Elastic Relaxations of Ionic Gel Associated with Hydrophobic Counterion

Shigeo Sasaki* and Shogo Koga

Department of Chemistry, Faculty of Science, Kyushu University, 33 Hakozaki, Higashiku, Fukuoka 812, Japan

Received: March 18, 2002; In Final Form: September 4, 2002

The tensile moduli of poly(acrylate) gel collapsed due to the hydrophobic dodecylpyridinium(DP) ion binding in the various salt concentrations were measured. It was found that the tensile force relaxed after the elongation and that the relaxation moduli strongly depended on the salt concentration, C_S. The differences between the moduli at initial, Y_i, and at equilibrium, Y_e, were 4×10^5 Pa at $C_S = 10$ mM and 3×10^3 Pa at $C_S = 100$ mM. The substantially constant moduli, ($Y_i \sim 5 \times 10^5$ Pa and $Y_e \sim 4 \times 10^4$ Pa) at C_S between 10 and 50 mM deeply drop at C_S between 80 and 100 mM, and level off ($Y_i \sim 11 \times 10^3$ Pa and $Y_e \sim 8 \times 10^3$ Pa) at C_S above 100 mM. However, the size of gel at $C_S = 100$ mM is essentially the same as that at $C_S = 10$ mM. This indicates that the C_S-dependent attraction between the ionic network and the hydrophobic counterions seriously affects the elasticity of the collapsed gel system. The relaxation moduli, $Y(t)$, of the gel is fitted to a function of $Y(t) = (Y_i - Y_e)\{\alpha_1 e^{-t/\tau_1} + \alpha_2 e^{-t/\tau_2} + (1 - \alpha_1 - \alpha_2)(1 + t/\tau_0)^{-\beta}\} + Y_e$.

1. Introduction

It is well-known that the highly cooperative hydrophobic counterion binding to ionic chains makes the chain affinity to the water molecules poor and collapses the polyelectrolyte gel.[1−3] We have revealed that the collapse of gel corresponds to the precipitation of polyelectrolyte.[1] The clarification of precipitation or collapsing mechanisms of polyelectrolyte chains related to the hydrophobic counterion binding is important for understanding the folding mechanisms of DNA and protein molecules in the biological systems where various kinds of amphiphilic moieties are distributed. Our interest is the role of the electrostatic interaction played in the mechanisms. The previous experiment[1] has revealed that the salt concentration, C_S, dependence of the transitional concentrations of the hydrophobic counterion, dodecylpyridinium (DP) ion, for inducing the collapse of ionic poly(acrylate) gel and precipitating the poly(acrylate) molecules, are very similar to each other in the solution at C_S below 300 mM but are not observed in the solution at C_S above 500 mM, even when the concentrations are beyond the critical micelle concentration of DPCl. The electrostatic attraction between the DP ions and the ionized chains as a principal force leading to the binding is reduced with an increase in C_S. The previous experiment has demonstrated that the transitional concentration of DP ion increases with C_S.

Small-angle X-ray scattering experiments[4−6] have revealed the existence of crystalline-like mesoscopic structures in the complex between hydrophobic counterions and polyelectrolytes or ionic gels. It is inferred that a unit cell of the ordered complex between ionized poly(acrylate) gels and hydrophobic dodecyltrimethylammonium counterions has a dimension of 8.21 nm, which is much longer than the size of a spherical micelle,[6] and that the ordered structure is the cubic phase with $Pm3n$ symmetry.[4]

Recently, we have found the slow relaxation in the tensile force of the collapsed *N*-isopropylacrylamide(NIPA) gel,[7] which is well-known to exhibit the volume phase transition with a change of temperature.[8] The cooperative dehydration of the chain induces the volume phase transition to collapse the gel chain.[9] The relaxation of the tensile modulus, $Y(t)$, has been found to be described by a function, $Y(t) = (Y_i - Y_e)(1 + t/\tau_0)^{-\beta} + Y_e$,[7] which can be explained by a gel model consisting of dangling chain ends in cross-linking networks with topological constraints. The volume phase transition of ionic gel is induced by the cooperative hydrophobic counterion binding to form the cubic structure of counterion aggregates.[4] The strong interaction between network chains and the counterion aggregates should affect the elastic properties of the gel system, which is different from those of the collapsed NIPA gel.

