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

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7     **Abstract**

8             A viscoelastic system was developed by forming hybrid wormlike micelles with poly  
9     (styrene-*co*-methacrylic acid) (P (St-*co*-MAA)) and cetyltrimethylammonium bromide (CTAB)  
10    in aqueous solution. The molar monomer ratio of St to MAA in the copolymer and the mixing  
11    ratio ( $r$ ) of P (St-*co*-MAA) to CTAB were the two key factors to obtain the viscoelastic system.  
12    Phase behaviors of P (St-*co*-MAA)/CTAB aqueous solutions as the functions of the monomer  
13    ratio in the copolymer, as well as the mixing ratio were investigated. It was found that there was  
14    no phase separation in any mixing ratios as monomer ratio of 6:4 and 7:3. On the other hand, the  
15    biggest viscosity was observed as the molar ratio of phenyl group in copolymer to CTAB was  
16    close to 1, rather than at charge stoichiometry between MAA and CTA<sup>+</sup>. It is found that as  $r$   
17    between 1.0 and 1.24 and the monomer ratio of St to MAA at 7:3, the mixing system had the  
18    largest viscosity. The effects of the total concentration of the mixture system, the salt  
19    concentration, the temperature, and the shear rate on the viscosity were studied in detail. The  
20    experimental results showed that the complex system had excellent thickening property even the  
21    copolymer concentration as low as 0.90% (w/v), good electrolyte tolerance as inorganic salt

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22 concentration lower than 1.8 M, and acceptable heat-resistance at room temperature. The  
23 complex system had a potential application as the thickeners in various fields.

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

26

## 27 **1. Introduction**

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

39 Further research found that a hybrid threadlike micelle could form between surfactant and  
40 polymer in an aqueous solution. Kenji Nakamura<sup>11</sup> constructed a hybrid threadlike micelle  
41 formed between CTAB, sodium p-toluensulfonate and sodium poly (p-vinylbezoate) (NaPVB) in  
42 an aqueous solution. The hybrid threadlike micelles were long enough to become entangled with  
43 each other and exhibit pronounced viscoelasticity. The findings suggested that incorporation of

44 long polymers into the hybrid threadlike micelle effectively hinders the crossing-through reaction  
45 between two micelles at an entanglement point and causes the rigidity of the hybrid threadlike  
46 micelle greater than that of the ordinary threadlike micelle. Oikonomou<sup>12</sup> had found that hybrid  
47 wormlike micelles could form upon mixing CTAB with Poly (methyl methacrylate-*co*-sodium  
48 styrene sulfonate) (P (MMA-*co*-SSNa)) copolymer in an aqueous solution. Usually, phase  
49 separation was often observed upon mixing a charged surfactant with an oppositely charged  
50 polyelectrolyte in an aqueous solution, especially as the mixing ratio approaches charged  
51 stoichiometry. In P (MMA-*co*-SSNa)/CTAB systems, monomer ratio in the copolymer and  
52 mixing charge ratio of the surfactant to polyelectrolyte were two key factors to affect the phase  
53 separation behavior. It was found that the phase separation was completely suppressed as the  
54 MMA content of the copolymers was about 30-40 mol %. On the other hand, specific  
55 stoichiometric cation- $\pi$  electron interactions between the surfactant and the phenyl rings was  
56 decisive for the formation of the polymer-induced hybrid wormlike micelle<sup>13</sup>. As known, the  
57 delicate balance among electrostatic attraction, cation- $\pi$  electron interactions, as well as  
58 hydrophobic interactions were crucial to form wormlike micelle and suppress phase separation.  
59 Though the effect of monomer ratio of MMA to SSNa on phase separation was investigated, the  
60 experimental results only revealed the equilibrium between hydrophobic interactions and  
61 electrostatic attraction. However, there was no way to change the ratio of styrene to sodium  
62 sulfonate to investigate the relationship between electrostatic attraction and cation- $\pi$  electron  
63 interactions, because both anionic sulfonate and phenyl groups came from the same monomer,  
64 sodium styrene sulfonate. As mentioned above, the relationship between electrostatic attraction  
65 and cation- $\pi$  electron interactions was decisive and should be controlled.

