Elastic and Osmotic Behavior and Network Imperfections of Nonionic and Weakly Ionized Acrylamide-Based Hydrogels

Sergey A. Dubrovskii* and Galina V. Rakova

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 4 Kosygin Street, Moscow 117977, Russia

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ABSTRACT: Elasticity of nonionic and weakly ionized acrylamide-based hydrogels was studied as a function of swelling degree Q and initial total monomer concentration c_0. The shear modulus decreases as Q^{-m} at low Q and then increases steeply because network chains no longer obey Gaussian statistics. The exponent m decreases from 0.7 to $^1/_3$ as c_0 increases from 5 to 30 wt %. Ionization of network leads to a decrease in the modulus, and this effect disappears at high concentrations of added salt, as predicted by a recent model. At swelling equilibrium, the modulus provides an "effective" measure of the osmotic pressure. The upturn in the modulus is described using the inverse Langevin function that allows estimation of an average network chain length. This length was compared with that of a perfect network chain, and the network density was evaluated from the modulus in the preparation state. This indicates that networks prepared with low c_0 contain a large amount of elastically ineffective segments. Their "chains" apparently have architecture typical of ideal random-branched macromolecules without loops. At high c_0, "effective" perfect networks with insignificant number of interchain trapped entanglements are formed.

Introduction

Acrylamide-based hydrogels are used in many applications such as superabsorbent materials and the medium for separation of biomacromolecules.[1,2] Their elastic and osmotic properties are very important in applications. From a more fundamental point of view, the relation between these properties and the network structure is of interest.

It is well-known that the properties of a polymer gel depend on the preparation conditions. In particular, the concentration of solvent at network formation is important as it controls interpenetration of polymer chains and hence the network topology. Polyacrylamide (PAAm) hydrogels are usually prepared by copolymerizing acrylamide with the cross-linking monomer in aqueous solution. The amount of water in the reaction mixture, or the initial total monomer concentration c_0, may be varied to change the hydrogel structure and thus alter its properties. The ionized acrylamide-based gels can be prepared from neutral PAAm gels without changing the network topology by hydrolysis of amide groups. Due to the high osmotic pressure of dissociated counterions, they can reach very large swelling degrees, where the non-Gaussian elasticity of network chains manifests itself.

Several studies have been reported on the elastic properties of acrylamide-based hydrogels as a function of c_0.[3−8] Experimental observations indicate that PAAm networks contain the topological defects affecting the shear modulus. First, the presence of elastically ineffective loops and dangling chains causes a decrease in the modulus from its expected value. Second, there are interchain trapped entanglements that add to the modulus by acting as effective cross-links. Concentrations of these defects depend on c_0.

Since both cross-links and trapped entanglements affect the elastic modulus, one cannot usually separate their contributions, and discriminate between the topological defects of two types, from the modulus data. However, an additional information can be obtained from the modulus values measured for ionized gels at high swelling degrees, when network chains are strongly stretched and cease to obey Gaussian statistics. In this case, an average length of elastically effective network chains can be evaluated using the inverse Langevin function to treat the modulus in the strong stretching regime.[9,10] It is expected that this allows characterization of the network imperfections in more detail.

As long as the network chains are weakly stretched, the shear modulus of a gel G decreases with the swelling degree Q as a power function of Q. The classical rubber elasticity theory predicts that G scales as $Q^{-1/3}$. However, the scaling exponents considerably larger than $^1/_3$ are often observed in experiments.[9,11] Obukhov et al.[12] used some recent ideas relating network strand configuration and modulus to describe the elasticity of neutral gels. Their model predicts $G \sim Q^{-7/12}$ for good solvent. The same ideas were applied by Rubinstein et al. to construct a theory for flexible polyelectrolyte gels.[13] This theory predicts G to scale as $Q^{-5/6}$ for salt-free gels at low swelling degrees. Also, it predicts a dependence of G on network charge and concentration of added salt. The effects of added salt and network ionization on the modulus have been observed experimentally at polymer concentrations close to c_0.[14]

The osmotic properties of weakly charged acrylamide-based hydrogels were recently studied by measuring the isotropic swelling pressure.[15] The ionic contribution to osmotic pressure was found to be mainly determined by the translational entropy of mobile ions in the gel. In polyelectrolyte gels, this contribution, associated with a Donnan equilibrium, dominates the polymer (mixing) contribution to osmotic pressure as long as the concentration of added salt is not very high. At the swelling equilibrium, the osmotic pressure is balanced by the elastic pressure, which arises from the stretching of network chains. In this case, the shear modulus can provide a reasonable measure of the osmotic pressure, as revealed by the experiments on neutral PAAm gels.[7]

In this paper we report a study on moderately cross-linked acrylamide-based hydrogels, both neutral and ionized by hydrolysis, prepared with different total

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monomer concentrations c_0. The aim of the present study is to better understand the effect of c_0 on the gel elastic behavior and the network topology. With this aim, we measured the shear modulus in a wide range of swelling degrees. Also, we apply to these data the approach to non-Gaussian elasticity quoted above[9,10] to evaluate the average length of network chains. A second aim is to clarify the dependence of shear modulus on the ionization degree of network and on concentration of added salt. With this aim, the *G(Q)* data for neutral gels, salt-free ionic gels, and ionic gels swollen in salt solutions are compared with the predictions of recently proposed models.[12,13] The next aim is to check if the equality between the shear modulus and the osmotic pressure determines the equilibrium swelling of polyelectrolyte gels. For this purpose, the modulus data on brine-equilibrated ionic gels are compared with the osmotic pressure of mobile ions calculated using the ideal Donnan equilibrium theory.

Experimental Section

Sample Preparation. PAAm hydrogels were prepared by radical copolymerization of acrylamide and *N,N'*-methylenebis(acrylamide) (BAAm), the cross-linking agent, in oxygen-free aqueous solution. The polymerization was initiated by the sodium persulfate−sodium thiosulfate system and carried out at 25 °C for 24 h; the concentration of each initiator component was held at a constant value of 0.5 g/L for all syntheses. In a series of gels, the cross-link density was fixed at 0.0046 while c_0 was varied; the c_0 values used were 0.050, 0.11, 0.15, 0.20, 0.25, 0.30. Here, the cross-link density is defined as the molar concentration ratio of BAAm to acrylamide. The initial total monomer concentration c_0 is defined as the mass fraction of monomer in the pregel reaction solution.

