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MOLECULAR THERMODYNAMICS OF AQUEOUS POLYMERS AND GELS

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SUMMARY

The phase behavior of aqueous polymer solutions and gels is often sensitive to prevailing conditions such as temperature, pH, ionic strength or solvent composition. For crosslinked polymer gels, this solution-sensitivity is indicated by large changes in gel volume in response to small changes in solution conditions. This chapter reviews recent work directed at developing a molecular-thermodynamic description of phase behavior in aqueous polymer systems. A theoretical description for hydrogel swelling equilibria correlates systematic experimental data obtained for model systems. Novel molecular-simulation studies of isolated polyelectrolytes provide detailed information on the relationship between expansion of polyelectrolytes in solution and pertinent parameters that characterize polymer and solution properties.

INTRODUCTION

Aqueous polymer systems have applications in a variety of areas including specialty chemicals, pharmaceuticals, personal-care products, enhanced-oil-recovery processes, and biomedical uses. In many applications, the polymer is in crosslinked form, i.e., as a hydrogel. Hydrogels are often superabsorbent, imbibing many times their weight in water. The large water affinity of certain hydrogels makes them particularly attractive for applications where biocompatability is important (e.g., for contact lenses or biological implants), and in applications where large water absorbency is desired (e.g., in disposable diapers, or agriculture in arid climates). Superabsorbent materials comprise an active area of materials research; hydrogels represent an important class of such materials.

The superabsorbent nature of a hydrogel is related to the hydrophilicity of the chains comprising the polymer network. For example, superabsorbent gels are often made of crosslinked polyelectrolytes. Polyelectrolytes expand significantly in solution as shown by their intrinsic viscosity and excluded-volume properties. The hydrophilic nature of the individual chains gives a gel with high water affinity.

The nature of the polymer and the conditions of the solvent determine the configurational (or expansion) behavior of isolated polymers in solution, in addition to the phase behavior (solubility properties) of concentrated polymer solutions. For example, it has been long known that temperature change can induce liquid-liquid phase separation in aqueous polymer solutions, and coil-globule transitions for isolated polymers in solution (ref. 1). Similarly, certain hydrogels have recently been shown to

exhibit phase behavior which is dramatically sensitive to changes in the surrounding solution conditions. Tanaka (ref. 2) observed discontinuous, order-of-magnitude volume changes in a partially-ionized polyacrylamide gel as a function of the surrounding acetone/water ratio. Since Tanaka's initial observation, phase transitions in gels have been reported in response to a number of solution variables, including temperature (ref. 3.), pH (ref. 4), and electric-field strength (ref. 5).

Large, reversible changes in hydrogel volume (water content) induced by changes in surrounding solution conditions suggest a new spectrum of potential applications for gels. Proposed applications include using gels in solute-recovery processes (refs. 6,7), in controlled-release devices (refs. 8,9), and in immobilized-enzyme reactors (ref. 10). It is now apparent that solution- or environmentally-sensitive hydrogels represent an important new class of materials. While many studies have investigated experimentally the properties of aqueous polymer solutions and gels, a quantitative theoretical description of their phase behavior has not as yet been established. Intermolecular forces in aqueous polymer systems are complex, including both orientation-dependent short-range interactions (e.g., hydrogen bonds) and long-range (electrostatic) interactions. These complex interactions, coupled with the connectivity of the polymer backbone (and for gels, the network topology), are responsible for both interesting phase behavior and for the difficulty in describing that phase behavior.

Recent work in our research group has been directed at obtaining a fundamental understanding of phase behavior in aqueous/polymer systems, including gels (refs. 11-16). We have pursued theoretical and experimental studies to identify and characterize the factors which influence the behavior of aqueous/polymer systems. One goal of this work has been to develop a molecular-thermodynamic model for describing swelling equilibria of environmentally-sensitive gels (refs. 11-13); such a framework should be useful for guiding the design of novel gels with specific properties. In addition, we have performed molecular-simulation studies of isolated polyelectrolytes in a dielectric 'solution' (refs. 14-16). These studies provide detailed information on the relationship between configurational properties, polymer structure (and energetics), and solution conditions. These molecular-simulation results provide a benchmark for comparison with analytical theories of polyion expansion. Through the analogy between isolated-polymer expansion and gel-swelling behavior, simulation studies give information on specific (electrostatic) factors which may influence gel swelling.

In this chapter we summarize our recent studies of phase behavior in aqueous/polymer systems. We begin by reviewing the thermodynamic framework for describing phase (swelling) equilibria in gel/solvent systems. We then introduce into this framework an oriented-lattice model for describing polymer/solvent mixing effects in aqueous systems (ref. 11); this model describes correctly lower critical-solution temperature behavior in aqueous polymer solutions, and temperature-induced volume

collapse for uncharged gels. An extension of this model for polyelectrolyte gels gives a semiquantitative description of isothermal swelling equilibria for ionized gels (ref. 12). In addition, the model predicts semiquantitatively the observed effect of gel charge density and solution ionic strength on temperature-induced gel collapse (ref. 13). Finally, we discuss molecular-simulation studies of isolated polyelectrolytes in solution (refs. 14-16).

THERMODYNAMIC FRAMEWORK

The framework which defines swelling equilibria in gel/solvent systems has existed for many years (ref. 1); it is a direct extension of the basis for defining phase equilibria in non-crosslinked systems. For equilibrium between two coexisting phases (phase ' and phase ") at the same temperature, the chemical potential μ of every component *i* is the same in both phases, i.e.,

$$\mu'_i = \mu''_i \tag{1}$$

For swelling of a gel in solvent, ' represents the gel phase, and " represents the surrounding solution, or external phase. Eqn (1) applies for all components which can exist in both phases, i.e., for all diffusible species. When *i* represents the solvent (component 1), Eqn (1) is usually written in the form:

$$\Pi = -\frac{\mu_1^{gel} - \mu_1^{ext}}{V_1} = -\frac{\Delta\mu_1}{V_1} = 0 \tag{1a}$$

where Π is the osmotic pressure of the solvent in the gel phase and V_1 is the solvent molar volume. Eqn (1a) is analogous to a mechanical equilibrium balance; solvent flows into or out of the gel until Π is zero, i.e., until the forces working to expand and contract the gel are balanced. Thus, Π can be thought of as a swelling pressure which, when nonzero, provides a driving force for gel volume change.

