Communications to the Editor

Low Dimensionality of Cross-Linked Carboxymethyldextran Chains in Swollen Gels

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1. Introduction. Recently the tremendous volume changes of polyion gels caused by a change in their electrostatic or thermodynamic conditions have attracted much attention with regard to their application to highly water-absorbing material and mechanochemical devices.[1] This swelling property of polyion gel was reported about 40 years ago[2] and subsequently followed by theoretical study.[3] A polymeric chain between two cross-links in a swollen gel is subject to traction. However, it was assumed that chain statistics under traction were not much different from those for chains free from traction. de Gennes has formulated the statistics for the former case which is different from the chain statistics for the latter.[4] An analysis on the basis of de Gennes' formulation is presented here.

The gel volume is determined by a force balance between expanding and contractile forces exerted on polymeric chains in the gel. The expanding force is due to osmotic Donnan effects, and the contractile one is elastic and originates from the entropy of chain conformation. Applying de Gennes' formula to the derivation of elastic force, a power relation between the osmotic Donnan force and the gel volume was obtained. We have experimentally determined the gel volumes of cross-linked carboxymethyldextran as a function of the degrees of ionization and the salt concentrations and thereby estimated the osmotic Donnan force. These data, when analyzed according to our simple theory, show that the dimensionality of a carboxymethyldextran network chain in swollen gel is much lower than 3.

2. Theory. The force balance between the Donnan expanding osmotic force and the contractile elastic force determines the swollen volume of an ionic polymer gel. The osmotic term is given as follows by the ideal Donnan without the counterion condensation[5]

$$\pi = kT\left[2C_s\left[\left\{1+\left(\frac{\alpha C_{pm}^*}{2C_s}\right)^2\right\}^{1/2}-1\right]\right] \quad (1)$$

The elastic force, P_{el}, is given by eq 2 in terms of the elastic free energy, F_{el}.

$$P_{el} = -\frac{\partial F_{el}}{\partial V} = \frac{C_{pm}^{\,2}}{N_m}\frac{\partial F_{el}}{\partial C_{pm}} \quad (2)$$

where

$$C_{pm} = N_m/V \quad \text{and} \quad C_{pm}^* = C_{pm}V/(V-V_{sk}) \quad (3)$$

Here α, C_s, V, V_{sk}, and N_m are, respectively, the ionization degree of an ionizable group, the salt concentration in the outer phase, the gel volume, the volume of chain skeletons, and the total number of ionizable groups in the gel.

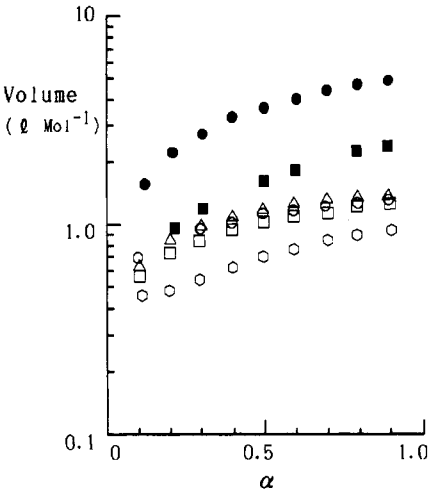

Figure 1. Gel volumes of C-50 (filled symbols) and C-25 (open symbols) as functions of the ionization degree α. $NaClO_4$ concentrations (10^{-3} M): 1 (△), 10 (○), 100 (●, □), 1000 (○), and 2000 (■).

According to the de Gennes theory, F_{el} is described as

$$F_{el} = \nu_p kT(R/R_F)^\delta \quad (4)$$

where ν_p, R, and R_F denote the number of polymer chains and the average end-to-end distances of chains in the gel and in the standard state (Flory state defined by de Gennes[4]), respectively. δ is related to the dimensionality of the chain d by eq 5.[4] Combining eqs 2–4 with a relation

$$\delta = (d+2)/(d-1) \quad (5)$$

$V = A_V R^3 \nu_p$ (A_V is a constant), we obtain P_{el}

$$P_{el} = -kTA_V^{-\delta/3}R_F^{-\delta}D_p^{-1+\delta/3}(\delta/3)C_{pm}^{1-\delta/3} \quad (6)$$

Here D_p ($=N_m/\nu_p$) is the number average polymerization degree of cross-linked chains. A relation $\pi + P_{el} = 0$ determines the gel volume, or equivalently C_{pm}, and we have eq 7.

$$\pi = kTA_V^{-\delta/3}R_F^{-\delta}D_p^{-1+\delta/3}(\delta/3)C_{pm}^{1-\delta/3} \quad (7)$$

3. Experimental Section. CM Sephadex C-25 and C-50 (Pharmacia, Sweden) were used as carboxymethyldextran gels. The gels were rinsed thoroughly with distilled water after soaking in 1 M HCl solutions for 12 h. Polyphosphate was prepared by fractionation of sodium phosphate glass in acetone. Details about the preparation are described elsewhere.[6] The molecular weight of polyphosphate determined by the end-group titration method was 15 000. Other chemicals used were reagent grades.

