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Charge density dependence of elastic modulus of strong polyelectrolyte hydrogels

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Abstract

The mechanical behavior of a series of strong polyelectrolyte hydrogels based on acrylamide and 2-acrylamido-2-methylpropane sulfonic acid sodium salt (AMPS) was investigated. The hydrogels were prepared at a fixed crosslinker ratio and monomer concentration, but at various charge densities, i.e. AMPS contents between 0 and 100 mol%. The elastic modulus of the hydrogels after their preparation first increases with increasing charge density but then decreases continuously. Investigation of the swollen state properties of the hydrogels shows existence of a large number of ionic groups inside the gel that are ineffective in gel swelling. The results indicate two opposite effects of charged groups on the elastic modulus of the hydrogels: formation of multiplets acting as additional crosslinks in the gel increases the elastic modulus of ionic hydrogels, whereas the effect of the electrostatic interaction of charged groups on elastic free energy decreases the modulus.

Keywords: Acrylamide; 2-Acrylamido-2-methylpropane sulfonic acid sodium salt; Elastic modulus

1. Introduction

In recent years, hydrogels derived from acrylamide (AAm) have received considerable attention for use as specific sorbents and as support carriers in biomedical engineering. AAm-based hydrogels are prepared mainly by free-radical crosslinking copolymerization of AAm monomer with *N*,*N*′-methylenebis(acrylamide) (BAAm) crosslinker. In order to increase their swelling capacity, an ionic comonomer is also included in the monomer mixture. Several studies have been reported on the properties of hydrogels as a function of their ionic group content [1–5]. Increasing number of ionic groups in the hydrogels is known to increase their swelling capacity. This is mainly due to the simultaneous increase of the number of counterions inside the gel, which produces an additional osmotic pressure that swells the gel [2]. The degree of gel swelling is, however, not a monotonically increasing function of the ionic group content of the hydrogels. It first increases with increasing ionic group concentration but then levels off after passing a critical concentration due to the finite extensibility of the network chains and due to the ion pair formation [6–8].

Our purpose of the present study is to measure the elastic properties of a series of hydrogels that are identical except for their ionic group contents. For this investigation, we selected 2-acrylamido-2-methylpropane sulfonic acid sodium salt (AMPS) as the ionic comonomer of AAm. AMPS received attention in recent years due to its strongly ionizable sulfonate group [6–10]; AMPS dissociates completely in the overall pH range, and therefore, the hydrogels derived from AMPS exhibit pH independent swelling behavior.

As will be shown later, elastic modulus of AAm–AMPS-based hydrogels varies depending on their ionic group contents. This is unexpected because both the polymer concentration and the chemical crosslink density of the hydrogels subjected to mechanical measurements were the same. The results are explained with the formation of multiplets in the gel acting as additional crosslink points and with the effect of the electrostatic interaction of charged groups on the elastic free energy.

2. Experimental

2.1. Materials

The sources of water, the monomers AAm and AMPS,

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the crosslinker BAAm, and the initiator potassium persulfate (KPS) were given before, as was also the mode of their purifications [6].

2.2. Synthesis of hydrogels

The hydrogels with a fixed chemical crosslink density but with various charge densities were prepared in the form of rods of 4 mm diameters. The crosslinking copolymerization was carried out in water at 40 °C in the presence of 0.474 mM KPS as the initiator. The reaction time was one day. The molar ratio of the monomers (AAm + AMPS) to the crosslinker BAAm was fixed at 82 throughout the study. The total monomer concentration was also fixed at 0.70 M, while the mole fraction of the ionic comonomer AMPS in the monomer mixture x_i varied between 0 and 1. Polymerization procedures have been given in detail previously [6]. The formation conditions of the hydrogels prepared in aqueous 0.2 M NaCl solutions instead of water were identical to those given earlier, except that the reaction time was increased to two weeks due to the low rates of reactions in the presence of NaCl. Both the gel fraction and the monomer conversion after given reaction times were found to be larger than 0.98 for all gel samples reported here.

