Polymer Bulletin 52, 83–90 (2004)
DOI 10.1007/s00289-004-0247-3

Polymer Bulletin

Non-Gaussian elasticity of poly(2-acrylamido-2-methylpropane sulfonic acid) gels

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Received: 22 March 2004 / Accepted: 16 April 2004

Summary

A series of strong polyelectrolyte hydrogels was prepared from the sodium salt of 2-acrylamido-2-methylpropane sulfonic acid (AMPS) as the monomer and N,N'-methylene(bis)acrylamide (BAAm) as a crosslinker. The hydrogels prepared between 9 and 50 mol % BAAm appeared homogeneous to eye but exhibited large spatial fluctuations of polymer concentration, as determined by the light scattering measurements. The elasticity tests show that the modulus of elasticity of gels increases with increasing degree of swelling, starting from the gel preparation state. Thus, the mechanical properties of the hydrogels are improved on their swelling in water. It was shown that the hydrogels even at a gel state just after their preparation are in the non-Gaussian regime due to the high degree of spatial gel inhomogeneity.

Introduction

Polymer gels have an important role in many emerging technological areas such as drug delivery, sensors, and superabsorbent materials. In many of the applications, precise information on the elastic properties of the gels is required. Polymer gels formed in the presence of a diluent are soft when handled in the swollen state; typically, swollen gels exhibit moduli of elasticity in the order of kilopascals. Therefore, the poor mechanical properties of highly swollen gels limit their technological applications. Another characteristic feature of gels formed by free-radical mechanism is the inhomogeneous distribution of their crosslink points along the gel volume, which is known as the spatial gel inhomogeneity [1,2]. The inhomogeneities present in gels are of considerable interest and importance in attempts to characterize such materials physically.

The aim of this study is to prepare hydrogels that improve their mechanical properties upon swelling. To achieve this aim, the concept presented here is to utilize the properties of highly inhomogeneous hydrogels. As schematically illustrated in Fig. 1, an inhomogeneous gel prepared in a dilute solution consists of regions of high polymer concentration (microgels), which are connected through the network chains locating in dilute regions. Since the network chains in the dilute phase are highly stretched, the gel should exhibit stiffened properties at swollen state due to the non-Gaussian elasticity. Preliminary experiments showed that the crosslinking copolymerization of the sodium salt of 2-acrylamido-2-methylpropane sulfonic acid (AMPS) monomer and N,N'-methylenebis(acrylamide) (BAAm) crosslinker in dilute aqueous solutions leads to the formation of highly inhomogeneous gels. To check our concept, hydrogels from AMPS and BAAm were prepared and subjected to swelling, elasticity and light scattering measurements. As will be seen below, the modulus of elasticity of gels increases monotonically as the gel swells beyond its swelling degree after preparation.

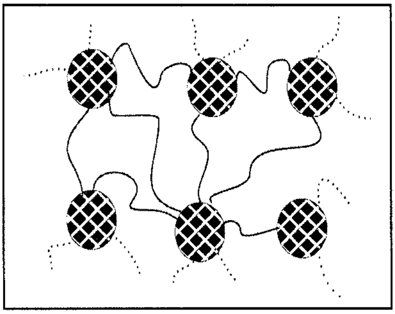


Figure 1. Schematic representation of the structure of an inhomogeneous gel prepared in dilute solution

Experimental

Materials

N,N'-methylenebis(acrylamide) (BAAm, Merck), ammonium persulfate (APS, Merck), and N,N,N',N'-tetramethylethylenediamine (TEMED) were used as received. 2-acrylamido-2-methylpropane sulfonic acid (AMPS-H^+, Merck) was crystallized from boiling methanol. It was neutralized with NaOH and a stock solution was prepared containing 0.966 M AMPS.

