming Gaussian statistics. The results could be explained with the non-Gaussian form of the rubber elasticity theory.[10,11]

In the present work, we used 4-vinylbenzenesulfonic acid sodium salt (styrene sulfonate, SSA) instead of AMPS as the ionic comonomer of NIPA. Our aim was to increase the stiffness of the polymer backbone of ionic PNIPA gels by replacing AMPS with SSA units. A gel with more rigid chain backbone is expected to show non-Gaussian properties at lower degrees of swelling than a flexible polymer. A series of hydrogels starting from the monomer NIPA and the ionic comonomer SSA was prepared in dilute aqueous solutions. The elastic behavior of gels was investigated at various gel volumes. The results were interpreted as the non-Gaussian elasticity of the hydrogels swollen to equilibrium.

EXPERIMENTAL

Materials

NIPA (Aldrich, Milwaukee, WI), 4-vinylbenzenesulfonic acid sodium salt (SSA, Fluka, Deisenhofen, Germany) BAAm (Merck, Darmstadt, Germany), ammonium persulfate (APS, Merck), and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED, Merck) were used as received.

Synthesis of hydrogels

PNIPA gels were prepared by free-radical crosslinking copolymerization of NIPA and SSA with a small amount of BAAm in aqueous solution at 5°C. The reaction time was 24 h. 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 SSA in the monomer mixture x_i was varied between 0

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and 1, whereas the crosslinker ratio X (mole ratio of the crosslinker BAAm to the monomers NIPA + SSA) was fixed at 1/85. The detail about the hydrogel preparation was described before.[10] The degree of dilution of PNIPA networks after their preparation was denoted by ν_2^0, the volume fraction of crosslinked PNIPA after the gel preparation. To determine ν_2^0, the hydrogels after preparation were first swollen in water to extract nonpolymerizable or soluble components and then dried to constant mass. ν_2^0 was then calculated as

$$\nu_2^0 = \left(1 + \frac{(q_F - 1)\rho}{d_1}\right)^{-1} \tag{1}$$

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 is the polymer density, and d_1 is the solvent density (1.00 g/ml). For the calculations, we assumed a constant density of 1.35 g/cm^3 for all the PNIPA networks. Assuming that the monomer conversion is complete after the crosslinking copolymerization, ν_2^0 can also be calculated from the initial molar concentration of the monomers C_0 (mol/l) as

$$\nu_2^0 = 10^{-3} C_0 \overline{V}_r \tag{2}$$

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 SSA repeat units as

$$\overline{V}_r = 83.7 + 68.9\, x_i \tag{2a}$$

The theoretical values of ν_2^0 calculated by using eqs. (2) and (2a) are shown in Figure 1 as the solid curve together with the experimentally determined ν_2^0 values (filled symbols). Although the initial monomer concentration was fixed at 0.70M, ν_2^0 increases with x_i because of the larger molar volume of SSA units compared to that of NIPA units [eq. (2a)]. Another point shown in Figure 1 is that the experimental ν_2^0 values are larger than the theoretical ones. This indicates the presence of residual water in the dried polymers. Indeed, previous work reveals that the ionic hydrogels always contain about 10–20 wt % water, even after several months of drying under vacuum.[12,13] Taking into account the residual water content of the dried networks, the experimental ν_2^0 values shown in Figure 1 indicate that both the monomer conversions and the gel fractions were complete after the crosslinking copolymerizations. In the following paragraphs, the theoretical ν_2^0 values were used for calculations.