66 In order to add another regulatory factor, anionic group and phenyl group should come from  
67 the different monomers in the copolymer. Thus, electrostatic attraction and cation- $\pi$  electron  
68 interactions could be adjusted independently by changing the monomer ratio in the copolymer. In  
69 the present work, we used poly (styrene-*co*-methacrylic acid) P (St-*co*-MAA) in replace of  
70 P(MMA-*co*-SSNa), and synthesized five kinds of P(St-*co*-MAA) with monomer ratio of St to  
71 MAA of 3:7, 4:6, 5:5, 6:4 and 7:3. Phase separation behaviors of P(St-*co*-MAA)/CTAB in the  
72 aqueous solutions as a function of the monomer ratio in the copolymer were investigated. It was  
73 found that there is no phase separation behavior in any mixing ratios between P(St-*co*-MAA) and  
74 CTAB as monomer ratio of 6:4 and 7:3. On the other hand, the thickening properties of these  
75 complex systems were studied in detail by changing the mixing ratios of P(St-*co*-MAA) (7:3) to  
76 CTAB. The biggest viscosity was observed as the molar ratio of phenyl group in copolymer to  
77 CTAB was close to 1, rather than at charge stoichiometry between MAA and  $\text{CTA}^+$ . Additionally,  
78 the effect of the concentration at the fixed ratio of P(St-*co*-MAA) to CTAB on the viscosity was  
79 investigated. Abilities of heat-resistance and salt-tolerance of the mixed systems were also  
80 studied for the actual application in various fields, including home and personal care, cosmetics,  
81 fracturing fluids, drag reduction agent, and other industrial fields<sup>14</sup>.

82

## 83 **2. Experimental Section**

### 84 *2.1. Chemicals*

85 The monomers styrene and methacrylic acid, as well as the initiator  $\alpha'$ ,  $\alpha'$ ,  
86 azobisisobutyronitrile (AIBN) were of chemical grade. 1, 4-diethylene dioxide, petroleum ether,

87 diethyl ether and cetyltrimethylammonium bromide (CTAB) were of analytical grade. All the  
88 chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

### 89 *2.2 Synthesis of the Copolymers.*

90 The copolymers P (St-co-MAA) with different monomer ratios were synthesized via free  
91 radical polymerization in 1, 4-diethylene dioxide using AIBN as an initiator. The desired  
92 quantities of the two monomers were dissolved in 180 ml 1, 4-diethylene dioxide to get total  
93 amount of the monomers approximately up to 1 mol. After the solution was degassed, the  
94 initiator AIBN (4.9263g, 0.03mol) was added. The reaction proceeded under vigorous stirring in  
95 a N<sub>2</sub> atmosphere in an oil bath at 65°C for 24 hours. After that, purification was carried out by  
96 dissolving it in 1, 4-dioxane and reprecipitating in petroleum ether and diethyl ether. At last, the  
97 product was dried in a vacuum oven at 60°C for 12 hours.

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

### 102 *2.3 Methods.*

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

108 The shear viscosity were performed at 35°C using a rheometer (TA DHR - 2 DSR dynamic

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

114 The morphology and size of the aggregates were characterized with transmission electron  
115 microscopy (TEM) (JEM-2100) at a 200 kV accelerating voltage. The sample solutions were  
116 deposited onto the surface of 300-mesh Formvar-carbon film coated copper grids. Excess  
117 solution was quickly wicked away with a filter paper<sup>15</sup>.

#### 118 *2.4 Preparation of solutions.*

119 Certain amount of P (St-co-MAA) with monomer ratio of St to MAA of 7:3, 6:4, 5:5, 4:6,  
120 3:7, respectively, was dissolved in 0.1 M NaOH aqueous solution by gentle stirring overnight to  
121 form the mother solution. The MAA group concentration in the mother solution for all monomer  
122 ratio was 50 mM. pH of the mother solutions were in the range of 11.0-12.0, for example, pH of  
123 P(St-co-MAA)(7:3) mother solution was 11.2.

