New Lecithin Organogels from Lecithin/Polyglycerol/Oil Systems

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Abstract: New liquid substances that induce the formation of lecithin organogels composed of reverse worm-like micelles were studied. The phase behavior and rheological properties of lecithin/polyglycerol (PGL)/oil systems were investigated in detail; the polymerization degrees of the glycerol residues were 3, 4, 6, 10, 20, and 40. From the partial phase diagrams of the lecithin/PGL/*n*-decane systems, it was apparent that highly viscoelastic reverse worm-like micelles formed upon the addition of small amounts of the PGL, except in the case of the PGL with a polymerization degree of 40. Steady-flow viscosity measurements showed that the zero-shear viscosity (η_0) of the reverse worm-like micelles rapidly increased with the concentration and polymerization degree of the PGLs, reaching a maximum value that was 750,000 times the viscosity of *n*-decane and thus resulting in the growth of these micelles. It is noteworthy that the η_0 values of lecithin organogels formed using PGLs were higher than the η_0 value of the lecithin organogel formed using glycerol (GL). From dynamic viscoelasticity measurements, it was shown that the viscoelastic behavior of the reverse worm-like micelles was consistent with the single Maxwell model, which is the basic model of a viscoelastic body. It follows from this study that PGLs are useful liquids because they can induce the formation of lecithin organogels with high viscoelasticity, as do other liquids such as water, glycerol, ethylene glycol, and formamide.

Key words: lecithin organogel; reverse worm-like micelle; lecithin; polyglycerols; small angle X-ray scattering; phase diagram; rheology

1 INTRODUCTION

Surfactants, which are amphiphilic molecules composed of both hydrophilic and hydrophobic groups, are used in a variety of commercial products such as cosmetics, medicines, foods, and ink because of their many advantages. One major advantage of surfactants is that they can be adsorbed at various interfaces (air-liquid, air-solid, liquid-liquid, and liquid-solid) and can alter the surface (or interfacial) tension, surface charge, wettability, and so on. This property is advantageous when using surfactants in emulsifiers, dispersing agents, forming agents, and surface-reforming agents. A second major advantage is that in combination with a solvent such as water or oil, surfactants can form a wide variety of molecular assemblies. It is well known that a surfactant at very low concentrations can dissolve in water as a monomer or adsorb at the air-water interface. However, when the surfactant concentration exceeds the critical micelle concentration (cmc), a large

variety of molecular assemblies such as spherical micelles, rod-like micelles, lamellar liquid crystals, and hexagonal liquid crystals can be formed. The shapes of these molecular assemblies are governed not only by the geometry, class, and concentration of the surfactant, but also by the temperature, pH, and class of the solvent. Although we have already mentioned above that various molecular assemblies are formed by surfactants in combination with water or oil, reports concerning the behavior of surfactants in oil are fewer than those concerning the behavior of surfactants in water.

One type of self-assembled structure that is formed in organic solvents, the reverse worm-like micelle, has attracted interest because of its structural and functional properties. Reverse worm-like micelles are cylindrically elongated reverse micelles. They entangle in an atypical fashion to form a transient three-dimensional network in solution, thus turning the liquid into a gel. The first report

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of this type of high-viscoelasticity organogel was a three-component lecithin/water/oil system discovered by Luisi et al. in 1988¹¹. Lecithin, a zwitterionic phospholipid with two alkyl tails, exists in all animal and plant cells. In general, lecithin forms spherical or ellipsoidal reverse micelles when added to oil. When trace amounts of water are added to this solution, the water molecules induce the formation of reverse worm-like micelles that turn the solution into an organogel (also called a lecithin organogel)¹⁻⁷. In this system, water is the key ingredient for the formation of reverse worm-like micelles.

