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Polymer 41 (2000) 141–147

polymer

Effects of polyelectrolyte complexation on the UCST of zwitterionic polymer

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Received 26 June 1998; received in revised form 16 November 1998; accepted 23 February 1999

Abstract

A zwitterionic polymer—poly-3-dimethyl(methacryloyloxyethyl)ammonium propane sulfonate (PDMAPS)—was synthesized and its complexation behaviors with polyanion: poly-2-acrylamido-2-methyl propane sulfonic acid (PAMPS); and polycation: poly-3-acryloylamino propyl trimethyl ammonium chloride (PDMAPAA-Q); or: x,y-ionene bromides ($x = 3,6$; $y = 3,4$) have been studied. One of the characteristic features of these complexes is that they are soluble, in spite of the abolishment of positive or negative charge of PDMAPS after the complexation and is able to exhibit UCST depending on the concentration and the mixing molar ratio. It was found that PDMAPS–PAMPS complex dramatically increases the viscosity to give a network structure through electrostatic interaction extensively decreasing the UCST, while the PDMAPS–polycation complex first decreases, but then increases the UCST without forming the network. The mechanism of different behaviors of these complexes has been discussed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Zwitterionic polymer; Poly-ion complexation; Network

1. Introduction

Sulfobetaines are special classes of zwitterions having ammonium cation and sulfonic anion isolated with alkyl, usually propyl or butyl group. Although their syntheses and properties have been studied and comprehensively described in books and reviews [1–9], systematic studies of solution and bulk properties of polyzwitterions are not many compared to those of aqueous polyelectrolytes. Salamone et al. [3], who studied the solution behaviors of a poly-vinylimidazolium sulfobetaine reported that inorganic salts disrupt the intramolecular interactions of the imidazolium and sulfonate groups and make them soluble in water. Schulz et al. [9] reported on the phase behavior of poly-3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate (PDMAPS) in aqueous salt solution and found the following general features: (1) the solubility of PDMAPS depends on polymer molecular weight as well as the concentration and species of added salts; (2) one of their samples exhibits the continuous phase separation in water both at an upper and lower critical solution temperature (UCST and LCST); and (3) solutions of PDMAPS do not exhibit common polyelectrolyte behavior, showing increase in viscosity with increasing salt concentration.

Thus, PDMAPS is considered to be in a collapsed coil in water below UCST due to intra- and/or inter-chain associations. This state is disrupted by addition of the salt, thereby allowing the chain expansion and solubilization due to screening effect of both ions.

Considering the sensitive nature of PDMAPS to the ions, we have made a detailed study of solution behaviors of PDMAPS in the presence of polymeric anion: poly(2-acrylamido-2-methyl-propane sulfonic acid) (PAMPS) or polymeric cations: poly-3-acryloylamino propyl trimethyl ammonium chloride (PDMAPAA-Q) and x,y-ionene bromides ($x = 3,6$; $y = 3,4$) (Fig. 1). We have found that the phase behaviors of PDMAPS are totally changed by the cooperative interaction with these polyelectrolytes, while the effect on UCST is quite different from each other. A possible mechanism of the interaction has been described.

2. Experimental

2.1. Materials

N,N-dimethylaminoethyl methacrylate was obtained from Tokyo Kasei Co., Ltd., and was purified by vacuum distillation. 2-Acrylamido-2-methyl-propanesulfonic acid

