Rubber Elasticity of Poly(*N*-isopropylacrylamide) Gels at Various Charge Densities

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ABSTRACT: The mechanical properties and the swelling behavior of a series of *N*-isopropylacrylamide copolymers with the sodium salt of 2-acrylamido-2-methylpropanesulfonic acid were investigated. The increase of the equilibrium gel volume V_{eq} with the charge density fN was considerably weaker ($V_{eq} \approx fN^{0.75}$) 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. The exponent 0.75 found indicates that the elastic free energy ΔG_{el} scales with the linear swelling ratio α as $\Delta G_{el} \approx \alpha^4$, thus deviating from $\Delta G_{el} \approx \alpha^2$ derived using Gaussian chain statistics. This expression for the elastic free energy explains the behavior of elastic modulus data of the equilibrium swollen hydrogels.

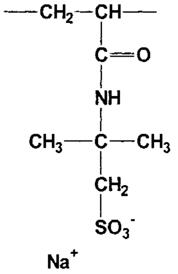
Introduction

Poly(*N*-isopropylacrylamide) (PNIPA) gel is a typical temperature-sensitive gel exhibiting volume phase transition at approximately 34 °C.[1,2] The temperature sensitivity of PNIPA gels has been studied both for its fundamental interest and technological application.[3−6] These materials are useful for drug delivery systems, separation operations in biotechnology, processing of agricultural products, sensors, and actuators. The experimental studies of PNIPA gels reported in the past focused essentially on their swelling behavior. To interpret the swelling data of PNIPA hydrogels, a number of theories were used.[2,7−10] However, fitting the existing theories to the swelling data requires PNIPA network cross-link density as an adjustable parameter 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.[11−13] 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 cross-links at high PNIPA network concentrations.[14] Muniz and Geuskens investigated the elastic modulus of semiinterpenetrated polymer networks of cross-linked polyacrylamide (PAAm) having linear *N*-isopropylacrylamide (NIPA) homopolymer inside.[15] 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.

Our aim of the present study was to investigate the elastic properties of a series of hydrogels denoted by PNIPA prepared by free-radical copolymerization of NIPA with the sodium salt of 2-acrylamido-2-methylpropanesulfonic acid (AMPS, Scheme 1) using *N,N′*-methylene(bis)acrylamide (BAAm) as a cross-linker. AMPS dissociates completely over the entire pH range so that AMPS containing hydrogels exhibit pH-independent swelling.[16−19]

Scheme 1. AMPS Repeating Unit of the Hydrogels



Here, we report the mechanical properties and the swelling behavior of PNIPA gels of various charge densities. As will be shown below, the volume and the elastic modulus data of equilibrium swollen hydrogels indicate non-Gaussian elasticity of PNIPA network, even at small charge densities. It was found both experimentally and theoretically that the elastic free energy ΔG_{el} scales with the linear swelling ratio α as $\Delta G_{el} \approx \alpha^4$, thus deviating from $\Delta G_{el} \approx \alpha^2$ derived using Gaussian chain statistics.

Experimental Section

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-methylpropanesulfonic 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. A stock solution containing NIPA and BAAm was prepared by dissolving 4 g of NIPA and 0.064 g of BAAm in 50 mL of distilled and deionized water.

Synthesis of Hydrogels. PNIPA gels were prepared by free-radical cross-linking copolymerization of NIPA and AMPS with a small amount of BAAm in aqueous solution at 5 °C in the presence of 3.51 mM APS initiator. The mole fraction of AMPS in the monomer mixture x_i was varied between 0 and 0.53, while the cross-linker ratio X (mole ratio of the cross-linker BAAm to the monomers NIPA + AMPS) was varied between 1/85 and 1/179. The synthesis parameters of the hydrogels are compiled in Table 1. To illustrate the synthetic procedure, we give details for the preparation of the hydrogel with $X = 1/86$ and $x_i = 0.010$ in the comonomer feed composition:

NIPA−BAAm stock solution (9.8 mL), AMPS stock solution (0.07 mL), and APS (0.008 g) were mixed and completed to 10 mL with distilled water. After bubbling nitrogen for 20 min,

