Viscosity behaviour of polymer solutions in the presence of complexing ions

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In the presence of complexing ions, dilute aqueous polymer solutions exhibit intriguing rheological properties that result from a delicate balance between complexation equilibria, polyelectrolyte effects and formation of reversible intrachain crosslinks. We present a theoretical Flory-type model describing the variation of the complexation constants and the intrinsic viscosity as a function of solution parameters (ionic strength, complexing-ion concentration, molecular weight of chains). In particular, we predict a quite specific molecular-weight dependence of the intrinsic viscosity and we show that, under certain conditions, the intrinsic viscosity may oscillate as a function of ionic strength. Some predictions of the model seem to be in a very good agreement with existing experimental observations, i.e. for poly(vinyl alcohol)–borax systems studied by Ochiai *et al.* Analogously, we expect that, for neutral chemical gels in water, the swelling degree may oscillate as a function of complexing-ion concentration.

(Keywords: complex formation; polyelectrolyte; added salt effect; reversible gel)

INTRODUCTION

The effect of complexing ions on the rheological properties of aqueous polymer solutions has raised considerable experimental interest stimulated by numerous industrial applications[1–7]. Such systems generally exhibit thickening and gelling properties resulting from the possible formation of complexes acting as tie points. The strength and lifetime of these crosslinks can be monitored by the choice of the complexing ion and external conditions such as the ionic strength of the solution, pH and the temperature.

The existence of a shear modulus plateau in semi-dilute solutions at low frequencies[8] and phase separation in both dilute and concentrated solutions[9] are examples of numerous observations that may be explained qualitatively by a delicate balance of polyelectrolyte effects, crosslinking and complexing chemical equilibria. It is difficult to take into account all these effects and little theoretical work has been devoted to model rheological and thermodynamic properties of polymer solutions complexed by ions.

This work presents a theory of the viscosity behaviour in the dilute regime. Many polymer–ion systems have been studied: e.g. polyvinylpyridine in the presence of Cu^{2+}, Fe^{3+} and Co^{2+} (ref. 10); poly(vinyl alcohol)–borax[5,6] and polysaccharide–borax[11]. For all these systems, spectacular effects are reported: the viscosity of dilute solution increases or decreases when complexing ions are added depending on the ionic strength of the solution. For instance, in *Figure 1* we have plotted the relative change of viscosity reported by Ochiai *et al.*[5] in poly(vinyl alcohol) (PVA)–borax systems. Without added monovalent salt, the viscosity increases monotonically when complexing borax salt is added (curve A). In the presence of the monovalent salt, the viscosity first decreases abruptly (curves B and C), passes through a minimum and then increases again monotonically when more borax is added. For a fixed borax concentration, the intrinsic viscosity decreases when passive salt is added (curve E) and can even reach a value well below that of neutral PVA in water. Ochiai *et al.* interpret this strange behaviour qualitatively by evoking the competition between electrostatic chain

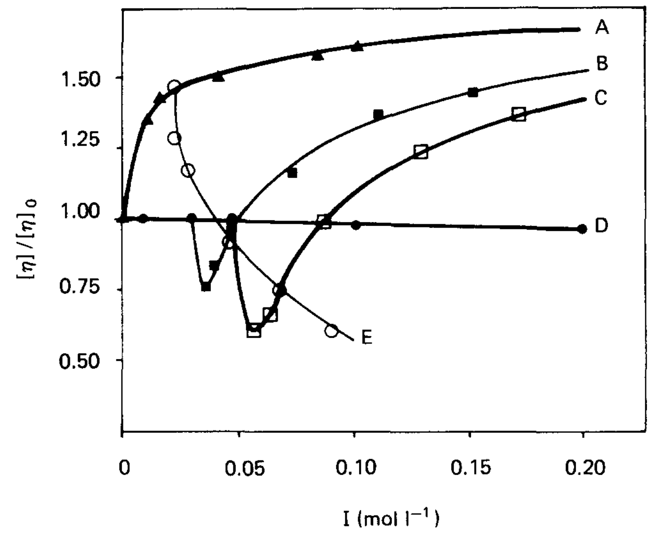

Figure 1 Relative variation of intrinsic viscosity $[\eta]/[\eta]_0$ of PVA–borax systems as a function of ionic strength $I = C_S + C_M$, according to the data of Ochiai *et al.*[5]: curve A, PVA + borax without NaCl; curves B and C, PVA + borax in the presence of 0.03 and 0.05 M NaCl solution, respectively; curve D, PVA + NaCl without borax; curve E, PVA + NaCl in the presence of 0.01 M borax solution

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expansion and contraction by intrachain crosslinking. We propose a detailed quantitative model that analyses the variation of the complexation equilibria with the respective concentration of added salt and complexing ions and discusses the influence of attached charges on the conformation of polymer chains in dilute solutions. We show that a simple Flory approach described the viscosity behaviour well and allows some interesting predictions.