The present experiment aims to reveal the elastic properties of the complex between the ionic gel chains and the hydrophobic counterions with the focus on the effect of the electrostatic interaction. The relaxation behavior of tensile moduli of the hydrophobic DP counterion binding ionic gel was examined with change in C_S.

2. Experiment

The chemical structures of ionic poly(acrylate) gel and dodecylpyridinium(DP) counterion are shown in Figure 1. The poly(acrylate) gels were prepared by the radical copolymerization[10,11] in the aqueous solution of 1 M acrylic acid and 0.01 M *N,N′*-methylenebis(acrylamide) at 60 °C. The gels were synthesized in a glass tube (inner diameter = 0.3 mm) and in a space between two glasses separated by a 1 mm thick spacer of poly(tetrafluoroethylene) sheet. The cylindrical gel was pushed out from the tube by applying pressure to it, rinsed thoroughly with 1 M HCl aqueous solution, dried, and used for observing the elastic behavior. The plate gel was cut into about 10 mm squares, and the squares were soaked in a 1 M HCl aqueous solution, dried, and used for the experiment of DP ion binding isotherm. All chemicals used were of analytical grade. Double distilled water was used.

Figure 2 schematically shows an apparatus for the tensile force measurement of the rod-like gel. A detail of the apparatus

---

* Corresponding author.

11894 *J. Phys. Chem. B, Vol. 106, No. 46, 2002*

Sasaki and Koga
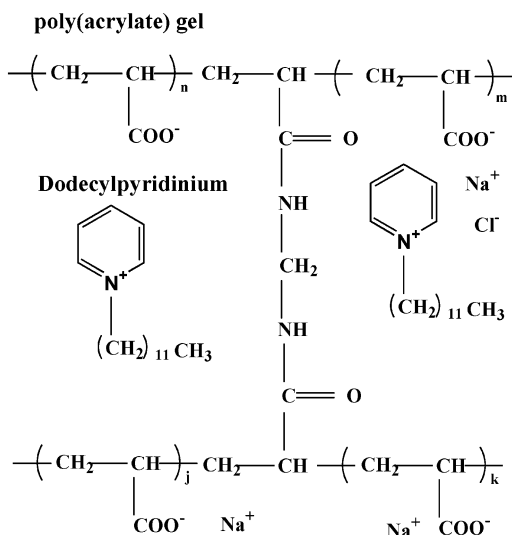
poly(acrylate) gel

Figure 1. Chemical structures of ionic poly(acrylate) gel and dodecylpyridinium counterion.
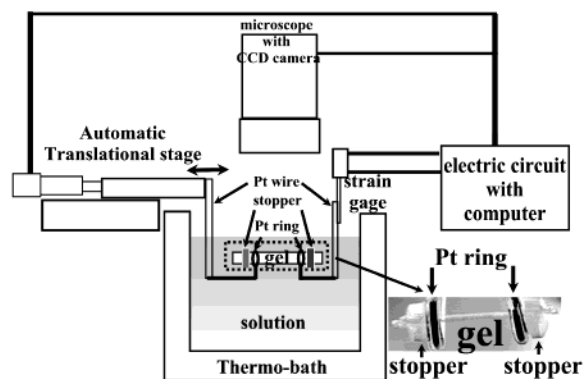
Figure 2. Schematic figure of the tension meter. The tensile force is measured by a strain gage, which is monitored by a computer. An inserted picture shows the gel held by two platinum rings. The rings covered with the silicon tubes are slightly open for insertion of the gel. The rings connect to the strain gage and an automatic translational stage. Silicone rubbers are capped as stoppers at the ends of the supporting gel. Silicone glue was used for fixing the cap to the gel. The gel is elongated with sliding the translational stage. The size of the gel is measured by using a computer-aided camera combined with a microscope.

