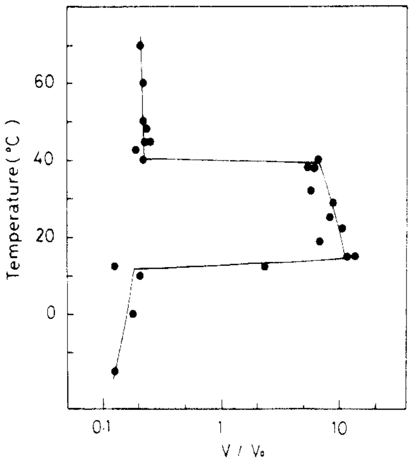

Figure 2. Temperature dependence of the volume swelling, V/V_0, of a cationic gel in a 40/60 acetone–water mixture. The cationic gel was prepared by copolymerization of acrylamide (1 g), trimethyl(*N*-acryloyl-3-aminopropyl)ammonium iodide (50.7 mg), and *N,N*′-methylenebisacrylamide (26.6 mg), described in the text.

whereas for shrunken gels $V/V_0 < 1$. Nonionized acrylamide gel in acetone–water mixtures shows a continuous change in equilibrium volume when the acetone concentration is changed (Figure 1a). As the density of cationic residues in the gel increases, a curve with a zero-slope inflection point first appears (Figure 1b), and then discrete transitions are observed (Figure 1c–g). The volume change at the transition increases gradually with increasing ionic density, and the acetone concentration at the transition shifts higher with increasing gel charge. The above behavior is the same as that of the anioic gels reported previously.[10,13] Consequently, the phase transition of the cationic gel can be relationalized by the theory proposed by Tanaka et al. as well.[10]

Figure 2 shows the relationship of temperature to the swelling ratio V/V_0. The cationic gel is observed to be in shrunken state in the high-temperature region. This is in marked contrast to the case of the acrylamide–sodium acrylate copolymer gel, which has a swollen state in the high-temperature region.[9] As the temperature decreases, the shrunken gel undergoes a tremendous volume change at 40 °C, falling into the swollen state. The swollen gel remains unchanged during subsequent temperature decrease. However, the swollen gel again undergoes a discrete volume change at 13 °C, returning to the shrunken gel state. The shrunken gel no longer changes with further temperature decrease. The above behavior can be summarized as follows. The cationic gel undergoes a convexo volume transition between the collapsed and swollen states, when the temperature is monotonically varied. This is, therefore, called a "convexo" phase transition. This phase transition is in marked contrast to that of an anionic gel, as noted previously.[10,13] The former is characterized by a convexo curve profile of a shrunken–swollen–shrunken cycle with temperature, while the later displays a concavo curve profile of a swollen–shrunken–swollen cycle with solvent composition (Me_2SO–water).[12] In the latter case, it has been referred to as a "reentrant" phase transition. The convexo phase transition containing the two discrete volume changes can be qualitatively understood by assuming that a "reduced" temperature, τ, which is theoretically defined in terms of ionic density and gel volume, is not a monotonic function of the actual temperature. Otherwise, the reduced temperature would be responsible for a phase transition of a stepwise curve profile which contains a single discrete volume change.[10]

In conclusion, the present paper is one of the first references to the phase transition of a cationic gel. The phase transition induced by solvent composition shows the same behavior as displayed by anionic gels,[6,8–13] and the phase transition induced by temperature change is characterized by specific convexo behavior with a monotonic temperature change.

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Registry No. (BIS)·(TMAAPAI)·(acrylamide) (copolymer), 98633-99-9; water, 7732-18-5; acetone, 67-64-1.

