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Effect of initial monomer concentration on the equilibrium swelling and elasticity of hydrogels

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Abstract

The linear swelling ratio α and the effective network chain length N of a series of poly(*N*,*N*-dimethylacrylamide) (PDMAAm) hydrogels were investigated as a function of the gel preparation concentration v_2^0. PDMAAm hydrogels were prepared at a fixed cross-linker ratio but at various initial monomer concentrations. It was found that α is not a monotonic function of v_2^0. As v_2^0 is increased, α first decreases up to about $v_2^0 = 0.10$ and remains constant in a narrow range of v_2^0, but then it increases continuously. The v_2^0-dependence of α is due to the variation of the network chain length N depending on the gel preparation concentration. In the range of v_2^0 below 0.1, N follows the scaling relationship $N \approx \left(v_2^0\right)^{-2}$, while at higher concentrations, N varies only slightly with v_2^0. The increase of α with N obeys the relation $\alpha \approx \left(v_2^0 N\right)^{1/5}$, as predicted by the Flory–Rehner theory.

Keywords: Swelling; Elasticity; Hydrogels; Gel preparation concentration; Poly(*N*,*N*-dimethylacrylamide)

1. Introduction

Hydrogels are cross-linked materials absorbing large quantities of water without dissolving. Investigations of the swelling behavior of acrylamide (AAm)-based hydrogels have received considerable attention in the last four decades. These hydrogels are prepared by free-radical cross-linking copolymerization of AAm monomer with a small amount of a hydrophilic cross-linker, e.g., *N*,*N'*-methylenebis(acrylamide) (BAAm). Since both AAm and BAAm are solid at the usual polymerization temperature, it is necessary to carry out the cross-linking reactions in an aqueous solution of the monomers.

Several studies showed that the hydrogel structure and thus, the hydrogel properties strongly depend on the initial monomer concentration of the reaction solution in which the polymer network is formed [1–11]. Thus, the description of a hydrogel structure requires not only information about the present state of gel, but also information about its history, i.e., about the state of the gel preparation. The state of gel preparation is usually given in terms of the polymer network concentration just after the gel preparation v_2^0. Decreasing v_2^0 causes the polymer chains to disentangle so that the network formed in

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a dilute solution can swell highly when exposed to a good solvent. On the other, decreasing v_2^0 increases the probability of intramolecular cross-linking reactions during polymerization, so that a large fraction of the cross-linker is lost in ineffective cross-links [12,13]. As a result, the network structure formed becomes increasingly loose as the degree of dilution increases. No continuous network is formed above a critical amount of solvent [12].

The equilibrium swelling of gels is often described in terms of the Flory–Rehner theory, in which the swelling equilibrium is determined by a competition between the volume interactions of segments and the gel rubber-like elasticity [14]. According to the theory of rubber elasticity of Gaussian chains, the free energy of elastic deformation ΔG_{el} scales with the deformation ratio as [14,15]:

$$\Delta G_{\mathrm{el}} \approx N^{-1}\alpha^2 \tag{1}$$

where N is the number of segments between two successive cross-links, i.e., the network chain length, and α is the linear deformation ratio relative to the after preparation state of gel. On the other hand, the free energy of volume interactions ΔG_{int} scales with α as [14,16,17]:

$$\Delta G_{\mathrm{int}} \approx B v_2^0/\alpha^3 + 2C\left(v_2^0/\alpha^3\right)^2 \tag{2}$$

where B and C are the second and third virial coefficients, respectively. Balancing the two opposite free energy contributions represented by ΔG_{el} and ΔG_{int} by minimizing their sum with respect to α, one obtains [17]:

$$\alpha^5 = B v_2^0 N + 2C\left(v_2^0\right)^2 N/\alpha^3 \tag{3}$$

For highly swollen gels in a good solvent, since $\alpha \gg 1$, $B > 0$, and $C \cong 0$, Eq. (3) becomes

$$\alpha \approx \left(v_2^0 N\right)^{1/5} \tag{3a}$$

which indicates, for a fixed value of v_2^0, a scaling parameter of 0.2 between the linear deformation ratio of gels and the network chain length. Under θ-conditions where the second virial coefficient vanishes, Eq. (3) reduces to Eq. (3b) and the scaling parameter becomes 0.125:

$$\alpha \approx \left(v_2^0\right)^{1/4} N^{1/8} \tag{3b}$$

Baker et al. [5] studied a series of poly(acrylamide) (PAAm) gels formed at a fixed cross-linker ratio but at varying v_2^0 between 0.11 and 0.30. They found that the degree of swelling decreases while the elastic modulus increases with increasing v_2^0. Shibayama et al. [18] observed that the linear swelling ratio α of swollen poly(N-isopropylacrylamide) (PNIPA) hydrogels is independent of the initial monomer concentration in the range of $v_2^0 = 0.03$–0.08. The invariance of α with v_2^0 was explained with chain entanglements acting as additional cross-link points, whose number increases with increasing concentration. However, our experimental data with poly(N,N-dimethylacrylamide) (PDMAAm) as well as with poly(acrylic acid) gels showed that, α increases linearly with increasing monomer concentration in the range of $v_2^0 = 0.1$–1 [19,20]. Bromberg et al. [21] studied systematically the equilibrium swelling degree of PDMAAm gels formed at various initial monomer concentrations. Assuming that the network chain length N is inversely proportional to the cross-linker ratio, they derived a scaling parameter between α and N, which deviates from that predicted by Eq. (3a). Furukawa [8] presented an equation predicting the equilibrium swelling of gels depending on the initial monomer concentration. However, there are six adjustable parameters in the Furukawa's equation so that it does not allow a definitive conclusion regarding the suitability of the model. Kinetic theories connecting the initial conditions of the gel forming systems to the final gel properties also require a large number of kinetic parameters [22].

In most of the experimental works testing the validity of the theories, however, the network chain length N is taken as an adjustable parameter or, N is assumed to be inversely proportional to the cross-linker concentration. Thus, fitting the existing theories only to the swelling data of hydrogels does not allow definitive conclusions regarding the suitability of the theories. Such conclusions are more appropriately obtained from independent swelling, elasticity, and gravimetric measurements, leading to the experimental values of α, N, and v_2^0, respectively.

In this note, we generalize the discussion about the monomer concentration dependence of the linear swelling ratio α and demonstrate that α is not a monotonic function of v_2^0. Further, we show that the scaling relation given by Eq. (3a) is valid for non-ionic gels formed over the entire range of the monomer concentration. We prepared a series of gels based on N,N-dimethylacrylamide (DMAAm) monomer at various polymer network concentrations v_2^0 but at a fixed chemical cross-link density. The selection of DMAAm as a monomer is due to the fact that it is a liquid at room temperature and is fully miscible with water. Thus, PDMAAm hydrogels could be prepared in aqueous solutions over the whole range v_2^0. PDMAAm hydrogels were characterized by swelling tests as well as by the elasticity tests at a state just after their preparation. It should be noted that, in our previous work, the lower limit of v_2^0 of PDMAAm hydrogels studied was 0.10 [19], whereas in the present work it is 0.03. As will be seen below, hydrogels formed in dilute solutions below $v_2^0 = 0.10$ exhibit different swelling behavior compared to those formed at higher polymer concentrations.

2. Experimental

2.1. Materials

N,*N*-Dimethylacrylamide (DMAAm, Fluka), *N*,*N*′-methylenebis(acrylamide) (BAAm, Merck), ammonium persulfate (APS, Merck), and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) were used as received. PDMAAm gels were prepared by free-radical cross-linking copolymerization of DMAAm and BAAm in aqueous solution at 5 °C in the presence of 3.51 mM APS initiator and 0.25 v/v % TEMED accelerator. The cross-linker ratio X (mole ratio of the cross-linker BAAm to the monomer DMAAm) was fixed at 1/83. The details about the preparation of the hydrogels have been published elsewhere [19].

2.2. Characterization

The degree of dilution of the networks after their preparation was denoted by v_2^0, the volume fraction of cross-linked polymer after the gel preparation. In order to determine v_2^0, PDMAAm hydrogels after preparation were first swollen in water to extract nonpolymerizable or soluble components and then dried to constant mass. v_2^0 was calculated as:

$$v_2^0 = \left[1 + \frac{(q_F - 1)\rho}{d_1}\right]^{-1} \qquad (4)$$

where q_F is the dilution degree after the gel preparation (mass of gel after preparation/mass of dried gel), ρ is the polymer density (1.21 g/ml) and d_1 is the solvent density (1.00 g/ml).