124

### 125 **3. Results and discussion**

#### 126 *3.1 Appearance of system upon mixing P(St-co-MAA) with CTAB*

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

130 As seen in Fig.1, as the monomer ratio of 3:7, the system of P(St-co-MAA) /CTAB did not

131 turn into be viscous at any mixing ratio. While the mixing ratio was less than 0.36, the  
132 precipitation generated. As  $r$  was bigger than 0.36, an opaque gel separated from the aqueous  
133 solution, i.e., syneresis was observed in the solution. As the monomer ratio of 3:7, the mixing  
134 ratio of 0.36 is the equal of the molar ratio of MAA to CTAB of 0.84, which approached to the  
135 charged stoichiometry in the system.

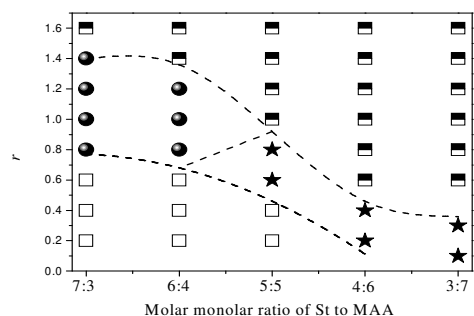
136 The situation of the system of P(St-co-MAA)(4:6)/CTAB was similar to that of  
137 P(St-co-MAA)(3:7)/CTAB. While  $r$  was between 0 and 0.46, the precipitation come out. As  $r$   
138 was bigger than 0.46, the syneresis took place. The charged stoichiometry of the system would  
139 be the mixing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

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

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

148 As was the case in the system P(St-co-MAA)(6:4)/CTAB, the system of  
149 P(St-co-MAA)(7:3)/CTAB was also stable at any mixing ratio. As  $r$  was smaller than 0.77, the  
150 system was transparent. As  $r$  ranged from 0.77 to 1.40, it became more and more viscous, and the  
151 entire solution turned into a transparent gel system. There came out syneresis while  $r$  was bigger  
152 than 1.4, and the opaque gel turned thinner.





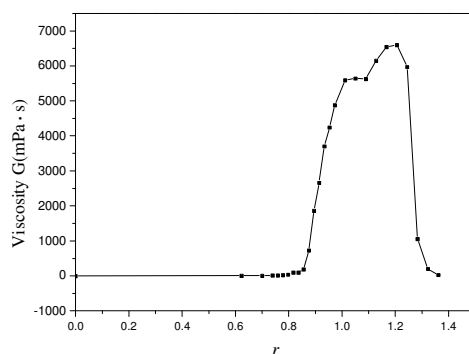
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154 Fig.1. Phase behavior of P(St-co-MAA)/CTAB aqueous solutions as the function of  $n(\text{St})$  to  $n(\text{MAA})$  of polymer  
 155 and the mixing ratio  $r$  of  $n(\text{St})$  to  $n(\text{CTAB})$ .

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

### 158 3.2 Influence of the mixing ratio on viscosity

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



172

173 Fig.2. Variation trend of viscosity as the mixing  $r$  of n(St) to n(CTAB) changed.

174 The amount of CTAB was fixed at 0.015mol, the temperature kept at 35°C.

### 175 3.3 Influence of the polymer concentration on viscosity

176 As the curve in Fig. 2, viscosity was biggest as the ratio  $r$  between 1.00 and 1.24. Therefore,

177  $r$  was fixed at 1 to measure the influence of the total concentration on the viscosity of the system.

178 The viscosity was measured by the digital viscosimeter. The copolymer P(St-co-MAA) (7:3)

179 concentration using MAA as a standard ranged from 5 mM to 45 mM while CTAB concentration

180 varied from 11.7 mM to 105 mM. As seen in Fig.3, the system was not viscous as the polymer

181 concentration lower than 15 mM. As larger than 15mM, the viscosity of the system increased

182 sharply. As the concentration between 30 mM and 40 mM, the value of viscosity reached

