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The elastic behaviour of weakly ionic gels

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Summary

The elastic modulus of polyacrylamide-acrylic acid hydrogels is studied in a wide range of swelling degrees. The modulus does not follow the concentration dependence predicted by the rubber elasticity theory. At low swelling degrees this can be attributed to the constrained state (non-phantom behaviour) of the network chains. The reason for the increase of modulus at high swelling degrees is seen in the finite extensibility and topological entanglements of the chains. A theory including these effects is proposed and verified by experiment.

Introduction

This work concerns the concentration dependence of the elastic modulus in polyelectrolyte gels where the presence of network-fixed ionizable groups makes possible a very large change in the swelling degree, and therefore also in the characteristics related. In spite of its importance both in science and technology, the behaviour of such gels has not been fully understood.

The widely used theory of phantom Gaussian networks [1-3] predicts the equilibrium shear modulus G to vary with the swelling degree w as $w^{-1/3}$ if the number of elastically effective chains in the network and their reference state remain unaltered. Some networks, neutral [4,5] and ionic [6,7], perfectly follow this prediction. For several systems it has been shown that the elastic modulus data also fit the power law but with the exponents differing from 1/3 [8,9]. Finally, the $G(w)$ curves with a minimum have been observed in the case of ionic polyacrylamide-based gels with rather high crosslink density [10], as well as for crosslinked cellulose ethers [11]. An increase in modulus of these gels with rising swelling degree was attributed to the finite extensibility of the network chains. However, the conclusion has not been verified by any quantitative estimates of the chain extension and non-Gaussian contribution to the modulus.

The aim of the present work is to clarify quantitatively the elastic behaviour of weakly ionic gels, and here we report our data on the equilibrium modulus of polyacrylamide-acrylic acid (PAAm-AAc) hydrogels with various low crosslink densities and ionizable group contents. We also present a theory of the elastic properties of gels which takes into consideration the

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non-phantom and non-Gaussian features of the network chains. It is verified by comparing with the data obtained and proves to agree well with experiment.

Experimental

Sample preparation: Gels were prepared by crosslinking copolymerization of acrylamide, acrylic acid (AAc), and *N,N* -methylene-bisacrylamide with AAc mole fraction of 0.047 (sample 1) and 0.196 (samples 2-5). The weight fraction of the crosslinking agent in the monomer mixture was 0.59% (for sample 1) and 0.58, 0.27, 0.15, 0.071% (for samples 2-5 respectively), total monomer concentration in aqueous solution was 0.095 g/ml. The polymerization was initiated with 1.0 g/l sodium persulfate-sodium tiosulfate (1:1) system, and proceeded i.vac. in sealed glass tubes of 5 and 10 mm in diameter at room temperature for 12 hours and then several hours at 40 °C to ensure completion of the reaction (gelation occurred in about 20 min).

Swelling and mechanical measurement: The samples were swollen for about 3 weeks in pure water and in aqueous solutions of NaCl with varying concentration, ranging from 1 X 10^{-4} to 1 M. To remove unreacted monomer and uncrosslinked polymer, as well as to ensure the gels were in equilibrium with the planed salt concentration, the solutions or water were replaced with fresh ones several times in the course of swelling. After this procedure the diameter D of the gel cylinders was measured with an Abbe comparator (Zeiss Jena) and the swelling degree was calculated according to

$$w = w^{*}(D/D^{*})^{3}$$

Here asterisk * denotes values referring to the sample state after preparation.

Deformation measurements were carried out by using the uniaxial compression technique described earlier [9] . The cylindrical specimen was compressed to a ratio λ (= l/l_{o}, where l, l_{o} ~ 1-2 cm respectively are the deformed and the initial specimen height) and the force f was determined after 30 sec of relaxation. Usually, fifteen λ_{i} and f_{i} values were measured over the range $0.7 < \lambda < 1$, and from this values the least squares estimate of the equilibrium shear modulus was calculated by using the relation

$$G = f/S_{o}(\lambda^{2} - \lambda^{-1})$$

in which S_{o} is the initial cross-section of the specimen. When measuring the weakest gels, which could not support their own weight in air, the sample was surrounded by the solution.

Results and Discussion

Like other polyelectrolyte gels, the hydrogels under study undergo a very large and reversible deswelling when increasing NaCl concentration in the outer solution (from 1 X 10^{-4} M and higher) [7], and thus we could determine their elastic modulus as a function of the equilibrium swelling degree.