Gel swelling experiments were carried out at 25 ± 0.5 °C. About 4 g of wet gels was suspended in a volume (20 mL) of a $NaClO_4$ solution of a given concentration. Neutralization of the gel was carried out with a NaOH solution. The gels were equilibrated with the solution phase for more than 48 h. Values of α were calculated from the added amount of NaOH and the pH of the suspensions. Sodium ion concentrations in the outer phase

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as determined by atomic absorption spectroscopy were close to those of the salt solutions. The gel volume V was obtained by subtracting the volume unoccupied by the gel network (V_u) from the total volume of the suspension. Determination of V_u was carried out as follows. A given amount of polyphosphate, w_1, was added to the gel suspension, and the suspension was shaken thoroughly. The polyphosphate concentration in the supernatant, C_{pp}, was measured by a colorimetric method. Then V_u was calculated according to the relation $V_u = w_1/C_{pp}$. Typical values of C_{pp} were on the order of 10^{-4} monomol/L. V_{sk} was obtained by subtracting the volume of the added salt solution from the total volume of the suspension. The measured V_{sk} values per mole of an ionizable unit were 0.11 and 0.15 L for C-25 and C-50, respectively.

4. Results and Discussion. Dependencies of the gel volumes per mole of carboxyl group on α are shown in Figure 1 for different salt concentrations C_s. The gel volume increases with α but decreases with C_s. The concentration C_{pm} was evaluated from the gel volume through eq 3, and log π was plotted against log C_{pm} in Figure 2. A power relation predicted from eq 7 holds irrespective of α and C_s. Values of δ were obtained through the least-squares fit of the data to eq 7. Chain dimensionalities d of the swollen gels were evaluated from the δ values through eq 5. They are shown in Table I. It is interesting that the dimensionalities are as low as about 1.4–1.5, which suggests that the chains are confined within something like a tube. The restriction force may be more effectively exerted on shorter chains as indicated by the fact that the dimensionality of the gel with shorter chains (C-25) is lower. Although the rigid skeletal backbone is considered to be a probable candidate for the constraining force, further study is required in this respect.

In the derivation of eq 7, a contribution from the mixing free energy of polymer segments is totally neglected. The validity of this approximation is partly supported by experimentally confirmed linear relations shown in Figure 2. Since the contribution from the mixing free energy becomes small as chains become stretched, the present results are self-consistent in this respect.

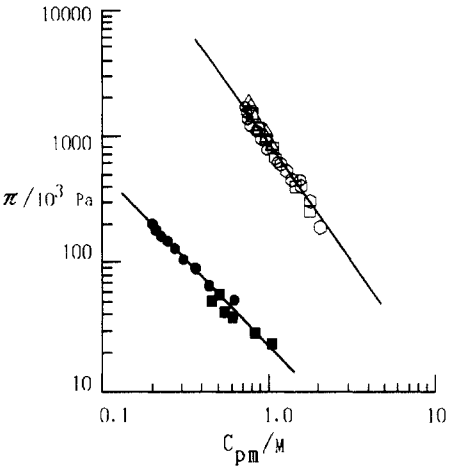

Figure 2. Osmotic pressures π versus residue concentration C_{pm} of C-50 (filled symbols) and C-25 (open symbols). Osmotic pressures were evaluated using eq 1. $NaClO_4$ concentrations (10^{-3} M): 1 (△), 10 (○), 100 (●, □), 1000 (○), and 2000 (■).

Table I
Measured δ Values and Dimensionalities

gel	C-50	C-25
δ	7.02 ± 0.18	8.91 ● 0.18
d	1.50 ± 0.03	1.38 ± 0.01

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References and Notes

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Registry No. Carboxymethyldextran, 9044-05-7; Sephadex C-25, 117079-76-2; Sephadex C-50, 108066-75-7.