The paper is organized as follows. In the next section we present a self-consistent model for the variation of the complexation constants with ionic strength of the solution. The important result here is that, due to a polyelectrolyte effect, the apparent complexation constant depends strongly on the concentration of complexing ions. It turns out that for most practical cases the concentration of free complexing ions is high enough to screen out electric interactions considerably and reduces the stiffening of the chains. We can thus formulate a simple Flory model that considers both charge repulsion and formation of intrachain tie points. Although the Flory model accounts well for the observed viscosity behaviour, it might not be well adapted for some systems for which excluded-volume effects are predominant. In the final section we discuss such situations and argue that small loops can be formed and influence strongly the molecular-weight dependence of the intrinsic viscosity.

COMPLEX FORMATION: INFLUENCE OF ADDED SALT

In most aqueous polymer solutions, the addition of complexing ions leads to the following chemical equilibria:

$$\mathrm{P}+\mathrm{M}\overset{K_1}{\rightleftharpoons}\mathrm{PM}$$

$$\mathrm{PM}+\mathrm{P}\overset{K_2}{\rightleftharpoons}\mathrm{PMP}$$

where P, M, PM and PMP denote, respectively, the polymer complexable site, the ion, the monocomplex and the dicomplex (PVP–Cu^{2+} and PVA–borate systems are typical examples). In chemical equilibrium, the chain may be viewed as a random copolymer with some units (monocomplexes) bearing electrical charges (*Figure 2*). The dicomplexes act as tie points, i.e. internal crosslinks in dilute solutions and intra- or intermolecular crosslinks in concentrated solutions. These systems are very different from polyelectrolytes bearing fixed charged groups. Not only is the number of charges on the chain determined by chemical equilibria, but also there are some free ions present in the solution. These free ions screen the electrostatic interactions even in the absence of passive salt.

The description of the chemical equilibria for polymer chains is much more involved than for small molecules: the number of complexes formed may depend not only on the concentrations of the ion and polymer but also on the chain molecular weight. Moreover, the dependence of the chemical equilibria on the ionic strength of the solution is expected to be much stronger and more important in the case of polymers since the charges induced by complexation are forced to be correlated as they are connected to the chain. In this section, we evaluate the importance of this last effect on monocomplex formation.

In dilute solution, the concentration of monocomplexes is given by:

$$C_{\mathrm{PM}}=\tilde{K}_1C_{\mathrm{P}}C_{\mathrm{M}} \qquad (1)$$

where C_{P} and C_{M} denote the concentration of free polymer sites and free ions, respectively. It should be remarked that the free-polymer site concentration C_{P} and the polymer concentration C are approximately related through the equation:

$$C\simeq C_{\mathrm{P}}(1+\tilde{K}_1C_{\mathrm{M}}) \qquad (2)$$

The effective monocomplexation constant $\tilde{K}_1$ depends on the ionic strength $I=C_{\mathrm{M}}+C_{\mathrm{S}}$ with C_{S} being the concentration of monovalent added salt. We assume that there are no cooperative effects, such as hydrogen bonding, that change the chain structure so that $\tilde{K}_1$ does not depend on the molecular weight of the chains.