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Table 1. Characteristic Data of the Hydrogels[a]

x_i	X^{-1}	C_0 (M)	G_0/kPa	$G_{r,eq}$	V_{eq}
0.000	85	0.71	6.12	0.92	1.6
0.010	86	0.71	6.48	0.77	3.2
0.022	87	0.71	6.94	0.71	5.8
0.030	88	0.71	7.14	0.80	7.4
0.046	89	0.71	7.33	0.76	9.0
0.055	90	0.71	6.48	0.84	10.8
0.059	91	0.71	7.06	0.83	11.0
0.109	96	0.72	5.21	0.84	15.8
0.217	109	0.72	4.62	0.90	27.2
0.322	126	0.73	3.94	1.16	46.4
0.435	151	0.74	3.16	1.40	73.8
0.525	179	0.74	1.76	*b*	*b*

[a] x_i = mole fraction of AMPS in the comonomer feed, X = cross-linker ratio (moles of cross-linker/moles of monomers), C_0 = initial monomer concentration, G_0 = elastic modulus of gels after their preparation, $G_{r,eq}$ = reduced modulus of equilibrium swollen gels, i.e., G_{eq}/G_0, and V_{eq} = normalized volume of equilibrium swollen gel. [b] These samples were too weak to withstand the mechanical and the swelling measurements at swelling equilibrium.

TEMED (0.025 mL) was added to the mixture. The solution was then poured into several glass tubes of 4.5−5 mm internal diameters and about 100 mm long. The glass tubes were sealed and immersed in a thermostated water bath at 5 °C, and the polymerization was conducted for 1 day. After the reaction, the hydrogels were cut into specimens of approximately 10 mm in length and immersed in a large excess of distilled water to remove the unreacted species.

PNIPA Network Concentration at the Stage of Gel Preparation. The presence of a solvent during the gel formation process is known to produce supercoiled polymer chains in the dry state so that the increase of their dimensions during swelling does not require much loss of their conformational entropy. As a result, the mechanical properties and the swelling behavior of gels sensitively depend on the degree of dilution at which they are formed.

The degree of dilution of PNIPA networks after their preparation was denoted by ν_2^0, the volume fraction of cross-linked 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. Assuming that the monomer conversion is complete after the cross-linking copolymerization, ν_2^0 can also be calculated from the initial molar concentration of the monomers C_0 (mol/L) as

$$\nu_2^0 = 10^{-3} C_0 \bar{V}_r \tag{1}$$

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

$$\bar{V}_r = 83.7 + 85.9\, x_i \tag{2}$$

The theoretical values of ν_2^0 calculated using eq 1 are shown in Figure 1 as open symbols together with the experimentally determined ν_2^0 values (filled symbols). It is seen that, although the initial monomer concentration was fixed at 0.7 M, ν_2^0 increases with increasing x_i due to the larger molar volume of AMPS units compared to that of NIPA units (169.6 vs 83.7 mL/mol). Another point shown in Figure 1 is that the experimental ν_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, elemental microanalysis results reveal that the cross-linked NIPA−AMPS copolymers always contain about 10−20 wt % water, even after several months of drying under vacuum.[20] Therefore, in the following paragraphs, the theoretical ν_2^0 values were used for further calculations.

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). 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 length taken from the same gel.

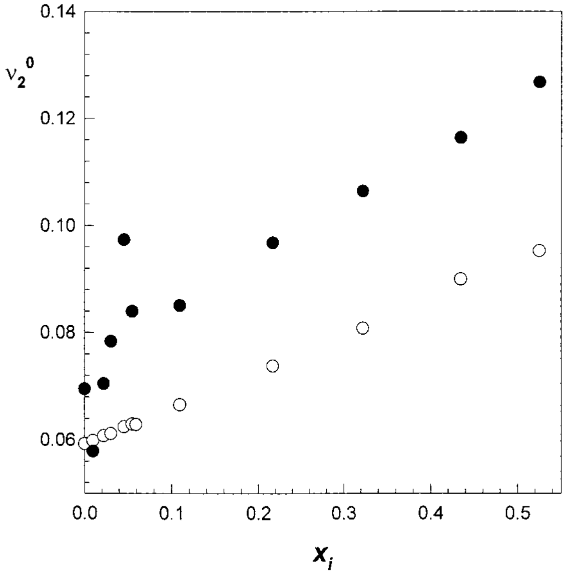

Figure 1. Variation of the polymer network concentration after the gel preparation ν_2^0 with the mole fraction of AMPS in the comonomer feed x_i. The filled symbols represent experimentally determined ν_2^0 values while the open symbols were calculated using eq 1 with the assumption that the monomer conversion is complete after the cross-linking copolymerization.