Equilibrium swelling measurements of the hydrogels in the form of rods of 4 mm in diameter were carried out in 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 linear swelling ratio with respect to the state of preparation, α, as determined by measuring the diameter of the hydrogel samples after equilibrium swelling in water D and after synthesis D_0 by a calibrated digital compass (Mitutoyo Digimatic Caliper, Series 500, resolution: 0.01 mm). α as calculated as:

$$\alpha = D/D_0 \qquad (5)$$

Uniaxial compression measurements were performed on gel samples 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 [23]. The elastic modulus G was determined from the slope of linear dependence $f = G(\lambda - \lambda^{-2})$, 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). For a network of Gaussian chains, the elastic modulus of gels just after their preparation, G_0, is related to the effective cross-link density v_e by [14,15]:

$$G_0 = A v_e R T v_2^0 \qquad (6)$$

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 cross-links, R and T are in their usual meanings. The network chain length N is related to the effective cross-link density v_e by:

$$N = (v_e V_1)^{-1} \qquad (7)$$

where V_1 is the molar volume of segment, which is taken as the molar volume of water (18 ml/mol). Since the gels prepared in this study were highly swollen, we used phantom network model ($\phi = 4$) to calculate the network chain length of PDMAAm hydrogels.

3. Results and discussion

PDMAAm hydrogels with at a fixed chemical cross-link density ($X = 1/83$) were prepared at various polymer concentrations ranging from dilute to concentrated solutions. In Fig. 1, the filled symbols show the linear swelling ratio α of the hydrogels in water plotted as a function of the cross-linked polymer concentration at the gel preparation v_2^0. For

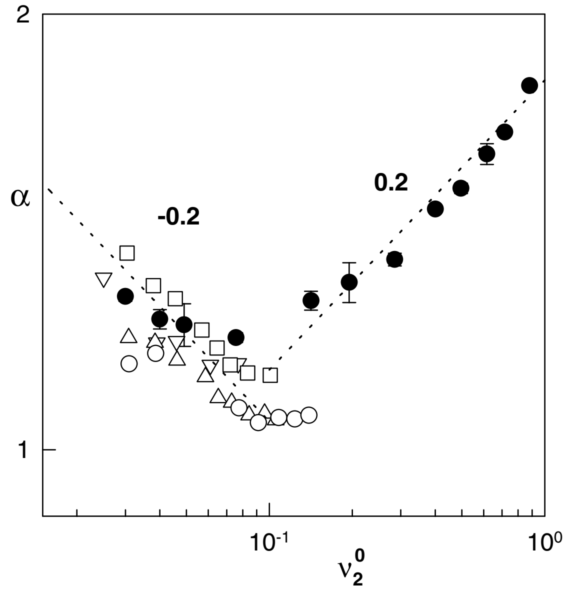

Fig. 1. Linear swelling ratio α of PDMAAm hydrogels with $X = 1/83$ (filled symbols) and of PAAm hydrogels (open symbols) shown as a function of ν_2^0. Data for PAAm hydrogels were taken from the literature [24,25]. $X = 1/50$ (○), 1/61.5 (△), 1/66 (▽), and 1/100 (□). The dotted lines were calculated using Eqs. (11a) and (11b). The corresponding slopes are shown.

comparison, swelling data reported for PAAm hydrogels of cross-linker ratios X varying between 1/50 and 1/100 are also shown in figure by the open symbols [24,25]. It is seen that α is not a monotonic function of the polymer concentration ν_2^0. Depending on the initial monomer concentration, the dependence of α on ν_2^0 exhibits three different regimes:

1. For $\nu_2^0 < 0.10$, α is a decreasing function of ν_2^0. Thus, in this regime, increasing the initial monomer concentration results in decreased expansion ratios of gels with respect to after preparation state.
2. In a rather narrow range of ν_2^0 around 0.10, α is ν_2^0 independent. The constancy of α in this regime is in agreement with the observation of Shibayama et al. [18] on PNIPA gels.
3. For $\nu_2^0 > 0.10$, α increases continuously with increasing ν_2^0 up to the bulk polymerization condition. This regime was also observed before in PDMAAm hydrogels [19].

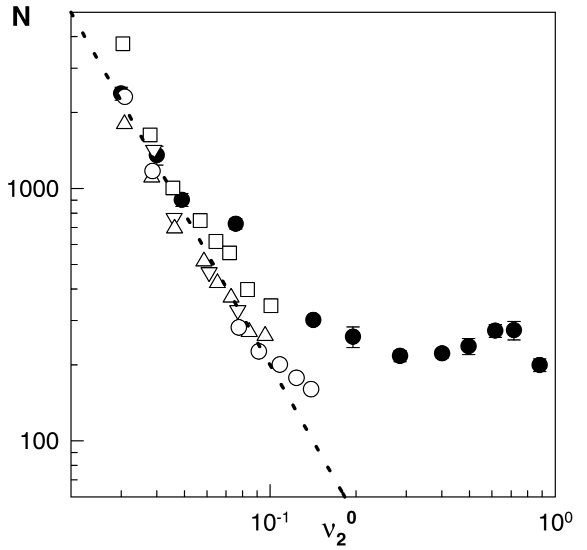

Fig. 2. Network chain length N of PDMAAm hydrogels with $X = 1/83$ (filled symbols) and of PAAm hydrogels (open symbols) shown as a function of ν_2^0. Data for PAAm hydrogels were taken from the literature [24,25]. $X = 1/50$ (○), 1/61.5 (△), 1/66 (▽), and 1/100 (□). The dotted line was calculated using Eq. (9).