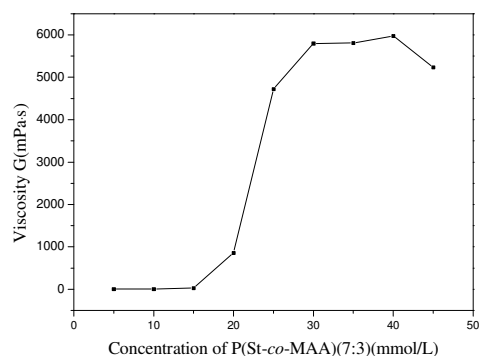
183 maximum and leveled off. After that, the viscosity of the system decreased slightly as the

184 polymer concentration increased. As the polymer concentration of 30 mM, i.e. 0.9% w/v, the

185 viscosity reached maximum value of 5500 mPa·s. The thickening efficiency was higher than that

186 of system of P(MMA-co-SSNa) /CTAB<sup>12</sup>, where the viscosity was only 1000 mPa·s at the

187 concentration of P(MMA-co-SSNa) of 1.5%w/v.



188

189 Fig.3. Variation trend of the viscosity as the function of total concentration of P (St-co-MAA)(7:3)/ CTAB

190

system.

191

The mixing ratio  $r$  of  $n(\text{St})$  to  $n(\text{CTAB})$  fixed at 1. The molar concentration of MAA in copolymer was used as

192

the criterion to mark the total concentration of the system. The temperature kept at 35°C.

193

### 3.4 Total salt concentration influence on viscosity

194

Inorganic salts have the ability of electrostatic shielding, which also decreases the

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cross-sectional area of head agent and increases the parameter  $P$ . Inorganic salts might change the

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viscosities of the systems. Sodium chloride, as a kind of common inorganic salt, was chosen to

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check the influence of the inorganic salt on the system viscosity.

198

NaCl (g) was added into the systems little by little to test whether the system had the good

199

salt tolerance. The rotational viscosimeter was used to measure the viscosities in different

200

situations. The concentration of MAA in copolymer of the research system was 45mM and  $r$  was

201

1. So, the initial salt concentration was 45 mM. As presented in Fig.4, firstly, the viscosity would

202

decrease partly while doubling or tripling the initial salt concentration. Then, the viscosity

203

seemed no big difference as the addition of NaCl until the total salt concentration up to 1.8 M.

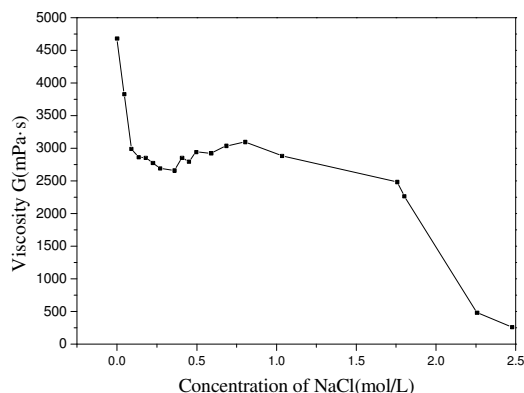
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Increasing salt concentration further, the system started to be thinner obviously. It could be

205

concluded that the system had a relatively good salt tolerance, since the system still maintained

206 viscosity as the salt concentration up to 1.8 M.



207

208

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

209 The concentration of P (St-co-MAA)(7:3) (using MAA as a standard) was 45mM. The concentration of P

210 (St-co-MAA)(7:3) (using MAA as a standard) was 45mM. The mixing ratio  $r$  of  $n(\text{St})$  to  $n(\text{CTAB})$  fixed at 1. The

211 temperature kept at 35°C.

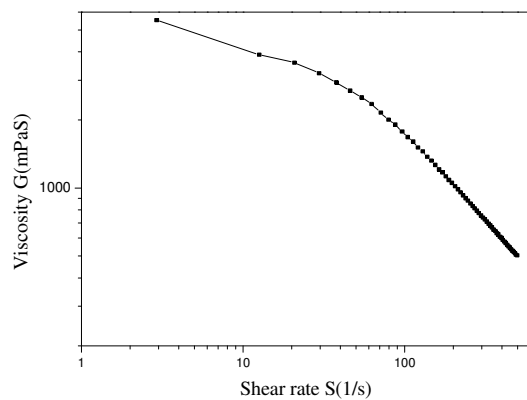
### 212 3.5 Rheological Behavior

213 DHR-2 Rheometer was used to test if the system has shear thinning behavior at a high shear

214 rates. As seen in Fig.5, the viscosity decreased while the shear rate was increasing in the whole

215 process. There was the non-Newtonian behavior of the system all the time in the process, so it

216 could be concluded that the system was not a typical Newtonian fluid.



