Highly Viscoelastic Reverse Wormlike Micellar Systems from a Mixture of Lecithin, Polyglycerol Fatty Acid Monoesters, and an Oil

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Abstract: We report new lecithin reverse wormlike micelles with high viscoelasticity formed using lecithin/polyglycerol fatty acid monoester (PGLFA)/oil systems. In this study, the influence of the amphiphilicity (i.e., hydrophile-lipophile balance, HLB) of PGLFA on the phase behavior and rheological properties of reverse wormlike micelles was investigated in detail. PGLFAs with degrees of polymerization of polyglycerol varying between 6-40 and constituent fatty acids with chains between 6-18 carbon atoms long were used. Partial phase diagrams of the lecithin/PGLFA/*n*-decane systems indicated that the appropriate PGLFA could change the lecithin/oil solution into a highly viscoelastic solution comprising reverse wormlike micelles. Rheological measurements showed that all systems that formed reverse wormlike micelles exhibited an unusual phenomenon called “shear-thickening”. Furthermore, reverse wormlike micelles grew as the PGLFA concentration increased and the zero-shear viscosity (η_0) of the solution rapidly increased. Our results indicate that the magnitude of the maximum η_0 depends on the degree of polymerization of the constituent polyglycerol in the PGLFA, while the size of the reverse micellar region and the highly viscous region in the phase diagram depends on the HLB value of the PGLFA.

Key words: reverse wormlike micelle, lecithin, polyglycerol fatty acid monoester, small angle X-ray scattering, phase diagram, rheology

1 INTRODUCTION

Surfactants are amphiphilic molecules which have both hydrophilic groups and hydrophobic groups. In solution, they self-assemble into micelles with various shapes (spherical, cylindrical, disk-like, etc.). Generally, in water, surfactant molecules are oriented with their hydrophilic groups toward the water phase and their hydrophobic groups away from it, whereas in non-polar solvents (“oils” for short) the structure of the micelle is similar but reversed, with the hydrophobic groups oriented toward the oil phase and the hydrophilic groups oriented toward the interior of the micelle¹. The shape of the micelle formed in both types of media is important in determining various properties of the surfactant solution, such as its viscosity

and ability to solubilize the substance². Recently, reverse wormlike micelles, a type of self-assembled structure, have attracted the interest of many researchers because of their unique rheological properties, such as high viscoelasticity, and fluid-like behavior described by the single Maxwell model, a fundamental model of a viscoelastic body. Reverse wormlike micelles are very long, cylindrical and flexible micelles formed in non-polar solvents. These micelles entangle to form a transient three-dimensional network in solution, thus turning the liquid into a highly viscoelastic solution. Reverse wormlike micelles are typically formed using the lecithin/water/oil system reported by Scartazzini and Luisi in 1988³. Lecithin is a zwitterionic phospholipid with two alkyl tails and forms spherical or ellipsoidal

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reverse micelles when added alone to oil, such as *n*-decane, liquid paraffin, and cyclohexane. When trace amounts of water are then added to this micellar solution, the water molecules attach to the phosphate groups of neighboring lecithins *via* hydrogen bonds and change the interface curvature of the molecular assemblies, thus inducing the formation of lecithin reverse wormlike micelles. Consequently, in this system, water is a primer to induce the formation of the lecithin reverse wormlike micelle^{4–7}. Recently, many researchers have reported that molecules other than water can act as primers. Shuchipunov reported that glycerol, ethylene glycol, and formamide can act as primers⁸, and Raghavan *et al.* reported that bile salts^{9, 10}, *p*-coumaric acid¹¹, and multivalent cations of inorganic salts (Ca^{2+} , Mg^{2+} , La^{3+} , and Ce^{3+}) can similarly act as primers¹². We reported that urea¹³, sucrose fatty acid monoesters¹⁴, D-ribose¹⁵, polyglycerols¹⁶, ascorbic acid¹⁷, and multivalent carboxylic acids¹⁸ can be used as primers. In our previous study¹⁶, we used branched polyglycerols (PGLs) as a primer for preparing lecithin reverse wormlike micelles and compared their phase behavior and rheological properties with those of conventional lecithin reverse wormlike micelles induced by glycerol (GL). The results of our experiments clearly showed that the viscosity and viscoelasticity of a reverse micellar solution can be improved by using PGLs instead of GL. Therefore, in the present study, we focused on polyglycerol fatty acid monoesters (PGLFAs), which are esters of polyglycerol and fatty acid. PGLFAs are nonionic surfactants that are used in food products, cosmetics, and toiletries in many countries. The hydrophile-lipophile balance (HLB) of PGLFAs is easy to control through the degree of glycerol polymerization and the chain length of the fatty acid.