Swelling measurements in water

The hydrogels in the form of rods of 4 mm in diameter were cut into samples of 10 mm length. Then, each sample was placed in an excess of water at 24 ± 0.5°C. To reach swelling equilibrium, the hydrogels were immersed in water for at least 2 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 lengths 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

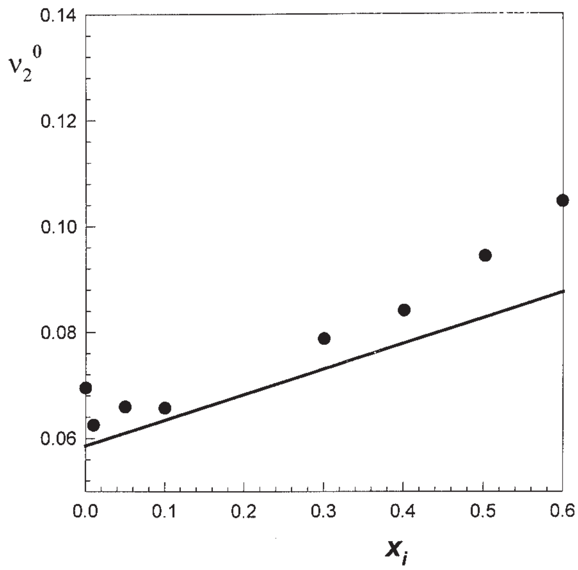

Figure 1 Variation of the polymer network concentration after the gel preparation ν_2^0 with the mole fraction of SSA in the comonomer feed x_i. The filled symbols represent experimentally determined ν_2^0 values, whereas the solid curve was calculated by using eqs. (2) and (2a).

$$V_{eq} = (D/D_0)^3 \tag{3}$$

where D and D_0 are the diameter of hydrogels after equilibrium swelling in water and after synthesis, respectively.

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.[10] 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 V were calculated.

Mechanical measurements

Uniaxial compression measurements were performed on gels at various degrees of swelling. All the mechan-

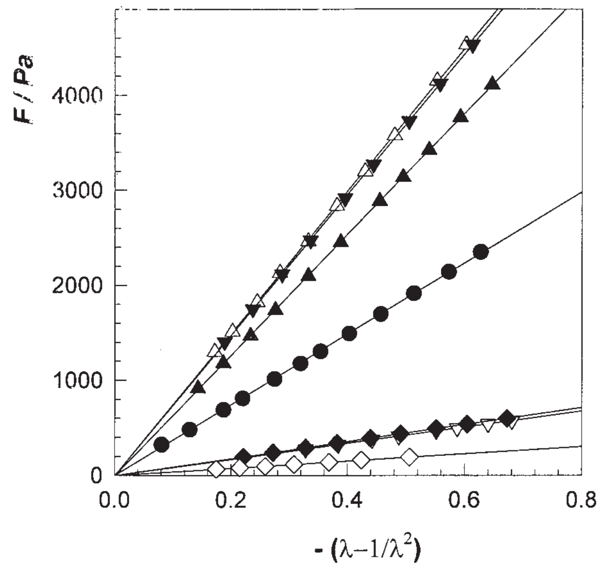

Figure 2. Typical stress–strain data for PNIPA hydrogels just after their preparation. The mole fraction of SSA x_i: 0.01 (●), 0.10 (▲), 0.20 (Δ), 0.30 (▼), 0.40 (▽), 0.50 (◆), and 0.60 (◇).

ical measurements were conducted in a thermostated room of 24 ± 0.5°C. The stress–strain isotherms were measured by using previously described apparatus.[12] 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 road 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 relations. From the repeated measurements, the standard deviations in the modulus value were $< 3\%$. 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

$$F = G(\lambda - \lambda^{-2}) \tag{4}$$

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. (4) are shown in Figure 2 for hydrogels with varying SSA contents.

For a homogeneous network of Gaussian chains, the elastic modulus of gels G is related to the network crosslink density by[14,15]

$$G = A\frac{\rho}{\bar{M}_c}RT(\nu_2^0)^{2/3}(\nu_2)^{1/3} \tag{5}$$

where $\bar{M}_c$ is the molecular weight of the network chains and ν_2 is the volume fraction of crosslinked copolymer in the swollen gel (i.e., $\nu_2 = \nu_2^0/V$). The front factor A equals 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

$$N = \bar{M}_c/(\rho V_1) \tag{6}$$

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

Because $\nu_2 = \nu_2^0$ for the hydrogels just after preparation, the modulus G_0 after preparation becomes $G_0 = A\,(\rho/\bar{M}_c)\,RT\,\nu_2^0$. From eq. (5), 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

$$G_r = \frac{G}{G_0} = \left(\frac{\nu_2}{\nu_2^0}\right)^{1/3} = V^{-(1/3)} \tag{7}$$

