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Conformational transition of poly(methacrylic acid-*co*-styrenesulfonic acid) in aqueous solution

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The conformational transition of poly(methacrylic acid-*co*-styrenesulfonic acid) (PMAS) in aqueous solution was investigated by the luminescence probe method using $Ru(bpy)_3^{2+}$ and viscometry. PMAS-8 (8 mol% styrenesulfonic acid (SS) residue) and PMAS-16 (16 mol% SS residue) revealed a unique conformational transition with changing negative charge on a polymer chain that had at least four conformations in aqueous solution. The luminescence behaviour of $Ru(bpy)_3^{2+}$ and the viscosity characteristics of PMAS solution indicated that the conformational transition was brought about by changing the negative charge of the polymer chain.

(Keywords: conformational transition; copolymer; luminescence)

INTRODUCTION

A number of photochemical and chemical reactions in microheterogeneous media such as micelles[1,2], vesicles[3], microemulsions[4] and polyelectrolytes[5,6] have been extensively investigated, since microheterogeneous media provide unique environments for the guest molecules with respect to controlling the reactions. The photoinduced electron-transfer reactions between $Ru(bpy)_3^{2+}$ and cationic quenchers such as methylviologen (MV^{2+}) and copper(II) ion are greatly enhanced in aqueous solutions containing poly(sodium styrenesulfonate) (PSS)[7–9]. The rate enhancement is ascribed to the concentration effect of both $Ru(bpy)_3^{2+}$ and quencher molecules in the anionic and hydrophobic polymer domains.

Earlier works have reported that poly(methacrylic acid) (PMA) undergoes unique pH-induced conformational transition from a compact coil to a compact micelle-like structure, and then to an expanded chain with increasing pH[10–13]. In PMA–$Ru(bpy)_3^{2+}$ solution below pH 5, the luminescence intensity and lifetime of the excited state of $Ru(bpy)_3^{2+}$ increase dramatically with an increase in pH and then decrease sharply with increasing pH through a maximum at pH 5. This is attributed to the fact that $Ru(bpy)_3^{2+}$ ions are incorporated into the micelle-like structure by electrostatic and hydrophobic interactions[13]. Further, the pH dependence of viscosity for PMA solution shows that PMA chains retain the compact structure until pH 5.5.

On the other hand, the conformational transitions for copolymers of methacrylic acid or maleic acid with other vinyl monomers have also been investigated by several workers[14–18] using viscometry and potentiometric titration. According to the literature[16,17], poly(styrene-*co*-maleic acid) undergoes pH-induced conformational transition in aqueous solution with dissociating primary carboxylic acid residue, and this transition seems to be similar to PMA, which changes from a tightly coiled structure to a looser one. Furthermore, free energy change for the conformational transition of poly(styrene-*co*-methacrylic acid) is larger than that of PMA[18]. These results indicate that the compact structure is stabilized by intramolecular long-range interaction such as the hydrophobic interaction between phenyl residues.

In this study, three kinds of poly(methacrylic acid-*co*-styrenesulfonic acid) were prepared, and the effect of SS residue on the pH-induced conformational transition of PMAS was investigated by the $Ru(bpy)_3^{2+}$ luminescence probe method and viscometry.

EXPERIMENTAL

Materials

Methacrylic acid (MA) was purified by distillation under reduced pressure. Sodium styrenesulfonate (NaSS) and α,α'-azobisisobutyronitrile (AIBN) were purified by recrystallization from water and methanol, respectively. Tris(2,2′-bipyridine)ruthenium(II)chloride hexahydrate ($[Ru(bpy)_3Cl_2]\cdot 6H_2O$) was prepared and purified by the method described elsewhere[19].

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Preparation of copolymers

Poly(methacrylic acid-*co*-styrenesulfonic acid)s were prepared by free-radical copolymerization of MA with NaSS by using AIBN as initiator in a mixture of water and ethanol (1 : 1 v/v) under an argon atmosphere. The reaction mixtures were dialysed in dilute hydrochloric acid of pH 2 with a cellulose tube (Nacalai Tesque, Inc., molecular weight cut-off = 8000) for 3 days. The dialysed solutions were evaporated to dryness, and copolymers were dried at 50°C *in vacuo* for 1 day. The copolymerization ratios of the poly(methacrylic acid-*co*-styrenesulfonic acid)s (PMAS) were determined by ^{1}H nuclear magnetic resonance (n.m.r.) spectroscopy.