The interaction energy between two neighbouring charges induced by complexation on a chain is given by:

$$U/kT=(Q/b)\exp(-\kappa b) \qquad (3)$$

where Q is the Bjerrum length ($Q=e^2/4\pi\varepsilon_0kT$) (typically $Q=7$ Å in water at 25°C), κ^{-1} is the Debye screening length:

$$\kappa^2=8\pi N_{\mathrm{A}}QI \qquad (4)$$

and b denotes the average spatial distance between two neighbouring monocomplexes on a chain. The distance b is a function of $\tilde{K}$ since the number of monomer units between two monocomplexes equals:

$$n=(1+\tilde{K}_1C_{\mathrm{M}})/\tilde{K}_1C_{\mathrm{M}} \qquad (5)$$

Hence, because of the polyelectrolyte effect of the repulsion between neighbouring charged complexes, the probability of complex formation is decreased:

$$\tilde{K}_1=K_1\exp(-\alpha U/kT) \qquad (6)$$

where K_1 is the complexation constant in the absence of electrostatic effects, i.e. at very large excess of added salt. A numerical factor α has been introduced into the exponential to represent an average increase of the

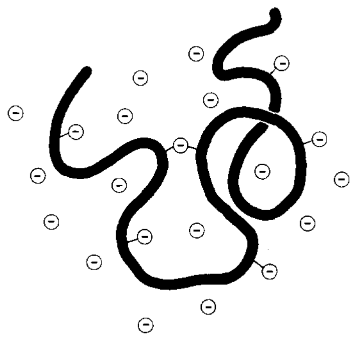

Figure 2 Schematic representation of a neutral polymer chain in the presence of complexing ions (anions). These ions may exist as three forms in equilibrium in the solution: free ions, charged monocomplexes carried by the chains, and dicomplexes forming intrachain crosslinks. Counterions are not represented

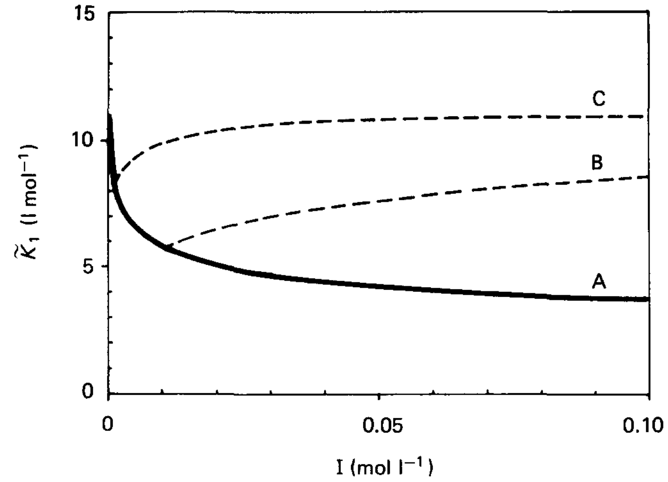

Figure 3 Variation of the apparent monocomplex equilibrium constant with ionic strength $I = C_S + C_M$: curve A, polymer + complexing ions without passive salt ($C_S = 0$); curve B, polymer + passive salt in the presence of complexing ions ($C_M = 10^{-3}$ M); curve C, polymer + passive salt in the presence of complexing ions ($C_M = 10^{-2}$ M). The constants are calculated for typical values of microscopic parameters ($K_1 = 11$ l mol^{-1}, $a = 5$ Å, $Q = 7$ Å)

electrostatic energy when a new complex is fixed in between two already existing charges. The simplest estimate gives $\alpha \simeq 4$. Equations (3) and (6) enable us to calculate the monocomplex formation constant self-consistently when the spatial distance between neighbouring charges $b(K_1)$ is known.

At this point, it is important to estimate the effect of chain stiffening due to the presence of electrical charges. The average contour distance d between two charged complexed polymer sites is $d = na$ where a is the length of a polymer site. In most practical cases $d > 3Q$ and the counterion condensation can be disregarded[12]. The persistence length can be estimated from the formula of Odijk[13] and Skolnick and Fixman[14]:

$$L_e = Q/4\kappa^2 d^2 \qquad (7)$$

In practice, the extra stiffening may be neglected when $L_e < Q$. From equations (7) and (4), it turns out that in most practical situations the range of extra stiffening is very small even for high complexing-ion concentration. Therefore, the spatial distance between two charges $b(\tilde{K}_1)$ can be estimated as the end-to-end distance of a strand of the (neutral) chain of n polymer units, i.e. $n^{1/2}a$.

The decrease of the apparent value of the complexation constant when complexing ions are added is quite spectacular. For example, for $\tilde{K}_1$ of the order of 10 l mol^{-1}, $a = 5$ Å and $C_M = 10^{-3}$ mol l^{-1}, one gets $Q/b \simeq 0.14$ and the drop of the apparent complexation constant is about 40%. In *Figure 3* we show the variation of the complexation equilibrium constant $\tilde{K}_1$ as a function of the ionic strength of the solution. In the absence of passive salt ($C_S = 0$), $\tilde{K}_1$ decreases rapidly when complexing ions are added and gently tends to a minimum. For a fixed free-ion concentration, adding a passive salt increases the apparent complexation constant $\tilde{K}_1$, whose value tends to K_1 at very high ionic strength.