The swelling pressure Π depends on gel and solution properties in a non-trivial manner. The commonly used Flory-Rhener approximation (ref. 1) assumes that Π consists of three independent contributions:

$$\Pi = 0 = \Pi_{mix} + \Pi_{elas} + \Pi_{ion} \tag{2}$$

where Π_{mix} represents the contribution from polymer/solvent mixing, Π_{elas} denotes the elastic contribution from deforming the network chains from their reference state, and Π_{ion} represents the contribution from ion/solvent mixing and electrostatic effects.

Eqn. (2) coupled with Eqns. (1) define the equilibrium gel composition (or degree of swelling) for specified conditions. To reduce Eqn. (2) to practice, we must specify the dependence of the three swelling pressure contributions on gel and solution properties. Considerable flexibility exists in this choice, and a number of swelling models based on Eqn. (2) can be found in the literature. However, in many cases, expressions used for the swelling-pressure contributions are not justified. As discussed in the next section, the unique swelling properties of hydrogels are largely a result of complex

polymer/water mixing effects; conventional polymer-solution models (used for Π_{mix} in existing gel-swelling models) do not account for these interactions. Little previous work has been concerned with the ability of existing models for Π_{elas} to represent the effects of network structural properties on swelling equilibria; we consider these effects here. Finally, various authors have included in Π_{ion} a contribution to account for intrachain fixed-ion repulsions; in the last section, we present molecular-simulation results which question the validity of current models for describing this contribution.

THERMALLY-INDUCED COLLAPSE OF UNCHARGED POLYMERS AND GELS

Before we turn our attention to gels, we must first understand the properties of linear (not crosslinked) polymers in aqueous solution. A particularly interesting class of aqueous/polymer systems are those mixtures which undergo phase separation in response to an increase in temperature. These systems exhibit a lower critical solution temperature (LCST). A well-characterized example is provided by poly(N-isopropylacrylamide) (NIPA) which has been studied at infinite dilution in water (ref. 17), in concentrated aqueous solution (ref. 18), and as a crosslinked gel in water (refs. 3,7,8). In each case, the aqueous/poly(NIPA) system undergoes a temperature-induced phase transition at approximately 31-33°C. In this temperature range, the infinitely-dilute polymer collapses from a random-coil to a compact configuration, the uncrosslinked polymer solution experiences liquid-liquid phase separation, and the crosslinked gel in water undergoes an order-of-magnitude volume decrease.

LCST behavior is observed in polymer solutions in two, fundamentally distinct situations. The first is observed when the polymer and solvent have large differences in compressibility; this situation is encountered often for nonpolar polymer/solvent mixtures at temperatures approaching the solvent's critical (ref. 19). The second is observed when specific, orientation-dependent interactions occur between polymer and solvent; aqueous/polymer mixtures (e.g. water/poly(NIPA)) provide an example.

Classical polymer-solution models (e.g., Flory-Huggins theory (ref. 1), Guggenheim's quasichemical theory (ref. 20)) are based on a rigid-lattice framework where compressibility effects not considered. In addition, these theories assume that all molecules or segments have interaction potentials which are independent of orientation; specific interactions are not considered. Thus, these theories cannot describe the physical mechanisms responsible for LCST behavior in either non-polar *or* specifically interacting systems. It is possible to describe LCST behavior using conventional Flory-Huggins theory when the polymer/solvent interaction parameter is given an *unreasonable* temperature-dependence, but such description has no scientific and therefore, little predictive value. Since lattice-fluid (ref. 21) and free-volume (ref. 22) equations of state account for compressibility effects, they describe correctly LCST behavior in nonpolar polymer solutions. However, these theories do not account for orientation-dependent interactions, and thus cannot describe the physical

mechanisms responsible for LCST behavior in hydrogen-bonding polymer mixtures such as aqueous poly(NIPA) systems.

For describing thermally-induced phase transitions in aqueous polymers and gels, we require a solution model which accounts for directionally-specific interactions. Prange et al (ref. 11) recently proposed such a model and applied it for describing LCST behavior in aqueous/polymer solutions and temperature-induced collapse in an aqueous/gel system. Here we review the physical premise of that model, the resulting expression for Π_{mix}, and some important results for the systems of interest here.

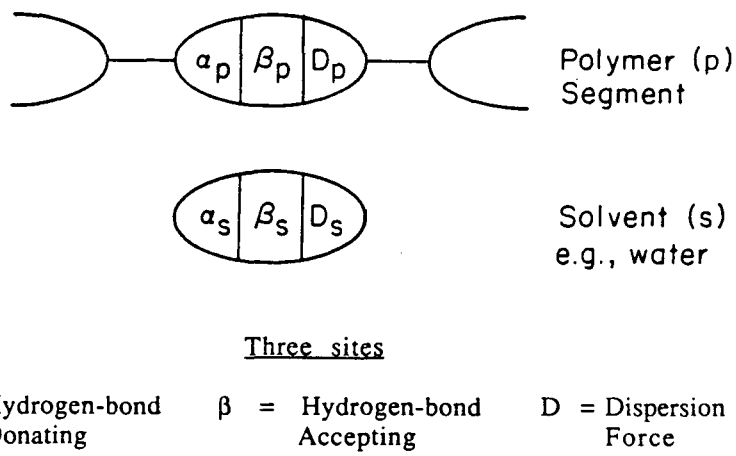


Fig. 1. Oriented-lattice model for polymer/solvent mixture (ref. 11). Each segment may possess up to three, energetically different types of contact sites; thus, interaction energies between neighboring segments are orientation-dependent.

Fig. 1 illustrates the qualitative features of the model developed by Prange et al. The model is formulated within a rigid-lattice framework, i.e., the solvent and polymer segments occupy discrete lattice spaces and no account is given to density (free-volume) effects. However, the model departs from conventional theories in the description of segment-segment interaction potentials. Here, each segment is allowed to possess up to three types of interaction sites: hydrogen-bond donating (α) sites, hydrogen-bond accepting (β) sites, and dispersion-force (D) interaction sites. With this major departure from conventional theories, interactions between neighboring lattice sites now depend on the orientations of the molecules or segments. For example, strong hydrogen-bonding interactions can occur between neighboring α (e.g., polarized hydrogen) and β (e.g., electronegative oxygen) sites, while weaker, dispersion force interactions occur between neighboring D sites. The frequencies of the different (orientation-dependent) interactions are obtained from the quasi-chemical assumption. This model describes the competition between hydrogen-bonding and dispersion-force interactions which results in LCST behavior for aqueous polymer systems.

