

Polymerized surface micelles formed under mild conditions†

Fang Liu, Mingfeng Wang, Zhiqiang Wang and Xi Zhang*

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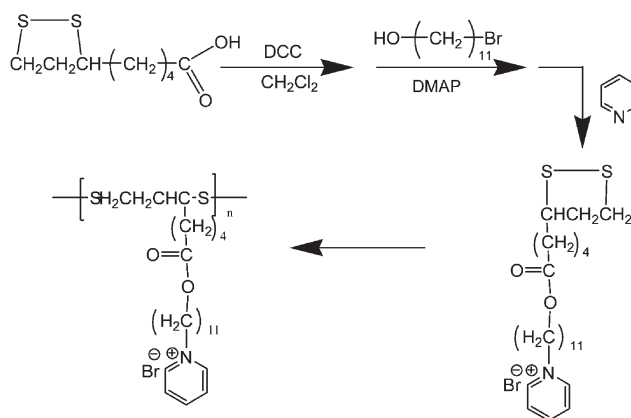
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A new polymerizable surfactant 1-[11-(lipoyloxy)-undecyl]-pyridinium bromide was synthesized, which provides a new approach for polymerizing micelles under mild conditions.

We describe the design and synthesis of a new surfactant and its utility in the formation of polymerized micelles. Our experiments have demonstrated that the surfactants are able to undergo ring-opening polymerization to form stable micelles by simply changing the pH of the solution. Surfactants containing long hydrophobic alkyl chains and hydrophilic head groups can self-organize into various micelles both in bulk solution and at an interface.^{1–4} However these micelles, associated by non-covalent interactions, are inherently dynamic and fluid, hence lacking the robustness required for detailed structural characterization and materials applications. We have developed methods of stabilizing surface micelles of a low molecular weight surfactant through *in situ* intramicellar polymerization initiated by Gamma ray irradiation⁵ or through the enhanced intermolecular interaction of the micelles by introducing mesogenic groups.⁶ Although the former method is effective to polymerize the surface micelles while maintaining their original cylindrical structures, the wide-application of Gamma ray sources is still very limited because of the specific and relatively expensive experimental setup. Therefore it is important to find some new surfactants which are able to polymerize under much milder conditions.

Inspired by the early work of Regen *et al.* on polymerized liposomes,^{7,8} we introduced a macrocyclic disulfide as a polymerizable moiety into a surfactant, and hoped that such a surfactant could give rise to a stable micellar nanostructure by ring-opening polymerization under mild conditions. The new surfactant of 1-[11-(lipoyloxy)-undecyl]-pyridinium bromide, abbreviated as LUPB, was synthesized from the esterification of 11-bromo-1-undecanol with lipoic acid anhydride in CH₂Cl₂ and subsequent quaternization with pyridine (Scheme 1). The concentration-dependent conductivity of LUPB aqueous solution showed a critical micelle concentration (CMC) of 3.3×10^{-3} M. We could anticipate that such surfactants with hydrophilic cationic heads and hydrophobic tails were segregated to form micelles by self-organization in water, and that the clustering of the hydrophobic tails with polymerizable groups of disulfide inside the micellar



Scheme 1 The synthetic routes used for the preparation of polymerizable surfactant LUPB and the polymerization of LUPB.

structure might show a polymerization kinetic much faster than those in the unclustering state.

The ring-opening polymerization in the micelles was followed by UV-Vis spectroscopy. We firstly checked an aqueous solution of LUPB. The ring-opening polymerization in the micelles was followed by a concentration of 6.6×10^{-3} M, above its CMC, at pH 7. We found that the UV absorption at 330 nm, which is characteristic of the five membered ring cyclic disulfide,⁹ decreased quickly with time. As shown in Fig. 1, there is an isosbestic point around 300 nm. The loss of the UV absorbance at 330 nm is indicative of the ring-opening polymerization. The polymerization underwent a very quick propagation and reached a termination within 30 min (Fig. 2a). This decrease in absorbance obeyed clean first-order kinetics ($k = 2.7 \times 10^{-3} \text{ s}^{-1}$). The polymerization was