CHAIN CONFORMATION IN THE PRESENCE OF COMPLEXING IONS: A FLORY MODEL

As a result of complexation equilibria, the polymer chains bear a certain amount of electrical charge (monocomplexes). The interaction between these charged units modifies the chain conformation. Even so, the modification is less dramatic than in the case of strongly charged polyelectrolytes, which in a very dilute solution behave like rods. This is because in chemical equilibrium no charge is fixed on a polymer chain without the presence of an excess of free complexing ions in solution. These free ions shield electrostatic interactions even in the absence of added salt. Thus the value of the complexation constant $\tilde{K}_1$ essentially determines both the number of charged units on a chain and the screening by free ions. In many cases $\tilde{K}_1$ is low enough so that the screening (Debye) length κ^{-1} is small. In fact κ^{-1} is smaller than the average distance between neighbouring charges $b(\tilde{K}_1) \simeq n^{1/2}a$, when $\tilde{K}_1 < 8\pi N_A a^2 Q$. The statistical segment length a is of the order of 5–10 Å, so that for $\tilde{K}_1 < 10$ l mol^{-1} we can consider that the charge density is low (cf. equation (7)) and the screening effects are strong even without passive salt. Therefore, in the practical cases we have in mind here, the Kuhn statistical length is not renormalized (cf. equation (7)), the polymers maintain spherical symmetry and they exhibit the conformation of chains with excluded-volume interactions.

In order to account for the distinct effects of free complexing ions and added passive salt, we apply a simple Flory model. We represent the chain as a random copolymer with excluded-volume interaction parameter v and $f = 1/n$, the fraction of complexed units repelling each other through the screened electrostatic interaction:

$$U/kT = (Q/r)\exp(-\kappa r) \qquad (8)$$

It is possible to define the extra virial coefficient between complexed units:

$$v' = \int [1 - \exp(-U/kT)]\, d^3 r \simeq 4\pi Q \kappa^{-2} \qquad (9)$$

The Flory energy of a complexed chain can be written as:

$$\frac{F_1}{kT} \simeq \frac{3R^2}{2Na^2} + v\frac{N^2(1-f)^2}{R^3} + v'\frac{f^2 N^2}{R^3} \qquad (10)$$

and after minimization we find the change of the radius of the chain due to the formation of monocomplexes:

$$\frac{R}{R_0} \simeq \left((1-f)^2 + \frac{f^2}{2vN_A I}\right)^{1/5} \qquad (11)$$

with $R_0 \simeq v^{1/5} N^{3/5} a^{2/5}$ being the Flory radius of a neutral chain. In the absence of the excluded-volume interactions ($v = 0$), this result, $R \simeq Q^{1/5} \kappa^{-2/5} N^{3/5}$, is equivalent to the classical expression for polyelectrolytes with added salt[15].

The variation of the intrinsic viscosity $[\eta] \simeq R^3/N$ with respect to $[\eta]_0$, the intrinsic viscosity of the non-complexed neutral polymer, is given by:

$$\frac{[\eta]}{[\eta]_0} \simeq \left((1-f)^2 + \frac{f^2}{2vN_A(C_M + C_S)}\right)^{3/5} \qquad (12)$$