RESULTS AND DISCUSSION

A series of gelation experiments was carried out at various mole fractions x_i of the ionic comonomer SSA in the feed. No gel formation was observed if x_i exceeds 0.6. In the range of x_i between 0 and 0.6, transparent and highly swellable hydrogels were obtained. In Figure 3, the equilibrium swollen volumes V_{eq} of the hydrogels are shown as a function of the mole fraction of SSA in the comonomer feed x_i. The open circles are the results of measurements. The filled symbols are data points for PNIPA hydrogels prepared at the same crosslinker ratio X and monomer concentration C_0 but by using AMPS as the ionic comonomer.[10,11] V_{eq} increases as the SSA content of the hydrogel x_i increases. This is a consequence of the osmotic pressure exerted by the counterions of SSA units in the network chains.[14] This osmotic pressure increases as x_i is increased. Figure 3 also shows that, in the range of x_i between 0 and 0.3, the hydrogels with SSA units swell less than those with AMPS units, probably due to the more hydrophobic character of the SSA units. Moreover, between $x_i = 0.3$ and 0.4, the volume of SSA gels increases sharply and becomes almost equal to the volume of AMPS gels.

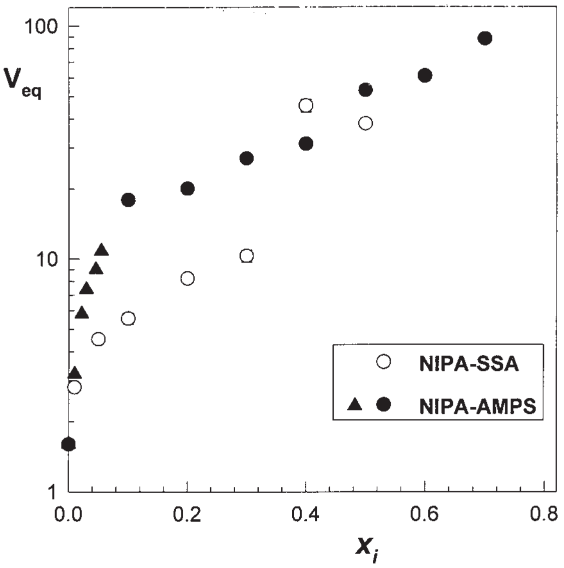

Figure 3 The equilibrium volume of the hydrogels in water V_{eq} shown as a function of the mole fraction of the ionic unit x_i. Open symbols are the results of measurements with SSA-containing hydrogels. Filled symbols are data points for AMPS containing hydrogels, taken from the literature [ref. 10 (▼) and ref. 11 (●)].

In Figure 4, open symbols show the elastic moduli of gels after preparation G_0 plotted against the mole fraction of SSA x_i. G_0 does not change much with x_i up to $x_i = 0.3$ but then rapidly decreases at higher values of x_i. 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 by using eqs. (5) and (6). The results are also shown in Figure 4 by the filled symbols. 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. Although the crosslinker ratio X was fixed at 1/85 in the experiments, N_{chem} slightly increases with increasing x_i because of the larger molar volume of SSA compared to that of NIPA units. 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.[16,17] Comparison of the swelling and the elasticity results collected in Figure 3 and 4 also shows that the rapid increase in the gel volume between $x_i = 0.3$ and 0.4 is due to the decrease of the effective crosslink density of the hydrogels in the same range of x_i.

