

## Chapter 2

# Thermo-responsive Wormlike Micelles

**Abstract** This chapter summarizes findings on the simplest trigger applied to wormlike micellar: temperature. Thermo-thinning systems are not discussed since a viscosity decrease with temperature is a rather general characteristic of most systems. Instead, the unique thermo-viscosifying behaviour displayed by some WLMs and the possibility of imparting a pseudo “sol/gel” transition in specific systems are extensively addressed. These two types of systems show a transition from either a low-viscosity fluid or a viscoelastic solution to a gel-like state by tuning the temperature. The thermo-thickening behaviour and the underlying mechanisms of various types of thermo-thickening wormlike micellar systems (non-ionic, cationic, anionic, and zwitterionic) are discussed in terms of molecular structure–property relationships.

**Keywords** Thermo-responsive • Thermo-thickening • Thermo-viscosifying • Wormlike micelles • Sol/gel transition • Surfactant gel

This chapter deals with the simplest possible trigger, which is temperature. Stimuli responsiveness can be defined as a physicochemical change resulting from a small external variation in environmental conditions. From this point of view, one may regard both thermo-thinning (i.e. a viscosity decrease with temperature) and thermo-thickening (i.e. a viscosity increase with temperature) fluids as examples of temperature responsiveness. Generally, however, the micellar contour length decays exponentially with increasing temperature, which in turn leads to an exponential decrease in zero-shear viscosity  $\eta_0$ , following an Arrhenius law [1]:

$$\eta_0 = G_0 A e^{E_a/RT} \quad (2.1)$$

where  $A$  is a pre-exponential factor,  $T$  is the absolute temperature,  $E_a$  is the flow activation energy, and  $R$  is the gas constant. Thermo-thinning is therefore a general characteristic of WLMs and for this reason will not be discussed here. Instead, we will focus in this chapter on the unique thermo-viscosifying behaviour displayed by some WLMs [2–10] (Sect. 2.1) and the possibility of imparting a pseudo

“sol/gel” transition in some systems, with a transition from either a low-viscosity fluid or a viscoelastic solution to a gel-like sample [11–13] by playing on the temperature (Sect. 2.2). It is worth noting from the start that thermo-viscosifying WLMs do not necessarily show a thermo-thickening response over the whole temperature range. Instead, a maximum value is usually present in the curve of  $\eta_0$  as a function of temperature; therefore, a thermo-thickening response can be obtained at low temperatures while a thermo-thinning behaviour at high temperatures, separated by a critical temperature.

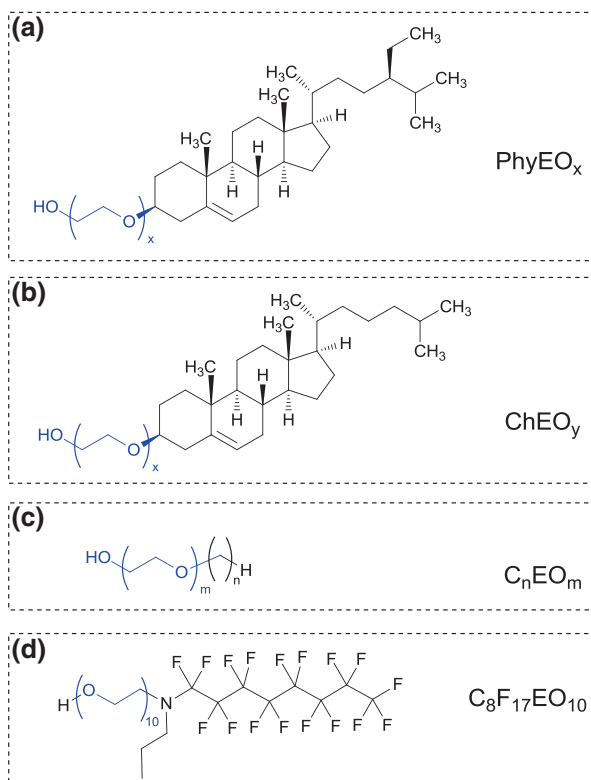
## 2.1 Thermo-thickening WLMs

Thermo-thickening WLMs have been reported for all types of surfactants: non-ionic, cationic, anionic, and zwitterionic. Their thermo-thickening behaviour and the underlying mechanisms are discussed in the following sections, which are organized according to the nature of the surfactant.

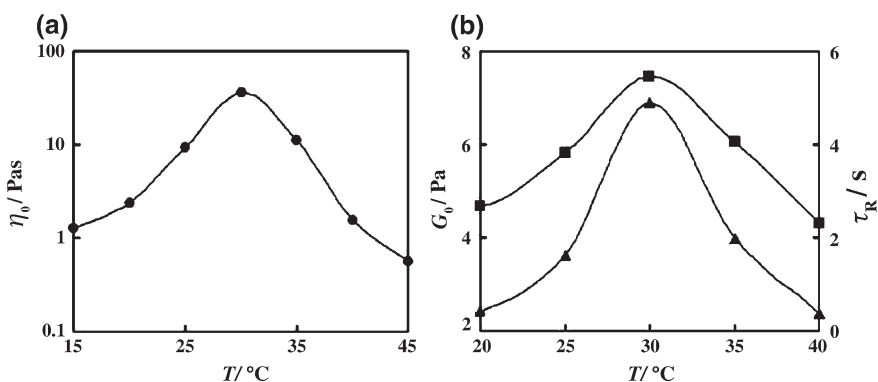
### 2.1.1 Thermo-thickening Non-ionic WLMs

Polyoxyethylene (PEG) is widely used as a responder to thermal stimulus, since the hydration of the oxyethylene unit is dramatically affected by temperature [14]: the hydration of PEG is weakened upon increasing the temperature, and thus, its solubility decreases. As a result, its corresponding aqueous solutions exhibit an upper miscibility gap with a lower critical solution point, usually referred to as a cloud point [15]. The biocompatibility of PEG is well known, and it has been approved for oral, subcutaneous, intramuscular, and intravenous injections into human bodies for biomedical applications [16]. Its unique thermo-responsiveness has been exploited to develop thermally responsive polymers [17–20], hydrogels [16, 21–23], molecular brushes [24], nanoparticles [25], nanofibres [26], and other thermally responsive materials [27]. In recent years, PEG has also been used to construct WLMs utilizing PEG-based non-ionic surfactants (Fig. 2.1), such as polyoxyethylene phytosteryl ether (PhyEO<sub>x</sub>, Fig. 2.1a) [14, 28], polyoxyethylene cholesteryl ether (ChEO<sub>y</sub>, Fig. 2.1b) [29, 30], polyoxyethylene alkyl ether (C<sub>n</sub>EO<sub>m</sub>, Fig. 2.1c) [31–34], and perfluoroalkyl sulphonamide ethoxylate (C<sub>8</sub>F<sub>17</sub>EO<sub>10</sub>, Fig. 2.1d) [35]. Similar to PEG-based macromolecules, these non-ionic wormlike micellar systems also display thermo-viscosifying behaviour [8, 14, 28, 30–34].

In a study on mixed non-ionic WLMs formed by PhyEO<sub>30</sub> and C<sub>12</sub>EO<sub>3</sub> in aqueous solutions, a maximum  $\eta_0$  was observed by Abe et al. [14] as a function of temperature, for a surfactant concentration of 5 wt% and mixing fraction ( $X$ , expressed as the weight fraction of C<sub>12</sub>EO<sub>3</sub>) of 0.36. As exhibited in Fig. 2.2a, upon increasing the temperature from 15 to 30 °C,  $\eta_0$  rises by more than one order of magnitude; upon a further increase in temperature,  $\eta_0$  decreases monotonically.