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 $V_{eq} = (D/D_0)^3$, where D and D_0 are the diameter of hydrogels after equilibrium swelling in water and after synthesis, respectively. The volume fraction of cross-linked polymer in the equilibrium swollen gel $\nu_{2,eq}$ was calculated as $\nu_{2,eq} = \nu_2^0/V_{eq}$.

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 weeks), the diameters of partially swollen gels were measured, from which their volumes and network concentrations (V and ν_2, respectively) were calculated.

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.[20] Briefly, a cylindrical gel sample of about 6 mm in diameter and 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

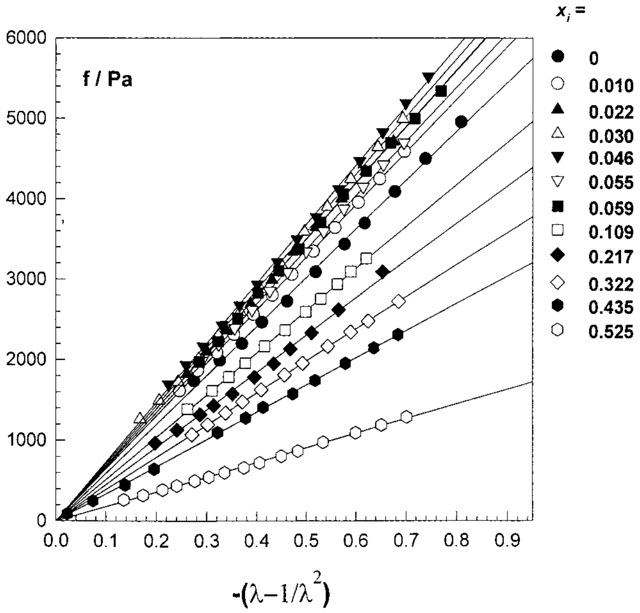

Figure 2. Typical stress−strain data for PNIPA hydrogels just after their preparation. The mole fraction of AMPS x_i is indicated in the figure.

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 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:

$$f = G(\lambda - \lambda^{-2}) \tag{3}$$

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 Figure 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 cross-link density by[21,22]

$$G = A\frac{\rho}{\bar{M}_c}RT(\nu_2^0)^{2/3}(\nu_2)^{1/3} \tag{4}$$

where ρ is the polymer density (1.35 g/mL) and $\bar{M}_c$ is the molecular weight of the network chains. 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 cross-links. The number of segments between two successive cross-links N is related to the molecular weight of the network chains $\bar{M}_c$ by $N = \bar{M}_c/(\rho V_1)$, where V_1 is the molar volume of a segment, which is taken as the molar volume of water (18 mL/mol).

Since $\nu_2 = \nu_2^0$ 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 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

$$G_r = \frac{G}{G_0} = \left(\frac{\nu_2}{\nu_2^0}\right)^{1/3} = V^{-1/3} \tag{5}$$

Results and Discussion

In the first subsection, we discuss the charge density dependence of the cross-link density of PNIPA hydrogels. In the second subsection, we discuss the power law dependence of the equilibrium gel volume on the charge density of the hydrogels and interpret the experimental observations. In the last subsection, we discuss the elastic modulus data of the hydrogels at various gel volumes.