The gel sheets were prepared in a rectangular glass mould containing a set of glass plates separated by spacers of different thickness (3.3, 4.7, 6.6, 10, and 17.6 mm). A part of the samples was used to measure the shear modulus at different degrees of swelling; some of these samples were tested in the initial state. The other gels were placed in 0.04 M aqueous NaOH solution to convert them into ionic gels.

In NaOH solutions, network-fixed amide groups were hydrolyzed to give carboxylate anionic groups.[5] To restrict the swelling of gels during hydrolysis, sodium chloride was added to the NaOH solution; the final NaCl concentration was 1 M. After 67 to 70 h, the gel plates were transferred in 1 M NaCl solution to stop the reaction of hydrolysis. Using this procedure, the ionic gels in salt form were obtained. The degree of hydrolysis was estimated for several samples by back potentiometric titration. The gels were cut into very small pieces and treated with aqueous HCl to convert all carboxylate groups into the acid form. Aqueous dispersion of the gel particles was neutralized by an excess of NaOH, and 0.1 M HCl was then added to the system in small portions; pH was measured at each step. The degrees of hydrolysis were 0.15, 0.18, 0.16, and 0.11 for gels prepared with c_0 = 0.11, 0.15, 0.25, and 0.30, respectively. The large variation in the results of titration is probably due to the difference in the hydrolysis temperature (which was not controlled).

Swelling Conditions. To investigate the effect of swelling on the elastic modulus, the gels were swollen to equilibrium in a large volume of appropriate solvent. The nonionic gels were swollen in pure water or water−acetone mixture; the acetone concentration ranged from 10 to 50 vol %. The polyelectrolyte gels were swollen in pure water or in aqueous NaCl; the salt concentration c_s ranged from 10^{-4} to 1 M. Approximately 1 to 2 weeks were needed to reach equilibrium. Once equilibrium was attained, the gels were weighed and their moduli were measured. The swelling degree *Q* is defined as the reciprocal of the volume fraction of polymer in the gel:

$$Q = 1 + (\rho_p/\rho_s)(Q_m/c_0 - 1) \tag{1}$$

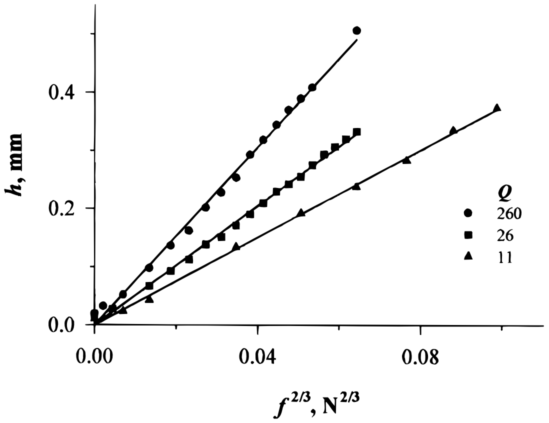

Figure 1. Penetration data for gels prepared with c_0 = 0.11 and swollen to different degrees *Q*: circles, neutral gel after preparation; squares, water-equilibrated neutral gel; triangles, ionized gel in equilibrium with 0.01 M NaCl.

where ρ_p (=1.3 g/cm^3) and ρ_s, respectively, are the densities of polymer and solvent and Q_m is the mass swelling ratio, i.e., the mass ratio of swollen gel to initial gel.

In parallel with the brine-equilibrated ionic gels, the salt-free nonequilibrium-swollen ionic gels were studied. Water was slowly evaporated from the ionic gel, swollen to equilibrium in water, until its swelling degree reached the equilibrium swelling degree of the corresponding neutral gel. Thereafter, the dried gel was swollen in steps by adding small portions of water. At each step, the gel was kept in a closed vessel for several days to restore uniformity. The weight and the modulus of the gel were measured during evaporation and at each step of swelling. These measurements gave close results, and, consequently, the modulus changed reversibly.

Mechanical Measurements. The shear modulus was obtained from penetration measurements. The technique used was described elsewhere.[16] The specimens were rectangular gel plates with typical thickness of 1 to 2 cm; thinner initial gel plates were used at higher swelling degrees and vice versa. The length and the width of each plate were approximately twice its thickness. A stainless steel sphere of radius *R* (1.9 or 3.4 mm) was forced down into a gel plate, and the penetration depth of the sphere *h* was measured after 30 s of relaxation as a function of applied force *f* (from 0.0001 to 0.01 N). All measurements were performed at deformation ratios $h/R \leq 0.2$. Measurements were made for two samples for each gel lot. The results were averaged.

The general relation between *h* and *f* at small deformations is given by[16]

$$h = h_0 + bf^{2/3} \tag{2}$$

where the factor *b* is related to the shear modulus *G*, $b = [3/(16GR^{1/2})]^{2/3}$. Figure 1 shows *h* plotted against $f^{2/3}$ for a series of gels swollen to different degrees. As predicted by eq 2, the data are reasonably described by straight lines except, possibly, for *f* close to zero. Shear moduli were calculated from the slopes of such lines.

Results and Discussion

A. Elastic Properties. We consider here the experimental *G(Q)* variation for both neutral and ionized gels. The dependencies are described by power functions at low *Q* and demonstrate the non-Gaussian features at high swelling degrees. To evaluate the effects of ionization degree and added salt, both salt-free ionized gels and ionized gels swollen in the presence of salt are considered. In addition, neutral gels with the same network topology are studied. The results are compared with the predictions of the Obukhov et al. and Rubinstein et al. models.[12,13]

