Contrasting Effects of Temperature on the Rheology of Normal and Reverse Wormlike Micelles

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Wormlike micelles are flexible polymerlike chains formed by the self-assembly of amphiphilic molecules either in water ("normal" worms) or in oil ("reverse" worms). Normal and reverse worms have both been studied extensively and have generally been found to exhibit analogous rheological properties (e.g., Maxwell fluidlike behavior). Here, we report a hitherto unexplored difference between these two classes of micelles pertaining to the effect of temperature on their rheological properties. For normal worms, the plateau modulus remains constant as the sample is heated while the relaxation time exponentially decreases. For reverse worms, however, both the plateau modulus and the relaxation time decrease exponentially upon heating. Consequently, the zero-shear viscosity of reverse worms decreases more rapidly with temperature than for normal worms. To explain these differences, we propose that increasing the temperature weakens the driving force for micellization in reverse worms whereas it only accelerates the dynamics of surfactant exchange in normal worms.

1. Introduction

The self-assembly of amphiphilic molecules results in a variety of remarkable structures of diverse shapes and sizes.[1] Among the most intriguing of these are the "wormlike micelles", which are flexible cylindrical chains with radii of a few nanometers and contour lengths up to several micrometers.[2−4] These structures have fascinated scientists because they are similar to polymer chains in their ability to entangle into viscoelastic networks.[2] At the same time, the micellar chains are held by weak physical bonds unlike the covalent bonds in polymers; consequently, the chains can break and recombine, and their contour length is not fixed by chemical synthesis but by solution thermodynamics. From a rheological standpoint, wormlike micellar samples are interesting because they can behave as Maxwell fluids (i.e., as model viscoelastic fluids having just a single relaxation time[3,4]).

Wormlike micelles can be formed both in water and in nonpolar organic solvents ("oils").[4] In water, a variety of surfactants (cationic, anionic, and zwitterionic) can give rise to these structures, although academic studies have largely focused on cationic surfactants combined with salt.[3] The salt is necessary to screen the ionic repulsions between the surfactant heads and thereby induce a molecular geometry that is optimal for packing into cylinders. Note that in these "normal" worms the polar surfactant heads are in contact with the solvent water whereas the nonpolar tails are buried in the interior of the micelle. "Reverse" or "inverted" worms formed in oils have the opposite structure, with the nonpolar tails extending into the oil and the polar heads sequestered in the interior of the micelle. A typical recipe for reverse worms requires adding the phospholipid lecithin to an organic solvent together with a small amount of water.[5,6] The added water is believed to serve a similar purpose as the salts do in the aqueous system in that it alters the geometry of the amphiphile to favor the formation of cylinders.

Normal and reverse worms are generally considered to be analogous.[4] Indeed, many theoretical considerations originally formulated to describe charge-screened worms in water have been shown to apply to reverse worms in oil as well.[5,6] Furthermore, experimental studies have also confirmed the similar rheological behavior of normal and reverse worms. For example, the characteristic Maxwellian response can be observed with both kinds of structures.[4,6] Also, key rheological parameters such as the zero-shear viscosity η_0 or the relaxation time t_R often exhibit a maximum as a function of a compositional variable in both types of systems.[3−6] Such viscosity maxima have been attributed to the branching of worms in both cases.

In this letter, we report a key difference between normal and reverse worms with respect to how their rheological properties change upon heating. Whereas both types of micelles show an exponential decrease in their viscosity with temperature, the decrease is more pronounced for reverse worms. We show that the rapid viscosity decrease of reverse worms is associated with an *exponential reduction in their plateau modulus* with temperature. This result is established for two different types of reverse worms, one being a lecithin/water mixture in oil[5,6] and the other a newer system based on mixtures of lecithin and bile salt in oil.[7] In contrast, the plateau modulus of normal worms remains constant with temperature as shown here for a typical aqueous sample based on the cationic surfactant cetylpyridinium chloride (CPyCl) in combination with the aromatic salt sodium salicylate (NaSal). This distinction in rheological behavior has not been highlighted so far to our knowledge. We believe that the drop in plateau modulus with temperature for reverse worms gives crucial insights into the mechanism for their formation. Specifically, it underscores the importance of hydrogen bonding as the driving force for the uniaxial growth of these micelles.

