Swelling equilibria of ionized poly(methacrylic acid) gels in the absence of salt

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The kinetic theory of rubber elasticity for polyelectrolytes has been modified by including an effect of the electrostatic persistence length. The relations for swelling equilibria as a function of the degree of neutralization in polyelectrolyte gels are derived. We find that the volume fraction of the polymer in the swollen gel does not decrease monotonically with increasing α, but instead exhibits a minimum near $\alpha \sim 0.1$. Beyond this value of α the extent of swelling decreases with increasing degree of neutralization. The theory has been verified by measurements of the swelling behaviour of weakly crosslinked polymethacrylic acid gels as a function of varying degree of neutralization.

(Keywords: polyelectrolyte gel; swelling; degree of neutralization)

INTRODUCTION

At present, great attention is being devoted to the structure and properties of polyelectrolytes (see, for example, Reference 1). The most complicated situation arises if we want to describe the behaviour of polyelectrolyte solutions without an added electrolyte of low molecular weight, where the electrostatic repulsive forces between polyions are weakly screened, and thus relatively long range. Several years ago, de Gennes *et al.*[2] used scaling concepts to describe the concentration dependence of characteristic quantities of polyelectrolyte systems in the absence of salt. Odijk[3,4] and Skolnick and Fixman[5] introduced the idea of the electrostatic persistence length L_e to describe the concentration-dependent flexibility of the polyelectrolyte chain. The total persistence length L_t, of the chain is split up into an intrinsic part L_p, which would characterize the chain in the absence of charge interactions, and an electrostatic part L_e, which decreases with increasing polymer concentration as a consequence of counterion screening of the charges on the macromolecule. This theory made possible a more exact description of conformational changes of polyelectrolyte coils in solvents without added salt.

For the description of some properties of polyelectrolyte gels the random coil model[6,7] has been successfully used. In this model the chain is regarded as an assembly of statistical segments, the distances between which are controlled by an appropriate distribution function. Assuming that the distribution function is Gaussian, a relationship for the free energy of the electrostatic interaction of charges on the polymer chain has been derived[7]. This theory describes titration curves[8] fairly well, and to a lesser extent swelling equilibria[9,10] and the equilibrium stress–strain behaviour[10,11] of polyelectrolyte gels. The same theory was successfully used for describing a pronounced change (collapse) in the degree of swelling of polyacrylamide[12,13] and poly(*N*,*N*-diethylacrylamide) gels[14].

In this paper we have included the effect of the electrostatic persistence length in the above mentioned kinetic theory of rubber elasticity for polyelectrolytes[10] and derived relations for the swelling equilibria in polyelectrolyte gels. The theory was verified experimentally by measuring the swelling behaviour of ionized gels of polymethacrylic acid (PMA) with a very low crosslink concentration. This system was selected because of the possibility of varying the charge per unit length of the chain by varying the degree of neutralization α of the acid by means of a suitable alkali.

THEORY

We view the polyelectrolyte gel with degree of ionization i as a network of wormlike chains with bare persistence length L_p (greater than the bond length a) bearing an elementary charge q per counterion distance $A = a/i$ (also called the segmental length), immersed in solvent with dielectric permittivity ε without any low molecular weight electrolyte. The following theory is based on three major assumptions:

(1) The interaction between charges is given by Debye–Hückel theory, i.e. we have computed the electrostatic energy using a simple screened form for the

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interactions:

$$\frac{q^2}{\varepsilon r}e^{-Kr}$$

where K^{-1} (the Debye–Hückel radius due to the counterions) is given by the relation $K^2 = 4\pi Qc$. Here $Q = q^2/\varepsilon kT$ is the Bjerrum length, k is the Boltzmann constant, T is the temperature and c is concentration, defined here as number of charge units per unit volume. We can write $c = i\rho N_A v_2/M_0$ where ρ is the density of the dry polymer, N_A is the Avogadro number, v_2 is the volume fraction of polymer in the swollen gel and M_0 is the molecular weight of the monomer.

(2) According to Manning[15] and Oosawa[16], if $A < Q$ (the strong coupling limit) a sufficient number of counterions will condense on the polyion to lower the reduced coupling constant Q/A to a value of unity. The Debye–Hückel screening is caused by uncondensed counterions only.