The physical premise of the oriented-lattice model is simple; however, extensive computations are required to reduce this model to analytical expressions for describing phase behavior in aqueous/polymer systems. Ref. 11 presents details of the model derivation. For our purposes here, we are interested primarily in the resulting expression for the polymer/solving mixing contribution in Eqn. (2):

$$\Pi_{mix} = -\frac{RT}{V_1}\left[\ln\phi_1 + \phi_2 - \frac{1}{2}z_1^{\alpha}q_1\ln\frac{\left[\Gamma_{11,pure}^{\alpha\alpha}\right]}{\left[\Gamma_{11,mix}^{\alpha\alpha}\right]} - \frac{1}{2}z_1^{\beta}q_1\ln\frac{\left[\Gamma_{11,pure}^{\beta\beta}\right]}{\left[\Gamma_{11,mix}^{\beta\beta}\right]} - \frac{1}{2}z_1^{D}q_1\ln\frac{\left[\Gamma_{11,pure}^{DD}\right]}{\left[\Gamma_{11,mix}^{DD}\right]}\right] \quad (3)$$

where R is the gas constant, T is temperature, ϕ_1 and ϕ_2 represent (respectively) the volume fraction of solvent and polymer in the gel, q_1 and the z_1's are solvent structural parameters, α, β, and D represent the different types of interaction sites on a segment, and the Γ's are factors which represent the degree of nonrandom mixing around each type of contact site.

Detailed explanations of all parameters in Eqn. (3) are given in ref. 11. It is important to note here that all parameters other than the Γ's are obtained from *known* structural properties of the solvent or polymer (i.e., V_1, q_1, and the z_1's), and are *not* adjusted to binary data. However, the non-random factors (Γ's) depend on three *adjustable* exchange-energy parameters (which are independent of temperature). These parameters describe interactions between different types of contact sites, and must be obtained from experimental phase equilibria for the binary polymer-solvent mixture.

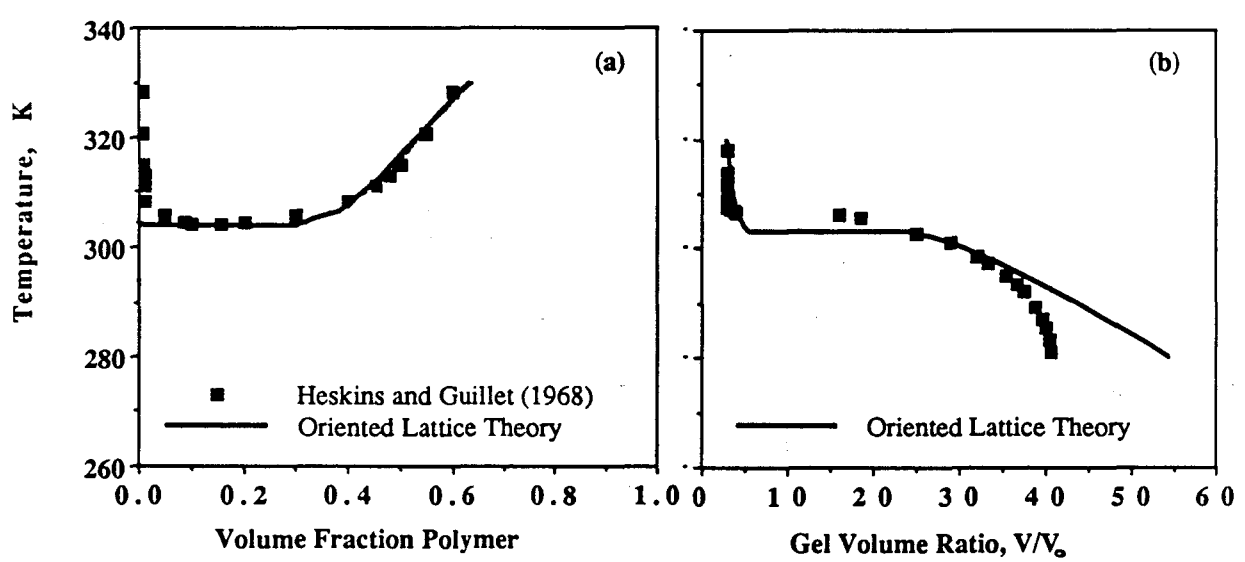


Fig. 2. (a) Liquid-liquid equilibria for uncrosslinked poly(NIPA) aqueous solution, and (b) swelling equilibria for crosslinked poly(NIPA) gel in water. Calculations for both systems were made using the same exchange-energy parameters. For the uncrosslinked polymer solution, a non-classical correction was applied in the critical region (see original paper for details). (Reproduced from ref. 11).

Prange et al showed that the oriented-lattice theory describes vapor-liquid and liquid-liquid equilibria in a number of specifically-interacting systems. Of particular interest here are liquid-phase equilibria in aqueous/polymer solutions and gels. Fig. 2 compares experimental and calculated equilibria for uncrosslinked poly(NIPA) aqueous solution and for crosslinked poly(NIPA) gel in water. The LCST behavior for the uncrosslinked polymer solution is correlated well by the oriented-lattice theory; similar results were obtained for other aqueous/polymer solutions exhibiting LCST behavior. For applying the oriented-lattice theory to crosslinked gels, Prange et al used for the elastic contribution in Eqn. (2) the simple affine network model (ref. 1). The resulting predicted swelling curve in Fig. 2 agrees reasonably well with experiment. This favorable agreement is especially encouraging because the same exchange-energy parameters were used in both calculations shown in Fig. 2.

ISOTHERMAL SWELLING EQUILIBRIA FOR POLYELECTROLYTE HYDROGELS

In the previous section we briefly reviewed the oriented-lattice theory for describing the complex, short-range intermolecular interactions in aqueous/polymer solutions and gels. Here we discuss an extension of this theoretical framework for describing swelling equilibria in *ionized* (polyelectrolyte) hydrogels. Attention in the previous section was directed at the effect of *temperature* on phase behavior in *uncharged* systems; here we are concerned with *isothermal* swelling equilibria of *ionized* hydrogels.

