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Effect of spatial gel inhomogeneity on the elastic modulus of strong polyelectrolyte hydrogels

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Summary

The effect of spatial inhomogeneity on the elastic modulus of ionic poly(acrylamide) (PAAm) hydrogels has been investigated with the static light scattering measurements. The gels were prepared by free-radical crosslinking copolymerization of acrylamide and 2-acrylamido-2-methylpropane sulfonic acid sodium salt (AMPS) monomers and N,N'-methylenebis(acrylamide) crosslinker. The crosslinker concentration of the hydrogels was fixed in our experiments while the mole fraction of AMPS in the comonomer feed (x_i) was varied over a wide range. Elasticity measurements show that the modulus of elasticity of gels increases with increasing x_i from 0 to 0.2. The excess scattering of gels, that is, the degree of spatial gel inhomogeneity rapidly decreases with increasing x_i and approaches to zero at $x_i = 0.05$. Debye-Bueche analysis of the light scattering data indicates frozen concentration fluctuations in gel; the size of the static structures increases while the extent of concentration fluctuations reduces with increasing x_i. It was shown that the macroscopic elastic properties of PAAm gels are mainly controlled by the microscopic gel structure determined by the scattering measurements.

Introduction

Hydrogels derived from acrylamide (AAm) have received considerable attention for use as specific sorbents and as support carriers in biomedical engineering. Poly(acrylamide) (PAAm) 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. 2-acrylamido-2-methylpropane sulfonic acid sodium salt (AMPS), as the ionic comonomer of AAm, was received attention in the last years due to its strongly ionizable sulfonate group; AMPS dissociates completely in the overall pH range, and therefore, the hydrogels derived from AMPS exhibit pH independent swelling behavior [1].

Several studies have been reported on the elastic properties of hydrogels as a function of their ionic group content [2-4]. It was shown that the modulus of elasticity of ionic PAAm hydrogels changes depending on the charge density of the network. At a fixed crosslinker concentration, the modulus first increases with increasing mole fraction x_i

of the ionic comonomer but then, decreases again after passing a critical concentration [5]. Similar results were reported by Tong and Liu for N,N'-dimethylacrylamide-AMPS hydrogels [6]. Ilavsky and co-workers 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 [7,8]. Their data also indicate an increase of modulus with increasing charge density of the network.

One possible explanation for the variation of the elastic modulus with the mole fraction of the ionic comonomer x_i is related to the contribution of electrostatic interaction of charged groups to the elastic free energy of ionic gels [2,3,6]. Theoretically, increasing charge density should monotonically decrease the elastic modulus of gels, which is indeed observed at large values of x_i. However, the initial increase of the modulus with x_i cannot be explained using the theory. 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 [8]. According to this approach, as the charge density of the polymer increases, the growing chains in the pre-gel 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. According to this hypothesis, addition of salt in the gel forming system should recover the modulus of the non-ionic gel since the electrostatic interactions in polymer coils are screened in the presence of salts. However, our measurements on ionic PAAm gels prepared in the presence of salts show that the modulus still increases with the charge density of the network chains [5]. Another explanation is connected with the condensation of counterions to ion pairs [5,9]. Ion pairs attract each other due to dipole-dipole interactions and form multiplets. After the gel preparation state, 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 [9].

Skouri et al proposed an alternate explanation for the effect of the charge density on the elastic modulus of gels [10]. Since real gels always exhibit an inhomogeneous crosslink density distribution known as the spatial gel inhomogeneity, the extent of the spatial concentration fluctuations in gels may change depending on the charge density. Thus, the chains in the dense regions of gel move apart due to the osmotic pressure of counter ions, so that the gel becomes increasingly homogeneous as the charge density is increased, which is responsible for the increased modulus of charged gels [10].

Our purpose of the present study is to investigate the structural changes in PAAm gels as a function of their ionic group content. We selected AMPS as the ionic comonomer of AAm in the hydrogel preparation at various mole fractions x_i. The changes in the microstructure of gels depending on x_i was monitored by the light scattering measurements. As is well known, gels exhibit an important scattering at low scattering vectors q, corresponding to concentration fluctuations at length scale between 10^0 and 10^2 nm [11,12]. Such large-scale concentration fluctuations, which are absent in polymer solutions, indicate existence of mesoscopic static structures in polymer gels due to the spatial inhomogeneity. The spatial inhomogeneity can thus be manifested by comparing the scattering intensities from the gel and from a semi-dilute solution of the same polymer at the same concentration. The excess scattering over the scattering from polymer solution is related to the degree of the inhomogeneities in gels [13]. In the present work, the variation of the excess scattering of PAAm gels was determined depending on their charge densities. In addition, macroscopic properties of gels in terms of elastic moduli were determined by the elasticity tests.

