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Photorheological Response of Aqueous Wormlike Micelles with Photocleavable Surfactant

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ABSTRACT: Recently, we have reported a new cinnamic acid-type photocleavable surfactant, C4–C–N-PEG9 that experiences a photocleavage through UV-induced cyclization in aqueous solution, yielding a coumarin derivative (7-butoxy-2H-chromen-2-one) and an aminated polyoxyethylene compound. Here, we have studied the effects of C4–C–N-PEG9 on the photorheological behavior of viscoelastic wormlike micelles formed by aqueous mixture of nonionic surfactants, polyoxyethylene phytosterol ether (PhyEO₂₀) and tetraoxyethylene dodecyl ether (C₁₂EO₄). The 4.9 wt % PhyEO₂₀/H₂O + 2.4 wt % C₁₂EO₄ solution forms wormlike micelles, and its viscosity is ~10 Pa·s. We have found that the addition of C4–C–N-PEG9 into this viscous, non-Newtonian fluid system decreases the viscosity. Viscosity decreased in parallel to the C4–C–N-PEG9 concentration reaching ~0.003 Pa·s at 2.5 wt % of C4–C–



N-PEG9. However, viscosity of the C4–C–N-PEG9 incorporated system increased significantly (~200 times at 1.5 wt % of C4– C–N-PEG9 system) upon UV irradiation. Small-Angle X-ray scattering studies have shown that addition of C4–C–N-PEG9 favors wormlike-to-sphere type transition in the micellar structure. However, UV irradiation in the C4–C–N-PEG9 incorporated system causes one-dimensional micellar growth. Since C4–C–N-PEG9 has relatively bigger headgroup size compared to the $C_{12}EO_{4^{\prime}}$ addition of C4–C–N-PEG9 into wormlike micelles reduces the critical packing parameter resulting in the formation of spherical aggregates. UV irradiation induced one-dimensional micellar growth is caused due to photocleavage of the C4–C–N-PEG9 into a less surface-active coumarin derivative and an aminated polyoxyethylene compound, as confirmed by UV–vis spectrometry and HPLC measurements. The hydrophobic coumarin derivative formed after cleavage of C4–C–N-PEG9 goes to the micellar core and is responsible for decreasing the viscosity. However, the hydrophilic aminated polyoxyethylene prefers to reside at the vicinity of headgroup of PhyEO₂₀ reducing the interhead repulsion, increasing the critical packing parameter and the viscosity as well.

1. INTRODUCTION

Surfactants self-assemble into a variety of microstructures, like spherical or cylindrical micelles, above the critical micelle concentration (CMC), and at high concentrations a range of lyotropic mesophases are formed.¹ Under certain conditions, the spherical micelles can transform into long micelles that overlap with each other, forming a transient network exhibiting both viscous and elastic properties, called wormlike micelles. Highly viscoelastic fluids find a wide range of applications as household and industrial products.² It is found that wormlike micelles formed by nonionic surfactants are preferred over ionic surfactants as they are environmentally friendly, simple with respect to charges, and avoid complex interactions. For practical applications, stimulus-responsive systems have gained much attention.^{3–8}Their application as carriers for drug delivery,^{9–11} nanoreactors for preparing nanosized materials,¹² and building blocks for the fabrication of smart surface coatings¹³ is highly recommended. In order to implement wormlike micelles into actual applications, studying the effects of various stimuli on rheology is a must. There are reports on reversible changes in

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Scheme 1. Molecular Structures of Polyoxyethylene Phytosteryl Ether (a) $PhyEO_{20}$, and Photocleavable Surfactant (b) C4–C–N-PEG9, and (c) Photocleavage Reaction of C4–C–N-PEG9 into Coumarin Derivative (7-Butoxy-2H-chromen-2-one) and Animated Polyoxyethylene Parts, Respectively



the viscoelastic properties of wormlike micellar solutions as a result of the trans-cis photoisomerization of azobenzenemodified cationic surfactants,14 cinnamic acid, and its derivatives;¹⁵⁻¹⁷ the effect of light on the self-assembly of aqueous mixtures of sodium dodecyl sulfate and a cationic, bolaform surfactant containing azobenzene;¹⁸ and the photoresponsive smart surface coatings based on the photoisomerization of a spiropyran-modified cationic surfactant adsorbed at a silica/aqueous solution interface.¹⁹ Light-sensitive surfactants provide interesting opportunities to create stimuliresponsive giant micellar systems because illumination of a solution can be easily patterned and modulated, and the benefits of using light as an external stimulus over pH, thermal, or electrical stimulation include miniaturization and limited chemical contamination, promoting the development of green, sustainable systems.²⁰ There are also reports on the effects of external stimuli (acid-base chemical reactions, thermal reactions, photoreactions) on cleavable surfactants.^{21–30}

