Macromolecules **1985**, *18*, 2781–2782

chain-length fluctuation, even though the center of mass of the polymer has not diffused more than a fraction of its end-to-end distance.

The relaxation of the tube stress through either reptation or chain-length fluctuation cannot happen without disentanglement of a neighboring chain. The unimportance of the constraint release in a linear viscoelastic relaxation of a monodisperse polymer indicates that such a disentanglement mainly occurring in a middle section of a chain does not cause immediate relaxation of stress or randomization of orientation in this part of tube (i.e., other than the tube ends). In other words the relaxation of stress in the middle part of a chain through disentanglement of a neighboring molecule is not as effective as through its own reptation or chain-length fluctuation at both ends of the tube. In the study of linear viscoelasticity of blend systems consisting of two nearly monodisperse components, the same effect was observed.[12]

Registry No. Polystyrene (homopolymer), 9003-53-6.

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Communications to the Editor

Phase Transition of a Cationic Gel

First referred to by Flory,[1] the tremendous swelling behavior of ionic gels has been studied by Tanaka and other researchers and led our attention to the phase transition of ionic gels. Nowadays, the phase transition has gained wider acceptance with the various findings of novel phenomena and theories.[1-13] Tanaka et al. have demonstrated that ionized polyacrylamide gels, under certain conditions, undergo discrete, reversible transitions in equilibrium volume with changes in solvent composition (acetone–water mixtures),[4-6] temperature,[7-10] pH,[10] salt concentration and species,[6] and electric field.[11] The above behavior can be taken as a phase transition between the swollen gel and the shrunken gel. The phase transition is governed by the sum of three terms: the osmotic pressure, which arises from the elasticity of the gel, the interaction between gel polymer networks, and the thermal motion of counterions in the ionic gel.[9]

Ilavsky et al.[5] reported a similar phase transition in acetone–water mixtures, using diethylacrylamide–sodium methacrylate copolymer gels. However, these conventional approaches to the phase transition of ionic gels were all limited to anionic, or negatively charged, gels. Therefore, whether cationic, or positively charged, gels undergo the same phase transition as anionic gels is one of the important current questions in this field. We report here the phase transition of a cationic gel in acetone–water mixtures, having examined temperature and solvent composition dependencies.

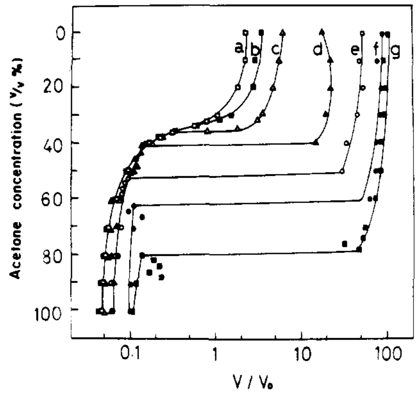

Figure 1. Equilibrium degree of swelling of cationic gels consisting of acrylamide (1 g), *N,N'*-methylenebisacrylamide (26.6 mg), and various amounts of trimethyl(*N*-acryloyl-3-aminopropyl)ammonium iodide: (a) 0 mg; (b) 3.2 mg; (c) 12.7 mg; (d) 50.7 mg; (e) 101.4 mg; (f) 405.8 mg; (g) 1902.1 mg.

Cationic gel samples used in the present experiment were prepared in the following way. Acrylamide (1 g) (the linear constituent), trimethyl(*N*-acryloyl-3-aminopropyl)ammonium iodide (TMAAPAI, 3.2–1902.1 mg) (the ionic component), *N,N'*-methylenebisacrylamide (BIS, 26.6 mg) (the cross-linking consitutent), and 2,2'-azobis(2-amidinopropane) dihydrochloride (V-50, 80 mg) (the initiator) were dissolved in distilled water to a final volume of 20 mL. Gel samples with the desired ion density were obtained after gelation of the solutions at 60 °C for 1 h. TMAAPAI was made by reacting ((dimethylamino)-propyl)acrylamide (DMAPAA) with methyl iodide. DMAPAA was obtained from Kojin Co. Ltd.

The sample preparation procedure is mostly the same as in previous works.[6,8-13] The prepared gels were washed in water and placed in acetone–water mixtures of various compositions. After the gels had reached equilibrium, the diameters of each cylindrical gel were measured.

Figure 1 shows the relationship of acetone concentration to the swelling ratio, V/V_0. The quantity V/V_0 represents the ratio of the final network volume to initial network volume for the cationic gels. The ratio is given by $(d/d_0)^3$, where d_0 and d are the initial and final equilibrium diameters of the gel, respectively. For swollen gels $V/V_0 > 1$,

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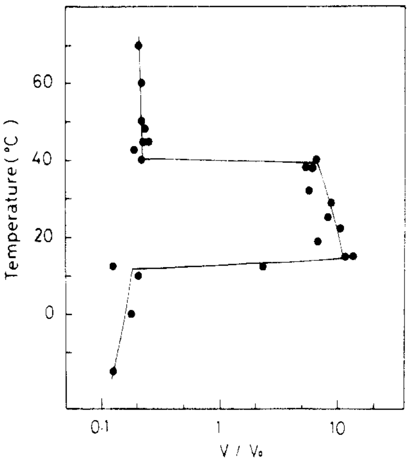

Figure 2. Temperature dependence of the volume swelling, V/V_0, of a cationic gel in a 40/60 acetone–water mixture. The cationic gel was prepared by copolymerization of acrylamide (1 g), trimethyl(*N*-acryloyl-3-aminopropyl)ammonium iodide (50.7 mg), and *N*,*N*′-methylenebisacrylamide (26.6 mg), described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

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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