has been described elsewhere.[7] The electric resistance of a strain gage (AE-801 Capto Co., Norway) was transformed to the electric voltage, which was monitored with a computer-aided instrument. A linear relation between the force and the voltage was checked before setting up the instrument. The force from 0.1 to 2000 dyne could be monitored with a time resolution of 0.1 ms. A solid dry gel was inserted into two platinum open rings, each of which was connected to the sensor and a translational stage through a platinum wire. The gel was immersed into the 1 mM NaOH solution to swell, and then the solution was altered with the other solution of given concentration of DPCl (C_{DPCl}) and NaCl (C_S), the pH of which was adjusted between 9 and 10 by adding a small amount of the 0.1 M NaOH solution. The volume of solution was about 100 mL, which was much larger than the gel volume, 50 μL. The gel was never exchanged for another one during measurements; that is, all data described here were obtained for one gel. It was confirmed that the observed tendencies were reproducible for the other gels. The diameter of the gel was measured by using an optical microscope equipped with a computer-aided CCD camera. The temperature of the solution was controlled 25 ±

0.1 °C. It took a few days for the gel to achieve the steady collapsing state from the swollen state. The equilibration was confirmed by monitoring the steady tension of the slightly elongated gel. The elongating length of gel was adjusted with an accuracy of 1 μm by sliding an automated translational stage. The gel was elongated after equilibrating it with the solution and the tensile force was recorded with the computer-aided instrument. The gel was elongated by a given distance (typically, several hundreds micrometers) within 0.1 s. The force observed at an initial, F_i, was found to decay to a time-independent value, F_e. During the measurement, the gel was held in the solution. An inflection point in a plot of F_e against the distance between the rings gives a natural length of the gel, l_0. The initial Young's modulus Y_i and Y_e at equilibrium, respectively, are given as

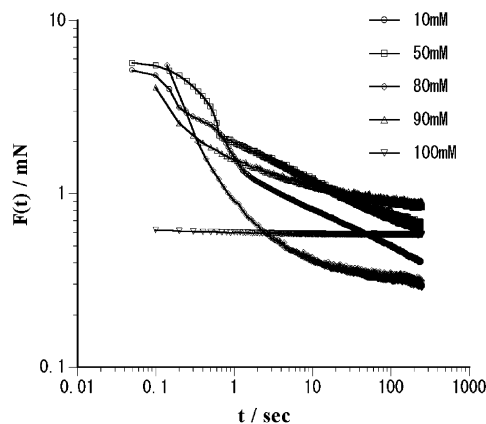$$Y_i = \frac{\lambda F_i}{\pi r_0^2 (\lambda - 1)} \quad (1)$$

$$Y_e = \frac{\lambda F_e}{\pi r_0^2 (\lambda - 1)} \quad (2)$$

where r_0 is a radius of gel in the tension free state and λ is an elongational ratio defined as $\lambda = l/l_0$, where l is the length of elongated gel.

The experiment of binding isotherm of DP ion was carried out as follows. The dry gel was weighed (W_{dry} = weight of dry gel) before putting in a small amount of 4 N NaOH aqueous solution to fully ionize it. After homogeneously swelling the gel, the small amount of about 1 M dodecylpyridinium chloride aqueous solution, which was the same mol amount as the carboxyl group of gel, was put on it to soak into it. Then the gel was immersed into a large amount (about 20 mL) of 2 mM DPCl aqueous solution of a given C_s. For achieving the equilibration, at which the turbid gels became transparent, the solution containing the gel was hold at 60 °C for more than a week and at room temperature for 1 day before the measurements. The collapsed gel was taken out of the solution, wiped, weighed (w_{col} = weight of collapsed gel), and immersed into the 1 M NaCl solution of a given volume, V. The solution was gently stirred for a day to diffuse the DP ion into it. The concentration of DP ion in the solution (C^S_{DP}) was evaluated from the optical absorbency at $\lambda = 259$ nm.