Recently, we have reported a new photocleavable surfactant, C4-C-N-PEG9 that undergoes photocleavage through UVinduced cyclization in aqueous solutions, yielding two functional materials including a coumarin derivative and an aminated polyoxyethylene compound.³¹ It is expected that the cleaved compounds may act as a perfume³² and a moisturizing agent,³³ respectively. To the best of our knowledge, this photocleavable mechanism has not been applied earlier in the wormlike micelles studies. In this context, systematic studies focusing on photoinduced structural modification have been carried out. Here, we study the effect of photocleavable surfactant, C4-C-N-PEG9, on the rheological behavior of environmentally friendly viscoelastic wormlike micelles formed by aqueous mixture of polyoxyethylene phytosteryl ether (PhyEO₂₀) and tetraoxyethylene dodecyl ether $(C_{12}EO_4)$.³⁴ The results are supported by rheology, UVvis spectroscopy and HPLC, and small angle X-ray scattering measurements. We expect that this new concept of the photorheological change with photocleavable surfactant can be of theoretical and practical importance. It is possible to design a photocleavable surfactant-based wormlike micellar system.

2. EXPERIMENTAL SECTION

2.1. Materials. Polyoxyethylene phytosteryl ether, (PhyEO₂₀, high purity, containing a percentage of isomers with branched structure) was kindly provided by Nikko Chemicals Co., Japan. Tetraoxyethylene dodecyl ether ($C_{12}EO_4$, purity >98%) was purchased from Nikko Chemicals Co., Japan. All chemicals were used as received without further purification. The water used in this study was deionized with a Barnstead NANO Pure Diamond UV system and filtered with a Millipore membrane filter (pore size 0.22 lm). The photocleavable surfactant C4–C–N-PEG9 was synthesized as previously described.³¹ Scheme 1 shows the molecular structures of (a) Polyoxyethylene phytosteryl ether (PhyEO₂₀), (b) C4–C–N-PEG9, and (c) photocleavage of C4–C–N-PEG9, respectively.

2.2. Preparation of Wormlike Micelles and Rheology. In this study, we focus on wormlike micellar solutions formed by an aqueous mixture of nonionic surfactants, polyoxyethylene phytosteryl ether (PhyEO₂₀) and tetraoxyethylene dodecylether ($C_{12}EO_4$), at a composition of 4.9 wt % PhyEO₂₀/H₂O + 2.4 wt % of $C_{12}EO_4$, as reported by Naito et al.³⁴ This mixture is biodegradable and less toxic. This composition forms viscoelastic wormlike micelles with the lowest concentration of surfactants in this system. In addition, if total concentrations of these surfactants are too high, the viscosity is so high that the handling of the samples is quite difficult.

Different amounts of C4–C–N-PEG9 were added to this micellar solution and mixed using a vortex mixer until a homogeneous mixture was achieved. The effect of UV irradiation as a function of time was studied on the C4–C–N-PEG9 added samples. The ultraviolet light irradiation was carried out by placing the 2 mL sample in a quartz cell (10×10 mm), with stirring at room temperature. Then the rheological measurements were performed after keeping the sample at equilibrium for 2 to 3 days. It was observed that the rheological parameters were almost the same when immediately performed. Measurements were performed in a stress-controlled rheometer, AR-G2 (TA Instruments) using cone–plate geometries (diameter 40 mm with a cone angle of 2° 0′ 4″). Frequency sweep measurements were performed in the linear viscoelastic regime of the samples, as previously determined by dynamic strain sweep measurements.