2. Experimental Section

Materials. The cationic surfactant CPyCl (99% purity), the aromatic salt NaSal (99%), the bile salt sodium deoxycholate (SDC) (97%), and *n*-decane (99%) were purchased from Sigma-Aldrich.

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The zwitterionic lipid soybean lecithin (95%) was purchased from Avanti Polar Lipids, Inc. All chemicals were used as received.

Sample Preparation. Normal worms of CPyCl/NaSal were prepared by adding ultrapure deionized water from a Millipore water-purification system to weighed quantities of CPyCl and NaSal. The samples were heated to ~65 °C under continuous stirring for approximately 1 h until the solutions became homogeneous.

Lecithin/water reverse worms were prepared in *n*-decane by adding the organic solvent to dry lecithin (dried in a vacuum oven at room temperature for 48 h), followed by stirring until the lecithin was completely dissolved. Water was then added to the lecithin solutions, followed by heating and stirring until the sample became homogeneous.

Lecithin/bile salt (SDC) reverse worms in *n*-decane were prepared by a procedure similar to that described in our earlier article.[7] First, lecithin and SDC were dissolved separately in methanol to form 200 and 100 mM stock solutions, respectively. Samples of the desired composition were prepared by mixing the stock solutions. Methanol was removed by drying the samples in a vacuum oven at room temperature for 48 h. The final samples with desired concentrations were obtained by adding *n*-decane, followed by stirring until the solutions became transparent and homogeneous. The above procedure ensured the removal of any residual water from the sample and thereby facilitated reproducibile sample preparation. All samples were equilibrated at room temperature at least 3 days prior to conducing experiments.

Rheology. Steady and dynamic rheological experiments were performed on an AR2000 stress-controlled rheometer (TA Instruments) using either parallel-plate or couette geometry with Peltier-based temperature control. A solvent trap was used to minimize sample evaporation. The samples were equilibrated for at least 10 min at each temperature prior to conducing experiments. Frequency spectra were recorded in the linear viscoelastic regime of the samples, as determined from dynamic strain sweep measurements. For the steady-shear experiments, sufficient time was allowed before data collection at each shear rate so as to ensure that the viscosity reached its steady-state value.

3. Results and Discussion

Rheological Data as *f*(*T*) for Normal Worms. We now describe the rheology of normal worms in water as a function of temperature, and we will subsequently contrast this behavior with that of reverse worms. Temperature effects on normal worms have been studied by a number of authors.[8−10] To illustrate the typical response, we show data for a cationic wormlike micellar fluid in Figure 1. The recipe we have used is a classic one involving the C_{16}-tailed cationic surfactant CPyCl combined with the aromatic salt NaSal.[3] Figure 1a shows dynamic rheological data (elastic modulus G' and viscous modulus G'' as functions of frequency ω) for a sample of 235 mM CPyCl and 125 mM NaSal in water at 22, 28, 34, and 40 °C. The data are typical of viscoelastic wormlike micelles, with a plateau in G' at high frequencies and terminal behavior of G' and G'' (slopes of 2 and 1, respectively) at low frequencies. Moreover, the sample is nearly a Maxwell fluid over the range of temperatures; fits are shown at 22 °C to a single-relaxation-time Maxwell model, given by the equations below:[4]

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

Here, G_p is the plateau modulus, and t_R is the relaxation time corresponding to $1/\omega_c$, where ω_c is the crossover frequency at which G' and G'' intersect. We note that the Maxwell model fits the data well, especially at low and intermediate frequencies, as has been shown for normal worms.[3,4]