References and Notes

(1) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, NY 1953.
(2) M. Ilavsky, *Polymer*, **22**, 1687 (1981).
(3) D. Nicili, C. Young, T. Tanaka, A. Pollak, and G. Whitesides, *Macromolecules*, **16**, 887 (1983).
(4) J. Hrouz, M. Ilavsky, K. Ulbrich, and J. Kopecek, *Eur. Polym. J.*, **17**, 361 (1981).
(5) M. Ilavsky and J. Hrouz, *Polym. Bull. (Berlin)*, **8**, 387 (1982).
(6) I. Ohmine and T. Tanaka, *J. Chem. Phys.*, **11**, 5725 (1982).
(7) M. Ilavsky, *Macromolecules*, **15**, 782 (1982).
(8) T. Tanaka, *Phys. Rev. Lett.*, **40**, 820 (1978).
(9) T. Tanaka, *Sci. Am.*, **244**, 110 (1981).
(10) T. Tanaka, D. J. Fillmore, S.-T. Sun, I. Nishio, G. Swislow, and A. Shah, *Phys. Rev. Lett.*, **45**, 1636 (1980).
(11) T. Tanaka, I. Nishio, S.-T. Sun, and S. Ueno-Nishio, *Science (Washington, D.C.)* **218**, 467 (1982).
(12) S. Katayama, Y. Hirokawa, and T. Tanaka, *Macromolecules*, **17**, 2641 (1984).
(13) Y. Hirokawa, T. Tanaka, and S. Katayama, "Microbial Adhesion and Aggregation", K. C. Marshall, Ed., Springer-Verlag, Heidelberg and New York, 1984, pp 177–188.

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Phase Transition of Positively Ionized Gels

Various ionic polymer gels have been experimentally found to undergo discontinuous volume phase transitions in response to small changes in the temperature,[1] solvent composition,[2–6] pH,[8] and ionic composition[9,10] or when an electric field is applied across the gel.[11] It has also been shown theoretically that for a gel to undergo a discontinuous volume phase transition, it is necessary that the gel have enough positive internal osmotic pressure (or equivalently, negative external osmotic pressure) and that the solvent in which the gel is immersed be sufficiently poor.[2] An adequately poor solvent can be readily found for any polymer network. A positive internal osmotic pressure can be created by ionizing the polymer network: the pressure originates in the translational degrees of freedom of the counterions trapped inside the Donnan potential well.[2] All gels that have been found to exhibit discontinuous volume transitions so far have negatively ionizable carboxyl groups or their salts in the polymer network.[1–6] Since the osmotic pressure theoretically depends only on the concentration of counterions, the swelling equilibrium should not depend on the sign of the charge of the ionizable group.

In this paper we present examples of positively ionized acrylamide gels that show a first-order phase transition. We also show an example of gels consisting of a nonacrylamide derivative monomer, styrenesulfonate, that undergo a discontinuous transition. These observations

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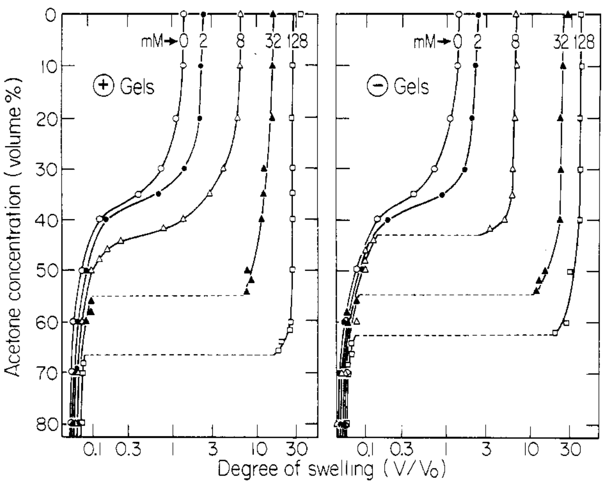

Figure 1. (a) Equilibrium swelling ratio (V/V_0) of positively ionizable acrylamide gels plotted as a function of acetone concentration. (Methacrylamidopropyl)trimethylammonium chloride (MAPTAC) is used as an ionizable group. MAPTAC concentration ranges from 0 to 128 mM. A discontinuous phase transition is observed in MAPTAC gels at high MAPTAC concentrations. (b) Equilibrium swelling ratio of negatively ionized acrylamide gels. Sodium acrylate is the ionizable group.

strongly support the theoretical prediction that the phase transition of ionized gels is universal and should not be confined to a specific group of gels.