The lecithin organogel is similar to general gelators such as polymer gelators and low-molecular-weight gelators in terms of its rheological behavior, with one slight but significant difference. In general, the relaxation times of polymers have a wide distribution because the polymers disentangle via reptation (a reptile-like motion)⁸⁻¹¹. In contrast, each surfactant in monomers and micelles is in a thermodynamic equilibrium state, and micelle-monomer exchange proceeds constantly. In other words, the micelles break and recombine at a rapid rate. Therefore, the rheological behavior of reverse worm-like micelles is determined by the balance between reversible breakage and reptation of the micelles. Single Maxwellian behavior is generally observed when the reversible breakage time is sufficiently shorter than the reptation time¹². In this situation, the relaxation time is represented by the geometric mean of the breaking time and reptation time.

Substances that can be used as substitutes for water in organogel preparation were explored by Shuchipunov⁷, who reported that glycerol, ethylene glycol, and formamide can induce the formation of lecithin organogels. It should be noted that all the substances mentioned so far are liquids at room temperature. Recently, however, Raghavan et al.¹³⁻¹⁵ reported that bile salts, which are solid substances at room temperature, induce the formation of a lecithin organogel composed of reverse worm-like micelles. The most remarkable aspect of this report was the method used for sample preparation. Even if lecithin, a bile salt, and a nonpolar organic solvent are mixed together simultaneously, reverse worm-like micelles do not form because the bile salts do not dissolve in nonpolar organic solvents. Therefore, these researchers homogeneously mixed the lecithin and bile salts in methanol in advance, and then removed the solvent to obtain a solid mixture. Next, they added a nonpolar solvent such as cyclohexane to the solid with agitation to obtain a gel-like substance. The method presented in Raghavan's paper seemed to be of use in searching for other solid substances that induce the formation of lecithin organogels. Indeed, we adopted their methods and discovered that urea¹⁶, sucrose fatty acid esters¹⁷, D-ribose and 2-deoxy-D-ribose¹⁸ also induce the formation of lecithin organogels. However, this preparation procedure is much more complicated than those involving the use of liquid

substances.

Topical drug delivery applications of lecithin organogel-based lecithin/water/oil systems have also been studied because of their functional benefits¹⁹. The advantages of lecithin organogels are their biodegradability, biocompatibility, and long-term stability; in addition, these organogels are easy to prepare and they can solubilize drug molecules having various polarities. On the other hand, drugs that undergo hydrolysis easily cannot be mixed with lecithin organogels of lecithin/water/oil origin. Thus, the aim of our study is to explore novel lecithin organogels that can be prepared easily and are stable against various drugs. In this study, we focused on polyglycerols (PGLs), i.e., polymers of glycerols, which can form linear, cyclic, and branched polymers. In general, polyglycerols are added to cosmetics and foods for the purpose of moisture retention and emulsification, respectively. In this study, we used branched polyglycerols to prepare lecithin organogels and compared the obtained organogels with the lecithin organogel induced by glycerol, which has already been reported by Shuchipunov⁶. Branched polyglycerols were used because they contain very few impurities and have narrow molecular weight distributions.

2 EXPERIMENTAL PROCEDURES

2.1 Materials

Soybean lecithin (PC content = 95%) was purchased from Avanti Polar Lipids, Inc. (AL, USA). Glycerol (GL) and *n*-decane were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Triglycerol (3PGL), tetraglycerol (4PGL), hexaglycerol (6PGL), decaglycerol (10PGL), icosaglycerol

Scheme 1 Molecular structures of (a) soybean lecithin and (b) decaglycerol (10PGL).

(20PGL), and tetracontaglycerol(40PGL) were donated by Daicel Co., Ltd. (Tokyo Japan). The moisture content of all PGLs was below 0.1%. All the chemicals were used without further purification. The molecular structures of lecithin and the PGLs are shown in Scheme 1.

2.2 Sample preparation

The required amounts of lecithin, PGLs, and *n*-decane were added to a vial and mixed using a magnetic stirrer. The vials were then maintained at 25°C for a few days to allow for equilibration. The samples containing GL were prepared by the same method.

