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Spatial inhomogeneity in poly(acrylic acid) hydrogels

Ilknur Yazici, Oguz Okay*

Department of Chemistry, Istanbul Technical University, 80626 Maslak, Istanbul, Turkey

Abstract

The crosslink density distribution in gels known as the spatial gel inhomogeneity has been investigated in poly(acrylic acid) (PAAc) gels with the static light scattering measurements. PAAc gels were prepared at a fixed chemical crosslink density but at various initial monomer concentrations. The gels were characterized by swelling and elasticity tests as well as by light scattering measurements. PAAc gels exhibit a maximum degree of spatial inhomogeneity at a critical monomer concentration ($\nu_{2,cr}^0$). $\nu_{2,cr}^0$ shifts toward higher concentrations as the gel swells beyond its dilution degree after preparation. Depending on the polymer concentration in gels, swelling reduces or enhances the extent of the spatial inhomogeneities. It was shown that the apparent degree of the spatial gel inhomogeneity is determined by the combination of three effects, namely the effects of the effective crosslink density, charge density and segment density. The relative magnitudes of these effects vary depending on the polymer concentration and lead to the appearance of a maximum degree of spatial inhomogeneity at a critical concentration.

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Keywords: Poly(acrylic acid) gels; Inhomogeneity; Static light scattering

1. Introduction

In contrast to ideal gels with a homogeneous distribution of crosslinks, real gels always exhibit an inhomogeneous crosslink density distribution, known as the spatial gel inhomogeneity [1,2]. The spatial inhomogeneity in gels mainly originates from the several non-idealities of the gel formation systems such as the different and conversion-dependent reactivities of the functional groups, cyclization, multiple crosslinking, microgel formation, and diffusion-controlled reactions [3,4]. The gel inhomogeneities are of considerable interest and importance in attempts to characterize such materials physically. From the practical point of view, spatial inhomogeneity is undesirable because it dramatically reduces the optical clarity and strength of gels, which are properties closely connected with many industrial applications such as contact lenses, super absorbents, etc.

Since the gel inhomogeneity results in static concentration fluctuations in gels, scattering methods have been employed to investigate the spatial inhomogeneities [5–21]. Scattering measurements show an important scattering in gels at low scattering vectors q, corresponding to concentration fluctuations at length scale between 10^0 and 10^2 nm. Such large-scale concentration fluctuations, which are absent in polymer solutions, indicate existence of meso-scopic static structures in polymer gels due to the spatial inhomogeneity. The gel inhomogeneity can 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 low-q scattering intensity from gels is always larger than that from the polymer solution. The excess scattering over the scattering from polymer solution is related to the degree of the inhomogeneities in gels. In general, the gel inhomogeneity increases significantly with the crosslink density or swelling degree of gels, while it decreases with the introduction of ionic units on the network chains. Candau and co-workers showed that the scattering intensity from poly(acrylic acid) (PAAc) gels is strongly reduced when the ionization degree of PAAc is increased [22,23]. This was explained as the rearrangement of the network chains as the ionization degree of PAAc is increased. Thus, the chains in the highly crosslinked regions

* Corresponding author. Tel.: +90 212 2853156; fax: +90 212 2856386.
  E-mail address: okayo@itu.edu.tr (O. Okay).

move apart due to the osmotic pressure of counterions, so that a less inhomogeneous structure will form at high charge densities [23]. They also showed that the addition of salt in the swelling medium (water) recovers the original non-ionized structure of PAAc gels. Recently, we have shown that the initial monomer concentration used in the hydrogel preparation also affects significantly the degree of inhomogeneity in poly(acrylamide) (PAAm) gels [24,25]. An inflection point was observed in the excess scattering versus monomer concentration plot, at which the inhomogeneity attained a maximum value. This behavior was interpreted as a result of two antagonistic effects of the initial monomer concentration on the spatial gel inhomogeneity [25]. As the monomer concentration is increased, the effective density of crosslinks also increases, so that the spatial inhomogeneity becomes larger. Opposing this, increasing monomer concentration, i.e., decreasing the degree of swelling of gels after preparation reduces progressively the concentration difference between densely and loosely crosslinked regions of gel, so that the apparent inhomogeneity decreases. The interplay of these two opposite effects determines the inhomogeneity in PAAm gels and results in the appearance of a maximum gel inhomogeneity at a critical monomer concentration.

