Colloid Polym Sci (2002) 280: 710–715
DOI 10.1007/s00396-002-0671-6

ORIGINAL CONTRIBUTION

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The effect of the heterogeneity of *N*-isopropylacrylamide-*co*-styrene sulfonate gel on the binding behavior of an ionic surfactant with the gel

Received: 9 January 2001
Accepted: 30 January 2002
Published online: 24 April 2002

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Abstract The effects of the heterogeneity of the gel on the swelling behavior and on the binding of surfactant counterions, dodecylpyridinium chloride (C12Py), were examined using copolymer gels of *N*-isopropylacrylamide and *p*-styrene sulfonate (pSS). The feed mole fractions of pSS, *X*, were 0.05, 0.1, 0.15, 0.20 and 0.25. The gels prepared at 40 ± 2 °C were turbid, indicating heterogeneous monomer densities on a microscopic scale, while the gels prepared at 4 ± 1 °C were transparent. Significantly different swelling behavior was observed on changing the temperature between the two kinds of gel: the change in gel volume in a given temperature interval was always smaller for the heterogeneous gels than for the homogeneous gels. The binding isotherms of C12Py were, in contrast, very similar between the two kinds of gel. The cooperative parameter of the binding, *u*, was rather small (2–4) for both types of gel. This small cooperativity was ascribed to relatively low charge densities. A small but significant decrease in *u* was found when *X* increased.

Keywords Heterogeneity of gels · Swelling behavior · Surfactant ion binding

Introduction

The interaction between polymers and surfactants in aqueous solutions has been a subject of great interest [1, 2, 3, 4, 5]. The case of polyelectrolyte and oppositely charged surfactant pairs is of special interest because of the especially strong interaction. The binding generally takes place cooperatively at a well-defined concentration, the critical association concentration (cac) just like micellization at a critical micelle concentration (cmc). The cac of a surfactant can be several orders of magnitude lower than the cmc, depending on the nature of the polyelectrolyte and the surfactant ion. The interaction has been investigated on the basis of the binding isotherms [6, 7, 8, 9]. The binding isotherm can be characterized in terms of two parameters: the cooperative binding constant, *Ku*, and the cooperative parameter, *u* [9].

On the other hand, the interaction between ionic gels and surfactants has been another subject of interest [10, 11, 12, 13, 14]. The volume of an ionic gel is determined by the balance between the swelling force of the osmotic pressure due to the counterions and the contractile force due to the elastic chains. The volume of a swollen gel varies with various medium conditions such as ionic strength, solvent composition, pH values or temperature [15, 16, 17, 18]. The gel volume is also changed by the binding of surfactant counterions.

Similar binding behavior was reported between a solution of linear polymers and the corresponding gels [11, 13], while a marked difference was reported [12] where *u* of the gel was more than 2 orders of magnitude smaller than that of the polymer solution. The reason for these inconsistent results is not well understood.

N-Isopropylacrylamide (NIPA) polymer aqueous solution exhibits a lower critical solution temperature

(LCST) at about 32 °C [19]. On the other hand, NIPA gel in water is known to show a volume phase transition in response to a temperature change at about 34 °C [18]. It is known that heterogeneous NIPA gels are synthesized in water at temperatures higher than the LCST [20, 21].

In the present study, we synthesized the NIPA-*co*-(*p*-styrene sulfonate) (pSS) copolymer gels at 40 and 4 °C, corresponding to above and below the LCST of NIPA, respectively, expecting homogeneous and heterogeneous structures. We investigated the effect of the heterogeneity of the gel structure on the temperature-induced volume change and the binding behavior of a surfactant conterion with the copolymer gel.

Experimental

Materials

NIPA was provided by Kojin Co. and was purified by toluene and hexane. Sodium pSS was purchased from Tokyo Kasei Kogyo Co.and was used as received. *N*,*N*′-Methylenebisacrylamide and ammonium peroxodisulfate were obtained from Kanto Chemical Co. and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) was purchased from Nacalai Tesque and was used as received. Dodecylpyridinium chloride (C12PyCl) was purchased from Tokyo Kasei Kogyo and purified by recrystallization four times from acetone. Surfactant stock solutions were prepared by dissolving C12PyCl in 0.1 molkg^{-1} NaCl stock solution. Deionized and distilled water was used in all the experiments.

