Soft Matter

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Soft Matter

www.rsc.org/softmatter

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/softmatter

Soft Matter

Soft Matter

ARTICLE

pH-Tunable Wormlike Micelles Based on an Ultra-long-chain "Pseudo" Gemini Surfactant

Yujun Feng[a,b] and Zonglin Chu*[b]

Smart surfactant wormlike micelles (SWLMs), responsive to external stimuli, are a particularly recent area of development, yet highly promising, given the versatility of the materials but simplicity of the design. Here, we developed a pH-switchable wormlike micellar system based on a "pseudo" gemini surfactant (named as EAMA) formed by a mixture of *N*-erucamido-*N,N*-dimethylamine (UC$_{22}$AMPM)

10 and maleic acid with molar ratio 2:1, and compared the "pseudo" gemini worm system with UC$_{22}$AMPM in the presence of hydrochloric acid (EAHCl). It was found both maleic acid and hydrochloric acid can protonate the ultra-long-chain tertiary amine into quaternary ammonium surfactant, thus forms wormlike micelles; however, much stronger viscoelastic behavior was evidenced in the maleic acid system because one protonated maleic acid molecule can "bridge" two quarternonized UC$_{22}$AMPM molecules *via*

15 electrostatic attraction. On the contrary, the EAHCl system just shows "mono" quaternary ammonium feature with weak viscosity buildup. In addition, the maleic acid-based worm system was found to be more thermo-sensitive than conventional wormlike micelles, which also originates from to its "pseudo" gemini architecture.

Introduction

20 Wormlike micelles (WLMs) are long flexible cylindrical aggregates resulting from self-assembly of surfactant molecules in aqueous media.[1–5] Above a threshold surfactant concentration, *i.e.*, overlapping concentration (*C**), the worms entangle into a dynamic reversible network that are continuously breaking and

25 recombineing, thus they are also called "equilibrium" or "living" polymers.[5–7] Compared with their traditional short chain counterparts, ultra-long-chain surfactants (tail length > C$_{18}$) exhibit excellent thickening ability even at very low concentration (< 1% w/w) due to their ultra-long hydrophobic

30 tail.[8–14] Nevertheless, the long-chain viscoelastic surfactants reported so far are only limited to erucyl bis-(hydroxyethyl)methylammonium chloride (EHAC)[8] and erucyl trimethylammonium chloride (ETAC),[8,9] erucyl dimethyl amidopropyl betaine (EDAB),[11] 3-(*N*-erucamidopropyl-*N,N*-

35 dimethyl ammonium) propanesulfonate (EDAS),[12,13] and sodium erucate (NaOE).[14] Gemini surfactant, made of two (or more) surfactants units in which the head-groups are connected by a spacer, represents another type of versatile viscoelastic surfactant, especially when the spacer is short.[1,2]

40 Switchable wormlike micelles are one type of stimuli-responsive smart fluids since their rheological behaviors could be reversibly regulated upon "triggering" the external stimulus such as electric current, ultraviolet/visible light, temperature, pH.[15–17] The activation of the trigger enables the active, tailored tuning of

45 micellar structures and consequently of the associated rheological response. This emerging multidisciplinary field opens the door to a range of potential applications, including clutches, microfluidics, valves, vibration control, clean fracturing fluids, tissue engineering, or even human muscle stimulators.[15] Amongst

50 various types of triggers,[18–21] pH offers a facile and economical way to control micellar assemblies and thereby the bulk properties of WLMs.[15,22,23] For instance, a simple and effective strategy towards SWLMs was first developed by Huang's group, utilizing cetyltrimethylammonium bromide as an amphiphile and

55 potassium phthalic acid as a responser.[22] The fluid can be switched between gel-like and water-like states within a narrow pH range.

A prototype surfactant system was developed with the unique feature that can be switched between an aggregated, amphiphilic

60 state and a nonaggregated, nonamphiphilic state using external stimuli.[24] This switchable surfactant system uses the reversible formation of a dynamic covalent bond for pH- and temperature-triggered on/off self-assembly of micellar aggregates by reversible displacement of the equilibrium between

65 nonamphiphilic building blocks and their amphiphilic counterparts.

Recently, we reported a novel gemini-like surfactant that is easily formed by simple mixing of isotropic aqueous precursor solutions.[23] The resulting dynamic surfactant shows fast

70 dissociation kinetics upon tuning solution pH. Such a responsive surfactant can be effectively used for the development of SWLMs, owing to their ultra-long tail and gemini-like structure. Here we extend the preliminary research to in-depth by rheological examination of the dynamic "pseudo" gemini surfactant worm

75 system, and compared it with UC$_{22}$AMPM in the presence of hydrochloric acid. It was found both maleic acid and hydrochloric

acid can protonate the ultra-long-chain tertiary amine into quaternary ammonium surfactant, thus forms wormlike micelles; however, much stronger viscoelastic behavior was evidenced in the maleic acid system as one protonated maleic acid molecule

5 can "bridge" two quanternonized $UC_{22}AMPM$ molecules *via* electrostatic attraction, behaving like a long-chain cationic "gemini" surfactant.