**Fig. 2.1** Structures of some amphiphiles involved in thermo-sensitive WLM formation and bearing polyoxyethylene headgroups: **a** PhyEO<sub>x</sub>, **b** ChEO<sub>y</sub>, **c** C<sub>n</sub>EO<sub>m</sub> and **d** C<sub>8</sub>F<sub>17</sub>EO<sub>10</sub>



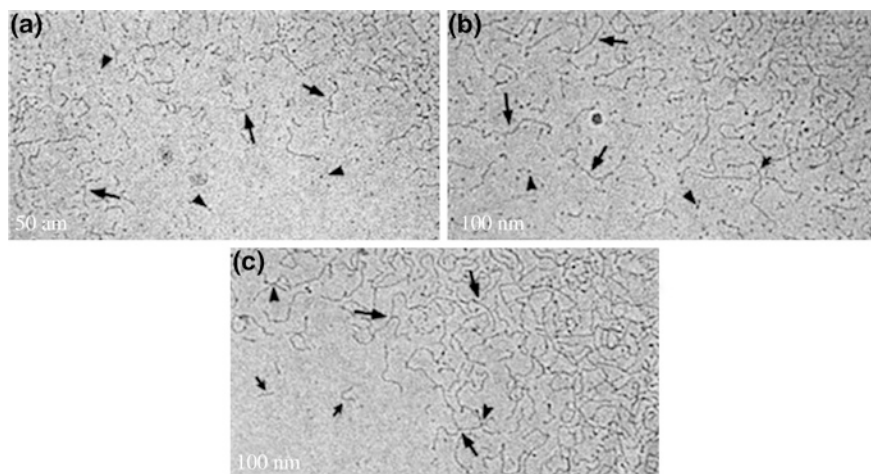
**Fig. 2.2** Variation of the zero-shear viscosity  $\eta_0$  (a) and plateau modulus  $G_0$  and relaxation time  $\tau_R$  (b) as a function of temperature ( $T$ ) for 5 wt% "PhyEO<sub>30</sub>/C<sub>12</sub>EO<sub>3</sub>" system at  $X = 0.36$ . Adapted with permission from Ref. [14]. Copyright (2009) American Chemical Society

Dynamic rheological experiments also demonstrated the thermo-viscosifying and thermo-thinning effects below and above 30 °C, respectively; that is, maximum values of  $G_0$  and  $\tau_R$  are present at 30 °C (Fig. 2.2b). From small-angle X-ray scattering (SAXS) measurements, micellar size, in terms of the maximum dimension of the aggregates ( $D_{\max}$ ), was seen to grow when increasing the temperature from 15 to 30 °C and then decrease at higher temperatures. The authors suggested that the thermo-viscosifying response below 30 °C could be understood in terms of the decrease in interfacial curvature of the aggregates due to the progressive dehydration of the PEG headgroups. Replacing  $C_{12}EO_3$  with monoglycerides such as monolaurin (ML) and monopalmitin (MP), the same group [30] again observed a thermo-thickening in the rheological response. For 10 wt% PhyEO<sub>30</sub>/ML solutions, when the mixing fraction  $X$ —expressed in weight fraction of ML (or MP for the other system)—ranged from 0.21 to 0.29, a gradual increase, followed by a decrease of the  $\eta_0$  versus  $T$  curve, was clearly observed. The behaviour of 10 wt% “PhyEO<sub>30</sub>/MP” was essentially similar, with the only exception that the viscosity growth was detected at higher temperatures, due to the longer hydrophobic chain of MP. The existence of a maximum was attributed to a temperature-induced micellar growth, followed by micellar branching. The interfacial curvature of the aggregates decreases with increasing temperature due to the progressive dehydration of the PEG headgroup and thus favours micellar growth; however, upon further increasing the temperature, intermicellar junctions are formed, and these connections can slide along the worms’ bodies, releasing the stress and thus resulting in a decrease of the viscosity, as speculated by the authors [30]. This “branching” has been widely documented in the WLMs literature, in general to explain the presence of a viscosity maximum as a function of salt or cosurfactant in mixed surfactant systems [36].

Very recently, the same authors [30] extended their work to the polyoxyethylene cholesteryl ether (ChEO<sub>20</sub>) wormlike micellar system, using cocamide monoethanolamine (C-11S) as a cosurfactant. For WLMs composed of 10 wt% ChEO<sub>20</sub> and 5.7 wt% C-11S, rheological measurements performed over a wide range of temperatures revealed changes in viscosity of various orders of magnitude upon small increases in the temperature. Ahmed and Aramaki [31] investigated the effect of PEG chain length on the temperature sensitivity of ChEO<sub>*x*</sub> WLMs, using ChEO<sub>15</sub> and ChEO<sub>30</sub> as a model surfactant and  $C_{12}EO_3$  as a cosurfactant. Again, the rheological properties of the worms were found to be highly sensitive to temperature, but largely dependent on the hydrophilic size of the surfactant: the ChEO<sub>30</sub> systems are less temperature sensitive than the ChEO<sub>15</sub> worm systems; that is, the increase of the PEG chain length reduces the thermo-sensitivity of the worms.

Aramaki et al. [8] also investigated the thermo-viscosifying effect of the non-ionic WLMs formed by  $C_{14}EO_3$  and Tween 80 in aqueous media. Upon increasing the temperature, the viscosity increased promptly. The authors suggested that one-dimensional micellar growth is enhanced at high temperature since the molecular cross-sectional area at the hydrophile–lipophile interface decreases gradually because of the dehydration of the polyoxyethylene chains, causing a reduction

in the spontaneous curvature and an increase in the end-cap energy. Constantin et al. [32] investigated the thermo-thickening mechanism of WLMs with the sole use of  $C_{12}EO_6$  as a model amphiphile, in the absence of any additives. For  $C_{12}EO_6$  concentrations between 5 and 35 wt%, it was found that the viscosity first increased with temperature and then decreased after reaching a maximum. The thermo-viscosifying temperature ranged from 0 to  $\sim 40^\circ\text{C}$ , depending on the surfactant concentration. Compared with  $C_{12}EO_6$  WLMs, the thermo-viscosifying range of  $C_{12}EO_8$  WLMs was shifted to higher temperatures [32], implying that an increase in PEG chain length can be used to tune the critical responsive temperature, in agreement with the findings by Ahmed and Aramaki discussed above [31]. Utilizing Cryo-TEM observation and light scattering techniques, Talmon et al. [33] examined the temperature sensitivity of WLMs formed by a similar polyoxyethylene alkyl ether,  $C_{12}EO_5$ . As shown in Fig. 2.3a, the coexistence of spheroidal (arrowheads) and rather short ( $<50$  nm) threadlike micelles (arrows) was observed at  $8^\circ\text{C}$ . Upon increasing the temperature to  $18^\circ\text{C}$  (Fig. 2.3b), longer flexible cylindrical micelles with contour lengths ranging between 50 and 100 nm were formed and a small number of threefold junctions or branching points (small arrows) were also observed. The micelles became much longer ( $>100$  nm) and the density of the threefold junctions higher (large arrows) with a further increase in temperature to  $29^\circ\text{C}$  (Fig. 2.3c). From static light scattering (SLS) measurements, the Rayleigh ratio was found to increase with temperature at a constant surfactant concentration, reflecting temperature-induced micellar growth.



**Fig. 2.3** Cryo-TEM images of a 0.5 wt% aqueous  $C_{12}E_5$  solution at three different temperatures. At  $8^\circ\text{C}$  (a), spheroidal (arrowheads) and rather short ( $<50$  nm) wormlike micelles (arrows) coexist. At  $18^\circ\text{C}$  (b), the coexistence of spheroidal (arrowheads) and cylindrical micelles (arrows) is again identified, but the worms are longer (50–100 nm) and threefold junctions (small arrow) are present. At  $29^\circ\text{C}$  (c), the worms are much longer ( $>100$  nm), and the density of the threefold junctions (larger arrows) is higher. Adapted with permission from Ref. [33]. Copyright (2000) American Chemical Society

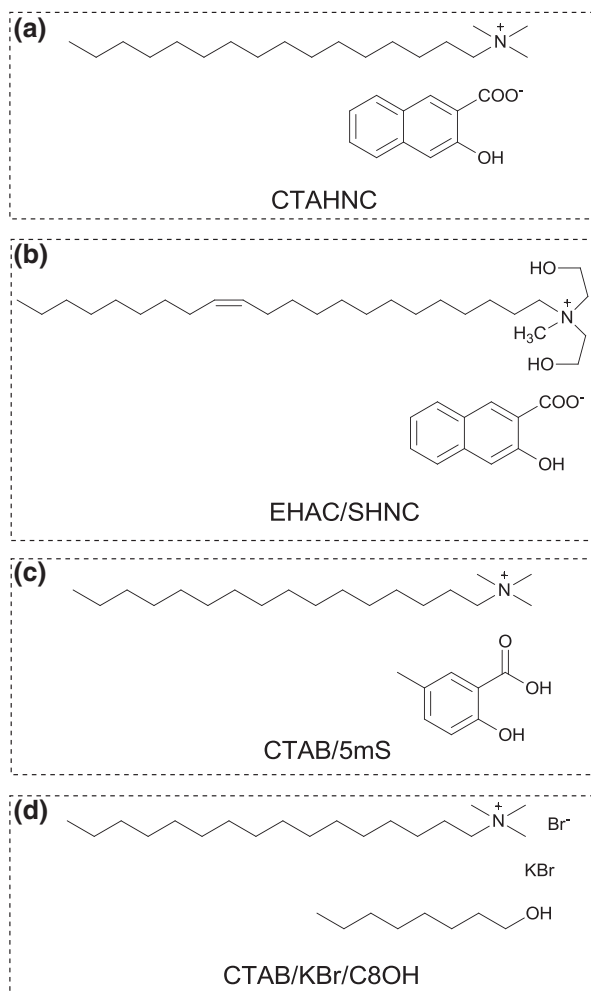
In addition to the above non-ionic thermo-thickening WLM systems, WLMs formed by the hybrid non-ionic surfactant perfluoroalkyl sulphonamide ethoxylate ( $\text{C}_8\text{F}_{17}\text{EO}_{10}$ ) were also found to display a thermo-thickening behaviour [35]. In this novel system, a thermo-viscosifying behaviour was detected at surfactant concentration as low as 1 wt%. Viscosity increased monotonously up to a critical temperature of ca. 35 °C, referred to as  $T_{\eta,\text{max}}$ , followed by a gradual decrease and ultimately phase separation. SAXS experiments revealed a gradual micellar growth until a slight “lamellar-like” structural pattern was observed at 45 °C. The authors speculated that this transition from WLMs to lamellar phase was probably related to the formation of micellar branching points. As the increase in temperature normally decreases the curvature, it is not yet clearly understood how a structural transition from WLMs to lamellar-like structures with a very low interfacial curvature could take place.