NIPA–pSS copolymer gels with constant total concentration (1.5 molkg^{-1}) of NIPA and pSS and varyious mole fractions of pSS were prepared by radical polymerization of NIPA with pSS in water as follows. NIPA, pSS, *N*,*N*′-methylenebisacrylamide (7.5×10^{-3} molkg^{-1}) as a cross-linker and ammonium peroxodisulfate (15×10^{-3} molkg^{-1}) as an initiator were dissolved in pure water and degassed for 1 h. TEMED, as an accelerator, was added, and then the solution was injected between glass plates separated by a Teflon gasket (1 mm). The polymerization reaction was performed at 40 ± 2 °C for 1 h and at 4 ± 1 °C for 24 h. Transparent and colorless homogeneous gels were obtained at 4 °C, but white, turbid heterogeneous gels were obtained at 40 °C. The gel plate was cut into a square (5 mm×5 mm) of 1-mm thickness, immersed in pure water for 2 weeks to remove all unreacted compounds, dipped into acetone, and then vacuum-dried at 40 °C.

The mole fractions of pSS at the gel preparation, X = pSS/(NIPA + pSS), were 0.05, 0.10, 0.15, 0.20 and 0.25, respectively. In the case of the heterogeneous gels, the fragile nature of the gels significantly increased with X. Especially, the heterogeneous gels with $X = 0.25$ often broke down during the purification process.

Measurements

In order to obtain the volume of the swollen copolymer gels, a dry gel was immersed in pure water overnight to establish the swelling equilibrium. Then, the area, S, (square millimeters) of the gel plate was measured with a slide caliper. The gel volume, V, (cubic millimeters) was determined from S. The volume per mole of the average monomer residue in the NIPA–pSS copolymer gel, V/n, was defined as follows:

$$V/n = S^{3/2}/n. \tag{1}$$

In order to obtain the binding isotherms of the surfactant with the copolymer gels, dry gels were swollen in 0.1 molkg^{-1} NaCl stock solution overnight. Then, a surfactant stock solution was added to the solution containing the gels, and then left to stand for at least 2 weeks at 25 ± 2 °C to establish a binding equilibrium state. A batch method was employed in all the measurements because of the long binding equilibration time. The free $C12Py^+$ ion concentration, c_f, was determined by UV absorption of the external surfactant solution at 259 nm. If necessary, the solutions were diluted so that the absorbance of the solution became around 1. The degree of binding, β, was defined as the ratio of the number of moles of surfactant that penetrated into the gel to the total number of monomeric units of the sulfonic group in the gel,

$$\beta = \frac{n_0 - n_f}{n_p}, \tag{2}$$

where n_0 and n_f, respectively, denote the number of moles of the surfactant initially present and that of free surfactant, and n_p is the total number of moles of the sulfonic groups in the gel.

Electron micrographs of the homogeneous and heterogeneous copolymer gel were taken by scanning electron microscopy (SEM) with a JEOL JSM-5200.

Results and discussion

Electron micrographs

The gels prepared at 4 °C were swollen in water and they were transparent, colorless, and homogeneous macroscopically. The gels prepared at 40°C, although swollen in water, were turbid and white. The formation of heterogeneous structures has been reported for a cross-linked NIPA gel prepared at synthesis temperatures above the LCST [20, 21, 22]. When the polymer solution is in the phase-separation regime, two different concentrations regions (i.e., NIPA-poor and NIPA-rich) appear during the gelation process. When the domain sizes of these two regions have a size of the order of the wavelength of visible light, the gel has a high turbidity. In this study, we observed high turbidity for the NIPA–pSS copolymer gels prepared at 40 °C above the LCST of NIPA, suggesting the domain structure with a size comparable to the wavelength of visible light. However, the turbidity of the swollen heterogeneous gel strongly depended on the irradiated position of the gel and hence reproducible results could not be obtained. This is probably due to the spatial heterogeneity on a large scale for the gel. Hereafter, we denote this gel as a heterogeneous gel. The degree of cross-linkage in NIPA-rich domains may be larger than that in NIPA-poor domains because of the hydrophobic interaction between NIPA-rich domains and methylenebisacrylamide.

In order to investigate the difference of the (microscopic) structure of the homogeneous and heterogeneous gels, electron micrographs of both gels were taken by SEM. The electron micrographs obtained are shown in

Fig. 1, which clearly shows that the surface of a homogeneous gel was very smooth, while large and deep cracks were observed for a heterogeneous gel. The cracks could be related to the fragile nature of the swollen state of the gel in water.