In this paper, we report an experimental study on crosslinked PAAc gels prepared in the acidic form. The aim of this study was to check whether the maximum observed in the spatial gel inhomogeneity vs. monomer concentration dependence still exists for weak polyelectrolyte gels and how this dependence is affected by the presence of charged groups. We prepared a series of PAAc gels by free-radical crosslinking copolymerization of acrylic acid (AAc) and N,N'-methylenebis(acrylamide) (BAAm) monomers in aqueous solutions. In our experiments, the crosslinker ratio was fixed at 1/80, while the initial monomer concentration vas varied over a wide range. For each gel sample, the spatial inhomogeneities were characterized by static light scattering measurements at two gel states: (a) at a gel state just after the preparation, and (b) at equilibrium swollen state in water. A semi-dilute PAAc solution of the same concentration as the equivalent gel served as a reference in the understanding of the inhomogeneities in gels. The excess scattering from the gels is taken as a measure of their inhomogeneities. In addition, swelling and elasticity measurements have as well been carried out to find the effective crosslink densities of gels formed at various concentrations. The experimental results were compared with the predictions of the statistical theory proposed by Panyukov and Rabin [26,27].

2. Experimental section

2.1. Synthesis of hydrogels

Acrylic acid (AAc, Fluka) was distilled under a reduced

pressure of 10 mmHg to remove its inhibitor. N,N'-methylenebis(acrylamide) (BAAm, Merck), and ammonium persulfate (APS, Merck) were used as received. PAAc gels were prepared by free-radical crosslinking copolymerization of AAc and BAAm in an aqueous solution at 70 °C in the presence of 0.79 mM APS initiator. The gels were prepared at a crosslinker ratio X (the mole ratio of BAAm to AAm) = 1/80 and at various initial monomer concentrations. The reaction time was one day. To illustrate the synthetic procedure, we give details for the preparation of a hydrogel at an initial monomer concentration of 6.0 w/v%.

BAAm (0.0156 g), AAc (0.56 ml), and APS (0.0018 g) were mixed and completed to 10 ml with distilled water. After bubbling nitrogen for 15 min, the solution was poured into several glass tubes of 5 mm internal diameters and about 150 mm long. For the light scattering measurements, the solution was filtered into the light scattering vials. The glass tubes and the vials were sealed, immersed in a thermostated water bath at 70 °C and the polymerization was conducted for 12 h.

2.2. Characterization of the hydrogels

The degree of dilution of the networks after their preparation was denoted by ν_2^0, the volume fraction of crosslinked polymer after the gel preparation. In order to determine ν_2^0, PAAc hydrogels after preparation were extracted in water over a period of at least 1 month. The hydrogels after extraction were first deswollen in water–acetone mixtures and then dried at 90 °C under vacuum to constant weight. Details about the extraction procedure were described previously [28]. Measurements showed that, in the range of ν_2^0 between 0.03 and 0.16, the experimental value of ν_2^0 is close to its theoretical value $\nu_2^0 = 10^{-3}$, C_0, V_r where C_0 is the initial monomer concentration (in M), and V_r is the molar volume of PAAc repeat units (47.5 ml/mol). This indicates that, under the reaction conditions, the monomer conversions and the gel fractions are complete.

For the swelling measurements of the hydrogels in water, the gel samples in the form of rods of 5 mm in diameter were cut into samples of about 10 mm length. Then, each sample was placed in an excess of water at 24 ± 0.5 °C. In order to reach swelling equilibrium, the hydrogels were immersed in water for at least two weeks replacing the water every other day. The swelling equilibrium was tested by measuring the diameter of the gel samples. To achieve good precision, three measurements were carried out on samples of different length taken from the same gel. The swelling capacity of the gels was determined by measuring the diameter of the hydrogel samples by a calibrated digital compass (Mitutoyo Digimatic Caliper, Series 500, resolution: 0.01 mm). The volume fraction of crosslinked polymer in the equilibrium swollen gel $\nu_{2,eq}$ and the volume swelling ratio q_v were calculated as

$$\nu_{2.eq} = (q_v)^{-1} = \nu_2^0/(D/D_0)^3 \qquad (1)$$

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

Uniaxial compression measurements were performed on gels just after their preparation. All the mechanical measurements were conducted in a thermostated room of $24 \pm 0.5\,^\circ$C. The stress–strain isotherms were measured by using an apparatus previously described [29]. The elastic modulus G_0 was determined from the slope of linear dependence $f = G_0(\sigma - \sigma^{-2})$, where f is the force acting per unit cross-sectional area of the undeformed gel specimen, and σ is the deformation ratio (deformed length/initial length). For a network of Gaussian chains, the elastic modulus at the state of gel preparation G_0 is related to the effective crosslink density ν_e by [30,31]

$$G_0 = A\, \nu_e\, RT\, \nu_2^0 \qquad (2)$$

where the front factor A equals to 1 for an affine network and $1 - 2/\phi$ for a phantom network, where ϕ is the functionality of the crosslinks, R and T are in their usual meanings. Since the gels prepared in this study were highly swollen, we used phantom network model ($\phi = 4$) to calculate the effective crosslink densities of PAAm gels.

