Thermosensitive Polymer Gel by Reversible Surfactant Binding

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ABSTRACT: A discontinuous volume collapse occurs on binding of tetraphenylphosphonium chloride (TPPC) to the anionic polyelectrolyte network poly[2-(acrylamido)-2-methylpropanesulfonic acid] (PAMPS) gel. The amount of TPPC inducing volume collapse decreases with increasing temperature. The TPPC binding to the gel is noncooperative and insensitive to temperature change in spite of the strong hydrophobic interaction of TPPC. The mechanism of the TPPC binding is discussed.

1. Introduction

Numerous studies have been reported on polymer gels capable of varying their shape and volume in response to changes in temperature.[1] The principle of such a thermosensitive response is mostly due to insolubilization/solubilization of the polymer network with a lower or higher critical solution temperature (LCST or HCST). Poly(*N*-isopropylacrylamide) (PNIPAM), a well-known example, is characterized in water solution by a LCST at about 31 °C.[2,3] The cross-linked PNIPAM gel has led to a number of applications which exploit the change in the dimensions of the gel to modulate the differential diffusion of species for selective removal[4,5] and delivery[6−8] of cosolutes by thermal-switching control.

Poly(vinyl methyl ether) (PVME) is another thermosensitive polymer having an LCST around 37 °C in aqueous media. A highly porous PVME network has been prepared by irradiating it with γ-rays and its thermomechanical responses were studied.[2,3,9]

Another example involves the temperature sensitive complexation between polymers such as poly(ethylene glycol) (PEG) with poly(methacrylic acid) (PMAA), where an increasing temperature favors complexation.[10,11] Based on this complexation, a transformation of chemical energy into mechanical work has been demonstrated.[12−14]

In this paper, we report a novel class of thermosensitive polymer gels which undergo volume phase transition in response to a change in temperature. Here, a negatively-charged polyelectrolyte gel, poly[2-(acrylamido)-2-methylpropanesulfonic acid], CH_2:$CHCONHC(CH_3)_2CH_2SO_3H$ (PAMPS), binds the cationic surfactant tetraphenylphosphonium chloride (TPPC), thus becoming strongly hydrophobic, leading to the thermosensitive behavior.

The interaction of surfactants with polyelectrolyte gels has been studied extensively.[15−20] We have investigated the thermodynamic and kinetic behaviors of the surfactant (*n*-alkylpyridinium chloride: C_nPyCl, $n = 4$, 8, 10, 12, 16, 18) binding to solubilized and the cross-linked PAMPS over a wide range of concentrations and ionic strengths. The binding was found to be cooperative through side by side hydrophobic interactions of *n*-alkyl groups.[21−23]

Here, we report on the binding of a surfactant with strong bulky hydrophobic groups. We show that TPPC, unlike *n*-alkylpyridinium ions, is not able to undergo cooperative binding to the PAMPS gel in spite of its large hydrophobicity. This indicates that for the cooperative process the arrangement of the binding molecules is important to produce an organized structure. The mechanism of the TPPC binding as well as the thermosensitive behavior of the complex will be described.

2. Experimental Section

Preparation. The preparation of the PAMPS gel was described elsewhere.[21,22] After the polymerization, the gel was immersed in a large amount of water to remove unreacted monomers and initiators until it swelled to equilibrium. The degree of cross-linkage (D.CL.) was defined by the molar ratio of cross-linking agent *N*,*N*′-methylenebis(acrylamide) (MBAA) to AMPS monomer. The degree of swelling of the gel (q) was determined as a weight ratio of the water swollen gel to its dry state.

Measurements. A piece of cubic PAMPS gel ($5 \times 5 \times 5$ mm^3, $q = 62$) was immersed in the prescribed concentration of 10 mL of TPPC solution, and the TPPC binding onto PAMPS gel was followed by measuring the change in UV absorption of the surrounding TPPC solutions at 268 nm (molar extinction coefficient of TPPC: $\epsilon = 4068$ M^{-1} cm^{-1}). TPPC solutions were diluted to a concentration lower than 10^{-4} M to measure the electronic spectra. It was confirmed that TPPC solutions have a constant extinction coefficient and absorption maximum in the measured concentration range. We assume that all of surfactants entered into the gel are bound to the polymer network and define the degree of binding β as the molar ratio of bound TPPC to the sulfonate groups in the gel. The volume change of the PAMPS gel was measured using a cathetometer after standing at least for 2 weeks in order to establish equilibrium.