To summarize, non-ionic WLMs composed of PEG hydrophilic blocks have been shown to display thermo-viscosifying properties, since micellar growth (which leads to increased entanglements and longer relaxation processes) is favoured by heating due to the dehydration of the polyoxyethylene blocks [37, 38]. It is worth noting that heat-induced micellar growth (generally from globular micelles to short rods) has been widely reported for other than PEG-derived surfactants [34, 39–41]; however, viscoelasticity was not studied because the rods were not long enough to form a three-dimensional network.

### 2.1.2 Thermo-thickening Cationic WLMs

Since the early studies on rodlike or WLMs carried out by Debye and Anacker [42], and Nash [43], WLMs based on cationic surfactants have been extensively investigated [44–49]. However, cationic wormlike micelles with thermo-thickening rheological response have scarcely been reported. As summarized in Fig. 2.4, thermo-thickening behaviour in cationic WLMs has been found for cetyltrimethylammonium 3-hydroxynaphthalene-2-carboxylate (CTAHNC, Fig. 2.4a) [2, 7, 9, 50, 51], erucyl bis-(hydroxyethyl)methylammonium chloride (EHAC, Fig. 2.4b) [3] or CTAB (Fig. 2.4c, d) [4, 52] in the presence of strongly hydrophobic organic compounds: 3-hydroxynaphthalene-2-carboxylate ( $\text{HNC}^-$ , Fig. 2.4b) [3], 5-methyl salicylic acid (5mS, Fig. 2.4c) [4] or *n*-octanol ( $\text{C}_8\text{OH}$ , Fig. 2.4d) [52]. The corresponding thermo-thickening mechanism is usually ascribed to a micellar shape transition upon heating.

The first known example of thermo-thickening cationic WLMs was reported for aqueous solutions of the surfactant CTAHNC (Fig. 2.4a) by Manohar et al. [2]. CTAHNC was simply prepared by mixing CTAB and sodium 3-hydroxynaphthalene-2-carboxylate (SHNC), followed by removal of the inorganic counterions ( $\text{Na}^+$  and  $\text{Br}^-$ ) through a solvent extraction technique using methyl isobutyl ketone [7, 9] and then further purifying via recrystallization from a mixture of benzene, petroleum ether [9]. At concentrations higher than 3 wt% at room temperature, the samples were turbid and solidlike, consisting of lamellar dispersions,



**Fig. 2.4** Structures of thermo-thickening cationic WLMs reported in the literature: CTAHNC (a), EHAC/SHNC (b), CTAB/5mS (c), and CTAB/KBr/C8OH (d)

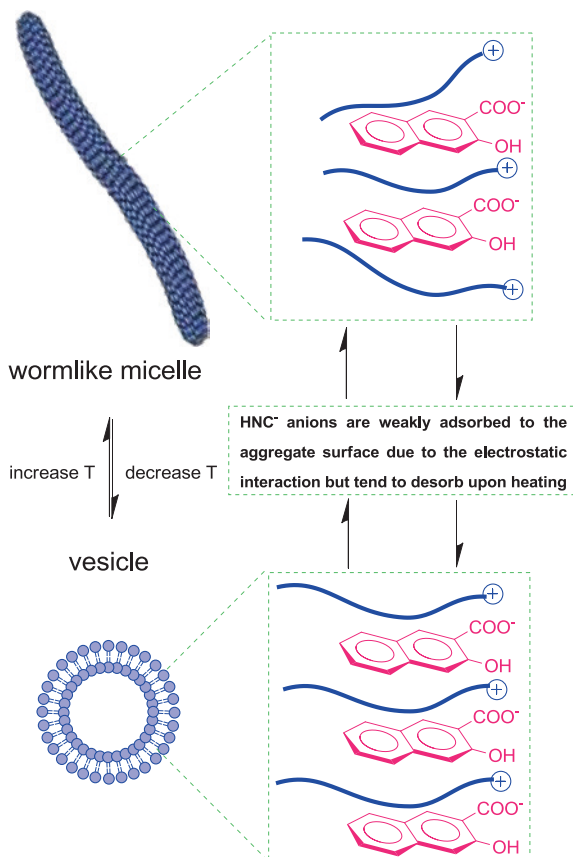
as demonstrated by polarized light microscopy [2]. Upon heating to well-defined temperatures, these samples turned into optically clear, strongly viscoelastic fluids, presumably consisting of long flexible WLMs. At 0.6 % (m/v), a CTAHNC solution also showed a turbid-to-clear transition, similar to the one observed at higher concentrations, accompanied by a viscosity increase by two orders of magnitude, as the solution became clear. However, the corresponding micellar transition was different from the concentrated samples. In the dilute regime, a vesicle-to-worm transition was detected by Cryo-TEM.

Soon after, Candau et al. [7] investigated the same micellar system, 0.6 wt% CTAHNC, at temperatures ranging from 30 to 70 °C. At temperatures up to 40 °C,

a low-viscosity vesicular solution phase was present, as demonstrated by rheology and optical microscopy. However, upon increasing the temperature to  $\sim 50$  °C or higher, highly elongated WLMs were formed, as suggested by rheological measurements. Rheological and optical experiments performed on mixed systems of 12 mM CTAHNC and small amounts of CTAB ( $\leq 2$  mM) also revealed a vesicle-to-worm transition upon heating [7]. SANS experiments performed by Mendes et al. [50] on the same solutions confirmed a phase transition from vesicles at 37 °C to WLMs at 55 °C. Differential scanning calorimetry (DSC) measurements on CTAHNC solutions carried out by Hoffmann et al. [51] showed a transition peak at 46 °C, independent of CTAHNC concentration, reflecting a transition within the lamellar phase at 46 °C due to the melting of the vesicle surface. Conductivity of the solution showed a jump at about the same temperature, implying the release of ions from the melting surface of the vesicles and implying a loss of surface-adsorbed  $\text{HNC}^-$  and their concomitant increase in the bulk water phase.

A possible mechanism for the vesicle-to-worm transition is schematically illustrated in Fig. 2.5 [52]. Vesicles are formed at low temperatures, because of the presence of an equimolar amount of  $\text{HNC}^-$  anions adsorbed at the aggregate

**Fig. 2.5** Mechanism of the vesicle-to-worm transition in the CTASHNC system. Reproduced from Ref. [52] with permission from The Royal Society of Chemistry

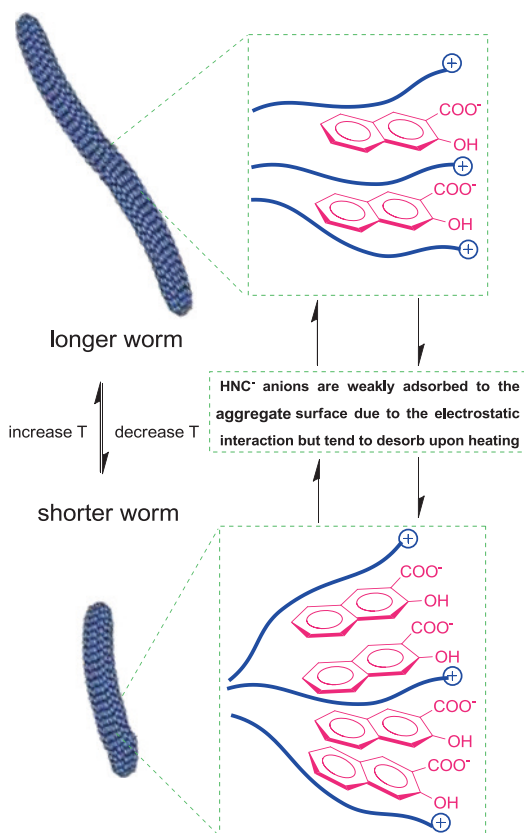




surface due to weak physical electrostatic forces. Upon heating, however, some of the  $\text{HNC}^-$  anions at the aggregate/water interface are transferred into the bulk as the weak physical adsorption is hindered by heating. This desorption changes the molecular geometry and hence reduces the interfacial curvature of the aggregates, inducing a transition from vesicles to WLMs. More details about the vesicle-to-worm transition of the CTAHNC systems can be found in the review by Narayanan et al. [9].