2.3. Swelling measurements in water

The hydrogels in the form of rods of 4 mm in diameter were cut into samples of about 10 mm length. Then, each sample was placed in an excess of water at room temperature (19 ± 1 °C). In order to reach the equilibrium degree of swelling, the hydrogels were immersed in water for at least two weeks during which water was replaced every other day; the swelling equilibrium was tested by measuring their diameters. 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_r (volume of swollen gel/volume of the gel just after preparation) was determined by measuring the diameter of the hydrogel samples by a calibrated digital compass. V_r was calculated as

$$V_r = \left(\frac{D}{D_0}\right)^3 \tag{1}$$

where D and D_0 are the diameter of hydrogels after equilibrium swelling in water and after synthesis, respectively. Equilibrium volume swelling ratio q_v (volume of swollen gel/volume of dry gel) was calculated as

$$q_v = \frac{V_r}{v_2^0} \tag{2}$$

where v_2^0 is the volume fraction of crosslinked polymer after the gel preparation. Since both the fractional monomer conversion and the gel fraction are close to unity, v_2^0 was calculated from the initial molar concentration of monomers C_0 (0.70 M) as

$$v_2^0 = 10^{-3} C_0 \bar{V}_r \tag{3}$$

where $\bar{V}_r$ is the average molar volume of polymer repeat units, i.e. [6]

$$\bar{V}_r = 52.6 + 117x_i \tag{4}$$

2.4. Mechanical measurements

Uniaxial compression measurements were performed on equilibrium swollen gels in water as well as on gels after their preparation. All the mechanical measurements were conducted in a thermostated room of 21 ± 0.1 °C. The stress–strain isotherms were measured by using an apparatus described before [11]. The elastic modulus G was determined from the slope of linear dependence

$$f = G(\alpha - \alpha^{-2}) \tag{5}$$

where f is the force acting per unit cross-sectional area of the undeformed gel specimen and α is the deformation ratio (deformed length/initial length). Typical stress–strain data correlated according to Eq. (5) are shown in Fig. 1 for hydrogel samples of various ionic comonomer (AMPS) contents.

For a homogeneous network of Gaussian chains, elastic modulus of gels swollen to equilibrium G relates to the network crosslink density through the equation [2,12]

$$G = A\frac{\rho}{\bar{M}_c} RT (v_2^0)^{2/3} (v_2)^{1/3} \tag{6}$$

where ρ is the polymer density, $\bar{M}_c$ the molecular weight of the network chains, v_2 the volume fraction of crosslinked polymer in equilibrium swollen gel, i.e. $v_2 = 1/q_v$, R and T are in their usual meanings. The front factor A equals to one for an affine network and $1 - 2/\phi$ for a phantom network, where ϕ is the functionality of the crosslinks. Since $v_2 = v_2^0$ for the hydrogels just after preparation, the modulus after preparation state G_0 becomes:

$$G_0 = A\frac{\rho}{\bar{M}_c} RT v_2^0 \tag{7}$$

From Eqs. (2), (6) and (7), the reduced modulus G_r defined as the ratio of the elastic modulus of the equilibrium swollen gel to that of the same gel after its preparation is given by the following equation:

$$G_r = \frac{G}{G_0} = \left(\frac{v_2}{v_2^0}\right)^{1/3} = V_r^{-1/3} \tag{8}$$

3. Results and discussion

Fig. 1 shows the variation of stress (compression) with strain for the hydrogels just after their preparation. The mole fractions of the ionic comonomer AMPS in the monomer mixture (x_i) are indicated in the figure. Although both the