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PII: S0032-3861(99)00161-5

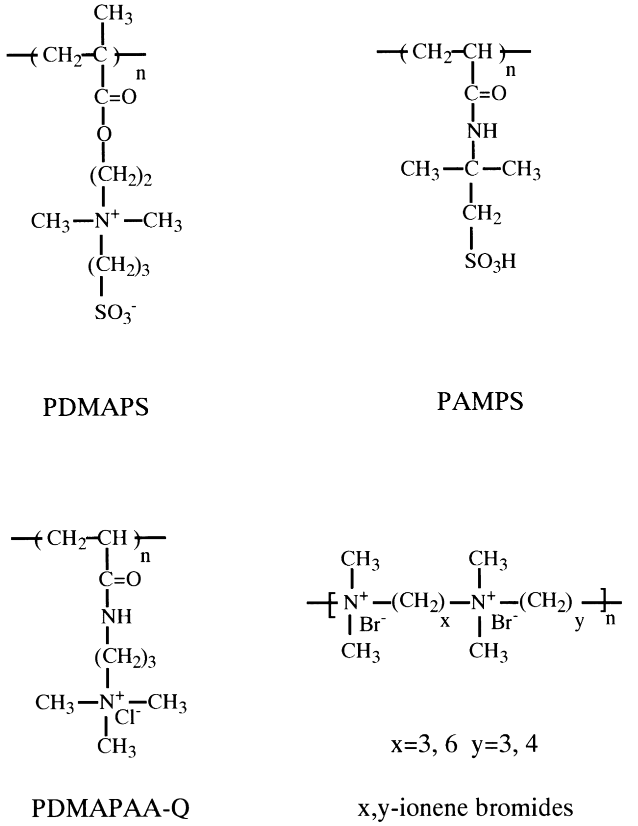

Fig. 1. Molecular structures of polymers used in this work.

(AMPS) was purchased from Kanto Chemicals Co., Ltd., potassium peroxosulfate ($K_2S_2O_8$) was from Tokyo Kasei Co., Ltd., and they were purified by repeated recrystallization. 1,3-Propane sulfone and 1,4-dibromobutane were obtained from Wako Pure Chemical Industries, Ltd., acryloylamino propyl trimethyl ammonium chloride (DMAPAA-Q) was from Kohjin Co., Ltd., 1,3-dibromopropane and *N*,*N*,*N*′,*N*′-tetramethyl-1,6-diaminohexane were from Kanto Chemicals Co., Ltd., and *N*,*N*,*N*′,*N*′-tetramethyl-1,3-diaminopropane was from Tokyo Kasei Co., Ltd., and they were all used as received.

2.2. Polymerization

N,*N*-dimethylaminoethyl methacrylate (8.75 g) and acetone (100 ml) were charged in a 500 ml volume flask equipped with a stirrer, water bath and a thermometer, and the contents were stirred at 30°C. A mixture of 1,3-propane sulfone (6.8 g) and acetone (3 g) was added dropwise for 30 min. Upon completing the addition, the mixture was stirred for 4 h at the same temperature and then allowed to stand at 5°C for 3 days. The precipitated white crystal was collected by filtration, washed with dry acetone several times, and dried under reduced pressure to obtain 3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate (DMAPS). Poly-3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate (PDMAPS) was obtained by radical polymerization of DMAPS in the presence of potassium peroxosulfate used as an initiator in water at 60°C for 15 h. The molecular weight is 49 000 according to gel-permeation chromatography (GPC) measurement. PAMPS [10], PDMAPAA-Q [11] and *x*,*y*-ionene bromides [12] were prepared by the method previously reported. The molecular weight of PAMPS is 650 000 from intrinsic viscosity measurement [10] and PDMAPAA-Q showed an intrinsic viscosity of 0.25 dl/g in a 0.1 g/dl NaBr solution. The intrinsic viscosities of 3,3-ionene bromide and 6,4-ionene bromide in 0.4 mol/l