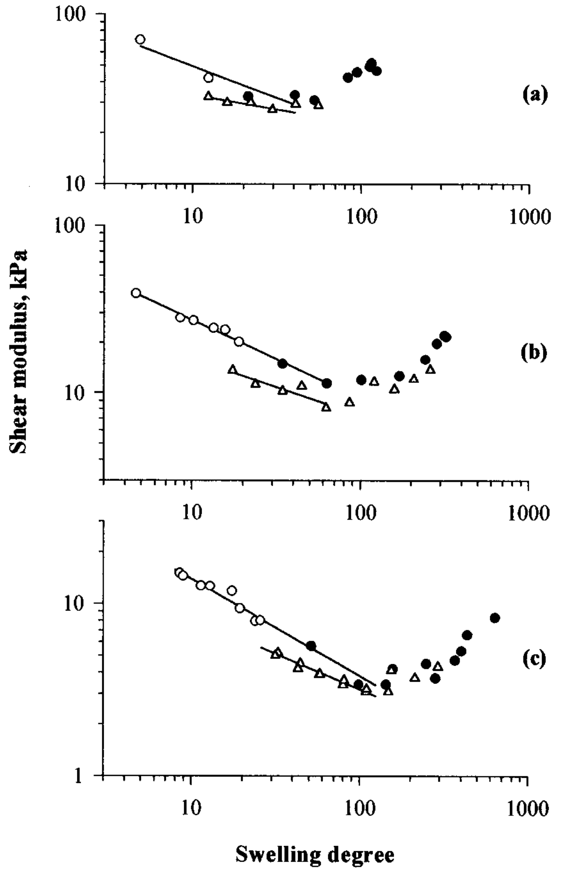

Figure 2. Variation of the shear modulus as a function of swelling degree for gels prepared with different c_0: (a) $c_0 = 0.25$; (b) $c_0 = 0.15$; (c) $c_0 = 0.11$. Key: open circles, neutral gels after preparation or at equilibrium with water–acetone mixtures; filled circles, ionic gels at equilibrium with aqueous NaCl solutions; triangles, salt-free ionic gels swollen to less than equilibrium swelling degree. At fixed c_0, the neutral and ionic gels have the same network topologies. The straight lines show the power law behavior at low swelling degrees.

Figure 2 shows the variation of the shear modulus with the swelling degree for neutral gels swollen to equilibrium in water–acetone mixtures, ionic gels swollen to equilibrium in salt solutions, and salt-free ionic gels. The modulus of a neutral gel decreases with an increase in swelling degree, and this variation is fitted in the log–log representation by a straight line. The modulus of an ionic gel decreases with increasing swelling degree only at comparatively low values of Q. At high swelling degrees, the modulus steeply increases with rising Q. Such an upturn in G was already observed for polyelectrolyte gels.[5,9,10,17] It was interpreted in terms of non-Gaussian elasticity of highly stretched network chains.[18] The upturn in G starts at a lower Q if c_0 is higher. This indicates that the network chains are shorter (the effective cross-link density is higher) when c_0 is higher.

The straight line drawn through the data for a neutral gel (open circles) fits the $G(Q)$ decrease observed for a brine-equilibrated ionic gel (filled circles), if these gels are prepared with the same c_0, and Q is not too high ($c_s \geq 0.1$ M). This is not surprising since these gels have identical networks, and the network charges are screened at high salt concentration. Thus, the shear modulus of a neutral gel crosses over smoothly to the modulus of the brine-equilibrated ionic gel prepared with the same c_0.

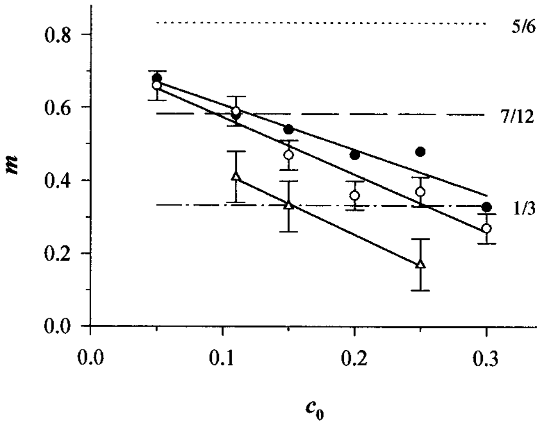

Figure 3. Exponent m of the power law $G \sim Q^{-m}$ for gels prepared with different c_0: circles, neutral gels and brine-equilibrated ionic gels; triangles, salt-free ionic gels. The values of m were determined whether as the slopes of best-fit lines in log–log coordinates (open symbols) or from the nonlinear regression using eq 8 (filled circles).

The moduli of salt-free ionic gels are lower than those of neutral gels or brine-equilibrated ionic gels (Figure 2). The difference is maximum at low swelling degrees. Ionization of network leads to a decrease in the shear modulus, while the addition of salt recovers the modulus of neutral gels. Similar results were obtained by Skouri et al.[14] for lower Q values close to the swelling degree at preparation. These effects can be qualitatively explained by the Rubinstein et al. model.[13] According to this model, the reference state (used to determine the elastic free energy of the gel) is changed upon ionization of the network chains. The size of a network strand in the reference state, which taken as the size the strand would have if it were a free chain, increases with rising degree of ionization. Thus, the shear modulus, which is inversely proportional to the square of this size, should decrease with increasing ionization degree. An alternate qualitative explanation[14] for the effect of electrostatic interactions on modulus takes into consideration the heterogeneous microstructure of PAAm gels and its modification upon ionization of the chains. As is seen from Figure 2, the difference between the moduli of brine-equilibrated and salt-free gels decreases with increasing Q. At some swelling degree, which is attained at a rather low salt concentration ($c_s \sim 0.01$ M), the modulus of a brine-equilibrated gel becomes equal, within experimental error, to the modulus of the appropriate salt-free gel. Therefore, the value of $c_s \sim 0.01$ M approximately corresponds to a crossover between low-salt and high-salt regimes[13] for our ionic gels that include ~15 mol % of charged monomer units.

The modulus variation observed for salt-free gels at low swelling degrees follows the power function $G \sim Q^{-m}$ (Figure 2). Within the experimental accuracy, the data are consistent with the prediction $G \sim Q^{-1/3}$ of the common network-elasticity theories[18,19] based on Gaussian statistics and assumption of affine expansion of network chains. The experimental values of exponent m (from 0.2 to 0.4) are considerably lower than the exponent $^5/_6$ predicted for salt-free ionic gels in the weak stretching regime by the Rubinstein et al. model.[13] Similar results were obtained by Nisato et al.[20,21] for salt-free poly(acrylic acid) gels with rather high cross-link densities. The stronger $G(Q)$ variation was observed for the smaller cross-link density.[21] It should be noted that m slightly decreases with increasing c_0 (Figure 3). At $c_0 = 0.25$, m is less than $^1/_3$. This is probably due to the finite extensibility of chains that adds to the modulus at high swelling degrees.