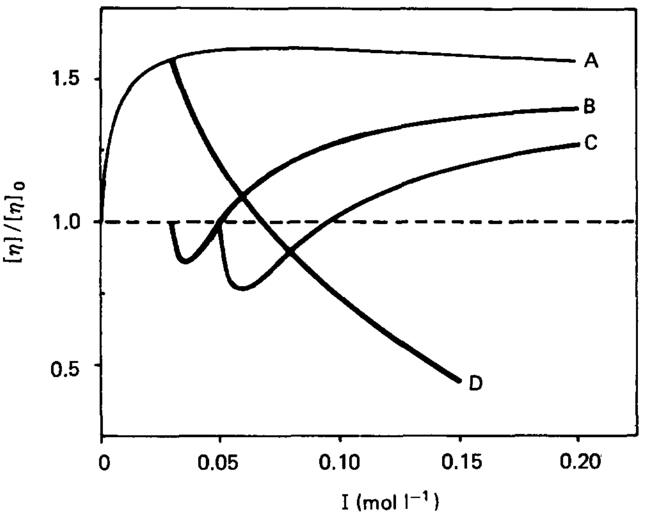

Figure 4 Theoretical dependences of relative intrinsic viscosity $[\eta]/[\eta]_0$ of a neutral polymer on ionic strength $I=C_S+C_M$ in the presence of complexing ions: curve A, polymer+complexing ions without passive salt ($C_S=0$); curves B and C, polymer+complexing ions with passive salt ($C_S=0.03$ M and $C_S=0.05$ M, respectively); curve D, polymer+passive salt for a fixed complexing-ion concentration. Typical values of microscopic parameters were used for the calculations ($K_1=11\,l\,\mathrm{mol}^{-1}$, $a=5$ Å, $v=\frac{1}{2}(7\text{ Å})^3$, $k_2uN_A=1\,l\,\mathrm{mol}^{-1}$)

The complexation constant $\tilde{K}_1(C_M,C_S)$ has to be calculated using equation (6). When complexing ions are added, repulsion between complexed units strongly increases the viscosity, e.g. the intrinsic viscosity doubles its value for C_M as small as 1.5×10^{-2} mol l^{-1} for typical values of $v=\frac{1}{2}(7\text{ Å})^3$ and $\tilde{K}_1\simeq6\,l\,\mathrm{mol}^{-1}$. For higher values of C_M, this effect is screened out and the viscosity shows a maximum and then decreases. The maximum increase in the viscosity strongly depends on the passive salt concentration C_S: it is lower for higher C_S.

However, as could be expected, sole monocomplex formation cannot explain the sharp drop in intrinsic viscosity observed in experiments when some complexing ions are added to a polymer solution with salt (*Figure 1*). To explain this spectacular effect, we consider the existence of intrachain crosslinks induced by dicomplex formation. Within the Flory approximation, one can treat dicomplex formation as a short-range attraction between non-complexed polymer sites and monocomplexes. The Flory energy can be written as[9]:

$$\frac{F}{kT}=\frac{F_1}{kT}-uk_2\frac{N^2}{R^3}f(1-f) \tag{13}$$

where kTu represents the energy gain when a crosslink is formed and k_2fN^2/R^3 is the average number of dicomplexes formed. The constant k_2 is typically of the order of 1–2 $l\,\mathrm{mol}^{-1}$ and represents the probability of dicomplex formation when a monocomplex is in contact with a monomer.

After minimization with respect to R, we find that the relative change of the intrinsic viscosity is given by:

$$\frac{[\eta]}{[\eta]_0}=\left((1-f)^2+\frac{1}{2vN_A}\frac{f^2}{C_M+C_S}-\frac{uk_2}{v}f(1-f)\right)^{3/5} \tag{14}$$

We see that for small complexing-ion concentrations C_M in the absence of added salt, the formation of intrachain crosslinks does not dominate electrostatic repulsion, when $\tilde{K}_1>2N_A(k_2u+v)$, i.e. when the energy gain due to crosslink formation is small. Thus the viscosity increases when the complexing ions are added and passes through a maximum resulting from both screening effects and crosslinking. On the other hand, when some amount of salt is present, the viscosity always decreases with the addition of a small amount of complexing ions and exhibits a characteristic minimum. The depth of the minimum depends on the passive-salt concentration. Typically, for $C_S\simeq0.05$ mol l^{-1} the viscosity decrease upon addition of $C_M=10^{-2}$ mol l^{-1} complexing ions may reach about 20% (for $\tilde{K}_1=6\,l\,\mathrm{mol}^{-1}$, $uk_2N_A\simeq1.5\,l\,\mathrm{mol}^{-1}$). The higher the salt concentration, the more abrupt is the drop of the viscosity (*Figure 4*). We see that the viscosity behaviour predicted from the Flory model (equation (14)) with typical values of microscopic parameters seems to be in a very good qualitative agreement with experimental observations for PVA–borax systems (*Figure 1*). We would like to stress that even in a dilute solution some interchain tie points may occur influencing the viscosity through aggregate formation. For PVA–borax systems, Ochiai *et al.*[5,6] examined this type of effect and concluded that they can be disregarded at least for their system.