217

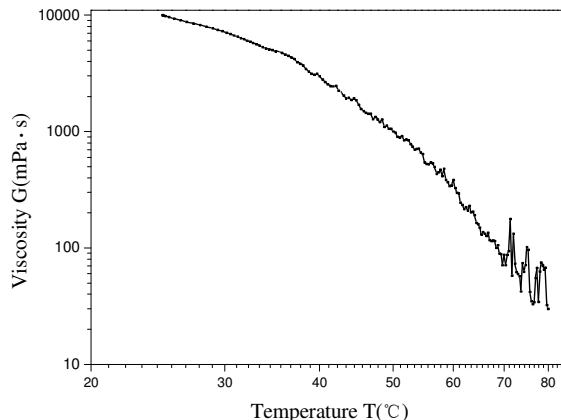
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Fig.5. Variation trend of viscosity as the shear rate turned greater.

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

### 221 3.6 Temperature influence

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



230

231 Fig.6. Variation trend of viscosity as the temperature ranged from 20 °C to 80 °C.

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

### 234 3.7 TEM characterization

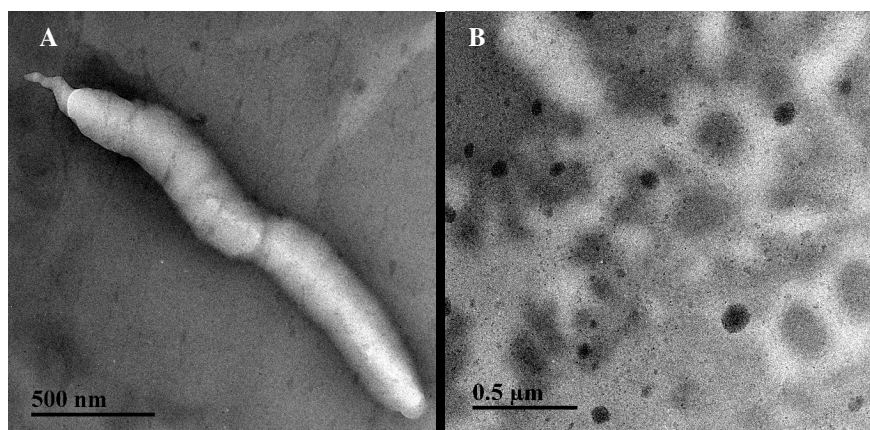


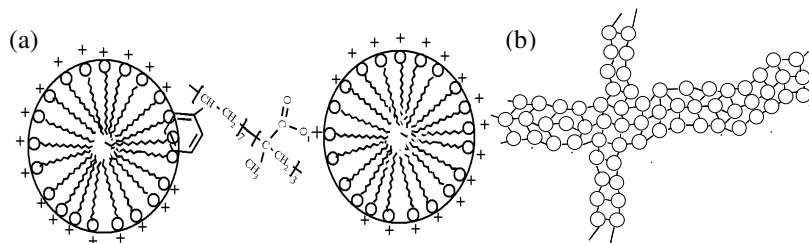
Fig.7 TEM images of the system of P(St-co-MAA)(7:3)/CTAB.