By simply mixing EHAC and SHNC without removing NaBr side product, Raghavan et al. [3] recently developed another type of thermo-viscosifying WLM system (Fig. 2.4b). A typical example of their experimental results on “40 mM EHAC/360 mM SHNC” is shown in Fig. 2.6 [52]. The sample is a low-viscosity, waterlike Newtonian fluid at 25 °C. However, upon gradual heating up to 45 °C, the viscosity increases steadily, while the fluid maintains its Newtonian behaviour. Upon raising the temperature further, the viscosity still increases continuously, but a shear-thinning response at high shear rates is observed for temperatures above 60 °C. When varying SHNC concentration, in some cases, the viscosity of the sample reaches a maximum at a critical temperature, beyond which it then

**Fig. 2.6** Mechanism of the rod-to-worm transition in the EHAC/SHNC system. Adapted with permission from Ref. [52]. Copyright (2013) Royal Society of Chemistry



decreases. The onset and magnitude of the viscosity increase, as well as the peak temperature, can all be altered by varying SHNC concentration. SANS data confirmed an increase in contour length of the micelles with temperature, at the origin of the thermo-thickening behaviour. The heat-induced increase in contour length was attributed to a temperature-dependent counterion binding at the micelle/water interface (Fig. 2.6). This is different from the case of CTAHNC since an excess of SHNC is present in such solutions.  $\text{HNC}^-$  anions are strongly hydrophobic, and the  $\text{HNC}^-$  ions in excess stay near the micelle/water interface, resulting in a higher interfacial curvature, thereby forming shorter rods at lower temperature. Upon heating, some of the  $\text{HNC}^-$  anions at the micelle/water interface shift to the bulk [3] as the weak physical adsorption forces are overcome, similar to the case of CTASHNC. However, in contrast to the former system, desorption reduces the interfacial curvature, thus favouring the growth of the worms.

Following this study, the same group developed another thermo-viscosifying WLM system (Fig. 2.4c) [4], based on the simple mixing of CTAB with the hydrotrope 5mS. A transition from a bluish, low-viscosity liquid around 48 °C to a colourless, perceptibly viscous and flow-birefringent fluid at about 54 °C was detected over a range of concentrations. A typical study of optical density at 500 nm and  $\eta_0$  as a function of temperature for a sample containing 12.5 mM CTAB and 20 mM 5mS suggested a micellar transition from vesicle to worm upon heating, and this interpretation was further confirmed by SANS. It is worth noting that the transition is temperature switchable; that is, vesicles that are disrupted into worms upon heating can be re-formed upon cooling. Both the transition temperature and the magnitude of the viscosity increase could be finely-tuned by varying sample composition. The mechanism responsible for the vesicle-to-worm transition upon heating was attributed to a temperature-dependent counterion binding at the micelle/water interface, similar to the CTAHNC system discussed above.

Sreejith et al. [53] investigated the mixture of CTAB and  $\text{C}_8\text{OH}$  in the presence of KBr (Fig. 2.4d) and observed a thermally-induced response for  $\text{C}_8\text{OH}/\text{CTAB}$  molar ratios above  $\sim 0.25$ . Based on rheological measurements, dynamic light scattering (DLS) analysis, and Cryo-TEM observation, the authors ascribed the thermo-response to a vesicle-to-worm transition. At low temperatures, a sufficient amount of  $\text{C}_8\text{OH}$  molecules were expected to be inserted between CTAB molecules to promote vesicle formation. However, upon increasing the temperature,  $\text{Br}^-$  ions were released into the bulk water, favouring the increase of the interfacial curvature and thus a transition to WLMs.

Thermo-thickening cationic WLMs have thus been prepared with long-chain cationic surfactants in the presence of strongly hydrophobic hydrotropes. The underlying thermo-thickening mechanism is usually attributed to a modification of the micellar architecture, caused by a change in the interfacial curvature prompted by a depletion of the hydrotropes at the micelle/water interface at high temperature.

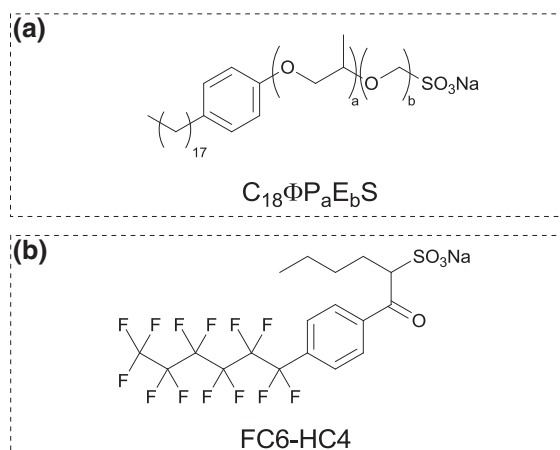
### 2.1.3 Thermo-thickening Hybrid WLMs

Pioneering studies on anionic thermo-thickening viscoelastic surfactants can be tracked back to 1988 [10], though no verification was made by Cryo-TEM observation at that time. Similar to PEG-derived non-ionic surfactants described above, the PEG-derived anionic surfactant octadecylphenylalkoxysulphonate ( $C_{18}\phi P_5E_{11}S$ , Fig. 2.7a) also shows a thermo-viscosifying behaviour, due to the presence of PEG units that are thermally responsive. For example, 10 mM  $C_{18}\phi P_5E_{11}S$  solution is a waterlike Newtonian fluid composed of globular micelles at temperatures below  $\sim 45^\circ\text{C}$  and becomes a shear-thinning fluid composed of WLMs at high temperatures. The mechanisms underlying the thermo-responsive behaviour of  $C_{18}\phi P_5E_{11}S$  WLMs, however, are similar to the PEG-based non-ionic surfactants discussed in Sect. 2.1.1, i.e. a dehydration of PEG chains, inducing micellar growth and a subsequent viscosity increase.

Apart from this particular example, no other common anionic WLMs have been found to show a thermo-thickening rheological response; however, some specific anionic surfactants with a hybrid structure, such as sodium 1-[4-(tridecafluorohexyl)phenyl]-1-oxo-2-hexanesulphonate (FC6-HC4, Fig. 2.7b) [5, 6], have been shown to possess such an unusual behaviour.

Yoshino et al. [54] synthesized the fluoro-hybrid anionic surfactant FC6-HC4 by reacting 1-[4-(perfluoroalkyl)phenyl]-1-alkanones with a sulphur trioxide/1,4-dioxane complex in 1,2-dichloroethane, followed by neutralization with aqueous sodium hydroxide, and then investigated its rheological behaviour as a function of temperature [6, 54]. A thermo-thickening response was detected for concentrations ranging from 7 to 15 wt%; the viscosity peak and corresponding temperature could be tuned by varying surfactant concentration [6]. Since thermo-viscosifying was not observed for monohydrocarbon chain surfactants, such as 1-pentanesulphonic