2.3 Phase diagrams

Phase diagrams of the lecithin/GL/*n*-decane and lecithin/PGL/*n*-decane systems were obtained by visual observation through crossed polarizers and by small-angle X-ray scattering (SAXS) analysis. SAXS was performed using a Nano-STAR instrument (Bruker AXS Inc., WI, USA) with a CuK α radiation source operating at 45 kV/120 mA. All measurements were performed at 25°C.

2.4 Rheological measurements

Steady and dynamic rheological measurements were performed using a stress-controlled rheometer (HAAKE RS600, Thermo Fisher Scientific Inc., MA, USA) with a cone-plate geometry (60 mm and 35 mm diameters, 1° cone angle), and a Peltier-based temperature control device was used for setting the temperature at 25°C. For steady-flow viscosity measurements, the samples were subjected to the desired shear stress for a sufficiently long time to achieve a steady state. Dynamic rheological measurements were performed using the strain (γ) value from the linear viscoelastic region. A solvent trap was used to prevent evaporation.

3 RESULTS AND DISCUSSION

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

The phase states of the lecithin/GL/*n*-decane and lecithin/PGL/*n*-decane systems were identified by visual observation through crossed polarizers or through SAXS analysis. Figure 1 shows the partial phase diagrams of the lecithin/GL/*n*-decane and lecithin/PGL/*n*-decane systems. In all systems, reverse micelles (Om) formed upon the addition of a small amount of PGL, and highly viscous regions (shaded areas) were confirmed within the Om regions. It was noteworthy that the Om regions slightly enlarged with an increase in the polymerization degree of the PGLs; however, the highly viscous regions were independent of the polymerization degree, except in the case of 20PGL. It was also found that the Om regions of the lecithin/PGL/*n*-decane systems were larger than those of the lecithin/

Fig. 1 Partial phase diagrams of lecithin/GL/*n*-decane and lecithin/PGL/*n*-decane systems in the dilute region at 25°C. The notation Om represents the reverse micellar phase. The region of high viscosity within the Om phase is shown by shading.

water/*n*-decane system (data not shown) and the lecithin/urea/*n*-decane system previously reported¹⁶⁾. Figure 2 shows the changes occurring at the solution surface of the lecithin/GL/*n*-decane [10:1.25:88.75 (wt%)] and lecithin/4PGL/*n*-decane [10:3:87 (wt%)] systems when the sample vials were inverted from the upright position. Each sample was transparent and optically isotropic when left stationary but showed weak birefringence when agitated. Furthermore, this photograph clearly shows that the lecithin/4PGL/*n*-decane system did not drip as easily as the lecithin/GL/*n*-decane system. The differences in viscosity

Fig. 2 Change in the surface of (a) lecithin/GL/*n*-decane [10:1.25:88.75 (wt%)] and (b) lecithin/4PGL/*n*-decane [10:3:87 (wt%)] systems when the vials were inverted from the upright position.

between these systems are discussed later. Further addition of GL and PGLs resulted in turbid solutions that retained their high viscosity (data not shown). This turbidity resulted from the droplets of excess GL and PGLs, whose concentration exceeded the solubility limit of the reverse worm-like micelles. A similar phase separation had previously been observed in the lecithin/urea/*n*-decane system¹⁶⁾. When 40PGL was used, the Om region narrowed considerably and the highly viscoelastic region was not observed. From this result, it is clear that the ideal polymerization degree of PGLs for the formation of lecithin organogels is 20 or lesser.