For highly swollen hydrogels such as those prepared in this study, 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.[18] According to the non-Gaussian theory of rubber elasticity, the change of elastic free energy of gels due to swelling is given by.[15,18]

$$\Delta G_{el} \approx N^{-1} \alpha n^{1/2} L^{-1}(\alpha n^{-1/2}) \tag{8}$$

where L^{-1} is the inverse Langevin function, α is the linear deformation ratio [i.e., $\alpha = (D/D_0) = V^{1/3}$], and 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. Replacing the inverse Langevin function by its Pade approximant, eq. (8) simplifies to[10,11]

$$\Delta G_{el} \approx N^{-1} \alpha^2 (3 + 2\alpha^2/n + 2\alpha^4/n^2) \tag{9}$$

According to eq. (9), 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. (9) 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.[14]

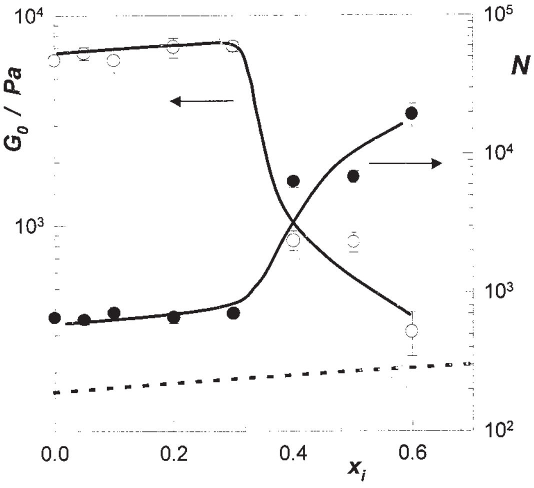

Figure 4 The elastic moduli of hydrogels after preparation G_0 (open symbols) and the effective crosslink densities of PNIPA gels in terms of N, number of segments between crosslinks (filled symbols), shown as a function of x_i. The solid curves show the trend of data. The dotted line shows the chemical values of N (N_{chem}), which would result if all the crosslinker molecules formed effective crosslinks in the hydrogel.

$$\Delta G_i \approx f \ln(f v_2^0/\alpha^3) \tag{10}$$

where f is the effective charge density of the network (i.e., the fraction of segments bearing ionic groups), which relates to x_i through the equation

$$f = x_i V_1/\overline{V}_r \tag{11}$$

Balancing the two opposite free-energy contributions represented by ΔG_{el} (eq. (9)] and ΔG_i [eq. (10)] by minimizing their sum with respect to α and, because $\alpha = V_{\mathrm{eq}}^{1/3}$ at the swelling equilibrium, one obtains

$$6\ V_{\mathrm{eq}}^{2/3} + 8\frac{V_{\mathrm{eq}}^{4/3}}{n} + 12\frac{V_{\mathrm{eq}}^{2}}{n^2} \approx fN \tag{12}$$

For the Gaussian chains, that is, when n approaches infinity, eq. (12) reduces to

$$V_{\mathrm{eq}} \approx (fN)^{3/2} \tag{12a}$$

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. (12) 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).

Figure 5 shows a double-logarithmic plot of the equilibrium gel volume V_{eq} versus the number of charges per network chains *fN*. Experimental data are shown by filled symbols. Experimental data for PNIPA gels prepared by using AMPS as the ionic comonomer are also shown in the figure by open symbols.[11] The solid curves in the figure are the best fitting curves to the data, which give scaling parameters 0.52 ± 0.08 and 0.68 ± 0.01, for SSA and AMPS hydrogels, respectively. The scaling parameter 0.52, thus found for the present hydrogels, is much smaller than the predicted value of 1.5 for Gaussian chains [eq. (12a)]. It is also smaller than the exponent 0.68 found for AMPS hydrogels. Moreover, fitting of eq. (12) to the experimental data by the method of least-squares gives the number of flexible units between crosslinks $n = 9.3 \pm 0.8$ and 34.9 ± 0.1 for SSA and AMPS hydrogels, respectively. The results demonstrate that the deviation from the predicted course of the Gaussian theory becomes more significant when the AMPS units in the PNIPA network chains are replaced with the SSA units. The effect of constraints restricting the chain motions seems to be more significant in SSA hydrogels because of the bulky side groups of SSA.