2.3. UV-vis Spectroscopy and HPLC. For the UV-Vis spectroscopy and HPLC measurements, light irradiation was carried out using a San-EI Supercure 203S Hg–Xe lamp (200 W) equipped with a UV filter. The transmission wavelength region is 260–390 nm; U-340 at an irradiation intensity of 50 mW cm⁻². Ultraviolet light irradiation was carried out by placing the 2 mL sample in a quartz cell (10 ×10 mm), with stirring at room temperature. The photocleavable behavior that occurs in bulk solution was monitored using an Agilent



Figure 1. (a) Photographs of 4.9 wt % PhyEO₂₀/H₂O/2.4 wt % $C_{12}EO_4$ and 4.9 wt % PhyEO₂₀/H₂O/2.4 wt % $C_{12}EO_4$ + 1.5 wt % C4–C–N-PEG9 solutions before and after 2 h of UV irradiation, (b) UV–vis absorption spectra of 4.9 wt % PhyEO₂₀/H₂O/2.4 wt % $C_{12}EO_4$ + 1.5 wt % C4–C–N-PEG9 solutions before and after 2 h of UV irradiation, and (c) steady-shear rheology of the corresponding system in parts (a) and (b) at 25 °C.

8453 UV-vis spectrophotometer with a quartz cuvette (0.1 mm path length). The photocleavable behavior was also characterized using an Agilent 1200 high-performance liquid chromatography system (ZORBAX Eclipse XDB C18 column, G1314B VWD variable wavelength detector, methanol mobile phase) equipped with a JEOL JMS-T100CS ESI mass spectrometer.

2.4. Small-Angle X-ray Scattering (SAXS). In order to investigate the microstructure transitions induced by the addition of C4-C-N-PEG9 and UV irradiation, SAXS measurements were performed using a SAXSess camera (Anton Paar, Austria) attached to a PW3830 laboratory X-ray generator with a long fine focus sealed glass X-ray tube (Cu $-K_{\alpha}$ wavelength of 0.154 nm) (PANalytical). The apparatus was operated at 40 kV and 50 mA. The SAXSess camera is equipped with a focusing multilayer optic and a block collimator for an intense and monochromatic primary beam with low background and a translucent beam stop for the measurement of an attenuated primary beam at zero scattering vector (q = 0). Samples were enclosed in a vacuum tight thin quartz capillary with an outer diameter of 1 mm and thickness of 10 μ m. Sample temperature was controlled with a thermostatted sample holder unit (TCS 120, Anton Paar). The 2D scattering pattern was collected on an image plate (IP) detection system Cyclone (Perkin-Elmer, U.S.), and was finally integrated into one-dimensional scattering curves as a function of the magnitude of the scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$ using SAXSQuant software (Anton Paar), where θ is the total scattering angle, and λ is the wavelength of X-ray. All data were normalized to the same incident primary beam intensity for the transmission calibration and were corrected for the background scattering from the capillary and water. All of the measured I(q) data were corrected for the background scattering from the capillary and the solvents, and the absolute scale calibration was made using water as a secondary standard. The SAXS data were analyzed by the generalized indirect Fourier transformation (GIFT) method³⁵⁻³⁸ to determine the pairdistance distribution function, p(r). The p(r) contains information on shape, size, internal structure, and inhomogeneity of scattering elements.³⁹⁻⁴³ Generally, GIFT relies on a basic equation of onecomponent monodisperse globular particle systems, I(q) = nP(q)S(q), where *n* is average number density of micelles, P(q) is average form factor, and S(q) is static structure factor. For the polydisperse systems, the S(q) is to be replaced with the so-called effective structure factor. It should be noted that in dilute systems where interparticle interactions are negligible, I(q) is apparently identical to the form

factor P(q) so that SAXS data can be evaluated by *indirect Fourier* transformation (IFT) without any problem in the evaluation procedure. However, in semidilute or concentrated systems, the I(q) deviates from the ideal particle form factor P(q) due to interactions between the micelles that are represented by the structure factor S(q). Under this situation, transformation of I(q) into real-space without separating out the influence of S(q) leads to a Fourier transform that can hardly be interpreted because of strong oscillations at higher r-values. This total distribution function describes the distance distributions of the overall density fluctuations around the mean value, which are related to the micellar density distributions, described by the correlation function $\gamma(r)$, and to the total correlation function h(r) = [g(r) - 1], describing the deviation of the particle distribution from the statistically uncorrelated situation, with g(r) being the radial distribution function and r the distance between the center of two micelles.