Figure 3 shows the exponent *m* as a function of c_0 for all gels analyzed. At fixed c_0, neutral gels and brine-equilibrated ionic gels are characterized by the same value of *m*. This value lies in the range from $^1/_3$ to 0.7 and decreases with increasing c_0. The behavior of neutral gels can be compared to the predictions of the Obukhov et al. model.[12] This model assumes affine displacement of network junctions on swelling and takes the free chain size as the size of a network strand in the reference state. It predicts the well-known dependence $G \sim Q^{-1/3}$ for swelling in a Θ solvent and a new dependence $G \sim Q^{-7/12}$ in the case of good solvent. As is seen, the low and upper limits of experimental exponents are close to predicted $^1/_3$ and $^7/_{12}$ values. The good-solvent behavior of neutral gels is observed only at low c_0, when relatively long network strands are likely to form. One can suggest that longer network strands better correspond to the assumption made in the Obukhov et al. model.[12]

For brine-equilibrated charged gels, the power law *G-(Q)* variation observed for high c_0 is consistent with the modulus variation measured by Nisato et al.[21] for poly(acrylic acid) gels with the rather high cross-link density. The values of *m* found for low c_0 are close to that predicted for uncharged polymers in good solvent (Figure 3). Following the Rubinstein et al. approach,[13] such a neutral-gel behavior can be expected at very high salt concentrations when the electrostatic screening length is lower than the electrostatic blob size. When the electrostatic screening length is not too low but c_s is still sufficiently high, the Rubinstein et al. model[13] predicts a dependence of the modulus on salt concentration, $G \sim Q^{-7/12}c_s^{1/4}$. In this case, the *G(Q)* decrease expected for brine-equilibrated ionic gels should be stronger than $G \sim Q^{-7/12}$ because increasing the equilibrium swelling degree of ionic gels is related to a drastic decrease in c_s. This inference seems inconsistent with the experimental data since the power law behavior with constant *m* value extends down to ionic gels in brines until the onset of non-Gaussian elasticity is observed (see Figure 2). However, this inconsistency can be fortuitous, resulting from a compensation between a decrease in the modulus caused by the salt effect and an increase due to the onset of non-Gaussian elasticity. The latter conclusion is supported by the fact that the values of *m* obtained with a non-Gaussian correction (Figure 3; see also section C) are slightly higher at large c_0 than the exponents discussed above.

It is worth mentioning that values of *m* larger than $^1/_3$ can be also attributed to deinterpenetration of network chains that causes their nonaffine expansion on swelling. However, the above discussion shows that our data agree with the affine assumption.

B. Osmotic Properties. According to the Flory-Rehner,[19] the swelling equilibrium of polymer networks is characterized by a balance between the osmotic and elastic pressures. Due to this, simple scaling relations are expected between the shear modulus *G* and the swelling degree *Q* at equilibrium, assuming that *G* linearly scales with the elastic pressure π_{el}. Such relations for polyelectrolyte networks[13] and uncharged networks[22] are independent of c_0 and the network chain length

$$G = B(RT/V)Q^{-n} \qquad (3)$$

where *R* is the gas constant, *T* is temperature, and *V* is the monomer unit molar volume. In the case of neutral gels, the exponent *n* is connected with the excluded volume exponent and equals to 2.25, 3.0, or ∞ for good, Θ and poor solvents respectively; the prefactor *B* depends on solvent quality. The values $n = 1$ and $n = 2$ independent of solvent quality are predicted for ionic gels in the low-salt and high-salt limits, respectively, when the polymer osmotic-pressure contribution can be neglected. The prefactor *B* for such gels depends on salt concentration (in the high-salt limit) and charge density of the network.

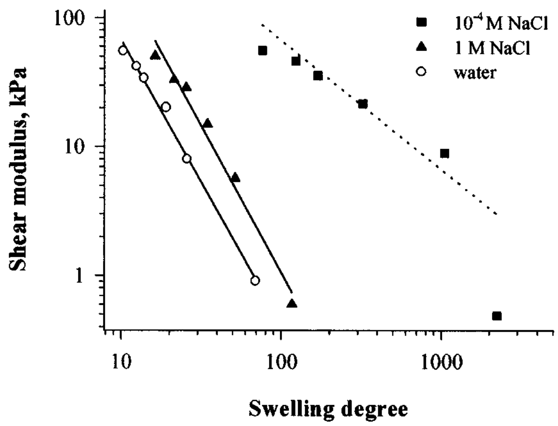

Figure 4. Shear modulus plotted as a function of equilibrium swelling degree in terms of eq 3. The concentration of salt is kept constant while c_0 is varied in each data series. The best-fit solid lines have slopes of 2.19 (circles) and 2.28 (triangles). The dotted line represents the osmotic pressure of dissociated counterions calculated by eq 4 with $\alpha = 0.15$.

Figure 4 shows the correlation between measured equilibrium values of *G* and *Q* in log−log coordinates. In each data series, the solvent composition is kept constant while c_0 is varied. The data for neutral gels in pure water and those for ionic gels at high salt concentration follow the prediction of eq 3. The straight lines drawn through the data have slopes (2.20 ± 0.09 and 2.28 ± 0.15, respectively) close to the expected values. The result for neutral hydrogels agrees with those reported by other authors.[6,7] It confirms that water is a good solvent for PAAm networks with a low content of BAAm. It is interesting to remark that the data for neutral gels equilibrated with water−acetone mixtures (not shown in Figure 4) are consistent with a crossover between the good-solvent behavior and Θ-solvent behavior. Indeed, the least-square estimates of exponent *n* in eq 3 are approximately equal to 2.2, 2.4, and 2.8 (±0.2) for 20, 30, and 40 vol % of acetone respectively.