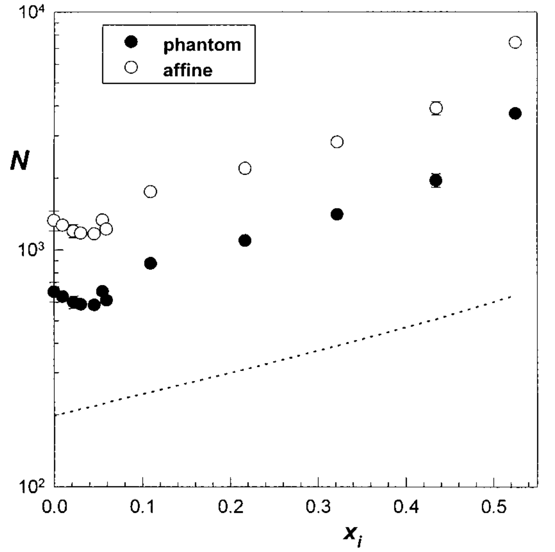

Figure 3. Effective cross-link densities of PNIPA networks in terms of N (number of segments between cross-links) calculated from the elastic moduli G_0 of the hydrogels shown as a function of the mole fraction of AMPS in the comonomer feed x_i. The filled and open symbols are calculation results for phantom ($\phi = 4$) and affine network models, respectively. The dotted line was calculated using eq 6.

(1) Cross-Link Density of the Hydrogels. The characteristic data of the hydrogels prepared at various charge and cross-link densities are listed in Table 1. The first three columns of the table contain the synthesis parameters of the hydrogels. Columns 4 and 5 show the elastic moduli of the hydrogels just after their preparation G_0 and their reduced elastic moduli at swelling equilibrium $G_{r,eq}$, respectively. In the range of x_i from 0 to 0.10, G_0 values lie at 6−7 kPa, whereas G_0 decreases as the AMPS content x_i further increases.

Using the values of G_0 and ν_2^0 of the hydrogels together with eq 4, one may calculate the effective cross-link densities of the hydrogels in terms on N, the number of segments between two successive cross-links. The results for phantom ($\phi = 4$) and affine network models are shown in Figure 3 as filled and open symbols, respectively, plotted against the mole fraction of AMPS x_i. The dotted line in the figure represents the chemical cross-link density, N_{chem}, which would result if all the cross-linker (BAAm) molecules formed effective cross-links in the hydrogel. N_{chem} was calculated from the cross-linker ratio X used in the gel preparation using the equation

$$N_{chem} = \frac{X^{-1}}{2}\frac{\bar{V}_r}{V_1} \tag{6}$$

It is seen that N of the nonionic PNIPA gel ($x_i = 0$) equals 665 or 1330 for phantom or affine network models, respectively, compared to its chemical value of 200. The difference between the effective and chemical cross-link densities of PNIPA hydrogels indicates that 70−85% of the cross-linker BAAm are wasted during the cross-linking copolymerization, probably due to the cyclization and multiple cross-linking reactions. The high degree of dilution during the gel preparation as well as the higher cross-linker reactivity compared to the monomer reactivity are mainly responsible for these reactions.[23−25]

Increasing the content of the ionic comonomer in the feed from $x_i = 0.059$ up to 0.53 increases continuously the number of segments between the cross-links N, i.e., decreases the cross-link density of PNIPA hydrogels (Figure 3). This is a consequence of the simultaneous decrease of the chemical cross-link density, as shown by the dotted line in Figure 3. Moreover, the contribution of electrostatic interaction of charged groups to the elastic free energy of ionic gels may also be responsible for this variation.[26] A somewhat different behavior was observed for slightly charged gels ($x_i < 0.05$). Here, N decreases; that is, the cross-link density increases with an increasing charge density (Figure 3). This type of variation of the cross-link density with x_i at small charge densities was also reported previously, and it is connected with the condensation of counterions to ion pairs.[27−29] Ion pairs attract each other due to dipole−dipole interactions and form multiplets. Multiplets act as additional (physical) cross-links in the hydrogel and thus contribute to the elastic modulus by increasing the effective cross-link density of the network.[30]

(2) Swelling Behavior of the Hydrogels. The equilibrium swelling ratios of the hydrogels in water are shown on the last column of Table 1, in terms of the normalized volumes V_{eq}. 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. This osmotic pressure increases as the concentration of the counterions increases.