Figure 1 shows the dependences of the reduced modulus ($Gw^{1/3}$) on the swelling degree for four gels with different fractions of crosslinker; the leftmost points refer to the state of the gels after preparation. Each of these curves considerably deviates from the ideal one, however there is a range of swelling degrees where the $Gw^{1/3}$ value is nearly constant in accordance with the theory of phantom Gaussian networks. The width of the range decreases with increasing crosslink density, so that the non-ideal features of the dependence observed are more pronounced in highly crosslinked gels. It is also clear that the ideal elastic behaviour can be expected for weakly crosslinked gels in a sufficiently narrow range of swelling degrees. These circumstances should be taken into consideration when comparing different data on the elastic modulus. In particular, they allow to understand the differences, pointed out in the introduction, in the data on PAAm-AAc gels [6,7,10].

Figure 1 also provides information about the effect of ionization on the mechanical properties of gels. It can be seen that the points corresponding to the samples 1 and 2 , being close in crosslink density, but quite different in AAc content, agree well with each other. This indicates that the ionization degree, and hence the electrostatic interaction of the network-fixed charges, does not play an important role in the behaviour observed. This also means that the flexibility (persistence length) of the network chains does not practically depend on the ionization degree for such weakly charged gels at least in sufficiently concentrated salt solutions.

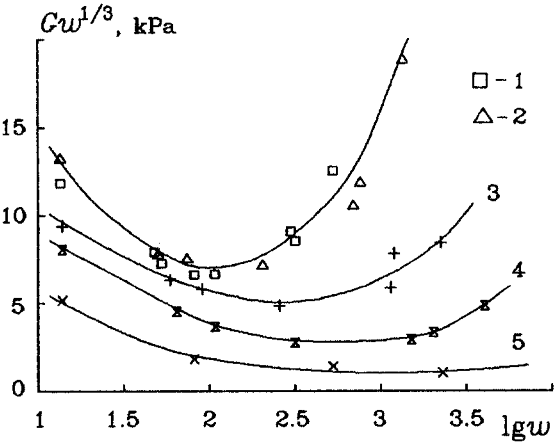

Fig.1. Plot of the reduced shear modulus of the PAAm hydrogels vs the equilibrium swelling degree in solutions of NaCl with varying concentration. The numbers indicated here and in Fig. 3 correspond to those of samples

Theoretical consideration: Two different features of the above curves have to be described: the drop of $Gw^{1/3}$ with increasing w at low swelling degrees and its rise at high w values. We suppose both of them are connected with the non-phantom nature of polymer chains, but in different ways. The former can be understood by considering that at large volume fractions of polymer each of the network chains is in a constrained state due to the presence of its neighbours. These surrounding chains form a "box" which compresses the enclosed chain. The size of the box is determined by the affinity condition and changes with swelling as the mean distance between adjacent junctions. Therefore, the spatial dimensions of the real network chain at low swelling degrees prove to be much lower than those of a phantom chain. As a result there is an additional entropy loss which has to be included in the elastic free energy of the network. This contribution (for the unit volume of gel) can be expressed [12] as

$$\Delta F_{el,compr}/RT = \phi n_c[(\lambda_x)^{-2}+(\lambda_y)^{-2}+(\lambda_z)^{-2}]/2 \qquad (1)$$

where $\phi=1/w$ is the volume fraction of polymer in the gel, λ_i is the deformation ratio of the gel in the i $(= x, y, z)$ direction with respect to the reference state, n_c is the molar concentration of elastically active chains in the dry network.

Using (1), the following expression for the shear modulus can be obtained

$$G = G_{id}[1 + (\phi/\phi_o)^{4/3}] \qquad (2)$$

in which $G_{id} = RTn_c\phi_o(\phi/\phi_o)^{1/3}$ is the modulus known from the rubber elasticity theory [1-3], ϕ_o is the volume fraction of polymer in the reference state. This equation is seen to predict the constancy of the reduced modulus at high swelling degrees ($\phi/\phi_o \ll 1$) and its rise with increasing polymer concentration. Therefore, a part of our problem is solved.