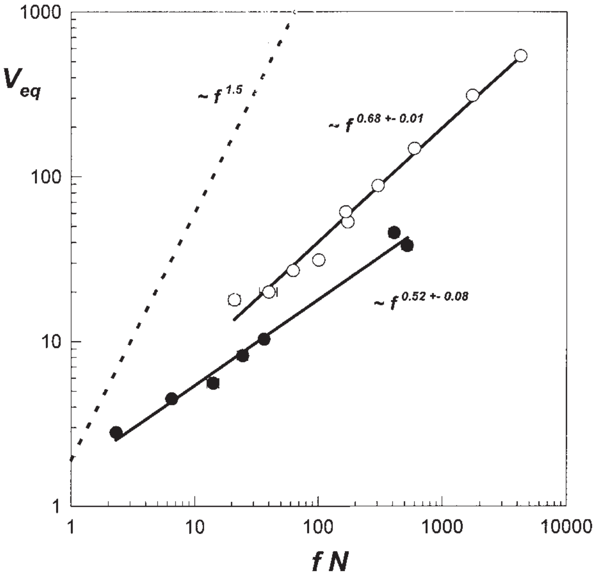

Figure 5. The equilibrium volume of the hydrogels normalized with respect to the after preparation state V_{eq} shown as a function of the number of charges per network chain *fN*. Experimental data obtained for hydrogels with SSA and AMPS units are shown by the filled and open symbols, respectively. Data for AMPS gels were taken from the literature.[11] The solid curves are the best fitting curves to the experimental data. The dotted curve represents the prediction of eq. (12a) for Gaussian chains.

The elastic moduli of the hydrogels were measured for hydrogel samples of various charge densities and swelling degrees. Results of the measurements are collected in Figure 6 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. 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, modulus decreases with increasing V with a slope close to the theoretical value of $-1/3$ [eq. (7)]. 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 the increase of the modulus with the gel volume. Recently, we showed that the reduced modulus of swollen gels can be given by.[10,11]

$$G_r = V^{-1/3} + \frac{2}{3}\frac{(1+\lambda^3)}{n\lambda}V^{1/3} + \frac{2}{3}\frac{(1+\lambda^3+\lambda^6)}{(n\lambda)^2}V + \frac{2}{3}\frac{(1+\lambda^3+\lambda^6+\lambda^9)}{(n\lambda)^3}V^{5/3} + \cdots \tag{13}$$

According to eq. (13), an infinite number of statistical segments per network chain ($n = \infty$) yields a straight line with a slope of $-1/3$, which is the result of the Gaussian approach [eq. (7)]. For finite values of n, the exponent deviates from $-1/3$ and G_r increases with increasing gel volume. The dotted lines in Figure 6(B) represent the theoretical slopes −1/3, 1/3, 1, and 5/3, predicted by eq. (13) for various gel volumes. It is seen that the dotted lines agree well with the experimental behavior of highly swollen PNIPA hydrogels.

In Figure 7, the reduced moduli of PNIPA gels with SSA (filled symbols) and AMPS units (open symbols) are shown as a function of the gel volume. $x_i = 0.30$ and 0.50 in Figure 7(A, B) respectively. It is seen that the upturn of the elastic modulus of SSA gels occurs at lower gel volumes than that of the AMPS gels. This behavior is also seen in Fig. 7(B), despite the fact that the crosslink density of the SSA gel is much lower. Thus, it is demonstrated that replacing AMPS with SSA in PNIPA hydrogels produces more rigid chain backbone so that the non-Gaussian properties become visible at lower gel volumes.