DISCUSSION AND CONCLUSIONS

The Flory picture presented in this work is well adapted to treating the case of moderately good solvents and high probability of dicomplex formation. The model seems to account well for the experimental observations of Ochiai *et al.*[5,6] on PVA–borax systems. It explains why, without passive salt, the viscosity increases when complexing ions are added, whereas the presence of a very low amount of passive salt leads to a sharp drop in the intrinsic viscosity. Moreover, the model predicts the existence of maximum viscosity, for a certain complexing-ion concentration. Hence, at high ionic strength, we expect a spectacular effect of intrinsic viscosity oscillating as a function of the complexing-ion concentration.

In the Flory-type approach, the excluded-volume interactions and reversible crosslinking are treated at the same level, as perturbations to the Gaussian chain conformation. However, for a very good solvent, when excluded-volume effects predominate, the probability of intrachain contacts and thus dicomplex formation is much smaller than a mean-field estimate. In fact, two monomers far apart on the chain have an extremely low probability of a close spatial encounter[16]. As a result, monocomplexes will tend to react with neighbouring units and the dicomplex equilibria lead to small-loop formation. In some respects, the situation is analogous to that described by Joanny[17] and Cates and Witten[18] for ionomer solutions when crosslinking is due to dipole–dipole interactions. The substantial difference is that for ionomers the chemical structure predetermines the possible size of the loops, whereas in the system we discuss here the monocomplexes can react with any free unit. Hence, in our systems the size of the loops is essentially determined by local chain properties (e.g. its stiffness) and their number should be proportional to the molecular weight of the chain. In a first approximation, the decrease of the intrinsic viscosity due to dicomplex formation is proportional to the number of small loops that are formed:

$$[\eta] \simeq [\eta]_r(1-\gamma N f) \qquad (15)$$

where $[\eta]_r$ represents the viscosity of a chain bearing only monocomplexes (equation (12)). The coefficient γ represents the product of the relative decrease of viscosity due to the formation of a single small loop and the probability of dicomplex formation through monocomplex–polymer site interactions. This probability will depend on the energy ΔF required to form a loop, $\gamma = \gamma_0 \exp(-\Delta F/kT)$. A crude estimate of the dependence of ΔF on C_M and C_S can be obtained from the Flory approach.

A comparison of equation (15) and of the Flory picture equation (14) shows that the formation of small loops may lead to a more pronounced minimum in the viscosity in the presence of passive salt, fitting the experimental results better. However, the most interesting prediction of the small-loop picture concerns the molecular-weight dependence of the relative change of the intrinsic viscosity $[\eta]/[\eta]_0$. For instance, in the presence of passive salt, when the complexing ions are added the drop in $[\eta]/[\eta]_0$ is proportional to the molecular weight.

In conclusion, several new predictions may be worth experimental consideration. We show how the monocomplex formation constant K_1 should depend strongly on complexing-ion and passive-salt concentrations. The process of dicomplex formation seems to be even more subtle. In dilute solution in a good solvent, dicomplex formation might be governed by the local conformational properties of the polymer chain. This implies that the concentration of dicomplexes might be proportional to the monomer concentration C_P rather than to C_P^2 and might be independent of the molecular weight of the chain. The mean-field (Flory-type) prediction would be proportionality to $C_P C^* \simeq N^{-4/5}$. For quantitative studies it would be interesting to couple the spectroscopic determination of the number of complexes formed with rheological measurements. If in dilute solutions the number of dicomplexes is proportional to C_P, it would be possible to define an apparent complexation constant for a total number of charged complexes linked to a polymer chain. This apparent complexation constant should depend on ionic strength as indicated by equation (6), but it is important to account for monomers 'lost' in small loops when calculating the mean distance.

The analogy between the conformation of a chain in dilute solution and a gel at swelling equilibrium[19] opens appealing perspectives. For water-soluble chemical gels in the presence of complexing ions, we expect variations of degree of swelling completely analogous to those predicted for intrinsic viscosity (cf. *Figure 4*). For instance, a neutral chemical gel at equilibrium in water should swell when complexing ions are added. On the other hand, in a saline solution the same gel should first shrink, then swell and shrink again when more complexing ions are added. We are currently studying such systems exhibiting 'oscillating' degrees of swelling.

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