Experimental

Materials

10 $UC_{22}AMPM$ with purity greater than 99.0% (HPLC) was synthesized previously.[25] The maleic acid was analytical grade and used without further purification; and the weight percent of HCl in the hydrochloric acid used is 36.5%. The water was triply distilled by a quartz water purification system.

15 The sample solutions were prepared by weighing surfactants and distilled water directly into glass bottles, treating the volume contribution of surfactant as 1 mL per gram, and then calculating to get molar concentration. This procedure is very similar to that reported by Candau *et al.*[26]

20 The pH was adjusted by adding 1–3 drops of dilute (0.1% w/w, for small tuning) or concentrated (10% w/w, for large tuning) NaOH and/or HCl solution to about 20 mL micellar solution, and determined by a Sartorius basic pH meter PB-10 (± 0.01). The viscoelasticity of the solution after tuning back to acidic

25 condition recovers almost completely in time scale of seconds. However, as a general rule for the freshly prepared wormlike micellar solutions, the samples were left at room temperature for at least 1 day prior to measurements.

Rheology

30 Rheological experiments were made on a Physica MCR 301 (Anton Paar, Austria) rotational rheometer equipped with a searle-type concentric cylinder geometry CC27 (ISO3219). Samples were equilibrated at the temperature of interest for no less than 20 min prior to the measurements. Dynamic frequency

35 spectra were conducted in the linear viscoelastic regime of the samples, as determined from dynamic stress sweep measurements. The temperature was set to ± 0.1 ℃ accuracy by a Peltier temperature control device, and a solvent trap was used to minimize water evaporation during the measurements. In the

40 steady rheological measurements, the shear duration of each measuring point is 100 s for concentration between 50 and 100 mM, 50 s for those between 10 and 40 mM, and 20 s for those lower than 10 mM. In the steady rheological test, all measurements were performed at steady state—the shear duration

45 of each measuring point is 100 s for concentration between 50 and 100 mM, 50 s for those between 10 and 40 mM, and 20 s for those lower than 10 mM.

Results and Discussion

Comparison the function of maleic acid and hydrochloric acid
50 ### on the pH-switchable wormlike micelles

In the previous report, we proved the formation of wormlike micelles of "50 mM $UC_{22}AMPM$ + 25 mM maleic acid", and its pH-response with switchability.[23] Since the stimuli-responsive

mechanism of the above worms could be attributed to the

55 reversible protonation of the tertiary amine $UC_{22}AMPM$ by the added acid/base, the aqueous solution of $UC_{22}AMPM$ in the presence of a common acid such as hydrochloric acid may also be used to construct pH-switchable wormlike micelles. For the convenience of expression, two $UC_{22}AMPM$ molecules in the

60 presence of one maleic acid molecule will be treated as one surfactant molecule, and abbreviated as EAMA (Mw = 961.53); one $UC_{22}AMPM$ molecule in the presence of one HCl molecule will be abbreviated as EAHCl (Mw = 459.19).
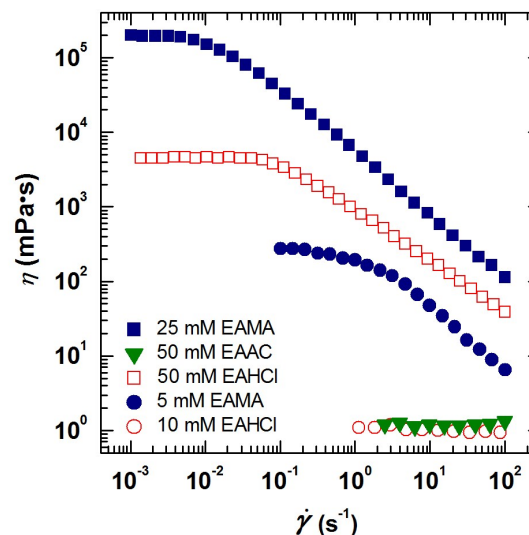

65

Fig. 1 Steady shear viscosity (η) plotted as a function of shear rate ($\dot{\gamma}$) for EAMA and EAHCl solutions at pH 6.20 and 25 °C.

Steady and dynamic rheologies of the EAMA and EAHCl solutions at pH 6.20 are investigated. Fig. 1 shows the

70 comparison of the steady rheological response of EAMA and EAHCl solutions. As can be seen, both the 25 mM EAMA and 50 mM EAHCl solutions show shear-thinning behavior when the shear rate exceeds a critical shear rate, indicating the presence of wormlike micelles in both solutions that undergo structural

75 change—alignment of the long micelles at high shear rates.[2,27] Extrapolation of viscosity to zero-shear rate in the steady-shear curve yields the zero-shear viscosity η_0. η_0 of the 25 mM EAMA solution is 10^5 times higher than of that of water (~1 mPa·s). The concentration of UC22AMPM in the 25 mM EAMA and 50 mM

80 EAHCl solutions is the same; however, the former solution is more viscous—η_0 of the former solution is one magnitude higher than that of the latter one. This means the EAHCl wormlike micellar solution is less efficient in thickening aqueous solution than EAMA worms. To further confirm this, 5 mM EAMA and