Swelling data collected in Table 1 show that the ionic PNIPA gels are highly swollen in water. For such highly swollen hydrogels, the swelling equilibrium is mainly determined by the mixing entropy of the counterions, which is balanced by the gel rubberlike elasticity. According to the theory of rubber elasticity of Gaussian chains, the free energy of elastic deformation ΔG_{el} scales with the deformation ratio as[21] $\Delta G_{el} \approx N^{-1}\alpha^2$, where α is the linear deformation ratio, i.e., $\alpha = (D/D_0) = V^{1/3}$. On the other hand, the existence of fixed ions on the network chains results in a nonequal distribution of mobile counterions between the inside and outside the gel. The ionic contribution to the free energy ΔG_i may be written as[21]

$$\Delta G_i \approx f \ln(f \nu_2^0/\alpha^3) \qquad (7)$$

where f is the effective charge density of the network, i.e., the fraction of segments bearing ionic groups. Balancing the two opposite free energy contributions represented by ΔG_{el} and ΔG_i by minimizing their sum with respect to α, one obtains

$$V_{eq} \approx (f N)^{3/2} \qquad (8)$$

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 $f N$.

It is important to note that the Flory−Huggins (FH) theory from which eq 8 was derived assumes an equivalent size for both the solvent molecules and the network segments. However, because of the different molar volumes of the monomer units and solvent of the present system, the mole fraction of AMPS units in the network x_i does not correspond to f (Scheme 1). f values of the hydrogels can be obtained from $f = x_i V_1/V_r$. The f values calculated are shown in Figure 4 as the solid curve plotted as a function of the mole fraction of AMPS units in the network x_i. It is seen that f is much smaller than x_i. This is due to the fact that each AMPS unit in the gel occupies a volume equal to 9-fold volume of a solvent molecule; i.e., each AMPS unit forms 9 segments but produces only one mobile ion in the gel. This size effect of the ionic comonomer results in a considerable lower charge density than expected from the chemical composition of the network chains.

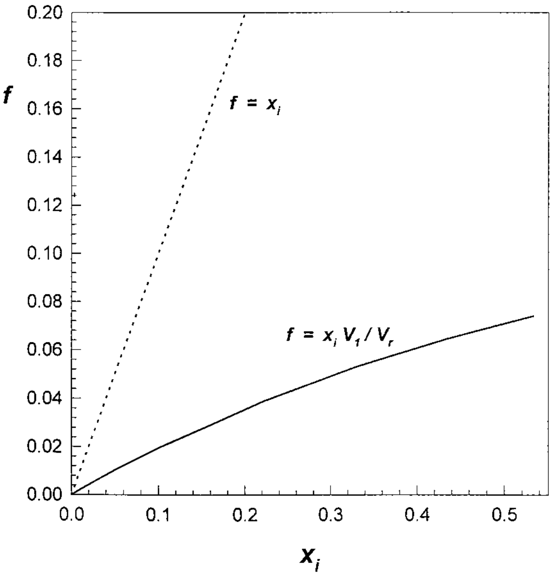

Figure 4. Charge density of the networks f shown as a function of the mole fraction of AMPS units x_i. Owing to the different molar volumes of the monomer units and solvent, f deviates from x_i, as shown by the solid curve.

Figure 5 shows a double-logarithmic plot of the equilibrium gel volume V_{eq} against the number of charges per network chains $f N$. Experimental data are shown by symbols. The dotted curve in the figure represents the prediction of eq 8 with a scaling parameter of 1.5. The solid curve in the figure is the best fitting curve to the experimental swelling data of the hydrogels, which gives a scaling relation:

$$V_{eq} \approx (f N)^{0.75} \qquad (9)$$

The scaling parameter 0.75 ($=^3/_4$), thus found, is much smaller than the predicted value of $^3/_2$ of the FH theory. Moreover, a curve fitting at low charge densities ($x < 0.10$) gives a scaling parameter 0.66; i.e., deviation from the theory further increases. An exponent between 0.6 and 0.8 has been reported before for both weak and strong polyelectrolyte hydrogels equilibrium swollen in water.[19,31−33]

The discrepancy between the theory and experiment may be related to the non-Gaussian behavior of fully swollen PNIPA gels in water.[34] The theory (eq 8) assumes that the polymer network is a collection of Gaussian chains, which can be extended to infinity. For the present hydrogels, $\nu_{2,eq}$ values vary between 0.0373 and 0.0012 depending on the charge density of the hydrogels. This indicates that the network chains in the equilibrium swollen hydrogels are 3−9 times as elon-