3. Results and Discussion

When the PAMPS gel is immersed in a TPPC solution, the gel shrinks with time. Figure 1 shows equilibrium volumes of PAMPS gels immersed in the surfactant solution with various concentrations. Dilute TPPC solutions result in a gradual and continuous contraction of the gel, while concentrated solutions bring about an abrupt collapse to about 4% of the initial volume. The concentration at which the abrupt collapse occurs depends on the temperature: an increase in the temperature brings about a decrease in the critical TPPC concentration. For example, at 45 °C, the collapse occurs in a TPPC solution of 0.002 M, while at 15 °C, it occurs in a TPPC solution of 0.007 M.

Since the sudden volume change of the PAMPS gel should be associated with the binding of TPPC, the profile of the volume change was plotted as a function

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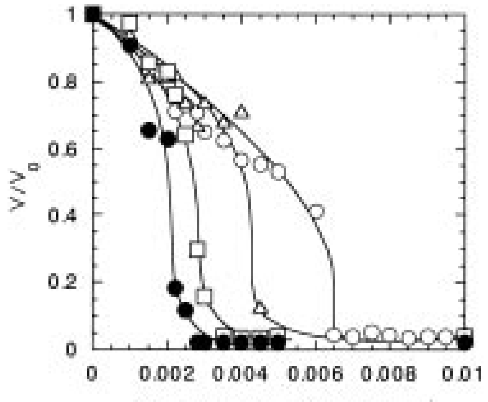

Figure 1. Profiles of volume change of PAMPS gel in TPPC solutions: (○) 15 °C; (△) 25 °C; (□) 35 °C; (●) 45 °C. D.CL. of PAMPS gel: 0.04, $q = 62$. V_0 is the initial volume of the gel swollen in water.

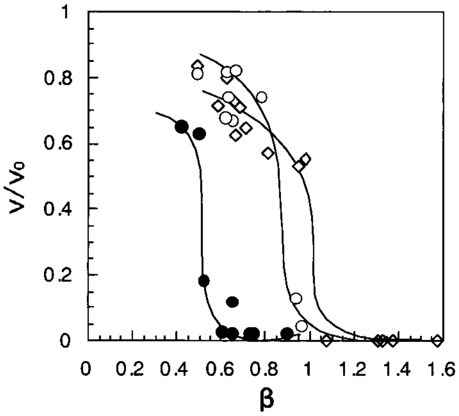

Figure 2. Volume changes as a function of β: (◇) 5 °C; (○) 15 °C; (●) 45 °C. Samples are the same as that used in Figure 1.

of degree of binding β (Figure 2). One can see that the collapse occurs abruptly at a β value which depends on temperature: the higher the temperature, the lower the β value to induce a collapse. The cooperative volume collapse at an elevated temperature suggests that hydrophobic interaction plays an important role.

The volume change can be repeated many times if temperature is cyclically changed (Figure 3). A large volume collapse occurs when the temperature is changed from 15 to 45 °C, while β changes only from 0.65 to 0.85. Thus, the large decrease of the critical β from 0.9 at 15 °C to 0.5 at 45 °C must be largely attributed to intramolecular aggregation of TPPC molecules bound on the gel due to the temperature-sensitive hydrophobic interaction.

A similar TPPC binding occurs with a PAMPS solution to form a temperature-sensitive aggregate. No aggregate is formed under 5 °C, while the solution becomes hazy at 45 °C and the aggregate disappeared when cooled again. The phenomenon can be observed as a change in the turbidity of the solution, and the result is shown in Figure 4. The decrease of the turbidity for the red light at high temperatures probably should be attributed to precipitation after the solution became hazy.

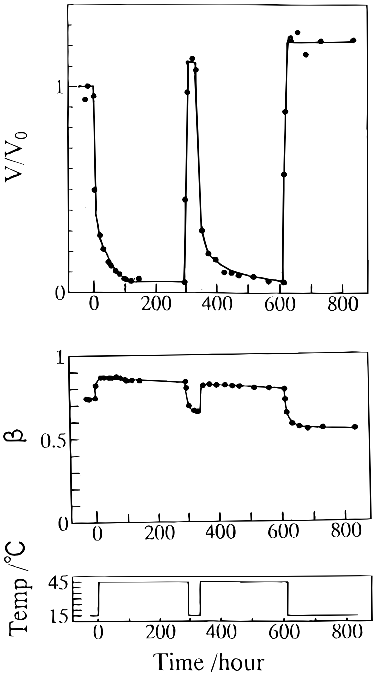

Figure 3. Time profiles of volume change (top), β (middle), and temperature (bottom). Sample is the same as that used in Figure 1.