In this contribution, we report on the influence of the degree of polymerization of the polyglycerol part of a PGLFA and the number of carbon atoms in the fatty acid part on the phase state and rheological properties of lecithin/PGLFA/*n*-decane systems. For this purpose, we used polyglycerol fatty acid monoesters with an HLB ≥ 14 , with a degree of polymerization of the branched polyglycerol between 6–40, and with a saturated fatty acid 6–18 carbon atoms long.

2 EXPERIMENTAL PROCEDURES

2.1 Materials

Soybean lecithin (PC content $\geq 95\%$) was purchased from Avanti Polar Lipids, Inc. (AL, USA). *n*-Decane was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). *n*-Decane was used as the oil component to compare with other lecithin reverse wormlike micellar systems. All polyglycerol fatty acid monoesters (hereinafter, referred to as PGLFAs, or PGL m FA n : where m is the degree of polymer-

Scheme 1 Schematic molecular structures of (a) soybean lecithin and (b) decaglycerol monodecanoic acid ester (PGL10FA10).

ization of the polyglycerol part and n is the number of carbon atoms in the saturated fatty acid part) were donated by Daicel Co., Ltd. (Tokyo, Japan). In this study, we used decaglycerol monohexanoic acid ester (PGL10FA6), decaglycerol monodecanoic acid ester (PGL10FA10), decaglycerol monotetradecanoic acid (PGL10FA14), decaglycerol monooctadecanoic acid ester (PGL10FA18), hexaglycerol monodecanoic acid ester (PGL6FA10), eicosaglycerol monodecanoic acid ester (PGL20FA10) and tetracontaglycerol monodecanoic acid ester (PGL40FA10). The moisture content of all PGLFAs was below 0.1%. All chemicals were used without further purification. The molecular structures of lecithin and a polyglycerol monofatty acid ester (PGL10FA10) are shown in **Scheme 1**.

2.2 Sample preparation

The required amounts of lecithin, PGLFA, and *n*-decane were placed in a vial and mixed using a magnetic stirrer. The vials were then maintained at 25°C for several days for equilibration.

2.3 Phase diagrams

Phase diagrams of the lecithin/PGLFA/*n*-decane systems were obtained by visual observation through crossed polarizers and by small-angle X-ray scattering (SAXS) analysis. SAXS measurements were conducted using the BL40B2

beamline (Structural Biology II Beamline) at SPring-8 (Hyogo, Japan) with a 4 m camera distance and using an imaging plate (30 × 30 cm) as a detector. The wavelength of the beam was 1.0 Å and the exposure time was about 100–130 s. The data are shown for the scattering intensity $I(q)$ versus the wave vector q [$q = (4\pi/\lambda)\sin\theta$, where λ is the X-ray wavelength and 2θ is the scattering angle]. All samples used for SAXS measurements were diluted five times in *n*-decane to eliminate structure-factor effects. All measurements were performed at 25°C. Particle shape, size, and size distribution were determined by fitting the SAXS data using Particle/Pore-size Analysis Software Nano-Solver (Rigaku, Japan).

2.4 Rheological measurements

Steady-flow viscosity and dynamic viscoelastic measurements were performed using a stress-controlled rheometer (HAAKE RS600, Thermo Fisher Scientific Inc., MA, USA) equipped with a cone-plate geometry (60 mm and 35 mm

diameter, 1°, 2°, and 4° cone angles), double cone-plate geometry (60 mm diameter, 1° cone angle), and a Peltier-based temperature control device. All measurements were performed at 25°C.