Figure 3 shows the SAXS scattering intensity [$I(q)$] as a function of the scattering vector (q) [$q = (4\pi/\lambda) \sin \theta$, where λ is the X-ray wavelength and 2θ is the scattering angle] for the lecithin/4PGL/*n*-decane [2:0.6:97.4 (wt%)] system. All samples used for SAXS measurements were diluted five times to eliminate the structure-factor effect. In the SAXS profiles of the lecithin/PGL/*n*-decane systems, the slope of the double logarithmic plot in the low- q region was -1. This indicated a cylindrical particle, i.e., the existence of a reverse worm-like micelle. Figure 4 shows cross-sectional plots of the SAXS profiles based on Eqs. 1 and 2²⁰⁾:

$$\ln qI(q) = \ln qI(0) - (1/2)R_c^2 q^2 \quad (1)$$

$$r = \sqrt{2}R_c \quad (2)$$

where R_c is the cross-sectional radius of gyration. The section radius (r) of a reverse worm-like micelle was 2.2 nm. In general, the length of a reverse worm-like micelle can be calculated from the low- q region, i.e., the Guinier region. However, the Guinier region could not be observed because of restrictions on the measurement range of SAXS. Therefore, the contour length (t) of a reverse worm-like micelle was estimated by a simulation based on Eq. 3²¹⁾

Fig. 3 SAXS scattering intensity [$I(q)$] as a function of the scattering vector (q) for lecithin/4PGL/*n*-decane [2:0.6:97.4 (wt%)] system. The result of fitting based on Eq. 3 is shown by a solid line.

Fig. 4 Cross-sectional plot of the SAXS profile of lecithin/4PGL/*n*-decane [2:0.6:97.4 (wt%)] system. The fitting result based on Eq. 1 is shown by a solid line.

with a fixed r value (2.2 nm), as shown in Fig. 3:

$$I(q) = \int_0^{\pi/2} \frac{\sin^2(q(t/2)\cos\theta)}{q^2(t/2)^2 \cos^2\theta} \frac{4J_1^2(qr\sin\theta)}{q^2 R^2 \sin^2\theta} \sin\theta d\theta \quad (3)$$

where J_1 is the Bessel function of order 1. As a result of

fitting, the contour length of the reverse worm-like micelle was found to be 50 nm or more. In our previous studies, we estimated that the contour lengths of the lecithin/urea/*n*-decane¹⁶⁾, lecithin/sucrose fatty acid ester/*n*-decane¹⁷⁾, and lecithin/sugar/*n*-decane¹⁸⁾ systems were also at least 50 nm. Although we also attempted to calculate the persistence length, which is a measure of flexibility of a reverse worm-like micelle, from the Kratky plot, we were unable to do so because of the measurement range. The formation of reverse worm-like micelles was confirmed in substances such as liquid paraffin, isopropyl palmitate, isopropyl myristate, cetyl caprylate, and isododecane (data not shown). These reverse worm-like micelles maintained their stability without phase separation for at least three years.

3.2 Formation mechanism of reverse worm-like micelles in lecithin/PGL/*n*-decane systems

In general, the molecular structure of a surfactant is an important factor that governs the shape of molecular assemblies, and this relationship is usually shown in terms of the critical packing parameter (*CPP*)^{22, 23)},

$$CPP = v_{\text{tail}} / (a_{\text{hg}} l_{\text{tail}}) = a_{\text{tail}} / a_{\text{hg}} \quad (4)$$

where v_{tail} is the volume of the hydrophobic group; a_{hg} , the effective area per hydrophilic group; l_{tail} , the length of the hydrophobic group; and a_{tail} , the effective area per hydrophobic group. It was clarified that the preferred molecular assembly depends on the *CPP* value. For instance, $CPP \leq 1/3$ corresponds to a spherical micelle; $1/3 < CPP \leq 1/2$, to a rod-like or worm-like micelle; $1/2 < CPP < 1$, to a vesicle; $CPP = 1$, to a planar bilayer; and $CPP > 1$, to reverse structures (reverse vesicle, reverse worm-like micelle, reverse spherical micelle, and so on). Although the relationship between the reverse structures and the *CPP* value has not been reported so far, it is thought that the structures of reverse aggregates change in the order reverse vesicle → reverse worm-like micelle → reverse spherical micelle, as the *CPP* value increases. Lecithin alone forms a sphere or ellipsoidal reverse micelles in oil,¹³⁾ and this means that the *CPP* value exceeds 1. It is important to clarify here that the *CPP* value must decrease slightly when a reverse spherical micelle transforms to a reverse worm-like micelle. The mechanism of formation of the reverse worm-like micelle