Hooper et al (ref. 12) investigated isothermal swelling equilibria in water and in aqueous salt solutions for gels prepared by copolymerizing acrylamide with the strong electrolyte methacrylamidopropyltrimethylammonium chloride (MAPTAC). For this system, the authors studied systematically the effects on swelling equilibria of gel charge density (%MAPTAC), gel crosslink density (%C) and monomer concentration at preparation (%T). We discuss here the primary results of ref. 12, with emphasis on the ability of the extended swelling model to predict the effects of gel and solution conditions on swelling equilibria.

For applying the oriented-lattice theory (Eqn. 3) to polyelectrolyte gels, we need expressions for the elastic and ionic contributions to the gel-swelling pressure (i.e, Π_{elas} and Π_{ion}). Prange et al (ref. 11) used the affine network model for providing a simple extension of the oriented-lattice theory to aqueous poly(NIPA) gel. Hooper et al were interested in describing the effects of gel structural properties (%C and %T) on swelling behavior; they used the more realistic *constrained junction* model (refs. 23, 24) in their calculations for the acrylamide/MAPTAC system.

The ionic contribution to gel swelling (Π_{ion}) includes, in principle, a number of separate physical effects. It is customary to assume that Donnan equilibria of mobile ions between the gel phase and surrounding solution provide the dominant contribution

to Π_{ion} (refs. 1, 25). However, some authors have proposed including in Π_{ion} an additional term to account for coulombic repulsions between fixed charged groups along the polymer chains (refs. 26, 27). Recent molecular-simulation results (see final section) indicate that existing theories for describing this intrachain fixed-ion repulsion contribution are inappropriate. Thus, we consider here only ideal Donnan equilibria for describing the ionic contribution to gel swelling.

Ref. 12 gives mathematical details concerning the use of constrained-junction theory for Π_{elas} and Donnan equilibria for Π_{ion}. Here we are concerned with the physical implications of these theories, and with the ability of the resulting swelling model to reproduce measurements for the acrylamide/MAPTAC system. The complete expression for the swelling pressure (Eqn. (2)) contains several parameters which describe gel and solution properties. However, the only *adjustable* parameters are the three exchange-energies in the oriented-lattice expression for Π_{mix}. In ref. 12 these adjustable energy parameters are obtained from swelling equilibria for *uncharged* polyacrylamide gels in water. The model is then used to *predict* swelling equilibria for *ionized* acrylamide/MAPTAC gels in aqueous NaCl solutions.

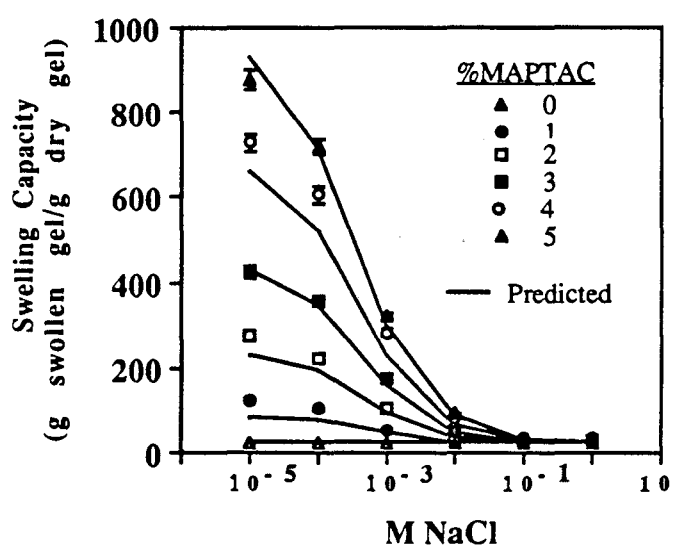


Fig. 3. Experimental and predicted swelling equilibria for acrylamide/MAPTAC copolymer gels in aqueous NaCl solutions. The model predicts semiquantitatively the effects of gel charge density and solution ionic strength on isothermal swelling equilibria. (Reproduced from ref. 12).

Fig. 3 presents the effect of gel charge density (%MAPTAC) on swelling equilibria in aqueous NaCl solutions in the concentration range 10^{-5} - 1.0 M. At low ionic strength, %MAPTAC dramatically influences water absorption properties; this effect is reduced (and eventually eliminated) as ionic strength rises. The swelling model provides semi-quantitative predictions for the effects of gel charge density and solution

ionic strength on the water absorption properties of this gel. This semi-quantitative agreement with experiment supports the argument that Donnan equilibria provide the dominant contribution to Π_{ion}, particularly for lightly ionized, strongly hydrophilic acrylamide/MAPTAC gels.

Fig. 4 presents the effects of crosslink density and monomer concentration at preparation on swelling equilibria of ionized gels in NaCl solutions. In both cases, the model predicts correctly the qualitative trends observed in response to variations in %C and %T. However, the sensitivity of predicted swelling capacities to %T is much smaller than that observed; this discrepancy is most apparent at low ionic strengths where the swelling capacities are largest. As discussed in ref. 12, the inability of the elastic expression to describe the observed %T effect appears related to the physical assumptions used in deriving this, and other common network-elasticity theories. In particular, the theory does not account for the ability of the network to form more chain entanglements with increasing %T, and the resulting contribution of these entanglements to network elasticity.

