

## Volume phase transition of polyelectrolyte gels in dimethyl sulfoxide/tetrahydrofuran mixtures

Xinxing Liu, Zhen Tong\*, Xianwu Cao and Ou Hu

Research Institute of Materials Science, South China University of Technology, Guangzhou 510641, China

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Copolymer gels were prepared from 2-(acrylamido)-2-methylpropanesulfonic acid (AMPS), *N,N*-dimethylacrylamide (DMAA, comonomer) and *N,N'*-methylenebis(acrylamide) (BIS). The mole fraction of AMPS were 0.2674 and 0.4318, respectively, with the same BIS mole fraction of 0.013. These gels with counterions  $H^+$ ,  $Na^+$ , and  $K^+$  were swollen at 25°C in mixtures of dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF). A volume phase transition was observed at the THF volume fraction of about 0.58, indicating that the volume phase transition in a polyelectrolyte gel occurs when the medium polarity decreases sufficiently for ion-pair formation. On changing the counterion, the fraction of DMSO in the solvent mixture which is required to initiate swelling decreases in the order  $Na^+$ ,  $H^+$ , and  $K^+$ , the same as for counterion condensation in identical gels. Copyright © 1996 Elsevier Science Ltd.

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### Introduction

Polymer gels, both synthetic and natural, are known to undergo a reversible, discontinuous volume phase transition in response to infinitesimal changes in their surrounding environment<sup>1–4</sup>. The concept and the knowledge of the phase transition will be the guiding principle in understanding bio-system and in developing artificial devices<sup>5</sup>. Gels showing this type of phase transition involve more or less ionization of the polymer chains, except *N*-substituted acrylamide gels<sup>6,7</sup>, and all such transitions have been described for gels swollen by aqueous solutions except for a specially designed charge transfer gel system swollen in benzene<sup>8</sup>. IImain *et al.*<sup>2</sup> presented a general scheme with examples of four types of gel volume phase transitions induced by van der Waals, hydrophobic, hydrogen bond, and ionic interaction forces, respectively. These studies indicated that the electrostatic interaction plays the dominant role, particularly in gels containing strongly dissociating ionizable groups on their side chains, since charge interactions control the chain conformation in the gel network<sup>9</sup>, which governs the macroscopic change in gel volume.

Recently, we found<sup>10</sup> that the volume phase transition takes place in highly charged copolymer gels containing sulfonic acid groups when swollen in a water/acetone mixture as the acetone concentration is raised. The acetone concentration in the mixture at which the phase transition occurs in the gel samples increases slightly with the charge density of the polyelectrolyte gels, falling in a narrow range of the mixture composition. This finding suggests that the ionization would be depressed by decreasing the solvent polarity, and a sudden drop in swelling osmotic pressure would be induced when the

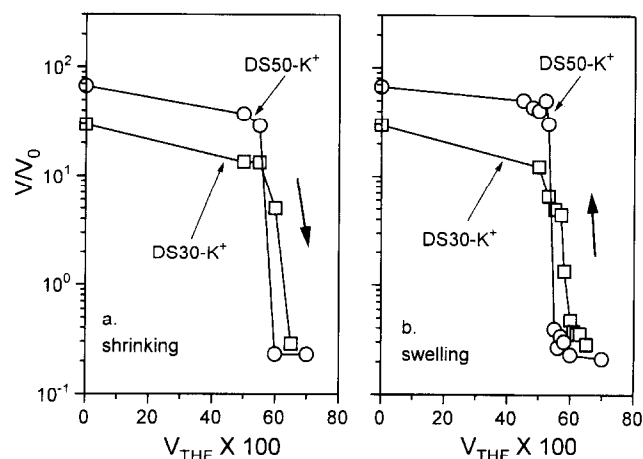
ionization degree declines below a certain value. The same volume phase transition should be observed when these gels are allowed to swell in the mixture of organic solvents if the change in polarity is sufficiently large.

To test this idea, we attempted to observe the discontinuous volume phase transition in crosslinked copolymer gels containing sulfonate groups exposed to mixtures of dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF).

### Experimental

Appropriate amounts of 2-(acrylamido)-2-methylpropanesulfonic acid (AMPS, ionizable monomer), *N,N*-dimethylacrylamide (DMAA, comonomer), and *N,N'*-methylenebis-(acrylamide) (BIS crosslinker) were dissolved in purified water to a total monomer concentration of 0.75 mol l<sup>-1</sup> and BIS mole fraction of 0.013<sup>10</sup>. The mole fraction of AMPS was varied to change the charge density in gel samples, and the final values in dried gel were 0.2674 and 0.4318, respectively, determined by elemental analysis. These samples were referred to as DS30 and DS50, respectively. The pregel solution was inserted into capillaries of about 2.8 mm inner diameter and polymerized at 70°C initiated by ammonium persulfate of *ca* 0.0015 g ml<sup>-1</sup>. The resultant gels were washed with water, neutralized with 0.015–0.02 mol l<sup>-1</sup> NaOH or KOH aqueous solutions as described previously<sup>11</sup>. The swelling experiment was conducted in dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF) mixtures with different compositions at 25°C. The gel samples were allowed to equilibrate firstly in pure DMSO after being transferred from pure water via several water/DMSO mixtures with increased DMSO content. The solvents were analysis reagents and used without further purification. For shrinking, the volume fraction  $V_{THF}$