Measurements

Acid dissociation constants (pK_a) and n, which represents the degree of the effect of neighbouring groups on the dissociation of protons, of PMAS were determined by potentiometric titration using a modified Henderson–Hasselbach equation[20]:

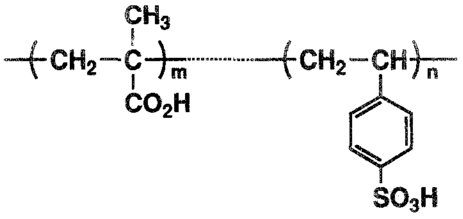
$$\mathrm{pH} = \mathrm{p}K_a - n \log[(1-\alpha)/\alpha] \qquad (1)$$

where α is the degree of neutralization of carboxylic acid residue on polymer chains. Sample solutions were adjusted to 10^{-3} mol dm^{-3} based on the unit concentration of carboxylic acid residues ($[CO_2H]_u$) and ionic strength was 0.06 (NaCl). The titrations were carried out by using 0.1 N NaOH aqueous solution at 25°C under an argon atmosphere.

Luminescence spectra of the excited state of $Ru(bpy)_3^{2+}$ were recorded on a Hitachi 150-60 spectrofluorometer using a 10 mm × 10 mm quartz cell. The excitation wavelength was 453 nm. The $Ru(bpy)_3^{2+}$ luminescence lifetime was measured by a Horiba NAES-550 nanosecond fluorometer. The viscosity of aqueous solutions of PMAS was measured using an Ubbelohde viscometer. The pH of solutions was adjusted by the addition of dilute hydrochloric acid or sodium hydroxide solutions of redistilled water.

RESULTS AND DISCUSSION

The chemical structure of PMAS is shown in *Figure 1*. Values of pK_a and n obtained from the intercept and the slope of the straight line of a plot of pH *versus* $\log[(1-\alpha)/\alpha]$ using the Henderson–Hasselbach equation are summarized in *Table 1*. The degree of dissociation of carboxylic acid residue and the ratio of negative charge on a polymer ($\alpha' = \alpha +$ molar fraction of SS residues) were calculated from the values of pK_a and n at each pH value.



	m	n
PMAS-8*	0.921	0.079
PMAS-16*	0.837	0.161
PMAS-43*	0.573	0.427

* : Numbers indicate the mole percentage of SS residues

Figure 1 Chemical structure of PMAS

Table 1 Values of pK_a and n of PMA, PMAS-8, PMAS-16 and PMAS-43

Compounds	pK_a	n
PMA	6.40	2.0
PMAS-8	7.02	1.81
PMAS-16	7.08	1.64
PMAS-43	7.00	1.68

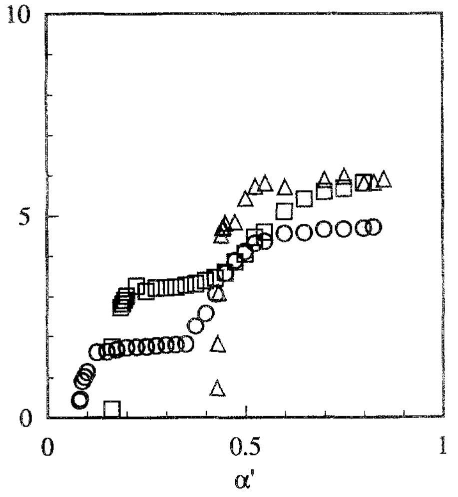


Figure 2 Dependence of the reduced viscosity (η_{sp}/c) on α' in PMAS-8 (○), PMAS-16 (□) and PMAS-43 (△) systems