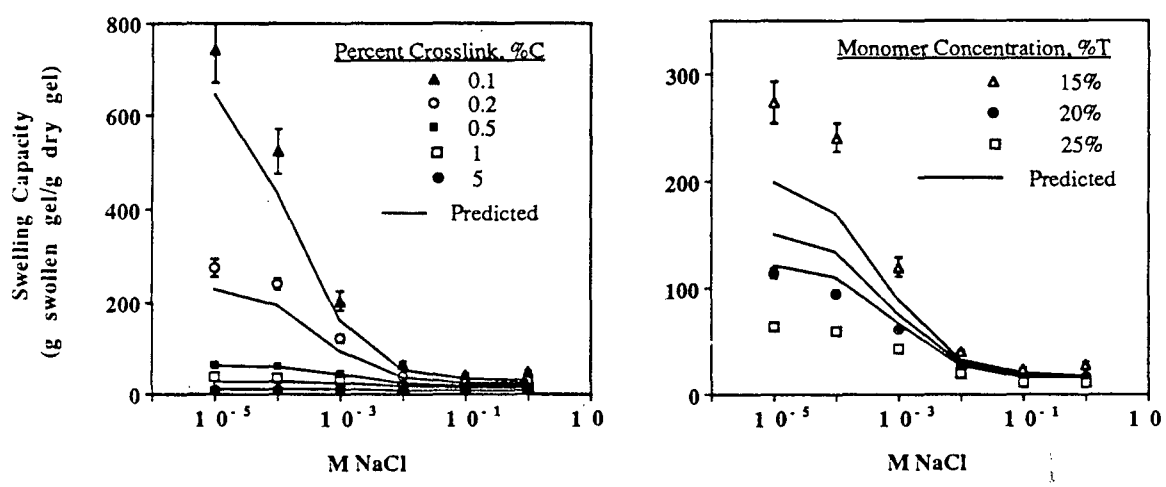


Fig. 4. Effect of network structural parameters on swelling equilibria of acrylamide/MAPTAC gels. The model predicts a smaller dependence of swelling equilibria on monomer concentration at preparation than that observed experimentally. (Reproduced from ref. 12).

The acrylamide/MAPTAC studies suggest some preliminary conclusions. For highly swollen gels, Donnan equilibria (coupled with the oriented-lattice mixing expression) describe well the effect of gel charge and solution ionic strength on gel swelling. The effect of crosslink density on swelling equilibria is described reasonably well by constrained-junction theory, while the effect of monomer concentration at preparation is not reproduced correctly. For improved representation of the data, we

require a better model for Π_{elas} to give the relation between monomer concentration and hydrogel-swelling properties.

SWELLING OF IONIZED TEMPERATURE-SENSITIVE HYDROGELS

In the previous two sections we considered first, temperature-sensitive phase behavior in nonelectrolyte polymer solutions and gels, and second, isothermal swelling equilibria of ionized gels. Here we consider temperature-sensitive swelling behavior for polyelectrolyte gels. For a model system, Beltran et al (ref. 13) studied gels prepared by copolymerizing N-isopropylacryamide (temperature-sensitive monomer) with MAPTAC (strongly dissociating electrolyte). Gel-swelling properties were measured as a function of temperature, gel-charge density, and solution ionic strength. Here we discuss the main results of ref. 13, with emphasis on our ability to describe (and predict) the effects of gel charge and solution ionic strength on temperature-induced gel collapse.

Fig. 5 presents swelling equilibria in water for NIPA gels containing 0-4% MAPTAC (gel structural parameters %C and %T are held constant). Gel ionization has a significant effect on absorption capacity and on the temperature of gel collapse. The calculated swelling curves are predictions based on exchange-energy parameters obtained from experimental swelling equilibria for the uncharged gel. At low temperatures (high degrees of swelling), the model predicts semiquantitatively the observed effect of gel charge on swelling capacity. The model also predicts the observed increase in temperature of the volume-transition region. However, absorption capacity at high temperature is not accurately predicted. Further, the theory predicts a discontinuous change whereas the data show a continuous transition.

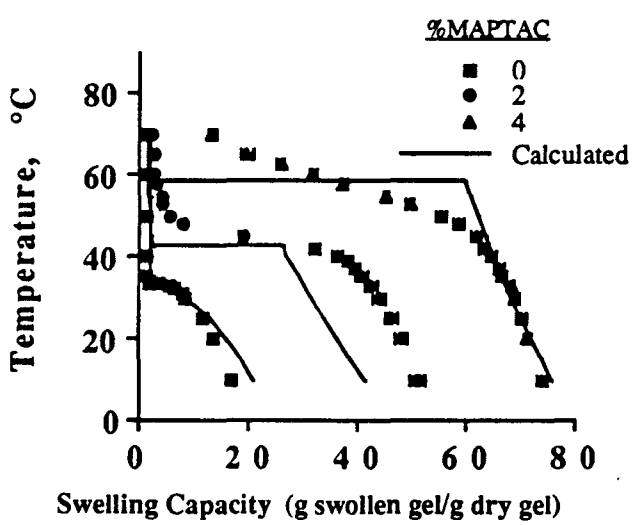


Fig. 5. Effect of network ionization on temperature-induced collapse of NIPA gel. Swelling measurements performed in aqueous solution (no added salt). Calculated swelling curves are predictions based on parameters obtained for uncharged NIPA gel in water. (Reproduced from ref. 13).

For a gel with constant ionization (4%MAPTAC), Fig. 6 shows the effect of solution ionic strength on temperature-sensitive gel swelling. As for the isothermal acrylamide/MAPTAC system, increasing ionic strength reduces the effect of gel ionization on water-absorption properties. Here this effect is confirmed over a wide temperature range. The 4%MAPTAC gel in 0.1M NaCl exhibits temperature-dependent swelling behavior nearly identical to that for uncharged NIPA gel. The swelling model predicts semiquantitatively the observed effect of solution ionic strength on the temperature-sensitive swelling properties of this gel. As in Fig. 5, there are discrepancies between theory and experiment in the order of the volume transition and in the swelling behavior at high temperatures.

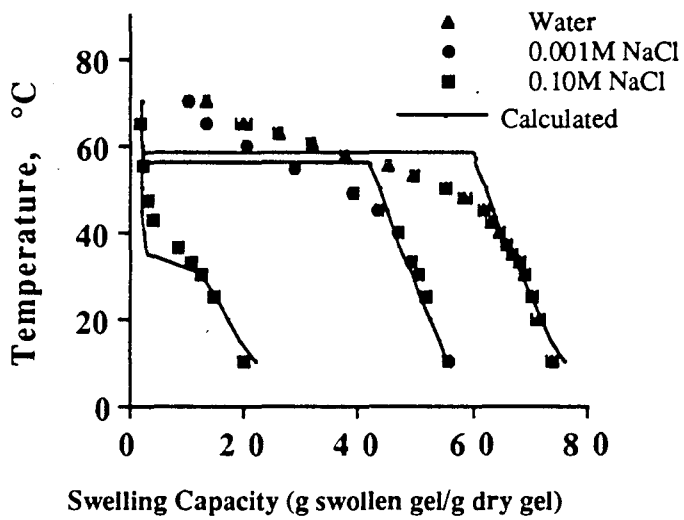


Fig. 6. Effect of solution ionic strength on temperature-induced collapse of an ionized (4% MAPTAC) NIPA gel. (Reproduced from ref. 13).