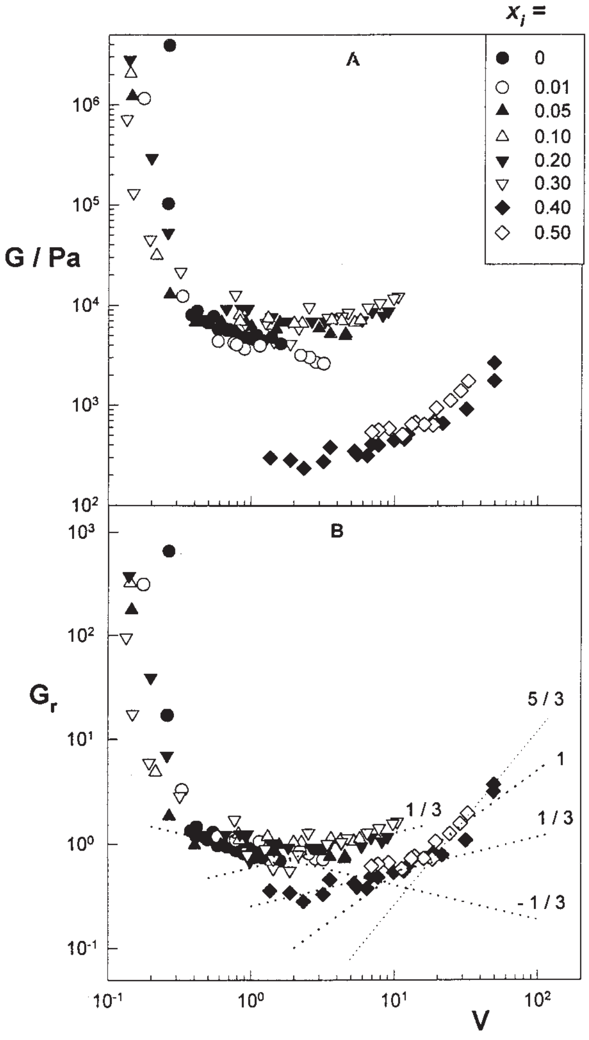

Figure 6. The elastic modulus G (A) and the reduced modulus G_r (B) of the hydrogels shown as a function of the normalized gel volume V. The mole fraction of SSA x_i is indicated in the figure. The dotted lines in (B) represent the theoretical slopes predicted by eq. (13) for different gel regimes.

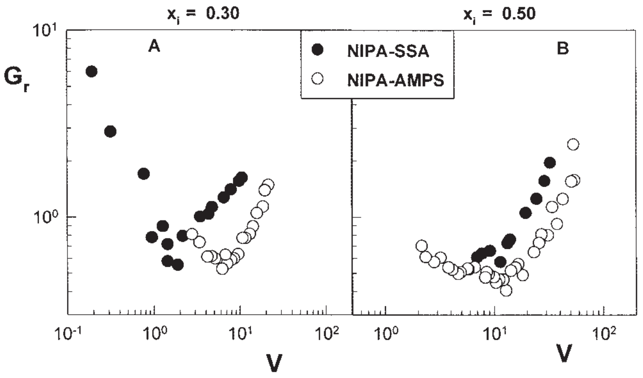

Figure 7. The reduced modulus G_r of the hydrogels with SSA (filled symbols) and AMPS units (open symbols) shown as a function of the normalized gel volume V. Data for AMPS gels were taken from the literature.[11] (A) $x_i = 0.30$, $N = 1259$ (AMPS gel) and 673 (SSA gel). (B) $x_i = 0.50$, $N = 2435$ (AMPS gel) and 6354 (SSA gel).

CONCLUSION

A series of hydrogels starting from the monomer NIPA and the ionic comonomer SSA was prepared in dilute aqueous solutions. It was shown that the increase of the equilibrium gel volume V_{eq} with the network charge density fN is considerably weaker ($V_{eq} \approx fN^{0.52}$) than expected assuming Gaussian statistics ($V_{eq} \approx fN^{1.5}$). This deviation is interpreted as the non-Gaussian elasticity of the hydrogels swollen to equilibrium. Elasticity data of swollen hydrogels also indicate striking departures from Gaussian behavior with large upturns in the modulus data. Non-Gaussian form of the rubber elasticity theory explains the exponents found in the dependence of the reduced modulus on the gel volume. It was also shown that the deviation from the Gaussian behavior becomes more significant if AMPS is replaced with the SSA units. This is due to the fact that the SSA-containing gels consist of rather stiff network chains due to the bulky side groups so that less statistical segments per network chain appears in the swollen state hydrogels.

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