3 RESULTS AND DISCUSSION

3.1 Phase diagrams of lecithin/PGLFA/*n*-decane systems

We first focused on the phase behavior of lecithin/PGLFA/*n*-decane systems. The effect of the degree of polymerization of the polyglycerol part and the number of carbon atoms in the fatty acid part of PGLFAs on the phase state was investigated by constructing ternary phase diagrams by visual observation through crossed polarizers or through SAXS analysis. Figure 1 shows the ternary phase diagrams of lecithin/PGLFA/*n*-decane systems in the dilute region at 25°C. Figure 1 (left) shows the ternary phase diagrams in which the degree of polymerization of the polyg-

Fig. 1 Partial phase diagrams of (left) lecithin/PGL10FA n /*n*-decane systems ($n = 6, 10, 14$, and 18), and (right) lecithin/PGL m FA10/*n*-decane systems ($m = 6, 10, 20$, and 40) in the dilute region at 25°C. The notation 'Om' represents the reverse micellar phase region. The region of high viscosity within the Om phase is shown by shading.

glycerol part was fixed at 10 and Fig. 1 (right) shows the ternary phase diagrams in which the number of carbon atoms in the fatty acid part was fixed at 10. In all systems, reverse micelles (Om) formed when a small amount of PGLFA was added. The width of the Om region increased with increasing lecithin concentration, and the size of the Om region depended on the amphiphilicity of the PGLFA. Increasing the number of carbon atoms in the fatty acid part of PGLFA or decreasing the degree of polymerization of the polyglycerol part enlarged the Om region in the phase diagram. Furthermore, highly viscous regions (shown by shading) were confirmed within the Om regions, except for the lecithin/PGL10FA18/*n*-decane system. Of note, in this study, we defined regions with a zero-shear viscosity (η_0) value of approximately ≥ 10 Pa·s as highly viscous. Interestingly, the highly viscous region enlarged the most when PGL10FA10 was used as a primer. The further addition of PGLFA resulted in the transparent solution becoming opaque. The Om regions and highly viscous regions of the lecithin/PGLFA/*n*-decane systems were significantly larger than those of the lecithin/PGL/*n*-decane systems we previously reported¹⁶⁾, for reasons discussed below.

Figure 2 shows the appearance of solutions changing from a viscous body to a highly viscoelastic body, using the lecithin/PGL10FA10/*n*-decane system as an example. At a low (2 wt%) PGL10FA10 concentration (Fig. 2(a)), the solution has a low viscosity. However, the viscosity of the solution monotonically increased with the addition of PGL10FA10 (to 6 wt%, Fig. 2(b)), and the solution finally changed into a highly viscoelastic transparent body at a PGL10FA10 concentration of 8 wt% or higher (Fig. 2(c)). Further addition of PGL10FA10 resulted in turbid solutions that retained their high viscosity (data not shown). Similar results were obtained for other lecithin/PGLFA/*n*-decane

systems, other than the lecithin/PGL10FA18/*n*-decane system.

We investigated in detail the differences in micellar structures formed by each lecithin/PGL10FA10/*n*-decane system, and by lecithin/PGL10FA18/*n*-decane system, by conducting SAXS measurements. Figures 3 and 4 show the results of SAXS measurements for the lecithin/PGLFA/*n*-decane system. All samples used for SAXS measurements were diluted five times with *n*-decane to eliminate structure-factor effects. Figure 3(a) shows the SAXS profile of the lecithin/PGL10FA10/*n*-decane = 2/1.2/96.8 (wt %) system, which was in a highly viscous state before dilution (Fig. 2(b)). The slope of the double logarithmic plot in the low-*q* region was -1, indicating a cylindrical particle, i.e., the existence of reverse wormlike micelles in solution¹⁹⁾. The size distribution of the section diameter of the cylindrical particles was determined by curve fitting with Nano-Solver software using a gamma distribution function. The fit and the section diameter distribution are shown in Fig. 3(a) and Fig. 3(b), respectively. The average section diameter of the reverse wormlike micelles was determined to be 4.3 nm with 11.5% dispersity. Cross section of reverse wormlike micelle is basically a core-shell structure. However, the hydrocarbon shell is almost invisible by X-ray since the hydrocarbon shell has almost the same electron density as the solvent (*n*-decane) has. Therefore, the average section diameter should be for the core. Accurate calculation of the contour lengths of the reverse wormlike micelles was impossible because the Guinier region was absent in the measurement range, indicating that the reverse wormlike micelles formed in these systems are rather long. The above results indicate that the highly viscous regions in the ternary phase diagrams originate from the formation of reverse wormlike micelles.

Fig. 2 Visual observations of (a) lecithin/PGL10FA10/*n*-decane = 10/2/88 (wt %), (b) lecithin/PGL10FA10/*n*-decane = 10/6/84 (wt %), and (c) lecithin/PGL10FA10/*n*-decane = 10/8/82 (wt %).

