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pH-sensitive Wormlike Micelle and Hydrogel Formation by Acylglutamic Acid–Alkylamine Complex

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pH-sensitive viscoelastic fluids were obtained through the formation of wormlike micelles and hydrogels. These assemblies result from the 1:1 stoichiometric complex formation of acylglutamic acid (C*n*Glu) with tertiary alkylamine. The pH-sensitive nature reflects a change in the charge density around the C*n*Glu headgroups, controlling the curvature of the molecular assemblies. The longer chain C*n*Glu analogues yield the hydrogel in a narrow pH region. This study proposes a unique way to obtain stimulus-responsive viscoelastic fluids by means of gemini-like amphiphiles.

Keywords: Wormlike micelle | Hydrogel | pH sensitive

Rheology control is a key process in developing various industrial products such as paints, foods, cosmetics, shampoos, dishwashing/laundry detergents, and so on. The addition of water- or oil-soluble polymers usually increases their solution viscosity, and hence they have been used as thickeners of liquid-based products. The use of wormlike micelles is also a potential method to yield highly viscoelastic aqueous or non-aqueous solutions. Here, wormlike micelles are formed as a result of the self-assembly of surfactants.[1] This means that wormlike micelles are reformable against shear motion, which is a fundamental difference from viscous polymer systems.

Wormlike micelles are typically formed in aqueous surfactant solutions in the presence of organic/inorganic salts or cosurfactants.[2–5] These additives control the packing geometry of surfactant molecules within micelles, i.e., the addition results in decreased head-to-head repulsion and/or an increased tail volume, achieving a suitable packing parameter for wormlike micelles. Interestingly, under appropriate conditions, gemini (or dimeric) surfactants can form wormlike micelles even in the absence of such additives.[6–9]

In our previous paper,[10] we demonstrated a possible method to form "gemini-like" amphiphiles through a very simple and handy process, i.e., a mixture of alkyl dicarboxylic acid and alkylamine yields a stoichiometric complex in aqueous solutions as a result of a proton transfer from the acid to the amine. We have also applied this concept to the formation of wormlike micelles.[11] In this earlier work, we employed an amino acid-based surfactant (dodecanoylglutamic acid, C12Glu) as an alkyl dicarboxylic acid compound and dodecyldimethylamine (C12DMA) to yield their 1:1 stoichiometric complex. Importantly, the rheological properties of their aqueous solutions were found to be strongly dependent on pH, resulting from the pH-dependent structural transformation of spherical–rodlike–wormlike micelles.

In this letter, we demonstrate the rheological properties of a series of acylglutamic acid–C12DMA complexes as a function of alkyl chain length. We abbreviate the acid to "C*n*Glu", where *n* refers to alkyl chain lengths of 8, 10, 12, 14, and 16. A typical chemical structure of the complex is shown in Figure 1.

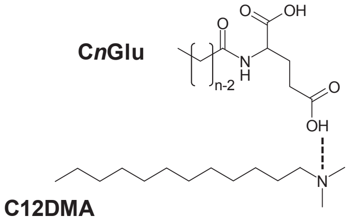

Figure 1. A typical chemical structure of C*n*Glu–C12DMA complex.

The C*n*Glu analogues were synthesized in our laboratory via a reaction of glutamic acid with octa-, deca-, dodeca-, tetradeca-, or hexadecanoyl chloride in the presence of triethylamine. C12DMA was purchased from Tokyo Chemical Industry and used without further purification. The acid-type C*n*Glu (1 equiv) was mixed with C12DMA (3 equiv) in ethanol at room temperature for 48 h under magnetic stirring. Then, the solvent was evaporated. The residue was recrystallized from either acetone or a mixture of hexane/ethyl acetate. After filtration, the residue was dried under reduced pressure. We confirmed the formation of a 1:1 stoichiometric complex of C*n*Glu–C12DMA on the basis of ^{1}H NMR (JEOL-ECP 500 MHz) and ESI-MS (FT-ICR MS Varian 910-MS) data. These characterization data are shown in Supporting Information, Table S1. In typical experiments, the complex (3 wt %) was mixed with a NaOH aqueous solution, and the system was heated up to 80 °C. Then the solution was stirred and finally kept for 4 days at a constant temperature of 25 °C. The sample pH was controlled by changing the NaOH concentration.

Figure 2 shows the maximum viscosity ($\eta_{\max}$) of the C*n*Glu–C12DMA complexes in aqueous media as a function of pH. These data were obtained through steady shear rate measurements by using a stress-controlled rheometer AR-G2 (TA Instruments) with a cone-plate.[12] The resultant viscosity against shear rate curves is given in Supporting Information, Figure S1.[13] It is clear in Figure 2 that the $\eta_{\max}$ data are strongly dependent not only on the pH but also on the alkyl chain length of C*n*Glu. As discussed in our previous paper,[11] the pH-dependent rheological behavior results from a change in the charge density (or acidity) around the carboxylic acid headgroups, i.e., the decreased pH results in a decreased charged density around the headgroups, leading to decreased head-to-head repulsion; hence, lower positively curved aggregates such as wormlike micelles tend to be formed at low pH values. The highest $\eta_{\max}$ observed at pH 5.7 in the C12Glu–

