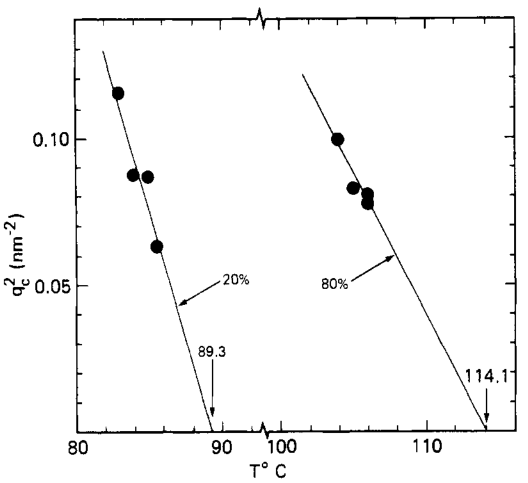

Figure 9. Square of the crossover point, q_c^2, as a function of temperature for an 80% and 20% mixture of PS(2K) with PBD(2.5K).

Conclusion

The initial stages of phase separation in low molecular weight mixtures of polystyrene with polybutadienes have been investigated by means of time-resolved small-angle X-ray scattering. The results presented only qualitatively agree with the classical theory of spinodal phase separation developed by Cahn and Hilliard. The data indicated that an additional contribution to the scattering equivalent to the Ornstein–Zernicke scattering from a homogeneous mixture at equilibrium was necessary in order to fully describe the scattering. A critical wavelength, q_c, was observed where the rate of intensity change was zero. This was used to evaluate the Flory–Huggins interaction parameter for the different mixtures. q_c^2 was found to vary linearly with the temperature and permitted the evaluation of the spinodal temperature. In addition, q_c was found to increase with an increase in the molecular weight of one of the components.

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Registry No. PS (homopolymer), 9003-53-6; PBD (homopolymer), 9003-17-2.

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Phase Transition in Ionic Gels Induced by Copper Complexation

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ABSTRACT: Acrylic acid–acrylamide copolymer gels immersed in water solutions of Cu(II) salts exhibit a discontinuous volume collapse upon continuous increase of Cu(II) concentration. The phenomenon, which occurs when the acrylic acid content of the gel exceeds a certain critical value, is attributed to formation of Cu(II) complexes with ligands attached to the network. A qualitative description of the phenomenon, based on an analogy between the formation of complexes in a copper salt solution and the formation of energetically favorable contacts between polymer segments in a poor solvent, is presented.

Introduction

In a previous study[1] we investigated the swelling of acrylic acid–acrylamide copolymer gels in water solutions of several simple electrolytes, focusing our attention on salts of alkali metals and alkaline-earth metals. When only monovalent ions are involved, the observed swelling is in good quantitative agreement with the predictions of the simple Donnan equilibrium theory. In the presence of

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divalent cations, such as Ca^{2+}, the quantitative agreement is not as good but the qualitative features remain well described. In these experiments the swelling was always a continuous function of the salt concentration, and we did not observe any evidence for a specific interaction between the metal cation and the ionized gels. Only the valency of the cation determined the swelling behavior.

A specific interaction, namely complexation, is known to occur in systems consisting of certain polyacids and transition metals.[2-6] The complexing of Cu(II), Ni(II), and Co(II) in gels of acrylic and methacrylic acid has been investigated in ref 5 and 6 but no attention was paid to the swelling behavior of the gels.

Here we report the observation of a new type of phase transition, which occurs in acrylic acid–acrylamide copolymer gels when immersed in water with varying amount of Cu(II) salts. We attribute this first-order transition to formation of Cu(II) complexes with network-fixed ligands. We also present a qualitative explanation of the observed phenomena.

Gel Preparation and Experiments

Gels were prepared by radical copolymerization of acrylamide, *N,N'*-methylenebis(acrylamide) (both Bio-Rad, electrophoresis purity), and acrylic acid (reagent grade). Total monomer concentration in the reaction solution (water) was 700 mM, the concentration of bis(acrylamide) was 8.6 mM, and the concentration of acrylic acid was varied between 0 and 350 mM. Gelation took place at 70 °C, initiated by ammonium persulfate. No accelerator was used. Details of the preparation procedure are described elsewhere.[1]

The prepared gels were dialyzed against pure water (resistivity 18 MΩ cm) and then immersed into a large volume of 0.1 mM NaCl solution. This concentration of NaCl was maintained in all subsequent swelling experiments. Sodium ions replace hydrogen in the gel and assure complete dissociation of the acrylic acid.[1] Their presence also speeds up the exchange of ions between the gel and the outer solution.

The gels were then immersed in solutions with varying concentrations of $CuCl_2$, $CuSO_4$, or $NiCl_2$ (all reagent-grade quality). The solutions were replaced several times over a period of 3 weeks until the gels reached equilibrium.[1]

The equilibrium diameter of the cylindrical gels was measured by using a microscope with a calibrated eyepiece. The swelling ratio $X = V/V_0$ was calculated from the equilibrium diameter and the original diameter at the time of the synthesis. Here V is the volume of the gel in equilibrium with a salt solution and V_0 is the volume at preparation.