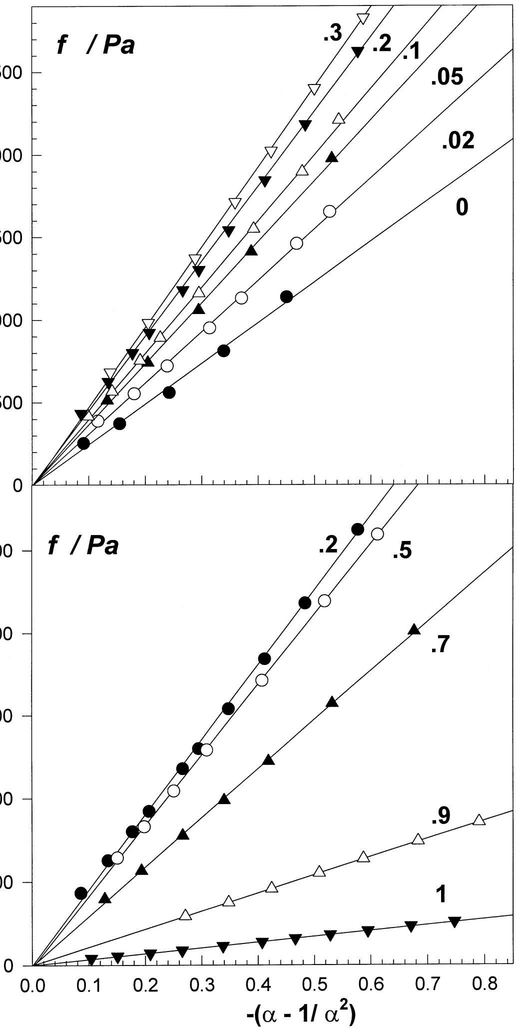

Fig. 1. Typical stress–strain data for AAm–AMPS-based hydrogels just after their preparation. The mole fraction of AMPS in the monomer mixture x_i is indicated in the figure.

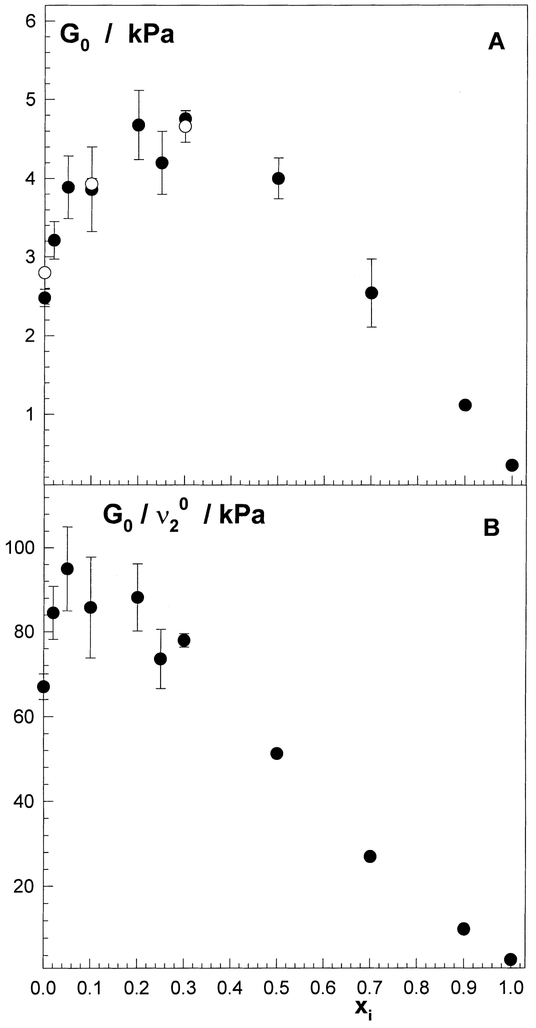

Fig. 2. Variations of the elastic modulus after the gel preparation G_0 (A) and G_0/v_2^0 (B) with the mole fraction of AMPS in the monomer mixture x_i. Filled symbols represent data for hydrogels prepared in water. Open symbols represent data for hydrogels prepared in 0.2 M NaCl solutions in order to screen the electrostatic interactions in polymer coils.