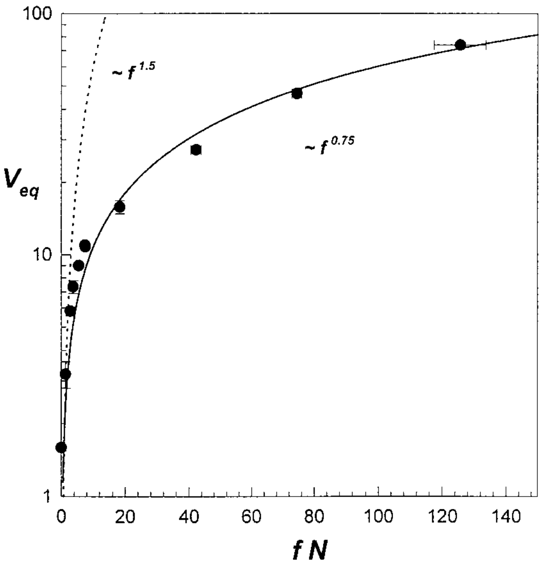

Figure 5. Equilibrium volume of the hydrogels normalized with respect to the after preparation state V_{eq} shown as a function of the number of charges per network chain $f\,N$. The dotted curve represents the prediction of the FH theory. The solid curve is the best-fitting curve to the experimental data. N was calculated using the phantom network model. Calculations using the affine model do not change the values of the exponents.

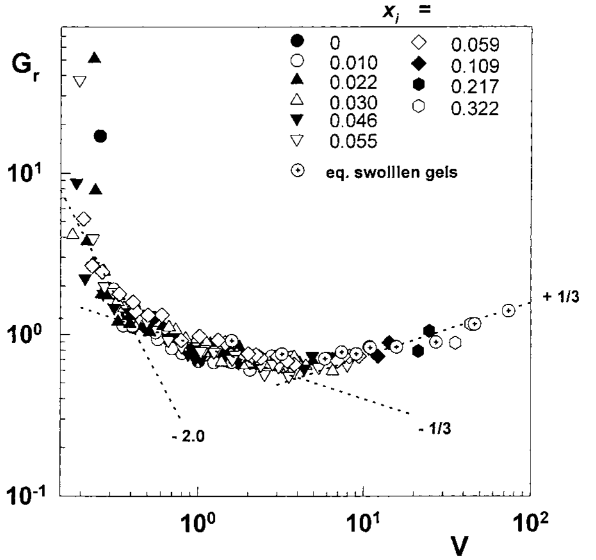

Figure 6. Reduced modulus G_r shown as a function of the normalized gel volume V. The mole fractions of AMPS are indicated in the figure. The symbols with cross hair represent data for equilibrium swollen hydrogels. Three different regimes and the corresponding slopes are also shown in the figure.

gated as in the dry state. At such high swelling ratios, deviation from the Gaussian statistics may appear due to the finite extensibility of the network chains.[35] A further evidence for the non-Gaussian behavior of the network chains in the swollen gels comes from the elastic moduli data of the hydrogels in their swollen states. As seen in Table 1, increase of the charge density x_i from 0 to 0.3 results in a 17-fold increase in the gel volume, while the reduced moduli of the equilibrium swollen hydrogels $G_{r,eq}$ remain constant at 0.82 ± 0.07. The reduced modulus even increases at larger charge densities (Table 1). This also suggests that the equilibrium swollen PNIPA hydrogels are in the non-Gaussian regime.

As the network chains deviate from the Gaussian statistics, elastic free energy ΔG_{el} will increase with a higher power of α. For example, assuming that ΔG_{el} increases with fourth power of α, i.e.,

$$\Delta G_{el} \approx N^{-1}\alpha^4 \tag{10}$$

minimizing the sum of eqs 7 and 10 gives

$$V_{eq} \approx (f\,N)^{3/4} \tag{11}$$

Thus, a scaling parameter $^3/_4$ can be obtained, which is exactly the same we observed in the experiments (Figure 5). Moreover, assuming that ΔG_{el} increases with the fifth power of α, a scaling parameter 0.6 can be obtained, which is close to the value 0.66 observed at low charge densities.

