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Viscoelastic system from mixing cetyltrimethylammonium bromide and poly (styrene-co-methacrylic acid) in aqueous solution

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Abstract

A viscoelastic system was developed by forming hybrid wormlike micelles with poly (styrene-co-methacrylic acid) (P (St-co-MAA)) and cetyltrimethylammonium bromide (CTAB) in aqueous solution. The molar monomer ratio of St to MAA in the copolymer and the mixing ratio \( r \) of P (St-co-MAA) to CTAB were the two key factors to obtain the viscoelastic system. Phase behaviors of P (St-co-MAA)/CTAB aqueous solutions as the functions of the monomer ratio in the copolymer, as well as the mixing ratio were investigated. It was found that there was no phase separation in any mixing ratios as monomer ratio of 6:4 and 7:3. On the other hand, the biggest viscosity was observed as the molar ratio of phenyl group in copolymer to CTAB was close to 1, rather than at charge stoichiometry between MAA and CTA\(^+\). It is found that as \( r \) between 1.0 and 1.24 and the monomer ratio of St to MAA at 7:3, the mixing system had the largest viscosity. The effects of the total concentration of the mixture system, the salt concentration, the temperature, and the shear rate on the viscosity were studied in detail. The experimental results showed that the complex system had excellent thickening property even the copolymer concentration as low as 0.90% (w/v), good electrolyte tolerance as inorganic salt...
concentration lower than 1.8 M, and acceptable heat-resistance at room temperature. The complex system had a potential application as the thickeners in various fields.

**Keywords:** Viscoelasticity; copolymer P (St-co-MAA); cetyltrimethylammonium bromide; phase behavior; wormlike micelle

1. Introduction

Above critical micellar concentration (CMC), a variety of surfactants self-assemble to form aggregates with plenty of morphologies. Israelachvili\(^1\) put forward critical accumulation parameter \(P\) to predict the morphologies of self-assembled aggregates by calculating geometric shapes of the surfactant molecules. Usually, the single-tailed surfactant, whose shape is like a cone and \(P\) is less than 1/3, can generally form globular micelles in an aqueous solution. However, single-tailed cationic surfactant such as cetyltrimethylammonium bromide (CTAB) can transform into wormlike micelle with addition of inorganic (e.g., \(\text{Cl}^-\) and \(\text{Br}^-\))\(^2\)\(^-\)\(^5\) or aromatic counterions (e.g., salicylate\(^6\),\(^7\) tosylate\(^8\), chlorobenzoate\(^9\), or hydroxynaphthalene carboxylate\(^10\)), as well as oppositely charged surfactant. The aromatic counterions bind to the surfactant more strongly owing to cation-\(\pi\) electron interaction and electrostatic attraction. Therefore, wormlike micelle occurs at much lower surfactant and counterion concentrations.