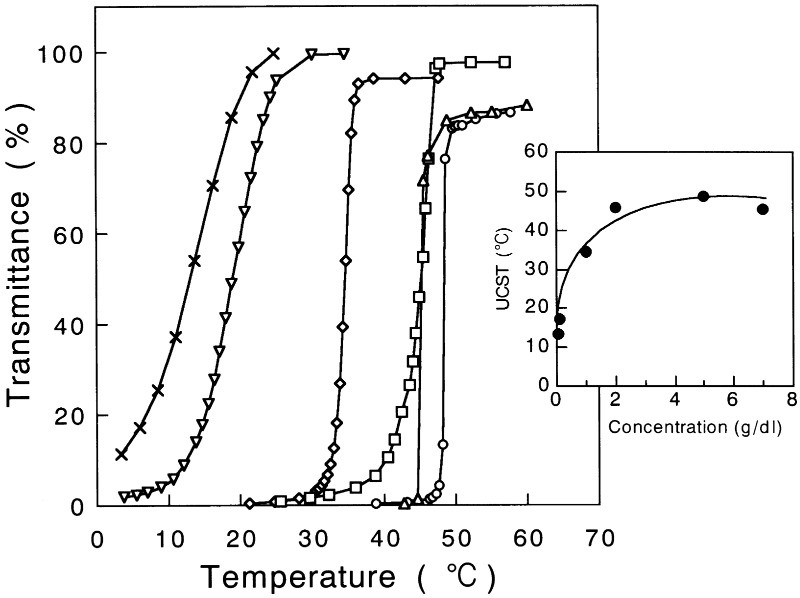

Fig. 2. Temperature dependence of the transmittance for aqueous solutions of PDMAPS at various concentrations: (×) 0.05 g/dl; (▽) 0.1 g/dl; (◇) 1 g/dl; (□) 2 g/dl; (○) 5 g/dl; and (△) 7 g/dl.

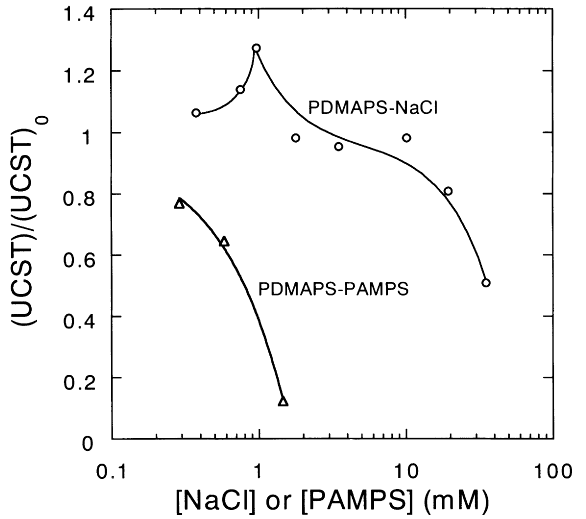

Fig. 3. UCST of PDMAPS in the presence of NaCl or PAMPS. $(UCST)_0$ is the UCST in pure water: (○) PDMAPS–NaCl, concentration of PDMAPS is 1.0 g/dl, UCST of PDMAPS is 35°C; (△) PDMAPS–PAMPS, concentration of PDMAPS is 0.81 g/dl, UCST of PDMAPS is 65°C. The difference in UCST of PDMAPS is attributed to different molecular weight used in the two experiments.

KBr aqueous solution at 25°C are 0.045 and 0.12 dl/g, respectively.

2.3. Measurement

The UCST of aqueous PDMAPS solution was characterized by measuring change in the transmittance at 500 nm using a spectrophotometer at various temperatures. The temperature was varied from 70 to 2°C.

The viscosity measurement of the polymer solutions was made by using Ubbelohde viscometer changing the temperature from 70 to 5°C.

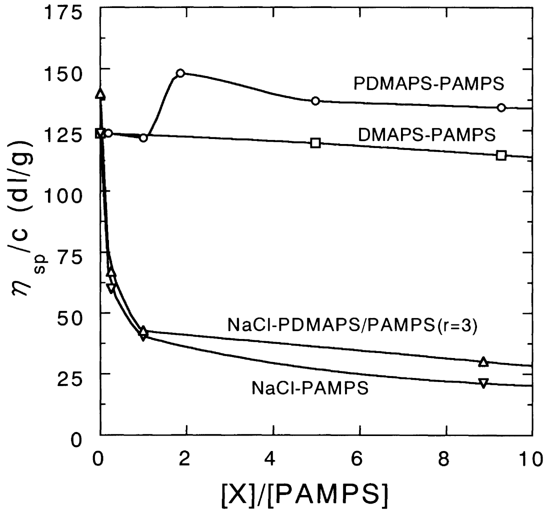

Fig. 4. Reduced viscosity change of diluted PAMPS solution by introducing various kinds of electrolytes. × stands for: (○) PDMAPS; (□) DMAPS; (▽) NaCl in PAMPS solution; and (△) NaCl in PDMAPS/PAMPS ($r = 3$) solution. Concentration of PAMPS is 1.0×10^{-2} g/dl. Temperature 25°C.