Theoretically, P(q) is the Fourier transformation of p(r) and can be described as follows,

$$P(q) = 4\pi \int_0^\infty p(r) \frac{\sin qr}{qr} dr$$
(1)

So one needs to calculate the IFT of the experimental P(q) to deduce the p(r) from the SAXS data. However, for concentrated systems, both the P(q) and S(q) have to be determined simultaneously within one procedure taking into account of interparticle interactions. Therefore, to suppress the influence of interparticle interference scattering on the evaluation of p(r) an interaction potential model for the structure factor has to be used during the data analysis. The P(q) is absolutely model free only a rough information on the maximum dimension of micelle is required while S(q) is calculated according to the Percus– Yevick^{44,45} so it is not model independent. In the present study, we have selected the averaged structure factor model^{46,47} for polydisperse hard-spheres and Percus–Yevick approximation is used to solve the Ornstein–Zernike (OZ) equation for the calculation of S(q).

3. RESULTS AND DISCUSSION

3.1. UV–visible Spectra and Rheology. Figure 1 shows the visual observation of 4.9 wt % PhyEO₂₀/H₂O/2.4 wt % $C_{12}EO_4$ and 1.5 wt % C4–C–N-PEG9 added 4.9 wt % PhyEO₂₀/H₂O/2.4 wt % $C_{12}EO_4$ solutions before and after UV irradiation. Visually they are quite different. The solution before

adding C4–C–N-PEG9 has high viscosity and shows shear birefringence when viewed under a crossed polarizer; however, when C4–C–N-PEG9 is added to the solution, the viscosity drops (samples are water-like that do not show any flow birefringence). The C4–C–N-PEG9 added system regains viscosity upon UV irradiation.

Figure 1b shows the UV-vis spectra for 4.9 wt % PhyEO₂₀/ $H_2O/2.4$ wt % $C_{12}EO_4$ + 1.5 wt % C4-C-N-PEG9 solutions before and after 2 h of UV irradiation corresponding to the irradiation energy 50 mW/cm². The sample shows an absorbance peak at 322 nm before UV. With UV light irradiation, absorbance at 322 nm decreases (A₃₂₂ assigned for the C4–C–N-PEG9) while absorbance at 194 nm (A_{194}) increases.³¹ The A_{194} absorption peak originates from the coumarin derivative formed in the process. It is suggested that the UV induced increased A₁₉₄ and decreased A₃₂₂ peaks are due to the photocleavage of C4-C-N-PEG9 into the coumarin derivative and aminated polyoxyethylene compound. Thus, irradiation will cause the C4-C-N-PEG9 molecule to absorb light, and this, in turn, can trigger a photocleavage of the C4-C-N-PEG9 to coumarin derivative and aminated polyoxyethylene compound. The photocleavage reaction of C4-C-N-PEG9 was also confirmed by LC-MS measurements before and after UV light irradiation.

The steady shear measurements for 4.9 wt % PhyEO₂₀/H₂O + 2.4 wt % C₁₂EO₄ solution (Figure 1c) show the shear thinning behavior, η decreases with the increase in shear rate, a trend commonly observed for solution with wormlike micelle matrix. It consists of a viscous matrix composed of long wormlike micelles³⁴ (the zero shear viscosity, $\eta_0 \approx 10$ Pa·s). When photodegradable surfactant, C4–C–N-PEG9 is added to it the η_0 decreases. On UV irradiation, gradually the system regains the viscosity and non-Newtonian behavior with time (~2 h after irradiation), see Figure 1 c.

The dynamic or oscillatory rheological response, which is one of the sensitive probes of the nanostructure in complex fluids, has been examined. Figure 2 shows the dynamic



Figure 2. Variation of elastic modulus (*G'*, closed symbols), and viscous modulus (*G"*, open symbols) as a function of oscillation frequency (ω) for the sample 4.9 wt % PhyEO₂₀/H₂O/2.4 wt % C₁₂EO₄, and 4.9 wt % PhyEO₂₀/H₂O/2.4 wt % C₁₂EO₄ + 0.5 wt % C4-C-N-PEG9 before and after UV irradiation at 25 °C.

rheology data—variation of elastic modulus (G') and viscous modulus (G'') as a function of oscillation frequency (ω) for the sample 4.9 wt % PhyEO₂₀/H₂O/2.4 wt % C₁₂EO₄. The sample shows a typical viscoelastic response; i.e., the behavior is elastic (G' > G'', plateau in G') at high frequencies or short time scales, while it is viscous (G'' > G', both moduli are strong functions of frequency) at low frequencies or long time scales. The G' and G" show a crossover at the intermediate frequency (exhibits viscoelasticity). This behavior resembles that of the Maxwell model observed for entangled wormlike micelles.³⁴ When C4–C–N-PEG9 is added the crossover is not observed in the whole frequency range (0.1–100 rad·s⁻¹) measured. The sample exhibits a purely viscous response over the entire range of frequencies, a response similar to liquid with short micelles.