Fig. 3 (a) SAXS profile (scattering intensity $I(q)$ versus the wave vector q) for the lecithin/PGL10FA18/ n -decane = 2/1.2/96.8 (wt %) system at 25°C. The curve fit using Nano-Solver software is shown as a solid line. (b) The size distribution of the section diameter of cylindrical particles.

Figure 4(a) shows the SAXS profile of the lecithin/PGL10FA18/ n -decane = 2/2/96 (wt %) system as an example, which did not provide a highly viscous region in the ternary phase diagram (Fig. 1). The solid line in Fig. 4 (a) is the fit obtained by assuming that spheroidal particles were formed, and Fig. 4 (b) shows the minor axis diameter distribution of the spheroidal particles. These data indicate that the spheroidal micelles had an average minor axis di-

Fig. 4 (a) SAXS profile for the lecithin/PGL10FA18/ n -decane = 2/2/96 (wt %) system at 25°C. The curve fit using Nano-Solver software is shown as a solid line. (b) The minor axis diameter distribution of spheroidal particles.

ameter of 6.3 nm, an aspect ratio of 2.3, and a dispersity of 10.2%, indicating that the micelles are oblate spheroids. Consequently, using PGL10FA18 as a primer, the micellar solution does not change into a highly viscous solution because spheroidal micelles are formed.

3.2 Plausible mechanism for the formation of reverse wormlike micelles in lecithin/PGLFA/*n*-decane systems

We investigated the influence of the amphiphilicity of PGLFA on the formation of reverse wormlike micelles. In general, lecithin forms a reverse spherical micelle, or a reverse, almost spherical ellipsoidal micelle when added alone to oil. When trace amounts of PGLFA are added to this solution, PGLFA molecules are solubilized into the lecithin reverse micelles and form mixed micelles. **Table 1** shows the inorganic/organic balance (IOB) values and hydrophile-lipophile balance (HLB) values of PGLFAs, calculated from organic conceptual diagrams^{20, 21}. As used herein, the IOB value is an index representing the polarity of a compound, i.e., a larger IOB value indicates higher hydrophilicity. Briefly, the IOB value represents the ratio of the inorganic value (IV) of a compound to the organic value (OV) of the compound. Furthermore, it is well known that the IOB value from an organic conceptual diagram can be converted to an HLB value using Eq. 1.²¹

$$HLB = IOB \times 10 \quad (1)$$

The HLB values of PGLFAs decreased as the number of carbon atoms in the fatty acid part increased and as the degree of polymerization of the polyglycerol part decreased. As described above, the size of the Om region in the phase diagram depends on the amphiphilicity of the PGLFA (**Fig. 1**). This can be explained by the formation of mixed micelles composed of lecithin and PGLFA: that is, PGLFA with a lower HLB value facilitates the formation of mixed micelles with lecithin in oil. The Om regions of the lecithin/PGLFA/*n*-decane systems are larger than those of lecithin/PGL/*n*-decane systems¹⁶, as expected, given that PGLFAs are less hydrophilic than PGLs because of the hydrocarbon chain in PGLFA.

Here, we would like to consider why the reverse micelle changes from a spherical to a wormlike or a disk-like shape. In general, the morphological shape or transition of surfactant aggregates is described by critical packing theory, and this relationship is explained using the critical packing pa-

rameter (*CPP*)^{22, 23}.

