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Elasticity of poly(acrylamide) gel beads

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Summary

The elastic behavior of swollen ionic poly(acrylamide) (PAAm) gel beads was investigated as a function of the bead diameter. For this purpose, an experimental setup was designed to measure the modulus of hydrogel beads. An inverse suspension polymerization technique was used to obtain spherical beads of sizes 3 to 11 mm. It was observed that the effective crosslink density of PAAm gel beads produced in the same synthesis batch increases with increasing bead diameter, which was attributed to the inverse suspension polymerization condition.

Introduction

Hydrophilic gels called hydrogels are important materials of both fundamental and technological interest. Hydrogels in the form of spherical beads have attracted attention as carrier matrices in a wide variety of medical and biological applications, such as affinity chromatography, immobilization technologies and drug delivery systems. Although significant progress has been made towards understanding of the formation – structure – properties relationships in polymer hydrogels, much less has been published about their structural characterization in the form of beads.

Mechanical measurements on gels provide information on their molecular characteristics such as the degree of crosslinking, molecular weight of the network chains, etc. Since tension tests cannot be applied to highly swollen gels due to fragility at the clamps, compression tests, in general, are preferable. Compression tests have been performed mainly on gel samples in the form of rods. For uniaxial compression of a cylindrical gel sample, the statistical theories of rubber elasticity yield for Gaussian chains an equation of the form [1,2]:

$$f = G\left(\alpha - \alpha^{-2}\right) \tag{1}$$

where f is the stress, α is the corresponding deformation ratio (deformed length/initial length) and G is the elastic modulus of the sample.

In contrast to a cylindrical gel sample, the interpretation of the compression test data of a spherical gel particle is complicated. This is due to the significant variation of the contact area between the wall and the originally spherical gel during deformation. For a sphere with a constant volume during deformation, Hertz derived the following equation for small deformation ranges [3-7]:

$$F = \frac{4}{3} G D_0^{0.5} \Delta D^{1.5} \quad (2)$$

where F is the force and ΔD is the deformation, $\Delta D = D_0 - D$, D_0 and D are the initial undeformed and deformed diameters of gel sample, respectively. The Hertz theory (eq. (2)) considers the contact deformation of elastic spheres under normal loads in the absence of adhesion and friction. Johnson, Kendall, and Roberts developed a model that included the effect of adhesion force on the deformation of an elastic sphere [8]. They demonstrated the importance of including surface adhesive forces in describing the contact mechanical behavior of spheres at very low loads. Only a few works have been reported on the mechanical measurements of individual gel beads. Knaebel et al presented an experimental device for measuring the modulus of poly(acrylic acid) gel beads [4]. They used eq. (2) to calculate the modulus of a series of gels of various swelling ratios. Tiihonen reported the effect of the solvent composition on the elasticity of ion-exchange resin beads [9]. Inci et al. developed an equation for the elasticity of gel beads under large compressive deformation [10].

In this work, we investigated the elastic behavior of swollen ionic poly(acrylamide) (PAAm) gel beads. For this purpose, an experimental setup was designed and a data treatment procedure was developed to calculate the modulus of hydrogel beads. PAAm beads were prepared by free-radical crosslinking copolymerization of acrylamide (AAm) with the sodium salt of 2-acrylamido-2-methylpropane sulfonic acid (AMPS) using N,N'-methylene(bis)acrylamide (BAAm) as a crosslinker. An inverse suspension polymerization technique was used to obtain spherical beads of sizes 3 to 11 mm. As will be seen below, we observed that the effective crosslink density of PAAm gel beads produced in the same synthesis batch varies strongly depending on the diameter of the beads. It must be noted that we only measured the macroscopic differences in the elastic behavior between the gel beads and not the inhomogeneity within the beads.