Further research found that a hybrid threadlike micelle could form between surfactant and polymer in an aqueous solution. Kenji Nakamura\(^11\) constructed a hybrid threadlike micelle formed between CTAB, sodium p-toluensulfonate and sodium poly (p-vinylbezoate) (NaPVB) in an aqueous solution. The hybrid threadlike micelles were long enough to become entangled with each other and exhibit pronounced viscoelasticity. The findings suggested that incorporation of...
long polymers into the hybrid threadlike micelle effectively hinders the crossing-through reaction between two micelles at an entanglement point and causes the rigidity of the hybrid threadlike micelle greater than that of the ordinary threadlike micelle. Oikonomou had found that hybrid wormlike micelles could form upon mixing CTAB with Poly (methyl methacrylate-co-sodium styrene sulfonate) (P (MMA-co-SSNa)) copolymer in an aqueous solution. Usually, phase separation was often observed upon mixing a charged surfactant with an oppositely charged polyelectrolyte in an aqueous solution, especially as the mixing ratio approaches charged stoichiometry. In P (MMA-co-SSNa)/CTAB systems, monomer ratio in the copolymer and mixing charge ratio of the surfactant to polyelectrolyte were two key factors to affect the phase separation behavior. It was found that the phase separation was completely suppressed as the MMA content of the copolymers was about 30-40 mol %. On the other hand, specific stoichiometric cation-π electron interactions between the surfactant and the phenyl rings was decisive for the formation of the polymer-induced hybrid wormlike micelle. As known, the delicate balance among electrostatic attraction, cation-π electron interactions, as well as hydrophobic interactions were crucial to form wormlike micelle and suppress phase separation. Though the effect of monomer ratio of MMA to SSNa on phase separation was investigated, the experimental results only revealed the equilibrium between hydrophobic interactions and electrostatic attraction. However, there was no way to change the ratio of styrene to sodium sulfonate to investigate the relationship between electrostatic attraction and cation-π electron interactions, because both anionic sulfonate and phenyl groups came from the same monomer, sodium styrene sulfonate. As mentioned above, the relationship between electrostatic attraction and cation-π electron interactions was decisive and should be controlled.
In order to add another regulatory factor, anionic group and phenyl group should come from the different monomers in the copolymer. Thus, electrostatic attraction and cation-π electron interactions could be adjusted independently by changing the monomer ratio in the copolymer. In the present work, we used poly (styrene-co-methacrylic acid) P (St-co-MAA) in replace of P(MMA-co-SSNa), and synthesized five kinds of P(St-co-MAA) with monomer ratio of St to MAA of 3:7, 4:6, 5:5, 6:4 and 7:3. Phase separation behaviors of P(St-co-MAA)/CTAB in the aqueous solutions as a function of the monomer ratio in the copolymer were investigated. It was found that there is no phase separation behavior in any mixing ratios between P(St-co-MAA) and CTAB as monomer ratio of 6:4 and 7:3. On the other hand, the thickening properties of these complex systems were studied in detail by changing the mixing ratios of P(St-co-MAA) (7:3) to CTAB. The biggest viscosity was observed as the molar ratio of phenyl group in copolymer to CTAB was close to 1, rather than at charge stoichiometry between MAA and CTA\(^+\). Additionally, the effect of the concentration at the fixed ratio of P(St-co-MAA) to CTAB on the viscosity was investigated. Abilities of heat-resistance and salt-tolerance of the mixed systems were also studied for the actual application in various fields, including home and personal care, cosmetics, fracturing fluids, drag reduction agent, and other industrial fields\(^{14}\).

2. Experimental Section

2.1. Chemicals

The monomers styrene and methacrylic acid, as well as the initiator \(\alpha^{'}, \alpha^{'},-\) azobisisobutyronitrile (AIBN) were of chemical grade. 1, 4-diethylene dioxide, petroleum ether,
diethyl ether and cetyltrimethylammonium bromide (CTAB) were of analytical grade. All the chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

2.2 Synthesis of the Copolymers.

The copolymers P (St-co-MAA) with different monomer ratios were synthesized via free radical polymerization in 1, 4-diethyl ether dioxide using AIBN as an initiator. The desired quantities of the two monomers were dissolved in 180 ml 1, 4-diethyl ether dioxide to get total amount of the monomers approximately up to 1 mol. After the solution was degassed, the initiator AIBN (4.9263g, 0.03mol) was added. The reaction proceeded under vigorous stirring in a N₂ atmosphere in an oil bath at 65°C for 24 hours. After that, purification was carried out by dissolving it in 1, 4-dioxane and reprecipitating in petroleum ether and diethyl ether. At last, the product was dried in a vacuum oven at 60°C for 12 hours.

The characterization data (^1H NMR, GPC) for all the polymers and yield of the polymerization reactions were shown in the support information. The data of ^1H NMR spectra demonstrated that the actual monomer ratio of St to MAA was similar to the monomer feed ratio. The yield of the polymer was in range of 46.5%-55.8%.

2.3 Methods.

Viscosity measurement was carried out at 35°C with a digital viscosimeter (NDJ-5S, Shanghai Geology Instrument Institute, China). The test solution was put in a beaker or other jar, whose diameter was greater or equal to 70 mm and the rotor should be put in the solution. The suitable rotor and rotational speed should be chosen to obtain the accurate results. During the measurement, the temperature should be kept the same.

The shear viscosity were performed at 35°C using a rheometer (TA DHR - 2 DSR dynamic...
shear rheometer, TA instruments, America) equipped with cone-plate geometry (diameter 40 mm, plate 0°, gap 0.055 mm). All the samples were left at least for 5 min in the apparatus to equilibrate before measurement. Air bubbles should be avoided in the samples. The shear rate ranged from 0 to 400 (1/s). The viscosities of the samples at the different temperature in the range of 20-80°C were also measured by the rheometer.

The morphology and size of the aggregates were characterized with transmission electron microscopy (TEM) (JEM-2100) at a 200 kV accelerating voltage. The sample solutions were deposited onto the surface of 300-mesh Formvar-carbon film coated copper grids. Excess solution was quickly wicked away with a filter paper.