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 $= 0.2\,\mu$m) 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 1.1×10^{-3} to $2.3 \times 10^{-3}\,\text{Å}^{-1}$, 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 (Rayleigh ratio at 690 nm $= 9.7801 \times 10^{-6}\,\text{cm}^{-1}$, DAWN EOS software). 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 PAAc solutions were calculated from the equilibrium swelling ratios of gels using the equation

$$V_{sol} = V_{0,sol}\left(\frac{D}{D_0}\right)^3 \qquad (3)$$

where $V_{0,sol}$ and V_{sol} are the solution volumes before and after dilution with water.

3. Results

PAAc hydrogels were prepared at various polymer network concentrations, denoted by ν_2^0, the volume fraction of the crosslinked polymer in the hydrogels after their preparation. The crosslinker ratio (mole ratio of crosslinker to monomer) was fixed at 1/80. Hydrogels formed between $\nu_2^0 = 0.02$ and 0.04 were too sticky and weak to withstand the elasticity and swelling tests. The characteristic data of the hydrogels formed between $\nu_2^0 = 0.04$ to 0.17 are compiled in Fig. 1. In Fig. 1(A), the modulus of elasticity G_0 and the effective crosslink density ν_e of the hydrogels are plotted against ν_2^0. Fig. 1(B) shows the swelling ratio of gels in terms of the volume swelling ratio (q_v) and the volume fraction of crosslinked polymer in the equilibrium swollen gel ($\nu_{2,eq}$) plotted as a function of ν_2^0. The curves show the trend of data. Elastic modulus G_0 increases from 1.4 to 50 kPa as ν_2^0 is increased. The inset to Fig. 1(A) shows that the modulus data can be described by a power law $G_0 \propto (\nu_2^0)^x$ where $x = 2.1 \pm 0.1$. The exponent found is much larger than the linear dependence predicted by the theory of rubber elasticity (Eq. (2)) and indicates existence of non-idealities during the gel formation process. Increasing number of wasted BAAm molecules in cycles on raising the dilution of the reaction solution, as reported for several vinyl–divinyl comonomer systems [3,4,32–34], may explain this discrepancy. Indeed, both $\nu_{2,eq}$ and ν_e are increasing functions of ν_2^0 (Fig. 1), that is, the higher the initial monomer concentration, the larger the effective crosslink density of the hydrogels and the smaller their swelling capacity.

Light scattering measurements were carried out on PAAc gels prepared between $\nu_2^0 = 0.02 - 0.15$, as well as on PAAc solutions prepared at the same polymer volume fractions ν_2^0. Measurements of the Rayleigh ratios $R(q)$ showed that there is a little variation of $R(q)$ with the scattering vector q for all the gel and solution samples. This is expected since we are probing length scales large compared with those typical for polymer gels. Therefore, in the following paragraphs, we focus on the scattering intensities measured at a fixed scattering vector $q = 1.7 \times 10^{-3}\,\text{Å}^{-1}$ (i.e., at a scattering angle $\theta = 90°$).

In Fig. 2(A), scattered light intensity from gels $R_{gel,q}$ (circles) and from solutions $R_{sol,q}$ (triangles) at $q = 1.7 \times 10^{-3}\,\text{Å}^{-1}$ are plotted as a function of ν_2^0. Results of
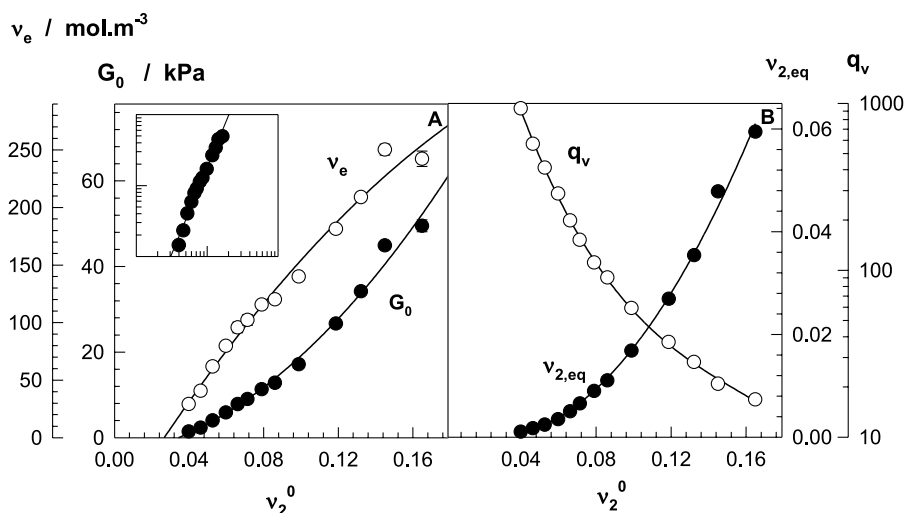
Fig. 1. (A) The modulus of elasticity G_0 and the effective crosslink density ν_e of the hydrogels shown as a function of the polymer network concentration ν_2^0. (B) The volume fraction of crosslinked polymer in the equilibrium swollen gel $\nu_{2,eq}$ and the volume swelling ratio q_v shown as a function of ν_2^0. The curves are polynomial best fits to each set of data. The inset to (A) shows a double logarithmic G_0 vs. ν_2^0 plot.