polymer concentration and the chemical crosslink density of the hydrogels are the same, the slope of stress–strain isotherms varies depending on the charge density of the hydrogels. In Fig. 2A, the slope of the isotherms, i.e. the elastic modulus of the hydrogels after their preparation G_0 is plotted against the mole fraction of AMPS x_i. Each data point in Fig. 2 is an average of three measurements carried out on samples taken from the same gel. G_0 changes depending on the charge density of the network x_i. G_0 first increases with x_i, reaching its maximum at $x_i = 0.2$–0.3, then decreases continuously. Results similar to those of Fig. 2A have been reported by Tong and Liu for *N,N'*-dimethylacrylamide-AMPS hydrogels [9]. Ilavsky and coworkers investigated the elastic properties of a series of hydrogels with various types of ionic comonomers over the range of x_i between 0 and 0.2 [13,14]. Their data indicate an increase in G_0 with increasing charge density of the network. In contrast, Schosseler [15], Skouri [5], and Takahashi [16] reported that, at a fixed crosslinker ratio, G_0 of poly(acrylic acid) gels monotonically decreases with an increase in charge density.

To explain the charge density dependence of G_0 shown in Fig. 2A, one has to first consider a possible variation of the dilution degree of the network after the gel preparation. Although the initial monomer concentration C_0 was fixed in our experiments ($C_0 = 0.70$ M), the volume concentration v_2^0 changes due to the different molar volumes of the monomers AAm and AMPS. For example, calculations using Eqs. (3) and (4) show that, with an increase of x_i from 0 to 0.2, v_2^0 increases from 0.037 to 0.053. According to Eq. (7), this will increase the modulus of the ionic hydrogels. In order to eliminate this effect, the ratio G_0/v_2^0 was calculated, which only depends on the effective crosslink density of the network (Eq. (7)). G_0/v_2^0 versus x_i data illustrated in Fig. 2B show, however, the same type of dependence as in Fig. 2A, except the maximum is shifted to $x_i \cong 0.05$.

Thus, the shape of the dependence of G_0 on x_i is real and, according to Eq. (7), this dependence originates from the variation of the effective crosslink density of the network depending on its charge density. The effective crosslink densities of the networks in terms of $\bar{M}_c$, calculated from the elastic modulus data together with Eq. (7), are shown in Fig. 3 as a function of x_i. The filled and open symbols are calculation results for phantom ($\phi = 4$) and affine network models, respectively. For the non-ionic gel ($x_i = 0$), $\bar{M}_c$ equals to 24 500 and 49 100 g mol^{-1} for phantom and affine network models, respectively, compared to the value of 2880 g mol^{-1}, calculated from the molar ratio of the monomers to the crosslinker used in the gel synthesis (82) and assuming that the gel is free of defects. From the difference between the experimental and theoretical $\bar{M}_c$ values, one may calculate that only one BAAm unit is involved in an effective crosslink out of 9–17 BAAm units, i.e. about 90% of crosslinker molecules used in the hydrogel synthesis are wasted, probably due to the cyclization and multiple crosslinking reactions. Previously, the fraction of wasted BAAm units in PAAm gels was reported to be as 80% using the determination of pendant vinyl group conversions [17]. This value was calculated as 95% from the swelling measurements [18]. Thus, previous analytical and swelling measurements together with the present mechanical measurements show that at least 80% of BAAm present in the feed are involved in ineffective crosslinks in non-ionic PAAm hydrogels.

Interestingly, addition of the ionic comonomer AMPS in the feed up to 5% ($x_i = 0.05$) decreases the molecular weight of the network chains $\bar{M}_c$, i.e. increases the crosslink density of the hydrogel (Fig. 3). Further increase in the ionic comonomer content, however, monotonically decreases the crosslink densities.