(3) Polyelectrolyte chains are near the rod limit ($KL_t > 1$). Under this assumption the electrostatic energy of curvature equal to the total electrostatic interaction between the charged groups minus the electrostatic energy of the rod configuration can be considered to be a perturbation to the elastic energy[3–5]. As a result the elastic properties are not determined by L_p but rather by the total persistence length, $L_t = L_p + L_e$, where $L_e = Q/4K^2A^2$. In the strong coupling limit ($A \leqslant Q$) the relation is modified to $L_e = 1/4QK^2$.

During swelling the gel is subjected to the swelling pressure given by[10,13]:

$$P = -\left(\frac{\partial \Delta F}{\partial V}\right)_{T,n_j} = \sum_{i=1}^{5} -\left(\frac{\partial \Delta F_i}{\partial V}\right)_{T,n_j} = \sum_{i=1}^{5} P_i \qquad (1)$$

where ΔF is the change in the free energy due to the volume changes of sample, V, during swelling, n_j is the number of moles of ions of the jth type in the gel, and $P_i = -(\partial \Delta F_i/\partial V)_{T,n_j}$. ΔF is determined by the sum of contribution due to the mixing of polymer segments with solvent (ΔF_1), mixing of ions with solvent (ΔF_2), configurational elasticity of the polymer network (ΔF_3), the electrostatic interaction of charges in the chain (ΔF_4) and the electrostatic interaction between charges on various chains (ΔF_5).

The pressure P_1 can be expressed as[17]

$$P_1 = -\frac{RT}{V_1}[\ln(1 - v_2) + v_2 + \chi v_2^2] \qquad (2)$$

where V_1 is the molar volume of the solvent, R is the gas constant, v_2 is the volume fraction of the polymer in the swollen gel and χ is the interaction parameter.

The pressure P_2 corresponds to the difference between the osmotic pressure in the gel and in the solute[17]:

$$P_2 = \left(\frac{RT}{M_0}\right) i\rho v_2 \qquad (3)$$

where M_0 is the molecular weight of the monomeric unit, i is the degree of ionization and ρ is the density of the dry gel.

The contribution P_3 has been calculated from ΔF_3 including the finite extensibility of chains[10]. If the total persistence length L_t is used instead of L_p, then

$$\begin{aligned} P_3 = {} & -\nu_d RT\left(\langle\alpha_0^2\rangle v_2^{1/3} - \frac{v_2}{2}\right) \\ & - v_d RT\left[\frac{3}{5}\langle\alpha_0^2\rangle^2 v_2^{-1/3} n^{-1}\left(1 + \frac{3}{4}\frac{L_e}{L_t}\right)\right. \\ & + \frac{99}{175}\langle\alpha_0^2\rangle^3 v_2^{-1} n^{-2}\left(1 + \frac{L_e}{L_t}\right) \\ & \left. + \frac{513}{875}\langle\alpha_0^2\rangle^4 v_2^{-5/3} n^{-3}\left(1 + \frac{9}{8}\frac{L_e}{L_t}\right) + \cdots\right] \end{aligned} \qquad (4)$$

where ν_d is the molar concentration of chains related to the dry volume, $\langle\alpha_0^2\rangle$ is the dilation factor of the dry state ($\langle\alpha_0^2\rangle = (v_0)^{2/3}$, where v_0 is the volume fraction of the polymer at network formation), and n is the number of statistical segments in the chain. The first term in equation (4) is the contribution of the Gaussian configurational free energy and the second term corresponds to the non-Gaussian free energy.

The contribution P_4 has been determined from the change in the electrostatic free energy of the chain, ΔF_4, with swelling. ΔF_4 is calculated by a pair-wise summation of the screened Coulomb interaction between charges separated by a distance A arranged on a rod. This simple one-dimensional model gives

$$P_4 = -RT\frac{Q\rho i}{M_0}\frac{v_2 K e^{-KA}}{1 - e^{-KA}} \qquad (5)$$

The last contribution P_5 can be estimated from the corresponding free energy for semidilute solutions of polyelectrolytes. It is difficult to give a sufficiently precise calculation of this energy. Several possible structures of semidilute polyelectrolyte have been considered[2]: hexagonal lattice of rigid rods; cubic lattice of rigid rods; and isotropic phase of partially flexible chains. All these structures appear to have very similar electrostatic energies[2] and therefore the hexagonal lattice has been used for further calculation. The electrostatic energy for this case is a function of the product Kd, where d is the nearest neighbour distance. Because d scales with v_2 like the screening radius K^{-1} it follows that ΔF_5 is practically independent of v_2 and thus of V, and $P_5 \simeq 0$.

