Communications to the Editor

Multiple Phases of Copoly(acrylic acid/styrene) Gels

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Multiple phases have recently been found in copolymer gels consisting of cationic and anionic groups that also form interpolymer hydrogen bonding.[1,2] As temperature of pH is varied, the gel changes its volume discontinuously among many phases distinguished by different volumes. The number of phases and the transition thresholds depend on the ratio of the cationic and anionic monomers in the polymer network. Each phase can be reached by following a different way of changing pH.

In this paper we present a study of copolymer gels of acrylic acid and styrene. The former interact with themselves through hydrogen bonding and ionic repulsion. Styrene has a strong hydrophobic attractive interaction among themselves. The composition of the gel determines the phase behavior, in particular, the number of phases and threshold pH for each transition. The largest number of phases was seven, and the smallest number was one. Four multiple phases were observed in the pure acrylic acid gel.

Gels were prepared by free-radical polymerization. Styrene (hydrophobic monomer, 3.02 mL × x), acrylic acid (anionic monomer with capacity of hydrogen bonding, 1.92 mL × (1-x)), divinylbenzene (cross-linker, 0.268 mL), and 2,2′-azobis(isobutyronitrile) (AIBN, initiator, 26.2 mg) were dissolved in 13.3 mL of dimethylformamide (DMF). Here x was chosen to be 0.0 (0.0 M styrene), 0.14 (0.20 M), 0.33 (0.47 M), 0.50 (0.70 M), 0.54 (0.75 M), and 0.57 (0.80 M). The total molar amount was fixed to be constant at 1.4 M per 1 L of DMF. The solution was brought to 60 °C and kept for 15 h for gelation in glass capillaries of inner diameter $d_0 = 140\ \mu$m. A piece of gel was taken out from a capillary and placed in a glass cell at room temperature. The gel was continuously flushed with aqueous solution whose pH was controlled using HCl for pH < 7 and NaOH for pH ≥ 7. In order to minimize the effect of carbon dioxide, the experiments were carried out under a nitrogen atmosphere. The gel diameter in equilibrium was measured under a microscope.

In Figure 1 the gel diameter, d, is plotted as a function of pH at 23 °C. There were four distinct volume phases in the pure acrylic acid gel at higher pH (upper left). The swelling curve was very complicated for some of the gels, and the following rule was adopted so that no branches of the swelling curves were missed. First, the gel was allowed to swell at high pH. Then pH was gradually lowered until the gel shrinks into a phase of smaller volume. The rule was that everytime a volume phase transition occurs the pH change was reversed. This way all the hysteresis cycles were completed. Each cycle was repeated at least twice for confirmation of reproducibility. Then the pH was changed in the opposite direction after the last swelling transition occurred.

Each phase is denoted by its diameter normalized by the original diameter: $d/d_0 = 0.9, 1.0, 1.8$, and 2.4. Below pH 3 the gel was shrunken in phase 0.9. As the pH was raised it swelled discontinuously to phase 1.8 at pH 7.3. As the pH was lowered from pH 7.3, the gel collapsed to phase 1.0 at pH 5.0, and further reduction of the pH caused the gel collapse back to phase 0.9 continuously. If, instead, the pH was increased from pH 7.3, the gel swelled continuously up to pH 9.5. As the pH was lowered from pH 12, the gel collapsed discontinuously into phase 0.9 at pH 5.5. Upon further reduction of pH, the gel collapsed into phase 0.9. These cycles were repeated with excellent reproducibility.

The phase behavior varied as the composition was gradually changed. For the pure acrylic acid gel there were four distinct phases. The maximum number of phases among the compositions chosen in the set of experiments was 7 for the composition of 1.26 M acrylic acid and 0.14 M styrene. Above a styrene concentration of 0.8 M there was only one phase.

It is important to note that the most shrunken state is not the fully collapsed phase, which can be brought by adding a poorer solution such as acetone to the gels.

Out of the multiple phases only one corresponds to the stable phase with the lowest free energy minimum at a particular pH, whereas the rest should be the metastable phases. Which one is the stable phase depends on the pH, and it switches from one phase to another as the pH is varied.