For ionic gels swollen in low-ionic-strength media, the agreement between the experimental data and the predictions of eq 3 is not very good. In this case, we do not draw a best-fit line through the data but compare the measured values of *G* with the calculated osmotic pressure. The contribution of osmotic pressure from polymer−solvent mixing can be neglected at high ionization degrees and low salt concentrations. Therefore, the osmotic pressure is found as the entropic pressure of dissociated counterions trapped in the gel volume

$$\pi_{osm} = RT\alpha c = (RT/V)\alpha Q^{-1} \qquad (4)$$

where *c* is the molar concentration of monomer units. The ionization degree α, defined as the fraction of charged monomer units, is taken consistent with the average degree of hydrolysis (0.15) of the gels. Considering the large variation in the results of titration, the agreement between the shear modulus and the osmotic

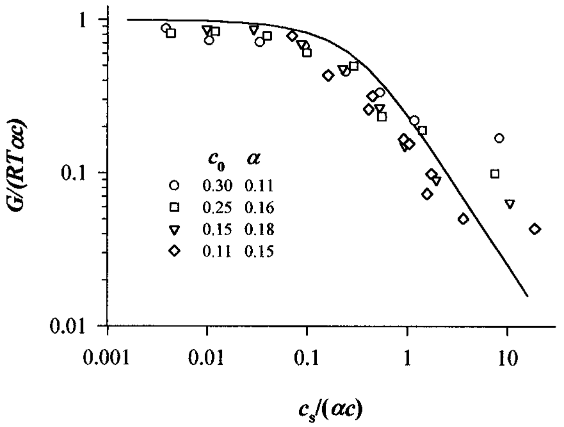

Figure 5. Reduced shear modulus $G/(RT\alpha c)$ and reduced osmotic pressure $\pi_{osm}/(RT\alpha c)$ (continuous line calculated by eq 5) as functions of reduced salt concentrations $c_s/(\alpha c)$. The total monomer concentrations used to prepare gels, c_0, and ionization degrees, α, are indicated in the plot area

pressure is satisfactory. Exception is the data point corresponding to the gel prepared with $c_0 = 0.05$. The deviation of this point may be attributed to a lower effective degree of ionization of this gel though the reason for such a low α is not fully understood. If this point is ignored, the data shown in Figure 4 seem to support the idea that the equality $G = \pi_{osm}$ determines the swelling equilibrium in the low-salt limit.

The effect of added salt on the dominant (ionic) part of osmotic pressure is described for weakly ionized acrylamide-based gels within the ideal-Donnan-equilibrium framework.[15] In this theory, the reduced osmotic pressure $\pi_{osm}/(RT\alpha c)$ is completely determined by the reduced salt concentration $\kappa \equiv c_s/(\alpha c)$

$$\pi_{osm}/(RTc) = \alpha\kappa(K_D + 1/K_D - 2) \tag{5}$$

where $K_D = 1/(2\kappa) + (1 + 1/(2\kappa)^2)^{1/2}$. This leads to the master curve shown in Figure 5. Here, we compare the calculated osmotic pressure and the measured shear modulus. These values are normalized to the value of $RT\alpha c$ and plotted against the reduced salt concentration in the log−log coordinates. It is expected that the modulus data points will be superimposed on the same curve for all ionic gels analyzed, if a linear relation between the modulus G and the elastic pressure π_{el} holds. We neglect the polymer contribution to osmotic pressure because it is small compared to that given by eq 5 as long as the salt concentration is not very high. Using $\alpha = 0.15$ and the Flory−Huggins theory[19] with a reasonable value for the polymer−solvent interaction parameter χ (0.48), our calculations show that the polymer contribution can be neglected when $c_s \leq 0.2$ M.

As is seen from Figure 5, the variation of $G/(RT\alpha c)$ is similar to that of $\pi_{osm}/(RT\alpha c)$ except in the range of the very high c_s (1 M, rightmost data points) where the polymer contribution to osmotic pressure cannot be neglected and the master curve representation is no longer valid. Outside this range, the reduced modulus is slightly lower than the reduced osmotic pressure and independent of c_0. In the low-salt limit, where $G/(RT\alpha c)$ and $\pi_{osm}/(RT\alpha c)$ tend toward constant values, G differs from π_{osm} by a factor $G/\pi_{osm} \approx 0.8$. At high c_s, this factor is about 0.7. The observed deviations can be caused by different reasons. First, eq 5 may be inexact as it does not consider the correlations between the free ions and the electric field of the charged chains. These correlations should reduce π_{osm}.[23] Second, an experimental error in titration or/and in the shear modulus can contribute to the deviations of the data points from the master curve.

The results shown in Figure 5 indicate that $G \cong \pi_{el}$ even in the range of non-Gaussian elasticity. However, there is no simple relation between G and π_{el} in the general case. In the classical theory,[19] $G = \pi_{el}$ when the so-called logarithmic term is neglected. This equality was verified experimentally for nonionic PAAm gels, i.e., in the low-swelling range.[7] At the same time, the difference between G and π_{el} should become significant when the network chains are strongly stretched. Our calculations based on the inverse Langevin function (see next section) show that the ratio G/π_{el} strongly increases when the end-to-end distance of a network chain tends to the chain contour length ($G/\pi_{el} \cong (G/G_G)^{1/2}$; G_G is the modulus for Gaussian networks).

The fair agreement between $G/(RT\alpha c)$ and $\pi_{osm}/(RT\alpha c)$ seen in the low-salt region in Figure 5 may be fortuitous. This is because the dissociation equilibrium of network acid groups is not taken into account and, hence, α used to calculate $G/(RT\alpha c)$ is overestimated. The actual ionization degree probably is not constant but decreases with lowering c_s as the salt cations are exchanged for H^+ ions in the gel volume. Due to this exchange, the hydrogen ion concentration inside the gel becomes much larger than the outer concentration,[24] and dissociation is suppressed. In light of this possibility, the shear modulus related to swelling equilibrium should be considered as an "effective" measure of the elastic pressure π_{el} and the osmotic pressure π_{osm}.

