CHAPTER 2

Wormlike Micelles: Solutions, Gels, or Both?

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2.1 A Brief History of Wormlike Micelles and Their Viscoelasticity

Wormlike micelles (WLMs or ''worms'' for short) have a history dating back to at least 40 years, *i.e.*, to 1976.[1] In that year, a Danish researcher named Signe Gravsholt published a paper titled ''Viscoelasticity in highly dilute aqueous solutions of pure cationic detergents''.[2] This paper reported that dilute solutions of C_{16}-tailed cationic surfactants with certain aromatic counterions (*e.g.*, salicylate) exhibited viscoelastic behavior. While Gravsholt did not prove the existence of worms in these solutions, he noted that ''... the aggregates in these solutions ... must differ fundamentally from ordinary micelles (spherical or rodlike).''

We now know that the above solutions indeed contain WLMs. Moreover, it is interesting that, from the time of the Gravsholt paper, these micelles have been intimately connected to the term ''viscoelasticity''. This term has been associated with 19th-century scientists like James Clerk Maxwell, Lord Kelvin, and Woldemar Voigt who developed the first models for viscoelastic

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materials (the Maxwell model and the Kelvin–Voigt model).[3,4] A viscoelastic material is one that shows both *viscous or liquid-like behavior* as well as *elastic or solid-like behavior*. The shift from elastic to viscous occurs as a function of the timescales over which the material is probed, *i.e.*, the material is elastic at short timescales and viscous at long time scales.

In the mid-20th century, viscoelasticity began to be associated with polymer solutions.[4,5] Polymers are macromolecules in which monomers are connected by covalent bonds into long chains (Figure 2.1a). Physical parameters characterizing polymers include their molecular weight, M, which dictates their end-to-end or contour length L. In addition, their persistence length l_p characterizes the flexibility of the chain. When polymer chains are in dilute solution, each chain is well separated from its neighbors. In this state, each chain forms a coil with a radius of gyration R_g. When the concentration of polymer in solution is increased above a threshold concentration, the chains overlap with their neighbors, resulting in an entangled network of the chains, which is then characterized by its mesh size ξ.

A major advance in our understanding of polymers came from "reptation theory," developed in the 1970s by Pierre-Gilles de Gennes, Masao Doi, and Sir Sam Edwards.[5–7] The theory proposed that polymers in solution undergo a snake-like motion (note that "reptation" is related to the word "reptile") within an imaginary confined "tube" formed by entanglements of individual chains with their neighbors. Reptation theory explains why the networks formed by polymers in solution are *transient*, *i.e.*, have a finite lifetime for stress relaxation. At short times, the chains are entangled with their neighbors and the network has elastic character. At long times, the chains reptate and thereby disentangle from the network, and eventually the material exhibits a viscous character. The time for the chains to reptate is thus the "relaxation time" of the transient network and it scales with polymer length as follows:

$$t_{\mathrm{rep}} \sim L^3 \tag{2.1}$$

Based on eqn (2.1), t_R can reach significantly high values for semidilute solutions of polymers that are very long, *i.e.*, of high molecular weight. An example is shown in Figure 2.1c and is discussed further below.[8]

Returning to WLMs, following the Gravsholt paper in 1976, there were numerous studies in the 1980s and early 1990s, especially from the groups of S. Candau in France and H. Hoffmann in Germany, that firmly established the viscoelastic nature of these micellar solutions.[9–13] What is more, many of these solutions were found to be "ideal" viscoelastic fluids, *i.e.*, their rheology could be modeled as that of a Maxwell fluid with a *single* relaxation time.[13,14] This is exemplified by Figure 2.1d, which shows data for mixtures of cetyl pyridinium chloride (CPyCl), a cationic surfactant with a saturated C_{16} tail, combined with an aromatic salt, sodium salicylate (NaSal).[13] The Maxwell model is schematically shown in the figure: it models the material as an elastic spring in series with a viscous dashpot.[3,4] The spring has an elastic modulus G_p while the dashpot has a viscosity η_0; in turn, the