2.4 Preparation of solutions.

Certain amount of P (St-co-MAA) with monomer ratio of St to MAA of 7:3, 6:4, 5:5, 4:6, 3:7, respectively, was dissolved in 0.1 M NaOH aqueous solution by gentle stirring overnight to form the mother solution. The MAA group concentration in the mother solution for all monomer ratio was 50 mM. pH of the mother solutions were in the range of 11.0-12.0, for example, pH of P(St-co-MAA)(7:3) mother solution was 11.2.

3. Results and discussion

3.1 Appearance of system upon mixing P(St-co-MAA) with CTAB

The quantity of CTAB fixed at 0.015 mol in all compounded systems, the phase behaviors were investigated as the functions of the monomer ratio in P(St-co-MAA) and the mixing ratio $\tau$, the molar ratio of St to CTAB.

As seen in Fig.1, as the monomer ratio of 3:7, the system of P(St-co-MAA) /CTAB did not
turn into be viscous at any mixing ratio. While the mixing ratio was less than 0.36, the precipitation generated. As \( r \) was bigger than 0.36, an opaque gel separated from the aqueous solution, i.e., syneresis was observed in the solution. As the monomer ratio of 3:7, the mixing ratio of 0.36 is the equal of the molar ratio of MAA to CTAB of 0.84, which approached to the charged stoichiometry in the system.

The situation of the system of \( P(St-co-MAA)(4:6)/CTAB \) was similar to that of \( P(St-co-MAA)(3:7)/CTAB \). While \( r \) was between 0 and 0.46, the precipitation come out. As \( r \) was bigger than 0.46, the syneresis took place. The charged stoichiometry of the system would be the mixing ratio of 0.4, close to 0.46.

The system of \( P(St-co-MAA)(5:5)/CTAB \) was transparent as \( r \) lower than 0.46, because the electrostatic attraction interaction weakened while cation-\( \pi \) action and hydrophobic action intensified. While \( r \) is between 0.46 and 0.92, the phase separation appeared. As \( r \) was bigger than 0.92, an opaque gel came out.

Phase separation did not appear at any mixing ratio in the system of \( P(St-co-MAA)(6:4)/CTAB \). As \( r \) was smaller than 0.68, the system was transparent but not viscous. It became thicken as \( r \) between 0.68 and 1.36. While \( r \) was bigger than 1.36, the syneresis took place and an opaque gel was observed.

As was the case in the system \( P(St-co-MAA)(6:4)/CTAB \), the system of \( P(St-co-MAA)(7:3)/CTAB \) was also stable at any mixing ratio. As \( r \) was smaller than 0.77, the system was transparent. As \( r \) ranged from 0.77 to 1.40, it became more and more viscous, and the entire solution turned into a transparent gel system. There came out syneresis while \( r \) was bigger than 1.4, and the opaque gel turned thinner.
Fig. 1. Phase behavior of P(St-co-MAA)/CTAB aqueous solutions as the function of n(St) to n(MAA) of polymer and the mixing ratio r of n(St) to n(CTAB).

The temperature fixed at 35°C. Marker: open squares: transparent; black round: viscoelastic; half-filled black squares: syneresis; black stars: precipitation.

3.2 Influence of the mixing ratio on viscosity

The polymer P (St-co-MAA) with monomer ratio of 7:3 was chosen as the research object, as the system of P(St-co-MAA)(7:3)/CTAB was stable at any case and the system had the biggest viscosity. The quantity of CTAB was fixed at 0.015mol in the compounded system, but the mixing ratio r of n(St)/n(CTAB) changed continuously by dropping the mother solution of P(St-co-MAA) into the CTAB solution. The viscosity of the systems at different r were measured by the digital viscosimeter, and the data was recorded in Fig. 2. While r was less than 0.80, the system did not turn to be viscous. As the ratio was bigger than 0.80, the system became more and more viscous. The viscosity increased sharply when the ratio grew from 0.80 to 1.00. While the ratio was between 1.00 and 1.24, the viscosity was at the top level. Then the system turned thinner as the ratio bigger than 1.24. The ratio r for the most viscous system was between 1.00 and 1.24, where the charged ratio of MAA to CTAB was between 0.43 and 0.53. It indicated that cation-π electron action, rather than electrostatic attraction was the decisive factor to form viscoelastic system.
Fig. 2. Variation trend of viscosity as the mixing rate of $n(\text{St})$ to $n(\text{CTAB})$ changed.

The amount of CTAB was fixed at 0.015mol, the temperature kept at 35ºC.