C. Description of Non-Gaussian Behavior. The description of highly stretched polymer chains via the inverse Langevin function[18,25] is well-known. Hasa et al.[26] used the power series expansion of this function to calculate the elastic modulus of a gel at high swelling degrees. Such an approach fails at strong stretching of network chains, and more general relations[9,27] were derived. The shear modulus measured at low deformations can be expressed by[9]

$$G = G_G(\beta/\gamma + \partial\beta/\partial\gamma)/6 \tag{6}$$

where G_G is the modulus in the weak stretching regime, β is the inverse Langevin function of γ ($\gamma = \coth\beta - 1/\beta$), and γ is the ratio of the stretched size r of a network strand to the contour length of the strand. The elasticity theory based on Gaussian statistics predicts[19]

$$G_G = ARTn_c\phi(r/r')^2 \tag{7}$$

where n_c is the concentration of elastically effective strands in the dry network, ϕ is the volume fraction of polymer in the gel, r and r' are the root-mean-square end-to-end distances of a network strand at the concentration ϕ and in its reference state. The prefactor A for a perfect tetrafunctional networks lies between the values of $^1/_2$ and 1 respectively predicted by the phantom[28] and affine[19] network models. The first of these limiting models assumes that network junctions fluctuate freely performing a Brownian motion about their mean positions while in the second model junction fluctuations are totally suppressed due to topological constraints.

To write the ratio of r/r' as a function of ϕ, we use the Obukhov et al. model.[12] Although this model is developed for nonionic gels, it allows the description of most of the effects observed in our experiments and has the advantage of simplicity. In this model, the stretched

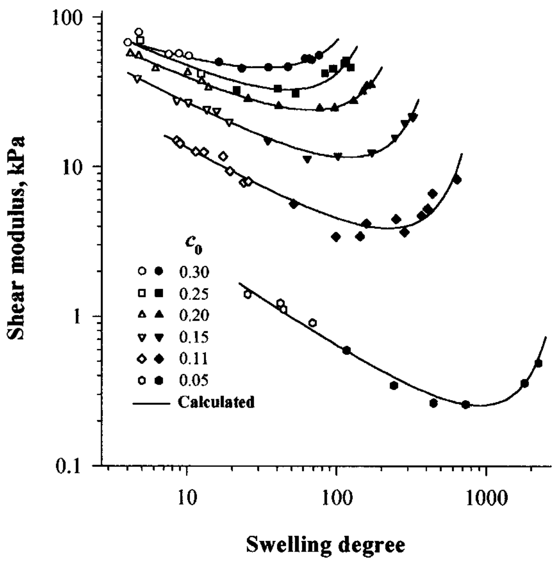

Figure 6. Shear modulus as a function of equilibrium swelling degree for neutral (open symbols) and ionic (filled symbols) gels prepared with varying total monomer concentration c_0. In each data series, c_0 and the network topology are kept constant while the solvent composition (acetone content or salt concentration) is varied. Continuous best-fit curves were generated by using eq 8 and parameters given in Table 1.

size of a network strand is $r = (\phi/\phi_0)^{-1/3}r_0$, where r_0 is the strand size in the preparation state. This assumes that strands expand on swelling affinely with the macroscopic gel. The scaling theory for semidilute solutions[22] is used to predict r_0 and r'. This assumes that the cross-linking does not perturb the free chain size and r' is identical to the free chain size in solution at concentration ϕ. Thus, eq 6 takes the form

$$G = G_0(\phi/\phi_0)^m(\beta/\gamma + \partial\beta/\partial\gamma)/6 \tag{8}$$

where ϕ_0 and G_0 relate to the preparation state. The exponent m lies between $^1/_3$ and $^7/_{12}$ depending on the solvent quality; in the Rubinstein et al. model,[13] the upper limit of m for ionic gels is as large as $^5/_6$. The value of G_0 is given by

$$G_0 = ARTn_c\phi_0 \tag{9}$$

To express the value of γ in terms of ϕ, we use the good-solvent prediction of the scaling theory[22] for the strand size in the preparation state

$$r_0 = aN^{1/2}\phi_0^{-1/8} \tag{10}$$

where N is the number of statistical units in the strand and a is the statistical unit length. This seems reasonable for PAAm hydrogels. Thus, the value of γ is written as

$$\gamma = N^{-1/2}\,\phi^{-1/3}\,\phi_0^{5/24} \tag{11}$$

A remark can be made with respect to the above model. Although eq 8 is true for both good solvent and Θ solvent, eqs 10 and 11 are valid only for good solvent. For this reason, the model is strictly consistent only when the exponent m in eq 8 is equal to $^7/_{12}$. In other cases, it should be considered as phenomenological.

In Figure 6 we compare the predictions of eq 8 with the experimental data for all neutral and ionized gels analyzed at swelling equilibrium. The curves shown here are fitted to the data by varying G_0, m and N as free parameters; a numerical method was used to compute the inverse Langevin function and its derivative. The observed $G(Q)$ variations quantitatively agree with the calculated curves. The best-fit values of the model parameters are also reasonable. In particular, the calculated values of G_0 are close to the observed ones (Table 1) considering the accuracy of measurements. The exponents m calculated by eq 8 are slightly higher than those discussed above especially at large c_0 (Figure 3). This might be expected since the finite extensibility of network chains slightly contributes to the shear modulus at medium swelling degrees.

Table 1. Parameters of Fits of Equation 8 to the Shear Modulus Data of Figure 6

c_0	G_0,[a] kPa	G_0, kPa	N	m
0.05	1.41	1.46	63.2	0.68
0.11	12.7	11.8	37.2	0.59
0.11	12.7	6.3[b]	37.7[b]	0.41[b]
0.15	28.0	27.1	28.9	0.54
0.20	45.4	44.8	24.9	0.47
0.25	70.1	58.2	21.2	0.48
0.30	67.9	63.1	22.6	0.33

[a] Measured values. [b] From the $G(Q)$ data for the salt-free gel (Figure 2c).

Two rows of the model parameters were obtained for gels prepared with $c_0 = 0.11$ (Table 1). The first row is related to the neutral gel and the ionic gel in brines while the second row refers to the salt-free ionic gel. The corresponding $G(Q)$ variations are shown in Figure 2c by circles and triangles respectively. As can be expected from the previous discussion, the values of G_0 and m for the salt-free ionic gel are lower than those for the neutral and brine-equilibrated ionic gels. This is consistent with the effect of electrostatic interactions on the modulus. At the same time, the values of N found from the two different $G(Q)$ variations are very close as one would expect for gels identical in the network topology.