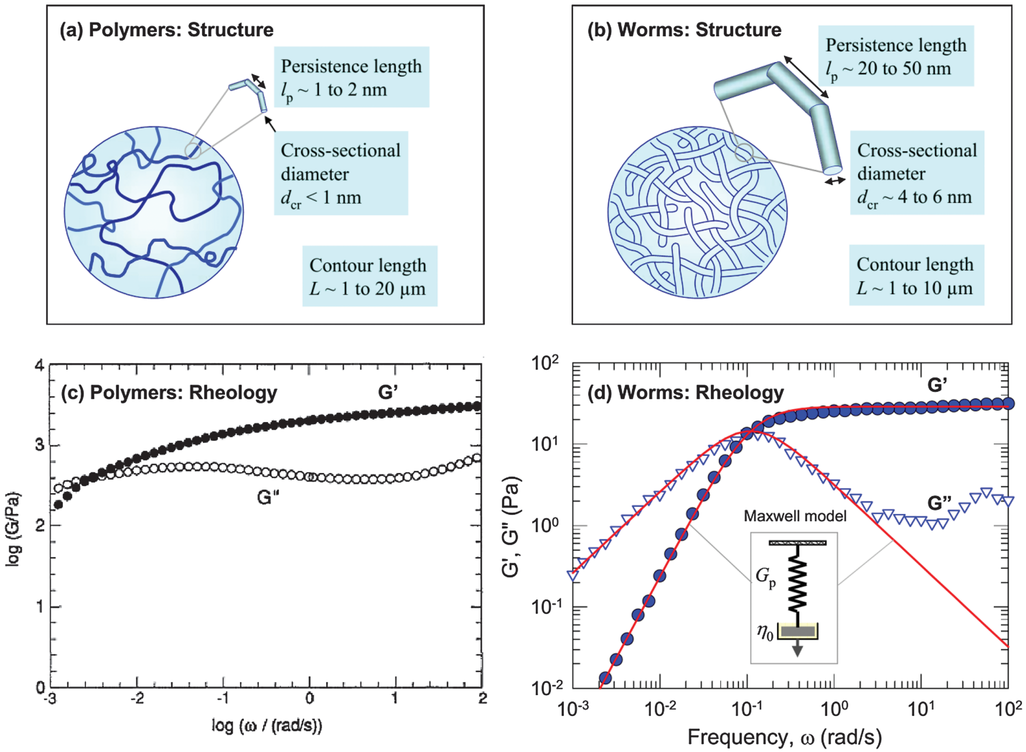

Figure 2.1 Contrasting the structure and rheology of polymers (in solution) and wormlike micelles. Typical values for structural length scales are indicated in (a) for polymers and (b) for WLMs. Typical data from dynamic rheology are shown for the two systems in (c) and (d), with the elastic modulus G' (filled symbols) and the viscous modulus G'' (unfilled symbols) plotted against frequency. The data in (c) are for polystyrene of $M = 4.7$ million at a concentration of 13.9 wt% in di(2-ethylhexyl)phthalate. Reprinted from K. Almdal *et al.*, *Polym. Gels Networks*, 1993, **1**, 5–17. Towards a phenomenological definition of the term 'gel', Copyright 1993 with permission from Elsevier.[8] According to the authors, this sample can be considered a gel. The data in (d) are for WLMs formed by 100 mM CPyCl and 60 mM NaSal at a temperature of 20 °C; this data is replotted from the paper by Rehage and Hoffmann.[13] The solid lines are fits to the Maxwell model for viscoelastic fluids (eqn (2.2)). The Maxwell model combines an elastic spring and a viscous dashpot in series, as shown in the inset.

relaxation time is $t_R = G_p/\eta_0$. The predictions of the Maxwell model for small-amplitude oscillatory shear (dynamic rheology) are:

$$G'(\omega) = \frac{G_p \omega^2 t_R^2}{1 + \omega^2 t_R^2}\ ;\ G''(\omega) = \frac{G_p \omega t_R}{1 + \omega^2 t_R^2} \tag{2.2}$$

Here, $G'(\omega)$ is the elastic or storage modulus and $G''(\omega)$ is the viscous or loss modulus, with the moduli being functions of the frequency ω of oscillations (ω is an inverse timescale).

Figure 2.1d shows that the Maxwell model fits the rheology of typical worms. Several features in the data are worth pointing out. First, at high ω (short timescales), the sample shows elastic behavior, *i.e.*, $G' = G_p = \text{constant}$, and also $G' > G''$. Second, at low ω (long timescales), the sample shows viscous behavior, *i.e.*, $G'' > G'$, with both moduli being functions of frequency ($G'' \sim \omega^1$, $G' \sim \omega^2$). Thus, the response is indeed viscoelastic. Third, G'' is symmetric near its peak and G' crosses G'' at this peak, which occurs at a crossover frequency ω_c. This frequency defines the relaxation time of the Maxwell fluid, $t_R = 1/\omega_c$. For the worms in Figure 2.1d, $\omega_c = 0.1\ \text{s}^{-1}$ giving $t_R = 10$ s. Many examples of viscoelastic worms have been published in the literature, and these results have been classified and summarized in several review articles.[13,14] A large fraction of these studies were done with cationic surfactants having C_{16} tails such as CPyCl or cetyl trimethylammonium bromide (CTAB).[9–13]

2.2 Comparing Wormlike Micelles and Polymers

Consider the dynamic rheological data in Figure 2.1c, which is for a solution of polystyrene (PS) of molecular weight $M = 4.7$ million.[8] Common synthetic polymers that are studied in the lab typically have $M < 1$ million. Thus, the PS in Figure 2.1c is at the high end of M and could be classified as "ultra high molecular weight" (UHMW). Also, the PS concentration in solution is rather high (13.9 wt%) and the temperature of the experiment is 25 °C. Under these conditions, the PS solution shows a response that is qualitatively similar to that of the worms in Figure 2.1d, *i.e.*, $G' > G''$ at high ω and $G'' > G'$ at very low ω. However, from the shapes of the G' and G'' curves, it is evident that the response does not follow that of a Maxwell fluid. That is, the sample does not have a single relaxation time, but instead has a *spectrum* of relaxation times.[3,4] It is generally accepted that the crossover frequency ω_c in such cases defines the *longest* relaxation time,[3,4] and the value of this time $t_R = 1/\omega_c \sim 200$ s for this PS solution.

Now, consider the physical parameters of typical WLMs, such as those in the CPyCl/NaSal sample from Figure 2.1d. Estimates for these parameters have been made possible by two main techniques: cryo-transmission electron microscopy (cryo-TEM) and small-angle neutron scattering (SANS).[15,16] These techniques began to be developed for routine use in the 1990s, which coincided with the increasing interest in worms. Figure 2.2 shows a couple of

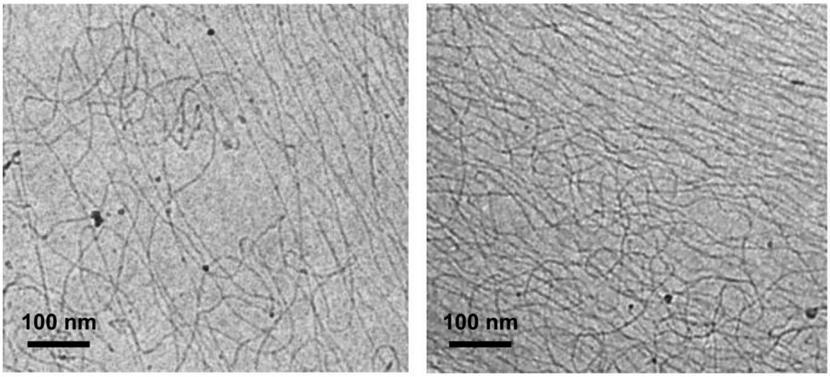

Figure 2.2 Cryo-TEM images of wormlike micelles at 25 °C. The WLMs are formed by the C_{22}-tailed zwitterionic surfactant EDAB in the absence of salt. Reproduced with permission from R. Kumar, G. C. Kalur, L. Ziserman, D. Danino and S. R. Raghavan, Wormlike micelles of a C22-tailed zwitterionic betaine surfactant: From viscoelastic solutions to elastic gels. *Langmuir*, 2007, **23**, 12849–12856. Copyright (2007) American Chemical Society.[17]

cryo-TEM images of worms.[17] Note that the worms are long chains, some entangled with one another, while others are aligned along a specific direction. The alignment is due to the shear imposed during sample preparation. Interestingly, the ends of the chains are not seen in the images, suggesting that the chains have contour (end-to-end) lengths L extending up to several micrometers. The cross-sectional diameter of the cylindrical chains d_{cr} can be measured quite accurately by SANS, and it is ~4–6 nm.[14,16] Finally, the persistence length l_{p} of the chains can also be extracted from SANS using appropriate models and assumptions, and the consensus is that l_{p} ranges from 20 to 50 nm.[14,16]