Viscosity studies

The dependence of the reduced viscosity (η_{sp}/c) on α' for PMAS-8, PMAS-16 and PMAS-43 is shown in *Figure 2*. The viscosity of PMAS-8 and PMAS-16 changed in two steps. When carboxylic acid residue was slightly dissociated ($\alpha' = 0.08$–0.10 for PMAS-8 and $\alpha' = 0.16$–0.18 for PMAS-16), the conformational transition occurred corresponding to the change of viscosity in the first step. Up to $\alpha' = 0.35$, the viscosity was almost constant regardless of α', and then the conformational transition corresponding to the change of viscosity in the second step occurred in the range of $\alpha' > 0.4$. Furthermore, the degree of viscosity change in the first step in PMAS-16 was larger than that in PMAS-8. It is clear that the change of viscosity becomes larger with increasing the introduction of SS residues into PMA. The viscosity of PMA was constant until $\alpha' \approx 0.40$, after which it increased steeply. The steep rise of viscosity is attributable to the conformational transition from the compact structure to the expanded one[4]. It should be mentioned that the two-step viscosity change was not observed in PMA. This indicates that SS residues participate in the conformational transition corresponding to the change of viscosity in the first step.

PMAS-43 revealed one viscosity change with increasing α'. The degree of the viscosity change in one step is equal to the sum of values in the first and second steps in PMAS-8 or PMAS-16. Therefore, it can be thought that two conformational transitions corresponding to the viscosity change in the first and second steps in PMAS-8 or PMAS-16 occur simultaneously in the case of PMAS-43.

As described above, it is found that the viscosity change takes place in two steps with increasing α' in the case of PMAS-8 and PMAS-16. The conformational transition corresponding to the change of viscosity in the first step, which is not observed in PMA, occurs when the carboxylic acid residue dissociates slightly. At high α', these copolymers have an expanded structure, although poly(styrene-*co*-methacrylic acid)[18] and poly(styrene-*co*-maleic acid)[16,17] keep a compact structure by hydrophobic interaction between phenyl residues. From these facts, it is suggested that hydrophobic interaction between SS residues is absent. Later, this will be considered in detail with respect to these conformational transitions.

Luminescence studies

The dependence on α' of the relative luminescence intensity (I/I_0: I_0 and I are the luminescence intensities in aqueous solution and aqueous PMAS solutions, respectively) and the maximum wavelength of the luminescence spectrum (λ_{max}) of $Ru(bpy)_3^{2+}$ are shown in *Figures 3* and *4*, respectively. In *Figures 3* and *4*, the enhancement of I/I_0 and the blue shift of λ_{max} are observed for PMAS-8 and PMAS-16 at $\alpha' = 0.2$ and 0.23, respectively. This behaviour of $Ru(bpy)_3^{2+}$ in aqueous PMAS-8 and PMAS-16 solutions is similar to that in aqueous PMA solution, as reported previously[10–13]. According to the previous works[10–13], the α' dependence of the luminescence of $Ru(bpy)_3^{2+}$ in aqueous solution can be explained as illustrated in *Scheme 1*.

At low α', I/I_0 and λ_{max} of $Ru(bpy)_3^{2+}$ in PMA solution are similar to those in aqueous solution, because the PMA chain has a compact coil structure and there is no interaction between $Ru(bpy)_3^{2+}$ and PMA chain. With increasing α', carboxylic acid residue dissociates and water permeates into the PMA domain. Since methyl groups gather by hydrophobic interaction, a hydrophobic, compact, micelle-like structure is newly formed on PMA chains at $\alpha' = 0.2$, during which time $Ru(bpy)_3^{2+}$ is incorporated and restricted into the hydrophobic micelle-like domain by both electrostatic and hydrophobic interactions. This is why the enhancement of I/I_0 and the blue shift of λ_{max} were observed. With further increase of α', PMA chains are expanded,

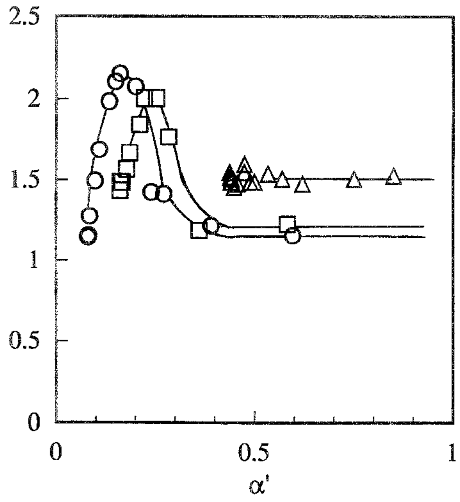


Figure 3 Dependence of the luminescence intensity (I/I_0) of the excited state of $Ru(bpy)_3^{2+}$ on α' for PMAS-8 (○), PMAS-16 (□) and PMAS-43 (△) systems