3. Results and discussion

3.1. Effect of Polyanion

An aqueous solution of PDMAPS has an UCST which depends on the concentration and molecular weight of PDMAPS [9]. Fig. 2 shows our results of temperature dependence of the transmittance of PDMAPS solutions. One can see that the transmittance of PDMAPS changes sharply in a narrow temperature range around UCST which strongly depends on the PDMAPS concentration: the higher the concentration, the higher the UCST and sharper the transition (Fig. 2, inset). It is considered that the ammonium cation and sulfo-anion in PDMAPS form an intra-chain or/and inter-chain pairing which brings about an insolubilization below the UCST [9]. A decrease in the UCST, i.e. an enhancement in the solubilization with decreased PDMAPS concentration might be associated with the partial dissociation of pairing of both ions.

When sodium chloride is added to the PDMAPS solution, the UCST increased first, then decreased as shown in Fig. 3. The decrease in UCST might be due to dissociation of the pairing of zwitterions by the electrostatic screening effect. An increase in UCST at the low concentration of sodium chloride is not fully understood yet, but we assume that it is due to an increased radius of the coil that leads to an enhancement in the inter-chain interaction.

It might be interesting to study how the UCST is changed if, instead of neutral salt, macro-ions are added since one can expect an eminent interaction due to the cooperative nature of macromolecules. So, we added various amounts of PAMPS to the 0.81 g/dl PDMAPS solution and the UCST of the mixed solution was measured. As shown in Fig. 3, the UCST decreased extensively when a small amount of PAMPS is added into the PDMAPS solution and the UCST even disappeared when the concentration of PAMPS is higher than 2.9 mM, which corresponds to a molar ratio of AMPS/DMAPS = 0.1. This pronounced change in the UCST suggests the strong interaction between PDMAPS and PAMPS.

In general, the characteristics of polyelectrolyte complexations should be affected by the molecular weights and concentrations of the component polyelectrolytes, but for the case of the polymers that have a molecular weight high enough to form the complex are considered to be less sensitive to these parameters. With regard to this, the experiments have been made mainly through changing the molar ratio of PDMAPS and polyanion (or polycation) under a fixed molecular weight.

In order to depict the conformational change due to polymer–polymer interaction, the viscosity of the PDMAPS–PAMPS mixed solution was investigated and compared with those of PDMAPS and PAMPS solutions. The reduced viscosity of PAMPS was as high as 125 dl/g, and that of PDMAPS was 0.1 dl/g below UCST and 1.0 dl/g above UCST. The extremely low value of PDMAPS below

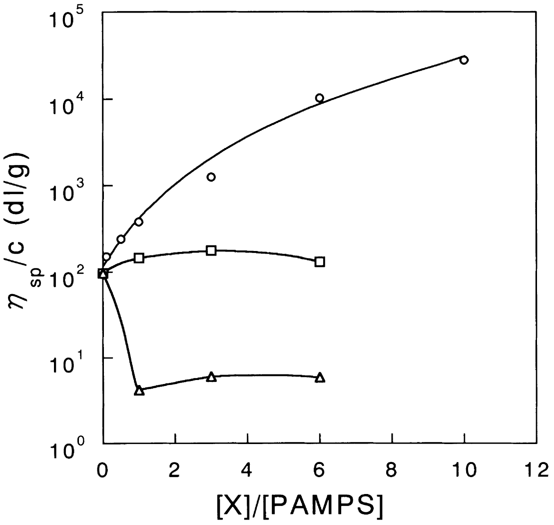

Fig. 5. Reduced viscosity change of concentrated PAMPS solution by introducing various kinds of electrolytes. The concentration of PAMPS is 1.0 g/dl. × stands for: (○) PDMAPS; (□) DMAPS; and (△) NaCl. Temperature 25°C.