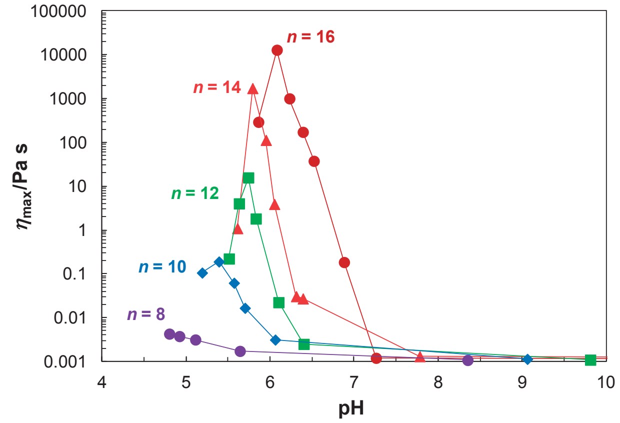

Figure 2. η_{max} of the C*n*Glu–C12DMA complexes in aqueous media as a function of pH.

C12DMA system reflects the formation of a highly entangled transient network structure of wormlike micelles.[11] We also suggested, on the basis of the dynamic viscoelastic data, that a further decrease in pH from 5.7 resulted in branching or interconnection of the wormlike micelles, inducing the decreased viscosity.[11]

Hereafter we focus on the effects of the alkyl chain length of C*n*Glu on the pH-dependent rheological behavior. The shortest analogue, C8Glu–C12DMA, yields a low viscous Newtonian fluid over the whole range of pH investigated, as shown in Figure S1a. In the case of C10Glu–C12DMA, the solution viscosity is dependent on pH, and a maximum η_{max} value is seen at pH 5.4. Non-Newtonian fluids were obtained in the pH range of 5.2–5.6 (Figure S1b); however, shear-birefringence was not observed for these relatively low viscous samples. These results indicate that both of the analogues form either spherical or rodlike micelles in the solutions, and further one-dimensional growth into wormlike micelles is not evidenced.

The longer chain analogues, C14Glu–C12DMA and C16Glu–C12DMA, yield non-Newtonian fluids in the pH ranges of 5.6–6.1 (C14) and 5.9–6.9 (C16), as shown in Figures S1c and S1d. In these pH regions, the viscosity drastically increased, and maximum η_{max} values were obtained at pH 5.8 (C14) and pH 6.1 (C16), respectively. In order to assess the viscoelastic properties of these samples, we performed oscillatory-shear rheological measurements. The results obtained for the C14Glu–C12DMA system are shown in Figure 3. At pH 5.8, over the whole range of angular frequencies, elastic behavior (storage modulus, G') dominates over viscous behavior (loss modulus, G''), indicating hydrogel formation at this pH. In contrast, at pH values of 5.6, 6.0, and 6.1, G' dominates at high frequencies, whereas G'' dominates at low frequencies. This behavior indicates the formation of highly entangled molecular assemblies in the viscoelastic fluids, and is typically seen in wormlike micellar systems. Indeed, we observed shear-birefringence for the three samples. On the basis of these results, we suggest wormlike micelle formation at these pH values, although the Maxwell model[14] does not always fit with the G' and G'' data. The dynamic rheology data obtained for the C16Glu–C12DMA system are given in Supporting Information, Figure S2, where one can see the hydrogel-type viscoelastic behavior in the pH range of 5.9–6.2 and the wormlike micellar behavior in the pH range of 6.4–6.5.

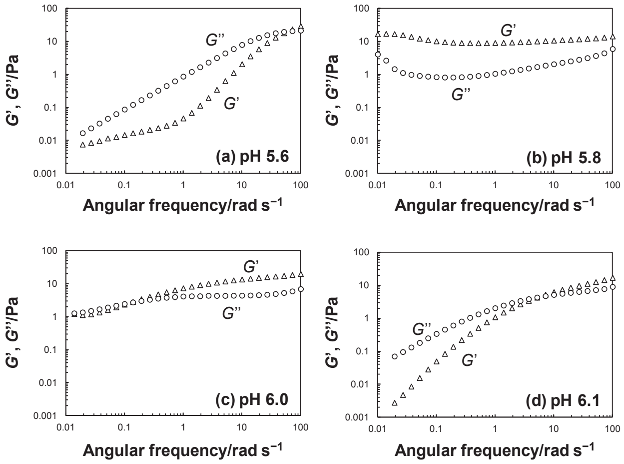

Figure 3. G' and G'' data obtained for the C14Glu–C12DMA complex system at various pHs.

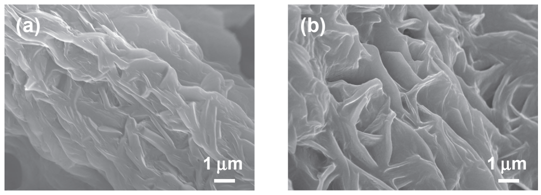

Figure 4. SEM images of the hydrogel samples: (a) C14Glu–C12DMA at pH 5.8 and (b) C16Glu–C12DMA at pH 6.1.