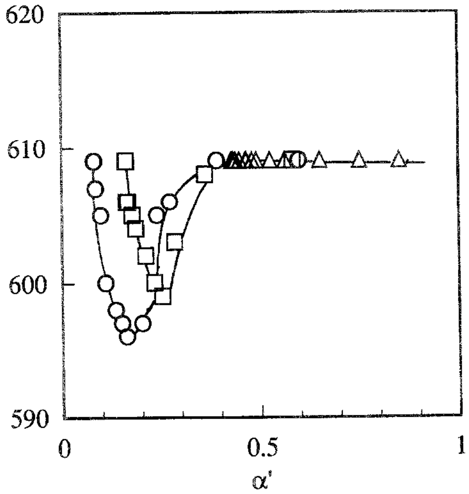
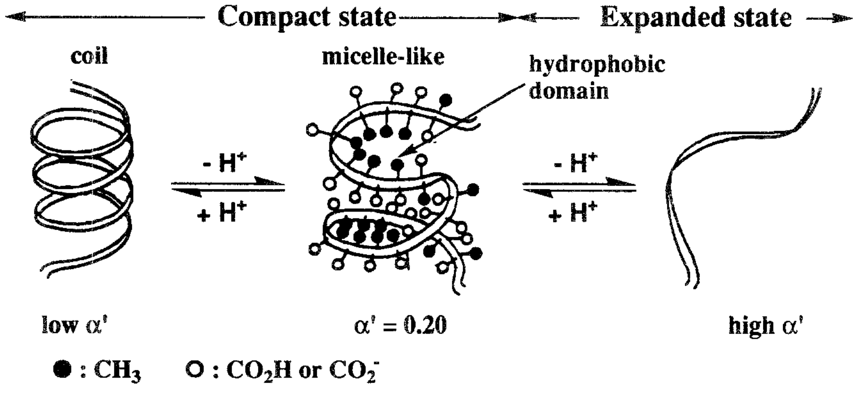


Figure 4 Dependence of the maximum wavelength (λ_{max}) of the luminescence spectrum on α' for PMAS-8 (○), PMAS-16 (□) and PMAS-43 (△) systems



Scheme 1 Tentative representation of the conformational transition of PMA in aqueous solution

and $Ru(bpy)_3^{2+}$ restricted in PMA chains is exposed to the bulk solution. At this time, I/I_0 and λ_{max} of $Ru(bpy)_3^{2+}$ become similar to those in aqueous solution.

For PMAS-8 and PMAS-16, the α' dependence of the luminescence behaviour of $Ru(bpy)_3^{2+}$ is similar to that for PMA. This indicates that PMAS-8 and PMAS-16 form the hydrophobic micelle-like structure by conformational transition, as described above. By comparison of PMAS-8 and PMAS-16, it is found that maximum values of I/I_0 almost coincide, but λ_{max} shifts from 609 to 595 nm for PMAS-8 and from 609 to 600 nm for PMAS-16. These results can be explained by taking into account differences of the hydrophobicity in the micelle-like structure and the interaction between polymer chains and $Ru(bpy)_3^{2+}$. Since PMAS-16 includes 16 mol% of SS residue on one polymer chain and the number of methyl groups responsible for the micelle-like structure is less than that of PMAS-8, the hydrophobicity in the micelle-like structure of PMAS-16 may be low. Therefore, λ_{max} shifts only up to 600 nm. Another factor that should be considered is the interaction between $Ru(bpy)_3^{2+}$ and SS residues.

A number of investigations of the luminescence behaviour of $Ru(bpy)_3^{2+}$ in aqueous solution containing PSS have been reported[5–9,21] According to these reports, the luminescence intensity of $Ru(bpy)_3^{2+}$ in PSS solution is enhanced due to π–π interaction between the bipyridine ligand and the phenyl ring of SS residue, but λ_{max} scarcely changes. Considering these reports, it is thought that $Ru(bpy)_3^{2+}$ in PMAS-16 interacted with the micelle-like domain as well as with the SS residues at $\alpha' = 0.23$. In other words, there are two kinds of $Ru(bpy)_3^{2+}$ species: one is incorporated into the micelle-like structure, and the other is restricted by SS residues through π–π interaction.