$$CPP = v_{tail} / (a_{hg} l_{tail}) = a_{tail} / a_{hg} \quad (2)$$

where v_{tail} is the volume of the hydrophobic part, a_{hg} is the effective area per hydrophilic part, l_{tail} is the length of the hydrophobic part, and a_{tail} is the effective area per hydrophobic part. The *CPP* values for the formation of spherical (spheroidal) micelles, rod-like (wormlike) micelles, vesicles, planar bilayer (lamellar phase), and reverse structures are $CPP \leq 1/3$, $1/3 < CPP \leq 1/2$, $1/2 < CPP < 1$, $CPP = 1$, and $CPP > 1$, respectively. Reverse structures, such as reverse vesicles, reverse rod-like (wormlike) micelles, and reverse spherical (spheroidal) micelles are formed in oil. Although the relationship between reverse structures and the *CPP* value has not been reported in detail, it is thought that the reverse structures change in the order reverse vesicles → reverse rod-like (wormlike) micelles → reverse spherical (spheroidal) micelles when the *CPP* value becomes larger than 1. As mentioned above, lecithin forms a reverse spherical micelle, or a reverse, almost spherical ellipsoidal micelle, when added alone to oil, indicating that the *CPP* value of lecithin is far greater than 1. Consequently, for reverse spherical micelles to grow into reverse wormlike micelles, the apparent *CPP* value of lecithin must decrease slightly. The above results show that when PGLFAs with an HLB of 15 or more are used, reverse spherical micelles transform into reverse wormlike micelles. As depicted in **Scheme 2**, we suggest that the mechanism underlying this transformation involves PGLFAs binding to lecithins through a hydrogen bond between a hydroxyl group in the polyglycerol part and the phosphate group of lecithin, resulting in widening of the gap between the head groups of neighboring lecithin molecules and an increase in the effective area per hydrophilic part (a_{hg}) of lecithin. On the other hand, a_{tail} may slightly increase because the fatty acid part of PGLFA slightly affects the hydrophobic group of lecithin. Therefore, use of a PGLFA with an HLB value of 15 or more as primer moderately decreases the apparent *CPP* value of lecithin and the reverse spherical micelle transforms into a reverse

Table 1 List of HLB values of PGLFAs calculated from organic conceptual diagrams.

	Inorganic value (IV)	Organic value (OV)	IOB value	HLB value
PGL40FA10	4940	2600	1.90	19.0
PGL20FA10	2540	1400	1.81	18.1
PGL10FA6	1340	720	1.86	18.6
PGL10FA10	1340	800	1.68	16.8
PGL10FA14	1340	880	1.52	15.2
PGL10FA18	1340	960	1.40	14.0
PGL6FA10	860	560	1.53	15.3

Scheme 2 Schematic illustration of reverse micelles formed by lecithin without and with PGLFA.

wormlike micelle.

In contrast, when a PGLFA with an HLB less than 15, such as PGL10FA18, is used as a primer, the reverse spherical micelles transform into reverse spheroidal micelles. We speculate that PGLFAs with low HLBs cannot effectively widen the gap between the head groups of neighboring lecithin molecules and thus the apparent *CPP* value of lecithin cannot significantly decrease.

The above results indicate that the HLB value of PGLFA affects the size of both the Om region and the highly viscous region of the ternary phase diagrams of lecithin/PGLFA/*n*-decane systems.

3.3 Rheological behavior of lecithin/PGLFA/*n*-decane systems

We used rheological techniques to characterize the reverse wormlike micellar solutions of lecithin/PGLFA/*n*-decane systems. For all measurements, micellar solutions were prepared at a fixed lecithin concentration of 10 wt% but with varying PGLFA concentrations.

First, we carried out steady-flow viscosity measurements on reverse micellar solutions. **Figure 5** shows the relationship between steady-flow viscosity and shear-rate for the lecithin/PGL10FA14/*n*-decane system as an example. Most reverse wormlike micellar systems, such as lecithin/water/oil³⁾, lecithin/glycerol/oil⁸⁾, lecithin/urea/oil¹³⁾, lecithin/D-ribose/oil¹⁵⁾, lecithin/polyglycerol/oil¹⁶⁾, lecithin/ascorbic acid/oil¹⁷⁾, and lecithin/multivalent carboxylic acid/oil¹⁸⁾, exhibit “shear-thinning”, and their viscosity decreases at high shear-rate. Shear-thinning is due to the transient three-dimensional network structure, which consists of reverse wormlike micelles, repeatedly collapsing and re-forming (i.e., reversible breakage). If the re-formation rate of the reverse wormlike micelle is sufficiently higher than the

Fig. 5 Steady flow-viscosity (η) vs. shear-rate curves for the lecithin/PGL10FA14/*n*-decane system at various concentrations of PGL10FA14 at 25°C. Lecithin concentrations were fixed at 10 wt%.

added shear-rate, the sample shows Newtonian flow (constant viscosity) because the three-dimensional network structure is apparently not broken. On the other hand, if the shear-rate is much higher than the re-formation rate, the viscosity decreases with increasing shear-rate because of the collapse of three-dimensional network structure. In contrast, our reverse wormlike micellar system shows “shear-thickening”, which is a very unusual response, and was observed with all lecithin/PGLFA/*n*-decane systems.