How do the above values for worms (Figure 2.1b) compare with those for polymers (Figure 2.1a)? Take the case of the PS with $M = 4.7$ million. The polymer-chain diameter is of atomic dimensions and is thus expected to be an order of magnitude smaller than that of worms (this is why individual polymer chains cannot be resolved by cryo-TEM).[5] The persistence length l_{p} of PS is reported to be ~1–2 nm, which is also an order of magnitude smaller than the corresponding values for worms.[5,18] In dilute solution, this very long PS is expected to form coils with a radius of gyration R_{g} of ~110–120 nm.[18] From these parameters, the contour length L for the above PS is estimated to be about 18 μm. The comparison shows that worms are undoubtedly thicker, and hence stiffer, than synthetic polymers. The contour length of worms is likely to be comparable to that of UHMW synthetic polymers. Also, note that if worms of $L \sim 5$ μm and $l_{\mathrm{p}} \sim 25$ nm were to form coils in dilute solution, the R_{g} of the coils would be ~500 nm due to the higher stiffness of the worms (since $R_g \sim \sqrt{L \cdot l_{\mathrm{p}}}$).[5] (In reality, diluting a solution of worms changes their length, and so this hypothetical scenario is not possible.)

Now we come to the key question. If the worms in Figure 2.1d have comparable dimensions to the polymers in Figure 2.1c, why does the polymer solution have a 20-fold longer relaxation time t_R? And why do the worms show a single t_R whereas the polymer solution has a spectrum of t_R? The answers to these questions were debated in the 1980s[9,10] and a convincing theory was provided by Michael Cates in 1987.[19] Worms are unlike polymers in one crucial respect, which is that they are held together by non-covalent bonds (hydrophobic interactions). As a result, much like spherical micelles, the surfactants in a given worm can leave it, diffuse through water, and add on to a different worm. That is, surfactants can be exchanged reversibly between different worms, which is why they are also called "living polymers" or "equilibrium polymers."[19] When a number of surfactant molecules leave a worm, the worm "breaks;" and when new surfactants are added, the broken worms "recombine." Cates[12,19] considered the scenario in which this breaking and recombination occurred rapidly, *i.e.*, over a timescale t_{br} much less than the time for the worms to reptate, t_{rep}. In that case, while each worm was reptating, it would break and recombine several times, which would provide a separate mode for stress relaxation. When both modes were factored in, the surprising result was that the system would have a *single* relaxation time t_R that is the geometric mean of t_{br} and t_{rep}, *i.e.*,[19]

$$t_R = \sqrt{(t_{br} \cdot t_{rep})} \tag{2.3}$$

Cates' theory explains why worms in the "fast-breaking limit" (*i.e.*, $t_{br} \ll t_{rep}$) show a single t_R (Maxwellian behavior) even though the worms are expected to be highly polydisperse in their contour length. In comparison, polymers like the PS in Figure 2.1c relax only by reptation and show a distribution of relaxation times. Incidentally, the breaking time t_{br} for worms like the ones in Figure 2.1d has been measured experimentally and values of 0.01–0.1 s have been reported.[20–22] These are much lower values than the t_R (~10 s) in Figure 2.1d, suggesting that "Maxwellian" worms can indeed fall in the "fast-breaking limit". For illustration, if we assume t_{br} is 0.1 s and that $t_R = 10$ s is the geometric mean of t_{br} and t_{rep} (by eqn (2.3)), then we obtain $t_{rep} = 1000$ s for the worms in Figure 2.1d. This is a very high value for t_{rep} and it suggests that the worms take much longer to reptate than even the UHMW PS in Figure 2.1c (possibly because the worms are nearly as long, but also stiffer). We restate this point in a different manner and with emphasis: *If reptation was the only mode for stress relaxation, worms would have extremely long (>100 s) relaxation times. It is only because worms break and recombine that their relaxation times are shorter.*

One more crucial difference between worms and polymers needs to be mentioned, which again derives from the non-covalent bonding in the former. The point is that the contour length L of worms is not a fixed quantity, but is a function of system variables including surfactant concentration, salt concentration, and temperature.[12,14] In particular, L is expected to decrease exponentially with increasing temperature:[12,23]

$$L \sim \phi^{1/2} \exp[E_c/2k_BT] \tag{2.4}$$

where E_c is the end-cap energy (extra energy associated with the hemispherical caps at the ends of the worms), k_B is Boltzmann's constant, T is the absolute temperature, and ϕ is the surfactant volume fraction. Consistent with the exponential reduction in length, it has been empirically found that the relaxation time t_R of worms also decreases exponentially with temperature, as does the zero-shear viscosity η_0.[23]

How could one *increase* the relaxation time t_R of worms in solution? Several strategies are worth considering, based on eqn (2.3) and (2.4). First, based on eqn (2.3), we see that the breaking of worms reduces their overall t_R. Thus, if we could design the worms to break slowly (*i.e.*, increase t_{br}), effectively converting them from "living" to "dead" polymers, then they would relax only by reptation, meaning a higher t_R. Second, consider the effect of temperature. If we cool a solution of worms below room temperature, it should increase their length (based on eqn (2.4)) and hence increase t_R. A third option is to use surfactants with longer tails. It is well known that increasing the tail length by just two carbons (while keeping the same headgroup) decreases the critical micelle concentration (cmc) by a factor of ~5 or more.[24,25] When the tail is longer, the end-cap energy E_c is expected to be higher,[12,23] and this should also increase the worm length L (by eqn (2.4)). However, there is a problem with the second and third options, which is related to the Krafft temperature T_K of surfactants.[24,25] Below T_K, surfactant tails are frozen and the surfactant tends to crystallize out of solution. Thus, at equilibrium, micelles exist only above T_K. For saturated C_{16} tails, T_K is ~20–26 °C, depending on the headgroup.[24] This means that if we cool a solution of worms formed by C_{16}-tailed cationics like CPyCl by just a few degrees Celsius below room temperature, the solution will fall below T_K and, given time, will separate into two phases. Likewise, if the surfactant has a saturated tail longer than C_{16} (*e.g.*, C_{18}), its T_K will be about 35 °C, *i.e.*, above room temperature.[24]

We will see in Section 2.4 that a viable strategy does exist to increase the t_R of worms, and that is to use surfactants with a longer tail (*e.g.*, C_{22}) but with a *cis*-unsaturation in the middle of the tail. Fatty acids with such tails are found in nature: *e.g.*, oleic acid (with an oleyl, *i.e.*, C_{18} tail) and erucic acid (with an erucyl, *i.e.*, C_{22} tail). These fatty acids can be used as feedstocks to synthesize other cationic, anionic, or zwitterionic surfactants. Despite their longer tails, these surfactants generally have Krafft temperatures T_K that are well below room temperature.[26] This is because the *cis*-unsaturation results in a sharp kink in the tail, and hence the tails do not pack close to each other in their crystal state. Because they are farther apart, the intermolecular (van der Waals) interactions between the tails are not as strong, and this allows the crystals to melt at lower temperatures.[24,25]

As we will show shortly, surfactants with long tails not only give rise to worms with long relaxation times, but in some cases, their samples exhibit the response of a gel. Before presenting this data, we first proceed to define the term "gel."