3.3 Influence of the polymer concentration on viscosity

As the curve in Fig. 2, viscosity was biggest as the ratio $r$ between 1.00 and 1.24. Therefore, $r$ was fixed at 1 to measure the influence of the total concentration on the viscosity of the system.

The viscosity was measured by the digital viscosimeter. The copolymer P(St-co-MAA) (7:3) concentration using MAA as a standard ranged from 5 mM to 45 mM while CTAB concentration varied from 11.7 mM to 105 mM. As seen in Fig. 3, the system was not viscous as the polymer concentration lower than 15 mM. As larger than 15mM, the viscosity of the system increased sharply. As the concentration between 30 mM and 40 mM, the value of viscosity reached maximum and leveled off. After that, the viscosity of the system decreased slightly as the polymer concentration increased. As the polymer concentration of 30 mM, i.e. 0.9% w/v, the viscosity reached maximum value of 5500 mPa·s. The thickening efficiency was higher than that of system of P(MMA-co-SSNa)/CTAB\textsuperscript{12}, where the viscosity was only 1000 mPa·s at the concentration of P(MMA-co-SSNa) of 1.5%w/v.
Fig. 3. Variation trend of the viscosity as the function of total concentration of P (St-co-MAA)(7:3)/CTAB system.

The mixing ratio $r$ of $n$(St) to $n$(CTAB) fixed at 1. The molar concentration of MAA in copolymer was used as the criterion to mark the total concentration of the system. The temperature kept at 35ºC.

### 3.4 Total salt concentration influence on viscosity

Inorganic salts have the ability of electrostatic shielding, which also decreases the cross-sectional area of head agent and increases the parameter $P$. Inorganic salts might change the viscosities of the systems. Sodium chloride, as a kind of common inorganic salt, was chosen to check the influence of the inorganic salt on the system viscosity.

NaCl (g) was added into the systems little by little to test whether the system had the good salt tolerance. The rotational viscosimeter was used to measure the viscosities in different situations. The concentration of MAA in copolymer of the research system was 45mM and $r$ was 1. So, the initial salt concentration was 45 mM. As presented in Fig. 4, firstly, the viscosity would decrease partly while doubling or tripling the initial salt concentration. Then, the viscosity seemed no big difference as the addition of NaCl until the total salt concentration up to 1.8 M. Increasing salt concentration further, the system started to be thinner obviously. It could be concluded that the system had a relatively good salt tolerance, since the system still maintained
viscosity as the salt concentration up to 1.8 M.

![Viscosity vs Concentration of NaCl](image1)

Fig. 4. Variation trend of viscosity as the addition of NaCl.

The concentration of P (St-co-MAA)(7:3) (using MAA as a standard) was 45mM. The mixing ratio $r$ of n(Si) to n(CTAB) fixed at 1. The temperature kept at 35°C.

3.5 Rheological Behavior

DHR-2 Rheometer was used to test if the system has shear thinning behavior at a high shear rates. As seen in Fig. 5, the viscosity decreased while the shear rate was increasing in the whole process. There was the non-Newtonian behavior of the system all the time in the process, so it could be concluded that the system was not a typical Newtonian fluid.

![Viscosity vs Shear Rate](image2)

Fig. 5. Variation trend of viscosity as the shear rate turned greater.
The concentration of P (St-co-MAA)(7:3) (using MAA as a standard) was 45mM. The mixing ratio \( r \) of \( n(St) \) to \( n(CTAB) \) fixed at 1. The temperature kept at 35°C.

### 3.6 Temperature influence

The effect of temperature ranged from 20°C to 80°C on the system viscosity was investigated by rheometer. As seen in Fig.6, the viscosity of the system decreased as the temperature increased. The curve in Fig.6 showed that the beginning of curve was almost accorded to the Newtonian behavior. As the temperature rose, the system showed some features of non-Newtonian fluid. It could be concluded that the system was a non-Newtonian fluid from the curves in Fig.5 and Fig. 6. The system was still viscous while the temperature was up to 40°C, but not as viscous as at 20°C. As the temperature was higher than 70°C, the system was just like water but a little milky. The system had a good ability in heat-resisting within room temperature.

![Figure 6: Variation trend of viscosity as the temperature ranged from 20 °C to 80 °C.](image)

Shear rate was 2/s. The concentration of P (St-co-MAA)(7:3) (using MAA as a standard) was 45mM. The mixing ratio \( r \) of \( n(St) \) to \( n(CTAB) \) fixed at 1.