UCST indicates the tightly collapsed conformation, which expands and solubilizes above UCST. Since the reduced viscosity of PDMAPS was much lower in comparison with that of PAMPS, we have plotted the viscosity change of the mixed solution as a function of the molar ratio r ($r = $ DMAPS/AMPS) while keeping the concentration of PAMPS constant at 10^{-2} g/dl (Fig. 4). As shown in Fig. 4, when PDMAPS was introduced into the PAMPS solution, an increase in the viscosity was observed at $r = 2$ and higher. In contrast to this, monomeric zwitterion (DMAPS) did not bring about any distinct change in the viscosity of PAMPS solution. The increase in the viscosity by addition of PDMAPS suggests the presence of cooperative interactions between PDMAPS and PAMPS. If we add sodium chloride into the PDMAPS–PAMPS mixture of $r = 3$, the viscosity decreased showing almost the same values of NaCl–PAMPS solution. This result suggests the electrostatic feature of the interaction between the sulfonate groups of PAMPS and the ammonium groups of PDMAPS. The PDMAPS–PAMPS mixture showed no UCST even at r greater than 9, which corresponds to a PDMAPS concentration of 0.12 g/dl. As shown in Fig. 2, the PDMAPS solution of this concentration exhibits UCST around 19°C.

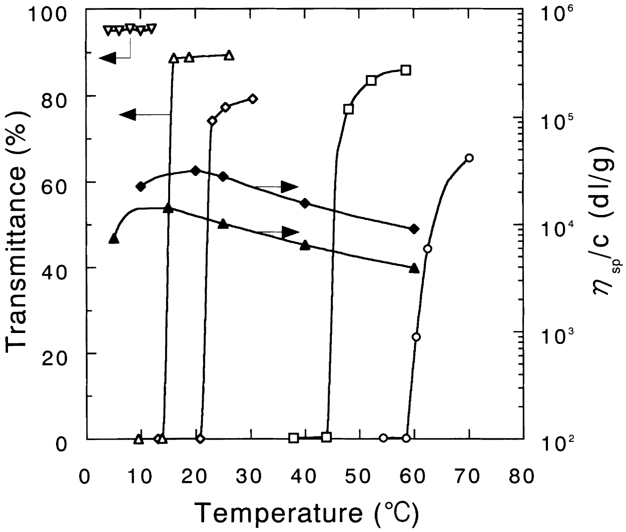

Fig. 6. Temperature dependence of the transmittance and viscosity of various solutions. (○) PDMAPS with a concentration of 13.5 g/dl; (□) mixture of PDMAPS and AMPS monomer, $r = 10$; (◇, ◆) mixture of PDMAPS and PAMPS, $r = 10$; (△, ▲) mixture of PDMAPS and PAMPS, $r = 6$; (▽) mixture of PDMAPS and PAMPS, $r = 3$. The concentrations of PAMPS and AMPS are 1.0 g/dl.

The steep increase in the viscosity of the mixture at $r = 2$ suggests the possibility of network structure. Thus, a similar experiment has been made using concentrated solutions of PAMPS and PDMAPS. As shown in Fig. 5, a subsequent viscosity increase was observed when PDMAPS is added to the concentrated (1.0 g/dl) PAMPS solution, which eventually could hardly flow and the viscosity of the mixture at $r = 10$ was more than 200 times larger than that of PAMPS solution. An addition of monomeric DMAPS to PAMPS solution did not change the viscosity and that of sodium chloride strongly decreased the viscosity, both of which are the same as those in the diluted cases. Such a drastic and progressive increase in viscosity by adding extra amount of PDMAPS into PAMPS solution obviously indicates the network formation occurred by a non-stoichiometric complexation between PDMAPS and PAMPS. The formation of gel-like network suggests the presence of free PDMAPS chains, capable to make the solvation and aggregation reversibly by change in temperature. Therefore, the transmittance of the complex solution with various mixing ratios was measured with changing temperatures (Fig. 6). As shown in Fig. 6, PDMAPS at the concentration of 13.5 g/dl showed UCST at 61°C and PDMAPS–monomeric AMPS mixture of $r = 10$ showed 45°C, while the complexes with PAMPS of $r = 6$ and 10 showed UCST at 15 and 21°C, respectively. The complex of $r = 3$ showed no UCST. One should note here that the transmittance changes of PDMAPS–PAMPS complexes are sharper than those of PDMAPS or PDMAPS–AMPS monomer.