85 10 mM EAHCl solutions are also compared: the former solution shows shear-thing behavior, and the η_0 is two magnitudes higher than that of water; on the contrary, the latter one just behaves as a water-like Newtonian fluid. This also demonstrates that EAMA shows better thickening ability. In addition, the solution

90 composed of $UC_{22}AMPM$ in the presence of equivalent amount acetic acid (named as EAAC) did not show thickening ability even at concentration as high as 50 mM. The comparison between these systems clearly demonstrates the advantage of the gemini-like structure of EAMA system.
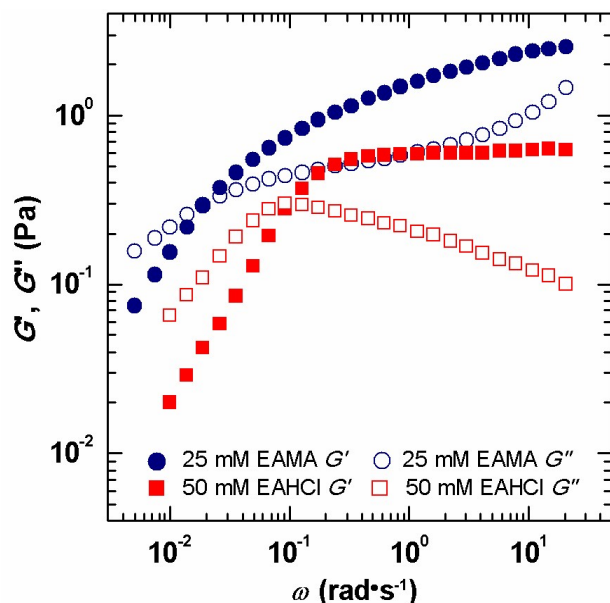
Fig. 2 Elastic (*G'*) and viscous (*G"*) moduli plotted as a function of angular frequency for the 25 mM EAMA and 50 mM EAHCl solutions at pH 6.20 and 25 °C.

5 Fig. 2 shows the plots of storage modulus (*G'*) and loss modulus (*G"*) as a function of oscillatory shear frequency (ω) for the 25 mM EAMA and 50 mM EAHCl solutions at pH 6.20 and 25 ºC. Both samples exhibits a typical viscoelastic response, *i.e.*, the behavior is elastic (*G' > G"*) at high frequencies or short time 10 scales, while it is viscous (*G' < G"*) at low frequencies or long time scales. The viscoelasticity of the solution is attributed to the entanglement of long worms to form a transient network.[2] However, compared with the 25 mM EAMA worm solution, the 50 mM EAHCl worm solution show lower plateau modulus, G_0, 15 and higher critical frequency, ω_c. This also confirms that the thickening ability of EAHCl is less effective than EAMA.

The samples with pH below 6.51 are high viscous wormlike micellar solutions, while those with pH between 7.29 and 9.45 are low viscous, turbid fluid (Fig. 3, inset). Under a weak basic 20 condition, oil-like UC$_{22}$AMPM was partially dissociated from the aqueous solution, resulting in the formation of oil-in-water emulsions, as confirmed by optical microscopy (insert, Figure 3, upper left corner). Upon further increasing pH, the water-soluble surfactant molecules can completely dissociated and precipitated 25 from the aqueous solution to give solid-like UC$_{22}$AMPM, implying that the thickening agent UC$_{22}$AMPM can be conveniently recycled by simply tuning the pH. Interestingly, in acid conditions, η_0 of the 25 mM EAMA worm solution is always higher than that of EAHCl worms, which further confirms that 30 EAMA possesses stronger thickening ability than EAHCl.

Both the 25 mM EAMA and 50 mM EAHCl show substantially responsive behaviors to the alteration of pH (Fig. 3); and the rheological properties of both samples can be switched via a facile way of tuning the pH through the addition of minor 35 acid or base (Fig. 4). The zero-shear viscosity (η_0) of the samples with pH 6.20 is several orders of magnitude higher than of those at pH 7.29. After being switched 7 times, the viscosity of the pH-switchable system at pH 6.20 can retain their initial values without any decay. As clearly shown, at pH 6.20, η_0 of the 25

40 mM EAMA worm solution is always higher than that of EAHCl worms, which is in also consistent with the above findings.
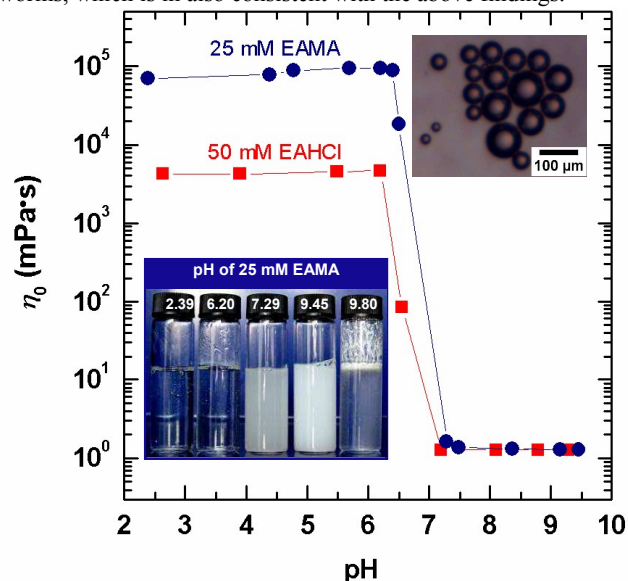