Experiment. Samples were prepared by free radical copolymerization in water at 20 °C. Positively ionizable gels were obtained from acrylamide (main polymer constituent), *N,N'*-methylenebisacrylamide (BIS, cross-linking agent), and (methacrylamidopropyl)trimethylammonium chloride (MAPTAC, positively ionizable group) at different relative compositions of acrylamide and MAPTAC. The total concentration of acrylamide and MAPTAC and the concentration of BIS were fixed at 700 and 8.6 mM, respectively. Styrene derivative gel was prepared from sodium styrenesulfonate (SSS, main polymer constituent and negatively ionizable group) and BIS. The concentrations of SSS and BIS were 970 and 162 mM, respectively. As initiators of polymerization, 40 mg of ammonium persulfate and 240 μL of tetramethylethylenediamine were added to 100 mL of a pregel solution. For comparison, we also prepared negatively ionized acrylamide gels using sodium acrylate in place of MAPTAC in the same molar concentration.

The pregel solutions were prepared under a nitrogen atmosphere, and the gelation was carried out in glass tubes having an inner diameter of 1.35 mm. After gelation was completed, the gels were taken out from the tubes and cut into small pieces approximately 1 mm long. The pieces of gel were then immersed in a large volumes of acetone–water mixtures of various mixing ratios. The mixtures contained 0.1 mM NaCl, which ensured full dissociation of the ionizable groups.

The gels reached equilibrium within a time ranging from an hour to a day, depending on the gel and solvent composition. The degree of swelling was determined by measuring the equilibrium diameter, d, under a microscope having a calibrated scale in the eyepiece. The degree of swelling, V/V_0, was calculated as $V/V_0 = (d/d_0)^3$, where $d_0 = 1.35$ mm.

Results and Discussion. Figure 1 shows the measured degree of swelling of the gels as a function of acetone composition for concentrations of ionizable groups ranging from 0 to 128 mM. The swelling curves for both positively and negatively ionized gels are similar. In both cases the volume transitions are discontinuous for higher concentrations of ionizable groups and continuous for lower concentrations.

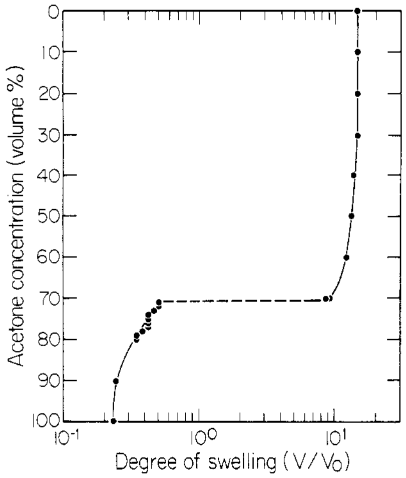

Figure 2. Equilibrium swelling ratio (V/V_0) of negatively ionizable styrene derivative gel plotted as a function of acetone content in acetone–water mixtures.

Slight differences can be observed between the swelling curves of positive and negative gels. It is easier for the negatively ionized gel to undergo a discontinuous phase transition: the minimum concentration of ionizable groups needed to induce the discontinuous volume transition is smaller for the negatively ionized gel, and the volume change at the discontinuous transition is slightly larger for negative gels. This may be due to the difference in bulkiness of the ionizable groups, which relates to flexibilities of polymer chains of the gels. The flexibility of the chains is considered to affect the internal osmotic pressure of the gels and, therefore, their phase properties.[2]

Figure 2 shows a swelling curve of a styrenesulfonate gel as a function of acetone concentration. In 100% acetone the gel is shrunken in a compact state. With an increase of water content, the gel swells slightly and at 29% water (71% acetone) its volume increases discontinuously 20-fold. The gel stays swollen at water concentrations higher than 29%.