To elucidate the molecular origin of the relation $\Delta G_{el} \approx N^{-1}\alpha^4$ thus found for fully swollen hydrogels, we assumed that the Gaussian statistics fail to describe the statistical properties of PNIPA chains in the equilibrium swollen networks. Instead, non-Gaussian statistics have to be introduced. We have used the well-known treatment based on the inverse Langevin function, L^{-1}, to derive a formula for the change of elastic free energy due to swelling:[22,35]

$$\Delta G_{el} \approx N^{-1}\alpha n^{1/2} L^{-1}(\alpha n^{-1/2}) \tag{12}$$

where n is the number of flexible units between cross-links, 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 12 by $\alpha n^{-1/2}$. It was shown that the inverse Langevin function can be accurately approximated by a Pade equation,[36,37] i.e.,

$$L^{-1}(x) = x(3 - x^2)/(1 - x^2) \tag{13}$$

When eq 13 is substituted in eq 12, one obtains

$$\Delta G_{el} \approx N^{-1}\alpha^2\left(1 + \frac{2}{1 - \alpha^2/n}\right) \tag{14}$$

For $\alpha^2/n \ll 1$, that is for moderate degrees of swelling, or at the onset of deviations from the Gaussian statistics, eq 14 reduces to

$$\Delta G_{el} \approx N^{-1}(\alpha^2 + \alpha^4/n) \tag{15}$$

Equation 15 explains what we observed experimentally. When n approaches infinity, the equation reduces to the Gaussian description. For finite values of n, the elastic free energy scales with the fourth power of the linear swelling ratio, as found by experiments.

(3) Elastic Modulus of the Hydrogels. The elastic moduli of the hydrogels were measured for 175 combinations of hydrogel samples of various charge and cross-link densities and swelling degrees. Results of the measurements are collected in Figure 6 as the dependence of the reduced modulus G_r on the normalized gel volume V. The ionic group contents of the hydrogels are indicated in the figure. The symbols with cross hairs represent the data obtained from equilibrium swollen hydrogels. Several interesting features can be seen from Figure 6. First, the dependence of the reduced modulus on the gel volume can be represented by a single curve, independent of the charge density of PNIPA hydrogels. Second, the data indicate that the volume dependence of reduced modulus cannot be described by a single scaling exponent. Three different regimes can be observed from Figure 6:

1. For the gel volumes V of less than 0.4, the reduced modulus G_r decreases sharply with increasing volume V. In the range of $G_r < 10$, the slope of the double-logarithmic G_r vs V dependence is -2.0.

2. In the range of the gel volume V between 0.4 and 3.5, G_r further decreases with increasing V. The slope of G_r vs V_r plot is -0.32, close to the theoretical value of $-^1/_3$ (eq 5). Thus, PNIPA hydrogels in this regime behave as Gaussian.

3. For gel volumes larger than 3.5, the reduced modulus G_r starts to increase with increasing gel volume with a slope 0.22.

The rapid decrease of G_r with increasing gel volume V from 0.2 to 0.4 in the first regime is usually interpreted as the transition of the polymer from the glassy to the rubbery state by addition of solvent. However, $V = 0.2-0.4$ corresponds to a more than 70% water content of the hydrogels. This means that the hydrogels are in the rubbery state during the mechanical measurements, and the observed behavior cannot be explained with the overall glassy-to-rubbery transition of the gels. A more plausible explanation is the effect of the gel inhomogeneities. As pointed out in the previous section, a large difference exists between the effective and chemical cross-link densities of the hydrogels, indicating that the cyclization and multiple cross-linking reactions occur predominantly during the gel formation of NIPA and BAAm monomers. These reactions result in an inhomogeneous distribution of cross-links in the final network and thus contribute to the formation of highly cross-linked (less swollen) regions connected by loosely cross-linked ones. These inhomogeneities in PNIPA gels have been detected by light scattering techniques.[38,39] As a laser beam scans through the PNIPA gel sample, the scattered intensity changes drastically depending on the location of the scattering points within the gel. Since the glass transition temperature increases with an increasing degree of cross-linking because more thermal energy will be needed for the system to become rubbery, the highly cross-linked regions pass from the glassy to the rubbery state later (i.e., at larger overall gel volumes) than the other regions. The rapid decrease of the modulus with increasing gel volume in this regime can thus be explained with the rubbery transition of the highly cross-linked and therefore less swollen regions of the hydrogel sample. The slope -2.0 found in this regime is close to the value of -2.3 reported for polyacrylamide gels.[40]