On the other hand, I/I_0 and λ_{max} of $Ru(bpy)_3^{2+}$ in PMAS-43 were independent of α', although I/I_0 was large in comparison with that in aqueous solution. From the fact that the luminescence behaviour of $Ru(bpy)_3^{2+}$ in PMAS-43 is similar to that in PSS, it can be said that $Ru(bpy)_3^{2+}$ interacted with SS residues, and PMAS-43 has a similar conformation to PSS in aqueous solution.

The dependence of I/I_0 and λ_{max} of $Ru(bpy)_3^{2+}$ in PMAS-16 solution on the unit concentration of SS residues ($[SS]_u$) at three different α' values ($\alpha' = 0.16$, 0.23 and 0.83) is shown in *Figures 5* and *6*, respectively. Different luminescence characteristics were observed at each value of α'. At $\alpha' = 0.16$, slight enhancement of I/I_0 and the blue shift of λ_{max} were observed until $[SS]_u = 3.0 \times 10^{-4}$ M, and they were constant at $[SS]_u > 3.0 \times 10^{-4}$ M. These results indicate that $Ru(bpy)_3^{2+}$ interacts with the hydrophobic domain formed by PMAS-16 at $\alpha' = 0.16$ and all of the $Ru(bpy)_3^{2+}$ complex is incorporated into the domain at $[SS]_u = 3.0 \times 10^{-4}$ M.

I/I_0 increased and λ_{max} shifted in the range of $[SS]_u = 0$–3.0×10^{-4} M at $\alpha' = 0.23$, and were approximately constant at $[SS]_u > 3.0 \times 10^{-4}$ M. As mentioned above, at $\alpha' = 0.23$, there are two kinds of $Ru(bpy)_3^{2+}$ species which are incorporated into the micelle-like structure and restricted by SS residues through π–π interaction. Therefore, all of the $Ru(bpy)_3^{2+}$ in PMAS-16 of high concentration, such as $[SS]_u = 3.0 \times 10^{-4}$ M, are assumed to interact with the polymer.

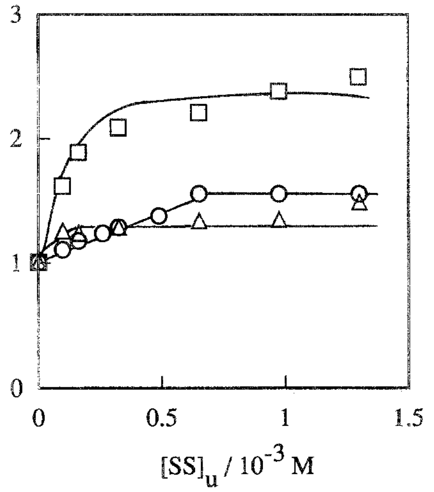


Figure 5 Dependence of the luminescence intensity (I/I_0) of the excited state of $Ru(bpy)_3^{2+}$ on the concentration of SS residues ($[SS]_u$) at $\alpha' = 0.161$ (○), 0.20 (□) and 0.83 (△) for PMAS-16 system

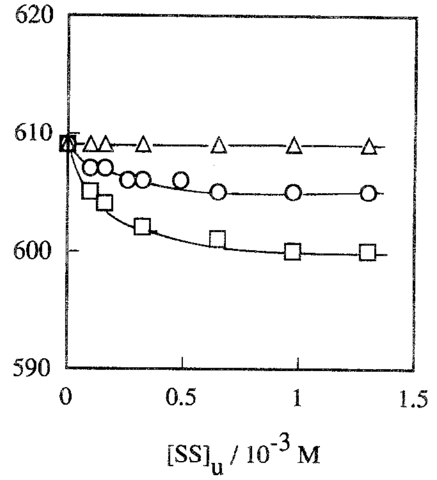


Figure 6 Dependence of the maximum wavelength (λ_{max}) of the luminescence spectrum on the concentration of SS residues ($[SS]_u$) at $\alpha' = 0.161$ (○), 0.20 (□) and 0.83 (△) for PMAS-16 system

In the case of $\alpha' = 0.83$, I/I_0 increased until $[SS]_u = 1.0 \times 10^{-3}$ M, followed by a plateau. In this case, λ_{max} was 609 nm and independent of $[SS]_u$.