The results presented in this paper not only support the concept of universality of the phase transition of ionized polymer gels but also suggest a wide variety of interesting experiments. For example, a negatively charged gel in an electric field deforms in such a way that the portion adjacent to the positive electrode collapses while the portion adjacent to the negative electrode swells.[11] The boundary between the swollen and collapsed portions moves with the amplitude of the electric field. It may be interesting to study such an electric field effect on positive gels.

The effect of various ions on positive and negative gels is another subject to be explored. The response of negative gels depends strongly on the kind and valency of the ions.[8] Since positive and negative counterions in general have different molecular stoichiometries, we may expect that the phase transition induced by changing the ionic composition will be different for positive and negative gels.

It is possible to prepare gels in which positive and negative gels are covalently junctioned. In a sense, such gels are similar to p–n junction diodes. The flow of counterions in such gels, corresponding to the flow of holes and electrons in a diode, would be curious to examine.

We have been able to prepare gels in which positive and negative groups are both incorporated in the same network. Studies of effects of pH and ionic composition on such gels are now under way. Such gels should show a reentrant volume transition[12] when the pH is continuously altered.

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Registry No. (BIS)·(MAPTAC)·(acrylamide) (copolymer), 98587-56-5; (BIS)·(SSS) (copolymer), 91293-65-1; acetone, 67-64-1; water, 7732-18-5.

References and Notes

(1) T. Tanaka, *Phys. Rev. Lett.*, **40**, 820 (1978).
(2) T. Tanaka, D. J. Fillmore, S.-T. Sun, I. Nishio, G. Swislow, and A. Shah, *Phys. Rev. Lett.*, **45**, 1636 (1980).
(3) M. Ilavsky, *Macromolecules*, **15**, 782 (1982).
(4) J. Hrouz, M. Ilavsky, K. Ulbrich, and J. Kopecek, *Eur. Polym. J.*, **17**, 361 (1981).
(5) M. Ilavsky, J. Hrouz, and K. Ulbrich, *Polym. Bull. (Berlin)*, **7**, 107 (1982).
(6) M. Ilavsky, *Polymer*, **22**, 1687 (1981).
(7) T. Tanaka, *Sci. Am.*, **244**, 110 (1981).
(8) I. Ohmine and T. Tanaka, *J. Chem. Phys.*, **11**, 5725 (1982).
(9) J. Ricka and T. Tanaka, *Macromolecules*, **18**, 83 (1985).
(10) Y. Hirokawa and T. Tanaka, in "Microbial Adhesion and Aggregation", K. C. Marshall, Ed., Springer-Verlag, Heidelberg and New York, 1984; see also, D. Nicoli, C. Young, T. Tanaka, A. Pollak, and G. Whitesides, *Macromolecules*, **16**, 887 (1983).
(11) T. Tanaka, I. Nishio, S.-T. Sun, and S. Ueno-Nishio, *Science (Washington, D.C.)*, **218**, 467 (1982).
(12) S. Katayama, Y. Hirokawa, and T. Tanaka, *Macromolecules*, **17**, 2641 (1984).
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Copolymer/Copolymer Blends: Effect of Sequence Distribution on Miscibility

In a previous paper,[1] we have discussed the effect of the sequence distribution of monomer units in a copolymer on the phase behavior of copolymer/homopolymer blends. Our model yielded an improvement to Flory–Huggins type theories for mixturs involving copolymers in that it was possible to make a distinction between the copolymer types (random, block, etc.) participating in the mixture. This was accomplished by introducing a parameter, Θ, which described the binary sequence distribution of the monomers in the copolymer. By varying Θ, we could describe a block, random, or alternating copolymer. Further, we assumed that the interaction energy between a monomer of homopolymer C and the monomer A (or B) in the copolymer AB is mediated by the nearest neighbors chemically bonded to the A (or B) structural unit. We showed that for a fixed composition, there is an optimal range of Θ values (or sequence distributions) for which the AB/C system may be miscible.