Synthesis of hydrogels

Poly(2-acrylamido-2-methylpropane sulfonic acid sodium salt) (PAMPS) hydrogels were prepared by free-radical crosslinking copolymerization of AMPS with BAAm in aqueous solution at 5^0C. The reaction time was 24 h. APS (3.51 mM) and TEMED (0.25 mL / 100 mL reaction solution) were used as the redox initiator system. The initial concentration of the monomers (AMPS +BAAm) was fixed at 5 w/v %. The crosslinker (BAAm) content in the monomer mixture was varied between 5 and 50 mol %. The detail about the hydrogel preparation was described before [3]. The weight fraction of gel W_g was determined by the extraction of the hydrogels in an excess of water and then drying the insoluble polymer to constant mass. W_g was then calculated as the ratio of the mass of extracted, dry polymer to the mass of the initial monomer.

Swelling measurements in water

The hydrogels in the form of rods of 4 mm in diameter were cut into samples of about 10 mm length. Then, each sample was placed in an excess of water at room temperature (24 ± 0.5^0C). 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. The normalized volume of the equilibrium swollen hydrogels V_{eq} (volume of equilibrium swollen gel/volume of the gel just after preparation) was determined by measuring the diameter of the hydrogel samples by a calibrated digital compass (Mitutoyo Digimatic Caliper, resolution: 0.01 mm). V_{eq} was calculated as $V_{eq} = (D/D_0)^3$, where D and D_0 are the diameter of hydrogels after equilibrium swelling in water and after synthesis, respectively. To obtain hydrogels at various degrees of swelling, equilibrium swollen gels were placed in sealed 50 mL - vials at room temperature to evaporate a desired amount of the gel water. This procedure ensured uniformity of the network concentration throughout the gel sample. After a given evaporation time (a few minutes up to a few months), the diameters of partially swollen gels were measured, from which their volumes V were calculated.

Mechanical Measurements

Uniaxial compression measurements were performed on gels at various degrees of swelling. All the mechanical measurements were conducted in a thermostated room of 24 ± 0.5 ^{0}C. The stress-strain isotherms were measured by using an apparatus previously described [4]. Briefly, a cylindrical gel sample of about 7 mm in length was placed on a digital balance (Sartorius BP221S, readability and reproducibility: 0.1 mg). A load was transmitted vertically to the gel through a road fitted with a PTFE end-plate. The compressional force acting on the gel was calculated from the reading of the balance. The resulting deformation was measured after 20 sec of relaxation by using a digital comparator (IDC type Digimatic Indicator 543-262, Mitutoyo Co.), which was sensitive to displacements of 10^{-3} mm. The measurements were conducted up to about 15 % compression. From the repeated measurements, the standard deviations in the modulus value were less than 3 %. The sample weight loss during the measurements due to water evaporation was found to be negligible. The elastic modulus G was determined from the slope of linear dependence:

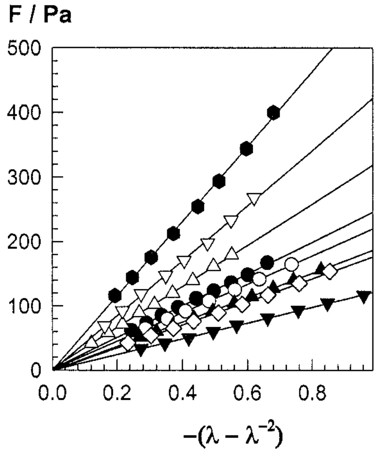
$$F = G\left(\lambda - \lambda^{-2}\right) \tag{1}$$

where F is the force acting per unit cross-sectional area of the undeformed gel specimen, and λ is the deformation ratio (deformed length/initial length). Typical stress-strain data correlated according to Eq. (1) are shown in Fig. 2 for hydrogels with varying BAAm contents. The interpretation of the elasticity measurements was made on the basis of the elastic modulus of gels just after their preparation and of the reduced modulus, designated by G_0 and G_r, respectively, where the reduced modulus is defined as the ratio of the elastic modulus of the gel at a given degree of swelling to that of the same gel after its preparation, i.e., $G_r = G/G_0$.

Light scattering experiments

For the light scattering measurements, the crosslinking copolymerizations 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. For the calculation of excess scattering from gels, all the crosslinking copolymerizations were repeated under the same experimental conditions except that acrylamide AAm was used as a comonomer of AMPS, in stead of the crosslinker BAAm [5,6].