Experimental

Materials

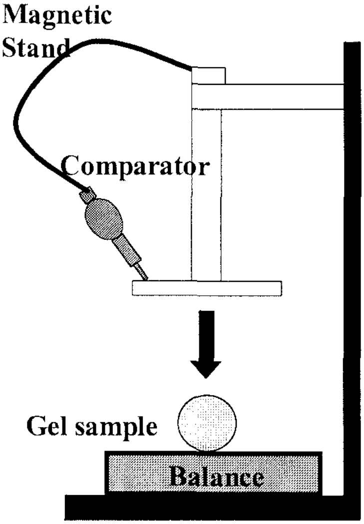
The monomer AAm (Merck) was crystallized from an acetone / ethanol mixture (70/30 by volume) below 30 °C . The ionic comonomer 2-acrylamido-2-methylpropane sulfonic acid was crystallized from boiling methanol. It was neutralized with NaOH and a stock solution was prepared containing 0.9728 M AMPS. The crosslinker BAAm, the initiator ammonium persulfate (APS) and the accelerator N,N,N',N'-tetramethylenediamine (TEMED) were obtained from Merck and were used without further purifications. Distilled and deionized water was used for the experiments.

Synthesis of PAAm gel beads

Clean PAAm gel beads were prepared by inverse suspension polymerization technique without using an external emulsifier. Paraffin oil was used as the water-insoluble continuous phase [11,12]. An aqueous monomer solution containing AAm, AMPS, BAAm, and APS was used as the water phase. The synthesis parameters were fixed as follows:

Initial monomer concentration in the aqueous phase = 9.6 w/v % (0.714 M)
Crosslinker ratio = 1 mol BAAm / 84 mol AAm + AMPS
Ionic group content (x_i) = 0.400 mol AMPS / mol AAm + AMPS
Aqueous phase / continuous phase = 1 / 10 (by volume)

The reactions were conducted in a 500 mL round-bottom, four-neck reactor, fitted with a mechanical stirrer, nitrogen inlet, condenser, and pipette outlet. 200 mL of paraffin oil were first introduced to the reactor and stirred at 100 rpm under nitrogen atmosphere at 24^0C. Then, 20 mL of an aqueous monomer solution of AAm (0.6018 g), BAAm (0.0260 g), APS (0.0410 g) and AMPS stock solution (5.8 mL) were transferred into the reactor. After 1 min, TEMED (0.12 ml.) was added to the mixture to initiate the polymerization. The reactions proceeded for 3 h at 24^0C. At the end of the polymerization, the gel beads were removed from the oil phase, washed several times with acetone and then dried in a vacuum at room temperature. Thereafter, they were placed in an excess of water and water was replaced many times. The diameter of PAAm gel beads in the swollen state ranged from 0.2 to 1 cm. The gel beads after equilibrium swelling were subjected to the elasticity measurements. It must be noted that the equilibrium swelling ratios of the beads were not measured due to the deformation of the beads during their drying.



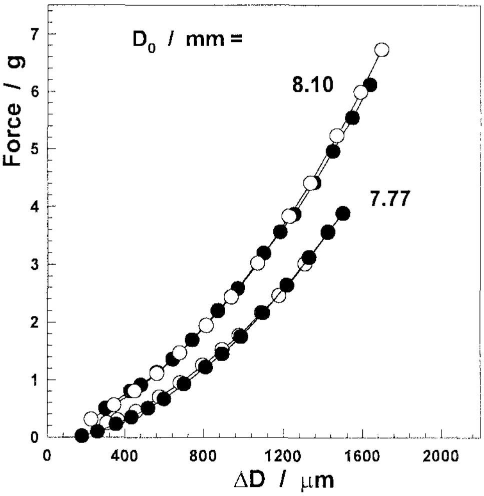


Fig. 1 (left): Uniaxial compression apparatus for measuring stress-strain data on gel beads.

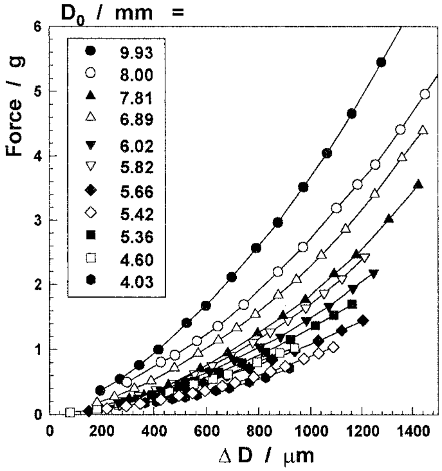
Fig. 2 (right): Force vs. deformation *ΔD* plots of two beads of different diameters. First run (●), second run (○).