measurements after preparation state and after equilibrium swelling in water (or after dilution with water) are shown by the filled and open symbols, respectively. Excess scattering $R_{ex,q}$ was calculated from $R_{gel,q}$ and $R_{sol,q}$ as:

$$R_{ex,q} = R_{gel,q} - R_{sol,q} \qquad (4)$$

Fig. 2(B) shows $R_{ex,q}$ after preparation (filled symbols) and after equilibrium swelling in water (open symbols) plotted against the concentration ν_2^0. Since the thermal fluctuations are eliminated in Eq. (4), excess scattering $R_{ex,q}$ is a measure of the degree of spatial inhomogeneities in gels. Several interesting features can be seen from the Figures. First, scattered light intensity from gels and the excess scattering attains a maximum value at a critical polymer network concentration $\nu_{2,cr}^0$. $\nu_{2,cr}^0 = 0.05$ and 0.09 for gels after preparation and after equilibrium swelling, respectively. Thus, $\nu_{2,cr}^0$ shifts toward higher polymer concentration as the gel swells beyond its swelling degree after preparation. Moreover, scattered light intensity from solutions ($R_{sol,q}$) also attains a maximum value at $\nu_{2,cr}^0 = 0.05$, i.e., at the same polymer concentration as the corresponding PAAc gel. However, in dilute solutions, the peak in the $R_{sol,q}$ vs. ν_2^0 plot disappears, or shifts toward a polymer concentration outside of the range of the measurements ($\nu_2^0 > 0.15$). Another point shown in the Figures is that, if $\nu_2^0 > 0.06$, swelling enhances the scattered light intensity from gels, i.e., the gel becomes increasingly inhomogeneous as it swells in water. This is expected [17]. Unexpected is the behavior of gels formed below $\nu_2^0 = 0.06$. In this range of ν_2^0, the excess scattering decreases, that is, the apparent degree of spatial inhomogeneity decreases during the gel swelling.

In Fig. 3, the ratio $R_{ex,q}/R_{gel,q}$, representing the contribution of the spatial inhomogeneities to the scattering light intensity from PAAc gels is plotted against ν_2^0 for gels

after preparation (filled symbols) and for the equilibrium swollen gels (open symbols). The solid curves show the trend of data, while the dotted curves were calculated using the Panyukov–Rabin theory, as will be explained later. It is seen that the spatial inhomogeneity contributes up to about 50% of the scattering of gels after preparation. This contribution increases to about 90% in swollen PAAc gels.
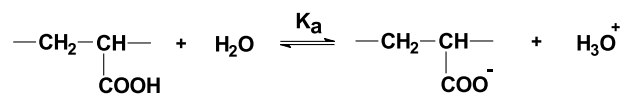
4. Discussion

In order to understand the physical origin of the light scattering results, we point the following effects determining the spatial inhomogeneity in a weakly charged hydrogel.

4.1. Effect of crosslink density

As shown in Fig. 1(A), increasing monomer concentration also increases the effective crosslink density ν_e of the hydrogels due to the more efficient consumption of BAAm in concentrated monomer solutions. Increasing crosslink density will increase the degree of spatial inhomogeneity in PAAc gels [2].