formed with polar solvents such as water and GL can be explained as follows. Polar molecules such as water and GL attach to the phosphate groups of lecithins via hydrogen bonds, and the gap between the head groups of the neighboring lecithin molecules widens. Thus, the a_{hg} value of lecithin increases. On the other hand, it can be considered that a_{tail} is constant because the polar molecules do not affect the hydrophobic groups of lecithin. Therefore, the apparent *CPP* value of these systems decreases so that the reverse spherical micelle transforms to a reverse worm-like micelle. The PGLs we used in this study contained some intramolecular hydroxyl groups, because of which they could bind to the phosphate groups of neighboring lecithin as well as to water, thus transforming the solution into a gel.

The Om regions in the phase diagrams slightly enlarged with increasing polymerization degree of the glycerol residues, as shown in Fig. 1. This phenomenon can be explained by the difference in the solubility of GL and PGLs in lecithin reverse micelles. In general, polar solutes such as water are primarily partitioned to the core region of the reverse micelle, while non-polar solutes are partitioned to the palisade layer of the reverse micelle²⁴⁾. Table 1 shows the inorganic/organic balance (IOB) values of GL and PGLs based on this organic conceptual diagram^{25, 26)}. As used herein, the IOB value is an index representing the polarity of substances, i.e., a larger IOB value indicates higher hydrophilicity. Briefly, the IOB value represents the ratio of the inorganic value (IV) of a substance to the organic value (OV) of the substance. As shown in Table 1, the hydrophilicity decreased in the order GL ≫ 3PGL > 4PGL > 6PGL > 10PGL > 20PGL. From this, it is apparent that the Om regions in the phase diagrams enlarged slightly with increasing polymerization degree because the PGLs dissolved in the core and palisade layers, while the GL primarily dissolved in the micellar core.

In contrast, it is noteworthy that the difference in molecular weight between GL and the PGLs hardly affected the highly viscous region within the Om region, except in the case of 20PGL. This result suggested that the dissolved status of GL in reverse worm-like micelles was similar to that of the PGLs, namely, GL was not distributed homogeneously in reverse worm-like micelles but formed a cluster

Table 1 List of IOB values calculated from organic conceptual diagram.

	Inorganic value (IV)	Organic value (OV)	IOB value
GL	300	60	5.0
3PGL	540	180	3.0
4PGL	660	240	2.8
6PGL	900	360	2.5
10PGL	1380	600	2.3
20PGL	2580	1200	2.2

with hydrogen bonds and dissolved in the micelles.

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

The rheological properties of the reverse micellar solutions, which were prepared at a fixed lecithin concentration of 10 wt% and varying GL and PGL concentrations, were examined.

First, we carried out steady-flow viscosity measurements for the reverse micellar solutions. **Figure 5** shows the results of the steady-flow viscosity measurements for the lecithin/4PGL/*n*-decane system. For all compositions, Newtonian flow occurred over the low-shear-rate range, as demonstrated by a nearly constant viscosity. This indicated that the three-dimensional network structure formed by the reverse worm-like micelles was apparently not broken in this range. As stated previously, the three-dimensional network structure of reverse worm-like micelles is not static like a synthetic polymer but is a transient network where collapse and formation are repeated (i.e., reversible breakage). Therefore, if the re-formation rate of the reverse worm-like micelle is sufficiently higher than the added shear rate, the sample shows Newtonian flow, because the network structure does not break. At higher shear rates, however, the solutions showed non-Newtonian flow, decreasing the viscosity of the solution with increasing shear rate. This phenomenon is a result of the collapse of the network structure, and it occurs when the shear rate is much higher than the re-formation rate.