Figs. 5 and 6 indicate both the value and limitations of our gel-swelling model. Using only experimental data for the uncharged gel, the model provides reasonable, semi-quantitative estimates for the effects on swelling equilibria of network ionization and solution ionic strength over a wide temperature range. Such estimates may be useful for guiding design of novel gels; they can reduce the required experimental effort by indicating the range of system variables which produce desired gel properties. However, the model does not provide quantitative predictions of swelling equilibria; model predictions cannot totally replace experimental measurements for the final conditions of interest.

MOLECULAR SIMULATION OF SINGLE POLYELECTROLYTES IN SOLUTION

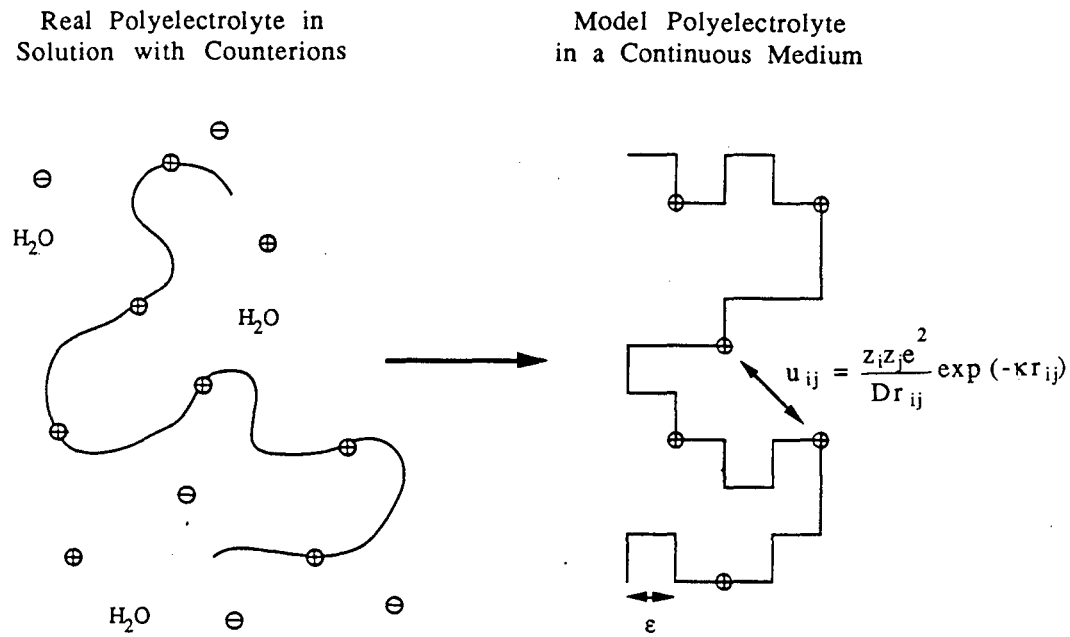
The simplest example of an aqueous/polymer system is provided by an isolated polymer at infinite dilution in water. The coil-globule transition of an isolated polymer in solution is analogous to liquid-liquid phase separation in concentrated polymer

solutions and to volume collapse of polymer gels. Thus, the isolated polymer represents a fundamental point of departure for examining interactions and conditions which influence phase behavior in more concentrated and more complex polymer systems.

Electrostatic interactions are of particular importance in aqueous/polymer systems, as indicated by the dominant effects of gel charge and solution ionic strength on swelling behavior of ionized hydrogels. Because of the complex nature of a hydrogel, it is not possible to isolate and examine the effects on swelling behavior of detailed electrostatic interactions (i.e., repulsions between fixed ions). However, the study of a single polyelectrolyte in solution may permit us to examine the effects of such detailed interactions on singe-chain expansion, thereby giving insight into the effects of these interactions in the more complex hydrogel system.

Experimental study of infinitely-dilute polymers is difficult and few direct measurements have been reported for configurational properties of isolated polymers in solution. Molecular simulation offers an alternate powerful method for studying the properties of model polymeric systems, including infinitely-dilute polymers in solution. Computer simulations have been performed in several cases for examining the conformational behavior of isolated, *uncharged* polymers (refs. 28-30) and, on a more limited basis, for studying isolated, *fully-ionized* polyelectrolytes (refs. 31, 32). Hooper et al (refs. 14, 15) recently performed Monte-Carlo computer simulations for a lattice model of an isolated, *partially-ionized* polyelectrolyte. Here, we present some of the primary results from refs. 14 and 15, and discuss how these results can improve our understanding of phase behavior in aqueous/polymer systems.

The first and most important step in performing a molecular-simulation study is choosing a *model* to represent the physical system of interest. In principle, we desire a complete, molecular-level description of a polyelectrolyte in aqueous solution; in practice, the computational requirements of such a model would severely limit the range of conditions (particularly, polymer length) that one could study by simulation. Fig. 7 illustrates the polyelectrolyte model used by Hooper et al. The polyelectrolyte is described as a self-avoiding walk on a cubic lattice with fixed charges equally spaced along the chain backbone. The discrete nature of the solvent is ignored; instead, the polymer is immersed in a continuum of dielectric constant D. The influence of the counterions and added salt are smeared; their effects on electrostatic interactions enter through the Debye screening length, κ^{-1}. The resulting model is characterized by three types of interactions: excluded volume (two segments cannot occupy the same lattice site), screened coulombic repulsions between all pairs of fixed charges, and attractive (hydrophobic) interactions between neighboring, non-bonded polymer segments. The model represented in Fig. 7 captures the essential physics of polyelectrolyte configurational behavior and is sufficiently simple to permit study of these properties by simulation over a wide range of system conditions.



Parameters in screened potential u_{ij}:

$z_i e$ = charge on monomer i
r_{ij} = distance between monomers i and j
D = dielectric constant (solvent property)
κ^{-1} = screening length
(determined by electrolyte concentration)

Fig. 7. Lattice representation of an isolated, partially-ionized polyelectrolyte used in Monte-Carlo simulations of refs. 14 and 15. The potential u_{ij} represents screened coulombic repulsions between all pairs of fixed charges on the chain; ε characterizes short-range, dispersion-force interactions between non-bonded nearest-neighbor segments.