4.2. Effect of charge density

The ionization degree α of PAAc in aqueous solutions or in gels, defined as the ratio of the number of carboxylate groups to the total number of monomers has a non-zero value due to the acid–base equilibrium,

$$-CH_2-CH- \;+\; H_2O \;\overset{K_a}{\rightleftharpoons}\; -CH_2-CH- \;+\; H_3O^+$$
$$\quad\quad | \qquad\qquad\qquad\qquad\qquad\qquad | $$
$$\quad COOH \qquad\qquad\qquad\qquad\qquad COO^-$$

where K_a is the dissociation constant. K_a was reported as 5.6×10^{-5} for gels of PAAc [35]. Assuming that the PAAc
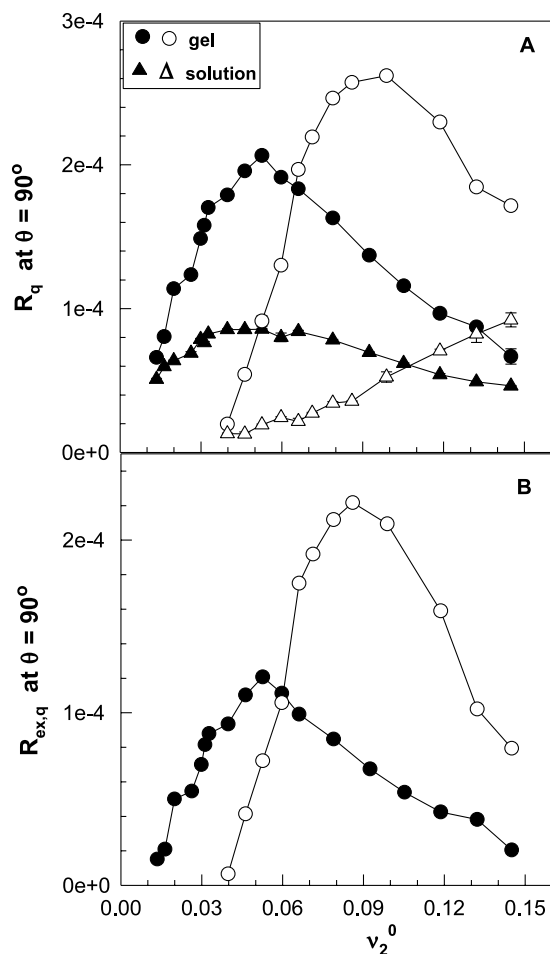
Fig. 2. (A) Scattering light intensities from gels $R_{\text{gel,q}}$ (circles) and from solutions $R_{\text{sol,q}}$ (triangles), both measured at $q = 1.7 \times 10^{-3}$ Å^{-1} shown as a function of ν_2^0. The filled and open symbols represent results of measurements on gels (or on solutions) after preparation and after equilibrium swelling in water (or after dilution with water), respectively. (B) Excess scattering intensities $R_{\text{ex,q}}$ at $q = 1.7 \times 10^{-3}$ Å^{-1} shown as a function of ν_2^0. The filled and open symbols represent data of gels at the state of their preparation and at the equilibrium swollen state in water, respectively.

density is 1.517 g/ml, one obtains the following relation between the ionization degree α and the polymer concentration ν_2

$$\alpha = \frac{1.63 \times 10^{-3}}{\sqrt{\nu_2}} \tag{5}$$

where $\nu_2 = \nu_2^0$ and $\nu_2 = \nu_{2,\text{eq}}$ for the preparation and equilibrium swollen (or diluted) state, respectively. According to Eq. (5), α is a decreasing function of the polymer concentration. Thus, as the gel preparation concentration is decreased or, as the gel swells, α increases, that is, the number of mobile ions in the gel or in the polymer coil increases. As reported before [22,23], increasing α will decrease the degree of spatial inhomogeneity in PAAc gels.
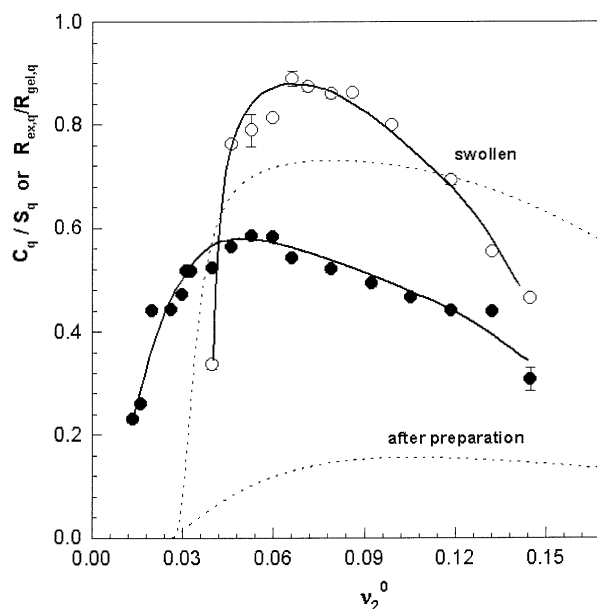

Fig. 3. The ratio $R_{\text{ex,q}}/R_{\text{gel,q}}$, (or C_q/S_q) representing the contribution of the spatial inhomogeneities to the scattering light intensity from PAAc gels is plotted against ν_2^0 for gels after preparation (filled symbols) and for the equilibrium swollen gels (open symbols). The solid curves show the trend of data. The dotted curves were calculated using the PR theory.