Shear-thickening is often defined as an increase in viscosity with increasing shear-rate²⁴⁾. The data shown in Fig. 5 clearly exhibit three regions: in the first region, η is constant at low shear-rate; in the second region, η reaches a maximum at a certain shear-rate; and in the third region, η suddenly decreases. The onset of the viscosity increase and the location of the viscosity maximum both shift to lower shear-rate as the PGLFA concentration increases. Shih-Huang *et al.*¹⁰⁾ previously reported the shear-thickening response of reverse wormlike micelles formed by the lecithin/sodium deoxycholate (SDC)/oil system. In their report, they proposed that shear-thickening is caused by increases in the connectivity between micelles at high shear-rate. It is known that the length of wormlike micelles has high polydispersity: the system includes not only entangled reverse wormlike micelles, but also short reverse wormlike micelles that do not take part in entanglement. They speculated that, at high shear-rate, these short reverse wormlike micelles become incorporated into the network of entangled reverse wormlike micelles, thus increasing the viscosity of the micellar solution. Our previous study¹⁴⁾ reported that the lecithin/sucrose fatty acid monoester/oil system also shows a shear-thickening response at high shear-rate (data not shown). It follows from this that the shear-thickening response of reverse wormlike micellar solutions is induced when surfactants, such as bile salts, sucrose fatty acid monoesters, and polyglycerol fatty acid esters, are used as a primer. We speculate that when a surfactant is used as a primer for the preparation of reverse wormlike micelles, the polydispersity of the reverse wormlike micellar length becomes higher compared to the use of other primers such as water or polyglycerol.

Figure 6 shows the relationship between zero-shear viscosity (η_0), obtained by extrapolation of the steady-flow viscosity curves to zero shear-rate, and the PGLFA concentration. The η_0 values for all systems increased steeply until the solution became opaque, except for the lecithin/PGL10FA18/*n*-decane system, indicating that the reverse wormlike micelles grow upon the addition of PGLFA. The range of zero-shear viscosity is almost same as that of lecithin/PGL/oil systems¹⁶⁾. Note from this figure that when PGLFA with a large HLB value is used, η_0 quickly rises and reaches its maximum value upon the addition of a small amount of PGLFA. Furthermore, the magnitude of the maximum η_0 depends on the degree of polymerization of the polyglycerol in the PGLFA. These results clearly show that both the HLB value of PGLFA and the degree of polymerization of the constituent polyglycerol affect the formation of reverse wormlike micelles. Note that the lecithin/PGL10FA18/*n*-decane system showed low viscosity mainly because of the formation of reverse spheroidal micelles by this system.

Next, we performed dynamic viscoelasticity measurements to characterize in detail the viscoelastic properties

Fig. 6 Zero-shear viscosity (η_0) of lecithin/PGLFA/*n*-decane systems as a function of PGLFA concentration at 25°C. Lecithin concentrations were fixed at 10 wt%.

of reverse wormlike micelles in lecithin/PGLFA/*n*-decane systems. Figure 7 shows the variation in the storage modulus (G') and loss modulus (G'') as a function of frequency (ω) for the lecithin/PGL10FA14/*n*-decane system as an example. Here, the G' and G'' values represent elasticity and viscosity, respectively. As shown in Fig. 7, G' and G'' intersect at a certain ω , where at low frequencies the viscosity component is predominant ($G'' > G'$), while at high frequencies the elasticity component is predominant ($G' > G''$). Moreover, the entire frequency spectrum moved to the upper left with increasing PGL10FA14 concentration. This indicates that the micellar solution changes from a viscous body to a viscoelastic body as the PGLFA concentration becomes higher. In Fig. 7, we also show fits to G' and G'' for each sample using a single Maxwell model based on Eqs. 3 and 4²⁵⁾:

$$G'(\omega) = \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} G_0 \quad (3)$$

$$G''(\omega) = \frac{\omega \tau}{1 + \omega^2 \tau^2} G_0 \quad (4)$$

$$\eta_0 = G_0 \tau \quad (5)$$

where G_0 is the plateau modulus and τ is the relaxation-time which reflects the disentanglement time of reverse wormlike micelles in the three dimensional network structure. When a sample fits a single Maxwell model, η_0 can be defined as Eq. 5. The fluid-like behavior exhibited by the single Maxwell model is indicative of the presence of entangled wormlike micelles. As shown in Fig. 7, the visco-

Fig. 7 Variation in G' and G'' as a function of ω at different PGL10FA14 concentrations in the lecithin/PGL10FA14/*n*-decane system at 25°C. Lecithin concentrations were fixed at 10 wt%. Maxwellian fittings to the experimental data are shown as solid lines.

elastic behavior of the reverse wormlike micelles fit well to a single Maxwell model based on Eqs. 3 and 4 at low and intermediate frequencies, and these results strongly support the presence of reverse wormlike micelles. In contrast, at high frequencies the fit was poor due to the Rouse mode, which is the faster relaxation mode related to micro-Brownian motion of the reverse wormlike micelle²⁶⁾.