**Fig. 2.7** Structures of hybrid anionic surfactants showing a thermo-thickening rheological response

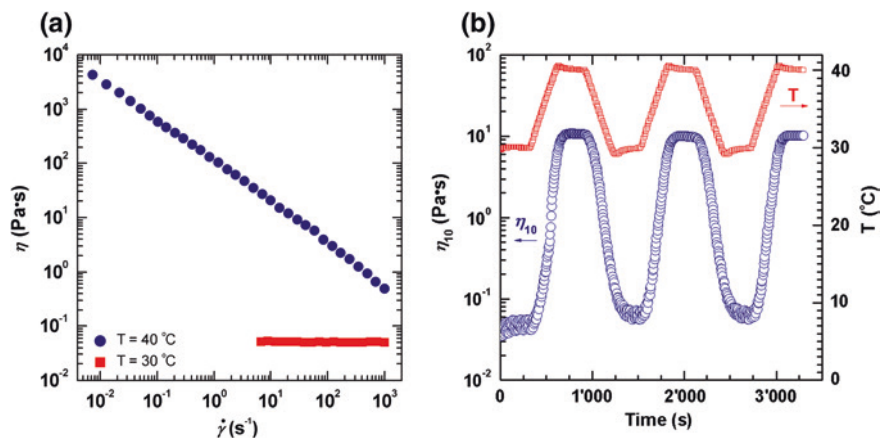


acid sodium salt and SDS, or monofluorocarbon chain-type surfactants such as perfluoroheptanoate, or neither fluoro-hybrid-type surfactants such as sodium 1-[4-(tridecafluorohexyl)phenyl]-1-oxo-2-butanedisulphonate (FC6–HC2), sodium 1-[4-(nonafluorobutyl)phenyl]-1-oxo-2-octadisulphonate (FC4–HC6), and its double hydrocarbon chain counterpart, sodium 1-(4-hexylphenyl)-1-oxo-2-hexanesulphonate (HC6–HC4), the authors assigned the unique thermo-responsive behaviour of FC6–HC4 micellar solutions to its peculiar chemical structure, i.e. a hybrid fluorocarbon/hydrocarbon double chain, with six carbon atoms in the fluorocarbon chain and four carbon atoms in the hydrocarbon chain [5, 6, 55]. Cryo-TEM measurements [56] were later undertaken, in combination with rheology, digital light microscopy, and self-diffusion NMR. Cryo-TEM revealed a heat-induced micellar transition from mainly short rodlike micelles at 20 °C to very large multilamellar vesicles at temperatures at 30 and 40 °C, and to a disordered lamellar phase at 50 °C and above [56]. Although the structure of the assemblies present at the temperature of 36 °C, i.e. where the viscosity showed a maximum—could not be elucidated by Cryo-TEM (due to an on-the-grid transformation during specimen preparation), rheology and self-diffusion NMR experiments indicated the presence around 40 °C of assemblies that are larger than those present at lower (mainly short rodlike micelles) and higher temperatures (a disordered multiconnected lamellar phase), which could explain the thermo-responsive behaviour [56].

### 2.1.4 Thermo-thickening Zwitterionic WLMs

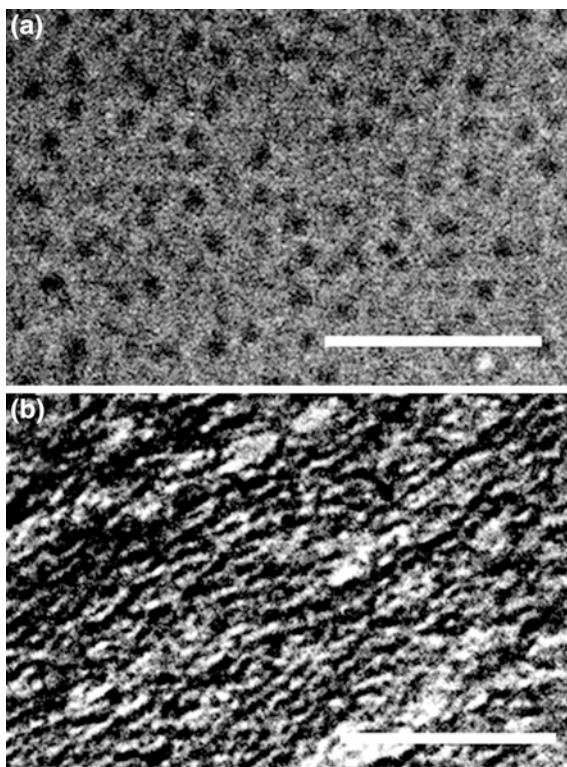
Despite being very gentle on the human skin and more environmentally friendly because of their neutral charge, zwitterionic surfactant WLMs have been scarcely reported [11, 57–61] compared to non-ionic, cationic, and anionic surfactants. To the best of our knowledge, only one type of thermo-thickening zwitterionic WLMs has been reported, which was recently developed by Chu and Feng using a synthesized sulphobetaine amphiphile, 3-(*N*-palmitamidopropyl-*N,N*-dimethyl ammonium) propane sulphonate (PDAS, Fig. 2.10d) [57].

The steady-state rheological behaviour of 1.0 M PDAS solution in the presence of 0.5 M NaCl is shown in Fig. 2.8. The shear viscosity of the sample (Fig. 2.8a) at 30 °C remains constant at 0.05 Pa s, regardless of shear rate, typical of Newtonian flow behaviour. Such low viscosity in surfactant solutions is usually attributed to the presence of globular micelles or short rodlike micelles (Fig. 2.9a). However, upon increasing the temperature to 40 °C, the same solution becomes shear thinning, which is well acknowledged as the evidence of WLMs becoming aligned in the flow field (Fig. 2.9b). The high viscosity of this solution could be switched on and off by altering the temperature. As exhibited in Fig. 2.9b, the apparent viscosity at a shear rate of  $10 \text{ s}^{-1}$  ( $\eta_{10}$ ) stays constant at 0.05 Pa s and 30 °C; however, when increasing the temperature from 30 to 40 °C,  $\eta_{10}$  increases 200-fold because of the thermal stimulus. Dynamic rheology also revealed an interesting thermo-switchable transition, which is discussed in the next section.



**Fig. 2.8** Thermal stimuli response of the PDAS/NaCl solution: shear viscosity  $\eta$  as a function of shear rate  $\dot{\gamma}$  (a) and thermo-reversible viscosity at shear rate of  $10 \text{ s}^{-1}$ ,  $\eta_{10}$  (b). Reproduced from Ref. [57] with permission from The Royal Society of Chemistry

**Fig. 2.9** Cryo-TEM observations of the  $30^\circ\text{C}$  (a) and  $40^\circ\text{C}$  (b) PDAS/NaCl solutions. Bars are 100 nm. Reproduced from Ref. [57] with permission from The Royal Society of Chemistry



## 2.2 WLMs with Thermo-induced “Sol/Gel” Transition

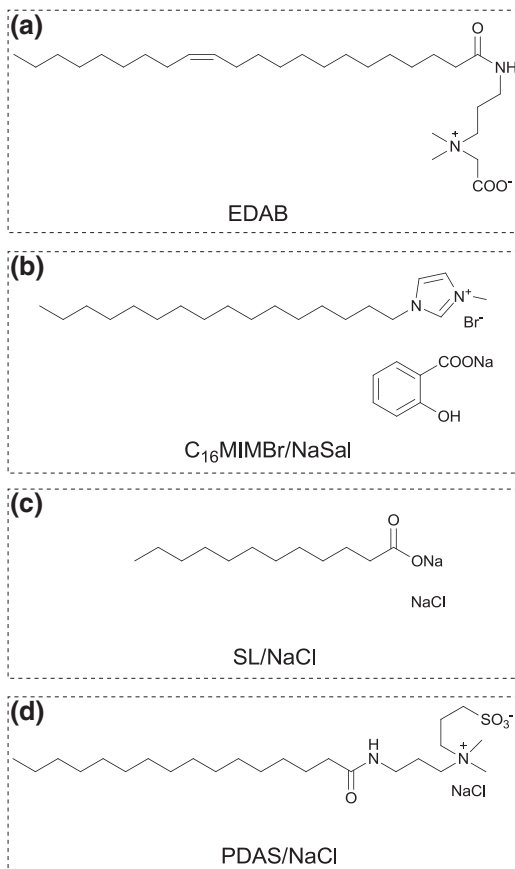
The typical rheological behaviour of WLM solutions follows the Maxwell model; namely, it displays a combination of viscous and elastic behaviour with a single relaxation time. However, a number of WLM systems have been reported which depart from this typical behaviour and are considerably stiffer, with very high values of  $G'$  and  $G''$ , showing very little dependence on shear frequency, thereby making them similar to gels. As such, they offer considerable potential for biomedical applications, in particular tissue engineering [62], if stimulus responsiveness can be imparted to them. In tissue repair, hydrogels are used as scaffolds, either combined with the patients' own cells or using the body as a bioreactor; injectable in situ gelling materials reactive to a range of stimuli are of interest, in particular responsiveness to temperature, in order to trigger gelation upon contact with the body. While the vast majority of thermally responsive gelators reported to date are polymers or peptides, surfactant gels based on the reversible formation and entanglement of long flexible wormlike micelles show considerable promise [11, 57, 59, 63].

We begin the discussion with a very brief account of gels and so-called surfactant gels. A gel is usually loosely identified on the basis of its ability to withstand its own weight under gravity in an inverted vial; more rigorously, in dynamic rheology, its elastic modulus  $G'$  is always higher than its viscous  $G''$ , and both are independent of shear frequency [64]. The strict definition of a “gel” has historically always been a topic of contention; the term is widely misused in the literature to describe a material that is “gel-like” but does not satisfy the strict rheological definition [64, 65]. The term “surfactant gel” has been applied to WLM networks in several reviews [63, 64], and we use it here to describe WLM systems showing a rheological behaviour characterized by  $G' > G''$  and largely independent of frequency over a very wide range.