Alternatively, after UV irradiation, this solution regains viscous behavior (G' < G'') at lower frequencies and elastic behavior (G' > G'') at higher frequencies, and a crossover around intermediate frequency is observed. Thus, dynamic rheology confirms a UV-induced transition from spherical micelles to wormlike micelles. It is found that (Figure 2), it is possible to control the rheology with C4–C–N-PEG9 and UV.

Figure 3a shows the effect of the amount of C4–C–N-PEG9 on the viscosity of the 4.9 wt % PhyEO₂₀/H₂O/2.4 wt % C₁₂EO₄. It is found that the η_0 decreases gradually with the continuous addition of C4–C–N-PEG9 and the solution eventually shows Newtonian flow behavior. It is almost constant beyond 2.5 wt % of the additive. With UV irradiation (50 mW/cm², 2 h), the η_0 for any amount of C4–C–N-PEG9 on the other hand switches a Newtonian fluid to a viscous, non-Newtonian fluid. With 1.5 wt % C4–C–N-PEG9, viscosity of the solution reduces to 0.01 Pa·s. It should be noted that the most significant change in η_0 before and after UV irradiation is when 1.5 wt % C4–C–N-PEG9 is added to the system, (200fold increase in viscosity from 0.01 Pa·s to 2 Pa·s).

Figure 3, parts b and c, shows the steady-shear rheology and the corresponding UV-visible spectra for 4.9 wt % PhyEO₂₀/ $H_2O/2.4$ wt % $C_{12}EO_4$ + 1.5 wt % C4–C–N-PEG9 solutions before and after UV irradiation for various periods of time corresponding to the irradiation energy 50 mW/cm², respectively. The viscosity gradually increases with UV irradiation time, and the time dependent UV- spectrum shows a gradual decrease in A₃₂₂ absorbance peak, assigned for the C4-C-N-PEG9 and an increased A194 absorbance peak, originated from the coumarin derivative. It is anticipated that at the fixed concentration of C4-C-N-PEG9 in the system, steady increase of viscosity occurs due to the gradual UV induced photocleavage of C4-C-N-PEG9 into coumarin derivative and aminated polyoxyethylene compound (decrease in A_{322} absorbance peak and increase in A_{194} absorbance peak increases with UV irradiation time).

3.2. HPLC and ESI-MS Measurements. HPLC measurements have been performed in order to calculate the degree of photodegradation of C4-C-N-PEG9 as a function of time and correlate with the viscosity change. Figure 4a shows the photocleavage ratio of C4-C-N-PEG9 as a function of irradiation time. The maximum degree of photocleavage has been evaluated as 85% (confirmed by HPLC measurements accompanied by the ESI-MS measurements). About 85% of photocleavage reaction completed within 30 min and reached photostationary state. Figure 4b shows the η_0 as a function of photocleavage ratio; the η_0 increases with the progress of photocleavage reaction. The η_0 increases abruptly at ~60% ratio, suggesting the existence of the critical composition which induces the abrupt growth of the wormlike micellar network. The photoinduced cleavage of C4-C-N-PEG9 and ultimately reduction of the interfacial curvature of the aggregate in the mixed system seems to be responsible for the increase in the viscosity.



Figure 3. (a) Zero shear viscosity of 4.9 wt % PhyEO₂₀/H₂O + 2.4 wt % $C_{12}EO_4$ solutions as a function of C4–C–N-PEG9 before and after UV irradiation, (b) steady-shear rheology and (c) UV–vis absorption spectra of the 4.9 wt % PhyEO₂₀ /H₂O/2.4 wt % $C_{12}EO_4$ +1.5 wt % C4–C–N-PEG9 system before and after UV irradiation for various periods of time at 25 °C.



Figure 4. (a) Photocleavable ratio for various periods of UV irradiation time and (b) zero shear viscosity as a function of photocleavage ratio of 4.9 wt % PhyEO₂₀/ $H_2O/2.4$ wt % $C_{12}EO_4$ + 1.5 wt % C4–C–N-PEG9 at 25 °C.

