Size Effect of the Alkyl Chain of the Surfactant on the Chemomechanical Motion of a Polymer Gel

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The chemomechanical behavior of a cross-linked poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) gel in the presence of *N*-alkylpyridinium chlorides with different chain lengths (C_nPyCl, n = 4, 8, 10, 12, 16, 18) has been investigated. It was found that C_{10}PyCl exhibits the greatest and quickest chemomechanical motion under dc current, while C_8PyCl induced practically no movement under the same conditions. Thus, the size of the alkyl chain of the surfactant is crucial to the total chemomechanical behavior of the gel. The role of alkyl chain size was explained in terms of cooperative hydrophobic interactions.

Introduction

When a water-swollen poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) gel (13 mm in diameter, 2 mm thick, and 5.6 mg dry weight) is immersed in 10 mL of a cationic surfactant *N*-alkylpyridinium chloride (C_nPyCl) solution, the surfactant molecules bind with the polymer network and the gel shrinks with time. This shrinking process is essentially a stoichiometric ion exchange reaction which is characterized by two processes. One is electrostatic salt formation of surfactant molecules with oppositely charged sulfonates in the gel (*initiation process*). The other is a hydrophobic interaction between adjacently bound surfactant molecules, which stabilizes the aggregate (*propagation process*).[1,2] The latter is called the "cooperative process".

When the surfactant undergoes a stoichiometric reaction, the overall stability constant (K) for the binding of the surfactant molecules with the gel can be calculated as[2]

$$K = (C_{s0} - C_s)/\{C_p - (C_{s0} - C_s)\}C_s \qquad (1)$$

where C_p is the exchanged molar concentration defined as the amount of sulfonic acid group in the total volume of the solution, C_{s0} is an initial concentration of the surfactant, C_s is the surfactant concentration surrounding the polymer gel at equilibrium.

For the cooperative binding, K is associated with K_0 and u as[3,4]

$$K = K_0 u = 1/(C_s)_{0.5} \qquad (2)$$

where K_0 is a binding constant of a surfactant molecule bound to an isolated binding site on a polymer, and u is a cooperativity parameter characterizing interaction between adjacently bound surfactants. Thus, K can be calculated as the value of the reciprocal of the equilibrium free surfactant concentration (C_s) at $\beta = 0.5$ and u is determined from the slope of the binding isotherm at the half-bound point:[4]

$$(\mathrm{d}\beta/\mathrm{d}\ln C_s)_{0.5} = \sqrt{u}/4 \qquad (3)$$

Thus, the formation of an aggregate, such as common micelles, is dominated by two opposing forces, a hydrophobic attractive force which favors the aggregation of alkyl chains, and an electrostatic repulsive force among the head groups which limits the growth of the aggregates. In our system the presence of a polyelectrolyte network considerably reduces the repulsive force due to its large cooperativity, consequently lowering the critical concentration required to give the stable aggregate.

On the basis of this phenomena, we have recently developed a new type of electrically driven chemomechanical system which shows quick responses with wormlike motility.[5,6] The principle of this movement is based on an electrokinetic molecular assembly reaction of solvated cationic surfactants, *N*-dodecylpyridinium chloride (C_{12}PyCl), onto a cross-linked polymer gel made from PAMPS. Here the electric field drives and controls the direction of the equilibrium to give anisotropic binding, i.e., when the dc voltage is turned on, the surfactant molecules move toward the cathode by electrophoresis and bind with the gel preferentially on the side of the PAMPS gel strip facing the anode. This causes an anisotropic contraction of the gel and bending toward the anode. Thus, a swinging of the gel was performed by applying electric field changing its polarity every 2 s. The motility of the gel is gentle and flexible and can serve as a new class of "soft acutator" or "molecular machine" fundamentally different from hydraulic engines and metallic machines.