235

236

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

239 Transmission electron microscopy (TEM) is one of the most powerful methods to study  
240 morphologies of the aggregate. Fig.7 showed the TEM images of copolymer aggregates. Fig.7A  
241 showed that wormlike micelle formed in the viscous system<sup>16</sup>. It was clearly seen in Fig.7B that  
242 the hybrid wormlike micelles entangled with each other to form network structure, which exhibit  
243 pronounced viscoelasticity. A schematic depicts the formation of the hybrid wormlike micelle  
244 from the polymer-surfactant complex and the mechanism of the origin of viscoelasticity. In  
245 CTAB micelle, the alkyl chains direct inward and headgroups direct outward. Upon addition of  
246 P(St-co-MAA), the phenyl group in P(St-co-MAA) might insert in CTAB micelle to interact with  
247 headgroup of CTAB owing to cation- $\pi$  electron interaction. Anionic MAA in polymer would  
248 move to the surface of CTAB micellar surface due to the electrostatic attraction. Two CTAB  
249 micelle could be lined by P(St-co-MAA) to form hybrid wormlike micelle or even network  
250 structure.



251

252

Schematic 1. Mechanism proposed for the origin of viscoelasticity.

253

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

254

### 3.8 <sup>1</sup>H NMR spectra

255

<sup>1</sup>H NMR spectra of the CTAB, P (St-co-MAA) (7:3) and the complex CTAB/P (St-co-MAA)

256

in D<sub>2</sub>O were measured, shown in Fig.8. In CTAB/P (St-co-MAA) system, mixing ratio *r* of n(St)

257

to n(CTAB) was fixed at 1, and the concentration of P (St-co-MAA) (using MAA as a standard)

258

was 45 mM. The chemical shift region 0-4 ppm, corresponding to the aliphatic protons of CTAB

259

and the backbone of the copolymer, was shown in Figure 8A. Compared with in CTAB, <sup>1</sup>H

260

NMR resonances of the headgroup ( $\eta$ ) of CTAB in the complex system, shifted upfield from

261

3.157 ppm to 3.042 ppm, which indicated that protons of headgroup shift to a more nonpolar

262

environment. In CTAB micelle, headgroups (trimethyl) were outward in water environment. In

263

CTAB/ P(St-co-MAA) system, both COO<sup>-</sup> anions intercalated among the CTAB head groups and

264

cation- $\pi$  electron interaction between CTA<sup>+</sup> and St would induce significant changes in the

265

position and shape of <sup>1</sup>H NMR peaks of CTAB headgroups. The chemical shift region 6-10 ppm,

266

corresponding to the benzene protons of P(St-co-MAA), was shown in Fig. 8B. Two <sup>1</sup>H NMR

267

bands were observed in this region attributed to the aromatic protons  $\alpha$  and  $\beta$  in P(St-co-MAA).

268

Upon addition of CTAB, <sup>1</sup>H NMR resonances of protons  $\alpha$  and  $\beta$  became weaker, and the two

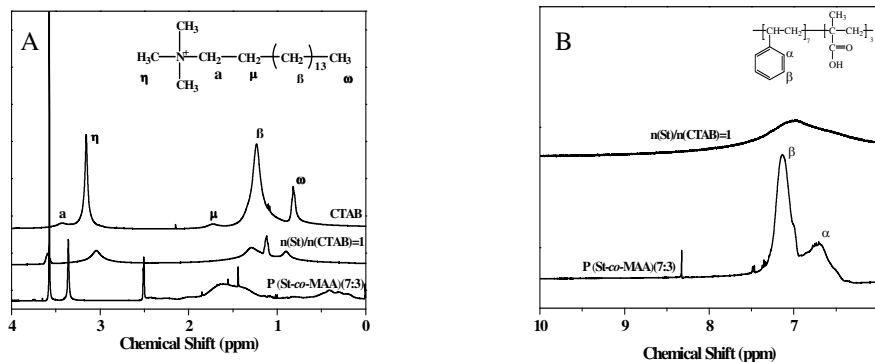
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band emerged. The mobility of aromatic protons was restricted because there was a strong

270

interaction between cation- $\pi$  electron between CTA<sup>+</sup> and phenol group in P(St-co-MAA). It

271 could be one direct evidence to be the support of the strong interaction between cation- $\pi$  electron,  
 272 reported by Rao et al.<sup>17</sup>



273

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

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

278

#### 279 4. Conclusions

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

288



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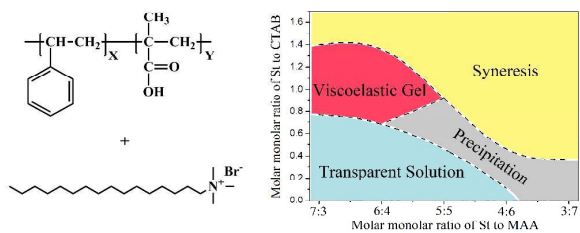
292