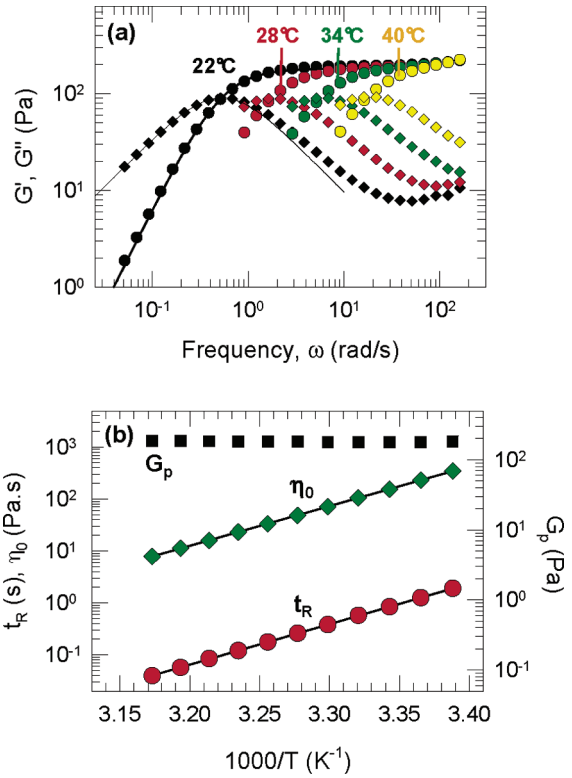

Figure 1. (a) Dynamic rheology of a normal worm sample (235 mM CPyCl + 125 mM NaSal in water) at different temperatures. Data is shown for the elastic modulus G' (circles) and the viscous modulus G'' (diamonds) as functions of frequency ω. The solid lines are fits to a single-relaxation-time Maxwell model. (b) Arrhenius (semilog) plot of the plateau modulus G_p, relaxation time t_R, and zero-shear viscosity η_0 as functions of $^1/_T$.

Turning to the effect of temperature on the rheological data, we can note several trends from Figure 1a. As temperature increases, the entire frequency spectrum moves to the right (i.e., to higher frequencies or shorter timescales), but the plateau modulus G_p remains constant.[8−10] The shift in crossover frequency ω_c to higher values means that the relaxation time t_R decreases with temperature. The variations of G_p and t_R with temperature are shown in Figure 1b on an Arrhenius plot (i.e., a semilog plot of the quantities vs $^1/_T$). We find that the t_R values fall on a straight line, indicating an exponential decrease that can be represented by the following equation[2,10]

$$t_R = A \exp\left(\frac{E_a}{RT}\right) \tag{2}$$

where E_a is the flow activation energy, R is the gas constant, T is the absolute temperature, and A is the pre-exponential factor. Figure 1b also plots the zero-shear viscosity η_0 as a function of $^1/_T$. The η_0 values are the viscosities in the Newtonian plateau at low shear rates from steady-shear rheological experiments. We obtain nearly the same values of η_0 from the dynamic data using the Maxwell fluid relation $\eta_0 = G_p t_R$. It is significant that the η_0 data in Figure 1b also fall on a straight line with approximately the *same* slope as for the t_R line. This result can be understood by combining the above Maxwell relation with eq 2:[10]

$$\eta_0 = G_p A \exp\left(\frac{E_a}{RT}\right) \tag{3}$$

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Equation 3 shows that when G_p is constant with temperature, η_0 will decrease exponentially with the same flow activation energy E_a. In other words, for a sample of normal worms, we can obtain E_a from the temperature dependence of either η_0 or t_R. For the present sample, we obtain E_a to be ca. 147 kJ/mol, which is comparable to reported values.[8−10]