Figure 8 shows the variation of dynamic rheological parameters with increasing PGLFA concentration. In all systems, both G_0 and τ increase with PGLFA concentration. Here, G_0 and τ reflect the volume fraction of the entangled reverse wormlike micelles and the length of the reverse wormlike micelles, respectively²⁵⁾. Therefore, the increase of G_0 with PGLFA concentration is related to an increase in the number of reverse wormlike micelles, whereas the increase of τ with PGLFA concentration is related to the one-dimensional growth of the reverse wormlike micelles. From Eq. 5, it appears that the incremental increase of both the number and the length of reverse wormlike micelles led to the rise in η_0 (Fig. 6).

We consider now the maximum values of the dynamic rheological parameters. It seems reasonable to suppose that the maximum G_0 is related to the maximum volume of entangled reverse wormlike micelles in the system, and that the maximum τ is related to the maximum length of the reverse wormlike micelle. As shown in Fig. 8, since the magnitude of the maximum G_0 remains essentially constant

Fig. 8 Variation in (a) G_0 and (b) τ at different PGLFA concentrations in lecithin/PGLFA/*n*-decane systems at 25 °C.

regardless of the PGLFA, there was little difference in the maximum amount of reverse wormlike micelles in either system. Interestingly, however, the magnitude of the maximum τ depends on the degree of polymerization of the polyglycerol constituent of the PGLFA, with the maximum length of the reverse wormlike micelle increasing as the degree of polymerization of the polyglycerol increases. A similar relationship is seen in lecithin/PGL/oil systems¹⁶⁾.

These results of our experiments clearly show that the number of hydroxyl functional groups in the polyglycerol part is the main factor controlling the growth of reverse wormlike micelles.

4 CONCLUSIONS

This study has demonstrated that polyglycerol fatty acid monoesters (PGLFAs) can induce the formation of lecithin reverse wormlike micelles with high viscoelasticity. Using PGLFAs instead of polyglycerol showed that the reverse micellar region (Om) and the highly viscous region in the ternary phase diagram are both enlarged. Rheological measurements confirmed the unusual phenomenon called “shear-thickening” in each system. The viscosity of the reverse micellar solution increased upon the addition of PGLFA because both the number and the length of reverse wormlike micelles increased with increasing PGLFA concentration.

The present results indicate that PGLFA is a useful primer due to its ability to induce the formation of lecithin reverse wormlike micelles in a manner similar to other compounds such as glycerol and polyglycerols.