3. Results

Figure 3 shows time profiles of the tension after elongating the shrunken gels immersed in the 1.3 mM DP ion solutions, NaCl concentrations of which are 10, 50, 80, 90, and 100 mM. The λ values of elongated gels were 1.1 except for the 100 mM salt solution. The λ value in the exceptional case was 1.6. The relaxed tensile forces in elongating the gels to these λ values were more than significant values for the present apparatus. A time when the maximum tension was observed after elongation was defined as $t = 0$. Very high tensions were observed just after elongating the gel to relax slowly in the solution at C_s less than 90 mM as shown in Figure 3. The initial high tensions and the slow relaxations were recovered when the once elongated gels stood in the tension-free state for longer than 30 min. However, the initial tensions of the gels staying in the tension-free state for shorter periods were lower than those plotted in Figure 3 but were a several times as high as the equilibrated tensions. It should be mentioned that the equili-

Elastic Complex of Ionic Gel with Hydrophobic Counterion

J. Phys. Chem. B, Vol. 106, No. 46, 2002 **11895**

Figure 3. Time profiles of the tensile force after elongating the DP ion binding gel. The NaCl concentrations of the solutions immersing the gels are 10 mM (○), 50 mM (□), 80 mM (◇), 90 mM (△), and 100 mM (▽).
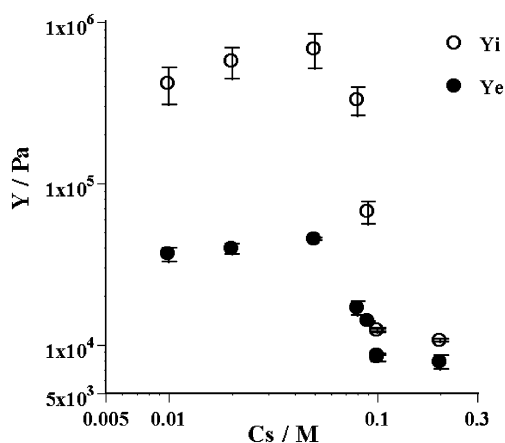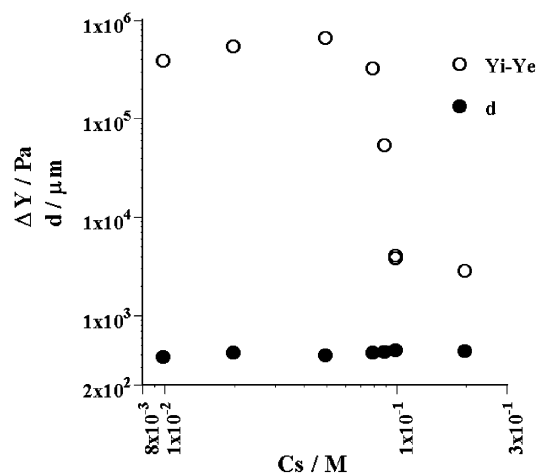

Figure 4. Young's moduli of the DP ion binding gel as functions of the salt concentration. The open and closed symbols represent the Young's moduli Y_i at the initial stage and Y_e at equilibrium, respectively.

Figure 5. Salt concentration dependence of the difference of the Young's moduli, $Y_i - Y_e$ (open symbols) and the diameter of gel(closed symbols).

Figure 6. The normalized relaxation tensile force of the DP ion binding gel. The tensile forces shown in Figure 3 are normalized as $\Delta F(t)/\Delta F(0)$, where $\Delta F(t) = F(t) - F_e$. The symbols are the same as those in Figure 3. Solid lines represent the functions of $\Delta F(t) = \Delta F(0)\{\alpha_1 e^{-t/\tau_1} + \alpha_2 e^{-t/\tau_2} + (1 - \alpha_1 - \alpha_2((1 + t/\tau_0)^{-\beta}\}$.