Results and Discussion

In Figure 1 the swelling ratio X of gels containing varying amounts of acrylic acid is plotted as a function of the $CuCl_2$ concentration in the outer solution. Both variables are plotted logarithmically. The volume of the uncharged gel (curve 0) shows no dependence on the Cu(II) concentration. At low Cu(II) salt concentrations, the charged gels exhibit swelling behavior similar to that of charged gels in solutions of salts of alkaline-earth metals.[1] The swelling ratio increases with increasing acrylic acid content. At higher Cu(II) concentrations this dependence is reversed, and the gels shrink with increasing acid content. The maximum observed volume fraction Φ of the shrunken polymer network is as high as 0.6. The collapsed gels are intensely blue, indicating the intake of copper ions from the dilute colorless solution.

For the highly charged gels, marked with 3 and 4 in Figure 1 and containing 145 and 212 mM acrylic acid, the dependence of X on $CuCl_2$ concentration exhibits a discontinuity. In the concentration range marked with vertical dashed lines, both a swollen and a collapsed state can be observed but never an intermediate state. When a collapsed gel is placed in a solution with a concentration below this range, the gel reswells. These findings indicate a first-order phase transition.

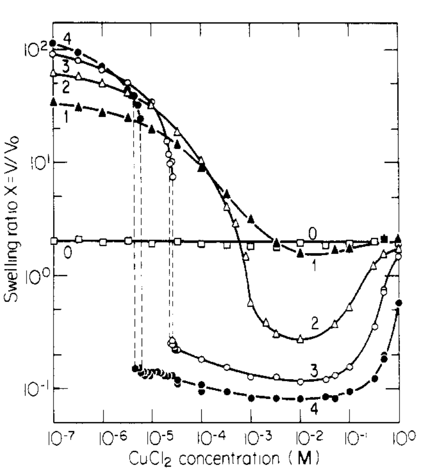

Figure 1. Swelling ratio X of gels containing varying amounts of acrylic acid as a function of $CuCl_2$ concentration in the outer solution. Both variables are plotted logarithmically. In the concentration range marked with vertical dashed lines, both a swollen and a shrunken state are observed, but no intermediate states. The solid line is to guide the eye. Curves are numbered with respect to increasing acrylic acid content: (0) 0, (1) 36.5, (2) 107, (3) 145, and (4) 212 mM.

At very high salt concentrations, all the gels swell, with the swelling ratio approaching that of an uncharged gel. Almost identical results are obtained when $CuSO_4$ is used instead of $CuCl_2$. In addition to these copper salts, we also investigated the effect of $NiCl_2$. Although Ni(II) is reportedly capable of forming complexes with polyacids,[2,5] we did not observe any collapse of the gels. Up to an acrylic acid concentration 350 mM (acrylic acid–acrylamide ratio 1:1) the swelling curves were continuous, resembling qualitatively curve 1 in Figure 1.

A rigorous theoretical description of copper–network complexation is not available, and we restrict ourselves to a qualitative discussion of the observed phenomena. The complexation, i.e., the coordination of a copper ion with several network-fixed ligands, has the effect of a short-range interaction between the polymer chains. When the complex stability is high, the complexation can be viewed as the formation of new cross-links. The theoretical task is to describe the swelling equilibrium of a gel with a variable number of cross-links, with the number of cross-links determined by the complexation equilibrium at a given state of swelling and a given copper concentration.

In the case of low complex stability, we make the analogy between the formation of complexes and the formation of energetically favorable contacts between polymer segments in a poor solvent. We restrict ourselves to this limit, sacrificing a consistent treatment of the complexation equilibrium for the sake of simplicity and to draw parallels with previous experiments on phase transitions in gels.

As first observed by one of us,[7,8] a polyacrylamide gel containing ionizable groups can undergo a discontinuous collapse as the solvent becomes progressively poorer. This behavior can be qualitatively understood in terms of a modified Flory–Huggins theory[8,9] of the swelling equilibrium. According to this theory the equilibrium value of the volume fraction Φ can be obtained from the following pressure-balance equation:

$$\Pi(\Phi)_{\mathrm{conf}} + \Pi(\Phi)_{\mathrm{ion}} + \Pi(\Phi)_{\mathrm{cont}} = 0 \qquad (1)$$

Here Π_{conf} represents the swelling pressure due to the conformational entropy of the network,[9] i.e., the so-called mixing entropy and rubber elasticity term.

Π_{ion} is the counterion swelling pressure, i.e., the difference between the osmotic pressures of mobile ions in the gel and in the outer solution. This contribution has been discussed in the previous paper.[1] It is always positive, causing the gel to expand, and increases with the amount of acrylic acid in the gel.