Experimental

Synthesis of hydrogels

PAAm gels were prepared by free radical crosslinking copolymerization of AAm and AMPS with a small amount of BAAm in an aqueous solution at 5°C in the presence of 3.51 mM ammonium persulfate initiator and 0.375 v/v % N,N,N',N'-tetramethylethylenediamine (TEMED) accelerator. The reaction time was one day. The total monomer concentration was fixed at 0.70 M. The mole fraction of the ionic comonomer AMPS in the monomer mixture x_i was varied between 0 and 0.5, while the crosslinker ratio (mole ratio of the crosslinker BAAm to the monomers AAm+AMPS) was fixed at 1/80 throughout the study. It should be noted that, due to the different molar masses of AAm and AMPS, the total concentration of the monomers at crosslinking polymerization increased from 5.0 to 10.0 w/v% as x_i is increased from 0 to 0.5. Details about the gel synthesis have been reported elsewhere [14].

Mechanical Measurements

For the elasticity tests, the crosslinking polymerizations were carried out in glass tubes of 5 mm internal diameters and about 150 mm long. Uniaxial compression measurements were performed on gel samples of about 10 mm in length just after their preparation. All the mechanical measurements were conducted in a thermostated room of 24 ± 0.5°C. The stress-strain isotherms were measured by using an apparatus previously described [15]. The elastic modulus G_0 was determined from the slope of linear dependence $f = G_0 \left(\Lambda - \Lambda^{-2}\right)$, 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).

Light scattering experiments

For the light scattering measurements, the crosslinking polymerizations were carried out in the light scattering vials. All glassware was kept dustfree by rinsing in hot acetone prior using. The solutions were filtered through membrane filters (pore size = 0.2 μm) directly into the vials. This process was carried out in a dustfree glovebox. All the gels subjected to light scattering measurements were clear and appeared homogeneous to the eye. The light scattering measurements were carried out at 24°C using a commercial multi-angle light scattering DAWN EOS (Wyatt Technologies Corporation) equipped with a vertically polarized 30mW Gallium-arsenide laser operating at $\lambda = 690$ nm and 18 simultaneously detected scattering angles. The scattered light intensities were recorded from 51.5° to 142.5° which correspond to the scattering vector q range $1.1 \mathrm{x} 10^{-3} - 2.3 \mathrm{x} 10^{-3}$ $\mathrm{A}^{\mathrm{o}\,-1}$, where $q = (4\pi n/\lambda)\sin(\theta/2)$, θ the scattering angle, λ the wavelength of the incident light in vacuum, n the refractive index of the medium. The light scattering system was calibrated against a toluene standard. To obtain the ensemble averaged light scattering intensity of gels, eight cycles of measurements with a small rotation of the vial between each cycle were averaged.

The measurements were carried out on gels both at the state of gel preparation and at the equilibrium swollen state in water. For the calculation of excess scattering from gels, all the crosslinking polymerizations were repeated under the same experimental conditions except that the crosslinker BAAm was not used. To calculate the excess scattering from swollen gels, polymer solutions were diluted to obtain solutions at the same polymer concentration as the swollen gels. Necessary dilution degrees for PAAm solutions were calculated from the equilibrium swelling ratios of gels using the equation:

$$V_{sol} = V_{0,sol} \left(D/D_0\right)^3 \tag{1}$$

where $V_{o,sol}$ and V_{sol} are the solution volumes before and after dilution with water, D_0 and D are the diameters of gel samples after preparation and after equilibrium swelling in water, respectively [13].

Results and Discussion

PAAm hydrogels were prepared at a fixed crosslinker ratio but at various AMPS mole fractions x_i. The equilibrium volume swelling ratio of the hydrogels in water increased from $4\text{x}10^1$ to $6\text{x}10^2$, as x_i is increased from 0 to 0.5. In Fig. 1, the modulus of elasticity G_0 of the hydrogels just after their preparation is plotted against x_i. As expected, G_0 first increases with x_i, reaching its maximum at x_i = 0.2, but then decreases continuously. This is in accord with the previous observations [5].