The swelling equilibrium for free swelling is given by

$$P_1 + P_2 + P_3 + P_4 = 0 \qquad (6)$$

α dependences of equilibrium v_2 calculated by relations of the theory published by Hasa, Ilavský and Dušek[10] (HID theory) and by the relations (2)–(6) are compared for $\nu_d = 5 \times 10^{-5}$ and 5×10^{-6} in *Figure 1*. The other parameters used correspond to PMA gels[10,11]*. It is seen in *Figure 1* that for $\nu_d = 5 \times 10^{-5}$, where the mean degree of the chain polymerization, Z, is low ($Z \simeq 309$) and the chains are already stiff ($n \simeq 31$), the effect of L_e is not significant. The differences between our results and the HID theory are more pronounced for $\nu_d = 5 \times 10^{-6}$. As expected, an increase of the chain stiffness with increasing α becomes more pronounced at higher values of Z and manifests itself by a decrease of the swelling degree. Contrary to the HID theory[10], v_2 is not a monotonically

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*The effective degree of ionization $i = \alpha$ was used for $A > Q$ and $i = a/Q = 0.36$ for $A < Q$ ($\alpha > 0.36$[18])

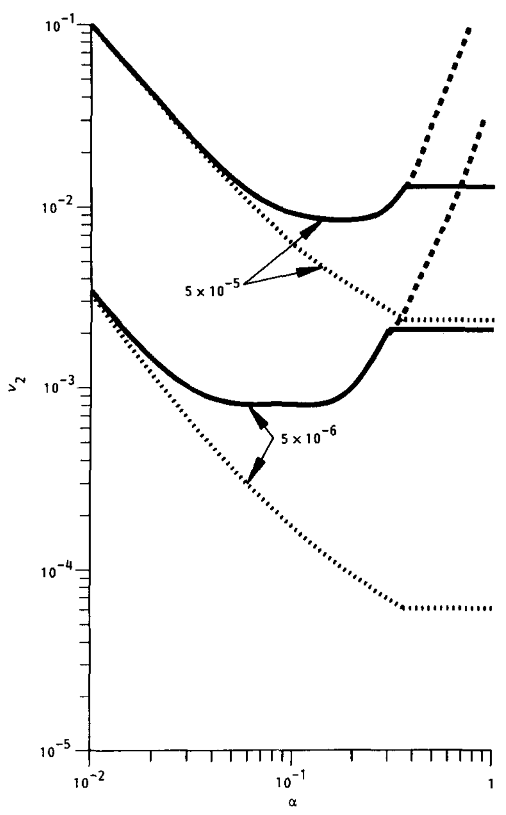

Figure 1 Dependence of the volume fraction v_2 of the polymer in the swollen gel on the degree of neutralization calculated from equations (2)–(6) (——) and using the HID theory[10] (·····). The parameters used correspond to crosslinked polymethacrylic acid: $M_0 = 86.1$ g mol^{-1}, $\rho = 1.33$ g cm^{-3}, $\langle \alpha_0^2 \rangle = 0.63$, $V_1 = 18.1$ cm^3 mol^{-1}, $\chi = 0.54$, $a = 2.55 \times 10^{-8}$ cm, $Q = 7 \times 10^{-8}$ cm, $L_p/a = 5$. v_d values in mol cm^{-1} are shown on the figure

decreasing function of α but shows a flat minimum at $\alpha \sim 0.1$. Beyond this value of α the volume fraction increases, i.e. the degree of swelling decreases with increasing ionization. Above $\alpha = 0.36$ the condensation of counterions causes v_2 to become independent of α. If this condensation did not occur, then according to the predictions of our model v_2 would continue to increase. This is indicated on *Figure 1* by the dashed lines.

EXPERIMENTAL

The PMA gel samples were prepared by block copolymerization of methacrylic acid with a small amount of ethylene dimethacrylate (0.5 and 1 wt%) in presence of water; the volume fraction v_0 of the monomer before polymerization was 0.5. The reaction was initiated with azobisisobutyronitrile (≈ 1 g dm^{-3}) and proceeded at 40°C for 72 h. The samples (rods with diameter of 6 and 20 mm length) were washed with water for several weeks.

Extracted gels were cut in plates about 1 mm thick and immersed in 100 ml of NaOH water solutions. The concentration of NaOH was selected to attain a desired degree of neutralization α of PMA gels. The swelling took place in closed bottles so that no air could enter. Equilibrium values of v_2 were achieved after 3 weeks. The volume fractions v_2 of the polymer in the swollen gels were calculated from the weight of gel samples swollen to equilibrium.