The light scattering measurements were carried out at 24^0C 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 from gels and solutions of PAMPS were recorded from 51.5^0 to 142.5^0, which correspond to the scattering vector q range $1.1\text{x}10^{-3} - 2.3\text{x}10^{-3}$ A^{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. During the measurements with gel samples, the vial was rotated eight times between each cycle of data sampling.



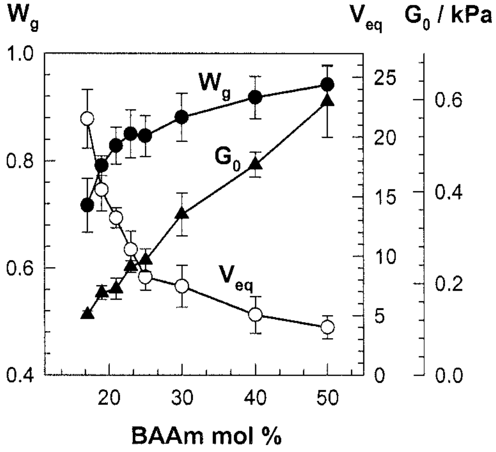


Figure 2. (left) Typical stress – strain data for PAMPS hydrogels just after their preparation. BAAm mol % = 17 (▼), 19 (◇), 21 (▲), 23 (O), 25 (●), 30 (△), 40 (▽), and 50 (●).

Figure 3. (right): The weight fraction of gel W_g, the elastic modulus G_0 and the normalized equilibrium volume swelling ratio of gels V_{eq} shown as a function of the BAAm content in the feed.

Results and Discussion

The crosslinking copolymerization of AMPS was carried out in the presence of various amounts of the crosslinker BAAm. No macrogel formation was observed if the BAAm concentration was less than 8 mol%. This critical BAAm content for the onset of gelation is about 30-fold larger than that reported for the crosslinking acrylamide (AAm) copolymerization under the same reaction conditions [6]. The gels formed between 9 and 15% BAAm were too weak to withstand the swelling and elasticity tests. Moreover, gels prepared above 50 mol % BAAm became first translucent and then opaque during the gel formation reactions. It is obvious that these gels have heterogeneities in a spatial scale of submicrometer to micrometer.

In Fig. 3, the weight fraction of gel W_g, and its elastic modulus G_0 are shown as a function of the BAAm content in the feed. The gels isolated from the reaction system were immersed in an excess of water and subjected to swelling measurements. Fig. 3 also shows how the normalized equilibrium volume swelling ratio of gels V_{eq} varies with BAAm %. Both W_g and G_0 increase, while V_{eq} decreases as the crosslinker content is increased. Thus, the amount of soluble chains decreases while the average gel crosslink density increases with increasing crosslinker content. In spite of the large amount of BAAm present in the reaction system, the gels exhibit moduli of elasticity in the range of 100 – 600 Pa, which are much lower than the moduli of polyacrylamide (PAAm) gels formed at 1 mol % BAAm (1500 Pa [6]). This suggests that only a small fraction of BAAm used in the hydrogel preparation forms elastically effective crosslinks in the final network. BAAm units involved in cycles, in multiple crosslinks as well as those bearing pendant vinyl groups may be responsible for this observation [7,8]. Such nonidealities in gel forming systems are known to produce spatial gel inhomogeneities.