Sedlakova et al. proposed that the charge density dependence of elastic modulus originates from the variation of the extent of cyclization reactions depending on the charge density of the polymer coil [14]. According to this approach, as the charge density of the polymer increases, the growing chains in the pregel regime will assume an extended conformation. This will result in a decrease of cycle formation reactions due to the thermodynamic excluded volume effect and therefore will increase the effective crosslink density of the final hydrogel [14]. If this hypothesis is correct, addition of salt in the gel forming system should decrease the modulus of the ionic hydrogels and, after complete neutralization, the gels should recover the modulus of the non-ionic gel. In order to check this point, we prepared hydrogels in 0.2 M NaCl solutions instead of water in order to screen the electrostatic interactions in polymer coils. The elastic moduli G_0 of these gels are also shown in Fig. 2A as open symbols. It is seen that G_0 still increases with x_i, indicating that the charge density dependence of G_0 is not due to the alteration of cyclization reactions.

One possible explanation for the variation of G_0 with x_i is related to the contribution of electrostatic interaction of charged groups to the elastic free energy of ionic gels [9]. Theoretically, increasing charge density should monotonically decrease the elastic modulus of the gels, which is indeed observed for $x_i > 0.05$ (Fig. 2B). However, the initial increase of the modulus with x_i cannot be explained using the theory. In order to clarify this point, in the following paragraphs, effective charge density of the hydrogels was calculated from their swollen state properties.

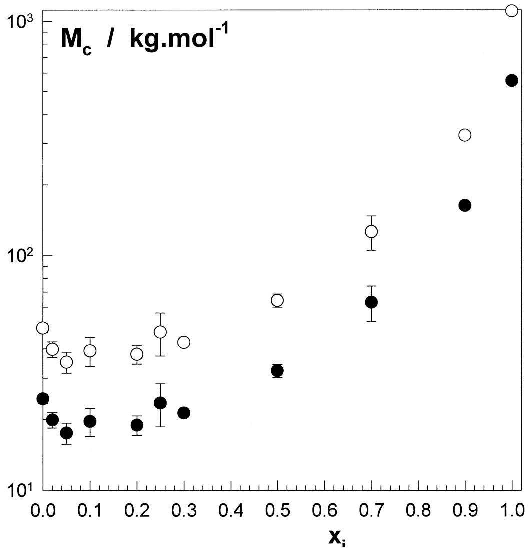

Fig. 3. The effective crosslink densities of the networks in terms of $\bar{M}_c$ calculated from the elastic moduli of the hydrogels shown as a function of the mole fraction of AMPS in the monomer mixture x_i. The filled and open symbols are calculation results for phantom ($\phi = 4$) and affine network models, respectively.

In Fig. 4, the swelling ratio q_v and the modulus G of the hydrogels swollen to equilibrium in water are shown as a function of the mole fraction of AMPS x_i. In Fig. 5, the reduced modulus G_r is plotted against the normalized gel volume V_r. For Gaussian chains, the slope of G_r versus V_r plot equals to $-1/3$ (Eq. (8)), which is represented in the figure by the dotted curve. Depending on the value of x_i, three different regimes can be seen from Figs. 4 and 5:

1. With increasing x_i from 0 to 0.05, the swelling ratio q_v increases and the modulus G decreases. The slope of G_r versus V_r plot is close to the theoretical value of $-1/3$, indicating that the hydrogels prepared in this regime behave Gaussian.
2. Over the range of x_i from 0.05 to 0.50, the swelling ratio q_v remains constant at about 600 while the modulus rapidly increases. The reduced modulus G_r also increases rapidly with increasing x_i at a fixed swelling ratio. This behavior is an indication of the limited extensibility of the network chains. The increase of the elastic modulus of the hydrogels in this regime is connected with the high stretching of the network chains. Indeed, $q_v = 600$ indicates that the network chains are about eightfold extended conformation than those in dry state.