A detailed rheological investigation of such a surfactant gel was carried out by Chu et al. [58] on 3-(*N*-erucamidopropyl)-*N,N*-dimethyl ammonium) propane sulfonate (EDAS) as a model system. Their results revealed a finite  $\eta_0$ , and that  $G'$  and  $G''$  should cross over at a very low shear frequency, not accessible; thereby, “surfactant gels” are strongly solidlike viscoelastic fluids with a finite  $\eta_0$  and ultra-long  $\tau_R$  rather than a “real” gel with infinite  $\eta_0$  and  $\tau_R$ . Based on these definitions, we can now discuss examples of thermo-induced “sol/gel” transitions in WLM systems reported in the literature (Fig. 2.9).

Raghavan et al. [11] investigated the “sol/gel” transition of WLMs formed by EDAB (Fig. 2.10a). At temperatures below 40 °C, concentrated EDAB solutions (for instance 50 and 100 mM) were strongly gel-like with  $G'$  exceeding  $G''$  over the entire experimental frequency range ( $10^{-2}$ – $10^1$  rad s<sup>-1</sup>), both of which were slight functions of shear frequency, which made these samples similar to elastic gels. However, one cannot exclude that  $G'$  and  $G''$  may cross over at a frequency much lower than the experimentally accessible range, for instance,  $10^{-3}$  rad s<sup>-1</sup> or even lower. In any case, the relaxation time  $\tau_R$  should be very long: at least  $10^3$  s from a simple estimate of  $1/\tau_R$ . Cryo-TEM and SANS revealed the presence of WLMs in

**Fig. 2.10** Thermo-responsive WLM systems reported in the literatures: EDAB (a), C<sub>16</sub>MIMBr/NaSal (b), SL/NaCl (c), and PDAS/NaCl (d)

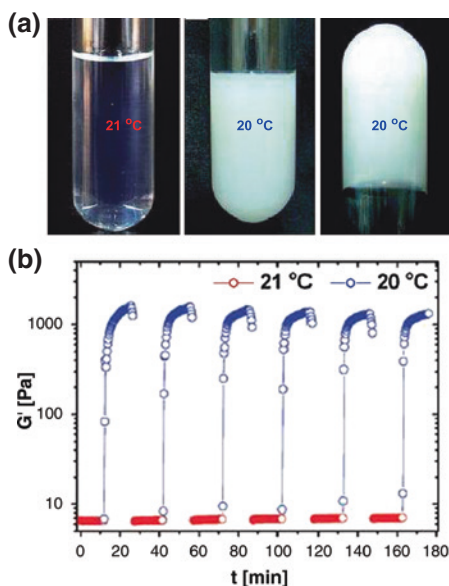


these concentrated EDAB solutions. Upon increasing the temperature to 60 °C and above, the EDAB gels became Maxwellian with much shorter  $\tau_R$ , about 300 and 40 s for 50 mM EDAB at 60 and 70 °C, and 100 and 15 s for 100 mM EDAB at 65 and 75 °C, respectively. The ultra-long  $\tau_R$  of concentrated EDAB samples at low temperatures was ascribed to its extremely long breaking time, possibly linked to its ultra-long C22 hydrophobic tail. Later, work on another C22-tailed zwitterionic surfactant EDAS by Chu and Feng [57] was also consistent with this speculation. Therefore, the “sol/gel” transition mechanism for EDAB WLMs is the decrease of  $\tau_R$  upon increasing the temperature. Interestingly, the “sol/gel” transition of EDAB is unusual since the plateau modulus  $G_0$  before and after the transition is almost the same.

Huang et al. [12] reported a novel thermo-responsive WLM gel (Fig. 2.11b) with a narrow temperature “window” based on a mixture of 1-hexadecyl-3-methylimidazolium bromide (C<sub>16</sub>MIMBr) and sodium salicylate (NaSal). Figure 2.11a depicts the visual appearance of the “sol/gel” transition of “40 mM C<sub>16</sub>MIMBr/28 mM NaSal” WLM solution. At 21 °C, the sample is transparent and shows low viscosity. Upon decreasing the temperature to 20 °C, it instantaneously becomes



**Fig. 2.11** The thermo-responsive “sol/gel” transition of the  $C_{16}MIMBr/NaSal$  WLM system. Adapted from Ref. [12] with permission from The Royal Society of Chemistry

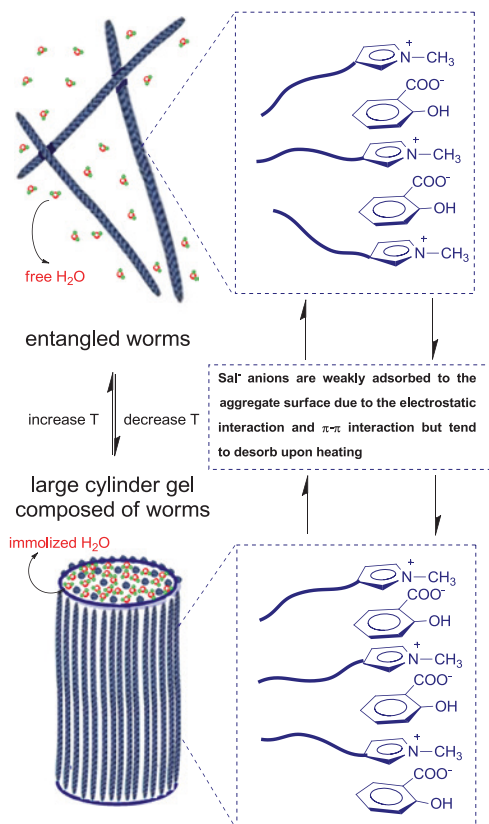


opalescent and can be turned upside down without flowing. This suggests a sol/gel transition upon cooling, which was further confirmed by dynamic rheology. As shown in Fig. 2.11b, the sol-to-gel transition is reversible, which means that a fluid and a gel can always be obtained by increasing and decreasing the temperature between 21 and 20 °C. In contrast to the case of EDAB WLMs described above, in which no detectable change in  $G_0$  occurred between the “sol” and “gel” states,  $G'$  in the  $C_{16}MIMBr/NaSal$  system showed an abrupt jump of over two orders of magnitude, before and after the transition. Scanning electron microscopy (SEM) at 20 °C revealed the presence of a network of large cylindrical structures with diameters ranging from 1 to 2  $\mu\text{m}$ , responsible for the formation of the hydrogel, since large amounts of water could be immobilized. Similarly, a previous work on another thermo-responsive gel formed by sodium laurate (SL, Fig. 2.10c) in the presence of NaCl, reported by Hao et al. [13], revealed the presence of a network of fibres composed of bundles of parallel WLMs, as assessed by high-resolution transmission electron microscopy (HR-TEM). In both systems [12, 13], the large cylinders were hypothesized to originate from the crystallization of WLMs, since the physical interaction between surfactant headgroups and added salt was modified upon cooling.

A possible mechanism for this type of thermo-responsive gels, taking the  $C_{16}MIMBr/NaSal$  system as an example, is illustrated schematically in Fig. 2.12. At 21 °C and above, the  $Sal^-$  anions are adsorbed at the micelle/water interface due to a combination of the following three physical interactions: the hydrophobic effect of the benzene ring, the electrostatic interaction between the ammonium cations and  $Sal^-$  anions, and the  $\pi$ - $\pi$  interaction between the benzene ring and the imidazolium ring. However, upon cooling to 20 °C and below, more  $Sal^-$  are

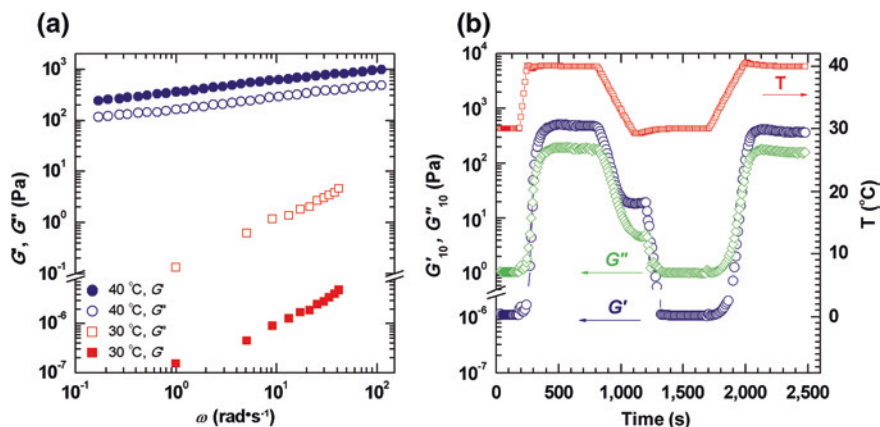


**Fig. 2.12** Mechanism of the “sol/gel” transition in the  $C_{16}MIMBr/NaSal$  WLM system. Adapted from Ref. [52] with the permission from The Royal Society of Chemistry

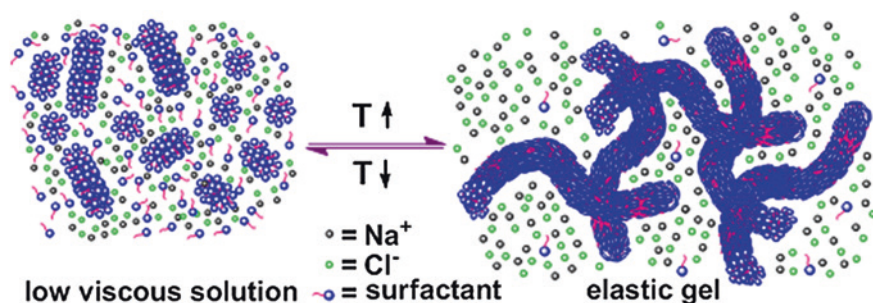


adsorbed at the interface since the physical interactions are slightly strengthened, which slightly increases the interfacial curvature, inducing the fusion of the WLMs and thereby the formation of large cylinders composed of WLMs [12].