The temperature dependence of the volume per weight of a swollen gel

The temperature dependence of the volume of swollen NIPA–pSS copolymer gels is shown in Fig. 2. The volume was normalized to a unit mole of the average monomer residue. As a whole, the volume tends to decrease with increasing temperature, where the (shrinking) tendency of the homogeneous gels is more remarkable than that of the heterogeneous ones. The most noticeable dependence is observed in the gels with the lowest composition studied ($X = 0.05$): the volumes of the homogeneous gels decrease by around 80% in contrast with a slight decrease of around 30% in the heterogeneous gels in the temperature region between 40 and 50 °C. It can be concluded that the heterogeneous gel did not shrink as much as the homogeneous gel. The NIPA-rich microdomains are dense even at temperatures below 30 °C and hence the extent of the volume shrinkage of the domains is much smaller than that of the homogeneous gel.

As to the effect of the contents, X, of the ionic monomer, the volume increase with X is more striking at higher temperature for both the homogeneous and the heterogeneous copolymer gels (Table 1). The increase in charge density, X in a gel results in the increased osmotic pressure that prevents the gels from shrinking even at high temperature. The present result is consistent with the previous finding that the introduction of electric charges prevents the NIPA gels from shrinking at high temperature [23].

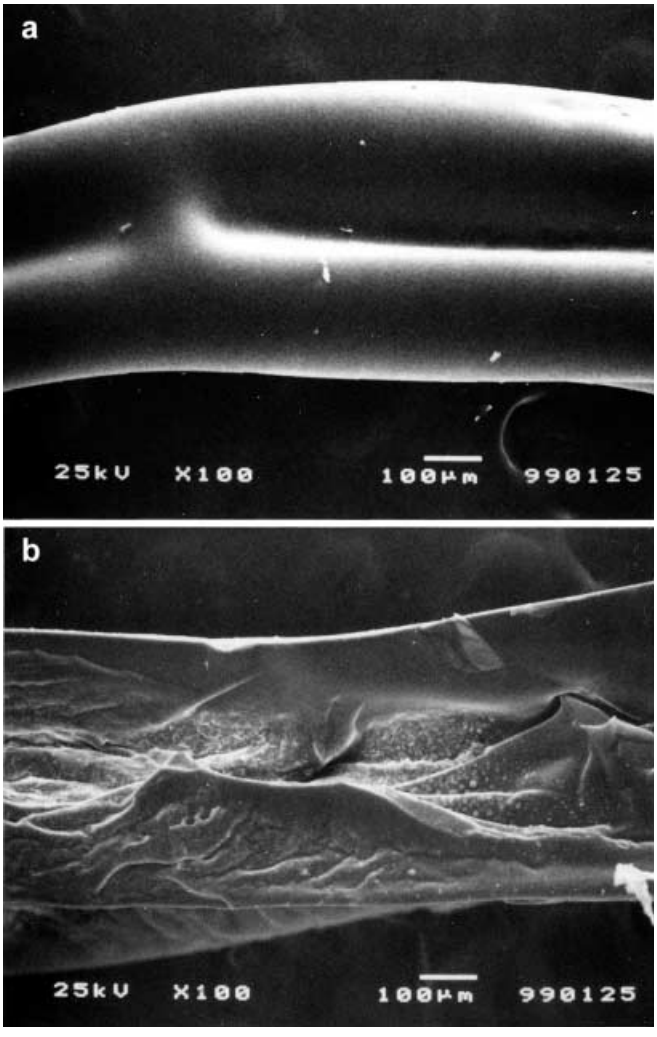

Fig. 1a,b. Electron micrographs of *N*-isopropylacrylamide (*NIPA*)–*p*-styrene sulfonate (*pSS*) gels ($X = 0.10$). **a** Homogeneous gel; **b** heterogeneous gel