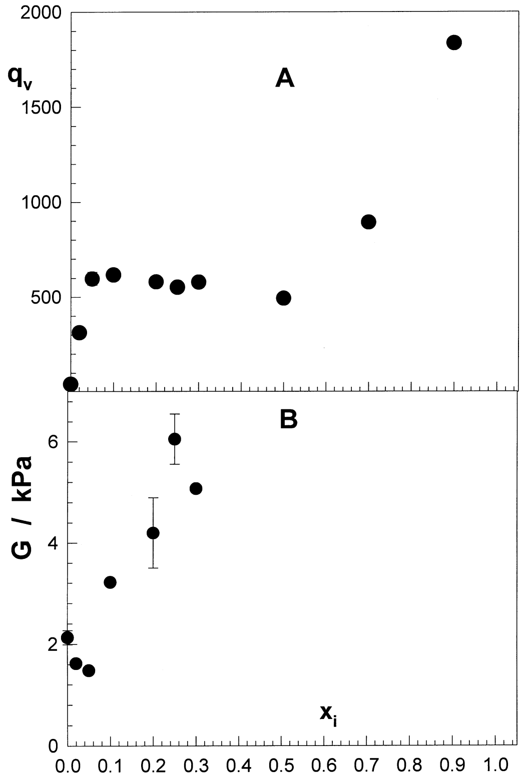

Fig. 4. The swelling ratio q_v and the modulus G of the hydrogels swollen to equilibrium in water shown as a function of the mole fraction of AMPS x_i.

3. For $x_i > 0.05$, the swelling ratio again increases with the charge density of the network. The hydrogels in this regime were too weak to withstand the mechanical measurements; therefore, no elasticity data are available for these equilibrium swollen hydrogels.

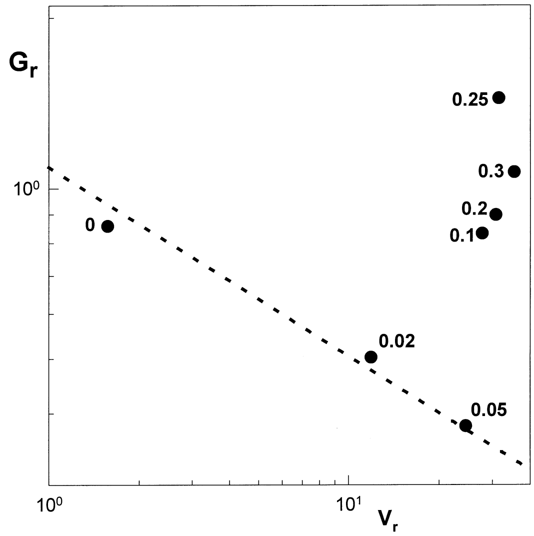

Fig. 5. The reduced modulus G_r shown as a function of the normalized gel volume V_r. The dotted curve represents the slope $-1/3$ predicted for Gaussian chains. The mole fractions of AMPS in the monomer mixture x_i are indicated in the figure.

In the following, the swollen state properties of the hydrogels were analyzed using the Flory–Rehner theory of swelling equilibrium. According to the theory, the osmotic pressure π of a gel is the sum of three contributions [2]

$$\pi = \pi_{\mathrm{mix}} + \pi_{\mathrm{el}} + \pi_{\mathrm{ion}} \tag{9a}$$

where π_{mix}, π_{el}, and π_{ion} are the osmotic pressures due to polymer–solvent mixing, due to deformation of network chains to a more elongated state, and due to the non-uniform distribution of mobile counterions between the gel and the solution, respectively. According to the Flory–Huggins theory, π_{mix} is given by [2]

$$\pi_{\mathrm{mix}} = -\frac{RT}{V_1}(\ln(1 - v_2) + v_2 + \chi v_2^2) \tag{9b}$$

where χ is the polymer–solvent interaction parameter and V_1 is the molar volume of solvent. To describe the elastic contribution π_{el}, we will use the phantom network model for tetrafunctional networks [2]:

$$\pi_{\mathrm{el}} = -RT\frac{\rho}{2\bar{M}_{\mathrm{c}}}(v_2)^{1/3}(v_2^0)^{2/3} \tag{9c}$$

