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Volume Phase Transitions of Gels in Hydrocarbons

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Polymer gels are known to undergo a discontinuous volume phase transition between the swollen and collapsed phases, but only in aqueous solutions. The volume transition is a result of the change in the balance of competition between forces of repulsive electrostatic interaction that act to swell the gel and attractive forces that act to shrink the gel. According to the mean field theory of gels, whether a gel has a continuous or discontinuous transition depends on two factors: the degree of ionization per chain and the persistence length of the chain. As the ionization or chain stiffness increases, the transition becomes discontinuous and the volume ratio at the transition increases. Only a couple of examples are known to show a discontinuous transition without ionization; *N*-isopropyl- and *N*-*n*-propylacrylamide gels in water. The ratio of the swollen and collapsed volumes at the transition is less than tenfold. In order for a larger discontinuous volume change to occur, it is necessary that a gel have sufficient swelling pressure, which is usually done by ionizing the gel. For this reason, observation of a discontinuous volume transition has been strictly limited to aqueous gels. However, if a gel can be ionized in an organic solvent, it may undergo a discontinuous volume phase transition.

Gels ionized in an organic solvent through a donor–acceptor reaction have been developed by Osada and colleagues[1] and Shiga and colleagues.[2] Their purpose was to develop gel actuators that can be triggered by an electric field. The hydrogels are not ideal due to electrochemical reactions that occur at the electrode. The problem may be solved if an organic solvent is used.

Stimulated by their work, we have designed a gel that undergoes the transition in organic solvents by ionizing the gel. The gel consists of a network of donor polymers that is swollen in an organic solvent with acceptor molecules dissolved in it. The electron transfer in the donor–acceptor reaction ionizes the polymer network in the organic solvent. The gel undergoes a discontinuous volume change in response to the changes in temperature, solvent composition, or acceptor concentration.

Furthermore, it is found that the collapsed phase is not a single phase but consists of two different phases having slightly different densities.

The gel was prepared by standard radical polymerization: 0.26 g of 4-vinylpyridine (donor and polymer constituent), 0.10 g of styrene (polymer constituent), 0.0098 g of divinylbenzene (cross-linker), and 1 mg of 2,2′-azobis(isobutyronitrile) (initiator) were dissolved in 100 mL of *N*,*N*-dimethylformamide (DMF). The solution was degassed and polymerized in capillaries of various diameters at 60 °C for 24 h. The gel was cut into small cylinders of 1-mm length and placed in benzene with various concentrations of tetrachloro-1,4-benzoquinone (acceptor). Figure 1 illustrates the possible ionization process of the donor gel in the acceptor solution through the donor–acceptor reaction.

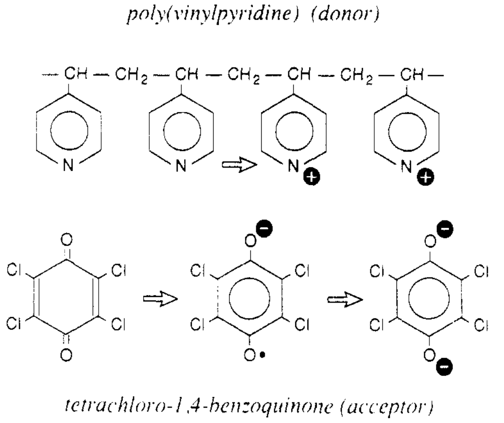

Figure 1. Donor–acceptor reaction between poly(4-vinylpyridine) gel (donor) and tetrachloro-1,4-benzoquinone (acceptor). The reaction allows ionization of the gel in an organic solvent.

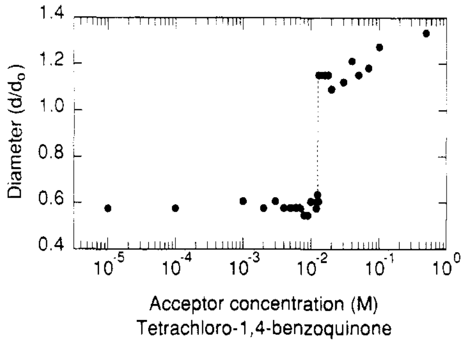

Figure 2. Diameter of a poly(4-vinylpyridine–styrene) copolymer gel in benzene where tetrachloro-1,4-benzoquinone was dissolved in various concentrations ranging from 10^{-5} to 0.5 M. A discontinuous volume change is observed at 10^{-2} M concentration.

The temperature of the samples was controlled within 0.1 °C by circulating temperature-controlled water around the capillary. The gel diameter was measured under a microscope using a microscaler to fit to the boundary of the gel on a video monitor. A discontinuous volume transition was observed at the acceptor concentration of 12.95 mM (Figure 2).

The temperature dependence of the gel volume was determined for acceptor concentrations near the transition threshold. The gel remained collapsed for acceptor concentrations from 8 to 12.9 mM at temperatures from 10 to 70 °C. The gel remained swollen for acceptor concentrations above 13.0 mM.