This paper is a further study of the chemomechanical behavior of the gel. We demonstrate here that the size of the alkyl chain of the surfactant molecule plays a crucial role for the effective chemomechanical motion of the polymer gel, i.e., C_{10}PyCl makes the maximum

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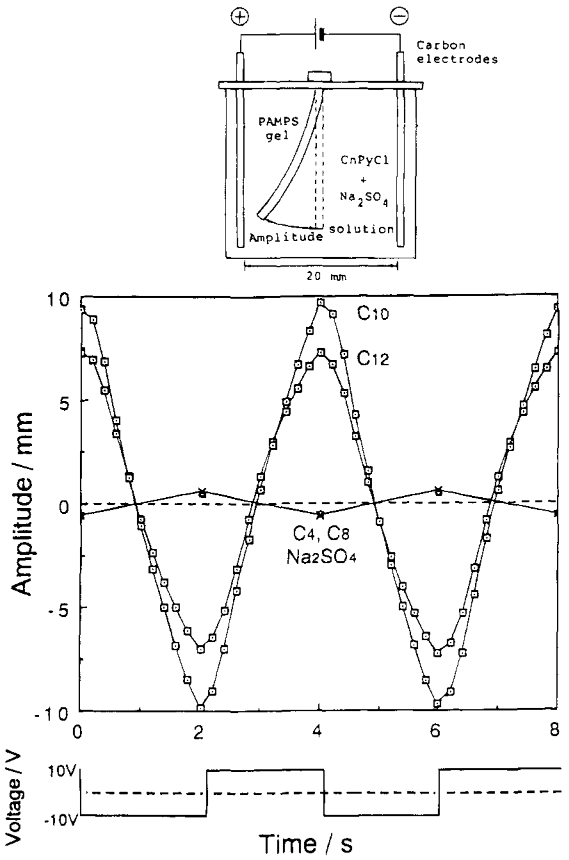

Figure 1. Time profiles of electrodriven chemomechanical swinging of the PAMPS gel in the presence of CnPyCl under dc 10 V and 70–80 mA. The polarity was changed at every 2 s. Temperature 25 °C. C_nPyCl (1×10^{-2} M) + Na_2SO_4 (3×10^{-2} M).

and quickest response of swinging of the gel under dc current, while C_8PyCl cannot induce any chemomechanical motion at all. The presence of such a threshold in alkyl chain length is explained in terms of cooperative hydrophobic binding.

Experimental Section

Materials. 2-Acrylamido-2-methylpropanesulfonic acid (AMPS, Nitto Chem. Co., Ltd.), *N,N'*-methylenebisacrylamide (MBAA) (Tokyo Kasei Co., Ltd.), and Potassium persulfite (Tokyo Kasei Co., Ltd.) were purified in the same manner in the previous paper.[5] *N*-Alkylpyridinium chlorides (CnPyCl) with $n = 4, 12, 16$ (Tokyo Kasei Co., Ltd.) were used as received, and those with $n = 8, 10, 18$ were synthesized according to the literature.[7]

Preparation of the gel: A cross-linked PAMPS gel was prepared by radical polymerization of AMPS with an appropriate amount of MBAA in the same manner described in the previous paper.[5]

Measurement. The profile of the binding of surfactant molecules with the gel was studied spectrophotometrically, i.e., by observing the change in UV absorption of an aqueous solution of surfactant molecules at 259 nm (1×10^{-2} M) containing a piece of cylindrical PAMPS gel (13 mm diameter, 2 mm thick) with time. The configuration of the apparatus in the measurement of the chemomechanical behavior (swinging pendulum) is shown in Figure 1. A sheet of PAMPS gel (20 mm long, 5 mm wide, 1 mm thick, dry weight 0.08 g) was suspended in 10 mL of the surfactant solution containing a certain amount of sodium sulfate, leaving the bottom end free.