2.3 Definition of a Gel

It has been said that the "gel state … is easier to recognize than to define."[8,27] To our knowledge, the best discussion of the term "gel" is in the introduction to the first issue of the journal *Polymer Gels and Networks* by Ole Kramer and coworkers.[8] The authors discuss various definitions of a gel proposed by scientists over the years.[28,29] The consensus is that a gel is distinguished by its *solid-like* rheological properties,[3,4] which are typically evidenced in tests under dynamic and/or steady-shear rheology (Criteria 1 and 2 below), and/or from a practical test involving visual observations (Criterion 3 below).

- *Criterion 1*: *Dynamic rheology*: When the shear moduli G', G'' are measured *vs.* ω, a gel shows a *plateau* in G' at low ω ($\sim$0.01–0.1 rad s^{-1}) and in this range, $G' > G''$ by a factor of 10 or more. The plateau (frequency-independence) means that the gel does not relax, *i.e.*, its relaxation time t_R (and in turn, its zero-shear viscosity η_0) are infinite.[3,4] Also, the dominance of G' over G'' implies that a gel is a predominantly elastic material.
- *Criterion 2*: *Steady-shear rheology*: When the apparent viscosity is measured *vs.* shear stress or shear rate, a gel shows a *yield stress* σ_y, *i.e.*, its viscosity is basically infinite at stresses $<\sigma_y$.[3,4] This is consistent with an infinite zero-shear viscosity η_0.
- *Criterion 3*: *Vial inversion*: When a gel is placed in a vial (or similar container) and the vial is overturned, the gel does not flow down the sides of the vial even when observed over a time scale of at least minutes. This is basically a reflection that the material has a yield stress σ_y.[30]

The above criteria for a gel are phenomenological; they say nothing about the underlying structure. The key is that *a gel behaves as a solid regardless of timescale* whereas a viscoelastic material has both solid-like and liquid-like character depending on the timescale. The time-invariance (lack of relaxation) is generally due to the presence of a connected nanostructure, such as a network of crosslinked chains.[4] When subjected to small-amplitude oscillations, the network stores the deformation energy and there is very little dissipation (loss) of this energy—which is why $G' > G''$.

What about a solution of entangled UHMW polymer chains such as the one in Figure 2.1c? This specific example was considered by Kramer *et al.*,[8] which is why it is included here in Figure 2.1c. They noted from the data that at $\omega \sim 0.1$ s^{-1}, G' is well above G''. Even though G' shows a weak slope rather than a plateau over this range of ω, they still proposed accepting this polymer solution as a ''gel'' for practical purposes. Of course, a rheological purist might question this classification, especially since the data at lower ω reveals a crossover of G' and G''. Still, this raises two questions. First, just because a sample has a very long relaxation time (>100 s), can it be deemed a gel? The second question is about the structure: the sample in Figure 2.1c is a solution of long polymer chains; there are no physical or chemical crosslinks, only chain entanglements. Therefore, is it possible that long chains can form a gel by entanglements alone?

2.4 Wormlike Micelles of Long-tailed Surfactants: Gel-like Behavior

The first long-tailed surfactant to be studied systematically was erucyl bis(hydroxyethyl)methyl ammonium chloride (EHAC). This cationic surfactant has an erucyl tail, which is 22 carbons long and bears a *cis*-unsaturation at the 13th carbon. Interest in worms of EHAC and other long-tailed surfactants came initially from the oilfield industry for use as ''fracturing fluids'' in hydraulic fracturing (''fracking'') operations[31,32] to replace crosslinked polymer gels. In fracking, gel-like fluids with suspended sand particles (called ''proppant'') are pumped underground into fractures in the bedrock, and the fluids experience temperatures >80 °C under these conditions.[32] Once the proppant is carried by the gels to the target fractures, the gels must be degraded to enable oil to flow back to the surface. In the case of crosslinked polymer gels (mainly based on guar gums), preplaced oxidative or enzymatic breakers are used to degrade the gels. Nevertheless, the notorious limitation of such polymeric systems is that the degraded polymer fragments continue to block the pores in the fracture and reduce its hydraulic conductivity significantly. On the contrary, surfactant-based worms collapse spontaneously into spheres when the fluid comes into contact with oil, leaving little or no residue. Thus, worms have advantages over polymeric fluids in fracking, and worms that can retain relative high viscosity at high temperatures are particularly advantageous for these applications. This motivated systematic rheological studies into EHAC and similar surfactants, which were first published in the early 2000s.[23,33–37] Typically, worms were created by combining these cationic surfactants with salts such as sodium salicylate (NaSal) or potassium chloride (KCl).

The first report of gel-like behavior in WLMs was for a system containing EHAC by Raghavan and Kaler in 2001.[23] Figure 2.3 shows data from this paper, which is for worms of EHAC/NaSal at 25 °C, with the EHAC concentration being 60 mM (~2.5 wt%) and for various concentrations of NaSal. For 18, 24, and 30 mM NaSal, a gel-like response is seen in dynamic rheology. That is, G' shows a plateau extending up to $\omega \sim 0.01$ rad s^{-1} at the low end, and $G' > G''$ at all ω by a factor of 10 or more. This is clearly a gel-like and elastic response, consistent with Criterion 1 in Section 2.3. It is very different