Fig. 3 Zero-shear viscosity (η_0) plotted as a function of pH at 25 °C for the 25 mM EAMA and 50 mM EAHCl solutions. Inset: optical 45 appearance of the 25 mM EAMA solution at different pH.
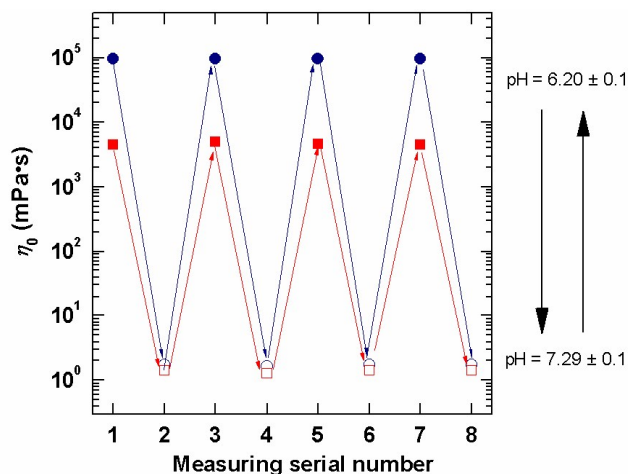

Fig. 4 Switchable zero-shear viscosity of the 25 mM and 50 mM EAHCl EAMA solutions at 25 °C.

The stimuli-responsive mechanism of both systems is 50 schematically illustrated in Fig. 5. Under acidic conditions, UC$_{22}$AMPM molecules are protonated and aggregated into long wormlike arrays, making the fluid viscoelastic. Upon the addition of an alkali solution, however, the dissociative tertiary amine UC$_{22}$AMPM desorbs from the worms and the network falls apart, 55 resulting in a low viscous turbid liquid. Therefore, both EAMA and EAHCl worms show pH stimuli-response with reversibility. The better thickening ability of the EAMA worms may find an explanation in terms of its unique molecular architecture— "gemini-like". EAMA bears two hydrophobic tails bridged by 60 one maleate via physical interaction, for example, electrostatic attraction and hydrogen bonding. This peculiar structure may allow it to behave as a "pseudo" gemini surfactant, which is well-known to have strong viscosifying ability due to the formation of wormlike micelles.[2] Though EAHCl bears one long hydrophobic

chain that favors to the formation of wormlike micelles, its thickening ability is much weaker than that of its twin-tailed counterparts.
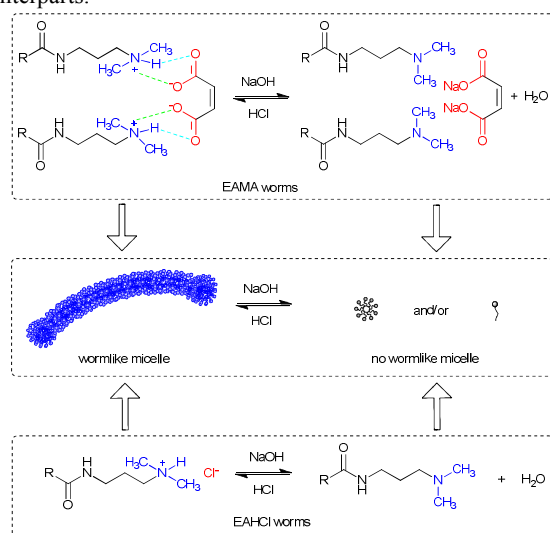

5 **Fig. 5** Schematic illustration of the switchable mechanism of the EAMA and EAHCl wormlike micelles.

Concentration dependence of rheological behaviors of EAMA worms at "on" state

In the above section, EAMA and EAHCl worms are compared in
10 terms of their thickening ability and pH-stimulus response. Both worms systems show pH response with reversibility; however, the "on" state (under acidic condition) EAMA worms are more efficient in thickening aqueous solution than those of EAHCl worms. Therefore, the EAMA worms are worthy of further
15 investigation, and thus concentration and temperature dependence of rheological behaviors of the "on" state EAMA worms are detailedly investigated in the following two sections.

Fig. 6 shows the variation of η as a function of shear rate $\dot{\gamma}$ for the EAMA solutions at pH 6.20. At low concentrations, for
20 example, 0.75 mM, η of the solution maintains constant regardless of the shear rate, which is a typical Newtonian flow behavior. However, the rheological response of the EAMA solution with higher concentrations is quite different. For instance, shear thinning occurs in the 2.5 mM EAMA solution
25 when the shear rate exceeds ~1 s^{-1}, which can be attributed to the alignment of long micelles at high shear rates.[2,27] On successively increasing the EAMA concentration, the wormlike micelles become highly entangled with each other, thereby enhancing the viscoelasticity of the fluid.