4.3. Effect of segment density

Increasing ν_2^0 or decreasing the degree of swelling necessarily increases the average segment concentration both in gels and solutions of PAAc. This will reduce the apparent degree of spatial inhomogeneity in PAAc gels.

The relative magnitudes of these three effects vary depending on the polymer concentration both in the history and in the present state of gel, and therefore, they play an essential role in the apparent degree of the spatial gel inhomogeneities. As ν_2^0 is increased, the spatial inhomogeneity of PAAc gels becomes larger due to the increase of their crosslink density (Fig. 1(A)) and due to the decrease of their charge density (Eq. (5)). Opposing this, increasing ν_2^0, that is, increasing segment density reduces the degree of spatial gel inhomogeneity. The ν_2^0 dependence of the gel inhomogeneity is thus determined by a competition of these effects. At low monomer concentrations, simultaneous effects of increasing crosslink density and decreasing charge density are more dominant than the concentration effect so that excess scattering increases with ν_2^0. At higher values of ν_2^0, the concentration effect starts to dominate over the other effects, resulting in a continuous decrease in the excess scattering. The location of the maximum ($\nu_{2,\text{cr}}^0$) in the excess scattering vs. monomer concentration ν_2^0 plot represents the transition point between these two regimes. Moreover, the shift of $\nu_{2,\text{cr}}^0$ toward higher polymer concentration during gel swelling is due to the weakening of the concentration effect in highly swollen gels. Thus, in swollen gels, the effect of segment density on the spatial gel inhomogeneity becomes

weaker, so that this effect starts to dominate later, i.e., at a larger value of $\nu_{2,cr}^0$.

Another point, which needs some comments, is the opposing behavior of gels formed above and below $\nu_2^0 = 0.06$ in response to the swelling process. The enhancement of the excess scattering during swelling of PAAc gels formed above $\nu_2^0 = 0.06$ is expected and can be explained as follows: since the crosslink density of the highly crosslinked (dense) regions of gel is larger than the average, these regions of gel partially shrink to ensure a micro-swelling equilibrium with the solvent in the environment. However, the matrix polymer is less crosslinked and, therefore, the swelling capacity of this region is generally higher than the degree of dilution after the gel preparation. Thus, if a good solvent is added, mainly the matrix polymer will swell further to attain the swelling equilibrium. As a consequence, concentration fluctuations and, therefore, the spatial gel inhomogeneities will increase during the swelling process.

However, an opposite behavior was observed if $\nu_2^0 < 0.06$ (Fig. 2). This can be explained with the low crosslink density and the high swelling capacity of PAAc gels formed in this region. As seen in Fig. 1(B), these gels exhibit swelling ratios q_v between 300 and 1000. For such loosely crosslinked gels, one may expect that both the dense and dilute regions of gel will swell significantly during the swelling process, which may decrease the extent of concentration fluctuations. To check this point, we used a simple two-phase gel model proposed by Weiss and Silberberg, and by Cohen et al. [36–38]. According to this model, the gel consists of two phases; one phase containing a high concentration of polymer and crosslinks; the other containing a low concentration of polymer and crosslinks. The model assumes that the two phases are weakly bound each other such that they swell independently [38]. The swelling equilibrium in each phase is given by the Flory–Rehner swelling theory. We apply this model to our data by taking the average crosslink density ν_e of the two-phase gel as one of the independent parameters. Calculations showed that, if ν_e of a two-phase gel is low, the concentration difference between the two phases decreases as it swells to equilibrium, i.e., the gel becomes increasingly homogeneous during swelling. The expected increase of the concentration fluctuation with ν_2^0 was observed at large values of ν_e.

As seen in Fig. 2(A), undiluted PAAc solutions also exhibit a maximum scattering intensity at a critical polymer concentration. This may be related to the variation of the ionization degree with the polymer concentration. As ν_2^0 is increased, i.e., as the degree of ionization decreases (Eq. (5), the scattered intensity due to the thermal fluctuations increases. This situation continues until the concentration effect dominates the charge density effect so that a decrease in $R_{sol,q}$ starts to appear at $\nu_{2,cr}^0$. To prove this explanation, we prepared a series of poly(sodium acrylate) (PSA) solutions (with $\alpha = 1$), as described in Ref. [39]. The initial polymer concentration ν_2^0 was varied between 0.05 and 0.15.