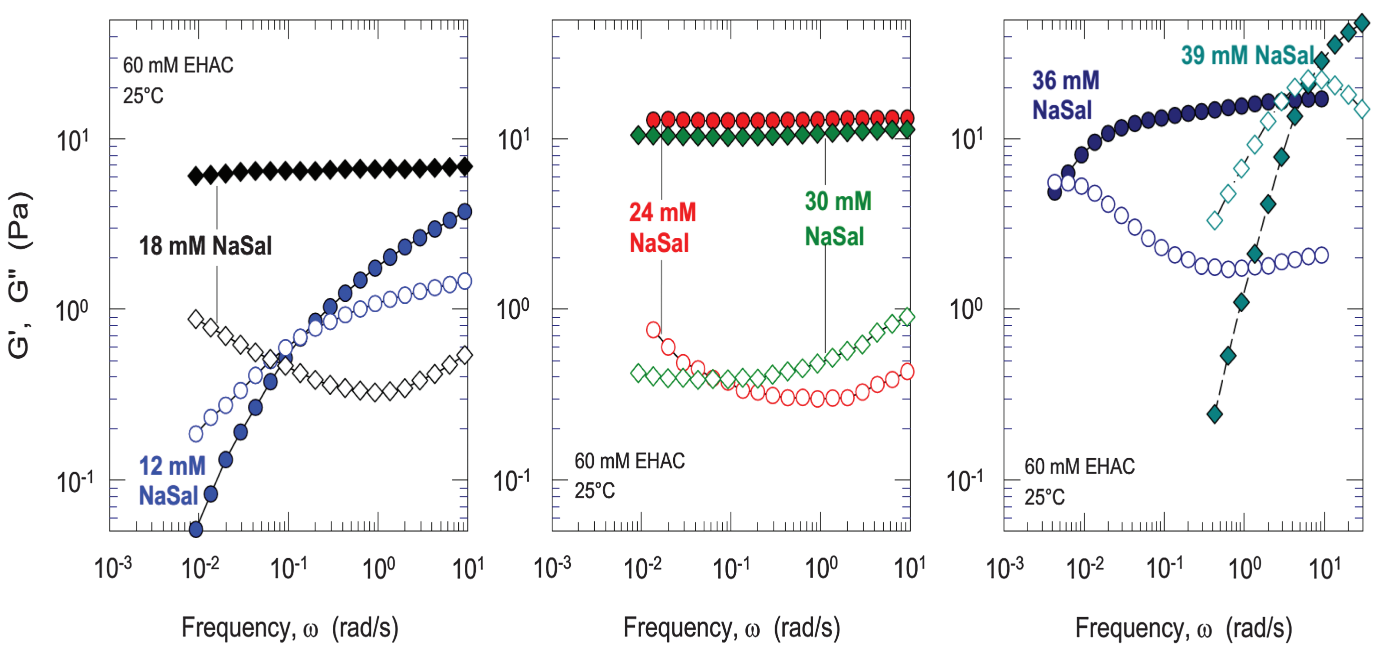

Figure 2.3 Dynamic rheology at 25 °C of WLMs that behave as gels. The worms are formed by the C_{22}-tailed cationic surfactant EHAC when combined with the aromatic salt NaSal. The plots show the elastic modulus G' (filled symbols) and the viscous modulus G'' (unfilled symbols) as functions of frequency. Data are for different NaSal concentrations, with the EHAC held constant at 60 mM. Samples at 18, 24, and 30 mM NaSal exhibit gel-like rheology.
Reproduced with permission from S. R. Raghavan and E. W. Kaler, Highly viscoelastic wormlike micellar solutions formed by cationic surfactants with long unsaturated tails. *Langmuir*, 2001, **17**, 300–306. Copyright (2001) American Chemical Society.[23]

from the viscoelastic response typically seen for worms (such as in Figure 2.1d). The above study did not discuss the gel-like response in much detail; rather, the focus was on the rheology of EHAC/NaSal worms at high temperatures. For the 60/30 EHAC/NaSal sample, the gel-like response persisted to about 60 °C, but above this temperature, the response was the conventional viscoelastic one. The zero-shear viscosity η_0 dropped with temperature, but even at 85 °C, η_0 was still quite high: ~10 Pa s, which is ~10 000 times that of water.

Thereafter, a study in 2007 by Raghavan *et al.* reported the rheology of worms formed by a zwitterionic surfactant, erucyl dimethyl amidopropyl betaine (EDAB).[17] This surfactant also had the same erucyl tail as in EHAC, but its headgroup had both cationic and anionic portions. Since the net charge on the head was low, the surfactant could form worms even in the absence of salt. Figure 2.4 shows the rheology of EDAB worms at 25 °C. For EDAB concentrations of 2.5 mM (~0.2 wt%) and higher, Figure 2.4a indicates a gel-like response in dynamic rheology (*i.e.*, $G' > G''$ with a plateau in G'). The ratio of G' to G'' is only a factor of ~2 at 2.5 mM, but this ratio becomes larger as the EDAB concentration is increased. Next, the data from steady-shear rheology (Figure 2.4b, which is a plot of the apparent viscosity η *vs.* shear stress σ) indicates the presence of a yield stress σ_y for the 8 mM and 25 mM EDAB samples, *i.e.*, their viscosity is infinite below a critical stress. For the 25 mM sample, σ_y is ~10 Pa while for a sample of 50 mM EDAB (data not shown), σ_y is ~50 Pa. Lastly, a sample of 50 mM EDAB is shown in an inverted vial in Figure 2.4c, and it is clear that the sample is able to hold its weight under these conditions (indicating a sufficient yield stress). We conclude that the EDAB samples satisfy all the three criteria for a gel discussed in Section 2.3, *i.e.*, from dynamic rheology, steady-shear rheology, and visual observation.

Next, the rheology of a 50 mM EDAB sample is shown as a function of temperature.[17] At low temperatures (25 and 40 °C, Figure 2.5a), the sample responds as a gel. However, at 60 °C and higher (Figure 2.5b), the response reverts to that of a viscoelastic solution, *i.e.*, $G' > G''$ at high ω and $G'' > G'$ at very low ω. This viscoelastic rheology is shown to conform to a single-t_R Maxwell model, which as noted earlier is characteristic of worms.[13,14] Thus, the unusual gel-like rheology is only seen at low temperatures and there is a smooth progression around 60 °C to the rheology of a highly viscoelastic solution. With further heating, the sample continued to remain viscoelastic but the t_R decreased exponentially. Note also that the plateau modulus G_p (value of G' at high ω) in the viscoelastic state is ~10 Pa and this is approximately the same as the ω-independent modulus G' in the gel state. This suggests that the nanostructures in the two states are similar.