30 As one can see, η_0 increases monotonously with increasing EAMA concentration. It is unusual when compared with short chain surfactant (hydrophobic tail no longer than C$_{16}$) worm systems,[28–31] but similar trends have been observed in the worm system formed by our previously reported C$_{22}$-tailed
35 amidosulfobetaine surfactant EDAS.[17] For the short chain surfactant worms, a maximum value of η_0 is usually observed in the concentrated regime[28–31] because of the formation of branched point that can slide along the wormlike micellar body, resulting in a decrease in η_0.[2,32,33] However, the presence of an ultra-long
40 hydrophobic chain in the hydrophobic tail can impart very long breaking times (τ_b, the mean time required for a chain of mean

length to break into two pieces) and long relaxation times (τ_R) to the corresponding worm solutions.[11,12] In such a case, the wormlike micellar networks behave as unbreakable polymer
45 networks instead of so-called "living" ones which follow the fast-breaking limit. Thus, the η_0 grows monotonously as that of water-soluble polymer solutions.
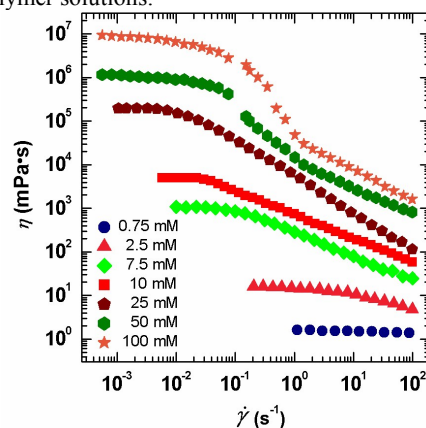

Fig. 6 Steady shear viscosity (η) plotted as a function of shear rate ($\dot{\gamma}$)
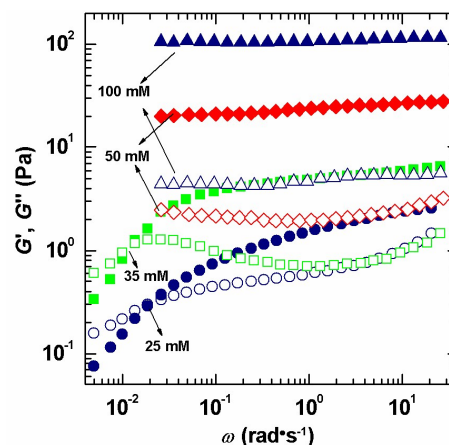50 for various EAMA solutions at pH 6.20 and 25 °C.

Fig. 7 Elastic (*G'*, filled symbols) and viscous (*G''*, open symbols) moduli plotted as a function of angular frequency for the different concentrations of EAMA solutions at pH 6.20 and 25 °C.

55 Exhibited in Fig. 7 are the plots of the elastic (*G'*) and viscous modulus (*G''*) as a function of the oscillatory shear frequency (ω) for EAMA solutions at pH 6.20. For the 25 and 35 mM samples at frequencies below a critical value (ω_c), the elastic modulus G' crosses over and drops below the viscous modulus *G''*. In other
60 words, the relaxation time τ_R is finite for these samples. The sample's response can be divided into two regimes on the basis of the relaxation time τ_R: on a timescale much shorter than τ_R ($\omega \gg \omega_c$), the response is elastic, whereas for a timescale much longer than τ_R ($\omega \ll \omega_c$), the response is viscous. The viscoelasticity of
65 the solution is usually attributed to the three-dimensional network formed by the long worms via entangling with each other.[2] The increasing EAMA concentration increases the entanglements, causing the increase of the plateau modulus (G_0, elastic modulus at high frequencies) and the decreases of ω_c. As a result, the ω_c of
70 the 50 mM and 100 mM EAMA solutions are too low to be detected, and the samples response like a strongly viscoelastic gel: *G'* is always above *G''*, and both moduli seem independent

of frequency. However, as we pointed out previously,[13] a surfactant worm gel should be a strongly viscoelastic solution with extremely long relaxation time (τ_R) instead of a real gel with infinite relaxation time. τ_R of the EAMA worm solutions can be estimated from the equation $\tau_R = \eta_0/G_0$. While this equation is normally used for Maxwellian fluids, it can also be used for the estimation of the τ_R of a "gel-like" sample.[13,34]

Usually, the dynamic rheological response of shorter-chain surfactant worms follows the Maxwellian model because of their short breaking times (τ_b) that allows fast-breaking of the so-called "living polymer" chains. However, it was suggested[11] that long-chain surfactant worms can have very long □b and do not allow the fast-breaking of the wormlike micellar chains, and thus show non-Maxwellian behaviors.
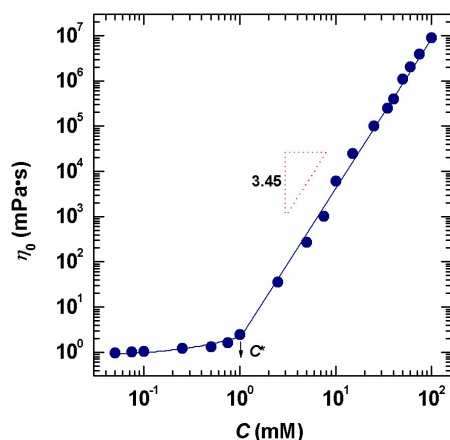

Fig. 8 Zero-shear viscosity (η_0) plotted as a function of EAMA concentration at pH 6.20 and 25 ºC.