Mechanical Measurements

Uniaxial compression measurements were performed on individual PAAm beads in their swollen states. All the mechanical measurements were conducted in a thermostated room of 24 ± 0.2 ^{0}C. The key parts of the apparatus used are shown in Figure 1.

Briefly, a gel bead of 3 to 11mm in diameter was placed on a digital balance. A load was transmitted vertically to the gel through a road fitted with a PTFE end-plate. The force acting on the gel was calculated from the reading of the balance m as $F = m\ g$, where g is the gravitational acceleration, ($g = 9.803\ m.s^{-2}$). The resulting deformation ΔD was measured using a digital comparator (IDC type Digimatic Indicator 543-262, Mitutoyo Co.), which was sensitive to displacements of 10^{-3} mm. The force and the resulting deformation were recorded after 20 sec of relaxation. The measurements were conducted up to about 20 % compression.

We first conducted the compression measurements on individual gel beads immersed in a large excess of water. However, no reproducible results were obtained from these measurements, probably due to the motion of the bead during compression. Measurements conducted outside of the water phase gave reproducible results. For example, Figure 2 shows force – deformation ΔD plots of two beads of different sizes. The filled symbols are the results from the first run. After the measurements, the beads were immersed in water and after two weeks, the measurements were repeated. These results are shown by the open symbols. It is seen that the two processes yield almost identical curves. The weight loss of single beads during the measurements due to water evaporation or due to the applied force was found to be negligible. This was achieved by keeping the measurement time as short as possible. One measurement took only less than 5 minutes involving 10 to 15 data points.



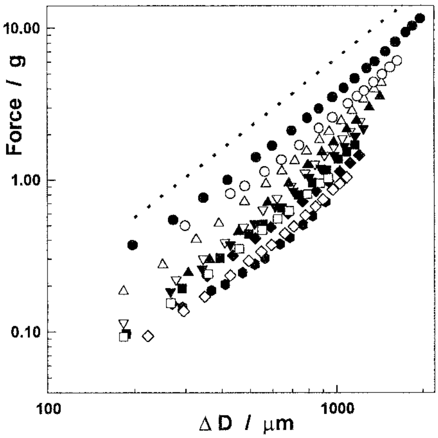


Fig. 3 (left): Force F (g) versus deformation ΔD (μm) plots of a series of beads of various original diameters D_0 indicated in the figure.

Fig. 4 (right): Double-logarithmic plot of the force F against the deformation ΔD. Experimental data are shown by symbols. The dotted curve represents the prediction of eq. (2) with a scaling parameter of 1.5.

Results and discussion

Elasticity measurements

The swollen ionic PAAm gel beads were compressed as described in Figure 1. All the gel beads subjected to the elasticity measurements were produced in the same inverse suspension polymerization batch with a crosslinker ratio 1/84. The deformation in the spheres was less than 20 % of their initial diameter. Figure 3 shows force F (g) versus deformation ΔD (μm) plots of a series of beads of various original diameters D_0. It is seen that the force is a non-linear function of the resulting deformation. Figure 3 also shows that the larger the bead diameter, the larger the force required obtaining a given degree of deformation.

According to eq. (2), a scaling parameter of 1.5 between the force acting on a sphere and the resulting deformation is expected. In order to check this exponent, we conducted measurements using 25 gel beads of various sizes between $D_0 = 4$ to 10 mm. Figure 4 shows a double-logarithmic plot of the force F against the deformation ΔD. Experimental data are shown by symbols. The dotted curve in the figure represents the prediction of eq. (2) with a scaling parameter of 1.5. An average slope of 1.55 ± 0.10 was found from the experiments indicating that eq. (2) works well. Eq. (2) also indicates that (3/4) $F/D_0^{0.5}$ vs. $\Delta D^{1.5}$ plots should be linear for a given bead, with a slope equals to its elastic modulus. Figure 5 shows such a plot. A discrepancy from the linear relationship is obvious at small compressions, which was observed in all gel beads studied. This deviation from theory can be attributed to the imperfect geometry of the surface of the sample, which decreases the contact area between the PTFE plate and the sample at low compression, and results in relatively high deformations at low stresses. Such deviations were also observed if the elasticity measurements were conducted using cylindrical gel samples [13,14]. In order to correct this imperfection, the isotherm was re-drawn by discarding the data at very low strains. The linear portion of the curve was fitted to the equation

$$F = \frac{4}{3} G (D_0 - x)^{0.5} (\Delta D - x)^{1.5} \tag{3}$$

with x and G as fit parameters, where x is the thickness of the imperfection. The data corrected in this manner are also shown in Figure 5 as open symbols. This initial slope correction resulted in an increase of the uncorrected moduli data of about 600 ± 100 Pa.