In Fig. 2, the filled symbols show the effective network chain length N of PDMAAm hydrogels plotted as a function of ν_2^0. As ν_2^0 is increased, N decreases first rapidly up to about $\nu_2^0 = 0.3$, but then, N changes only slightly with ν_2^0. The slight variation of N in this high concentration regime is due to the reducing reactivity of pendant vinyl groups during cross-linking as well as due to the increasing extent of chain entanglements [19]. Literature data reported for PAAm gels are also shown in the figure by the open symbols [24,25]. It is seen that both gels exhibit similar behavior in the range of ν_2^0 below 0.3. Thus, the effective cross-link density of hydrogels is very sensitive to the initial monomer concentration if ν_2^0 is below 0.3. One may explain this behavior with decreasing probability of cyclization as the monomer concentration during polymerization is increased.

In order to quantify the above results, we consider the gel growth process during polymerization as a set of random walks of the growing radicals, as proposed by Bromberg et al. [21]. The process of gel growth is schematically illustrated in Fig. 3. The random walk of the propagating radical, shown in the figure by the solid curve, occurs between two successive hits of the radical center with the other kinetic chains, i.e., between A and B, B and C, etc. Each random walk is succession of g steps, during which the radical adds the monomer AAm, the cross-linker BAAm and involves cyclization reactions with the pendant vinyl groups located on the

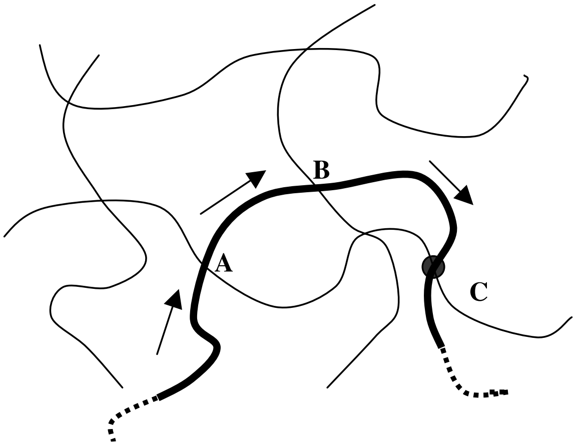

Fig. 3. Gel growth during free-radical cross-linking copolymerization. The random walk of a propagating radical is shown by the solid curve. The growing chain hits another chains at A, B, and C. The dot represents a cross-link point.

same chain. Since in a random walk the path length R (the end-to-end distance) of a chain after g steps is $g^{1/2}$, the polymer segments concentration v_2^0 during the cross-linking copolymerization scales with $g/g^{3/2} = g^{-1/2}$, or [21]:

$$g \approx \left(v_2^0\right)^{-2} \tag{8}$$

After g steps, i.e., at point A, B, or C, the growing chain will hit another chains. The probability p that the radical end will meet a cross-linker unit on another chain is proportional to the cross-linker concentration, i.e., to the cross-linker ratio X. After $1/p$ hits, the growing chain will succeed to form an effective cross-link, for example at point C in Fig. 3. The network chain length N will then be equal to:

$$N = \frac{g}{p} = \left(v_2^0\right)^{-2} X^{-1} \tag{9}$$

which indicates a scaling parameter of −2 between the network chain length of gels formed at a fixed cross-linker ratio and the polymer concentration v_2^0. The dotted line in Fig. 2 represents N versus v_2^0 dependence predicted by Eq. (9). It is seen that the theoretical line is in good agreement with the experimental data of gels formed below $v_2^0 = 0.1$. Eq. (9) is valid if the number of steps g per random walk of the growing radical is large enough and if the chain is Gaussian. For larger values of v_2^0, g becomes too small due to the high polymer concentration in the reaction system, where the chains during polymerization are strongly entangled. In this case, the end-to-end distance R, i.e., the path length of a growing chain between two successive collisions with the other chains cannot be described by the Gaussian statistics. For example, assuming that R scales with g as $R \sim g^{1/3}$ instead of it $R \sim g^{1/2}$, N becomes independent of v_2^0. The relation $R \sim g^{1/3}$ means that the chain portion between two successive hits during polymerization is compressed very strongly or, in other words, it is collapsed [17]. As a consequence, N is v_2^0 invariant because the polymer chains represent approximately homogeneous spheres. Moreover, in dilute reaction solutions, the path length of the growing chain becomes very long so that the radical end would have an enhanced probability to involve cyclization reactions. One may expect that if $v_2^0 \ll 1$, the radical end cannot make a favorable collision with the pendant vinyl group on the other chains so that no macroscopic network forms after the reaction.