Figure 7 shows the $[SS]_u$ dependence of I/I_0 and λ_{max} of $Ru(bpy)_3^{2+}$ in PMAS-43 at $\alpha' = 0.43$. I/I_0 was enhanced until $[SS]_u = 1.0 \times 10^{-3}$ M and was then constant at $[SS]_u > 1.0 \times 10^{-3}$ M. λ_{max} was equal to that in aqueous solution over the whole range of $[SS]_u$. The present luminescence characteristic was similar to that for PMAS-16 at $\alpha' = 0.83$ and PSS. It is assumed that $Ru(bpy)_3^{2+}$ in PMAS-43 interacted with SS residues.

Conformational transition

As shown in *Scheme 1*, PMA has at least three conformations in aqueous solution and two conformational transitions with increasing α'. Relationships between these conformational transitions and the luminescence and viscosity behaviour can be explained as follows. A conformational transition from a compact coil to a compact micelle-like structure occurs, accompanied by enhancement of I/I_0 and the blue shift of λ_{max},

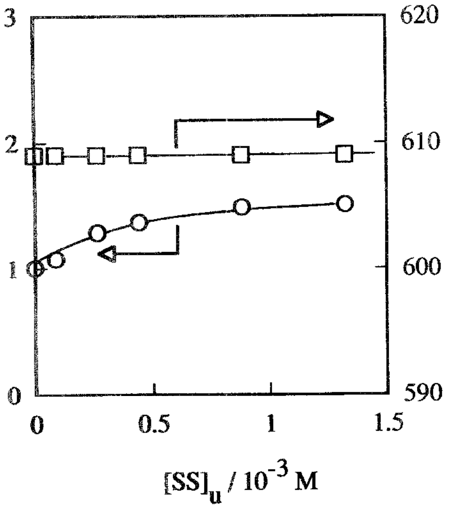


Figure 7 Dependence of the luminescence intensity (○) and maximum wavelength (□) of the excited state of $Ru(bpy)_3^{2+}$ on the concentration of SS residues ($[SS]_u$) at $\alpha' = 0.43$ for PMAS-43 system

during which time the viscosity hardly changes. When a conformational transition from the compact micelle-like structure to an expanded structure takes place, I/I_0 and λ_{max} are consistent with the values observed in aqueous solution, and viscosity sharply increases.

The α'-induced conformational transitions of PMAS-16 and PMAS-43 are discussed below on the basis of the luminescence and viscosity behaviour.

PMAS-16 has at least four conformations and three conformational transitions with increasing α'. When these four conformations are abbreviated as C_0, C_1, C_M and C_S in the order of increasing α', the α'-induced conformational transition is shown in equation (2):

$$C_0(\alpha' < 0.16) \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} C_1(\alpha' = 0.18)$$

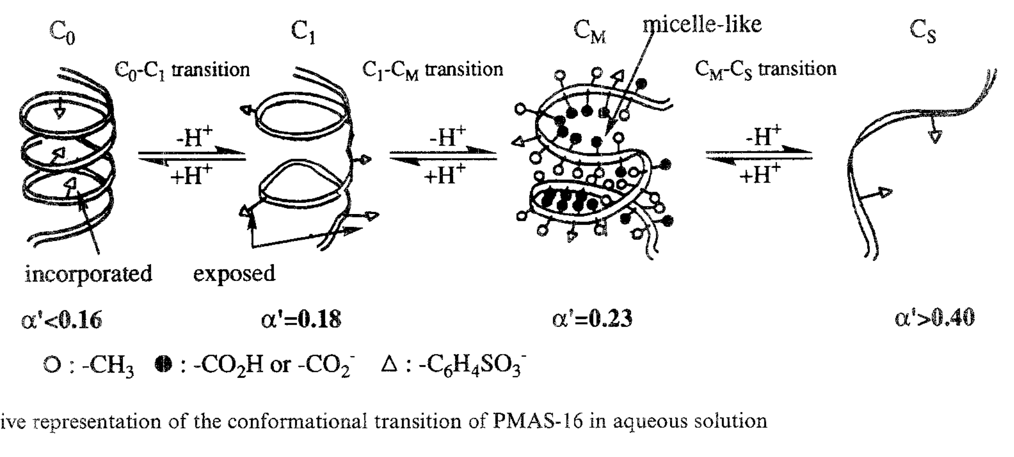
$$\underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} C_M(\alpha' = 0.23) \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} C_S(\alpha' > 0.40) \qquad (2)$$