\* To whom correspondence should be addressed

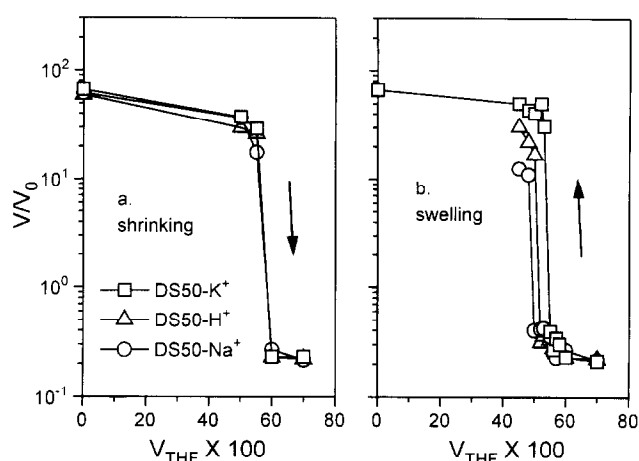


**Figure 1** Swelling ratios  $V/V_0$  of DS50 and DS30 gels with the counterion  $K^+$  in DMSO/THF mixtures as a function of THF volume fraction  $V_{THF}$  at 25°C: (a) shrinking curves obtained by increasing  $V_{THF}$  in the mixture; (b) swelling curves obtained by decreasing  $V_{THF}$  in the mixture. The mole fraction of ionized monomer AMPS in the samples DS30 and DS50 are 0.2674 and 0.4318, respectively

of THF in the DMSO/THF mixture was increased from 0 to about 0.7; while for swelling  $V_{THF}$  was decreased until the volume of the shrunken gel recovered. The swelling equilibrium was confirmed by monitoring gel diameters. The equilibrated swelling ratio  $V/V_0$  was determined from the gel diameter after swelling equilibrium related to the original one monitored with a scaled microscope on the assumption that swelling is isotropic.

### Results and discussion

Figure 1 shows the shrinking and swelling curves obtained on the samples DS30 and DS50 with counterion  $K^+$  as the volume fraction  $V_{THF}$  of THF in the DMSO/THF mixtures increases or decreases. The gels are in the swollen state when  $V_{THF}$  is lower than 0.55 and collapse as  $V_{THF}$  is higher than 0.6. The discontinuous volume change is clearly seen in the DS50 gel, but the volume change of the DS30 gel is less sharp. The  $V_{THF}$  values where the sudden volume change occurs in DS30 and DS50 are rather similar. These phenomena can be attributed to the abrupt change in the electrostatic force between ionizable groups. The dielectric constant  $D$  characterizing the solvent polarity is 48.9 for DMSO and 7.58 for THF, respectively, at 25°C<sup>12</sup> so that the sulfonate groups can entirely dissociate in the DMSO but become ion pairs connecting an anion and a cation in THF<sup>13</sup>. The strong repulsive force between ionized groups leads to a large swelling of the gels; while the dipolar attraction will dominate between the ion pairs, making the gels shrink. Although the macroscopic composition of the mixed solvent is changed continuously, the composition in the solvated layer around the ionized groups may change discontinuously. The difference in ionized state induced by the micro-medium polarity will cause the volume phase transition. We found that ethanol/THF mixtures could not initiate the phase transition in the same samples, since the dielectric constant of ethanol (24.3)<sup>12</sup> is too small where the gel cannot swell sufficiently<sup>14</sup>. It may be concluded that the sudden volume shrinkage of charged gels is mainly driven by dipolar attractions of the ion pairs in nonpolar or low-polarity media<sup>15</sup>. This finding indicates that the



**Figure 2** Shrinking (a) and swelling (b) curves for DS50 gels containing the counterions  $K^+$ ,  $H^+$ , and  $Na^+$  in DMSO/THF mixtures at 25°C

volume phase transition in a polyelectrolyte gel can be initiated when the medium polarity decreases sufficiently low to lead to ion-pair formation.

The shrinking curves for DS50 gels with the counterions of  $K^+$ ,  $H^+$ , and  $Na^+$  coincide with each other (Figure 2a), showing the independence of counterion species. However, the swelling curves vary with the counterion species (Figure 2b). The value of  $V_{THF}$  at which the shrunken DS50 gel begins to swell decreases in the counterion sequence,  $K^+$ ,  $H^+$ , and  $Na^+$ ; in other words the fraction of DMSO increases. This fact suggests that the affinity of these counterions bound to the sulfonate group in the gel increases in the order of  $K^+$ ,  $H^+$ , and  $Na^+$ , which is consistent with the order of counterion condensation<sup>11</sup>. By close examination, one will find that there may be a hysteresis between shrinking and swelling curves for the DS50 gels with  $H^+$  and  $Na^+$  counterions for they follow the same shrinking curve but different swelling curves. This hysteresis appears to reflect extra energy needed to swell a shrunken polyelectrolyte gel, which seems to be a common behaviour in many gel systems<sup>4,6,8,16,17</sup>.

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