As described before, the UCST of aqueous PDMAPS is associated with the reversible expansion and collapse of the coil to give a mesoscopic aggregate above and below the UCST. The observation of UCST for the complex solution suggests the presence of PDMAPS, which can form the coiled conformation before UCST to give the aggregate, while keeping the PAMPS network in expanded conformation. In order to confirm such mesoscopic aggregate formation in the network, the viscosity change of the complex was measured using the complex solution of $r = 10$ and $r = 6$ under various temperatures. The viscosity measurement was carried out immediately after the temperature was equilibrated. As shown in Fig. 6, the transmittance of solution abruptly decreased at the UCST, while the viscosity

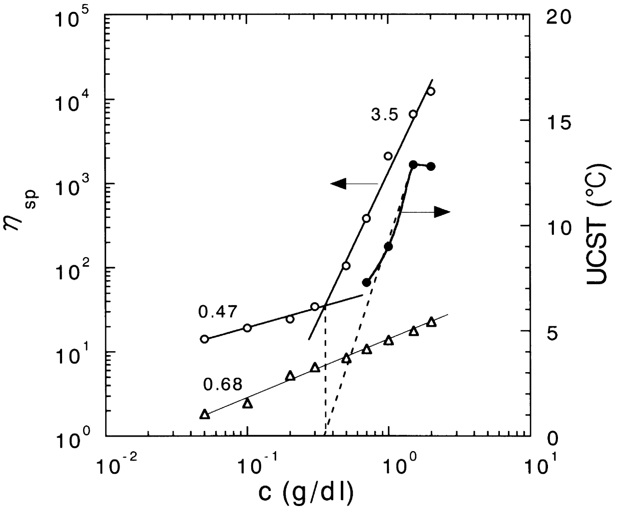

Fig. 7. Viscosity (○) and UCST (●) of PDMAPS–PAMPS mixture ($r = 5$) upon the concentration change of PAMPS. (△) is the viscosity of aqueous PAMPS solution. The numbers in the figure are the slopes of the lines. Temperature 25°C.

decreased only slightly and retained high viscosity even after the solution became cloudy for both cases.

Further, we have changed the concentration of the complex keeping r constant at 5.0, then measured the viscosity and the UCST of the solution. As shown in Fig. 7, the viscosity of mixed solution is higher than PAMPS solution even at low concentrations, indicating the presence of interaction between PDMAPS and PAMPS. The plot of viscosity of the mixed solution showed very good linear relation with an inflection point at a PAMPS concentration of 0.32 g/dl. Above the inflection point, the slope of the line $a = 3.5$, which is much higher than that below the inflection point ($a = 0.47$). In contrast, PAMPS solution showed a single slope with a slope of 0.68 through the whole concentration range. These results clearly demonstrate that the network of the complex is formed above the critical PAMPS concentration of 0.32 g/dl. One can also see from Fig. 7 that UCST appears if PAMPS concentration is higher than 0.32 g/dl and the value increases with increase in the concentration. The complex solution lower than 0.32 g/dl showed no UCST. Since the minimum concentration to exhibit the UCST coincides with the threshold concentration to form intermolecular network, we assume that the network formation might be critical to reveal the UCST by reversible interchain aggregation and dissolution by the free PDMAPS chains. Increase of UCST with increase in the concentration can also be explained by the same reasoning as described in Fig. 2.

A schematic illustration of the complexation and network formation is shown in Fig. 8. As easily predicted from the viscosity result, PAMPS keeps in the expanded conformation due to its electrostatic repulsion, while PDMAPS is in