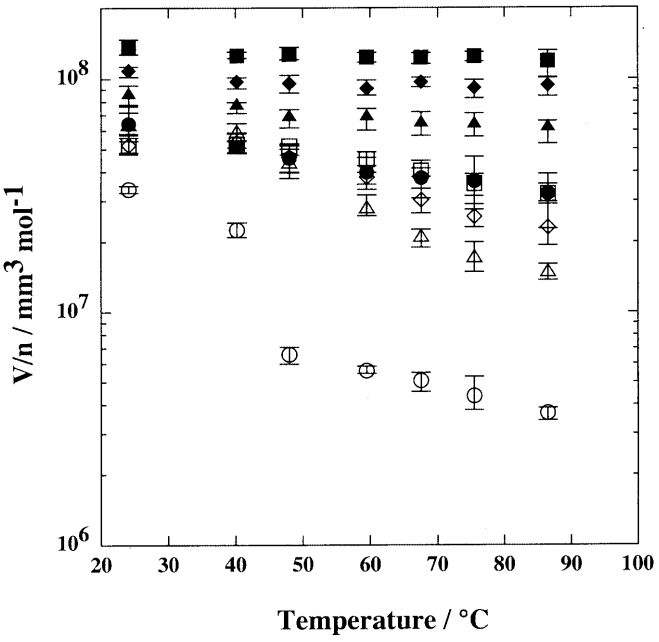

Fig. 2. Temperature dependence of the volume per mole of the average monomer residue in the NIPA-pSS copolymer gel, V/n, with various compositions. $X = 0.05$ (*circles*), $X = 0.10$ (*triangles*), $X = 0.15$ (*diamonds*) and $X = 0.20$ (*squares*). *Open* and *closed symbols* denote homogeneous and heterogeneous gels, respectively

Binding isotherm

Binding isotherms of $C12Py^+$ to NIPA–pSS copolymer gels in 0.1 molkg^{-1} NaCl at 25 °C are shown in Figs. 3 and 4. In the case of $X = 0.05$, the binding isotherm of

Table 1. Values of the volume per mole of the average monomer residue in the *N*-isopropylacrylamide–*p*-styrene sulfonate copolymer gel (V/n) at around 90 °C in water. X represents the feed mole fraction of *p*-styrene sulfonate

	X	V/n (10^7 mm^{3}mol^{-1})
Homogeneous	0.05	0.37 ± 0.02
	0.10	1.5 ± 0.2
	0.15	2.3 ± 0.6
	0.20	3.2 ± 0.4
Heterogeneous	0.05	3.2 ± 0.9
	0.10	6.2 ± 0.9
	0.15	9.4 ± 1.0
	0.20	11 ± 2

the heterogeneous gel coincided with that of the homogeneous gel as shown Fig. 3A. As shown in Figs. 3B and 4, on the other hand, the binding isotherms of the heterogeneous copolymer gels shifted slightly toward higher free surfactant concentrations, c_f in the case of $X = 0.10$, 0.15 and 0.25. The binding isotherms themselves of the two kinds of gel were of similar shape for a given X value. These binding curves were reproducible for both the homogeneous and the heterogeneous copolymer gels. The results shown in Figs. 3 and 4 clearly indicate that the counterion binding takes place in a similar manner for both the homogeneous and the heterogeneous gels in spite of the significant difference in the swelling behavior.

It is expected that the solubilization of surfactant ions into hydrophobic regions (NIPA-rich microdomain) through the hydrophobic interaction affects the biding isotherms [24]. Actually, this solubilization was scarcely observed in the binding isotherms of the heterogeneous gels. Thus, the results can be interpreted by assuming the dominant role of the electrostatic interaction in the binding. Under this condition, the amount bound is

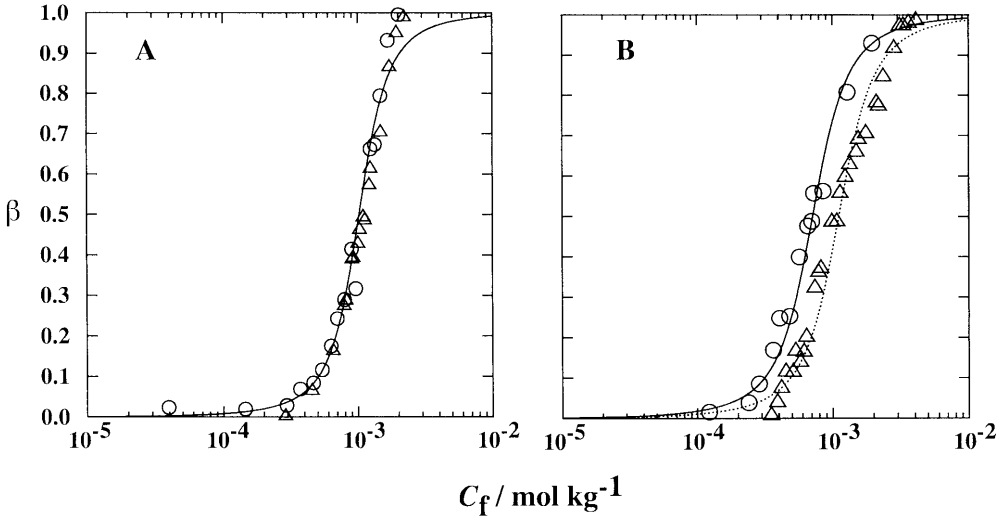

Fig. 3A,B. Binding isotherms of dodecylpyridinium chloride (*C12Py*) to NIPA–pSS gels with various compositions in 0.1 molkg^{-1} NaCl at 25 °C and theoretical curves calculated from Eq. (3). Homogeneous gels (*circles*) and heterogeneous gels (*triangles*). **A** $X = 0.05$. *Solid line*: $Ku = 1.0\times10^3$ and $u = 14$. **B** $X = 0.10$. *Solid line*: $Ku = 1.4\times10^3$ and $u = 10$. *Dashed line*: $Ku = 0.9\times10^3$ and $u = 10$