On the other hand, the increase of the elastic modulus G_r in the third regime is an indication of the limited extensibility of the network chains and is connected with the high stretching of the network chains. As seen in Figure 6, all the equilibrium swollen hydrogels with $x_i > 0.01$ are in the third regime. For the equilibrium swollen hydrogels, since the elastic free energy scales as $\Delta G_{el} \approx N^{-1}\alpha^4$, their moduli should vary as $G \approx N^{-1}\alpha^4 \nu_2$ and $G_0 \approx N^{-1}\nu_2^0$. Thus, the reduced modulus of swollen gels should scale with the gel volume as $G_r \approx V^{1/3}$; i.e., an exponent of $^1/_3$ is expected for fully swollen hydrogels. Indeed, the exponent $^1/_3$ shown in Figure 6 by the dotted line agrees well with the experimental data in the third regime. 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[22,35]

$$f = \frac{1}{3}\frac{\rho}{\bar{M}_c} RTn^{1/2}\nu_2^0\alpha^{-2}\{L^{-1}(\lambda\alpha n^{-1/2}) - \lambda^{-3/2}L^{-1}(\alpha(n\lambda)^{-1/2})\} \quad (16)$$

Replacing the inverse Langevin function by its Pade approximant (eq 13), eq 16 simplifies to

$$f = G'\left(\lambda - \frac{1}{\lambda^2}\right) \quad (17)$$

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

$$G' = G\left(1 + \frac{2}{3}\frac{\alpha^2(1+\lambda^3)}{n\lambda}\right) \quad (18)$$

The reduced moduli of the networks follow from eqs 5 and 18 as

$$G_r = V^{-1/3} + \frac{2}{3}(\lambda^2 + 1/\lambda)\frac{V^{1/3}}{n} \quad (19)$$

According to eq 19, 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 approaches $^1/_3$ at high gel volumes.

Conclusions

The equilibrium swelling degrees and the elastic moduli of PNIPA hydrogels were studied at various charge densities. The increase of the equilibrium gel volume V_{eq} with the charge density fN was found to be considerably weaker ($V_{eq} \approx (fN)^{0.75}$) than expected assuming Gaussian statistics ($V_{eq} \approx (fN)^{1.5}$). The deviation is interpreted as the non-Gaussian elasticity of equilibrium swollen PNIPA hydrogels. The scaling parameter 0.75 thus found indicates that the elastic free energy ΔG_{el} scales with the fourth power of the linear deformation ratio α., i.e., $\Delta G_{el} \approx \alpha^4$. This expression for the elastic free energy explains the behavior of elastic modulus of equilibrium swollen PNIPA hydrogels.

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(34) It might be argued that the free energy of mixing of polymer segments with solvent molecules cannot be neglected in analyzing the swelling equilibrium. We tried to fit the experimental swelling and mechanical data to the Flory−Rehner equation[21] with the polymer−solvent interaction parameter χ as a fit parameter. Calculations showed that χ increases drastically from 0.495 (or from 0.485 for phantom network) up to about 50 with an increasing ionic group content of the hydrogel. Thus, the swelling behavior of PNIPA gels cannot be explained using the Flory−Rehner equation, unless the interaction parameter is given an unrealistic dependence on the charge density. On the other hand, adhering the χ parameter value found for swollen uncharged PNIPA network (0.485 and 0.495 for phantom and affine network models), but taking the effective charge density f as a fit parameter, the experimental data can be explained using the Flory−Rehner equation, if only a small fraction of charged units is osmotically active in the gel swelling. This effective fraction of charged units was found to decrease from 0.6 to 0.07 with an increasing charge density of the gel. However, because of the strong polyelectrolyte nature of AMPS, such a high fraction of undissociated AMPS units in water is unrealistic.

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