The above trends for G_p, η_0, and t_R as functions of temperature have been observed for numerous kinds of normal worms.[2,8−10] It is worth reviewing the mechanistic underpinnings for these results. As mentioned earlier, the average worm length $\bar{L}$ is a thermodynamic quantity, and it is predicted to decrease exponentially with temperature according to the equation[2]

$$\bar{L} \simeq \phi^{1/2} \exp\left[\frac{E_c}{2k_B T}\right] \tag{4}$$

Here, ϕ is the volume fraction of worms, E_c is the end-cap energy (i.e., the excess energy associated with the hemispherical caps compared to the cylindrical body of the worm), and k_B is Boltzmann's constant. A decrease in $\bar{L}$ will affect the dynamics of micellar stress relaxation. The relaxation time t_R is determined by a competition between micellar breaking and chain reptation, and Maxwellian behavior is generally observed when the breaking time τ_B is much lower than the reptation time τ_{rep}.[2] In this fast-breaking regime, the relaxation time t_R is equal to $(\tau_{rep}\tau_B)^{1/2}$. Because $\tau_{rep} \sim \bar{L}^3$, a decrease in $\bar{L}$ will cause a drastic reduction in τ_{rep}, and this is the dominant effect on t_R.[2] Thus, as the worms grow exponentially shorter, they will relax exponentially faster, and this is indeed what is found empirically. The decrease in worm length will have no effect on the plateau modulus G_p, however. This is because G_p is primarily related to the mesh size ξ of the entangled network, and in the semidilute regime, ξ is a function only of the volume fraction ϕ of entangled worms:[2]

$$G_p = \frac{k_B T}{\xi^3} \qquad \xi \approx \phi^{-0.75} \tag{5}$$

Thus, with increasing temperature, as long as the volume fraction ϕ remains the same, the network mesh size will be independent of worm length, and G_p will remain constant.

Rheological Data as *f*(*T*) for Reverse Worms. We now describe the temperature dependence of the rheology of reverse worms. Again, we have chosen a classic recipe for forming these worms, involving 125 mM soybean lecithin and 250 mM deionized water added to the nonpolar solvent, *n*-decane.[5,6] Figure 2a shows the dynamic rheological data for this sample at 22, 28, 34, and 40 °C. Here again, we observe the viscoelastic behavior typical of entangled networks. Maxwell model fits (eq 1) are shown at 22 °C, and the fit is again reasonable at low to moderate frequencies. (Deviations at high frequencies can be attributed to alternate "breathing" modes of stress relaxation.[6]) As temperature is raised, the entire frequency spectrum moves both downward and to the right (i.e., toward decreasing moduli and increasing frequency). Specifically, note the behavior of the plateau modulus G_p. In contrast to the constant G_p observed for normal worms (Figure 1a), G_p for the reverse worms is seen to decrease upon heating (Figure 2a). Figure 2b plots the variation of G_p, η_0, and t_R versus $^1/_T$, and we find that all three quantities decrease exponentially with temperature. Note that the G_p values have been estimated from Maxwell model fits (or equivalently from Cole−Cole plots; see Supporting Information).[6] Figure 2b also shows the slope of the Arrhenius plot for η_0 to be greater than that for t_R, indicating that the viscosity decreases more rapidly with temperature than the relaxation time.