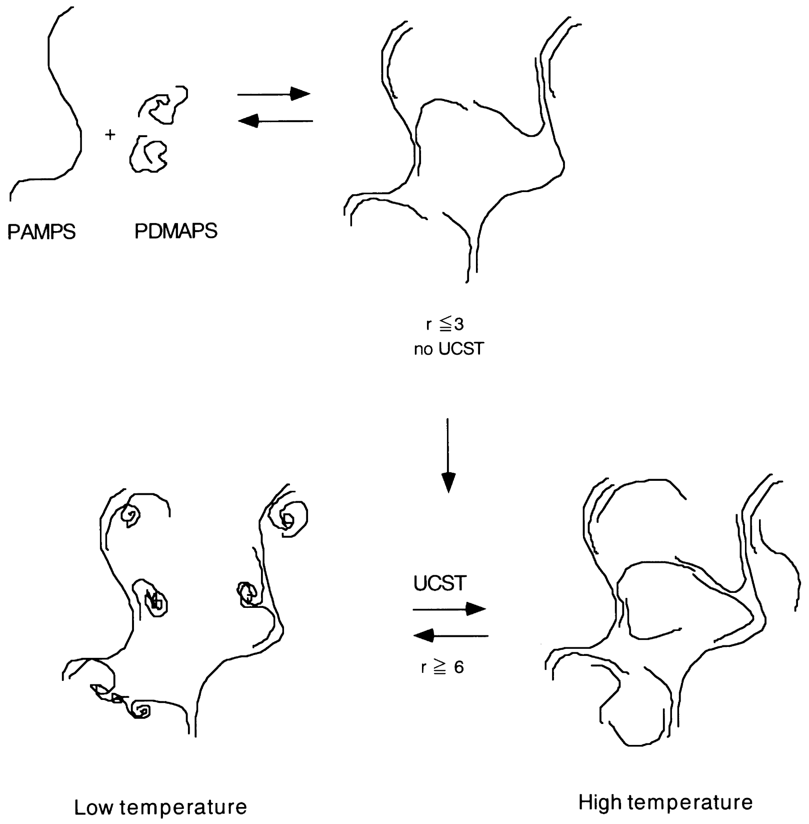

Fig. 8. Schematic illustration of the complexation and network formation between PDMAPS and PAMPS solutions at various r compositions.

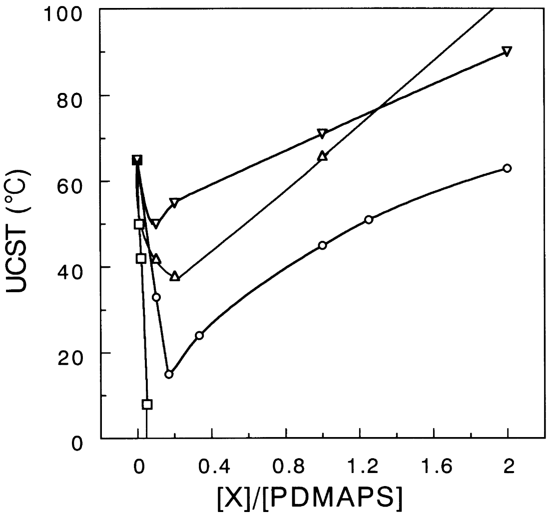

Fig. 9. Relationship between unit molar ratio and UCST for mixed solution of PDMAPS and various polyelectrolytes. The concentration of PDMAPS is 0.81 g/dl. × stands for: (□) PAMPS; (○) PDMAPAA-Q; (▽) 6,4-ionene; and (△) 3,3-ionene.

the tightly coiled state below UCST. When the *r* is not large enough, PDMAPS has not enough free PDMAPS chains to form the mesoscopic aggregate even below UCST and the mixture of two polymers forms a soluble complex without showing the UCST. However, if *r* becomes larger, the complex has more free PDMAPS chains, which are able to make the aggregation–dissolution in the network by change in temperature and shows UCST.

3.2. Effect of polycation

Instead of PAMPS, a PDMAPS mixture with PDMAPAA-Q has been made and the effect on UCST was studied. In this case the ammonium cation of PDMAPAA-Q might undergo the electrostatic interaction with sulfonate anion of PDMAPS. If the complexation is formed through the electrostatic interaction, one can expect the similar result obtained by the PDMAPS–PAMPS mixture. In fact as shown in Fig. 9, an introduction of PDMAPAA-Q until $R = 0.17$ (*R* is defined as a molar ratio of polyelectrolyte/PDMAPS) decreases UCST from 65 to 15°C. This behavior is similar with that observed for the PDMAPS–PAMPS complex (Fig. 9). However, further addition of PDMAPAA-Q to PDMAPS increased the UCST, which was totally different from the case between PDMAPS and PAMPS. We have further investigated the effect of polycation using *x,y*-ionene bromides ($x = 3,6$; $y = 3,4$) having charge on the chain backbone. As shown in Fig. 9, the mixture with ionene polymers showed a similar UCST change as that of PDMAPS–PDMAPAA-Q mixture, showing a minimum UCST at $R = 0.1$–0.17. Thus, when aqueous polycation is added to PDMAPS, UCST decrease first, then increases via a minimum. Different from the case of PAMPS, the viscosity of complexes decreases with increase in *R* showing no evidence of network formation.