Plotted in Fig. 8 is the concentration dependence of η_0 for the EAMA solutions at pH 6.20. The η_0–C curve can be separated into two parts at the critical surfactant concentration C^*. Below C^*, η_0 increases linearly in accordance with the Einstein equation[30]

$$\eta_0 = \eta_{water}(1 + KC) \tag{1}$$

where K is on the order of unit; above C^*, η_0 increases drastically following scaling law[29,35]

$$\eta_0 \propto C^n \tag{2}$$

wherein n is the power-law exponent. As shown in Fig. 8, C^* of the EAMA worms is 1 mM (~0.96‰, w/w), which is very close to that of the long-chain surfactant worms formed by EDAS,[12] and much lower than those of shorter-chain surfactant worms whose C^* ranges from ~ 1 mM to higher than 100 mM, depending on the composition of the wormlike micellar solution.[29] The extremely low C^* of the EDAS worms can be ascribed to its long hydrophobic tail and zwitterionic (non-charged) headgroup of which the repulsion between different headgroups is much weaker than that of the ionic surfactants. As compared to EDAS reported previsously,[12] C^* of EAMA should be much higher since it is a cationic surfactant with stronger repulsion between different headgroups, but why its C^* is as low as that of EDAS? Noting the structural feature of EAMA, one

may easily understand this. As stated above, EAMA is a "pseudo" gemini bearing two hydrophobic tails bridged by one maleate. This peculiar chemical structure probably allows it to behave as cationic gemini surfactants which are excellent thickening agents and tend to self-assemble into worms at very low surfactant concentration.
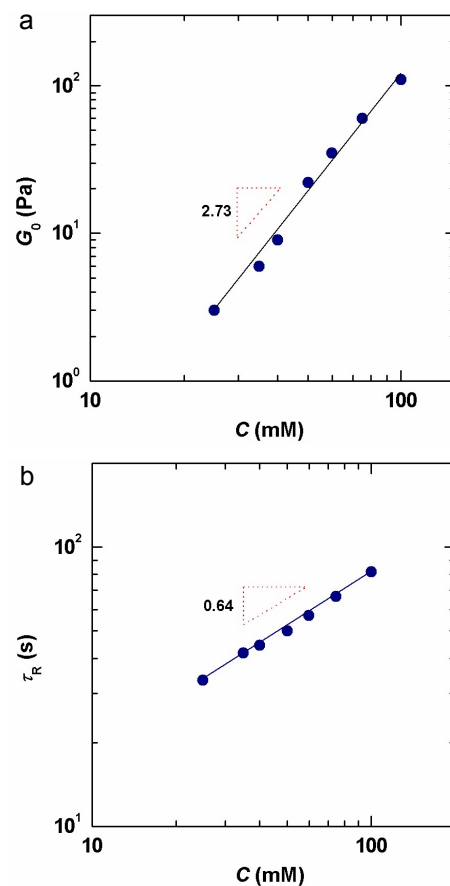

Fig. 9 Plateau modulus G_0 (a) and Relaxation time τ_R (b) plotted as a function of EAMA concentration at pH 6.20 and 25 ºC.

In the semidilute regime ($C > C^*$), the power-law exponent n reaches 3.45 (Fig. 8), which is quite in accordance with both theoretical predictions and experimental results for entangled worms.[36,37,38] The curves of plateau modulus G_0 and relaxation time τ_R (estimated by η_0/G_0) as a function of EAMA concentration also satisfy power law behavior, and the corresponding power-law exponents are 2.73 (Fig. 9a) and 0.64 (Fig. 9b), respectively. Both values are not so close to the corresponding theoretical forecast values 9/4 and 5/4 respectively;[36,37] however, as reviewed by Berret[39] different experimental tools can give different exponents.

Temperature dependence of rheological behaviors of EAMA worms at "on" state

Both theory and experiments suggest that zero-shear viscosity decreases exponentially with increasing temperature, following the Arrhenius plot[40]

$$\eta_0 = G_0 A e^{Ea/RT} \tag{3}$$

where T is the absolute temperature in K, Ea is the flow activation energy in J·mol⁻¹, R is the gas constant (8.315 J·mol⁻