The effect of ionization degree on N obtained by eq 8 is worth consideration. We have not made a systematic study on gels with different degrees of ionization. However, we applied eq 8 to the data[9] on gels prepared by copolymerizing acrylamide, acrylic acid, and BAAm. The value of N is found to increase from 37 to 47 as the acrylic acid content increases from 5 to 20 mol %. We also analyzed the data reported by Skouri et al.[14] on poly(acrylic acid) gels swollen to equilibrium in salt solutions. In this case, N is weakly sensitive to the network charge; it increases from 30 to 32 with the ionization degree rising from 0.1 to 0.2. The increase in N is caused by a shift of the modulus upturn to larger Q values. This shift is probably due to a change in free chain configuration upon ionization. It is qualitatively consistent with the prediction of the Rubinstein et al. model.[13] Anyhow, the effect of network charge on N is not very strong. Therefore N can be used as a measure of the average number of segments between junctions for networks close in the ionization degrees.

The results shown in Figure 6 indicate that eq 8 quantitatively describes the elastic behavior of ionic gels though it is derived for nonionic gels and does not include the dependence of the modulus on ionization degree and salt concentration. This agreement between theory and experiment may be caused by fortuitous compensation. As discussed above, the effect of added salt on modulus can be compensated by the finite extensibility of the network chains in some range of swelling degrees. For this reason, the parameter N

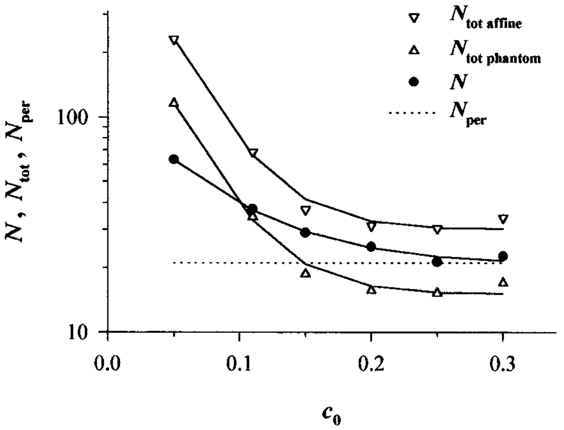

Figure 7. Number of statistical segments between junctions in networks prepared with different c_0: triangles, total number N_{tot} calculated from the initial modulus G_0 by eq 9 for phantom and affine (turned over triangles) models; filled circles, number of elastically effective segments N determined by eq 8; horizontal dotted line, N_{per} characterizing a perfect network with 0.46 mol % of tetrafunctional cross-linker units.

determined by eq 8 from the experimental $G(Q)$ variation should be considered as an "effective" characteristic of the network chain length. The correlation between this parameter, the cross-link density, and the number of elastically effective network chains is considered in the next section.

D. Characterization of Network Imperfections. Parameters of a perfect network can be calculated from the molar ratio of BAAm to acrylamide used to prepare the gels. In the perfect network, all the cross-linker molecules are incorporated in such a way that they connect elastically effective network strands. As the cross-linking reaction with BAAm leads to tetrafunctional cross-links, the number of network chains is just twice the number of cross-linker molecules. At the cross-link density used in this study (0.0046), the average number of monomer units between two consecutive cross-links is about 109. Taking $s = 5.2$ for the number of monomer units in the statistical segment,[29] we get the average number of statistical segments in the perfect network chain $N_{per} = 21$. It is worth noting that N_{per}, as well as N and the defined below N_{tot}, is considered as an average value because the polydispersity of strand lengths is inherent to networks (such as PAAm ones) prepared by radical copolymerization.

Actual PAAm networks are imperfect, and the perfect network parameters are merely a useful standard of comparison. As a next approximation, the network densities are estimated from the G_0 values by eq 9. The average total number of statistical segments per one elastically effective chain is calculated from the network density as $N_{tot} = 1/(n_c V s)$. In an imperfect network, each macromolecule connecting adjacent junctions is not linear but branched, and only a part of this molecule contributes to the elastic modulus. Therefore, the value of N_{tot} includes not only elastically effective segments but also those belonging to dangling chains and loops. On this basis, N_{tot} can be expected to be higher than N obtained from the modulus in the strong stretching regime. The value of N includes only elastically effective segments, and the fraction of such segments is evaluated as the ratio of N/N_{tot}.

In Figure 7 we compare the values of N and N_{tot} plotted as functions of the initial total monomer concentration c_0. The average number of segments in the perfect network chain N_{per} is also shown here. At low c_0, both N_{tot} and N are higher than N_{per} with N_{tot} larger than N. This is consistent with the idea of a significant fraction of cross-links wasted in network defects in these conditions.[5,6,8] As c_0 increases, N_{tot} and N decrease. Hence, the efficiency of cross-linking rises, and more perfect networks are formed. At $c_0 \sim 0.2$, N_{tot} and N become independent of c_0 with N close to N_{per} and N_{tot} only somewhat different from N_{per}. This suggests that the networks prepared with $c_0 > 0.2$ have an insignificant fraction of elastically ineffective units and a considerably higher density of cross-links than trapped entanglements. In fact, these networks can be considered as "effective" perfect networks. As is seen from Figure 7, N_{per} is between the low limits of N_{tot} calculated with the phantom[28] and affine[19] network models. This result related to gels in the preparation state seems to show that the topological interactions (constraints) have some effect on cross-link fluctuations and gel elasticity.