3.3. SAXS Measurements. In order to investigate the microstructure transitions of phytosterol wormlike micelles induced by the C4-C-N-PEG9, and upon UV irradiation in the C4-C-N-PEG9 incorporated system, SAXS measurements were performed on the 4.9 wt % PhyEO₂₀/H₂O + 2.4 wt % C12EO4 system at different concentration of C4-C-N-PEG9 (0, 1.5, and 2.5%), and on the 4.9 wt % $PhyEO_{20}/H_2O +$ 2.4 wt % C₁₂EO₄ + 1.5% C4-C-N-PEG9 system after UV irradiation. All of the measurements were performed at 25 °C and experimental data were evaluated using the GIFT method as described in the Experimental Section. Figure 5a shows the SAXS spectra on absolute scale (symbols) of the 4.9 wt % PhyEO₂₀/H₂O + 2.4 wt % C₁₂EO₄ system at different concentrations of C4-C-N-PEG9 with solid lines representing GIFT fit to the experimental SAXS data and dashed lines, the calculated form factors as obtained by the GIFT method. The results of the GIFT procedure, i.e., the pair-distance

distribution function, p(r), are presented in Figure 5b. Figure 5, parts c and d, shows SAXS spectra and corresponding p(r)curves of the 1.5% C4-C-N-PEG9 system before and after UV irradiation, respectively. First we discuss the effect of C4-C-N-PEG9 on the microstructure of the 4.9 wt % PhyEO₂₀/ $H_2O + 2.4$ wt % $C_{12}EO_4$ system. As can be seen in Figure 5a, all of the SAXS spectra are typical of core-shell particles displaying local minimum and maximum in the middle-q regime. This local minimum (or inner central peak) in the SAXS spectrum is usually affected by the interparticle interference and the side maximum represents the particle form factor. As can be seen in Figure 5a, the inner central peak (indicated by arrows) and side maximum of SAXS pattern shifted toward higher-q side upon addition of C4–C–N-PEG9. Besides, the calculated form factor curve decays differently in the low-*q* regime. The low-*q* slope is roughly "-1" representing the rodlike structure⁴⁸⁻⁵⁰ of the aggregates in the system



Figure 5. (a) Normalized X-ray scattered intensities, I(q), for the 4.9 wt % PhyEO₂₀/H₂O + 2.4 wt % C₁₂EO₄ system at different concentrations of C4–C–N-PEG9 (0, 1.5, and 2.5%) obtained in absolute scales, (b) the corresponding pair-distance distribution function, p(r), (c) the I(q) curves for the 4.9 wt % PhyEO₂₀/H₂O + 2.4 wt % C₁₂EO₄ + 1.5 wt % C4–C–N-PEG9 before and after UV irradiation, and (d) the corresponding p(r) curves. The solid and broken lines in panels (a) and (c) represent the GIFT fit and the calculated form factor for *n* particles existing in unit volume, nP(q), respectively. The downward arrows on the high-*r* side of panels (b) and (d) represent the maximum dimension, $D_{max'}$ of spheroid type micelles and maximum length, $L_{max'}$ of elongated rodlike micelles, respectively. Schematic models show the microstructure transitions.

without C4–C–N-PEG9. Addition of C4–C–N-PEG9 decreased the low-q slope, demonstrating the modulation of the rodlike structure of aggregates into a globular-type object. Relatively smaller values of the I(q = 0) in the C4–C–N-PEG9 incorporated systems also indicate smaller size aggregates.