Light scattering measurements showed no peak in the $R_{sol,q}$ vs. ν_2^0 plot of PSA solutions, supporting our explanation that the appearance of a peak is due to the variation of the ionization degree of PAAc depending on the polymer concentration.

The light scattering results were also interpreted using the statistical theory of Panyukov and Rabin (PR) [26,27]. The Panyukov–Rabin (PR) theory assumes that the gel is prepared by instantaneous crosslinking of semi-dilute polymer solutions. The advantage of PR theory is that it predicts the correlations between the synthesis parameters of gels and their scattering properties. The PR theory takes into account the effect of the network structure at preparation on the structure factor $S(q)$ under condition of measurements. The structure factor of this theory consists of two contributions, one from the thermal fluctuations $G(q)$ and the other from the static inhomogeneities $C(q)$. Theoretical prediction of the PR theory requires the network parameters at the state of the gel preparation as well as at the state of the measurements. According to the PR theory, these structure factors are given by the following equations

$$S(q) = G(q) + C(q) \tag{6}$$

$$G(q) = \frac{a^{-3}\nu_2 N g(q)}{1 + w g(q)} \tag{7}$$

$$C(q) = \frac{a^{-3}\nu_2 N}{(1 + w g(q))^2 (1 + Q^2)^2} \tag{8}$$
$$\times \left(6 + \frac{9}{w_0 - 1 + 0.5 Q^2 (\nu_2^0/\nu_2)^{2/3}} \right)$$

where a is the segment length, ν_2 is the volume fraction of crosslinked polymer in the gel at the measurement, N is the number of segments between two successive crosslinks, and $g(q)$ is the thermal correlator in the absence of the excluded volume effect,

$$g(q) = \frac{1}{0.5 Q^2 + (4 Q^2)^{-1} + 1} + \frac{2(\nu_2/\nu_2^0)^{2/3}}{(1 + Q^2)^2} \tag{9}$$

w and w_0 are the excluded volume parameters at the state of measurement and at gel preparation, respectively,

$$w = (1 - 2\chi + \nu_2)\nu_2 N + \frac{l_B \alpha^2 \nu_2 N^2}{Q^2 + l_B f \nu_2 N} \tag{10}$$

$$w_0 = (1 - 2\chi_0 + \nu_2^0)\nu_2^0 N + \frac{l_B \alpha_0 \nu_2^0 N^2}{Q^2 + l_B f_0 \nu_2^0 N} \tag{11}$$

Q is the reduced scattering vector normalized by the monomer fluctuating radius, $Q = a N^{1/2} q$, χ is the polymer–solvent interaction parameter, l_B is the dimensionless Bjerrum length, $l_B = 4\pi L_B/a$, L_B is the Bjerrum length, α is the degree of ionization, and the initial and final states of the gels are assumed to be in the mean field regime. The parameters with and without the subscript 0 denote those of

the initial state and final state, respectively. Note that N is related to the effective crosslink density ν_e through

$$N = 1/(\nu_e a^3 N_A) \tag{12}$$

where N_A is the Avogadro's number.

The solution of the above equations requires several parameters, which were evaluated as follows. We already know the crosslink density ν_e (or N) and the swelling capacity $\nu_{2,eq}$ of gels as a function of ν_2^0 (Fig. 1). Non-linear curve fits to the experimental ν_e vs. ν_2^0 and $\nu_{2,eq}$ vs. ν_2^0 data shown in Fig. 1 give the following equations:

$$\nu_e = -66.9 + 2617\nu_2^0 - 4065(\nu_2^0)^2 \quad \text{(for } \nu_2^0 < 0.17) \tag{13}$$

$$(\text{mol m}^{-3})$$

$$\nu_{2,eq} = 2.1419 \times 10^{-3} - 0.16039\nu_2^0$$
$$+ 3.13955(\nu_2^0)^2 \quad \text{(for } \nu_2^0 < 0.17) \tag{14}$$

which were solved as a function of ν_2^0. The degree of ionization α for PAAc is given by Eq. (5). Bjerrum length L_B for aqueous solutions at 25 °C is 7 Å. The interaction parameter for PAAc–water system was reported as $\chi = \chi_0 = 0.45$ [40]. The evaluation of χ assumes an equivalent size of both solvent (water) molecules and PAAc segments. Therefore, for the following calculations, the volume of segment (a^3) was assumed to be equal to the molar volume of water (18 ml/mol), which leads to a segment length $a = 3.1$ Å. By substituting $\nu_2 = \nu_2^0$ and $\nu_2 = \nu_{2,eq}$ in Eqs. (6)–(12) for gels at the state of preparation and at the swollen state, respectively, the structure factor $S(q)$, its thermal fluctuations correlator $G(q)$ and the part of static density

Fig. 4. Variation of the theoretical structure factor for gels (S_q) and for solutions (G_q) at $q = 1.7 \times 10^{-3}$ Å^{-1} with the polymer network concentration ν_2^0. Calculations were using the PR theory and for PAAc gels after preparation (solid curves) and after equilibrium swelling in water (dashed curves).

inhomogeneities $C(q)$ were calculated. Calculations were for the scattering vector $q = 1.7 \times 10^{-3}$ Å^{-1}.