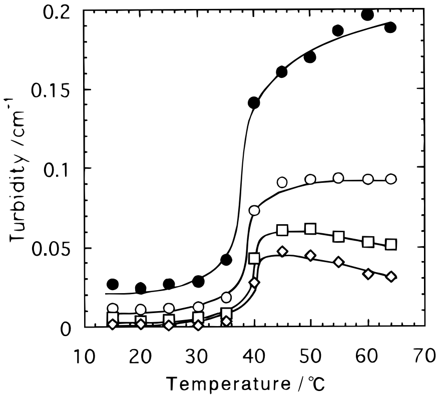

Figure 4. Turbidity changes of the TPPC−PAMPS solution in response to temperature changes observed at various wave lengths: (●) 400 nm; (○) 500 nm; (□) 600 nm; (◇) 700 nm.

In order to investigate the mechanism of the binding, we have plotted isotherms of β vs the free surfactant concentrations at various temperatures (Figure 5, curves group A). One can see that the binding of TPPC starts at a concentration of 10^{-5} M and β increases monotonically with the increase in TPPC concentration. Binding isotherms of TPPC are not sensitive to temperature changes.

We have extensively investigated the binding between PAMPS and C_nPyCl surfactants with different alkyl chain lengths.[20−23] The binding of C_nPyCl surfactants with linear PAMPS is highly cooperative, due to the strong hydrophobic interaction between the nearest neighbor bound surfactant molecules. This cooperative behavior is greatly reduced when the PAMPS is cross-linked to a gel.[23] A cooperativity parameter u is defined by[19]

$$u = \exp(-\Delta F_{\mathrm{h}}/kT) \qquad (1)$$

where ΔF_{h} is the free energy gain through the hydrophobic interaction between adjacently bound surfactants. It can be shown that u is obtained from the slope of the binding isotherm at half-saturation:[19]

$$(\mathrm{d}\beta/\mathrm{d}\ln C_{\mathrm{s}})_{\beta=0.5} = \sqrt{u}/4 \qquad (2)$$

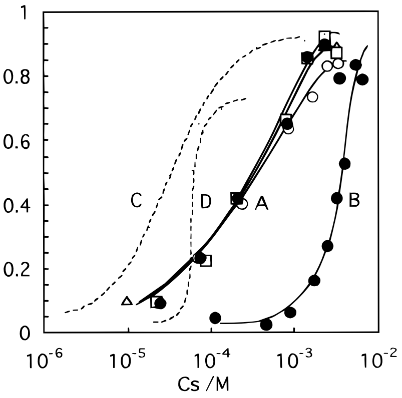

Figure 5. Binding isotherms of TPPC onto PAMPS gel in the absence (A) and presence (B) of sodium sulfate (1×10^{-2} M in concentration) under various temperatures: (○) 15 °C; (△) 25 °C; (□) 35 °C; (●) 45 °C. Samples are the same as that used in Figure 1. Dotted lines indicate the binding isotherm of C_{12}-PyCl with PAMPS gel at 25 °C in the absence (C) and presence (D) of 1×10^{-2} M sodium sulfate. Curve B was measured at 45 °C.

Table 1. Interaction Parameters of Surfactants with PAMPS Gel

		TPPC	C_{12}PyCl
K/L mol^{-1}	no salt	3.2×10^3	3.2×10^4
	with salt[a]	3.1×10^2	1.7×10^4
u	no salt	0.8	5.5
	with salt[a]	6.6	710

[a] 1×10^{-2}/mol L^{-1} sodium sulfate.

where C_s denotes the free surfactant concentration. The cooperativity parameter u for C_{12}PyCl binding with linear PAMPS is as high as 630, but that of the polymer network is about 5.5. The low cooperativity observed for the charged network is due to the high osmotic pressure created by the mobile counterions, which promote an expansion in competition with the shrinkage due to surfactant binding.[19] The gel binding becomes cooperative on addition of a large amount of neutral salt to suppress the network expansion.