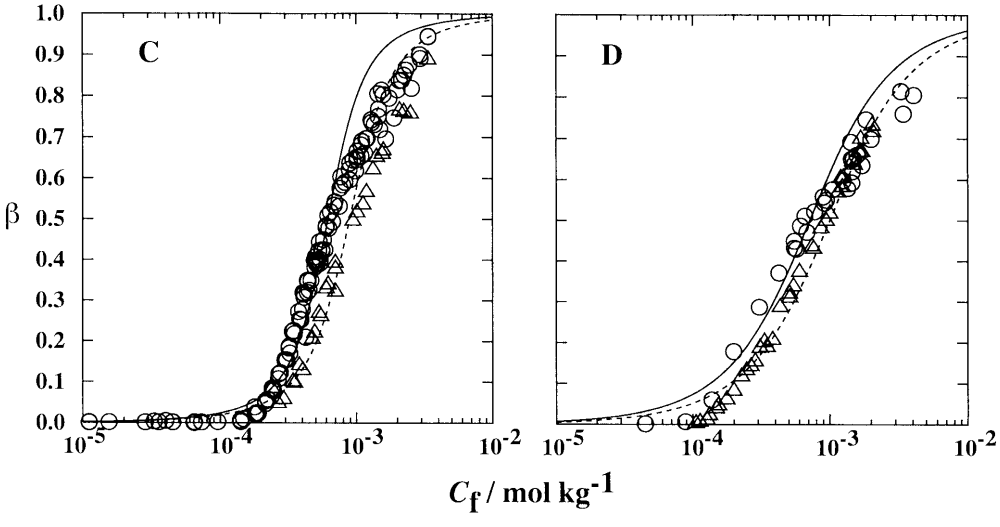

Fig. 4A,B. Binding isotherms of C12Py to NIPA–pSS gels with various compositions in 0.1 molkg^{-1} NaCl at 25 °C and theoretical curves calculated from Eq. (3). Homogeneous gels (*circles*) and heterogeneous gels (*triangles*). **A** $X = 0.15$. *Solid line*: $Ku = 1.6\times10^3$ and $u = 9$. *Dashed line*: $Ku = 1.2\times10^3$ and u = 7. **B** $X = 0.25$. *Solid line*: $Ku = 1.4\times10^3$ and $u = 2$. *Dashed line*: $Ku = 1.2\times10^3$ and $u = 2$

Table 2. Values of the critical association concentration (*cac*) and binding parameters of gels of various compositions in 0.1 molkg^{-1} NaCl

	X	cac ± 0.5 (10^{-4} molkg^{-1})	Ku ± 0.3 (10^3 kgmol^{-1})	u ± 1
Homogeneous	0.05	3.5	1.0	14
	0.10	2.1	1.4	10
	0.15	1.7	1.6	9
	0.25	1.0	1.4	2
Heterogeneous	0.05	3.5	1.0	14
	0.10	2.6	0.9	10
	0.15	2.0	1.2	7
	0.25	1.0	1.1	2

expected to be determined by the content of the charged monomers, which is proportional to X. On the other hand, the distribution of charged monomers is likely to be heterogeneous; X is greater in NIPA-poor domains and vice versa. In spite of this probably uneven distribution of X between the two kinds of microdomains, the amount bound was still determined by the overall value of X because the gels used in the present study were of sufficiently large size in order to average the microscopic heterogeneity of the gels. The present results also suggest that the heterogeneous structure of a gel scarcely produces any specific effect on the binding isotherm, in contrast to the results of the swelling behavior.

Bindings take place at a well-defined concentrations and this concentration was referred to as the cac. The values of the cac of both gels are summarized in Table 2. The values of the cac clearly decreased as X or the charge density of the gel increased. This result indicates the dominant role of the electrostatic interaction in the initial binding step.