With the elastic behaviour at low and medium swelling degree being understood, we can now concentrate on the high w values and take into consideration the effect of the finite extensibility of chains. This effect has been previously discussed in the framework of the so-called Langevin approximation [1], and a relation for the gel modulus as a function of the chain extension ratio (γ) has been derived [13]. The relation, however, is restricted to rather small chain extensions ($\gamma <$ 0.5), and here we present its generalization:

$$G_L = G_{id}(L^*(\gamma)/\gamma + dL^*(\gamma)/d\gamma)/6 \qquad (3)$$

which is applicable up to $\gamma \sim 1$. In this equation L^* is the inverse Langevin function of γ which can be found numerically. Defining the γ value as the ratio of the mean-square end-to-end distance of the network chain to its length, and using the fact that in the reference state the chain obeys Gaussian statistics, we have

$$y = (\phi_0/\phi)^{1/3}(x_c/s)^{-1/2} \qquad (4)$$

Here $x_c = 1/(n_c v)$ and s respectively are the number of monomer units in the chain and in the statistical segment, v is the molar volume of the unit. Thus, the G_L value is expressed as a function of the swelling degree and the network parameters x_c, ϕ_0 and s.

Combining (3) and (2), we obtain an equation for the elastic modulus

$$G = G_{id}[(L^*/y + dL^*/dy)/6 + (\phi/\phi_0)^{4/3}] \qquad (5)$$

which includes both finite extensibility of chains and their topological repulsion at high polymer concentrations ($\phi >$ or $\sim \phi_0$). The $Gw^{1/3}$ curves calculated according to (5) are shown in Fig.2 as a function of the swelling degree for various chain parameters x_c and s. The straight lines here express the dependences for the corresponding ideal networks. As seen in Fig.2, there is a very good qualitative agreement between the theory and the experiment (Fig.1). All the features discussed above are observed. The almost ideal elastic behaviour does take place over a narrow range of swelling degrees near the minimum in the $Gw^{1/3}$ curve. For low x_c and high s values, however, even the minimal reduced modulus can be considerably large than the ideal one. This fact is worth taking into account in using the classical expression for G_{id} to determine the crosslink density from the modulus data.

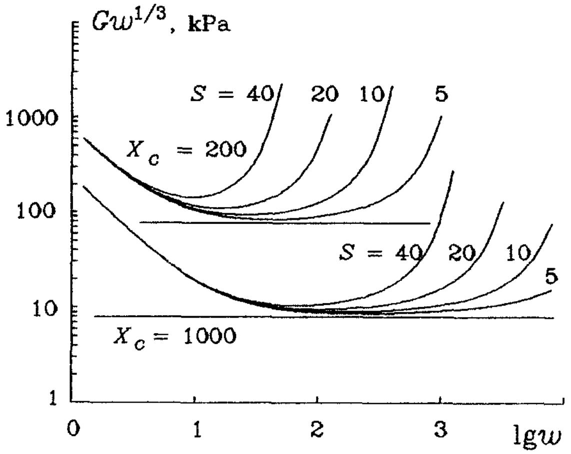

Fig.2. The reduced gel modulus plotted as a function of the swelling degree for various values of the network parameters x_c and s

Testing the theory: To test the quantitative consistency of (5) the experimental data including those of Ref.[10] were fitted to this dependence by adjusting the values of x_c, ϕ_0 and s; as a preliminary we obtained an analytical representation of function (3). The standard nonlinear regression procedure was applied to reach the point of minimum variance between the theory and the experiment. The calculated curves are confronted with the experimental data in Fig.3. For all samples the agreement is very good in the whole range of swelling degrees. Equation 5 thus describes the elastic behaviour of weakly charged ionic gels in a quantitatively correct way.

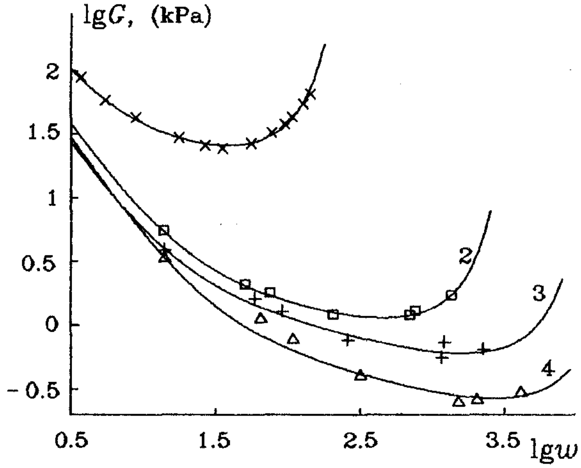

Fig.3. Dependence of the shear modulus on the swelling degree. Points: experimental data of this work (for samples 2-4) and those of Ref.[10] (X). Solid lines: theoretical curves calculated using eq.5