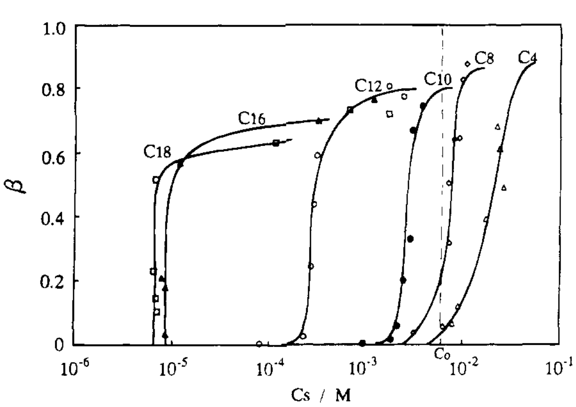

Figure 2. Binding isotherms of surfactant molecules with the PAMPS gel at 25 °C. Equilibration time 30 days. The degree of binding (β) is defined as the molar ratio of bound surfactant to total sulfonate group in the gel. Na_2SO_4 (3×10^{-2}M). △ C_4PyCl, ◇ C_8PyCl, ● $C_{10}PyCl$, ○ $C_{12}PyCl$, ▲ $C_{16}PyCl$, □ $C_{18}PyCl$.

The ionic strength of the solution was kept constant ($\mu = 0.1$). A pair of parallel plate carbon electrodes (30 mm long, 10 mm wide, 1 mm thick) was inserted into the solution with a 20 mm distance and dc voltage was applied through the electrodes from an electric source using a potentiometer (HA-501, Hokuto Denko, Co.). The chemomechanical response of the PAMPS gel to the electric field was observed by a video camera and the time profile was analyzed by means of a personal image analyzing system (XL-500, Olympus).

Results and Discussion

The binding isotherm for CnPyCl of various chain lengths onto the PAMPS gel was obtained by plotting the degree of binding (β), defined as the molar ratio of bound surfactant to total sulfonate group in the gel, vs the free surfactant concentration. Figure 2 shows the results obtained in the presence of 3×10^{-2} M of sodium sulfate at 25 °C. Figure 2 demonstrates that the slope of the binding curve for each surfactant is very high, starting and completing the binding in a very narrow range of the surfactant concentration, and the slope, which indicates the cooperativity of the binding, increases with an increase in alkyl chain size. It is also seen that an increase in the chain length of the surfactant lowers the concentration at which the binding starts, suggesting that the hydrophobic interaction favors the binding equilibrium and stabilizes the complex.

Due to the presence of strong cooperativity, an increase in the alkyl chain length of the surfactant brings about a drastic change of the β value under a constant surfactant concentration. For example, $C_{10}PyCl$ can bind to the gel with a β of 0.8 at the surfactant concentration of 7×10^{-3} M as seen in Figure 1, while the β for C_8PyCl is only 0.2 This nature of the binding has led us to make a chemomechanical system which shows specific dependence on the alkyl chain length of the surfactant.

When an electric field is applied to a sheet of PAMPS gel suspended in the surfactant solution (C_nPyCl, $n = 4, 8, 10, 12, 16, 18$), the gel showed bending only when the alkyl size of the surfactant became C_{10} or larger. Among the surfactants used, $C_{10}PyCl$ and $C_{12}PyCl$ showed intensive and steady swinging and the magnitude of bending attained 7–9 mm within 1 s or about 25° in angle (Figure 1). If the polarity of the electric

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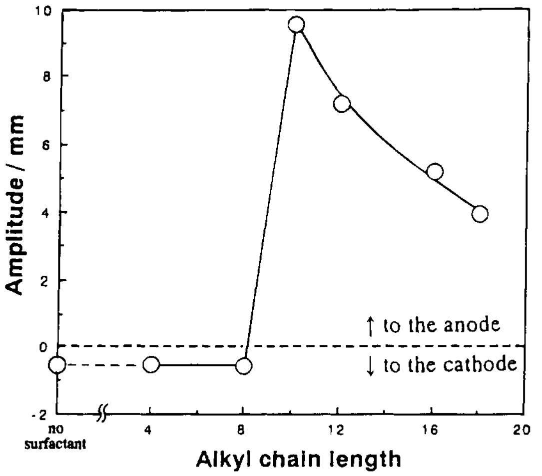

Figure 3. Dependence of alkyl chain size of the surfactant on the amplitude of the swinging of the PAMPS gel. The amplitude of the swinging was measured at 1 s after applying the electric field. Temperature 25 °C.

field is altered every 2 s, the gel showed repeated swinging like a pendulum more than 3000 times.[8,9] The swinging profiles are shown in Figure 1.