The term Π_{cont} arises from interactions among polymer segments and solvent molecules. In a simple mean-field approximation, which takes into account only binary contacts between the polymer segments, it is given by[9]

$$\Pi(\Phi)_{cont} = -k_B T \chi (\Phi^2/v) \qquad (2)$$

The factor Φ^2/v, where v is the molecular volume of the solvent, reflects the increase in the number of the binary contacts with increasing density (shrinking) of the gel. The interaction parameter[9] χ is proportional to the free energy change ΔF due to dissolution of one contact. In a poor solvent χ is positive and increases with decreasing compatibility between the polymer and solvent.

In the experiments of ref 8, the value of χ was varied by changing the water–acetone ratio of the solvent. An uncharged acrylamide gel ($\Pi_{ion} = 0$) was found to deswell continuously when the acetone concentration was increased. Correspondingly, eq 1 holds for a single value of Φ over the entire range of acetone concentration. However, when the amount of network-fixed ionizable groups exceeds a certain critical value, the deswelling becomes discontinuous: a first-order phase transition occurs. For a particular value of χ, eq 1 has three solutions, corresponding to two stable states and one unstable state.

We propose to include the effect of copper complexation by introducing a new "contact" term Π_{comp} into eq 1. There is some uncertainty about the number of ligands participating in the formation of one complex.[3,4,6] We assume a complex is formed when two ionized acid groups and one copper ion can be found in a certain small volume. The probability for such ternary encounters increases with the density of the gel as $c_{Cu}c_a{}^2$, where c_{Cu} and c_a are the concentrations of noncomplexed copper and of ionized acid groups in the gel. This leads to the proportionality relation

$$\Pi_{comp} \propto -(\Delta F) c_{Cu} c_a{}^2 \qquad (3)$$

where ΔF is the change in free energy associated with the dissociation of one complex. The concentration c_a is a monotonically increasing function of the total acrylic acid concentration c_0. In the present qualitative treatment we assume $c_a \propto c_0$. Denoting by r the ratio of monomers carrying an acid group to the total number of monomers and using the obvious relation $c_0 \propto r\Phi$, we write an expression analogous to eq 2

$$\Pi_{comp} = -k_B T \chi_c (\Phi^2/v) \qquad (4)$$

$$\chi_c = p(\Delta F) c_{Cu} r^2 \qquad (5)$$

Equation 5, where p is a proportionality constant, defines an effective interaction parameter χ_c, which describes the effect of copper complexation on gel swelling.

An increase in either the acrylic acid content r or the copper concentration c_{Cu} within the gel increases the value of χ_c and is thus equivalent to lowering the polymer–solvent compatibility.

Using this simple model we can not interpret the data in Figure 1. As the conformation term $\Pi(\Phi)_{conf}$ is approximately the same for all gels, the swelling behavior is determined by the relative importance of the complexation term Π_{comp} and the ion swelling pressure Π_{ion}. The latter increases with r, but it decreases with increasing salt concentration in the outer solution.[1] In the present case, this decrease is enhanced by depletion of the ionized acrylic acid groups due to the formation of complexes.

The equilibrium copper ion concentration in the gel depends on the concentration in the outer solution. In our experiments, Na^+ and Cu^{2+} compete to neutralize the gel. We can assume the distribution of these ions is described by the Donnan theory.[1] At $CuCl_2$ concentrations below 10^{-6} M, relatively few of the Na^+ ions are replaced by Cu^{2+}. The effective interaction parameter χ_c is small, and Π_{ion} dominates the swelling behavior. The swelling ratio X increases with increasing acrylic acid content r.

In the concentration range between 10^{-4} and 10^{-2} M, the counterion Na^+ is replaced by Cu^{2+}. Now Π_{comp} dominates and the dependence of swelling on r is reversed as an increase in r is analogous to a decrease in the solvent quality.

For gel 1 the parameter r and thus Π_{comp} are too small to cause the gel to collapse. The only important effect of increasing the $CuCl_2$ concentration is to reduce Π_{ion} to zero. The acrylic acid content of gel 2 is sufficiently high to bring about a collapse of the gel but the deswelling with increasing copper concentration is continuous. In analogy to gels in water–acetone mixtures, there is a critical value of r above which the opposing pressures Π_{ion} and Π_{comp} are both large enough to make a phase transition possible (gels 3 and 4). The higher the acrylic acid content, the lower the copper concentration necessary to induce the collapse, in accordance with the proposed model.

It remains to explain the increase in swelling at high $CuCl_2$ concentrations in solutions. It is conceivable the gel becomes "overcrowded" with copper.[6] The concentration of Cu^{2+} ions in the gel is high enough to make Bjerrum-type ion association important. Positively charged copper–carboxylate pairs would be prevalent, and their electrostatic repulsion would prevent the formation of complexes.

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Registry No. $CuCl_2$, 7447-39-4; $CuSO_4$, 18939-61-2; $NiCl_2$, 7718-54-9; (acrylamide)·(*N,N'*-methylenebis(acrylamide))·(acrylic acid) (copolymer), 27791-59-9; (acrylamide)·(*N,N'*-methylenebis(acrylamide)) (copolymer), 25034-58-6.

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