All the above WLM gels exhibit a common characteristic of gelation upon cooling. Instead, the thermo-switchable gel based on PDAS (Fig. 2.10d) shows the remarkable characteristic of gelation upon heating [57]. As discussed above, concentrated PDAS solutions showed a thermo-thickening behaviour in steady-state rheology. Dynamic rheology measurements (Fig. 2.13a) show a clear viscous response for a 1.0 M PDAS solution in the presence of 0.5 M NaCl at 30 °C, with a characteristic  $G'$  much lower than  $G''$  over the entire shear frequency range. Upon heating to 40 °C, both  $G'$  and  $G''$  increase by several orders of magnitude, and the rheological response becomes elastic, with  $G'$  exceeding  $G''$  for all shear frequencies measured. The gelling process could be reversed by cooling, which enables one to switch the gel between an “on” and “off” state simply by heating and cooling, respectively (Fig. 2.13b). As schematically illustrated in Fig. 2.14, the mechanism of the switchable gelation was ascribed to the strengthened “salting-out” effect at increased temperature. At lower temperatures (ca. 30 °C), the “salting-out”



**Fig. 2.13** Thermal response of the PDAS/NaCl solution: elastic ( $G'$ ) and viscous ( $G''$ ) modulus as a function of oscillatory shear frequency  $\omega$  (a) and thermo-reversible gelling processes (b). Reproduced from Ref. [57] with permission from The Royal Society of Chemistry



**Fig. 2.14** Schematic illustration of the switchable gelation mechanism. Reproduced from Ref. [57] with permission from The Royal Society of Chemistry

effect of PDAS caused by the added salt is weaker, and thus, more PDAS molecules are present as monomers. However, upon increasing the temperature to 40 °C, the “salting-out” effect becomes stronger, and thus, the solubility of the hydrophobic moieties of PDAS tail worsens, enhancing micellization and the growth of the micelles from short rods into entangled long worms. The micellar structures immobilize the water, thereby resulting in the formation of a hydrogel. Upon decreasing back the temperature to its initial value, the entangled worms are lost due to the transfer of amphiphiles from the micellar phase to the bulk, and the self-assembly structures as well as the rheological properties revert back to the initial state.

Some WLM systems have thus proven to be effective thermo-switchable gelators and could therefore find interesting applications, offering generally, over traditional gelators, facile synthesis, simple mechanisms of gelation, and cost-effectiveness.

## References

1. Candau SJ, Hirsch E, Zana R, Delsanti M (1989) Rheological properties of semidilute and concentrated aqueous solutions of cetyltrimethylammonium bromide in the presence of potassium bromide. *Langmuir* 5:1225–1229
2. Salkar RA, Hassan PA, Samant SD, Valaulikar BS, Kumar VV, Kern F, Candau SJ, Manohar C (1996) A thermally reversible vesicle to micelle transition driven by a surface solid–fluid transition. *Chem Commun* 10:1223–1224
3. Kalur GC, Frounfelker BD, Cipriano BH, Norman AI, Raghavan SR (2005) Viscosity increase with temperature in cationic surfactant solutions due to the growth of wormlike micelles. *Langmuir* 21:10998–11004
4. Davies TS, Ketner AM, Raghavan SR (2006) Self-assembly of surfactant vesicles that transform into viscoelastic wormlike micelles upon heating. *J Am Chem Soc* 128:6669–6675
5. Abe M, Tobita K, Sakai H, Kamogawa K, Momozawa N, Kondo Y, Yoshino N (2000) Thermoresponsive viscoelasticity of concentrated solutions with a fluorinated hybrid surfactant. *Colloid Surf A-Physicochem Eng Asp* 167:47–60
6. Tobita K, Sakai H, Kondo Y, Yoshino N, Kamogawa K, Momozawa N, Abe M (1998) Temperature-induced critical phenomenon of hybrid surfactant as revealed by viscosity measurements. *Langmuir* 14:4753–4757
7. Hassan PA, Valaulikar BS, Manohar C, Kern F, Bourdieu L, Candau SJ (1996) Vesicle to micelle transition: rheological investigations. *Langmuir* 12:4350–4357
8. Varade D, Ushiyama K, Shrestha LK, Aramaki K (2007) Wormlike micelles in Tween-80/ $C_mEO_3$  mixed nonionic surfactant systems in aqueous media. *J Colloid Interface Sci* 312:489–497
9. Narayanan J, Mendes E, Manohar C (2002) Vesicle to micelle transition driven by surface solid–fluid transition. *Int J Mod Phys B* 16:375–382
10. Greenhill-Hooper MJ, O'Sullivan TP, Wheeler PA (1988) The aggregation behavior of octadecylphenylalkoxysulfonates: I. Temperature-dependence of the solution behavior. *J Colloid Interface Sci* 124:77–87
11. Kumar R, Kalur GC, Ziserman L, Danino D, Raghavan SR (2007) Wormlike micelles of a C22-tailed zwitterionic betaine surfactant: from viscoelastic solutions to elastic gels. *Langmuir* 23:12849–12856
12. Lin Y, Qiao Y, Yan Y, Huang J (2009) Thermo-responsive viscoelastic wormlike micelle to elastic hydrogel transition in dual-component systems. *Soft Matter* 5:3047–3053
13. Yuan Z, Lu W, Liu W, Hao J (2008) Gel phase originating from molecular quasi-crystallization and nanofiber growth of sodium laurate-water system. *Soft Matter* 4:1639–1644
14. Sharma SC, Shrestha LK, Tsuchiya K, Sakai K, Sakai H, Abe M (2009) Viscoelastic wormlike micelles of long polyoxyethylene chain phytosterol with lipophilic nonionic surfactant in aqueous solution. *J Phys Chem B* 113:3043–3050
15. Strunk H, Lang P, Findenegg GH (1994) Clustering of micelles in aqueous solutions of tetraoxyethylene-*N*-octyl ether (C(8)E(4)) as monitored by static and dynamic light-scattering. *J Phys Chem* 98:11557–11562
16. Moon HJ, Ko DY, Park MH, Joo MK, Jeong B (2012) Temperature-responsive compounds as in situ gelling biomedical materials. *Chem Soc Rev* 41:4860–4883
17. Lee H, Pietrasik J, Sheiko SS, Matyjaszewski K (2010) Stimuli-responsive molecular brushes. *Prog Polym Sci* 35:24–44
18. Lutz J-F, Akdemir O, Hoth A (2006) Point by point comparison of two thermosensitive polymers exhibiting a similar LCST: is the age of poly(NIPAM) over? *J Am Chem Soc* 128:13046–13047
19. Lutz J-F, Hoth A (2006) Preparation of ideal PEG analogues with a tunable thermosensitivity by controlled radical copolymerization of 2-(2-methoxyethoxy)ethyl methacrylate and oligo(ethylene glycol) methacrylate. *Macromolecules* 39:893–896