In this communication, we apply the above model to the mixture of two copolymers that differ only in composition, one containing f_A units of A comonomer and f_B units of B comonomer ($f_A + f_B = 1$) and the other g_A units of A and g_B units of B ($g_A + g_B = 1$). A special case of interest is where both copolymers have the same composition ($f_A = g_A$) and differ only in the sequence distribution of their monomers. An interesting question is: Are there circumstances under which these polymers are immiscible? Experimentally it is known that blends of PVC and chlorinated polyethylene (CPE) are immiscible even when the CPE has the same Cl content as PVC.[2] In this context, CPE may be considered as a random copolymer of CH_2 ($\equiv$A) and CHCl ($\equiv$B), while PVC is the alternating copolymer composed of these units.

The theoretical formulations presented below will be compared to recent experimental observations of the phase behavior of blends of CPE.[2] It will be shown that these data allow the determination of the various interaction parameters required by theory.

The Model. The free energy of mixing for a mixture of two copolymers that differ only in polymer composition is given by[3]

$$\Delta G/RT = (\phi_{AB}/N)\ln\phi_{AB} + (\phi_{AB}'/N')\ln\phi_{AB}' + \phi_{AB}\phi_{AB}'(f_A - g_A)^2\chi_{AB} \qquad (1)$$

where ϕ_{AB} is the volume fraction of one copolymer with degree of polymerization N and composition f_A, while ϕ_{AB}' is the volume fraction of the other copolymer with degree of polymerization N' and composition g_A($\phi_{AB} + \phi_{AB}' = 1$). This free energy is identical with the usual Flory–Huggins one, when the following identification is made:

$$\chi_{\text{blend}} \equiv (f_A - g_A)^2\chi_{AB} \qquad (2)$$

Here, we will consider a binary mixture of two copolymers with compositions f_A and g_A but assume that the interaction energy for an A–B pair is influenced by the units that are chemically bound to A (and B). This requires that all the possible pairs of triplets, with A or B occupying the central site, be enumerated. Next, the probability of occurrence for each specific triplet is calculated and an energy is assigned to each A–B interaction. To reduce the large number of χ parameters required to properly describe the energetics, the following simplifications are introduced: it will be assumed that all A–A and B–B interactions are equivalent and equal to zero. Although there are 16 possible A–B interactions, a unique energy is assigned only to the triplet pairs (AAA–BBB) and (BAB–ABA): $\chi_{AAA;BBB}$ for the former and $\chi_{BAB;ABA}$ for the latter. The remaining 14 pairs of A–B interacting triplets are assigned an average value of $\bar{\chi}_{AB}$. The required pair probabilities f_{AB}, f_{BB} and f_{AA} are the joint probabilities of AB, BB, and AA pairs; ϕ_A and ϕ_B are the volume fractions of A and B comonomers for the copolymer with composition f_A. These variables are related as follows:

$$\begin{gathered} f_A = f_{AA} + f_{AB}; \qquad f_B = f_{BB} + f_{BA}; \qquad f_{AB} = f_{BA} \\ f_A + f_B = 1; \qquad \phi_A + \phi_B = \phi_{AB} \\ f_A\phi_{AB} = \phi_A; \qquad f_B\phi_{AB} = \phi_B \end{gathered} \qquad (3)$$

An identical set of relationships apply to the g_A and g_B variables with $\phi_A' + \phi_B' = \phi_{AB}'$.

The probability of the AAA triplet of the f_A copolymer interacting with the BBB triplet of the g_A copolymer is given by the probability of the AAA configuration, $\phi_A(f_{AA}/f_A)^2$, times the probability of the BBB configuration, $\phi_B'(g_{BB}/g_B)^2$, which yields

$$\phi_{AB}\phi_{AB}'(f_{AA}g_{BB})^2/f_A g_B \qquad (4)$$

Similarly, the probability of a BAB triplet interacting with an ABA triplet is

$$\phi_{AB}\phi_{AB}'(f_{AB}g_{AB})^2/f_A g_B \qquad (5)$$

On the other hand, an AAA–BBB triplet interaction involving the same f_A copolymer is given by

$$(1 - \phi_{AB}')\phi_{AB}(f_{AA}f_{BB})^2/f_A f_B \qquad (6)$$

and a BAB–ABA triplet interaction is given by

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