We have not enough data to elucidate the different effects of polycation from those of polyanion. However, one can attribute this difference to the different geometrical structure of the complexes (Fig. 10). As described in the previous section, the appearance of UCST of PDMAPS–PAMPS complex originates from the presence of free sulfonates located at the end of side-chain and these free sulfonates give the expanded conformation above UCST and coiling below UCST. Since PDMAPS has an ammonium cation in the middle and the sulfonate anion at the end of side chain, the complex is able to have a free sulfonate at the end of the side chain that makes it possible to solubilize in water even after PAMPS bound. In contrast with this, PDMAPS forms the complex with PDMAPAA-Q or ionene through the sulfonates located at the end of the side chain, which means that the free ammonium cation of PDMAPS is located in the middle of the side chain. This brings about a strong limitation of solubilization of the ammonium cations since they are surrounded by two hydrophobic main chains of the PDMAPS and PDMAPAA-Q (or ionenes). Besides, this gives a restricted freedom of molecular motion (i.e. decrease in the entropy). Thus, the specific UCST behavior of the PDMAPS–polycation complex should be associated with the chemical structure of the complex.

The above discussion suggests that PDMAPS complexation with polyanion PAMPS dramatically increases the viscosity to form a network and decreases the UCST extensively with increase in a molar ratio of PAMPS/PDMAPS due to the presence of free sulfonates located at

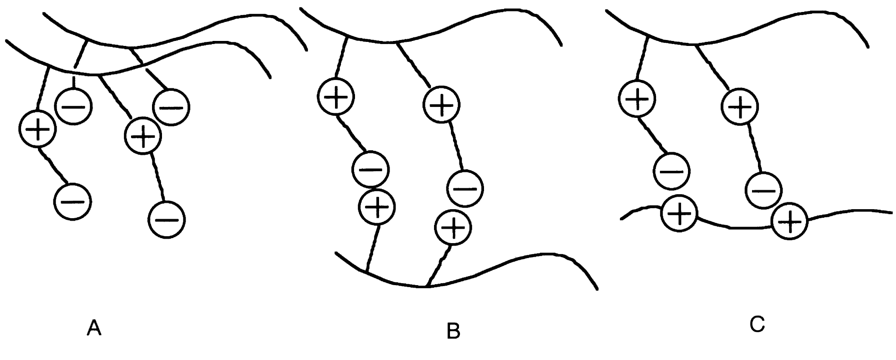

Fig. 10. Schematic illustration of the complexation of PDMAPS with: (A) polyanion; (B) polycation; and (C) polymer ionene.

the end of side-chain, while the PDMAPS–polycation complexes first decrease the UCST, which are similar with that of PDMAPS–PAMPS complex, and then increase with increase in a molar ratio of polycation/PDMAPS and do not form the network since the free ammonium cation of PDMAPS is located in the middle of the side chain.

The structural analyses of the complexes of PDMAPS with polyelectrolytes have also been tried by X-ray measurement. We have previously reported that 3,3-ionene is crystalline and its insoluble polymer–surfactant complexes with sodium alkyl sulfates ($n = 6$, 12) and sodium alkanesulfonates ($n = 8,10$) showed both short and long-range ordering [12]. However, the dried complexes of PDMAPS with 3,3-ionene of $R = 1$ and 2 showed no long-range ordering.

Although we could not elucidate the mechanism of different behaviors in these complexes explicitly, we come to the conclusion that the differences of these complexes are attributed to the different chemical structure of these complexes.

Acknowledgements

This research is supported by a Grant-in-aid for the Special Promoted Research Project “Construction of Biomimetic Moving Systems Using Polymer Gels” from the Ministry of Education, Science, and Culture, Japan.

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