As we have mentioned in the Experimental Section, essential information on the particle shape and size can be obtained from the pair-distance distribution function p(r). One can estimate the maximal dimension $(D_{\text{max}} \text{ for sphere and } L_{\text{max}} \text{ for rods})$ within one particle from the abscissa value where the p(r)function reaches to zero in the higher-r side. Experimental SAXS spectra of the 4.9 wt % PhyEO₂₀/H₂O + 2.4 wt % C12EO4 system with different surfactant concentrations of C4-C-N-PEG9 were therefore transformed from the reciprocal into the real-space by the GIFT method, which separates out the disturbing interparticle contribution from the overall scattering intensity. The shape of the p(r) functions (see Figure 5b) indicates inhomogeneous (core-shell) rodlike and globular structures with differences in the core and shell scattering contrast. The local maximum and minimum in the lower-*r* side of the p(r) curves, which originate due to electron density difference in the core and shell, are the characteristic features of core-shell type micelles. In the absence of C4-C-N-PEG9, the shape of p(r) function is characteristic of rodlike micelles: long tail in the higher-r regime. The maximum length of the rod, L_{max} is ca. 18.5 nm, which is very interestingly! The shape of the p(r) functions of the C4-C-N-PEG9 incorporated systems have a characteristic of spheroid type micelles with maximum dimensions, D_{max} , ca. 10.4 and 9.7 nm for the 1.5 and 2.5 wt % C4–C–N-PEG9, respectively. Thus, judging from the p(r) function, we have observed a clear rod-to-sphere microstructure transition induced by the C4–C–N-PEG9, as illustrated by a schematic model in Figure 5b. These results obtained from the SAXS measurements well explain the change in rheological behavior of the phytosterol wormlike micelles upon addition of C4–C–N-PEG9. As shown in Figure 3a, the η_0 of phytosterol womlike micelles decreases by approximately 4 orders of magnitude upon incorporation of 2.5 wt % C4–C–N-PEG9. This massive decrease in viscosity is caused by the microstructure transitions. Addition of C4–C–N-PEG9 destroys the network structures of wormlike micelles and eventually favors the formation of spherical type micelles.

Next, we discuss the effect of UV irradiation on the microstructure of the 1.5 wt % C4–C–N-PEG9 incorporated system. Note that this system consists of spheroid type micelles having maximum dimension ca. 10.2 nm before UV irradiation (see Figure 5b). One can clearly see the difference in the SAXS patterns before and after UV irradiation. The scattering intensity in the low-q regime ($q < 0.6 \text{ nm}^{-1}$) decreased and the inner central peak shifted slightly toward the forward direction after UV irradiation. It should be noted that the decrease in the I(q = 0) value is caused due to poor contrast of system not due to smaller particle size as the calculated form

factor decays following approximately q^{-1} behavior in the low-q regime indicating rodlike shape of the micelle.

The UV induced microstructural transition can best be seen in the real-space p(r) curves shown in Figure 5d. After UV irradiation, the p(r) curve decays slowly in the higher-r side, which is characteristic of elongated scattering object. The maximum length of elongated micelles after UV irradiation is ca. 14.5 nm. This demonstrates the fact that UV irradiation in the C4-C-N-PEG9 incorporated system favors sphere-to-rod type transition resulting in the formation of long rodlike micelles, which again strongly supports the results obtained from the rheometry (viscosity of the sample increased from 0.01 to 2.1 Pas upon UV irradiation, see Figure 3a). From visual observation, we found that the sample of the 4.9 wt % PhyEO₂₀/H₂O/2.4 wt % C₁₂EO₄ + 1.5% C4-C-N-PEG9 system flows easily before UV irradiation. However, after 2 h UV irradiation, the sample did not flow even after the glass vial was turned upside-down.

The results obtained from the GIFT evaluation of the scattering data very well support the results derived from rheological measurements. However, we note that the maximum length of micelles that we have determined from the real-space p(r) curves, particularly for the rodlike or wormlike micelles, may not be the actual length of rods. Generally, the maximum size that one can detect from scattering measurements depends on the maximum resolution of the SAXS measurement $(q_{\min}, D_{\max} = \pi/q_{\min})$ and on the overall contrast of the system. Nevertheless, with the available contrast of the systems and sensitivity of our SAXS equipment $(q_{\min} \sim 0.1 \text{ nm}^{-1})$, we could outline the qualitative information on microstructure transition induced by the C4–C–N-PEG9 and UV irradiation to explain the rheological behavior.

Figure 6 shows the proposed mechanism for the different rheological behavior induced by the addition of C4-C-N-



Figure 6. Wormlike micellar structure formed by the 4.9 wt % $PhyEO_{20}/H_2O + 2.4$ wt % $C_{12}EO_4$ system, and the effect of C4–C–N-PEG9 and UV irradiation. The $PhyEO_{20}$ molecule is shown as an orange head and black tail, the $C_{12}EO_4$ molecule is shown with a blue head and black tail, while the C4–C–N-PEG9 is shown with a green head and green tail.