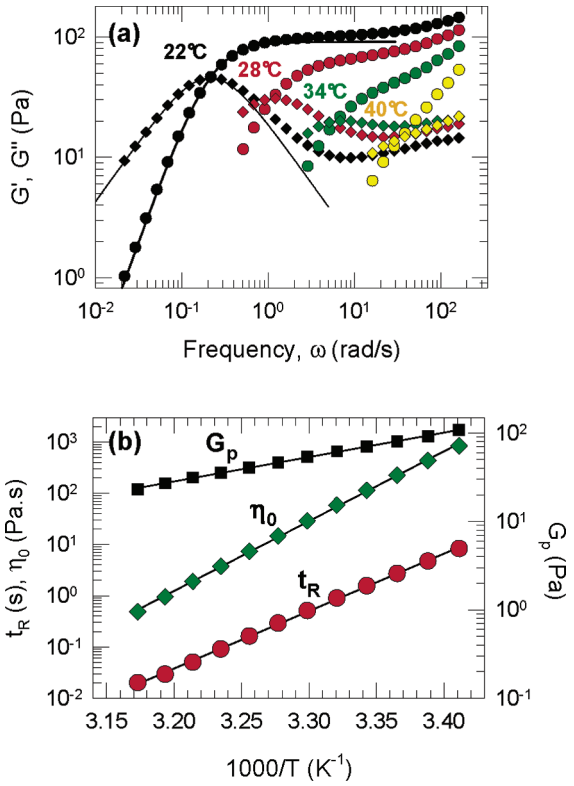

Figure 2. (a) Dynamic rheology at different temperatures of a water-induced reverse worm sample (125 mM lecithin + 250 mM water in *n*-decane). The elastic modulus G' (circles) and the viscous modulus G'' (diamonds) are shown as functions of frequency ω. The solid lines are fits to a single-relaxation-time Maxwell model. (b) Arrhenius (semilog) plot of the plateau modulus G_p, relaxation time t_R, and zero-shear viscosity η_0 as functions of $^1/_T$.

Figure 2 thus indicates a qualitatively different rheological variation with temperature for reverse worms compared to that for normal worms. We have observed similar results for *all* reverse worm samples in the lecithin/water/*n*-decane system as well as with other nonpolar solvents. One might wonder if the same pattern occurs for reverse worms that do not involve water as an additive. Recently, we have reported that bile salts, which are naturally occurring "facial" amphiphiles, act just like water and induce reverse worms of lecithin in organic solvents.[7] It is therefore useful to examine temperature effects for these bile salt-based reverse worms. We show results in Figure 3 for a reverse worm sample obtained by combining 125 mM lecithin and 18.75 mM bile salt sodium deoxycholate (SDC) in *n*-decane. This sample also shows a viscoelastic response characteristic of entangled micelles (Figure 3a), and once again, the entire frequency spectrum moves to lower moduli and higher frequencies as temperature is increased. Thus, for bile salt-induced reverse worms also, the plateau modulus G_p decreases upon heating. Figure 3b confirms the exponential drop in G_p, η_0, and t_R with temperature, as was seen in Figure 2b. Note that, here again, the zero-shear viscosity decreases more rapidly with temperature than does the relaxation time.

A notable feature exists with regard to the variation of G_p, η_0, and t_R for the two reverse worm samples (Figures 2b and 3b). Both of these samples are sufficiently close to being Maxwell fluids such that the relation $\eta_0 = G_p t_R$ holds to a good approximation. (The η_0 from steady-shear rheology and the η_0 calculated by the above relation match to within 6%.) As a result, the slopes of the straight lines in Figures 2b and 3b obey the rule of exponents (i.e., $E_a[\eta_0] = E_a[G_p] + E_a[t_R]$), where we have assigned activation energies for each rheological parameter. In