The morphology of the hydrogels formed by C14Glu–C12DMA (at pH 5.8) and C16Glu–C12DMA (at pH 6.1) was observed using a JEOL JSM-7600F scanning electron microscope (SEM). A droplet of the hydrogel sample was placed on a SEM grid coated with carbon tape, and then the grid was dried at 25 °C for 1 day under reduced pressure. Finally, the dried sample was sputtered with platinum. As shown in Figure 4, a three-dimensional network structure formed by fibrous molecular assemblies was observed. A similar network structure has been reported in the hydrogel system consisting of stearic acid and amines.[15]

In summary, we have demonstrated the pH-sensitive formation of wormlike micelles and hydrogels by changing the alkyl chain length of the C*n*Glu–C12DMA complex. The pH-dependent nature primarily results from a change in the charge density around the carboxylic acid headgroups of C*n*Glu, controlling the curvature of the molecular assemblies in aqueous media. The longer chain analogues experience structural transformation from/into wormlike micelles and hydrogels in the narrow pH region.

The development of stimulus-responsive "smart" wormlike micellar systems is an interesting research topic in the field of surfactant chemistry.[16] pH is a typical trigger in such systems. Recently, pH-responsive wormlike micellar systems have been proposed in mixtures of tertiary alkylamine with dicarboxylic acid[17–19] or tricarboxylic acid.[20] These stoichiometric complexes are sometimes called "pseudo-gemini (dimeric)" or "pseudo-trimeric" surfactants. In our case, the wormlike micelles can be transformed into hydrogels in the narrow pH region, and hence the observed change in the viscoelastic properties is greater than the results reported in the previous papers. These stoichiometric complexes, including ours, can be obtained through a very simple, handy, and cost-effective process without difficulty of organic synthesis. We expect, therefore, that this concept is versatile in developing a wide variety of stimulus-responsive materials as well as “pseudo” polymeric surfactants.

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Supporting Information is available on http://dx.doi.org/10.1246/cl.160231.

References and Notes

1 M. E. Cates, S. J. Candau, *J. Phys.: Condens. Matter* **1990**, *2*, 6869.
2 D. Varade, C. Rodríguez-Abreu, L. K. Shrestha, K. Aramaki, *J. Phys. Chem. B* **2007**, *111*, 10438.
3 L. Ziserman, L. Abezgauz, O. Ramon, S. R. Raghavan, D. Danino, *Langmuir* **2009**, *25*, 10483.
4 R. G. Shrestha, L. Abezgauz, D. Danino, K. Sakai, H. Sakai, M. Abe, *Langmuir* **2011**, *27*, 12877.
5 R. G. Shrestha, K. Sakai, H. Sakai, M. Abe, *J. Phys. Chem. B* **2011**, *115*, 2937.
6 R. Oda, I. Huc, J.-C. Homo, B. Heinrich, M. Schmutz, S. Candau, *Langmuir* **1999**, *15*, 2384.
7 F. Kern, F. Lequeux, R. Zana, S. J. Candau, *Langmuir* **1994**, *10*, 1714.
8 E. Buhler, E. Mendes, P. Boltenhagen, J. P. Munch, R. Zana, S. J. Candau, *Langmuir* **1997**, *13*, 3096.
9 D. P. Acharya, H. Kunieda, Y. Shiba, K. Aratani, *J. Phys. Chem. B* **2004**, *108*, 1790.
10 H. Sakai, Y. Okabe, K. Tsuchiya, K. Sakai, M. Abe, *J. Oleo Sci.* **2011**, *60*, 549.
11 K. Sakai, K. Nomura, R. G. Shrestha, T. Endo, K. Sakamoto, H. Sakai, M. Abe, *Langmuir* **2012**, *28*, 17617.
12 Dynamic rheology measurements were performed in the case of highly elastic samples, where complex viscosity was measured as a function of angular frequency.
13 Basically, we equated the $\eta_{\max}$ with the zero-shear viscosity in the observed shear rate curve. However, it was not possible to estimate the zero-shear viscosity in highly viscoelastic samples. In such case, the highest viscosity measured in the low shear rate (or low angular frequency) region was employed as the $\eta_{\max}$.
14 R. G. Shrestha, L. K. Shrestha, K. Aramaki, *J. Colloid Interface Sci.* **2007**, *311*, 276.
15 H. Basit, A. Pal, S. Sen, S. Bhattacharya, *Chem.—Eur. J.* **2008**, *14*, 6534.
16 Z. Chu, C. A. Dreiss, Y. Feng, *Chem. Soc. Rev.* **2013**, *42*, 7174.
17 Z. Chu, Y. Feng, *Chem. Commun.* **2010**, *46*, 9028.
18 Y. Feng, Z. Chu, *Soft Matter* **2015**, *11*, 4614.
19 H. Lu, Q. Shi, B. Wang, Z. Huang, *Colloids Surf., A* **2016**, *494*, 74.
20 Y. Zhang, P. An, X. Liu, *Soft Matter* **2015**, *11*, 2080.