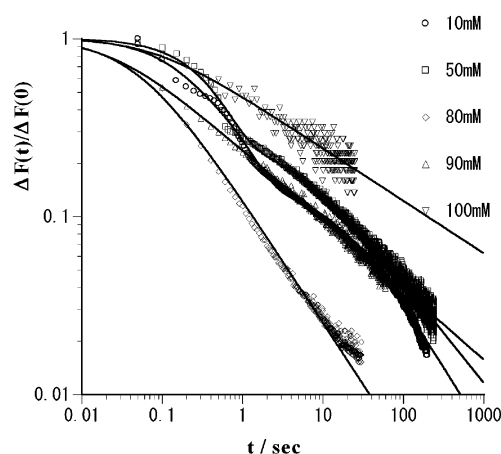brated tensions were not affected by the periods of the tension-free state before the elongation.

The Young's moduli, Y_i and Y_e, are estimated from the relaxation data of tensile force measurements by using eqs 1 and 2, and are plotted against the C_S to show in Figure 4. The DP ion concentrations of the solutions were 1.3 mM at C_S between 10 and 100 mM and 2 mM at $C_S = 200$ mM. It should be mentioned that a little change (3%) in the moduli at $C_S = 100$ mM was observed with the DP ion concentration change from 1.3 to 2 mM. It is obvious that the moduli of Y_i and Y_e change drastically between C_S of 50 and 100 mM and are unchanged above 100 mM and below 50 mM. The transition-like change in the moduli at C_S between 80 and 100 mM is more obvious in plotting the difference between Y_i and Y_e against C_S as shown in Figure 5. However, the diameter of the gel was changed little at C_S between 10 and 200 mM as shown in Figure 5.

The relaxation tensile force, $F(t)$ shown in Figure 3 is normalized by a difference of F_i and F_e as shown in Figure 6, which demonstrates that the relaxation force decays according to such a function of t as

$$F(t) - F_e = (F_i - F_e)\{\alpha_1 e^{-t/\tau_1} + \alpha_2 e^{-t/\tau_2} + (1 - \alpha_1 - \alpha_2)(1 + t/\tau_0)^{-\beta}\} \quad (3)$$

Equation 3 gives a normalized tensile modulus of

$$\Delta Y(t) = \Delta Y(0)\{\alpha_1 e^{-t/\tau_1} + \alpha_2 e^{-t/\tau_2} + (1 - \alpha_1 - \alpha_2)(1 + t/\tau_0)^{-\beta}\} \quad (4)$$

where $\Delta Y(t) = Y(t) - Y_e$, since the diameter of gel is substantially time independent. The solid lines in Figure 6 represent the curves described by eq 3 with the best fitted parameters which are tabulated in Table 1. Adding to the power decay function of t at the long t, single and double exponential decays are observed at the short t in the relaxation tensile forces of gel in the solutions at $C_S = 50$ and 10 mM, respectively, but no exponential decays are observed at C_S above 80 mM.