RESULTS

The equilibrium values of v_2 for PMA gels as a function of α are shown in *Figure 2* together with the theoretical $v_2(\alpha)$ functions calculated by the HID and the theory presented in this paper. The values of v_d for the theoretical calculations were selected so that $v_2(\alpha)$ functions match the experimental data for $\alpha > 0.36$, at which point v_2 becomes independent of α. In the absence of any added NaOH, i.e. $\alpha = 0$, the gel with 1% crosslink content swells to give $v_2 = 0.412$ and the gel with 0.5% crosslink content swells more, as expected, to give $v_2 = 0.117$. These values are indicated by arrows on the vertical axis in *Figure 2*. As the degree of neutralization increases, the swelling ratio increases, i.e. v_2 decreases. However, unlike the predictions of the HID theory, this decrease of v_2 does not continue indefinitely. The degree of swelling begins to decrease, i.e. v_2 increases for $\alpha > 0.2$. The minimum in v_2 is more pronounced for the gel with 0.5% crosslink content than for the 1% gel.

The experimental data for v_2 *versus* α of the gel with 0.5% of crosslink content show a minimum near $\alpha \approx 0.1$ which is only slightly shifted against the minimum of the $v_2(\alpha)$ function predicted by the above proposed theory. In addition, this theoretical $v_2(\alpha)$ function, calculated by the relations including the effect of the electrostatic persistence length, describes the experimental data better

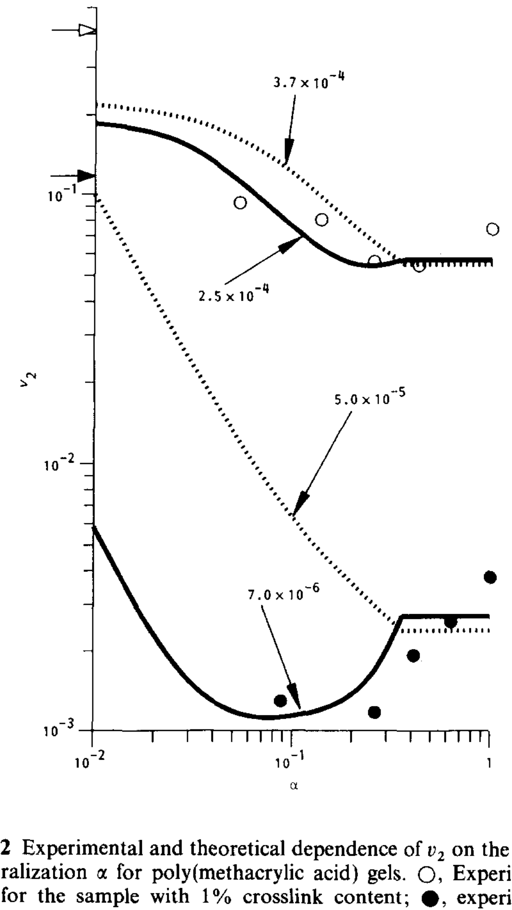

Figure 2 Experimental and theoretical dependence of v_2 on the degree of neutralization α for poly(methacrylic acid) gels. ○, Experimental values for the sample with 1% crosslink content; ●, experimental values for the sample with 0.5% crosslink content; ——, theoretical curves calculated according to relations (2)–(6); ·····, HID theory[10]. v_d values in mol cm^{-1} are indicated on the figure. The arrows on the vertical axis correspond to the volume fraction in the unneutralized, swollen gel (i.e. gel swollen in pure H_2O with no added NaOH). The filled arrow corresponds to v_2 (at $\alpha = 0$) for the 0.5% crosslink sample and the open arrow to the 1% sample

than the functions calculated by the relations of HID theory.

As for the gel sample with 1% crosslink content, the difference between the two theories is not significant and both describe swelling equilibria fairly well. As mentioned earlier, this is to be expected when the mean degree of chain polymerization is low and the chains are already stiff.

In conclusion it can be said that the effects of including the electrostatic persistence length produce significant changes in the description of the swelling behaviour of weakly crosslinked ionized gels and the results are in better qualitative agreement with experiment than the theories published up to now (e.g. the HID theory). Quantitative verification of the derived relations is not feasible without independent measurements of ν_d, which is rather complicated for such weakly crosslinked gels.

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