The data presented in Figure 7 indicate that interchain trapped entanglements play a minor role in the elastic behavior of the gels in this study. Opposite results were reported for similar gels, consistent with the concept of rising entanglement density with increasing c_0.[3,8] However, one has to bear in mind that the effect of trapped entanglements should be more pronounced for weaker cross-linked networks prepared with higher c_0. In this connection it is interesting to compare the values of N and N_{tot} with the length of an entanglement strand at the preparation concentration c_0. This length can be estimated from the viscosity data for solutions of linear PAAm.[29] As is seen from Figure 35 of ref 29, the zero shear specific viscosity plotted against the reduced polymer concentration $c[\eta]$ (where $[\eta]$ is the intrinsic viscosity) shows a typical crossover between two power laws. The intersection of these two laws corresponds to the entanglement onset of PAAm chains in solution. It takes place at $c[\eta] \cong 6.6$. Using this result and the molecular weight dependence of intrinsic viscosity,[29] $[\eta] = 6.31\times10^{-3}M^{0.8}$, the number of segments in an entanglement strand is found as $N_e \cong 16c^{-1.25}$. This leads to $N_e \approx 72$ for the maximum preparation concentration used in our experiments ($c_0 = c = 0.3$). Clearly, this value of N_e is considerably higher than the observed low limits of N or N_{tot}. Thus we confirm that interchain trapped entanglements have no effect on elasticity of analyzed gels even at large c_0.

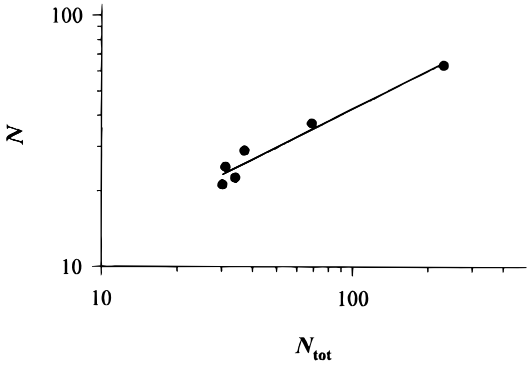

Figure 8. Number of segments in an interjunction chain as a function of total number of segments related to the chain for acrylamide-based gels prepared with different c_0. Unlike N, N_{tot} includes dangling chains and loops. The best-fit line has a slope of 0.51.

Figure 8 shows the correlation between N and N_{tot} in the log−log representation. This correlation is independent of entanglement density because N and N_{tot}

vary in the same proportion or remain unchanged (if the cross-link density is high enough) as the entanglement density changes. The data shown in Figure 8 are reasonably fitted by a straight line with the slope close to 0.5 (0.51 ± 0.05). This provides some new information on the architecture of PAAm networks. Indeed, the observed $N \sim N_{tot}^{1/2}$ variation can be compared to the following theoretical relation derived for an ideal random-branched macromolecule without loops:[30]

$$N \sim N_{tot}^{1/2} n^{1/2} \qquad (12)$$

Here, N is the average number of statistical segments between arbitrary ends of the molecule, N_{tot} is the total number of segments in the molecule, and n is the average number of segments between branch points. For the network analyzed, the value of n, inversely proportional to the cross-link density, is constant. Therefore, the observed $N \sim N_{tot}^{1/2}$ relation coincides with relation 12. This coincidence implies an analogy in architecture between the network "chains" and random-branched macromolecules without loops. This analogy confirms that PAAm networks contain a large amount of elastically ineffective segments, especially at low c_0. Also, it is consistent with the concept of an insignificant fraction of intramolecular cyclization (loops) in networks prepared with low cross-linker concentrations.[31]

Conclusion

We have studied the shear modulus as a function of the swelling degree for acrylamide-based hydrogels prepared by radical copolymerization with total monomer concentration c_0 ranging from 5 to 30 wt % and cross-link density fixed at 0.46 mol %. To attain high swelling degrees, a small amount of ions was fixed to a polymer network by hydrolysis that leaves the network topology unchanged. The results reported in this paper illustrate the effect of c_0 on the elastic properties and the network topology of neutral and ionic gels.

The shear modulus plotted against the swelling degree demonstrates a typical crossover from a power law decrease at low swelling ratios ($Q/Q_0 < 7$) to an abrupt upturn caused by stretching of network chains above Gaussian limit. We observe a new feature: the decrease in modulus becomes weaker when the concentration of preparation c_0 is higher. The modulus decreases with ionization degree; however, at high salt concentrations ionic gels follow the power law behavior of neutral gels. The exponent of this law, common for an ionic gel swollen in brine and the corresponding neutral gel, is higher than the exponent for the salt-free ionic gel. The effects of added salt and network charge support the idea that the electrostatic interactions affect the reference state used to determine the elastic part of the gel free energy.[13]

The modulus of ionic gels measured at swelling equilibrium is only slightly lower than the osmotic pressure of mobile ions calculated within the ideal Donnan framework. The observed deviation can be attributed to the presence of the osmotic coefficient associated with the correlation between the free ions and the charged polymer. Anyhow, the modulus provides an "effective" measure of the elastic and osmotic pressures. Further experiments involving networks with the strong electrolyte groups (having a larger dissociation constant) are needed to better understand the relation between G and π_{el} at high stretching of network chains.

The upturn in the modulus related to non-Gaussian elasticity of chains is quantitatively described using the inverse Langevin function, which allows evaluation of an average length of network chains. This length is related to the number of elastically effective segments between adjacent junctions regardless of whether these are trapped entanglements or chemical cross-links. At low c_0, the number of elastically effective segments N is considerably lower than N_{tot}, the total number of segments in a macromolecule between junctions, determined from the modulus of gel at preparation. Thus we conclude that the networks prepared with low c_0 contain a large amount of elastically ineffective segments. The correlation between N and N_{tot} shows that the network "chains" have architecture typical of an ideal random-branched macromolecule without loops. At large c_0, N, and N_{tot} become independent of c_0 and close to N_{per}, the number of segments in a perfect network chain, calculated from the cross-link concentration used in gelation. This suggests that the density of trapped entanglements is lower than the density of chemical cross-links in the gels under study. The entanglement strand length estimated from the viscosity of PAAm solutions[29] confirms this conclusion.

One further remark should be made, concerning the heterogeneity of gels. Several studies have shown that PAAm gels are very heterogeneous and can be considered as a medium in which dense and more dilute regions coexist.[6,14,32] However, the structure and properties of these gels depend on the cross-link density. The elastic properties of weakly cross-linked gels seem consistent with the theoretical predictions made for homogeneous networks. Significant changes in the physical properties and structure of PAAm gels occur only at cross-link densities higher than 2.5 mol % (BAAm/all monomers). It appears that the results of the present study related to networks with low BAAm content of 0.46 mol % support a simple picture of homogeneous structure of weakly cross-linked PAAm gels.

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