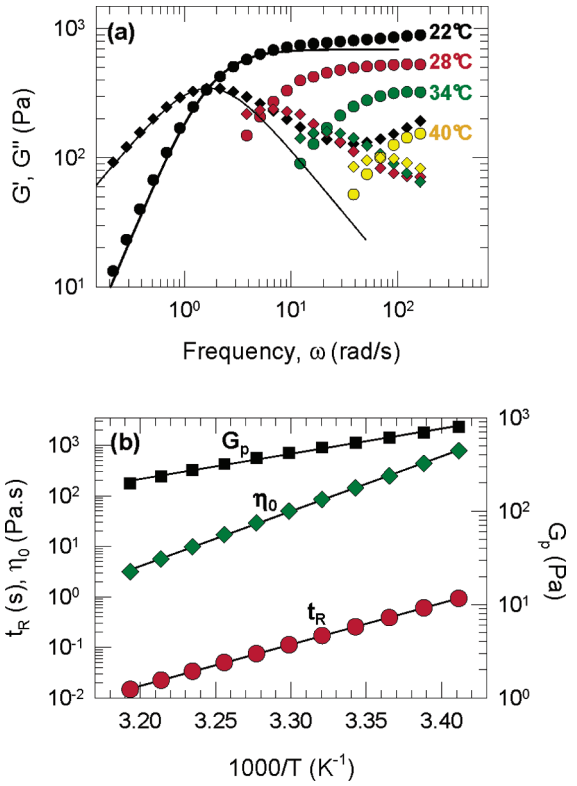

Figure 3. (a) Dynamic rheology at different temperatures of a bile salt-induced reverse worm sample (125 mM lecithin + 18.75 mM SDC in *n*-decane). The elastic modulus G' (circles) and the viscous modulus G'' (diamonds) are shown as functions of frequency ω. The solid lines are fits to a single-relaxation-time Maxwell model. (b) Arrhenius (semilog) plot of the plateau modulus $G_{p,}$ relaxation time t_R, and zero-shear viscosity η_0 as functions of $^1/_T$.

particular, for lecithin/water/*n*-decane reverse worms (Figure 2b), we find $E_a[G_p] = 53$ kJ/mol, $E_a[t_R] = 215$ kJ/mol, and the sum of these quantities is close to the empirical value of $E_a[\eta_0]$, which is 261 kJ/mol. Similarly, for lecithin/SDC/*n*-decane reverse worms, we find $E_a[G_p] = 52$ kJ/mol and $E_a[t_R] = 157$ kJ/mol, and their sum almost exactly matches the empirical $E_a[\eta_0]$ of 208 kJ/mol. Note that the quality of Arrhenius fits in Figures 1−3 is uniformly very good so that the error in E_a is low (<1%). It is interesting that the activation energies for G_p are nearly identical for the two reverse worm samples. Also, note that the activation energies for η_0 are higher for the reverse worms than for the normal worms in Figure 1 (implying a more rapid decrease in viscosity with temperature for the reverse worms).

Mechanistic Differences Between Normal and Reverse Worms. We now put forward a plausible explanation for the observed contrast in behavior between normal and reverse worms. For normal worms, the derivation of eq 4 for their contour length assumes that they have a constant end-cap energy E_c.[2] In other words, the driving force for forming worms is assumed to be independent of temperature. The dominant driving force for micellization in general arises from the hydrophobic effect.[1] For CPyCl/NaSal micelles to grow from spheres to worms in water, strong electrostatic binding of the salicylate anions to the cationic pyridinium headgroups is also necessary,[3] but neither the hydrophobic interaction nor the electrostatic binding is expected to be strongly temperature-dependent,[1] which is why it is indeed reasonable to assume a constant E_c as a function of temperature for normal worms. (Indeed, this conclusion has been validated by both theoretical[2] and experimental[10] studies.) The predominant effect of temperature on the micelles is thus simply to accelerate the dynamics of surfactant exchange between them.[2] This rapid