In Fig. 4, the linear expansion ratio α of both PDMAAm and PAAm hydrogels is plotted as a function of the product Nv_2^0 on logarithmic coordinates. The solid curve in the figure is the best fitting curve to the experimental data of the hydrogels. It can be seen that while both the initial monomer concentration and the cross-linker ratio vary greatly, all

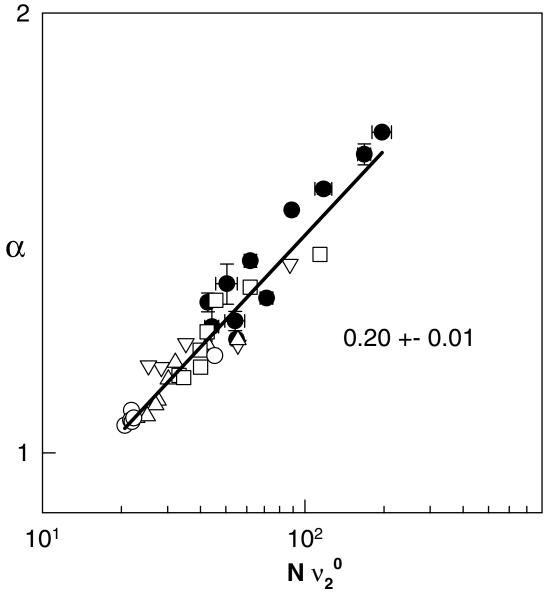

Fig. 4. Linear swelling ratio α of PDMAAm hydrogels with $X = 1/83$ (filled symbols) and of PAAm hydrogels (open symbols) shown as a function of Nv_2^0. Data for PAAm hydrogels were taken from the literature [24,25]. $X = 1/50$ (○), 1/61.5 (△), 1/66 (▽), and 1/100 (□). The solid line was calculated using Eq. (3a). The corresponding slope is shown.

the data of the gels fall onto a single curve with a scaling parameter 0.20 ± 0.01, as predicted by Eq. (3a). It should be noted that α versus N plot for each set of gel is non-linear, indicating the importance of the gel preparation concentration in the treatment of the swelling and the elasticity behavior of hydrogels. Using the elasticity data of PDMAAm hydrogels, we can now explain the monomer concentration dependence of the swelling ratio α. Differentiating Eq. (3a) with respect to v_2^0, we obtain:

$$\frac{\mathrm{d}\ln\alpha}{\mathrm{d}\ln v_2^0} \approx \frac{1}{5} + \frac{1}{5}\frac{\mathrm{d}\ln N}{\mathrm{d}v_2^0} \tag{10}$$

Since $N \approx \left(v_2^0\right)^{-2}$ at low polymer concentrations, we arrive

$$\alpha \approx \left(v_2^0\right)^{-1/5} \quad (\text{for } v_2^0 < 0.1) \tag{11a}$$

while at high polymer concentrations, since N is nearly v_2^0 independent, we obtain

$$\alpha \approx \left(v_2^0\right)^{1/5} \quad (\text{for } v_2^0 > 0.1) \tag{11b}$$

The dotted lines in Fig. 1 represent the scaling parameters −0.2 and 0.2 predicted by Eqs. (11a) and (11b), respectively. It is seen that the dotted lines agree well with the experimental swelling behavior of the hydrogels.

4. Conclusions

The equilibrium swelling degrees and the elasticity of PDMAAm hydrogels were studied at various gel preparation concentrations v_2^0. The increase of the linear swelling ratio α with the network chain length N follows the relationship $\alpha \approx \left(v_2^0 N\right)^{1/5}$, as predicted by the Flory–Rehner theory. In the range of v_2^0 below 0.1, N varies depending on the gel preparation concentration as $N \approx \left(v_2^0\right)^{-2}$, while at higher concentrations, N varies only slightly with v_2^0. The results can be explained with the concentration dependence of the probability of cross-link formation during the free-radical cross-linking reactions. The linear swelling ratio α first decreases but then increases as the gel preparation concentration is increased. The v_2^0-dependence of α is due to the variation of the network chain length N depending on the gel preparation concentration.

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