Light scattering measurements were carried out on gels and solutions of PAAm prepared between x_i = 0 to 0.5. For each gel sample, the spatial inhomogeneities were characterized at two gel states; 1) at a gel state just after the preparation, and 2) at equilibrium swollen state in water. For $x_i > 0.2$, non-linear Rayleigh ratio R(q) versus

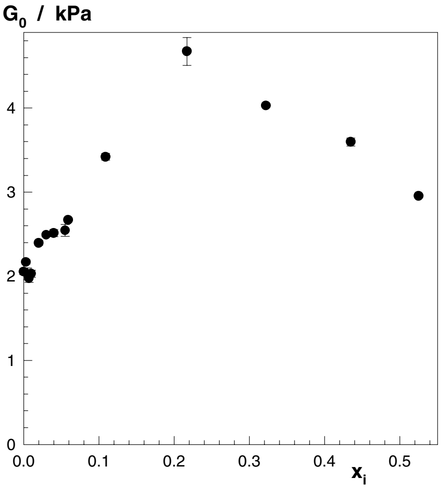

Figure 1. Elastic moduli G_0 of PAAm gels shown as a function of the AMPS mole fraction x_i.

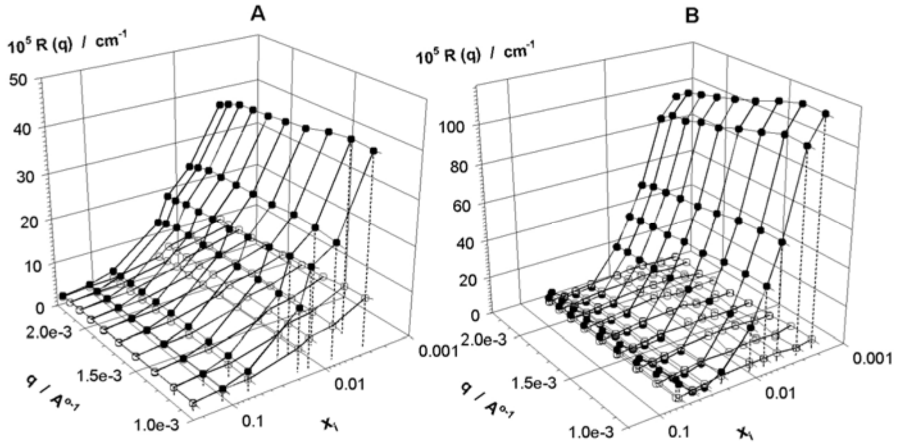

Figure 2. Rayleigh ratio *R(q)* versus scattering vector *q* and AMPS mole fraction x_i plots for PAAm gels (filled symbols) and for the corresponding PAAm solutions (open symbols). (A): At the state of preparation. (B): At equilibrium swollen (or diluted) state.

q plots were obtained for both gels and solutions, probably due to the high concentration of counterions in these samples. For $x_i < 0.2$, results of measurements of *R(q)* at the state of preparation and at the equilibrium swollen (or diluted) state of the samples are shown in Figs. 2A and 2B, respectively, plotted as functions of the scattering vector *q* and the AMPS content x_i. The filled and open symbols represent data obtained using gel and solution samples, respectively. Note that the *R(q)* scale of Fig. 2B is about twice that of Fig. 2A. Light scattering intensity from gels $R_{gel}(q)$ rapidly decreases as x_i is increased and approaches to the scattering intensity from solutions $R_{sol}(q)$. It is seen that, replacing a small fraction of AAm units with AMPS (about one out of hundred AAm units) significantly affects the scattering behavior of gels. Light scattering intensity from solutions $R_{sol}(q)$ also decreases with x_i, but this decrease is much slower than that observed in the gel samples. Moreover, at low charge densities, swollen gels scatter much more light than gels after preparation state, indicating increasing extent of spatial inhomogeneities in gels during their swelling process. Another point is that there is a little variation of *R(q)* with *q* for all the gel and solution samples. Therefore, in the following paragraphs, we focus on the scattering intensities measured at a fixed scattering vector $q = 1.7\text{x}10^{-3}$ A^{o-1} (i.e., at a scattering angle θ = 90°). The excess scattering $R_{ex,q}$ was calculated from the data in Fig. 2 as:

$$R_{ex,q} = R_{gel,q} - R_{sol,q} \tag{2}$$

Fig. 3 shows $R_{ex,q}$ of PAAm gels plotted against the AMPS mole fraction x_i. Open symbols are for swollen gels while filled symbols are for gels after preparation. Since the thermal fluctuations are eliminated in Eq. (2), excess scattering $R_{ex,q}$ is a measure of the degree of spatial inhomogeneities in gels. Excess scattering rapidly decreases with increasing charge density and approaches to zero at about $x_i = 0.05$. Thus, at this charge density, the scattering behavior of gel becomes similar to that of a semi-dilute polymer solution. The inset to Fig. 3 showing the behavior of gels in the range of x_i between 0 and 0.02 indicates that the excess scattering of swollen gel approaches to that of gels after preparation state at $x_i = 0.01$.

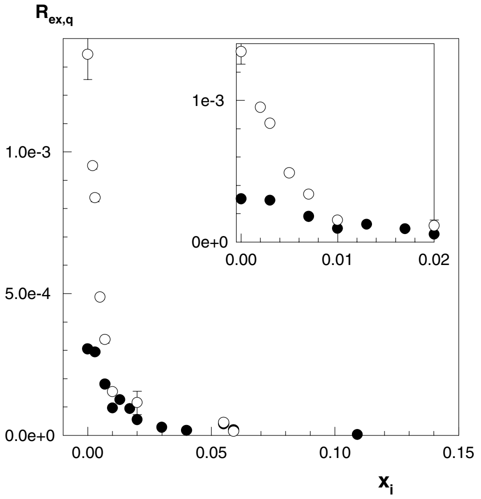

Figure 3. Excess scattering $R_{ex,q}$ versus AMPS mole fraction x_i for gels after preparation (●) and after equilibrium swelling in water (○).

Light scattering results from gels were interpreted by the Debye-Bueche (DB) function [16]:

$$R_{ex}(q) = \frac{4\pi\, K \xi^3 \langle \eta^2 \rangle}{\left(1 + q^2 \xi^2\right)^2} \tag{3}$$

where K being the optical constant, $K = 8\pi^2 n^2 \lambda^{-4}$, ξ is the correlation length of the scatterers, and $\langle \eta^2 \rangle$ is the mean square fluctuation of the refractive index. ξ of the DB theory is a characteristic length scale for gels and it corresponds to the size of the highly crosslinked regions. According to Eq. (3), the slope and the intercept of $R_{ex}(q)^{-1/2}$ *vs.* q^2 plot (DB plot) give ξ and $\langle \eta^2 \rangle$ of a gel sample. In Fig. 4, some of the

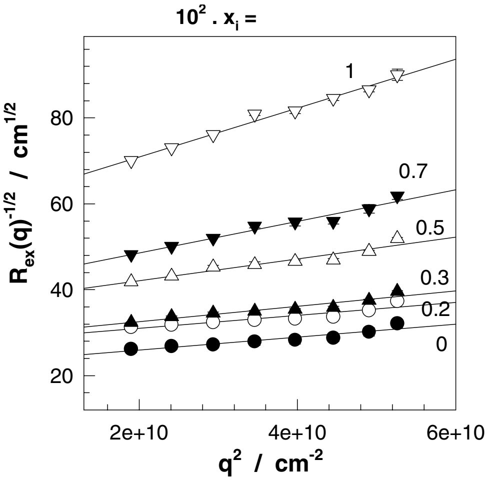

Figure 4. Debye-Bueche plots for swollen PAAm hydrogels at various x_i indicated in the Figure.