The physical basis of multiple phases has not been fully understood. The mean-field free energy of a gel consists of terms for rubber elasticity, osmotic pressure by counterions, net charge repulsion, and virial interactions.[1,2] These six or seven terms with different powers of polymer density can create free energy minima at three distinct densities. Clearly it is not enough to describe the seven multiple phases. It is necessary to introduce new order parameters in addition to the polymer density to predict more than three phases. Hydrogen bonding density may

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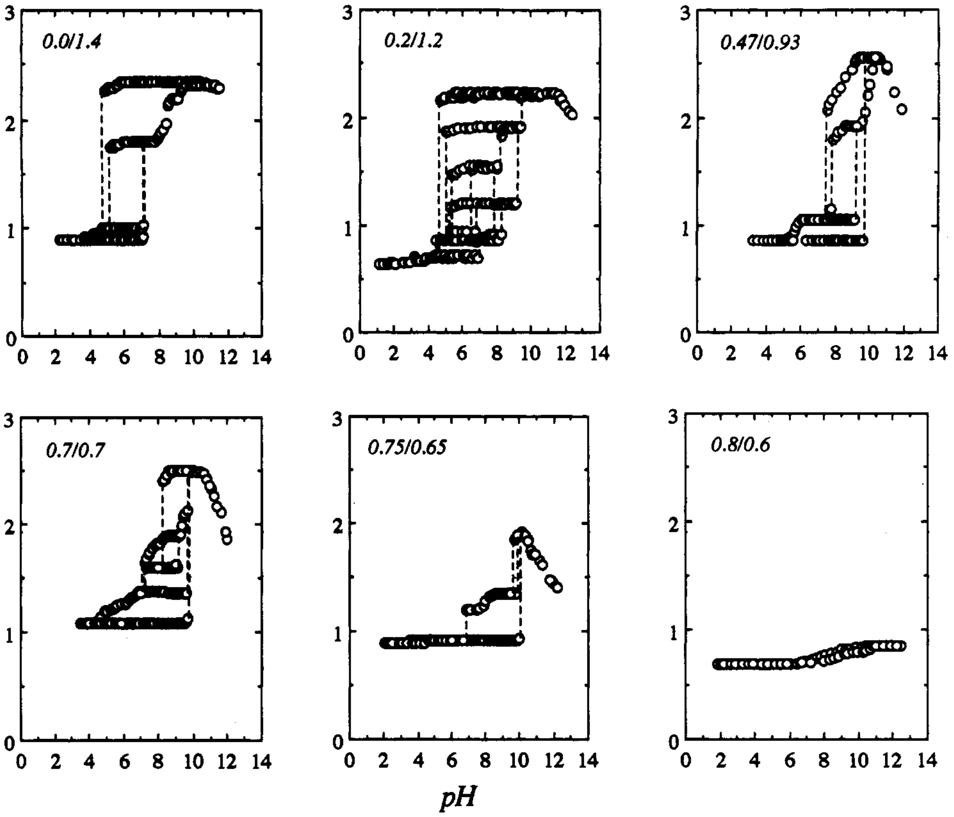

Figure 1. Diameters of copoly(acrylic acid–styrene) gels in aqueous solutions as a function of pH. The total monomer amount of the gels was fixed at 1.4 M per 1 L of DMF, and the acrylic acid concentration was varied from 0 to 0.6 M. The chemical compositions of the gels are indicated in each figure. The pH was controlled by adding HCl for pH ≤ 7 and NaOH for pH ≥ 7. The number of phases depends on the composition and was seven at maximum in this set of data and decreases as the composition deviates from the value.

be a natural choice for a new order parameter. Formation of hydrogen bonding is energetically favorable but entropically undesirable since it restricts the freedom of chain configurations. Another possibility is randomness of interactions in heteropolymers introduced by Shakhnovich and Gutin.[3] Randomness could add another phase transition and thus double the number of phases. Construction of a theory is under way.

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References and Notes

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