Are EDAB worms *structurally* different in some way that could explain their gel-like behavior? EDAB samples were probed using SANS and cryo-TEM, and no unusual structural features were found.[17] For example, SANS data showed the scattering intensity $I \sim q^{-1}$ at low q, where q is the scattering vector. Such a power law is typical of cylindrical micelles. Also, the micellar

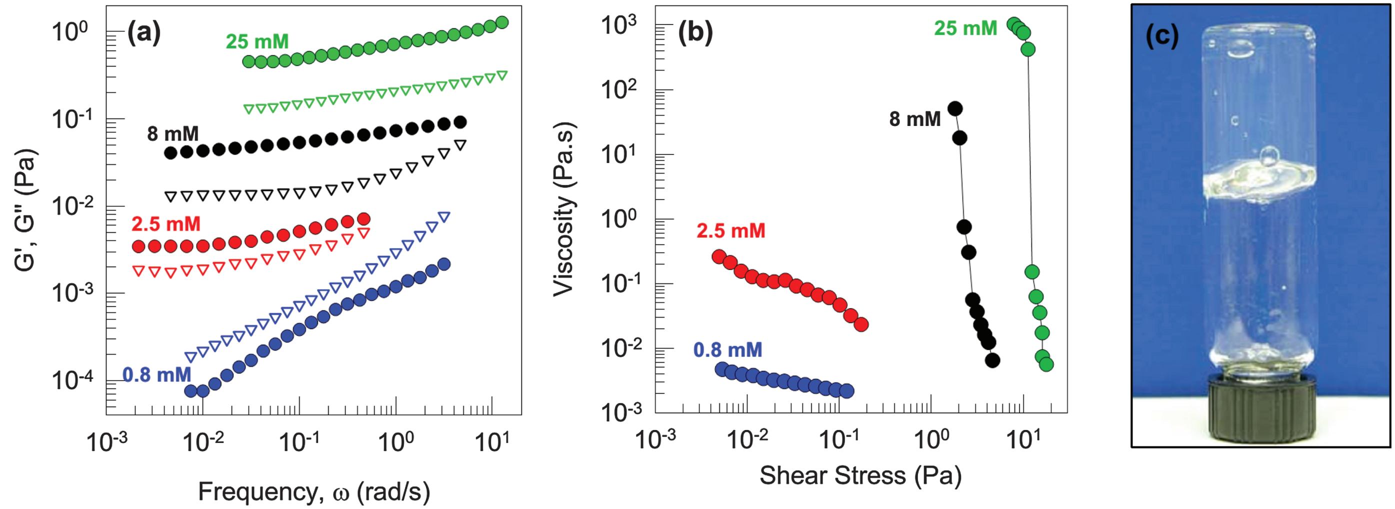

Figure 2.4 Rheology and visual observation of gel-like WLMs at 25 °C formed by the C_{22}-tailed zwitterionic surfactant EDAB. (a) Data from dynamic rheology showing the elastic modulus G' (filled circles) and the viscous modulus G'' (unfilled triangles) as functions of frequency. (b) Data from steady-shear rheology for the apparent viscosity as a function of shear stress. (c) Photograph of a 50 mM EDAB sample that holds its weight in the inverted vial.

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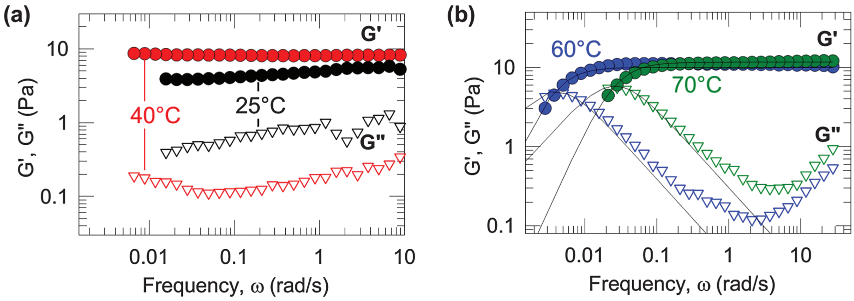

Figure 2.5 Dynamic rheology of a 50 mM EDAB sample at various temperatures. The elastic modulus G' is shown as filled circles and the viscous modulus G'' as unfilled triangles. At low temperatures (a), the sample behaves like a gel, whereas at high temperatures (b), it behaves as a viscoelastic fluid. The solid lines in (b) are fitted to the Maxwell model (eqn (2.2)). Reproduced with permission from R. Kumar, G. C. Kalur, L. Ziserman, D. Danino and S. R. Raghavan. Wormlike micelles of a C_{22}-tailed zwitterionic betaine surfactant: From viscoelastic solutions to elastic gels. *Langmuir* 2007, **23**, 12849–12856. Copyright (2007) American Chemical Society.[17]

diameter d_{cr} for EDAB worms was determined to be 5.8 nm from SANS, which is within the expected range for C_{22}-tailed surfactants. Regarding cryo-TEM, images of EDAB worms were shown earlier in Figure 2.2. The worms in this image appear exactly like those reported for worms from C_{16}-tailed surfactants.[15] No unusual features are evident in the EDAB worms that might point to a gel, such as junction points or zones. EDAB worms appear just to be long, entangled chains. Finally, the photo of an EDAB gel in Figure 2.4c shows a homogenous, transparent gel. No evidence of crystallites or a separate phase is evident.

In the last few years, similar gel-like behavior has been reported for a range of WLM systems.[38–46] The common aspect to all these systems is that they feature a long-tailed surfactant with an overall tail length of C_{22} or longer. Much of the pioneering work on long-tailed surfactants has been done by the group of Feng,[26] who have developed new methods to synthesize several of these surfactants. Surfactants reported to form gels include zwitterionic surfactants with the same erucyl (C_{22}, unsaturated) tail as in EHAC and EDAB, including an amidosulfobetaine[39,40] and an amidopropyl amine oxide.[45] In addition, an anionic carboxylate surfactant, sodium erucate, also having an erucyl tail, has been shown to form gels when combined with hydrotropes such as benzyl trimethyl ammonium bromide, or choline.[41,42]

In the above cases, the surfactants had a single long tail, with the unsaturation in the tail ensuring that the Krafft point remained low.[26] Gels of worms have also been demonstrated in solutions of some "gemini" surfactants. The term refers to surfactants with two tails and two heads separated by a spacer. For example, Zhao *et al.*[38] reported gels of a carboxylate gemini surfactant with an azobenzene spacer, denoted as $C_{14}(azo)C_{14}$. This surfactant has two saturated C_{14} tails that together give a total of C_{28}. Chen *et al.*[43] studied butane-1,4-bis(hydroxylethylmethylalkyl-ammonium)bromides, and for an alkyl length of C_{16} (denoted as 16-4-16 MEA), gels were found. Here again, there are two saturated C_{16} tails, which add up to a total of C_{32} in the molecule. Lastly, Feng *et al.*[44] have introduced the concept of a "pseudo-gemini", formed by combining an erucyl (C_{22}) amine with maleic acid at a molar ratio of 2 : 1. The maleic acid bridges the amine, thereby leading to a gemini-like structure with a total of C_{44}, and this mixture formed worms that exhibited gel-like rheology.