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References

- 1) Holmberg, K. *Handbook of Applied Surface and Colloid Chemistry*, Vol. 2. Wiley, New York (2002).
- 2) Rosen, M.J. *Surfactants and Interfacial Phenomena*, 2nd ed. Wiley, New York (1989).
- 3) Scartazzini, R.; Luisi, P.L. Organogels from lecithins. *J. Phys. Chem.* **92**, 829-833 (1988).
- 4) Schurtenberger, P.; Scartazzini, R.; Luisi, P.L. Viscoelastic properties of polymerlike reverse micelles. *Rheol. Acta* **28**, 372-381 (1989).
- 5) Luisi, P.L.; Scartazzini, R.; Haering, G.; Schurtenberger, P. Organogels from water-in-oil microemulsions. *Colloid Polym. Sci.* **268**, 356-374 (1990).
- 6) Angelico, R.; Palazzo, G.; Colafemmina, G.; Cirkel, P.A.; Giustini, M.; Ceglie, A. Water diffusion and headgroup mobility in polymer-like reverse micelles: Evidence of a sphere-to-rod-to-sphere transition. *J. Phys. Chem. B* **102**, 2883-2889 (1998).
- 7) Angelico, R.; Ceglie, A.; Olsson, U.; Palazzo, G. Phase diagram and phase properties of the system lecithin-water-cyclohexane. *Langmuir* **16**, 2124-2132 (2000).
- 8) Shchipunov, Y.A. Lecithin organogel: A micellar system with unique properties. *Colloids Surf. A Physicochem. Eng. Asp.* **183-185**, 541-554 (2001).
- 9) Tung, S.H.; Huang, Y.E.; Raghavan, S.R. A new reverse wormlike micellar system: mixtures of bile salt and lecithin in organic liquids. *J. Am. Chem. Soc.* **128**, 5751-5756 (2006).
- 10) Tung, S.H.; Raghavan, S.R. Strain-stiffening response in transient networks formed by reverse wormlike micelles. *Langmuir* **24**, 8405-8408 (2008).
- 11) Kumar, R.; Ketner, A.M.; Raghavan, S.R. Nonaqueous photorheological fluids based on light-responsive reverse wormlike micelles. *Langmuir* **26**, 5405-5411 (2010).
- 12) Lee, H.Y.; Diehn, K.K.; Ko, S.W.; Tung, S.H.; Raghavan, S.R. Can simple salts influence self-assembly in oil? multivalent cations as efficient gelators of lecithin organosols. *Langmuir* **26**, 13831-13838 (2010).
- 13) Hashizaki, K.; Chiba, T.; Taguchi, H.; Saito, Y. Highly viscoelastic reverse worm-like micelles formed in a lecithin/urea/oil system. *Colloid Polym. Sci.* **287**, 927-932 (2009).
- 14) Hashizaki, K.; Taguchi, H.; Saito, Y. A novel reverse worm-like micelle from a lecithin/sucrose fatty acid ester/oil system. *Colloid Polym. Sci.* **287**, 1099-1105 (2009).
- 15) Hashizaki, K.; Taguchi, H.; Saito, Y. New lecithin organogels with sugars of RNA and DNA. *Chem. Lett.* **38**, 1036-1037 (2009).
- 16) Hashizaki, K.; Sakanishi, Y.; Yako, S.; Tsusaka, H.; Imai, M.; Taguchi, H.; Saito, Y. New lecithin organogels from lecithin/polyglycerol/oil systems. *J. Oleo Sci.* **61**, 267-275 (2012).
- 17) Hashizaki, K.; Watanabe, N.; Imai, M.; Taguchi, H.; Saito, Y. Possibility of vitamin C to induce the formation of lecithin organogel. *Chem. Lett.* **41**, 427-429 (2012).
- 18) Imai, M.; Hashizaki, K.; Taguchi, H.; Saito, Y.; Motohashi, S. A new reverse worm-like micellar system from a lecithin, multivalent carboxylic acid and oil mixture. *J. Colloid Interface Sci.* **403**, 77-83 (2013).
- 19) Shrestha, L.K.; Yamamoto, M.; Arima, S.; Aramaki, K. Charge-free reverse wormlike micelles in nonaqueous media. *Langmuir* **27**, 2340-2348 (2011).
- 20) Fujita, A. Prediction of organic compounds by a conceptual diagram. *Pharm. Bull.* **2**, 163-173 (1954).
- 21) Nihon Emulsion Co. Ltd. Formulation design with organic conception diagram. Tokyo (1997).
- 22) Israelachvili, J.N.; Mitchell, D.J.; Ninham, B.W. Theory of self-assembly of hydrocarbon amphiphiles into micelles and bilayers. *J. Chem. Soc. Faraday Trans. 2* **72**, 1525-1568 (1976).

- 23) Israelachvili, J.N.; Mitchell, D.J.; Ninham, B.W. Theory of self-assembly of lipid bilayers and vesicles. *Biochim. Biophys. Acta - Biomembr.* **470**, 185-201 (1977).
 - 24) Hu, Y.T.; Boltenhagen, P.; Pine, D.J. Shear thickening in low-concentration solutions of wormlike micelles. I. Direct visualization of transient behavior and phase transitions. *J. Rheol.* **42**, 1185-1208 (1998).
 - 25) Cates, M.E.; Candau, S.J. Statics and dynamics of worm-like surfactant micelles. *J. Phys. Condens. Matter* **2**, 6869-6892 (1990).
 - 26) Rouse, P.E. A theory of the linear viscoelastic properties of dilute solutions of coiling polymers. *J. Chem. Phys.* **21**, 1272-1280 (1953).
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