The molalities of acrylic acid, C_{AA}, and DP ion, C_{DP}, in the gel, respectively, are obtained from the measured values of W_{dry}, w_{col}, C^S_{DP}, and V by using the relations of $C_{AA} = W_{dry}/(72 w_{col})$ and $C_{DP} = C_{AA}\cdot\gamma$, where γ is a binding amount of DP ion per a monomeric unit of gel chain given by $\gamma = 72\cdot V\cdot C^S_{DP}/W_{dry}$. Figure 7 shows the plots of C_{AA}, C_{DP}, and γ against C_s. It is characteristic that the increases in C_{AA}, C_{DP}, and γ with decrease in C_s are significant, but not so large as the changes in the moduli shown in Figures 5 and 6.
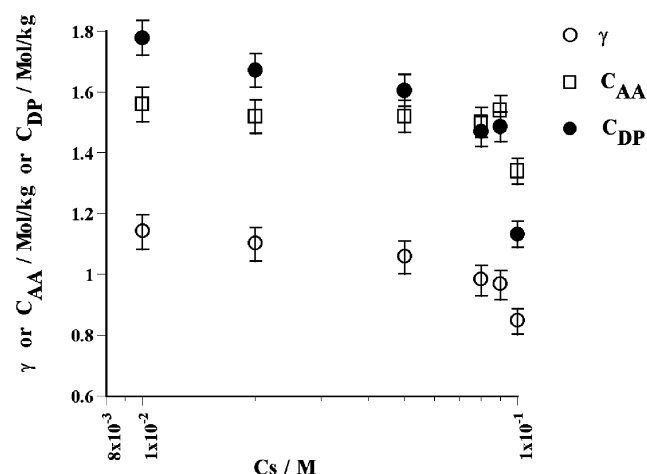
Figure 7. Salt concentration dependence of molalities of acrylic acid (C_{AA}) and DP ion (C_{DP}) in the gel, and a binding amount of DP ion (γ) per monomeric unit of the chain.

TABLE 1: Parameter Values Obtained after Fitting of the Data Shown in Figure 6 to Eq 3

C_s(mM)	β	τ_0(s)	α_1	τ_1(s)	α_2	τ_2(s)
10	0.75	14.5	0.39	0.14	0.46	0.77
50	0.57	3.93	0.73	0.40	0.0	
80	0.70	0.051	0.0		0.0	
90	0.39	0.026	0.0		0.0	
100	0.3	0.081	0.0		0.0	

4. Discussion

The hydrophobic counterions bound to the ionic chains aggregate in the gel network where the concentration of DP ion is about 1 M, which is estimated from the concentration of monomer concentration acrylate in the gel.[1] The deformed structure of hydrophobic counterions' aggregates accompanied with the network deformation generates the stress of the system. The stress converts the network to be detected as the tensile force if the binding force is strong. The binding strength, whether they bind loosely or tightly, depends on the strength of interaction between the ionic chains and the counterions. The addition of salt shields the electrostatic interaction and has the effect of loosening the binding. The C_S-dependent behavior of moduli observed in the present experiments reveals the elastic abnormalities of the hydrophobic counterion aggregates as well as the networks themselves of the shrunken gel.

The exponential decays observed for the gels in the solutions at $C_S = 10$ and 50 mM are inferred to be elastic responses to the deformations of the aggregates. The observed behavior is very similar to the reported results of the surfactant solutions; the viscoelastic relaxation time of the 1 M cetyltrimethylammonium bromide solution is a sub second[12] and the cole−cole plots of viscoelastic data of highly concentrated surfactant solutions show exponential decays.[13] However, the moduli of aggregates in the network are estimated to be on the order of 10^5 Pa ($\sim\alpha_i$ ($Y_i - Y_e$)) which is much larger than that of the solution, an order of 10^2−10^3 Pa.[13] This difference is considered to be due to the difference in their morphologies.

The power decay function of t has been also observed in the tensile force relaxation of shrunken N-isopropylacrylamide gel as reported elsewhere.[7] The power decay relaxation of modulus can be theoretically explained by the liberation of dangling chains from the topological constraints in the network.[7,14,15] The theory presumes that a time, t, for l units of the dangling chain having n units to reach equilibrium is given by $t = \tau_0 \exp(\alpha l)$ and gives the relation of $\beta = q/\alpha$, where τ_0, α, and q,

respectively, are a primary time of the reptation in the constraint, a characteristic density of mesh and a degree of cross-linking of the gel.