Ionic contribution π_{ion} to the swelling pressure is caused due to the counterions (Na^+ ions of AMPS units) inside the gel. When the gel is immersed in water, Na^+ ions cannot escape outside the gel due to the condition of electroneutrality. As a result, the concentration difference of Na^+ between the gel and the outer solution (water) creates this additional osmotic pressure [2]

$$\pi_{\mathrm{ion}} = CRT \tag{9d}$$

where C is the counterion concentration in the swollen gel which is equal to

$$C = \frac{f_i}{V_1}v_2 \tag{9e}$$

where f_i is the effective charge density, i.e. the mole fraction of the charged units in the network chains that are effective in gel swelling.

Substitution of Eqs. (9b)–(9e) into Eq. (9a) and since the osmotic pressure π equals to zero at swelling equilibrium, one obtains the following equation for equilibrium swollen gels:

$$\ln(1 - v_2) + v_2 + \chi v_2^2 + \frac{\rho}{2\bar{M}_{\mathrm{c}}}V_1(v_2)^{1/3}(v_2^0)^{2/3} - f_i v_2 = 0 \tag{10}$$

For the solution of Eq. (10) for the effective charge density f_i of the hydrogels, the values used were $\rho = 1.35\ \mathrm{g\ cm^{-3}}$, $V_1 = 18\ \mathrm{g\ ml^{-1}}$. v_2^0 was calculated using Eqs. (3) and (4). Both v_2 $(= 1/q_v)$ and $\bar{M}_{\mathrm{c}}$ are also known from the swelling and elasticity measurements, respectively. The remaining parameter χ was evaluated as follows: Since $f_i = 0$ for the non-ionic gel, substitution $v_2 = 1/42.4$ and $\bar{M}_{\mathrm{c}} = 24\,500 \pm 1100\ \mathrm{g\ mol^{-1}}$ into Eq. (10) gives the interaction parameter as $\chi = 0.480 \pm 0.002$. This value of χ is in good agreement with the reported value of 0.48 by Prausnitz and coworkers [19]. Moreover, respective calculations using the affine network model leads to $\chi = 0.490 \pm 0.001$. In the following calculations, χ was held constant at 0.480. The use of a single χ parameter for all the hydrogels also requires some comments. First, it is to be noted that χ is independent of the number of charges on the network chains, since this effect is included in Eq. (9d). Second, increasing AMPS content in the hydrogels from 0 to 100 mol% changes the chemical structure of the network chains, which may alter the value of the χ parameter. In our previous work, we calculated χ parameter of AAm–AMPS hydrogels of various compositions using swelling measurements in concentrated NaCl solutions, in which each network chain behaves more like an uncharged polymer [6]. Calculations gave a constant value for χ indicating that χ does not change with the AMPS content of the hydrogels.

After finding the χ parameter for the present system, the effective charge density f_i can now be evaluated using Eq. (10) together with the experimental swelling and elasticity data of the hydrogels. The calculation results are collected in Fig. 6 as the dependence of the effective charge density f_i plotted as a function of the mole fraction of AMPS x_i. If one assumes that all the AMPS units are effective in gel swelling, the chemical charge density f_{chem} can be calculated from x_i as

$$f_{\text{chem}} = x_i \frac{V_1}{\bar{V}_{\text{r}}} \tag{11}$$

which is also shown in Fig. 6 as the dotted curve.