PEG9 into 4.9 wt % PhyEO₂₀/H₂O/2.4 wt % $C_{12}EO_4$ and UV irradiation in C4–C–N-PEG9 added solutions. PhyEO₂₀ forms spherical micelles with cone geometry at dilute concentration due to interhead repulsion of its larger polyoxyethylene chain headgroup.⁵¹ When $C_{12}EO_4$ is added to the micellar solution of PhyEO₂₀, it goes to the palisade layer of the latter. The additive reduces the effective headgroup area and thus leads to a sphere

to cylinder micellar transition. The long cylinders are entangled with each other to form a transient network of wormlike micelles as the C12EO4 concentration is increased. A mixture of 4.9 wt % PhyEO₂₀/H₂O + 2.4 wt % $C_{12}EO_4$ tends to form wormlike micelles (Figure 6).³⁴ When C4–C–N-PEG9 (with a large hydrophilic group) is added to the 4.9 wt % PhyEO₂₀/ H_2O + 2.4 wt % $C_{12}EO_4$ solution, being a short chain surfactant, it too tries to reside in the palisade region of PhyEO₂₀ micelle (competing with $C_{12}EO_4$), ultimately disturbing the wormlike micellar system. The larger hydrophilic part of C4-C-N-PEG9 decreases the critical packing parameter of the surfactant leading back to the spherical micelles with cone geometry. On UV irradiation, photocleavage of C4-C-N-PEG9 into the hydrophobic coumarin derivative (7-butoxy-2H-chromen-2-one) and a hydrophilic aminated polyoxyethylene moiety occurs. The hydrophobic coumarin derivative goes into the hydrophobic core of 4.9 wt % $PhyEO_{20}/H_2O$ + 2.4 wt % $C_{12}EO_4$ micelle while the hydrophilic aminated portion locates itself in the vicinity of hydrophilic environment. The hydrophobic coumarin derivative that goes to the core of the micelle plays a role in decreasing the viscosity of the solution. The N-atom of aminated polyoxyethylene can bond with the H₂O molecule hydrating the PhyEO₂₀ headgroup or with the bulk H₂O near the PhyEO₂₀ headgroup. The molecule still reduces the interhead repulsion between PhyEO₂₀ molecules. However, the net reducing-effect is diminished. The hydrophilic aminated polyoxyethylene is unlikely to form micelles after the cleavage of a large hydrophobic part. Therefore, we believe that the cleaved hydrophilic portion still remains near the hydrophilic part of PhyEO₂₀ rather than going completely to the bulk. This again alters the net geometry from a cone to a truncated cone and thereby induces again the spherical micelles to grow into flexible cylinders.

4. CONCLUSIONS

Rheology of viscoelastic wormlike system, 4.9 wt % PhyEO₂₀/ $H_2O + 2.4$ wt % $C_{12}EO_4$ could be modified by incorporating photocleavable surfactant, C4-C-N-PEG9 into the matrix. The system loses viscoelasticity with the addition of C4-C-N-PEG9. The addition of C4–C–N-PEG9 with large headgroup decreases the Critical Packing Parameter of the micelles. This leads to a microstructure transition from wormlike to spherical micelles. The viscoelasticity of the system recovered upon UV irradiation. UV irradiation induces photocleavage of C4-C-N-PEG9 (as confirmed by UV-visible spectroscopy and HPLC measurements) giving hydrophobic coumarin derivative (7butoxy-2H-chromen-2-one) and the hydrophilic aminated polyoxyethylene compound. The net effect of C4-C-N-PEG9 is minimized by this cleavage. It is anticipated that the coumarin derivatives are solubilized in the core of the surfactant. This promotes formation of spherical micelles and plays a role in reduction of the viscosity. However, the aminated polyoxyethylene remains in the vicinity of hydrophilic environment of PhyEO₂₀. This promotes a progressive reduction of the interfacial curvature of the aggregate in the mixed system and transforming spherical/short cylinder back to wormlike micelles. Therefore, the formation of wormlike micelles is promoted due to the UV-induced decomposition of C4-C-N-PEG9. A transition of Newtonian to non-Newtonian fluids has been observed with UV irradiation, the viscosity increased by 200 times. This viscosity control is far different from that observed with other photoisomerization

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material. The results derived from the rheological measurements are well supported by the small-angle X-ray scattering. This work presents new way of controlling the rheology of system using a less expensive type of stimulus, light. We anticipate that such photocleavable surfactant-based wormlike micelles will find applications in the formulation of highperformance chemical products in the field of cosmetics, personal care, and medicine.

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Notes

The authors declare no competing financial interest.

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