$^1 \cdot K^{-1}$), and A is a pre-exponential factor. It is reported that Ea of the entangled linear wormlike micelles formed by the C_{22}-tailed surfactants, erucyl dimethyl amidopropyl betaine (EDAB),[11] and erucyl bis-(hydroxyethyl)methylammonium chloride (EHAC),[41]
5 is about 200 kJ·mol^{-1}; and in such a case, the increase of temperature by 10 ºC decreases the η_0 by about one order of magnitude. However, it is found that the EAMA worms in this work are more thermosensitive than those reported, *i.e.*, the increase of temperature by 5 ºC decreases the η_0 by about one
10 order of magnitude (Fig. 10). This can be further confirmed by plotting of η_0 versus 1/T (Fig. 10, inset). As is clearly exhibited, the slope of the experimental fitting line is 34, corresponding to Ea about 280 kJ·mol^{-1}. This is much higher than those of EDAB and EHAC, both of which are also C_{22}-tailed surfactants.
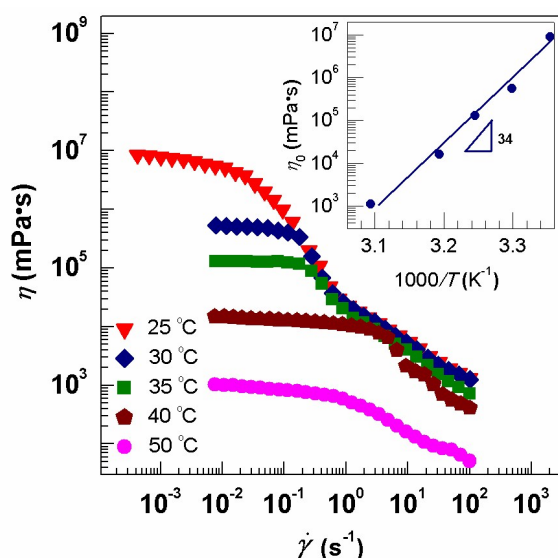
15

Fig. 10 Steady shear viscosity (η) plotted as a function of shear rate ($\dot{\gamma}$) for the 100 mM EAMA solution at pH 6.20 and varied temperatures. Inset: zero-shear viscosity (η_0) plotted as a function of T^{-1} for the 100
20 mM EAMA solution at pH 6.20. Solid circle stands for the experimental data, and the solid curve are the corresponding Arrhenius fitting line.
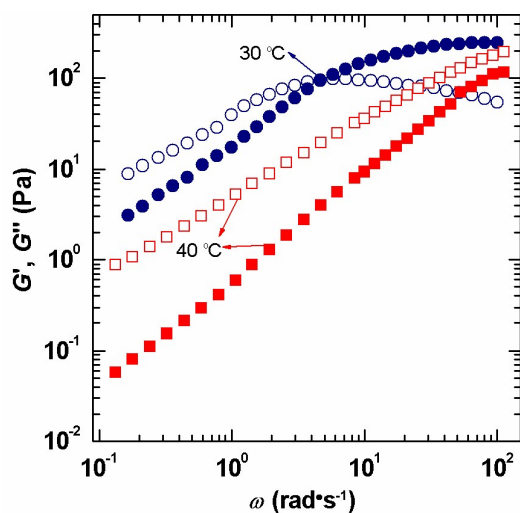

Fig. 11 Elastic (G', filled symbols) and viscous (G", open symbols) moduli plotted as a function of angular frequency for the 100 mM EAMA
25 solution (pH=6.20) at 30 and 40 °C.

The thermosensitive nature of the EAMA worms can also be demonstrated by dynamic rheological experiments. As described above, the 100 mM EAMA sample at 25 ºC behaves as a strongly elastic gel with G' always higher than G" (Fig. 7). However,
30 when the temperature is increased by just 5 ºC, the gel changes into a viscoelastic fluid with a very short relaxation time; when the temperature is further increased to 40 ºC, it becomes a viscous solution, *i.e.*, G' is always lower than G" , and both modulus are strong function of shear frequency (Fig. 11).
35 The thermosensitive nature of the EAMA worms may also find an explanation in terms of their "gemini-like" molecular architecture. The so-called "gemini-like" structure is not so stable as that of a real spacer in gemini surfactant since the electrostatic attraction is a weaker physical force as compared to a chemical
40 bond. When the temperature is increased, the weak electrostatic force will probably decrease substantially, as a result, the "gemini-like" structure will be destroyed. Therefore, the worms formed by "gemini-like" EAMA are more thermosensitive than other worms.

45 ## Conclusions

Rheological properties of wormlike micelles based on a pseudo Gemini surfactant EAMA, ultra-long-chain tertiary amine in the presence of maleic acid with molar ratio 2:1, were investigated. EAMA worms exhibit pH-responsiveness with reversibility. The
50 stimuli-responsive mechanism of the worms was attributed to the reversible protonation of the ultra-long-chain tertiary amine $UC_{22}AMPM$ by the added acid/base. EAMA worms possess excellent thickening ability and high thermosensitivity, which can be interpreted in terms of its "gemini-like" chemical structure.
55 When replacing the maleic acid by other acids such as hydrocloric acid, the worms also show pH stimulus response with switchability, but the viscosity maximum is much smaller than that of EAMA because of the absence of the Gemini-like architecture.

Notes and references

65 *^{a} State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute, Sichuan University, Chengdu 610065, P. R. China.*
^{b} Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, P. R. China. E-mail: zonglinchu@gmail.com

70 1   S. Lerouge and J.-F. Berret. *Adv. Polym. Sci.*, 2010, **230**, 1.
2   C. A. Dreiss. *Soft Matter*, 2007, **3**, 956.
3   H. Hoffmann. *Adv. Mater.*, 1994, **6**, 116–129.
4   H. Hoffmann and G. Ebert. *Angew. Chem. Int. Ed. Engl.*, 1988, **27**, 902.
75 5   M. E. Cates. *J. Phys. Fr.*, 1988, **49**, 1593.
6   M. E. Cates. *Macromolecules*, 1987, **20**, 2289.
7   H. Rehage and H. Hoffmann. *Mol. Phys.*, 1991, **74**, 933.
8   V. Croce, T. Cosgrove, G. Maitland, T. Hughes and G. Karlsson. *Langmuir*, 2003, **19**, 8536.
80 9   S. R. Raghavan, H. Edlund and E. W. Kaler. *Langmuir*, 2002, **18**, 1056.
10 Z. Chu and Y. Feng. *ACS Sustainable Chem. Eng.*, 2013, **1**, 75.