The present experimental result that τ_0 values increase with decrease in C_S at C_S below 90 mM as shown in Table 1 is due to the strong attractive interaction between the ionic gel chains and the counterion aggregates. The remarkable difference of τ_0 values at $C_S = 50$ and 80 mM suggests that the states of binding change drastically between these C_S. A hydrophobic counterion is trapped in the deep electrostatic potential valley at an ionized carboxyl group in the solution of lower C_S while it can widely move in the potential trough along the ionic chains in the solution of higher C_S. The former is called the site binding and the latter the atmospheric binding. A time-consuming process for the counterion to jump from one ionic site of chain to the others induces the exponential decay relaxations and the long τ_0 values as observed in the solutions at $C_S = 10$ and 50 mM. The counterions in the atmospheric binding state can move along the trough with low resistance along the vicinity of the ionic chains. This situation of the atmospheric binding state induces the disappearance of exponential decays and the short τ_0 values shown in Table 1.

The β-value change with C_S is considered to be induced by a change in the α-value because of no q-value changes with C_S. The result that the β increase with a decrease in C_S indicates that the α increases with C_S. The increase in the mesh density of the isometric gel, α, corresponds to the decrease in the mesh size. The mesh size is related to the cluster size of the hydrophobic counterion aggregates. The C_S dependence of β mentioned above suggests a cluster size decrease with C_S. The morphologies of aggregates might change with C_S.

The power decay relaxation moduli of the gel in the solution at C_S higher than 100 mM are remarkably smaller than those at $C_S = 90$ mM as shown Figure 3. A 10% change in the shielding effect of salt on the interaction between hydrophobic counterion aggregates and ionic network chains is quite difficult to explain more than 10 times change in the stress of dangling chains. It can be speculated that the change of hydrophobic counterion aggregates from the solid-like state at $C_S = 90$ mM to the liquid-like one at $C_S = 100$ mM induces the result mentioned above. The C_{DP} change from 1.5 M/kg at $C_S = 90$ mM to 1.1 M/kg at $C_S = 100$ mM as shown in Figure 7 might induce the change of state mentioned above by cooperating with the gel network. For clarifying the change of state, another experiment such as the rheology measurements of the polyelectrolyte complex with hydrophobic counterion is needed.

References and Notes

(1) Sasaki, S.; Koga, S.; Imabayashi, R.; Maeda, H. *J. Phys. Chem.* B **2001**, *105*, 5852.

(2) Khokhlov, A. R.; Kramarenko, E. Yu.; Makhaeva, E. E.; Starodubtzev, S. G. *Macromolecules* **1992**, *25*, 4779.

(3) Khandurina, Yu. V.; Rogacheva, V. B.; Zezin, A. B.; Kabanov, V. A. *Polym. Sci.* **1994**, *36*, 195.

(4) Hansson, P. *Langmuir* **1998**, *14*, 4059.

(5) Zhou, S.; Hu, H.; Burger, C.; Chu, B. *Macromolecules* **2001**, *34*, 1772.

(6) Ashbaugh, H. S.; Lindman B. *Macromolecules* **2001**, *34*, 1522.

(7) Sasaki, S.; Koga, S. *Macromolecules* **2002**, *35*, 857.

(8) Hirokawa, Y.; Tanaka, T. *J. Chem. Phys.* **1984,** *81*, 6379.

(9) Sasaki, S.; Maeda, H. *Phys. Rev. E* **1996**, *54*, 2761.

(10) Sasaki, S.; Maeda, H. *J. Colloid Interface Sci.* **1999**, *211*, 204.

(11) Sasaki, S.; Fujimoto, D.; Maeda, H. *Polymer Gels and Networks* **1995**, *3*, 145.

(12) Candau, S. J.; Hirsch, E.; Zana, R.; Adam, M. *J. Colloid Interface Sci.* **1988**, *122*, 430.

(13) Kern, F.; Lemarenchal, P.; Candau, S. J.; Cates, M. E. *Langmuir* **1992**, *8*, 437.

(14) Curro, J. G.; Pincus, P. *Macromolecules* **1983**, *16*, 559−562.

(15) De Gennes, P. G. In *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca and London, 1979; p 23.