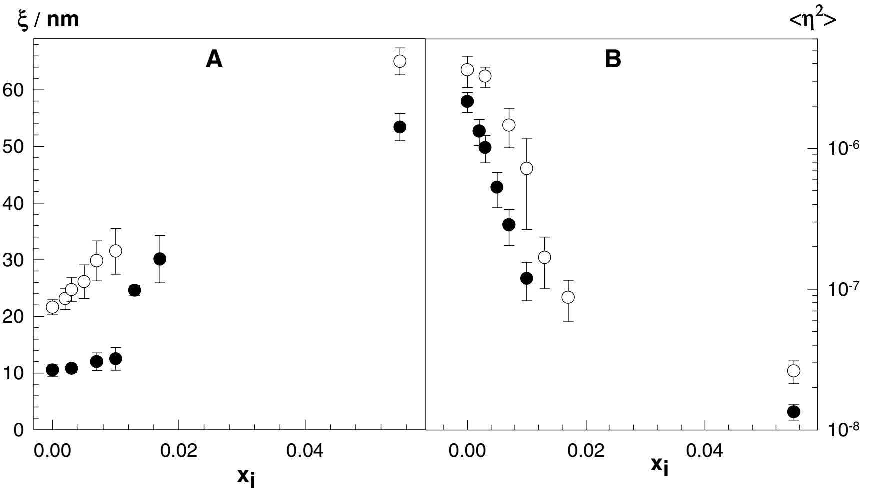

Figure 5. The correlation length of the scatterers ξ (A) and the mean square fluctuation of the refractive index $\langle \eta^2 \rangle$ (B) in PAAm gels after preparation (●) and after equilibrium swelling in water (○) shown as a function of x_i.

data points are replotted in the form of DB plots. It is seen that straight lines were obtained from the DB analysis, from which ξ and $\langle \eta^2 \rangle$ parameters were calculated, as described before [17].

Calculated values of ξ and $\langle \eta^2 \rangle$ from DB analysis are shown in Fig. 5 plotted as a function of x_i. Open symbols are for swollen gels while filled symbols are for gels after preparation. The correlation length of the scatterers ξ and the mean square fluctuations $\langle \eta^2 \rangle$ are in the range of 10 – 60 nm and 10^{-8} – 10^{-5}, respectively. ξ increases while $\langle \eta^2 \rangle$ decreases as the charge density is increased. Moreover, a general trend is that both ξ and $\langle \eta^2 \rangle$ slightly increases during swelling of ionic PAAm gels.

In order to understand the physical origin of the experimental results, we consider a PAAm gel sample as consisting of highly crosslinked (dense) regions, which are interconnected by the less crosslinked (dilute) interstitial regions, i.e., it consists of regions of high and low polymer concentrations. For a given average concentration of the ionic comonomer AMPS, the local charge density (number of AMPS units per gel volume) in the dense regions will thus be higher than in the dilute regions. Due to the condition of electroneutrality, the concentration of the counterions will also be higher in the dense regions. The concentration difference of counterions between the inside and outside the dense regions will create an osmotic pressure resulting in the swelling of these regions. Thus, water from dilute regions of the gel moves to the dense regions due to the additional osmotic pressure of excess counterions. As a result, increasing average charge density will result in increased degree of swelling of the dense regions of gel so that their size, represented by ξ, increases while the extent of concentration fluctuations $\langle \eta^2 \rangle$ reduces.

Moreover, since the crosslink density of the dense regions is larger than the average, these regions of gel after preparation state shrink to ensure a micro-swelling equilibrium with the solvent in the environment. However, the crosslink density of the dilute regions is lower than the average and thus, the swelling capacity of this region is higher than the degree of dilution after the gel preparation. Therefore, this region of gel is not in thermodynamic equilibrium. If a good solvent is added, the dilute regions will swell more than the dense regions. As a result, the spatial inhomogeneities represented by $\langle \eta^2 \rangle$ will increase during the swelling process.

A comparison of the elasticity results (Fig. 1) with the results of the light scattering measurements (Fig. 3) shows that, the decrease of the degree of spatial gel inhomogeneity is accompanied with an increase of the elastic modulus of gels. Even addition of 5 % AMPS in the gelation system results in an increase in the elastic modulus of gels; this increase cannot be explained with the ion-pair formation mechanism due to the fact that the AMPS content of the network chains is too low to produce multiplets acting as additional crosslinks. A more plausible explanation is the reducing degree of spatial gel inhomogeneity on rising the charge density of the network chains. Thus, since a homogeneous gel will exhibit a higher modulus of elasticity compared to an inhomogeneous gel of the same average crosslink density, increase of x_i provides a more homogeneous distribution of crosslink points along the gel sample, so that the macroscopic elasticity increases.

The results thus demonstrate that the macroscopic elastic properties of PAAm gels are mainly controlled by the microscopic gel structure determined by the scattering measurements.

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