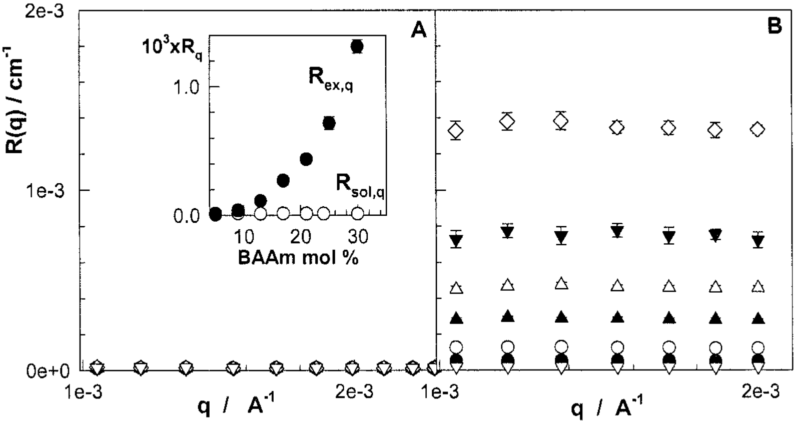


Figure 4. Rayleigh ratio $R(q)$ versus scattering vector q plots for PAMPS gels (B) and for the corresponding linear PAMPS solutions (A). BAAm (or AAm) mol % =5 (▽), 9 (●), 13 (○), 17 (▲), 21 (△), 25 (▼), and 30 (◇). The inset to Figure 4A shows scattering light intensities from PAMPS solutions $R_{sol,q}$ (open circles) and the excess scattering $R_{ex,q}$ (filled circles) measured at $q = 1\text{x}10^{-3}$ A^{o-1} as a function of BAAm %.

To determine the extent of the spatial gel inhomogeneity, light scattering measurements were carried out. For this purpose, PAMPS gels and the corresponding PAMPS solutions were subjected to the light scattering measurements. The spatial gel inhomogeneity was manifested by comparing the scattered intensities from gels and solutions of PAMPS at the same concentration [5]. In Fig. 4, the Rayleigh ratios R(q) from solutions (A) and from gels (B) are plotted against the scattering vector q. Both for gels and solutions, R(q) is independent on q over the range of the light scattering measurements. Comparison of Fig. 4A and 4B shows that PAMPS gels scatter much more light than the corresponding PAMPS solutions. Excess scattering $R_{ex}(q)$ of gels over the scattering from polymer solutions was calculated as $R_{ex}(q) = R_{gel}(q) - R_{sol}(q)$, where $R_{gel}(q)$ and $R_{sol}(q)$ are the Rayleigh ratios for gel and polymer solution, respectively. Since the thermal fluctuations are eliminated in $R_{ex}(q)$, it is a measure of the degree of spatial inhomogeneity in PAMPS gels. To compare the excess scattering of different gels, we will focus on the scattering intensity measured at a fixed scattering vector q = 1x10^{-3} A$^{o\,-1}$. The inset to Figure 4A shows $R_{sol,q}$ (open circles) and the excess scattering $R_{ex,q}$ (filled circles) plotted as a function of BAAm %. In polymer solutions, the scattered light intensity $R_{sol,q}$ does not change much with AAm %. However, as soon as a macroscopic gel forms in the reaction system, $R_{ex,q}$, that is the degree of inhomogeneity rapidly increases with increasing BAAm content. To interpret the light scattering results from gels, several scattering functions have been proposed. For example, the excess scattering $R_{ex}(q)$ was given by the Debye-Bueche (DB) function as [9]:

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

where K being the optical constant, $K = 8\,\pi^2 n^2 \lambda^{-4}$, ξ is the correlation length of the scatterers, and $\left\langle \eta^2 \right\rangle$ is the mean square fluctuation of the refractive index. Note that the correlation length ξ of DB theory is a characteristic length scale in the gel and, it is a measure of the spatial extent of the fluctuations. According to eq. (2), the slope and the intercept of $R_{ex}(q)^{-1/2}$ vs q^2 plot (DB plot) give ξ and $\left\langle \eta^2 \right\rangle$ of a gel sample.

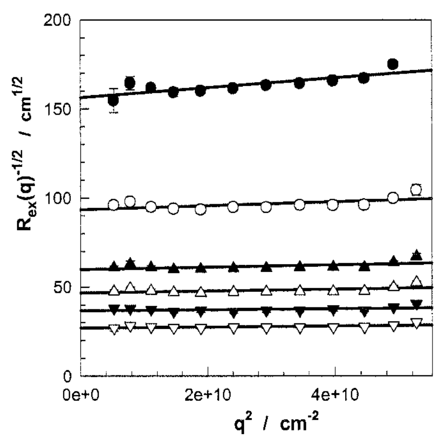


Figure 5. (left) Debye - Bueche plots for PAMPS gels prepared at 9 (●), 13 (○), 17 (▲), 21 (△), 25 (▼), and 30 mol% BAAm (▽).