It is seen that the effective charge density f_i increases with x_i up to 0.05 then remains constant. Thus, additional AMPS units above $x_i = 0.05$ does not lead to the increase of the effective charge density of the chains. Moreover, f_i is always less than f_{chem} indicating that all the counterions inside the gel are not effective in the gel swelling. Even in the first regime ($x_i < 0.05$) in which the network chains behave Gaussian (Fig. 5), only a small portion of the counterions inside the ionic gel contributes to the gel swelling while this value further decreases as the AMPS content increases and becomes nearly constant between $x_i = 0.05$ and 0.30. Thus, a large fraction of counterions in the gel is ineffective in the swelling process. Recent experimental and theoretical results also indicate the existence of 'osmotically passive' counterions inside the swollen gels, which do not contribute to the swelling process [6,7,20,21]. A possible explanation is the hydrophobic interactions between the alkyl groups of the AMPS units leading to the formation of aggregates; the counterions in these aggregates may condense and lead to a decrease in the osmotic pressure. Gel heterogeneities may also be responsible for the condensation of counterions. The counterions in the highly crosslinked (less swollen) regions of the gel may condense on the network chains and become passive in the gel swelling.

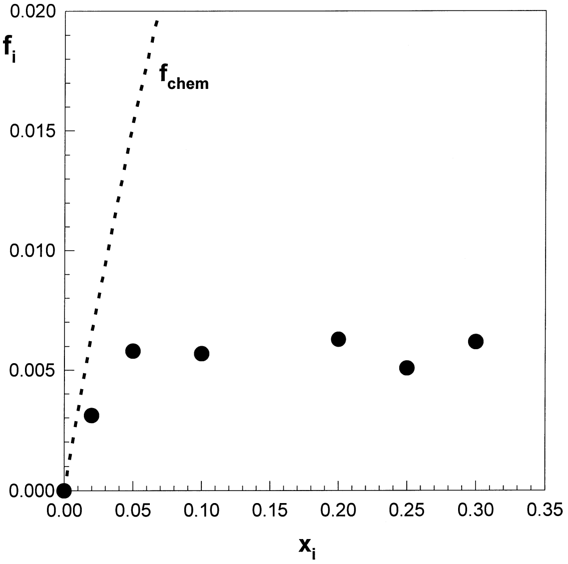

Fig. 6. The dependence of the effective charge density f_i on the mole fraction of AMPS x_i. The chemical charge densities f_{chem} are shown as the dotted curve.

From these findings, we propose that the initial increase of the modulus G_0 with increasing charge density between $x_i = 0$ and 0.05 shown in Fig. 2B is connected with the condensation of counterions to ion pairs. Ion pairs attract each other due to dipole–dipole interactions and form multiplets [21]. After the gel preparation, the concentration of polymer inside the gel is high enough to make formation of multiplets more favorable. Multiplets act as additional (physical) crosslinks in the hydrogel and thus contribute to the elastic modulus by increasing the effective crosslink density of the network.

Moreover, the decrease of modulus at higher ionic group content is connected with the contribution of electrostatic interactions to the conformational change of the network chains. Theories show that this contribution is always negative [9], i.e. the modulus should decrease continuously with increasing charge density. Moreover, calculations show that the higher the flexibility of the network chains, the steeper is the decrease of the modulus G_0 with the charge density. For the flexible acrylic acid units, the effect of the electrostatic interactions on the modulus dominates over the entire range of x_i so that G_0 monotonically decreases with increasing charge density, as was observed by Candau and coworkers [5,15]. However, for ionic units bearing 4–16 carbon atoms used by Ilavsky et al. [13], or for AMPS units of the present work, this effect is small at low charge densities compared to the effect of multiplet formation. As a result, modulus increases with increasing charge density below $x_i = 0.05$.

4. Conclusions

A series of AAm–AMPS-based hydrogels was prepared at a fixed crosslinker ratio and monomer concentration, but at various charge densities, i.e. AMPS contents between 0 and 100 mol%. The elastic modulus of the hydrogels after their preparation first increases with increasing charge density but then decreases continuously. Investigation of the swollen state properties of the hydrogels shows existence of a large number of ionic groups inside the gel, which are ineffective in gel swelling. The results indicate two opposite effects of charged groups on the elastic modulus of the hydrogels: Formation of multiplets acting as additional crosslinks in the gel increases the elastic modulus of ionic hydrogels, whereas the effect of the electrostatic interaction of charged groups on elastic free energy decreases the modulus.

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