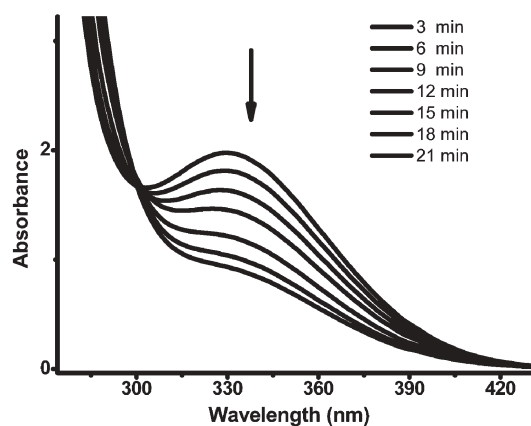


Fig. 1 UV-Vis spectral changes accompanying the polymerization in micelles of surfactant LUPB at pH 7.

Key Lab of Organic Optoelectronics & Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084 and Key Lab for Supramolecular Structure & Materials, College of Chemistry, Jilin University, Changchun 130023, China.

E-mail: xi@mail.tsinghua.edu.cn

† Electronic supplementary information (ESI) available: Synthesis and characterization of LUPB monomer, measurement of the CMC, experiment details for UV-Vis, *in situ* AFM and DLS characterization. See DOI: 10.1039/b600498a

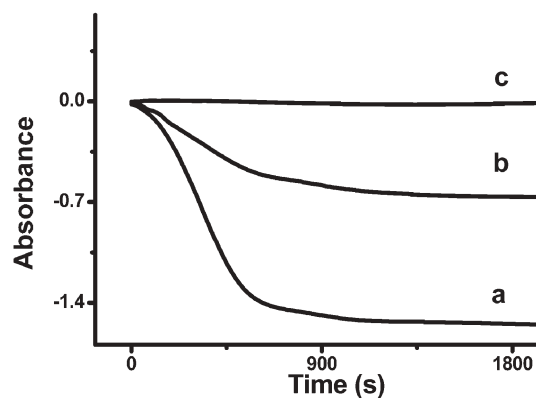


Fig. 2 The decrease of the LUPB absorbance at 330 nm with extension of time of polymerization at pH 7 with the concentration of (a) 6.6×10^{-3} M (b) 3.3×10^{-3} M and (c) 1.5×10^{-3} M.

also rationalized by ^1H NMR, all proton signals of LUPB lost their fine profiles and broadened after polymerization.¹⁰

The LUPB has shown different polymerization behaviors depending on the concentration of the aqueous solution of LUPB as well as on the pH values of the solution. When the concentration of the aqueous solution of LUPB was 1.5×10^{-3} M, below its CMC, there was a slight change in the UV absorbance at 330 nm at pH 7 within the same time period (curve c in Fig. 2), suggesting that the surfactants underwent a very slow polymerization under these conditions (Fig. 2). Since the only difference between the three samples of curves a, b and c in Fig. 2 was whether the concentration was above or below the CMC, the significant difference in absorption change between them suggests that the close packing of the surfactants in the micellar structure facilitates ring-opening polymerization of the disulfide.

In addition, the ring-opening polymerization of LUPB is pH dependent. For an aqueous solution of LUPB with a concentration above its CMC but at a low pH (pH 3), the UV absorbance at 330 nm changed only a little bit within 4 h, which means that only a small amount of surfactants were converted into polymers. It took about 20 h to terminate the polymerization under these conditions. The rate of polymerization became faster and faster with the increase in pH value of the solution, which can be explained in terms of the reaction being hydroxide initiated and the higher pH providing more hydroxide than the lower pH.¹¹ For example, at pH 10, the polymerization became too fast to be followed.

We wondered what kind of micellar structure the LUPB could form at an interface before and after polymerization. In order to address this question, we applied tapping mode fluid atomic force microscopy (*in situ* AFM) to image the surface micelles at the mica/liquid interface. For a concentration of 6.6×10^{-3} M and under a pH of 3, *in situ* AFM observation indicated that LUPB self-organized spontaneously into worm-like micelles at the mica/liquid interface (Fig. 3a). The section analysis showed that the micelles have a uniform diameter of about 5.5 nm. These interfacial micelles are meandering and show different alignment on the substrate. The low pH can guarantee that LUPB does not polymerize during the time period of the *in situ* AFM operation. For a concentration of 6.6×10^{-3} M and under a pH of 7, we made similar *in situ* AFM observations and found that similar