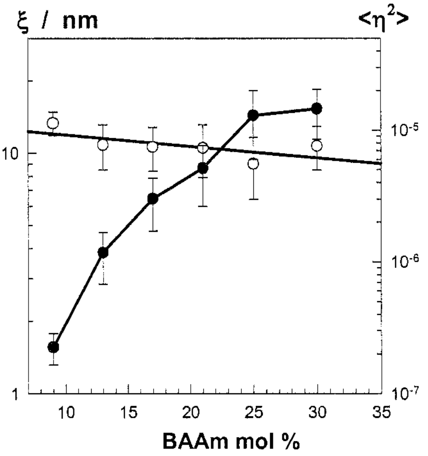
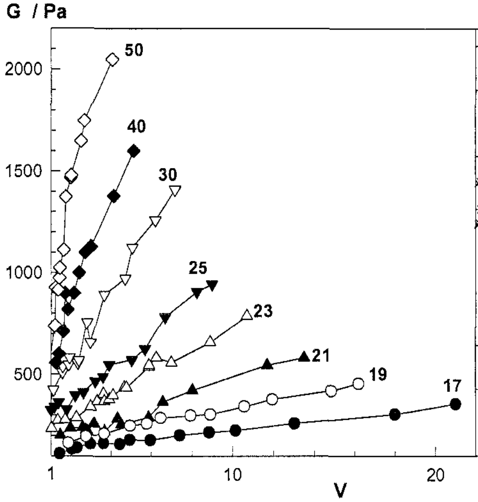


Figure 6. (right): The correlation length of the scatterers ξ (open symbols) and the mean square fluctuation of the refractive index $\left\langle \eta^2 \right\rangle$ (filled symbols) in PAMPS gels shown as a function of BAAm %.

Fig. 5 shows the DB plots of the PAMPS gels. Calculated values of ξ and $\left\langle \eta^2 \right\rangle$ from DB analysis are shown in Fig. 6 plotted as a function of BAAm %. The size of the highly crosslinked regions ξ is about 10^1 nm and slightly decreasing function of the crosslinker content. The spatial extent of the fluctuations of polymer concentration in gel, represented by $\langle \eta^2 \rangle$, rapidly increases with BAAm % from 10^{-7} to 10^{-5}.

The gels were subjected to the elasticity tests at various gel volumes between $V = 1$ (at a gel state just after preparation) and $V = V_{eq}$ (at equilibrium swollen state). The results are plotted in Fig. 7, where the elastic moduli of gels G are shown as a function of the gel volume V (i.e., gel swelling). For a network of Gaussian chains, one may expect a continuous decrease of G with the gel swelling due to the decrease of the concentration of elastically effective network chains. Fig. 7 shows however an opposite behavior. The modulus monotonically increases as the gel swells beyond its swelling degree after preparation. A two to three fold increase in the moduli of elasticity was observed upon swelling of gels in water. Indeed, visual observations showed that, as the gel swells, they become more resistant to the physical tests. Thus, mechanical properties of gels are improved on their swelling.



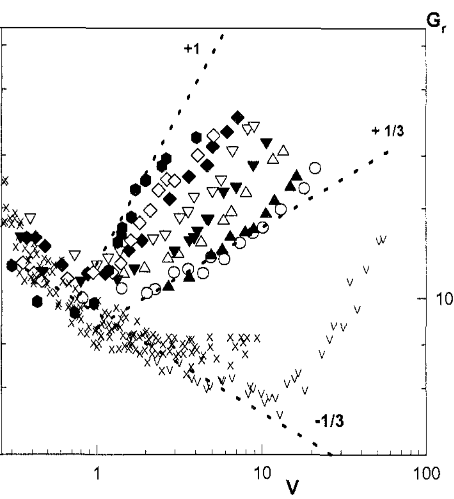


Figure 7. (left): Elastic modulus of gels G of gels shown as a function of the gel volume V. BAAm contents (mol %) are indicated in the Figure.