In order to characterize the interaction between two nearest neighbor bound TPPC molecules, we have also investigated the binding isotherm in the presence of 1×10^{-2} M sodium sulfate, and the results are shown in Figure 5 (curve B). The cooperativity parameter u and the equilibrium constant K, which is the reciprocal of the free surfactant concentration at half-saturation are calculated from Figure 5 and shown in Table 1. The presence of the salt increases the TPPC concentration at which the binding starts by as much as 2 orders of magnitude. This indicates that the initiation process of binding is dominated by electrostatic interactions. However, there is little cooperativity in TPPC binding. Addition of salt increases u only from 0.8 to 6.6. This is quite different from the case of C_{12}PyCl, where the slope of the binding curve increased sharply in the presence of simple salt (Figure 5, curve D) and u increased from 5.5 to 710.

As reported previously,[22] the binding of C_nPyCl is cooperative through side-by-side molecular interaction of n-alkyl chains. The cooperativity parameter u of C_nPyCl increases with an increase in the alkyl chain length, i.e., with an increase in the hydrophobicity. In the case of TPPC, however, the nearest neighbor hydrophobic interaction is very weak in spite of their strongly hdyrophobic groups. The absence of cooperativity of TPPC binding might be associated with a stereochemical effect. The branched structure of TPPC should be unfavorable for hydrophobic stacking and oppose the cooperative process.

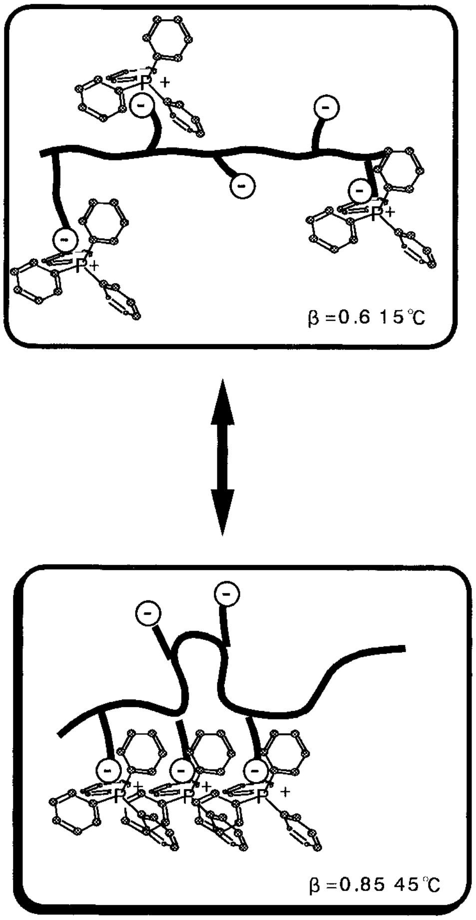

Figure 6. Schematic illustration of the reversible aggregate formation in response to the change in the temperature.

The structure of PAMPS gel–TPPC complexes has been studied using wide- and small-angle X-ray diffraction. Unlike PAMPS gel–C_{12}PyCl aggregates which exhibited an ordered structure with a hexagonal lattice,[20] no appreciable diffraction pattern appeared for the PAMPS–TPPC complexes.

As described, the binding process itself is not cooperative and not temperature sensitive in the temperature range from 15–45 °C. Nevertheless, the volume change occurred abruptly and cooperatively. Thus, the binding of TPPC on the PAMPS gel might be characterized by two stages (Figure 6).

First, TPPC molecules associate with the PAMPS gel, where the electrostatic interaction plays a dominant role. The addition of neutral salt strongly interferes with the binding. This process is not temperature sensitive and not cooperative.

This is followed by an intramolecular aggregation of TPPC molecules bound to the PAMPS gel through hydrophobic interaction. This process is temperature sensitive and a rise in temperature favors the formation of aggregates. When the aggregation proceeds to some extent, the gel shrinks (in the case of solvated PAMPS, it becomes insoluble) and a volume phase transition occurs.

The results indicate that although the hydrophobic interaction between nearest neighbor surfactant molecules is important for the cooperative binding, it is not crucial. The geometric structure which enables an appropriate stacking of the binding molecules is important.

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