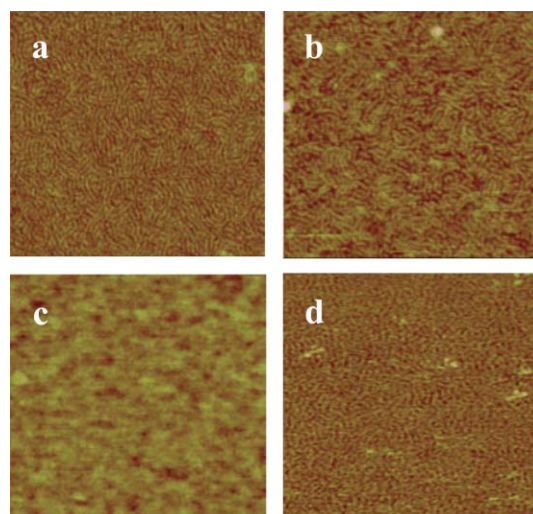


Fig. 3 *In situ* AFM phase images (400×400 nm) at the mica/liquid interface of (a) LUPB with a concentration of 6.6×10^{-3} M under a pH of 3; (b) polymerized LUPB with a concentration of 6.6×10^{-3} M under a pH of 7; (c) LUPB with a concentration of 3.5×10^{-4} M under a pH of 3; and (d) polymerized LUPB with a concentration of 3.3×10^{-4} M under a pH of 7.

worm-like micelles were formed at the mica/liquid interface (Fig. 3b). As discussed before, the LUPB can undergo a ring-opening micellar polymerization within 30 min under a pH value of 7. So, what we observed in Fig. 3b are polymerized surface micelles. The similarity between AFM images of Fig. 3a and 3b indicates that the surface micellar structure can remain well after the polymerization. Moreover, the *in situ* AFM observation is well complemented by dynamic light scattering.

To demonstrate furthermore that the polymerized surface micelles are more stable than unpolymers, we used *in situ* AFM to observe the change of surface structure of LUPB in diluted conditions. As shown in Fig. 3c, the unpolymers surface micelles were destroyed when diluted. Instead, the cationic surfactants of LUPB were physically adsorbed onto the mica sheet, forming a flat surface structure. In contrast, the polymerized surface micelles were maintained very well when subjected to similar dilution treatments (Fig. 3d). In other words, polymerized surface micelles have shown an enhanced stability over unpolymers ones.

In summary, we have provided a way of making polymerized micelles. A similar molecular design could be applied to synthesize many new surfactants which contain some functional moiety but undergo polymerization under mild conditions, thus opening a new route for fabricating supramolecular nanomaterials.

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Notes and references

- 1 T. Kunitake, Y. Okahata, M. Shimomura, S. Yasunami and K. Takarabe, *J. Am. Chem. Soc.*, 1981, **103**, 5401.
- 2 S. H. Manne and E. Gaub, *Science*, 1995, **270**, 1480.
- 3 W. A. Ducker and E. J. Wanless, *Langmuir*, 1999, **15**, 160.
- 4 D. Cochin, F. Candau and R. Zana, *Macromolecules*, 1993, **26**, 5755.
- 5 X. Zhang, M. F. Wang, T. Wu, S. C. Jiang and Z. Q. Wang, *J. Am. Chem. Soc.*, 2004, **126**, 6572.

6 B. Zou, M. F. Wang, D. Qiu, X. Zhang, L. F. Chi and H. Fuchs, *Chem. Commun.*, 2002, 1008.
7 S. L. Regen, K. Yamaguchi, N. K. P. Samuel and M. Singh, *J. Am. Chem. Soc.*, 1983, **105**, 6354.
8 M. Wakita and S. L. Regen, *Macromolecules*, 1987, **20**, 2029.

9 P. R. Brown and J. O. Edwards, *J. Org. Chem.*, 1969, **34**, 3131.
10 M. Summers, J. Eastoe, S. Davis, Z. P. Du, R. M. Richardson, R. K. Heenan, D. Steytler and I. Grillo, *Langmuir*, 2001, **17**, 5388.
11 A. J. Parker and N. Kharasch, *Chem. Rev.*, 1959, **59**, 583.

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