In order to estimate the parameters of binding, we analyzed the binding isotherms after the method of Satake and Yang [9]. According to this method, the degree of binding, β, is given by

$$\beta = \frac{1}{2}\left(1 + \frac{Kuc_f - 1}{\sqrt{(Kuc_f - 1)^2 + 4Kc_f}}\right), \quad (3)$$

where K is the binding constant between the surfactant ion and an isolated binding site on the copolymer gel and u is the cooperativity parameter between two bound surfactants on adjacent binding sites: $u > 1$ for cooperative binding, $u = 1$ for noncooperative binding and $u < 1$ for anticooperative binding. The solid and dashed lines in Figs. 3 and 4 are the best fit of the experimental data to Eq. (3) for the homogeneous and heterogeneous copolymer gels, respectively. The values of Ku and u for both gels are also summarized in Table 2, which shows that the Ku values for both copolymer gels were nearly constant irrespective of X; $Ku = 1.4\times10^3$ for the homogeneous copolymer gel and $Ku = 1.1\times10^3$ for the heterogeneous copolymer gel. The values of u for both copolymer gels were also very similar to each other and the u values decreased as the X values increased.

The u values obtained in this study show two features: the values of u are very small and the decrease of u with increasing X. This means that the binding behavior is almost noncooperative ($u = 1$). Three factors that potentially influence the cooperativity are considered here. For the effect of the ionic strength, no marked effect on u has been reported, but u is expected to increase with ionic strength as a general trend [3]. The relatively high ionic strength (0.1 molkg^{-1} NaCl) in the present study cannot explain the small u values.

It is known that u decreases with decreasing charge density of linear polymers, as observed in the binding of tetradecylpyridinium ions, C14Py$^+$, to pectinates with various degrees of esterification [3]. The general trend of small u values could be explained by relatively low charge densities ($X \le 0.25$) in the present study; however, the second feature mentioned earlier, $\partial u/\partial X < 0$, is opposite to the expected outcome of this explanation.

The third factor to be considered is the effect of crosslinks in the case of gels. The effect was studied by comparing the binding isotherms between ionic gels and linear polyions in solution. Two mutually inconsistent results are obtained. No marked difference between the gels and the linear polyions has been observed on polyacrylamide [11] and copolymer of NIPA and poly(aminepropyl)methylsiloxane (PAMPS) [13]. (In the binding of C12Py with the latter copolymer, on the other hand, a small difference for the u values was also reported [14]. The values of u for $X_{PAMPS} = 0.1$ were 11 and 2.47 for the linear polyion and the gel, respectively [14]. This u value for the gel is about one-quarter of the u value of the gel ($X = 0.1$) in the present study. On the other hand, the marked decrease in the u values of the gels ($u = 2.42$) compared with the linear polyions ($u = 630$) was observed in the binding of C12Py and PAMPS [12].

Conclusion

Copolymer gels of NIPA and pSS with various mole fractions of the latter ($X = 0.05$, 0.10, 0.15, 0.20 and 0.25) were polymerized at 4 and 40 °C. The homogeneous gels prepared at 4 °C were transparent and colorless. On the other hand, the heterogeneous gels prepared at 40 °C were turbid and white, indicating the existence of the microdomain structure with a size comparable to the wavelength of visible light. It consists of NIPA-rich and NIPA-poor microdomains.

The swollen gel volume decreased with increasing temperature for the homogeneous and the heterogeneous gels. The shrinking tendency of the homogeneous

gels was more remarkable than that of the heterogeneous ones for all compositions because the NIPA-rich microdomain with the larger degree of cross-linkage swells slightly even below 30 °C and the NIPA-poor microdomain is prevented from shrinking owing to the higher osmotic pressure. On the other hand, with increasing X at a given temperature, the degrees of volume shrinkage of both copolymer gels decreased with increasing osmotic pressure.

The effect of the existence of the hydrophobic microdomains (NIPA-rich microdomains) of submicron size on the binding of surfactant-counterions of C12Py was examined. The binding isotherms of C12Py of both gels were very close to each other. The results suggest that the hydrophobic maicrodomains in the heterogeneous gels scarcely contribute to the binding of surfactant counterions. Thus, the results can be interpreted by assuming the dominant role of the electrostatic interaction in the binding. The cooperative binding constants (Ku) for the homogeneous and the heterogeneous gels were 1.4×10^3 and 1.1×10^3 kg mol^{-1}, respectively, irrespective of the X values. The cooperative parameters of the binding for both copolymer gels were rather small ($u = 2$–4) and depended slightly on X.

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