20. Munoz-Bonilla A, Fernandez-Garcia M, Haddleton DM (2007) Synthesis and aqueous solution properties of stimuli-responsive triblock copolymers. *Soft Matter* 3:725–731
21. Yin XC, Stover DH (2003) Hydrogel microspheres formed by complex coacervation of partially MPEG-grafted poly(styrene-alt-maleic anhydride) with PDADMAC and cross-linking with polyamines. *Macromolecules* 36:8773–8779
22. Lutz J-F, Weichenhan K, Akdemir O, Hoth A (2007) About the phase transitions in aqueous solutions of thermoresponsive copolymers and hydrogels based on 2-(2-methoxyethoxy)ethyl methacrylate and oligo(ethylene glycol) methacrylate. *Macromolecules* 40:2503–2508
23. Hwang MJ, Suh JM, Bae YH, Kim SW, Jeong B (2005) Caprolactonic poloxamer analog: PEG-PCL-PEG. *Biomacromolecules* 6:885–890
24. Yamamoto S, Pietrasik J, Matyjaszewski K (2007) ATRP synthesis of thermally responsive molecular brushes from oligo(ethylene oxide) methacrylates. *Macromolecules* 40:9348–9353
25. Otsuka H, Nagasaki Y, Kataoka K (2003) PEGylated nanoparticles for biological and pharmaceutical applications. *Adv Drug Deliv Rev* 55:403–419
26. Moon K-S, Kim H-J, Lee E, Lee M (2007) Self-assembly of T-Shaped aromatic amphiphiles into stimulus-responsive nanofibers. *Angew Chem Int Ed* 46:6807–6810
27. Kim J-K, Lee E, Kim M-C, Sim E, Lee M (2009) Reversible transformation of helical coils and straight rods in cylindrical assembly of elliptical macrocycles. *J Am Chem Soc* 131:17768–17770
28. Sharma SC, Shrestha LK, Sakai K, Sakai H, Abe M (2010) Viscoelastic solution of long polyoxyethylene chain phytosterol/monoglyceride/water systems. *Colloid Polym Sci* 288:405–414
29. Afifi H, Karlsson G, Heenan RK, Dreiss CA (2011) Solubilization of oils or addition of monoglycerides drives the formation of wormlike micelles with an elliptical cross-section in cholesterol-based surfactants: a study by rheology, SANS, and Cryo-TEM. *Langmuir* 27:7480–7492
30. Shrestha RG, Sakai K, Sakai H, Abe M (2011) Rheological properties of polyoxyethylene cholesteryl ether wormlike micelles in aqueous system. *J Phys Chem B* 115:2937–2946
31. Ahmed T, Aramaki K (2009) Temperature sensitivity of wormlike micelles in poly(oxyethylene) surfactant solution: importance of hydrophobic-group size. *J Colloid Interface Sci* 336:335–344
32. Constantin D, Freyssingeas É, Paliarne J-F, Oswald P (2003) Structural transition in the isotropic phase of the C<sub>12</sub>EO<sub>6</sub>/H<sub>2</sub>O lyotropic mixture: a rheological investigation. *Langmuir* 19:2554–2559
33. Bernheim-Groswasser A, Wachtel E, Talmon Y (2000) Micellar growth, network formation, and criticality in aqueous solutions of the nonionic surfactant C<sub>12</sub>E<sub>5</sub>. *Langmuir* 16:4131–4140
34. Bulut S, Hamit J, Olsson U, Kato T (2008) On the concentration-induced growth of nonionic wormlike micelles. *Eur Phys J E: Soft Matter Biol Phys* 27:261–273
35. Acharya DA, Sharma SJ, Rodriguez-Abreu C, Aramaki K (2006) Viscoelastic micellar solutions in nonionic fluorinated surfactant systems. *J Phys Chem B* 110:20224–20234
36. Dreiss CA (2007) Wormlike micelles: where do we stand? Recent developments, linear rheology and scattering techniques. *Soft Matter* 3:956–970
37. Johansson H, Karlstrom G, Tjerneld F (1993) Experimental and theoretical study of phase separation on aqueous solutions of clouding polymers and carboxylic acids. *Macromolecules* 26:4478–4483
38. Zhang KW, Karlstrom G, Lindman B (1994) Ternary aqueous mixture of a non-ionic polymer with a surfactant or a 2nd polymer—a theoretical and experimental investigations of the phase behavior. *J Phys Chem* 98:4411–4421
39. Wennerström H, Lindman B (1979) Micelles—physical chemistry of surfactant association. *Phys Rep—Rev Sec Phys Lett* 52:1–86
40. Lindmann B, Wennerström H (1991) Nonionic micelles grow with increasing temperature. *J Phys Chem* 95:6053–6054
41. Corti M, Minero C, Degiorgio V (1984) Cloud point transition in non-ionic micellar solutions. *J Phys Chem* 88:309–317

42. Debye P, Anacker E (1951) Micelle shape from dissymmetry measurements. *J Phys Chem* 55:644–655
43. Nash T (1958) The interaction of some naphthalene derivatives with a cationic soap below the critical micelle concentration. *J Colloid Sci* 13:134–139
44. Raghavan SR, Kaler EW (2001) Highly viscoelastic wormlike micellar solutions formed by cationic surfactants with long unsaturated tails. *Langmuir* 17:300–306
45. Gravsholt S (1976) Viscoelasticity in highly dilute aqueous solutions of pure cationic detergents. *J Colloid Interface Sci* 57:575–577
46. Porte G, Appell J, Poggi Y (1980) Experimental investigations on the flexibility of elongated cetylpyridinium bromide micelles. *J Phys Chem* 84:3105–3110
47. Imae T, Kamiya R, Ikeda S (1985) Formation of spherical and rodlike micelles of cetyltrimethylammonium bromide in aqueous NaBr solutions. *J Colloid Interface Sci* 108:215–225
48. Rehage H, Hoffmann H (1988) Rheological properties of viscoelastic surfactant systems. *J Phys Chem* 92:4712–4719
49. Li J, Zhao W, Zheng L (2012) Spontaneous formation of vesicles by *N*-dodecyl-*N*-methylpyrrolidinium bromide (C<sub>12</sub>MPB) ionic liquid and sodium dodecyl sulfate (SDS) in aqueous solution. *Colloid Surf A-Physicochem Eng Asp* 396:16–21
50. Mendes E, Oda R, Manohar C, Narayanan J (1998) A small-angle neutron scattering study of a shear-induced vesicle to micelle transition in surfactant mixtures. *J Phys Chem B* 102:338–343
51. Horbaschek K, Hoffmann H, Thunig C (1998) Formation and properties of lamellar phases in systems of cationic surfactants and hydroxy-naphthoate. *J Colloid Interface Sci* 206:439–456
52. Chu Z, Dreiss CA, Feng Y (2013) Smart wormlike micelles. *Chem Soc Rev* 42:7174–7203
53. Sreejith L, Parathakkat S, Nair SM, Kumar S, Varma G, Hassan PA, Talmon Y (2011) Octanol-triggered self-assemblies of the CTAB/KBr system: a microstructural study. *J Phys Chem B* 115:464–470
54. Yoshino N, Hamano K, Omiya Y, Kondo Y, Ito A, Abe M (1995) Synthesis of hybrid anionic surfactants containing fluorocarbon and hydrocarbon chains. *Langmuir* 11:466–469
55. Tobita K, Sakai H, Kondo Y, Yoshino N, Iwahashi M, Momozawa N, Abe M (1997) Thermoresponsive viscoelasticity of sodium 1-oxo-1-[4-(tridecafluorohexyl)phenyl]-2-hexanesulfonate aqueous solutions. *Langmuir* 13:5054–5055
56. Danino D, Weihs D, Zana R, Orädd G, Lindblom G, Abe M, Talmon Y (2003) Microstructures in the aqueous solutions of a hybrid anionic fluorocarbon/hydrocarbon surfactant. *J Colloid Interface Sci* 259:382–390
57. Chu Z, Feng Y (2011) Thermo-switchable surfactant gel. *Chem Commun* 47:7191–7193
58. Chu Z, Feng Y, Su X, Han Y (2010) Wormlike micelles and solution properties of a C22-tailed amidosulfobetaine surfactant. *Langmuir* 26:7783–7791
59. Chu Z, Feng Y (2010) Amidosulfobetaine surfactant gels with shear banding transitions. *Soft Matter* 6:6065–6067
60. Chu Z, Feng Y, Sun H, Li Z, Song X, Han Y, Wang H (2011) Aging mechanism of unsaturated long-chain amidosulfobetaine worm fluids at high temperature. *Soft Matter* 7:4485–4489
61. Fisher P, Rehage H, Grüning B (2002) Linear flow properties of dimer acid betaine solutions with and without changed ionic strength. *J Phys Chem B* 106:11041–11046
62. Lee KY, Mooney DJ (2001) Hydrogels for tissue engineering. *Chem Rev* 101:1869–1879
63. Trickett K, Eastoe J (2008) Surfactant-based gels. *Adv Colloid Interface Sci* 144:66–74
64. Raghavan SR (2009) Distinct character of surfactant gels: a smooth progression from micelles to fibrillar networks. *Langmuir* 25:8382–8385
65. Kavanagh GM, Ross-Murphy SB (1998) Rheological characterisation of polymer gels. *Prog Polym Sci* 23:533–562

Smart Wormlike Micelles

Design, Characteristics and Applications

Feng, Y.; Chu, Z.; Dreiss, C.A.

2015, XV, 91 p. 42 illus., 37 illus. in color., Softcover

ISBN: 978-3-662-45949-2