In the above studies on worms that exhibit gel-like rheology, the experimental trends are similar to those in Figures 2.3–2.5. That is, such rheology is seen (1) at high surfactant concentrations and (2) at low temperatures, typically around room temperature. When the gels are heated, they revert to viscoelastic solutions, similar to the data in Figure 2.5. Also, in studies where cryo-TEM images were acquired, the worms look similar to those in Figure 2.2. In our discussion, we have focused on those systems in which the surfactant concentration is moderate (2–5 wt%, or ~10–100 mM) and where there is substantial evidence for the existence of worms. A key point in this regard is that if a gel is formed by worms, the modulus (G') of the gel should be ~10 Pa for 2–5 wt% surfactant, as was indicated in Figures 2.3–2.5. A much higher gel modulus (~1000 Pa for the same surfactant concentration) suggests a different structure, *e.g.*, one formed by crystalline fibers.[47]

2.5 Why do Certain Wormlike Micelles Form a Gel?

The common factor in gel-forming worms is that the surfactant has a C_{22} or longer tail, and for the rest of this article, we will refer to these as "C_{22} worms." How are these worms different from the typical "C_{16} worms" that form viscoelastic solutions? The hypothesis, first advanced by Raghavan *et al.*,[17,48] is that C_{22} worms have breaking times t_{br} that are much longer than those of C_{16} worms. An increase in tail length from C_{16} to C_{22} affects many properties. For example, the cmc decreases by a factor of 200–1000. The cmc is also the concentration of surfactant unimers that are in equilibrium with its micelles.[24,25] Thus, a low cmc means that very few surfactant molecules are present outside the micelles, which is understandable because the C_{22} tail is longer, and hence more hydrophobic, compared to a C_{16} tail (indeed, the cmc is akin to the "solubility" of the surfactant[24]). Now consider the breaking of a micelle: individual surfactant molecules must leave the micelle and others must take its place. But since the C_{22} tails are so hydrophobic, it is unfavorable for surfactants to diffuse through water, either out of a micelle or into another one. This explains why the t_{br} of C_{22} worms should be much higher. (To our knowledge, no measurements of t_{br} exist for C_{22} worms, and so this hypothesis is yet to be verified.)

The implications of a high t_{br} can now be discussed. Consider the limit of $t_{br} \rightarrow \infty$, *i.e.*, if the worms are "unbreakable" or "dead" (*i.e.*, breaking is entirely prohibited), very much like polymer chains. In this case, the worms would be entangled, and reptation would be the only mode for stress relaxation, *i.e.*, $t_R = t_{rep}$. Then, as noted in Section 2.2, we expect these "unbreakable" worms to have a very long t_R. Another factor to consider is that the contour lengths L of C_{22} worms are also likely to be longer than those of C_{16} worms. The reasons were already mentioned in Section 2.2, and they include the lower cmc and the higher end-cap energy E_c of C_{22} surfactants.[12,23] Longer contour lengths would imply higher reptation times since (by eqn (2.1)), $t_{rep} \sim L^3$, and this would further increase t_R.

Table 2.1 provides some numbers to illustrate the differences between C_{16} and C_{22} worms at 25 °C. For the C_{16} worms, the values for t_{rep}, t_{br}, and t_R are reproduced from Section 2.2 and correspond to the data in Figure 2.1d. Note that t_R is extracted from this data while t_{br} and t_{rep} are estimates. The estimates are consistent with $t_{br} \ll t_{rep}$, meaning that the worms are in the fast-breaking limit. The net t_R therefore follows eqn (2.3) and the worms show Maxwellian rheology. In comparison, the C_{22} worms are estimated to have at least a 10-fold higher t_{rep} due to their higher L. In addition, their t_{br} is also postulated to be higher by several orders of magnitude. These values imply that the C_{22} worms no longer fall in the fast-breaking limit, and hence eqn (2.3) no longer applies. What can we say about t_R in this case? There are two possibilities. One is that the t_R of these C_{22} worms is infinite, and this possibility is further considered below. The other is that t_R is a high, but finite value (>1000 s, as seen by the lack of G' and G'' crossover even at $\omega \sim 0.001\ s^{-1}$). In this case also, for all practical purposes, the sample can be classified as a "gel," as per the definition of a gel by Kramer *et al.* (see Section 2.3).

What about the transition of C_{22} worms from a gel to a viscoelastic solution at higher temperatures? Table 2.1 provides some estimates for C_{22} worms at 60 °C. In this case, the t_R of ~200 s is extracted from the data in Figure 2.5b. The rheology at this temperature follows the Maxwell model, suggesting that the worms are now in the fast-breaking limit ($t_{br} \ll t_{rep}$) and that eqn (2.3) applies. To satisfy these conditions, we estimate values of $t_{rep} \sim 4000$ s and $t_{br} \sim 10$ s. At 60 °C both these values are considerably lower than at 25 °C. The decrease in t_{rep} is explained by a combination of eqn (2.4) and eqn (2.2). That is, the contour length L of worms is expected to decrease exponentially with T (eqn (2.4)), and since $t_{rep} \sim L^3$ (eqn (2.1)), a decrease in L implies a dramatic decrease in t_{rep}. As for t_{br}, the diffusion of surfactant molecules would be much more rapid at higher T, and hence, C_{22} surfactants

Table 2.1 Parameters for different wormlike micelles.

	C_{16} worms at 25 °C: Sol	C_{22} worms at 25 °C: Gel	C_{22} worms at 60 °C: Sol
Reptation time t_{rep}	1000 s	> 10 000 s	4000 s
Breaking time t_{br}	0.1 s	> 1000 s	10 s
Breaking regime	Fast-breaking, $t_{br} \ll t_{rep}$	Slow-breaking	Fast-breaking, $t_{br} \ll t_{rep}$
Overall t_R	$(1000 \times 0.1)^{0.5} = 10$ s	> 1000 s (infinite?)	$(4000 \times 10)^{0.5} = 200$ s

would be able to traverse from one worm to another while reducing the time that water is in contact with their long tails. This means that breaking would be enhanced, *i.e.*, t_{br} reduced, at higher T. The combination of these two effects ensures that t_{R} has a finite (but large) value at 60 °C, whereas t_{R} is infinite at lower T.