At $\alpha' = 0.16$–0.18, a conformational transition from C_0 to C_1 structure (C_0–C_1 transition) occurs. In the case of the C_0–C_1 transition, I/I_0 and λ_{max} hardly change, but the change of viscosity corresponding to the first step is observed. A conformational transition from C_1 to C_M structure (C_1–C_M transition) occurs at $\alpha' = 0.18$–0.23, in which the enhancement of I/I_0 and the blue shift of λ_{max} are observed, but not the change of viscosity. Further, a conformational transition from C_M to C_S structure (C_M–C_S transition) takes place at $\alpha' > 0.4$, and only the change of viscosity is observed. As described above, the conformational transitions would be associated with the luminescence and viscosity behaviour. The presumed microstructures and conformational transitions of PMAS-16 with increasing α' are illustrated in *Scheme 2*. As shown in *Figure 2*, the change of viscosity corresponding to the C_0–C_1 transition increases with increasing molar fraction of SS residue in PMAS. It suggests that SS residue in PMAS plays an important role in the C_0–C_1 transition. In addition, the results of *Figures 5* and *6* indicate that there is no interaction between $Ru(bpy)_3^{2+}$ and SS residue at $\alpha' = 0.16$, because both the enhancement of I/I_0 and the blue shift of λ_{max} were observed. Only the enhancement of I/I_0 should be observed if there is interaction between them[21]. It can be said that most of the SS residue of the compact C_0 structure at $\alpha' = 0.16$ exists in the interior of the polymer domain, and the C_0–C_1 transition is the conformation change caused by the exposure of SS residues existing in the polymer domain to bulk solution. Therefore, it is thought that C_1 formed at $\alpha' = 0.18$ is the compact structure, in which most of the SS residues are exposed to the surrounding water. C_M is a micelle-like structure, which is similar to that formed by PMA at $\alpha' = 0.20$. Since the results of viscosity study suggest that C_S is an expanded structure, the C_M–C_S transition is the conformational transition from the compact structure to the expanded one.

On the other hand, PMAS-43 has two conformations in aqueous solution. When these structures are abbreviated as $C_0'(\alpha' < 0.43)$ and $C_S(\alpha' < 0.45)$, the α'-induced conformational transition of PMAS-43 is shown in equation (3):

$$C_0'(\alpha' < 0.43) \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} C_S(\alpha' > 0.45) \qquad (3)$$

At $\alpha' < 0.43$, PMAS-43 retains a compact structure (C_0' structure) by hydrogen bonding between carboxylic acid residues. In the α' region of about 0.43–0.45, the C_0'–C_S transition is induced by the electrostatic repulsion between negatively charged residues such as carboxylate and SS residues. Even after the C_0–C_1 and C_1–C_M



Scheme 2 Tentative representation of the conformational transition of PMAS-16 in aqueous solution

transitions have occurred, PMAS-16 is able to retain the compact state by hydrogen bonding between carboxylic acid residues and Van der Waals interaction between methyl groups. That is to say, PMAS-16 changes in a stepwise manner from the compact C_0 to the expanded C_S through C_I and C_M structures. On the contrary, *Figures 3* and *4* indicate that PMAS-43 changes from C_0' to C_S at once. Probably, PMAS-43 cannot form compact structures such as C_I and C_M owing to the collapse of hydrogen bonding between carboxylic acid residues by slight dissociation of carboxylic acid. This is supported by the fact that the change of viscosity from C_0' to C_S for PMAS-43 is equal to the sum of the change of viscosity in the first and second steps observed for PMAS-16, as described in the results of *Figure 2*. Therefore, PMAS-43 has two conformations in aqueous solution and only one conformational transition (C_0'–C_S transition) takes place.

In conclusion, a new conformational transition, which was not observed in PMA, was induced by introducing 8 and 16 mol% of SS residues into the PMA chain. Both PMAS-8 and PMAS-16 have at least four conformations in aqueous solution and PMAS-43 has at least two conformations in aqueous solution. Further, microstructures of four conformations were assumed from relationships between the conformational transitions and the luminescence and viscosity behaviour. In both PMA and PMAS, it is clear that the conformational transition to the micelle-like structure occurs when the ratio of negative charge on one polymer is about 0.2.

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