On the other hand, C_4PyCl and C_8PyCl caused extremely weak and slow swinging and the direction of bending was opposite to that of $C_{10}PyCl$ and $C_{12}PyCl$. Since this swinging motion is the same as that of the sodium sulfate solution, one can conclude that there is no effect of those surfactants on the chemomechanical behavior. In other words, C_4Py^+ and C_8Py^+ cations penetrate into the gel network without making extensive stoichiometric binding, and this is also the case for the sodium cation.

Figure 3 shows the dependence of the amplitude of the swinging on the alkyl chain length. One can see that the amplitude and the direction of the swinging abruptly changes at the interval of C_8PyCl and $C_{10}PyCl$. As is easily understood from the binding isotherm curve in Figure 2, this is due to the fact that the surfactant molecules with an alkyl chain shorter than C_8PyCl can not bind with the gel at this concentration (7×10^{-3} M) enough to induce the effective swinging. On the other hand, $C_{10}PyCl$ and $C_{12}PyCl$ results in an intensive swinging of the gel attaining $\beta = 0.8$. Thus, a difference of two carbon atoms of surfactant significantly dominates the chemomechanical behavior of the gel.

A further increase in alkyl chain length of the surfactant decreases the amplitude and response of the swinging. This should be associated with the kinetic nature of the binding, i.e., $C_{16}PyCl$ and $C_{18}PyCl$ are largely in a form of aggregated micelle structures at this (10^{-2} M) concentration (the critical micelle concentration of $C_{16}PyCl$ is 0.9×10^{-3} M without salt), which significantly restricts their diffusive penetration through the polymer network and consequently lower the β value bound within 2 s.[8] As reported in our previous paper,[1] the diffusion coefficient of $C_{18}PyCl$ in the PAMPS network is 2 orders of magnitude smaller than that of $C_{10}PyCl$.

Table 1. Interaction Parameters of C_8PyCl and $C_{10}PyCl$ with the PAMPS Gel at 25 °C in the Presence of Na_2SO_4 (3×10^{-2} M)

	K/ L mol^{-1}	cooperativity parameter u	K_0/ L mol^{-1}	$\Delta G°$/ kJ mol^{-1}	$\Delta H°$/ kJ mol^{-1}	$\Delta S°$/ J K^{-1} mol^{-1}
C_8PyCl	130	18	7.4	−12.2	−2.2	34
$C_{10}PyCl$	340	39	8.7	−14.7	16.0	105

The dramatic size effect of the alkyl chain length of the surfactant can be associated with hydrophobic binding between adjacent surfactant molecules and this can be explained by a thermodynamic analysis of the binding isotherm. According to the procedure reported in the previous paper,[1] interaction parameters of the surfactant with the gel can be calculated from the binding isotherm and the results are summarized in Table 1. From the table, one can see that the binding constant of the initiation process (K_0) of $C_{10}PyCl$ is almost the same as with C_8PyCl, while the cooperativity parameter (u), characterizing the interaction between adjacently bound surfactants of $C_{10}PyCl$, is twice that of C_8PyCl.

Enthalpy and entropy changes of the binding were calculated from the temperature dependence of the binding isotherm and the results are summarized in Table 1. As we know,[10] the hydrophobic interaction is well characterized as having a large and positive entropy change while nearly zero or small positive enthalpy change, which is interpreted as a net breakdown of the "iceberg structure" of water molecules bound onto alkyl chains of the surfactant. As seen in Table 1, the binding of C_8PyCl has a negative enthalpy and positive entropy, suggesting that the binding is largely dominated by the electrostatic interaction. In contrast, $C_{10}PyCl$ has large positive enthalpy and entropy values, which indicates an extensive contribution of the hydrophobic interaction.

Thus, a chemomechanical swinging performed by the reversible molecular assembly reaction of the surfactants at the polymer gel is extremely sensitive to the alkyl chain length of the surfactant, and the hydrophobic interaction dominates the total behavior of the movement.

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