Hooper et al examined two situations: first, in the *hydrophilic* polyelectrolyte limit (i.e., when the segment-segment interaction energy ε /kT is zero); and second, for *hydrophobic* polyelectrolytes (i.e., ε /kT < 0). In both cases, configurational properties were calculated as a function of degree of chain ionization and solution ionic strength (i.e., Debye screening length); for the first case, the effect of polymer chain length was also examined.

We first consider results for the *hydrophilic* polyelectrolyte limit. Fig. 8 presents the effect of charge screening (denoted here by electrolyte concentration) on the reduced, end-to-end distance of partially-ionized 100-segment polyelectrolytes. The polymer end-to-end distance provides a measure of excluded volume, or space occupied by the polymer. The maximum of the vertical axis represents the fully-extended, or rodlike conformation of the polyion; this conformation is approached for

fully-ionized chains at low ionic strengths (low charge shielding). As ionic strength rises, the polyelectrolytes transform from extended rods to random coils.

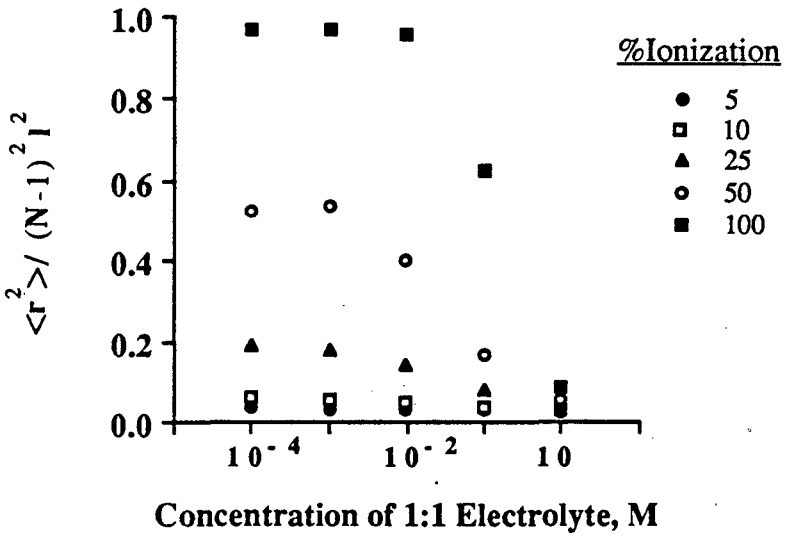


Fig. 8. Effect of ionic-strength on reduced end-to-end distance for 100-segment partially-ionized polyelectrolytes. Note the qualitative similarity of the single-chain behavior to the gel swelling equilibria shown in Fig. 3. (Reproduced from ref. 14).

Fig. 8 shows results similar to the swelling equilibria curves for partially-ionized gels in aqueous salt solutions (Fig. 3). In both cases, a large reduction in volume (gel volume, or polymer excluded volume) is induced by an increase in system ionic strength. Clearly, differences exist between the two cases, and the comparison is qualitative. Nevertheless, we see similarities between single-chain behavior and behavior of more complex aqueous/polymer systems.

The effect of intrachain, fixed-ion repulsions on polyelectrolyte expansion has been discussed extensively in the literature, particularly for describing the contribution of these repulsions to the behavior of semi-dilute or concentrated polyelectrolyte solutions, or to the swelling behavior of ionized gels. The theory of Katchalsky and Lifson (ref. 33) has been used often for describing fixed-ion repulsion effects on single-chain expansion (ref. 33), and on gel-swelling equilibria (refs. 26, 27). However, due to lack of well-characterized experimental data, justification has never been given to the Katchalsky-Lifson (K-L) theory.

In the hydrophilic limit, the simulation model of Fig. 7 corresponds directly with the model used by K-L in deriving their analytical theory for polyelectrolyte expansion. Hooper et al (ref. 14) compared simulation results for electrostatic energies and expansion factors with predictions of K-L theory, along with predictions of a revised version of this model known as *uniform-expansion* theory (ref. 34). Fig. 9 presents typical results from this comparison. In general, poor agreement was found between simulation and theory for various chain lengths, chain ionizations, and screening

lengths. This disagreement clearly indicates that K-L theory does not accurately represent the physical model on which it is based. Possible reasons for this disagreement, and suggestions for improving the theoretical predictions, are discussed in ref. 14. As a result of this comparison, we conclude that there is little justification for using K-L theory for describing the contribution of intrachain fixed-ion repulsions to polyelectrolyte expansion or gel-swelling equilibria. Unfortunately, an alternate theory for describing this contribution in such calculations is not currently available.

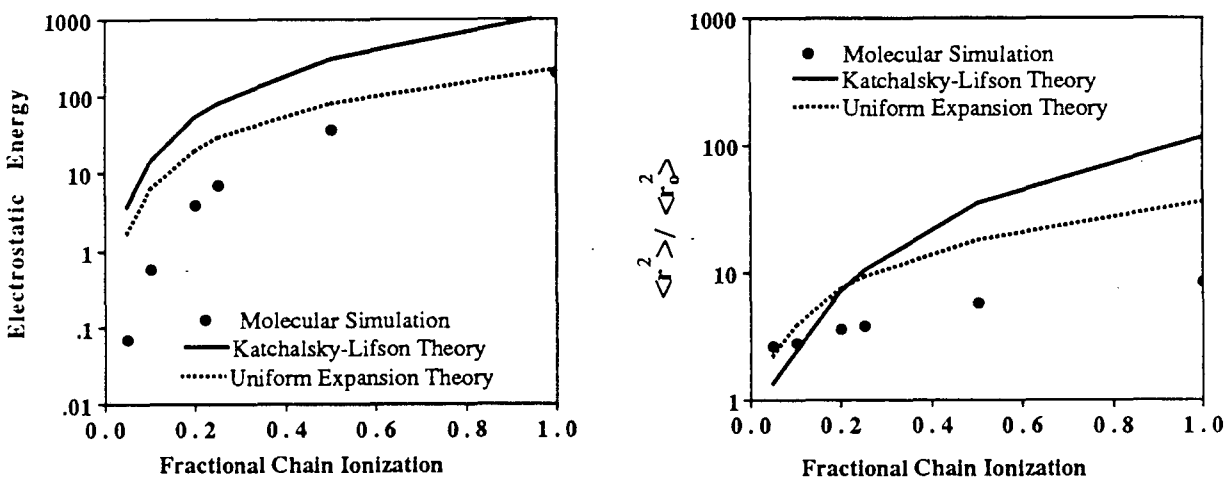


Fig. 9. Comparison of theoretical and simulated electrostatic energies and expansion factors for 100-segment polyelectrolytes in 1.0M 1:1 electrolyte. (Reproduced from ref. 14).