Crosslink density of gel beads

Figure 6 shows stress- strain data for a series of beads of various diameters in the form of Hertz plots. The slopes of such plots, i.e., the elastic moduli of the gel beads are shown in Figure 7 plotted against the bead diameter. It is seen that the modulus increases with increasing bead diameter.

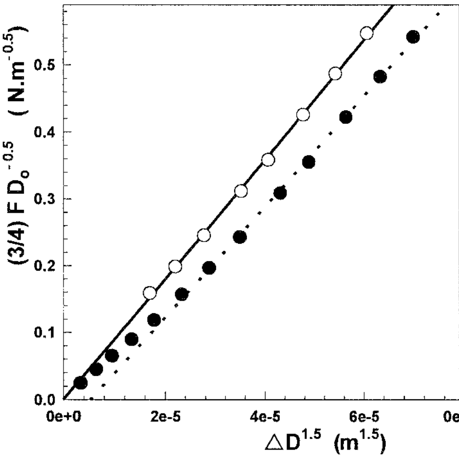
For a homogeneous phantom network of Gaussian chains, the elastic modulus of gels G relates to the network crosslink density by [1]:

$$G = \frac{\rho}{2\overline{M}_c} RT \left(v_2^0\right)^{2/3} \left(v_2\right)^{1/3} \tag{4}$$

where ρ is the polymer density, v_2 and v_2^0 are the polymer volume fractions after equilibrium swelling and after gel preparation, respectively, and $\overline{M}_c$ is the molecular weight of the network chains. Moreover, the crosslink density relates to the equilibrium swelling ratio of an ionic phantom network of Gaussian chains by an equation of the form [1]:

$$\ln(1-v_2)+v_2+\chi v_2^{\,2}+\frac{\rho}{2\overline{M}_c}V_1 v_2^{\,1/3}\left(v_2^0\right)^{2/3}-f v_2=0 \tag{5}$$

where χ is the polymer–solvent interaction parameter, V_1 is the molar volume of solvent and f is the charge density of the network.



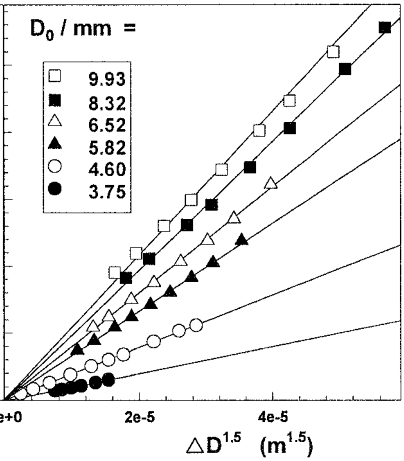


Fig. 5 (left): Typical stress-strain data for a PAAm gel bead of initial diameter D_0 = 8.32 mm. (●) Uncorrected data, (○) corrected data.

Fig. 6 (right): Stress-strain data for PAAm gel beads of various initial diameters D_0.

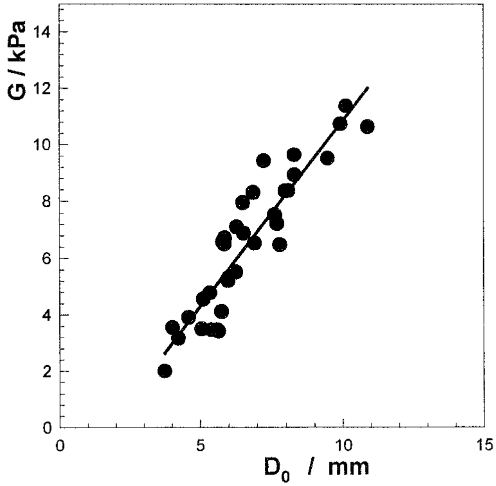


Fig. 7: Elastic moduli *G* of PAAm gel beads shown as a function of their initial diameters D_0.