In Fig. 4, S_q and G_q for PAAc gels after preparation (solid curves) and after equilibrium swelling in water (dotted curves) are shown as a function of ν_2^0. Note that S_q and G_q are proportional to $R_{gel,q}$ and $R_{sol,q}$, respectively. Comparison of the theoretical curves in Fig. 4 with the experimental data given in Fig. 2(A) clearly shows that the theory qualitatively predicts the experimental behavior of gels. Both S_q and G_q vs. ν_2^0 plots for gels after preparation exhibit peaks at a critical concentration. During gel swelling, the S_q peak shifts toward a higher concentration, while the G_q peak disappears in the range of ν_2^0 investigated. However, the predicted values of $\nu_{2,cr}^0$ are 0.09 and 0.16 for gels after preparation and after equilibrium swelling in water, respectively, which are much larger than those found by experiments. In Fig. 3, the dotted curves show ν_2^0-dependence of the ratio C_q/S_q, which corresponds to the experimental $R_{ex,q}/R_{gel,q}$ data. It is seen that, although the PR theory predicts a large increase in the fraction of excess scattering during gel swelling, the predicted course significantly deviates from the experimental behavior. Moreover, theory predicts a small difference between S_q and G_q for gels after preparation (Fig. 4, solid curves) while experiments show that S_q is much larger than G_q (Fig. 2), that is, the degree of inhomogeneity is much larger than that predicted by the theory. These differences are probably due to the random crosslinking assumption of the PR theory, which is unrealistic for gels formed by free-radical mechanism [3,4].

5. Conclusions

We have reported results on the swelling, elasticity and scattering of a series of PAAc gels prepared at a fixed crosslinker ratio (1/80) but at various initial polymer network concentrations ν_2^0. Light scattering measurements showed that both gels and solutions of PAAc after their preparation exhibit a maximum scattering at a critical polymer concentration $\nu_{2,cr}^0$. $\nu_{2,cr}^0$ shifts toward a higher polymer concentration as the gel swells in water, while the maximum disappears as the solution is diluted with water. The scattering measurements also showed that, if $\nu_2^0 > 0.06$, swelling enhances the scattered light intensity from gels, while an opposite behavior was observed in the range of ν_2^0 below 0.06; Here, excess scattering decreases via swelling, that is, the apparent degree of spatial inhomogeneity decreases during gel swelling.

We have shown that the apparent degree of spatial inhomogeneity in PAAc gels is determined by the combination of three different effects, namely the effects of the effective crosslink density, charge density, and segment density. The relative magnitudes of these effects vary depending on the polymer concentration both in the history and in the present states of gel, and lead to the
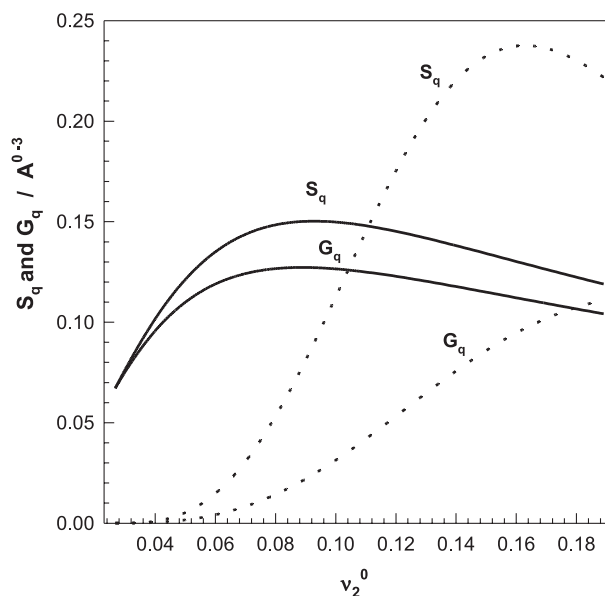
appearance of a maximum degree of spatial inhomogeneity at a critical polymer concentration.

Acknowledgements

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