Figure 8. (right): Reduced modulus of gels Gr shown as a function of the gel volume V. Large symbols are results of measurements with PAMPS gels. BAAm mol % = 17 (○), 19 (▲), 21 (△), 23 (▼), 25 (▽), 30 (◆), 40 (◇), and 50 mol % (●). Small symbols are data for PNIPA gels with 1.19 mol % BAAm and various AMPS contents. AMPS mol % = 0 – 6 (X) and 50 (V).

One may explain the elastic behavior of PAMPS gels with the non-Gaussian elasticity of highly stretched network chain. Recently, we have shown that the reduced modulus of polymer networks obeying non-Gaussian chain statistics is given by [3,10]:

$$G_r = V^{-1/3} + \frac{2}{3}\frac{(1+\lambda^3)}{n\lambda}V^{\frac{1}{3}} + \frac{2}{3}\frac{(1+\lambda^3+\lambda^6)}{(n\lambda)^2}V + \frac{2}{3}\frac{(1+\lambda^3+\lambda^6+\lambda^9)}{(n\lambda)^3}V^{\frac{5}{3}} + \dots \tag{3}$$

where n is the number of flexible units between crosslinks, which includes the non-Gaussian properties of the network. The value of n depends on the stiffness of the polymer backbone and on the molar mass of the network chains. According to Eq. (3), an infinite number of statistical segments per network chain ($n = \infty$) yield a straight line in G_r vs V dependence with a slope of –1/3, which is the result for the Gaussian approach. For finite values of n, the exponent deviates from –1/3 and G_r increases with increasing gel volume.

In Fig. 8, large symbols are the reduced modulus (G_r) data of PAMPS gels plotted against the gel volume V in a double logarithmic plot. The dashed curves represent several theoretical slopes predicted by eq. (3) for various gel volumes. For comparison, data of elasticity and swelling of strong polyelectrolyte poly(N-isopropylacrylamide) (PNIPA) hydrogels were taken from the literature and are also shown in the figure by the small symbols [3,10]. These gels contain 1.2 % BAAm and various amounts of AMPS; their elastic moduli are in the range of 2500-4200 Pa, i.e., about 10-fold larger than that of PAMPS gels. Several interesting features can be seen from Fig. 8. Deviations from the Gaussian behavior in PAMPS gels are arising at gel volumes $V \cong 1$. Thus, despite the fact that the moduli G_0 of PAMPS gels are lower than that of PNIPA gels, the upturn of G_r in PAMPS gels occurs at much smaller gel volumes. The slope of G_r vs V plot increases from about 1/3 to 1 with increasing BAAm %, that is the reduced modulus shows a steeper increase with increasing crosslinker content. In case of PNIPA gels, deviation from the Gaussian slope appears at about $V = 10$.

We propose the following picture to explain the observed phenomena: As was found from the light scattering measurements, PAMPS hydrogels consists of highly crosslinked (dense) regions of sizes 10^1 nm, which are connected to a macronetwork through PAMPS network chains (Fig. 1). The low modulus of elasticity of the hydrogels even at BAAm contents as high as 50% suggests that the dense regions of gel mainly consist of agglomerates of BAAm molecules. Increasing BAAm content leads to the further deswelling of the dense regions so that their size decreases, while the extent of concentration fluctuations increases (Fig. 5). Since the interstices between the dense regions are highly diluted, the network chains in these regions are in an extended conformation. Thus, swelling shifts these chains in the non-Gaussian regime, even at a gel state just after their preparation.

In conclusion, this report introduces a novel concept to design soft gels that stiffen upon swelling in good solvents.

Acknowledgements. We express our sincere thanks to Ms. Handan Cerid for the light scattering measurements.

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