Eqs. (4) and (5) were used to calculate the molecular weight of the network chains $\overline{M}_c$ and the equilibrium polymer volume fraction v_2. For these calculations, v_2^0 value was estimated from the initial molar concentration of the monomers C_0 as $v_2^0 = 10^{-3}\, C_0\, \overline{V}_r$, where $\overline{V}_r$ is the average molar volume of the polymer repeat unit [15]. The charge density f was calculated using the equation $f = x_i\, V_1 / \overline{V}_r$ where x_i is the mole fraction of AMPS in the monomer mixture [16]. The following values of parameters were used: ρ = 1.35 g/mL, V_1 = 18 mL/mol, $\overline{V}_r$ = 99.4 mL/mol, v_2^0 = 0.071, f = 0.0724, and χ = 0.48 [17, 18]. The results of calculations are collected in Figure 8 as the dependences of v_2 and $\overline{M}_c$ on the bead diameter D_0. The polymer volume fraction in the equilibrium swollen gel v_2 increases and the molecular weight of the network chains $\overline{M}_c$ decreases as the bead diameter increases. Thus, the beads produced in the same batch absorbs the swelling agent (water) heterogeneously, that is, in swollen state, small beads are more diluted than the large beads.

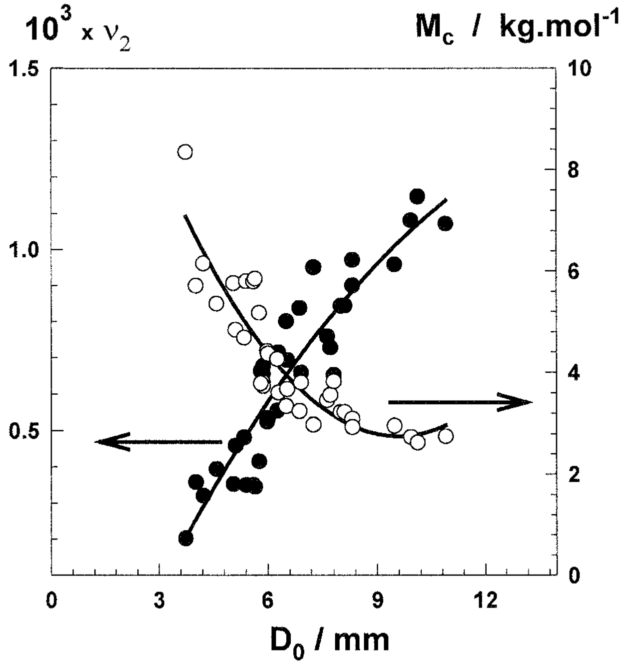


Fig. 8: The polymer volume fraction in the equilibrium swollen gel v_2 (filled symbols) and the molecular weight of the network chains $\overline{M}_c$ (open symbols) shown as a function of the diameter D_0 of PAAm gel beads.

Such a size dependent variation of the crosslink density of hydrogel beads was not reported before. However, for crosslinked poly(2-hydroxy ethyl methacrylate) gels obtained by suspension polymerization, it was observed that the swelling ratio of the beads decreases with increasing bead diameter, which is in accord with our finding [19]. More recently, in cylindrical PAAm gel samples, it was reported that the elastic modulus of the gel depends on the location, at which the mechanical measurements are carried out [20]. The modulus increases with increasing distance from the bottom of the gel rod.

We propose that the size dependent crosslink density of the gel beads is connected with the inverse suspension polymerization condition. During the inverse suspension polymerization, the reactions at the surface layer of the monomer droplets are expected to slow down due to the contact of this region with the continuous oil phase. This will reduce the crosslinking density of the surface layer of the resulting gel beads. Since decreasing size of the monomer droplets increases surface-to-volume ratio of the final gel beads, the smaller the bead diameter, the smaller its average crosslink density or the higher its swelling capacity.

In concluding, an experimental setup was designed to measure the modulus of hydrogel beads. It was observed that the effective crosslink density of ionic PAAm gel beads produced in the same synthesis batch increases with increasing bead diameter, which was attributed to the inverse suspension polymerization condition.

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