Fig. 5 Steady shear rate-viscosity (η) curves for lecithin/4PGL/*n*-decane system at various concentrations of 4PGL. Lecithin concentration was fixed at 10 wt%.

Figure 6 shows the relationship between zero-shear viscosity (η_0), given by extrapolation of the steady-flow viscosity curve to zero shear rate, and the GL and PGL concentrations. The η_0 values of all systems increase monotonously until phase separation occurs, and then, the entire η_0 curve shifts to the right (i.e., to higher PGL concentrations) as the polymerization degree of the PGLs increases. It follows from this that the reverse worm-like micelles can grow upon PGL addition, as they did in the system containing GL, and that a small amount of PGLs can induce the formation of reverse worm-like micelles with sufficient length for entanglement when using PGLs with smaller polymerization degrees. We also note that the gels formed using PGLs showed higher viscosities than did the gel formed using GL. The maximum η_0 values of the lecithin/GL/*n*-decane and lecithin/20PGL/*n*-decane systems are approximately 40 Pa·s and 550 Pa·s, respectively. The difference between these systems is discussed later.

Next, to characterize the viscoelasticity of the lecithin/PGL/*n*-decane systems, we carried out dynamic viscoelasticity measurements. **Figure 7** shows the variation in the storage modulus (G') and loss modulus (G'') as a function of frequency (ω) for the lecithin/4PGL/*n*-decane system, at a fixed lecithin concentration of 10 wt% and varying 4PGL concentrations. Here, G' and G'' represent elasticity and viscosity, respectively. G' and G'' intersect at a certain ω . At high frequencies, the elasticity component is predominant ($G' > G''$), while at low frequencies, the viscosity

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

Fig. 7 Variation in G' and G'' as a function of ω at different 4PGL concentrations in the lecithin/4PGL/*n*-decane system at 25°C. Lecithin concentration was fixed at 10 wt%. Maxwellian fittings to the experimental data are shown by solid lines.

component is predominant ($G'' > G'$). It is well known that the dynamic viscoelastic behavior of reverse worm-like micelles follows a single Maxwell model. This relaxation time indicates the disentanglement time of reverse worm-like micelles. In general, the relaxation time of linear polymers has a wide distribution because the polymers disentangle via reptation and the relaxation time is proportional to the third power of the molecular weight⁸⁻¹¹. Here, reptation implies the mode of motion by which the entangled polymers gradually disentangle from the chain end under the influence of their own Brownian motion. In contrast, the rheological behavior of reverse worm-like micelles is determined by the balance between reversible breakage and reptation of the micelles, and single Maxwellian behavior is generally observed when the reversible breakage time is sufficiently shorter than the reptation time^{12, 13}. If the viscoelastic behavior of reverse worm-like micelles follows the single Maxwell model, Eqs. 5 and 6 fit well to the data obtained by the dynamic viscoelasticity measurements. In this situation, relaxation time is represented by the geometric mean of the breaking time and reptation time (Eq. 7)¹²,

$$G' = \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} G_0 \quad (5)$$

$$G'' = \frac{\omega \tau}{1 + \omega^2 \tau^2} G_0 \quad (6)$$

$$\tau = (\tau_b \tau_{\text{rep}})^{1/2} \sim \bar{L} \quad (7)$$

where $\bar{L}$ is the average length of the reverse worm-like micelle and τ reflects the length of the reverse worm-like micelle^{12, 13}. G_0 is the plateau modulus, as calculated by Eq. 8^{12, 13}.