293 **References**

- 294 [1] Israelachvili, J. N.; Mitchell, D. J.; Ninham, B. W. *J. Chem. Soc., Faraday Trans 2:*  
295 *Molecular and Chemical Physics* **1976**, 72, 1525-1568.
- 296 [2] Magid, L. J.; Li, Z.; Butler, P. D. *Langmuir* **2000**, 16, 149-156.
- 297 [3] Magid, L. J. *J. Phys. Chem. B.* **1998**, 102, 4064-4074.
- 298 [4] Khatory, A.; Lequeux, F.; Kern, F.; Candau, S. *J. Langmuir* **1993**, 9, 1456-1464.
- 299 [5] Jain, N. J. Aswal, V. K.; Goyal, P. S. *Colloids and surfaces A.* **2000**, 173, 85-94.
- 300 [6] Ali, A. A.; Makhloufi, R. *Phys. Rev. E* **1997**, 56, 4474-4478.
- 301 [7] Rehage, H.; Hoffmann, H. *J. Phys. Chem.* **1988**, 92, 4712-4719.
- 302 [8] Soltero, J. F. A.; Puig, J. E.; Manero, O. *Langmuir* **1996**, 12, 2654-2662.
- 303 [9] Carver, M.; Smith, T. L.; Gee, J. C.; Delichere, A.; Caponetti, E.; Magid, L. J. *Langmuir*  
304 **1996**, 12, 691-698.
- 305 [10] Mishra, B. K.; Samant, S. D.; Pradhan, P.; Mishra, S. B.; Manohar, C. *Langmuir* **1993**, 9,  
306 894-898.
- 307 [11] Kanae Yamanaka,† and Toshiyuki Shikata. *Langmuir* 2003, 19, 8654-8660.
- 308 [12] Oikonomou E, Bokias G, Kallitsis J K, Iliopoulos I. *Langmuir* **2011**, 27, 5054-5061.
- 309 [13] Fundin J, Brown W. *Macromolecules* **1994**, 27, 5024-5031.
- 310 [14] Yang J. *Current Opinion in Colloid & Interface Science* **2002**, 7, 276-281.

- 311 [15] Wang BN, Ni XJ, Yu MJ, Cao YH. *Journal of Chromatography A* **2012**, 1245, 190-198.
- 312 [16] Danino, D; Groswasser, A. B.; Talmon, Y. *Colloids and Surfaces A: Physicochem. Eng.*  
313 *Aspects* **2001**, 183-185, 113-122.
- 314 [17] Rao, U. R. K.; Manohar, C.; Valaulikar, B. S.; Iyer, R. M. *J. Phys. Chem.* **1987**, 91,  
315 3286–3291.
- 316 [18] Yamada Shinji, Azuma Yuka, Aya Kanae. *J. Phys. Chem. B* **2014**, 55, 2801–2804.
- 317 [19] Ferdani, R.; Barbour L J, Gokela G W. *Journal of Supramolecular Chemistry* **2002**, 2,  
318 343–348.
- 319 [20] Li RQ, Winterb R, Kramerb J, Goke G W. *Supramolecular Chemistry* **2010**, 22, 73–80.
- 320 [21] Estarellas C, Frontera A, Quiñonero D, Deyà P M. *Central European Journal of Chemistry*  
321 **2011**, 9(1), 25–34.
- 322 [22] Lin C, Chinnappan R, Acharya K, Pellequer K L, Jankowiak R. *Biophysical Chemistry* **2011**,  
323 154, 2801–2804.
- 324 [23] Gao JL, Chou L, Auerbach A. *Biophysical Journal* **1993**, 65, 43–47.
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333 **For Table of contents use only**



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336 **Title of the paper:**

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

339

340 **List of authors:**

341 Lu Zhang, Xinjiong Ni, Yuhua Cao\*, Xinyu Ma, Guangqun Cao.

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