Figure 2.5 shows a continuous and smooth transition from a gel regime (infinite t_{R}) at low T to a viscoelastic regime (high but finite t_{R}) at high T for the case of 50 mM EDAB. This behavior is reversible as well, *i.e.*, when a hot viscoelastic solution is cooled, it reverts to a gel. The same trends are found at all surfactant concentrations studied, with the only difference being in the value of the temperature demarcating the end of the gel regime. The continuous transition and reversibility strongly suggest that there is no dramatic structural difference between the low and high T states. Indeed, a continuous change from gel to solution has been observed in all studies that have investigated the temperature-dependent rheology of worms formed by other long-tailed surfactants.[38–46] Thus, results from the literature are consistent with the hypothesis that, upon heating, there are gradual changes in both the structure (*i.e.*, the contour length of the worms) and the dynamics (*i.e.*, the breaking time of the worms). This brings us back to the question raised at the end of Section 2.3: is a gel then nothing more than a very highly viscoelastic solution? Or is there something ''special'' or distinct about the gel state that sets it apart from the viscoelastic state?

2.6 Can a Gel Be Formed by ''Entanglements'' Alone?

We have noted that C_{22} worms appear to simply be long, linear chains, and yet they give rise to gels. No crosslinks (bonds) between the chains are evident; the chains are simply expected to ''entangle'' with each other, very much like polymers in solution. Can such ''entanglements'' alone lead to a gel? As discussed in Section 2.1, in the case of polymers, entanglements are expected to be *transient* connections between the chains with a lifetime of t_{rep} (eqn (2.1)). In contrast, the crosslinks between polymer chains in a gel are supposed to be permanent, *i.e.*, to have an infinite lifetime. Is it possible that somehow the ''entanglements'' between worms are different from those in polymers?

In this context, a useful analogy has been made between C_{22} worms and other systems composed only of long chains that show gel-like behavior.[48] The first class of such systems are generally termed *molecular gels*,[27,49,50] and they are formed by adding a small organic molecule (''gelator'') to a solvent, whereupon the gelator self-assembles into a network of fibers (in the literature, many equivalent terms are used for chain-like objects, including fibers, fibrils, and filaments). The fibers usually have diameters in the nanoscale range while their lengths are in the micron range. A second class of systems are the filamentous gels formed by peptides[51,52] or proteins such as actin or microtubules (such filaments exist in the cytoplasm of every eukaryotic cell).[53,54] In this case, the building blocks often are globular proteins ($M \sim 30$ kDa) that are folded into compact nanoscale spheres. These globules assemble into filaments with nanoscale diameters and lengths of several microns. Clear evidence exists that the above systems are indeed gels: they satisfy all the criteria listed in Section 2.3, including frequency-independence of G' and G'', and the ability of samples to hold their weight under tube inversion. At the same time, micrographs of these gels do not reveal anything more than long fibers/filaments, *i.e.*, no obvious crosslinks are evident.[48]

What is common to the fibers in molecular gels, the filaments in protein gels, and surfactant worms in general? In all cases, the chains have *nanoscale* dimensions, *i.e.*, ranging from 4–6 nm to ~100 nm in diameter. Due to their relatively large diameter, these chains are quite stiff and their persistence length l_p ranges from 25–50 nm for worms to more than 10 μm for protein filaments. Chains with such l_p values are categorized as *semi-flexible* or *wormlike*.[4,53] In comparison, polymer chains have much lower l_p values of 1–10 nm (see Section 2.2) and are categorized as *flexible*.[5] Conversely, a *rigid* chain would have an l_p that exceeded its contour length L, while a perfectly rigid rod would exhibit an $l_p \rightarrow \infty$.[53]

Raghavan and Douglas have suggested that the "entanglements" between semi-flexible (or rigid) chains may have a different character compared to their counterparts between flexible chains, which could explain the formation of gels.[48] Semi-flexible or rigid chains are less likely to form loops and knots, and so even the very term "entanglement" is a misnomer (a more appropriate term would be "topological constraint").[55,56] Recent theoretical studies by Douglas and coworkers have suggested that the topological interactions between chains become stronger (*i.e.*, more long-lived) as the chains become stiffer.[57,58] One prediction from these studies is that the chain relaxation time t_r will vary with chain length L through a higher exponent than that predicted by reptation theory (*e.g.*, $t_r \sim L^5$ compared to $t_{rep} \sim L^3$).[59,60] The theories all predict that the relaxation time will diverge as the chain length L increases. Thus, perhaps it is possible that beyond a critical length, t_r becomes long enough that the topological constraints act like permanent crosslinks.[48] If so, this could explain the onset of gel-like behavior in a diverse range of systems containing long, semi-flexible chains. In terms of a practical analogy, these topologically constrained systems could be envisioned to be like a bowl of spaghetti!

To close this section, we outline a plausible set of requirements to form a gel from wormlike micelles, or more generally from any type of linear chains:[48]

1. *The chains must have a huge contour length.* The chain contour length L must be much larger than the chain diameter d_{cr}, with the aspect ratio $L/d_{cr} > 1000$ or so.
2. *The chains must be stiff (semi-flexible).* The persistence length l_p must be >10 nm so that the chains can be considered as semi-flexible or

wormlike. This is often ensured simply by having the chain diameter d_{cr} in the nanometer range.

3. *The chains must be temporally persistent.* The chains must not relax by molecular exchange or chain scission, or at least the timescale for such alternative relaxation processes must be very long.

If the above three conditions are all satisfied, then a gel could form simply by topological constraints ("entanglements") between the chains. In the case of surfactant worms, Conditions 1 and 2 are frequently met, but Condition 3 is rarely met. It is only when we have C_{22} worms that Condition 3 is met, and then only at low to moderate temperatures.

2.7 Conclusions

Historically, worms have been closely associated with their viscoelasticity, *i.e.*, their combination of viscous and elastic rheology. Recent studies, however, have shown that some worms can instead exhibit the rheology of a gel (*e.g.*, their $G' > G''$ at all ω and G' shows a plateau at low ω). Gel-like worms all appear to be based on surfactants with long hydrophobic tails, typically at least 22 carbons long and with a *cis*-unsaturation in the middle of the tail. The gel-like rheology is only exhibited at low T; upon heating, the rheology reverts to that of a highly viscoelastic solution.

Regarding the origin of gel-like rheology in these "C_{22} worms", a plausible hypothesis is that it arises because: (1) C_{22} worms are longer than typical worms due to the long tail of the surfactant; and (2) C_{22} worms have very long breaking times, again due to the hydrophobicity of the long surfactant tails. Under these conditions, the worms are postulated to form a gel, *i.e.*, a "permanent" network, due only to topological interactions ("entanglements") between the chains.

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