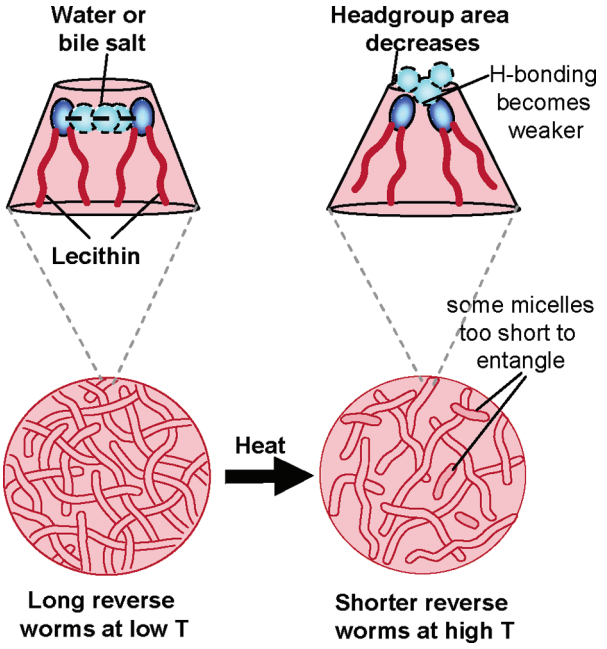

Figure 4. Schematic depiction of structural changes in lecithin-based reverse worms as a function of temperature. At low temperatures, the worms are very long and entangled. At higher temperatures, the worms are much shorter, and some of them are so short that they are not entangled with the rest (i.e., the volume fraction of entangled worms drops with temperature). A contributing factor to the decrease in worm length is the weakening of H-bonding interactions between lecithin and the polar additive (water or bile salt). In turn, the effective geometry of the amphiphile is altered in such a way as to disfavor the growth of reverse worms.

exchange of surfactant unimers weakens the impact of having unfavorable end-caps (i.e., individual surfactant molecules spend less time in their end-caps at a higher temperature). As a result, more end-caps can be formed, and this implies shorter worms. Although the worms get shorter upon heating, they are presumably still long enough to entangle so that the volume fraction of entangled worms remains constant, and this in turn explains why G_p is constant with temperature for normal worms.

In the case of reverse micelles, for spheres to grow into worms, the area per headgroup has to increase. In both the lecithin/water[6] and lecithin/bile salt[7] systems, the binding of water or bile salt to the lecithin headgroups is postulated to cause this increase. The binding in each case is believed to occur by hydrogen bonding between pairs of hydroxyl moieties on the headgroups and the additives.[6,7] In contrast to electrostatic or hydrophobic interactions, hydrogen bonds are expected to be temperature-sensitive. Indeed, both theoretical and experimental studies show that hydrogen-bonding interactions decay exponentially with temperature.[11,12] A weakening of hydrogen bonds would, in turn, reduce the driving force for the growth of long reverse worms. Thus, there are two factors at play for reverse worms as temperature is increased: first, the accelerated dynamics of surfactant exchange (same as in normal worms) and second, a reduced driving force for micellar growth (unique to reverse worms because they are dependent on hydrogen-bonding interactions). In other words, whereas the end-cap energy E_c is approximately constant for normal worms, it may be a decreasing function of temperature for reverse worms (and this decrease could be related to $E_a[G_p]$). The net result would be to cause a rapid decrease in contour length for reverse worms upon heating (Figure 4). Moreover, because a population

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of worms is always highly polydisperse,[2] we believe that the worms at the tail of the distribution quickly fall below a length that is sufficient for entanglement, as shown in Figure 4. If this is true, then the volume fraction of *entangled* reverse worms would drop, which (by eq 5) can explain the drop in plateau modulus G_p with temperature for these samples.

4. Conclusions

We have presented rheological data to show that normal and reverse worms respond differently to temperature. For normal worms, the plateau modulus G_p remains constant with temperature, and the relaxation time t_R and zero-shear viscosity η_0 drop exponentially. For reverse worms, in addition to t_R and η_0, G_p also decreases exponentially with temperature. This result has been confirmed for two different reverse worm samples (lecithin/water/n-decane and lecithin/bile-salt/*n*-decane). We suggest that the decrease in G_p for reverse worms is due to a weakening of the hydrogen-bonding interactions that control the effective amphiphile geometry in these systems. The results presented here emphasize the importance of hydrogen bonding as the key factor that dictates the self-assembly and growth of reverse micelles.

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Supporting Information Available: Cole−Cole plots of the dynamic rheological data along with the full range of frequency spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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