The network parameters estimated as a result of the fit of eq.5 are listed in Table 1. The estimates of ϕ_0 are of interest in connection with the problem of the reference state choice. As seen in Table 1, for samples 1-3 the values of ϕ_0 are close to the concentration of polymer network after preparation (ϕ_{prep} = 0.073 and 0.11 for all our samples and that of Ref.[10] respectively); in the other cases, ϕ_0 considerably differs from ϕ_{prep}. The general tendency is that the ϕ_0 value decreases with increasing x_c. This rather provides an argument for the idea that for the network prepared at high dilutions the reference state corresponds to the θ-temperature for the proper linear macromolecule, and hence $\phi_0 = k(x_c)^{-1/2}$ [14]. The k value estimated from the data of Table 1 is about 2.5. It is

Table 1. The characteristic parameters of hydrogels

Sample	x_c[1]				ϕ_0	s	β
	a	*b*	*c*	*d*			
1	180	1160	1170	1340± 70	0.064±0.008	57±7	3.3
2	190	1070	1090	1210± 40	0.064±0.004	33±2	2.5
3	400	1500	1410	1610±180	0.072±0.017	17±5	1.8
4	750	2650	2160	2030±200	0.040±0.008	23±7	2.1
5	1530	5560	3770	–	–	–	–
from [10]	40	130	190	293± 9	0.210±0.010	21±1	2.0

[1] calculated with v = 54.6 cm^3/mol from the crosslinker content in the monomer mixture (*a*), the minimal $Gw^{1/3}$ value at $\phi_0 = \phi_{prep}$ (*b*), the minimal $Gw^{1/3}$ value at $\phi_0 = 2.5(x_c)^{-1/2}$ (*c*), and the $G(w)$ curve using eq.5 (*d*)

noteworthy here that the ϕ_0 values obtained in this work, and thus also the function $\phi_0(x_c)$, evidently leave some room for speculations. However, with the detailed modulus data, eq.5 opens a good way to the reference state characterization.

The x_c values obtained by different procedures (Table 1) are worth comparing with each other. Considering the remark made in discussing Fig.2 and experimental errors, the values found when using (5) are in agreement with those estimated on the basis of the classical approach from the minimal values of $Gw^{1/3}$. All these x_c values are considerably higher than those calculated from the crosslinker content, which is in accordance with the low efficiency of gelation found previously in PAAm gels [15]. Therefore, the comparison indicates that eq.5 leads to the consistent x_c values.

The s values (Table 1) are much higher than the number of monomer units in the statistical segment known from other sources. For example, according to our calculations based on the characteristic ratio data for the linear PAAm chain [16], the s value ranges from 5.2 to 12.1; the most reliable value is 5.2. At first sight this discrepancy speaks against the theory proposed. However, it appears to be not so. The contradiction can be avoided taking into account the topological constraints, viz. the entanglements between different network chains which manifest themselves at high swelling degrees as additional crosslinks [17]. Their role can also be understood considering that for the entangled chain it is not the end-to-end distance but the length of the primitive path that determines the chain extension; this path may be defined as the shortest line between crosslinks which is equivalent in topology to the network chain [12]. Therefore, instead of γ defined above, which characterises the extension of an individual chain, we have to use a larger quantity:

$$\gamma_{new} = \mu\gamma \qquad (6)$$

Here μ > or = 1 is the ratio of the primitive path length to the mean-square end-to-end distance of chain. The parameter μ is a characteristic of gel depending on the method and conditions of gelation but independent of the swelling degree. For the gels under study the μ values calculated with s = 5.2 are given in Table 1. For all samples $\mu > 1$, and thus the gels do consist of the partially entangled coils.

The theory proposed therefore opens some new possibilities in the network structure characterization. In particular, in addition to the network density it allows to obtain a measure of the chain entanglements. It is worth mentioning that for highly ionic gels the parameter μ estimated from the *G(w)* curve can include not only a topological contribution, but also that of the electrostatic persistence length. In principle, this contribution can be considered by analogy with the work [18].

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