A small discontinuous volume transition was observed for an acceptor concentration of 12.9 mM. There was a hysteresis; i.e., the swelling and shrinking temperatures were different. They were 52 and 57 °C, respectively (Figure 3). This implies that the collapsed phase may not be a single phase but instead consist of at least two different phases. They may be random ordered phases similar to the ones recently found in hydrogels.[3]

Similar transitions were observed in a pure 4-vinylpyridine gel without styrene in a solvent mixture of toluene and DMF as a function of their volume ratio (Figure 4). Tetracyanoethylene (TCNE) at different concentrations was used as an acceptor. The transition was maximum for 1 mM TCNE.

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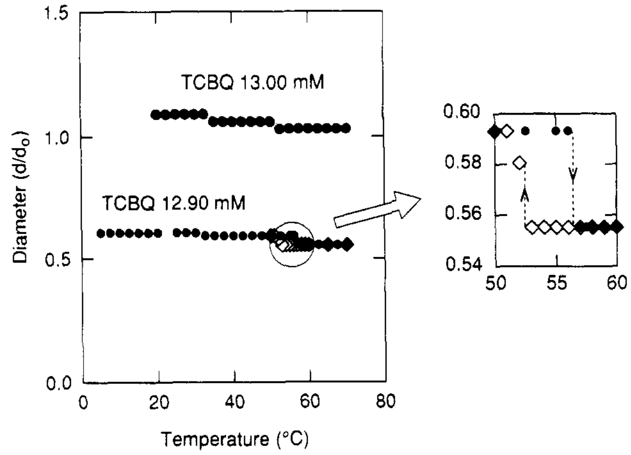

Figure 3. Temperature dependence of the diameter of a poly(4-vinylpyridine–styrene) copolymer gel in benzene solutions of tetrachloro-1,4-benzoquinone (TCBQ) at a concentration of 12.9 mM. A hysteresis is observed that proves a discontinuous volume transition between two different collapsed phases. A similar curve is shown for TCBQ at 13.0 mM. There is not much change in the diameter. The volume change is reversible.

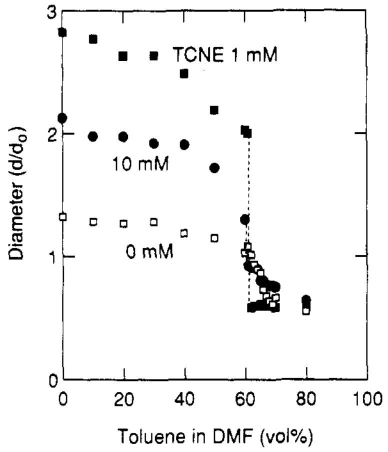

Figure 4. Diameter of a poly(4-vinylpyridine) gel in mixtures of toluene and *N,N*-dimethylformamide (DMF) at various volume ratios as a function of the concentration of tetracyanoethylene (TCNE, acceptor). The volume transition is maximum for a TCNE concentration of 1 mM.

Similar experiments were carried out with 7,7,8,8-tetracyanoquinodimethane (TCNQ). The largest volume change was observed for the highest solubility concentration of 1 mM.

It is interesting to observe that large volume changes occurred as a function of acceptor concentration, but not as a function of temperature. This means that a concentration change of 0.05 mM of the acceptor has a larger effect than a temperature change of 70 °C. We are puzzled by this observation.

The finding of the phase transition of gels in oil will substantially expand the scientific and technological scope of research on the phase transition of gels, which has so far been limited only to aqueous media.[4-7] Technologically, it will allow development of actuators, sensors, delivery systems, and controlled absorbents in organic solvents.

The high swelling power of the so-called superabsorbent gels is a result of the electrostatic repulsion and the counterion osmotic pressure due to ionization of the gel and has therefore been limited only to water. Molecular design using a donor–acceptor reaction[1,2] would lead to development of oil superabsorbents.

The electric field induced phase transition in hydrogels has been studied extensively, but it has the problem of electrochemical reactions at the electrode. To solve this problem, Osada et al.[1] and Shiga et al.[2] have recently studied the electric field effect on gels in an organic solvent. They have successfully obtained a clear picture on the migration process of counterions within the gels. Combining their finding and the work presented here suggests the possibility to observe the electric field phase transition of gels in an organic solvent.

Interactions between biological or synthetic polymers fall into four categories: hydrogen bonding, van der Waals interaction, hydrophobic interaction, and electrostatic interaction. Recently, the volume transition was induced in gels where only one of the fundamental interactions was present,[8] and extensive studies of these interactions have begun using the gel swelling behavior. The gel phase transition in an organic solvent will allow quantitative evaluations of these forces in environments totally different from the previous experiments that were carried out in aqueous solutions, which will be of vital importance for a better understanding of molecular recognition mechanisms in the biological and chemical world.

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