### 3.7 TEM characterization
Fig. 7 TEM images of the system of P(St-co-MAA)(7:3)/CTAB.

The concentration of P (St-co-MAA)(7:3) (using MAA as a standard) was 45 mM. The mixing ratio \( r \) of \( n(\text{St}) \) to \( n(\text{CTAB}) \) fixed at 1. The temperature kept at 35°C.

Transmission electron microscopy (TEM) is one of the most powerful methods to study morphologies of the aggregate. Fig. 7 showed the TEM images of copolymer aggregates. Fig. 7A showed that wormlike micelle formed in the viscous system\(^6\). It was clearly seen in Fig. 7B that the hybrid wormlike micelles entangled with each other to form network structure, which exhibit pronounced viscoelasticity. A schematic depicts the formation of the hybrid wormlike micelle from the polymer-surfactant complex and the mechanism of the origin of viscoelasticity. In CTAB micelle, the alkyl chains direct inward and headgroups direct outward. Upon addition of P(St-co-MAA), the phenyl group in P(St-co-MAA) might insert in CTAB micelle to interact with headgroup of CTAB owing to cation-π electron interaction. Anionic MAA in polymer would move to the surface of CTAB micellar surface due to the electrostatic attraction. Two CTAB micelle could be lined by P(St-co-MAA) to form hybrid wormlike micelle or even network structure.
Schematic 1. Mechanism proposed for the origin of viscoelasticity.

(a) Hooking of the micelles. (b) Formation of hybrid wormlike micelles through the linking mechanism.

3.8 \textit{¹H NMR spectra}

\textit{¹H NMR spectra} of the CTAB, P (St-co-MAA) (7:3) and the complex CTAB/P (St-co-MAA) in D$_2$O were measured, shown in Fig. 8. In CTAB/P (St-co-MAA) system, mixing ratio $r$ of $n$(St) to $n$(CTAB) was fixed at 1, and the concentration of P (St-co-MAA) (using MAA as a standard) was 45 mM. The chemical shift region 0-4 ppm, corresponding to the aliphatic protons of CTAB and the backbone of the copolymer, was shown in Figure 8A. Compared with in CTAB, 1H NMR resonances of the headgroup (η) of CTAB in the complex system, shifted upfield from 3.157 ppm to 3.042 ppm, which indicated that protons of headgroup shift to a more nonpolar environment. In CTAB micelle, headgroups (trimethyl) were outward in water environment. In CTAB/P(St-co-MAA) system, both COO$^-$ anions intercalated among the CTAB head groups and cation-π electron interaction between CTA$^+$ and St would induce significant changes in the position and shape of \textit{¹H NMR} peaks of CTAB headgroups. The chemical shift region 6-10 ppm, corresponding to the benzene protons of P(St-co-MAA), was shown in Fig. 8B. Two \textit{¹H NMR} bands were observed in this region attributed to the aromatic protons α and β in P(St-co-MAA). Upon addition of CTAB, 1H NMR resonances of protons α and β became weaker, and the two band emerged. The mobility of aromatic protons was restricted because there was a strong interaction between cation-π electron between CTA$^+$ and phenol group in P(St-co-MAA). It
could be one direct evidence to be the support of the strong interaction between cation-π electron, reported by Rao et al.  

![Chemical Shift (ppm)](image)

Figure 8. The $^1$H NMR spectra of P(St-co-MAA), CTAB and P(St-co-MAA)/CTAB system

The concentration of P(St-co-MAA) (7:3) (using MAA as a standard) was 50mM, and the concentration of CTAB was 50mM. The concentration of P(St-co-MAA)/CTAB system was 30mM while the mixing ratio $r$ of $n$(St) to $n$(CTAB) fixed at 1.

4. Conclusions

Based on experimental results, there came to three important conclusions. Firstly, as the monomer ratio of 6:4 and 7:3 in the system P(St-co-MAA) /CTAB, phase separation did not occur at any mixing ratio, and viscoelasticity appeared at appropriate mixing ratios. Secondly, the cation-π electron action$^{18-23}$ between CTA$^+$ and phenyl ring in the copolymer, rather than electrostatic attraction between cationic CTAB and polyanion, was decisive factor to form hybrid wormlike micelle, even network structure, because the biggest viscosity in the system P(St-co-MAA) /CTAB was located close to equal ratio of St to CTAB, instead of charged stoichiometry. Thirdly, the system had good performances in salt-tolerance and heat-resistance.
Acknowledgement

This work was supported by the National Natural Science Foundation of China (no.21405133) and MOE & SAFEA for the 111 Project (B13025).

References


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