$$G_0 = \nu k T = \frac{k T}{\xi^3} \quad \xi \approx \phi^{-0.75} \quad (8)$$

Here, ν is the numerical density of the entanglement point; k , Boltzmann's constant; T , the absolute temperature; ξ , the mesh size of the entangled network; and ϕ , the volume fraction of reverse worm-like micelles. Therefore, G_0 reflects the volume fraction of the entangled reverse worm-like micelles. When a sample follows a single Maxwell model, η_0 can be defined by Eq. 9.

$$\eta_0 = G_0 \tau \quad (9)$$

Here, η_0 is determined by the balance between the number and length of the reverse worm-like micelles. The fitted curves (solid lines) based on Eqs. 5 and 6 are shown in Fig. 7. The rheological behavior of the reverse worm-like micelles showed a good fit with the Maxwellian curves at low frequencies. However, the fit was not good at high frequencies, which indicated that the relaxation mode of the reverse worm-like micelles formed in this system did not strictly follow the single Maxwell model and that faster relaxation occurred in addition to the relaxation of reversible breakage. This faster relaxation mode is thought to be related to micro-Brownian motion (i.e., the Rouse mode²⁷) of the reverse worm-like micelles. Figures 8 and 9 show the variation in G_0 and τ as a function of the GL and PGL concentrations in these systems. As shown in Fig. 8, all the G_0 curves shifted to the right and the maximum value of G_0 decreased slightly with increasing polymerization degree of the PGLs. It follows from the small decrease in G_0 that the volume fraction of entangled reverse worm-like micelles decreased slightly with increasing polymerization degree of the PGLs. On the other hand, as shown in Fig. 9, the maximum τ value dramatically increased with the polymerization degree of the PGLs, because all the τ curves moved significantly to the upper right. We believe the reason for the rapid increase in τ to be as follows. As mentioned above, it is well known that the relationship for τ expressed in Eq. 7 holds when the experimental data follow a single Maxwell model^{12, 13}. Here, τ_{rep} increased as the length of the reverse worm-like micelle increased, and τ_b increased as the breakage of reverse worm-like micelles became difficult. It is reasonable to think that elongated and/or relatively unbreakable reverse worm-like micelles were formed by the addition of the PGLs. Here, we would like to explain how the relatively unbreakable reverse worm-like micelles were formed in lecithin/PGL/*n*-decane systems. We suggested above that glycerols formed clusters in the reverse worm-like micelles of the lecithin/GL/

Fig. 8 Variation in G_0 at different GL and PGL concentrations in the lecithin/GL/*n*-decane and lecithin/PGL/*n*-decane systems at 25°C.

Fig. 9 Variations in τ at different GL and PGL concentrations in the lecithin/GL/*n*-decane and lecithin/PGL/*n*-decane systems at 25°C.

n-decane system and that these clusters were formed by hydrogen bonding between the glycerol molecules. In contrast, the PGLs in the reverse worm-like micelles were formed via covalent bonds with the glycerol residues, and hence, the bonding strength of the glycerols in the PGLs was considerably stronger than that in a glycerol cluster. It is certain that the difference in the bonding strength between the PGLs and the GL clusters affected the breakage of all the reverse worm-like micelles. Therefore, we

suggest that the increase in the maximum η_0 value of the system containing the PGLs is affected by not only the increase in the length of the reverse worm-like micelles but also the increase in the bonding strength. The results of our experiment clearly show that the viscosity and viscoelasticity of reverse micellar solutions can be improved by using PGLs instead of GL.

4 CONCLUSIONS

We developed new lecithin organogels with lecithin/PGL/oil systems and compared their phase behavior and rheological properties with those of the conventional lecithin/GL/oil system. The most important findings in this study are the following. All the PGLs used in this study can induce the formation of lecithin organogels that consist of reverse worm-like micelles, except for 40PGL. The zero-shear viscosity of the micellar solutions depends on the concentration and polymerization degree of the PGLs. Thus, we conclude that PGLs are useful liquids because of their ability to induce the formation of lecithin organogels, as do substances such as water and glycerol.

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