Much current research is directed at polymers where some or all of the monomers are hydrophobic but where the presence of bound charges induces water solubility. Because these *hydrophobic polyelectrolytes* have interesting solution behavior, they are actively studied for applications as additives and viscosifiers in aqueous solution (refs. 35-37). Crosslinked gels of hydrophobic polyelectrolytes show large volume transitions in response to small pH changes (ref. 38); these systems are of interest for potential applications in controlled-release devices (ref. 39).

Molecular simulations of hydrophobic polyelectrolytes (ref. 15) can provide fundamental qualitative information on the properties of this interesting class of systems. In particular, such studies indicate the range and magnitudes of interactions which influence polymer properties. Fig. 10 illustrates charge-induced order-of-magnitude structural transitions seen in simulations for hydrophobic polyelectrolytes. At low ionizations, the chains exist in a compact globular form, with the density of the collapsed chain determined by the polymer hydrophobicity (i.e., the magnitude of ε/kT). At high ionizations, the chains expand to rod-like conformations. Over an intermediate range of ionization, the chains experience a transformation from the collapsed to the expanded

conformation; the transition becomes increasingly sharp for the more hydrophobic chains.

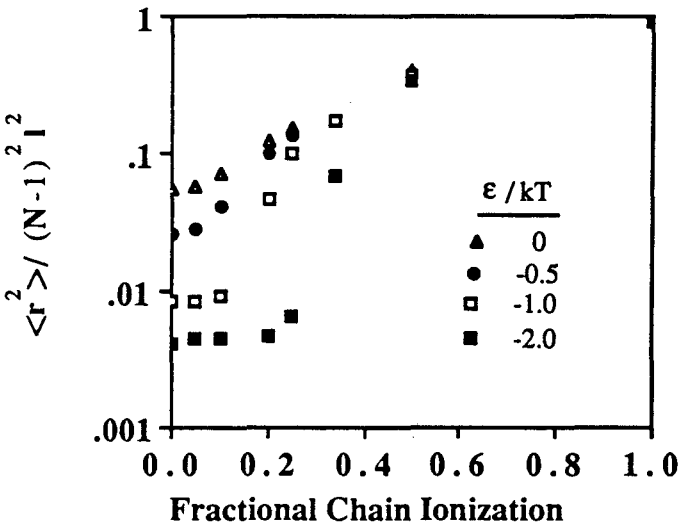


Fig. 10. Charge-induced structural transitions of hydrophobic polyelectrolytes. Results are for 40-segment chains in 0.001M 1:1 electrolyte. (Reproduced from ref. 15).

The simulation results of Fig. 10 (and ref. 15) provide direct evidence for a global structural transition in model hydrophobic polyelectrolytes due to an increase in chain ionization. The occurrence of such a transition has been suggested previously by a number of authors (40-42) with indirect experimental evidence (i.e., intrinsic viscosity measurements) used to support their arguments. Molecular simulation studies of model hydrophobic polyelectrolytes are valuable for providing direct observations of polymer behavior for well-defined system conditions.

Refs. 14 and 15 consider configurational properties of isolated polyelectrolytes at *isothermal* conditions. Current work (ref. 16) is directed at determining the effect of *temperature* on the properties of isolated polyelectrolytes. Temperature-induced coil-globule transitions of infinitely-dilute uncharged polymers have been examined experimentally (43, 44) and by computer simulation (refs. 28-30). Using molecular simulation, Sassi et al (ref. 16) are examining the influence of chain ionization on temperature-induced collapse of isolated polymers.

CONCLUSIONS

Aqueous polymer systems exhibit unique solution behavior due to complex intermolecular interactions, to the large number of chain conformational degrees of freedom, and for gels, to the intricate topology of crosslinked networks. This chapter has summarized recent work directed at improving our understanding of aqueous/polymer systems.

We presented the essential basis of a recently proposed polymer-solution model which accounts for specific (hydrogen-bonding) interactions, and describes correctly LCST behavior in aqueous/polymer solutions. We examined the uses and limitations of a gel-swelling model which uses the oriented-lattice theory for describing polymer/solvent mixing effects. The model predicts semiquantitatively swelling equilibria for isothermal acrylamide/MAPTAC gels in aqueous salt solutions and swelling equilibria for ionized temperature-sensitive NIPA/MAPTAC gels in water and in aqueous salt solutions. The model does not describe well the effect of monomer concentration at preparation on the swelling behavior of acrylamide/MAPTAC copolymer gels. The failure of the model to describe monomer-concentration effects is related to the assumptions in the elastic equation of state.

We have used molecular simulation to examine configurational properties of isolated polyelectrolytes in solution. Studies on hydrophilic polyelectrolytes indicate that existing polyelectrolyte-expansion theories are inconsistent with the physical model on which they are based. Studies on hydrophobic polyelectrolytes are useful for examining the nature of structural transitions in polymers with competing attractive and repulsive interactions, and for determining the range of conditions under which such transitions occur.

This work discusses new models and techniques for improving our understanding and description of phase behavior in aqueous/polymer systems. We have considered only some of the potentially important classes of aqueous/polymer systems; this work provides a framework on which to base further studies in this area. Important classes of hydrogels not considered here are pH-sensitive gels (refs. 4, 38), and gels in mixed-solvent solutions (ref. 4). A satisfactory theoretical description has not yet been obtained for the large volume transitions observed in these systems. It is likely that volume transitions induced by changing solvent composition (i.e., acetone/water ratio) may be explained by the oriented-lattice framework extended to ternary systems.

The molecular-simulation studies discussed here consider the relatively simple case of a single polymer at infinite-dilution on an infinite lattice. Many interesting features of polymer solutions result from interchain interactions (e.g., aggregations in hydrophobic polyelectrolytes) and from interactions of polymers with interfaces (e.g., adsorption and adhesion properties). Computer simulation may also prove useful for studying such polyelectrolyte systems.

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