11 R. Kumar, G. C. Kalur, L. Ziserman, D. Danino and S. R. Raghavan. *Langmuir*, 2007, **23**, 12849.
12 Z. Chu, X. Su, Y. Han and Y. Feng. *Langmuir*, 2010, **26**, 7783.
13 Z. Chu and Y. Feng. *Soft Matter*, 2010, **6**, 6065.
14 Y. Han, Y. Feng, H. Sun, Z. Li, Y. Han and H. Wang. *J. Phys. Chem. B*, 2011, **115**, 6893.
15 Z. Chu, C. A. Dreiss and Y. Feng. *Chem. Soc. Rev.*, 2014, **42**, 7174.
16 X. Liu and N. L. Abbott. *J. Colloid Interface Sci.*, 2009, **339**, 1.
17 Yujun Feng, Zonglin Chu, Cécile A. Dreiss, *Smart wormlike micelles: design, characteristics and applications*, Berlin Springer Verlag, 2015.
18 K. Tsuchiya, Y. Orihara, Y. Kondo, N. Yoshino, T. Ohkubo, H. Sakai and M. Abe, *J. Am. Chem. Soc.*, 2004, **126**, 12282.
19 A. M. Ketner, R. Kumar, T. S. Davies, P. W. Elder and S. R. Raghavan, *J. Am. Chem. Soc.*, 2007, **129**, 1553.
20 Z. Chu and Y. Feng, *Chem. Commun.*, 2011, **47**, 7191.
21 Z. Yuan, W. Lu, W. Liu and J. Hao, *Soft Matter*, 2008, **4**, 1639.
22 Y. Lin, X. Han, J. Huang, H. Fu and C. Yu, *J. Colloid Interface Sci.*, 2009, **330**, 449.
23 Z. Chu and Y. Feng. *Chem. Commun.*, 2010, **46**, 9028.
24 C. B. Minkenberg, L. Florusse, R. Eelkema, G. J. M. Koper and J. H. van Esch. *J. Am. Chem. Soc.*, 2009, **131**, 11274.
25 Z. Chu and Y. Feng. *Synlett*, 2009, (**16**), 2655.
26 R. Oda, J. Narayanan, P. A. Hassan, C. Manohar, R. A. Salkar, F. Kern and S. J. Candau. *Langmuir*, 1998, **14**, 4364.
27 V. Corce, T. Cosgrove, C. A. Dreiss, S. King, G. Maitland and T. Hughes. *Langmuir*, 2005, **21**, 6762.
28 S. J. Candau and R. Oda. *Colloids Surf. A*, 2001, **183–185**, 5.
29 F. Kern, R. Zana and S. J. Candau. *Langmuir* 1991, **7**, 1344.
30 H. Hoffmann. Viscoelastic surfactant solutions, In Structure and Flow in Surfactant Solutions; Herb, C. A., Prud'homme, R. K., Eds.; American Chemical Society: Washington, DC, 1994.
31 H. Rehage and H. Hoffmann. *J. Phys. Chem.*, 1988, **92**, 4712.
32 A. Khatory, F. Kern, F. Lequeux, J. Appell, G. Porte, N. Morie, A. Otta, and W. Urbach. *Langmuir*, 1993, **9**, 933.
33 S. C. Sharma, L. K. Shrestha, K. Tsuchiya, K. Sakai, H. Sakai and M. Abe. *J. Phys. Chem. B*, 2009, **113**, 3043.
34 E. Buhler, S. J. Candau, E. Kolomiets and J.-M. Lehn. *Phys Rev. E*, 2007, **76**, 061804.
35 J.-F. Berret, J. Appell and G. Porte. *Langmuir*, 1993, **9**, 2851.
36 M. E. Cates and S. J. Candau. *J. Phys.:Condens. Matter*, 1990, **2**, 6869.
37 Y. A. Schipunov and H. Hoffmann. *Langmuir*, 1988, **14**, 6350.
38 H. Fan, Y. Yan, Z. Li, Y. Xu, L. Jiang, L. Xu, B. Zhang, J. Huang, *J. Colloid Interface Sci.*, 2010, **348**, 491.
39 J.-F. Berret. In Molecular Gels: Materials with Self-Assembled Fibrillar Networks; Weiss, R. G.; Terech, P. Eds., Springer, Dordrecht, The Netherlands, 2006.
40 S. J. Candau, E. Hirsch, R. Zana and M. Delsanti. *Langmuir*, 1989, **5**, 1225.
41 S. R. Raghavan and E. W. Kaler. *Langmuir*, 2001, **17**, 300.

Soft Matter Accepted Manuscript