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CO_2-responsive smart wormlike micelles based on monomer and "pseudo" gemini surfactant

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ABSTRACT

CO_2-responsive wormlike micelles based on monomer *erucic acid 3-(N,N-dimethylamino)propylamide* (EADP) with or without *sodium salicylate* (NaSal) in aqueous solution were studied and compared with "pseudo" gemini system. The "pseudo" gemini system were formed by a mixture of EADP and *maleic acid* (MA) with molar ratio between 2:1–1:1. Different morphological transformations of microstructures in response to EADP concentrations, additives and CO_2 stimuli were further investigated in these systems, the wormlike micelle or vesicles can be obtained. The mechanism of these transitions were further investigated by rheology, cryo-TEM and DFT calculation, the results showed that the mechanism behind this transition involved reversible reaction of CO_2 with EADP. The mechanism in this research may give further evidence to the self-assembly of CO_2-responsive surfactants.

Introduction

In biological and environment fields, morphological transformations of microstructures in response to environmental stimuli are important integral to the processes. Synthetic various systems of self-assembly can similarly undergo morphological transitions in response to physical or chemical stimuli [1]. Wormlike micelles (WLMs), which are long flexible, linear or branched polymer-like aggregates, resultes from the self-organization of small structural motifs, such as low-weight molecules, nanoclusters or macro-ions. WLMs have drawn strong attention in wide areas of biology, energy, and environmental sciences [2–6]. WLMs with polymer like characters can easily entangle with each other and form a transient network structure [7,8]. The transformation of aggregation behavior results in solution phase changing into high viscoelastic solution. Therefore, to build such a flexible and elongated framework, the strength and directionality becomes important [9,10]. Meanwhile, the construction of WLMs is related to non-covalent interactions, such as hydrophobic attraction and hydrogen bonding, as well as electrostatic and π–π interactions, which have aroused extensive attention [11–13]. In contrast to the traditional covalent interaction, non-covalent interactions affect the self-assembled structures with facile and green controllability. In this case, electrostatic attraction as one of the non-covalent interactions is widely used for surfactants self-assemble in aqueous solutions due to its superior performance [6,14–16]. Moreover, studying the role of non-covalent interactions in such self-organized behavior is still one of the most important issues in the field of molecular self-assembly.

Recently, reversible WLMs have attracted growing attention, both from the theoreticians and experimentalists, due to their peculiar unique rheological response and a broad spectrum of applications, such as enhanced oil recovery (EOR) [17], heat transfer [18,19] and drag reduction [20,21]. The viscoelasticity of these reversible WLMs can be instantaneously changed in the properties *via* environmental stimuli, such as light [22], pH [23], temperature [16], CO_2 [24], magnetic field [25] or combined stimuli [26]. Among these physical or chemical stimuli, CO_2-responsive WLMs present superior advantages, because environmentally benign and renewable CO_2 is a truly mild and "green" trigger [27]. Comparatively, CO_2 is readily available and has no additives to the solutions, which can avoid changes in the composition and easy to remove, neither accumulates nor contaminates the production. As a widely available, biocompatible resource, CO_2-trigger has received a great deal of interest [28–30]. The traditional CO_2-responsive surfactants mainly contain four types of CO_2-responsive functional groups (tertiary amine, amidine, guanidine and imidazoline) [31]. Comparing with the

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others, tertiary amines as a conventional functional group is a classic chemical product. It has great CO_2 responsiveness and simple synthesis methods.

Meanwhile, gemini surfactants have attracted considerable attentions because their superior performance and rich self-assembly behavior [5,32,33]. The preparation of gemini surfactants always required complicated synthetic routes which are not easy to control, limiting the development and industrial applications of gemini surfactants. Gemini-type self-assemblies provide a new facile approach to construct gemini surfactants, which can be fabricated by strong electrostatic attractions between a short chain of bola-type molecule and oppositely charged single chain surfactants [34]. Also, the "pseudo" gemini surfactant formed by non-covalent interactions can avoid complicated synthetic routes and is easy to achieve through simple surfactants. The construction and evolution of the self-assemblies in gemini type surfactant system generally depend on the control of the non-covalent interaction by varying the proportion of surfactant, changing solvent properties or adding an organic salt. Relative to other non-covalent interaction, electrostatic interactions play a major role in the molecular self-assembly [34]. The effect of the other non-covalent interactions may be too weak to induce the transformation of self-assemblies, so the research of gemini type surfactants mainly focuses on the electrostatic interaction. Recently, our research group [12] has reported the smart WLMs that can be responsive to both pH and CO_2, the mechanism of transformation is mainly governed by electrostatic interactions. Such a responsive surfactant can be efficiently used for better development of WLMs, the introduction of stimuli-responsive functional groups may also enrich the self-assembly structures.

Herein, we report a CO_2-responsive viscoelastic system on the basis of the ultra-long tail surfactant *Erucic acid 3-(N,N-dimethylamino)propylamide* (EADP) [33]. By carefully choosing counter ions, molar ratios and conditions, we could control the different microstructures of aggregation. We thus anticipated to clarify the role of non-covalent interactions in the aggregation behavior, achieving readily controllable self-assembly and disassembly of organized assemblies. Here, we compared EADP system with EADP in presence of *sodium salicylate* (NaSal) and *maleic acid* (MA), respectively, with varying ratios. The various morphologies of aggregates are observed in both monomer (NaSal) and "pseudo" gemini (MA) system, such as sphere micelles, wormlikes and vesicles. Owing to the reversibility of tertiary amine and quaternary ammonium, viscoelastic and low viscous solutions with several recycles can still be readily changed in response to the changes of CO_2.

Experimental section

Materials

Maleic acid (MA, 99.0%) and *sodium salicylate* (NaSal, 99.5%) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China) and used as received. EADP with purity greater than 99.0% (HPLC, high performance liquid chromatography) was synthesized according to the previous report [35]. The detail synthesis method and analysis of this compound, including HPLC, ESI-MS data and ^1H NMR, shown in supporting information. The structure of EADP is further confirmed by ^1H NMR. As shown in Fig. S1, the signal of methyl protons directly attached to terminal nitrogen atom can be clearly observed as a sharp singlet at about 2.23 ppm. The chemical shifts of double bond proton are observed downfield at about 5.35 ppm. Meanwhile, the UPLC characterization of EADP with the gradient of 5–95% CH_3CN in H_2O is shown in Fig. S2, two peaks at 3.25 and 3.40 min indicate the *cis–trans* isomerism of double bonds in the EADP. The ESI-MS characterization of EADP is shown in Fig. S3.

Sample preparation

The sample was prepared by weighing certain surfactant and desired distilled water into sample bottles, treating the volume contribution of surfactant as 1 mL per gram, and then calculating the molar concentration. This procedure is very similar to that reported by Oda et al. [36].

The NaSal or MA solid was directly added to the surfactant solution, hereafter, solutions were heated and stirred vigorous, then sealed and kept at 25 °C in a thermostat for at least 1 week prior to measurements (The synthetic route of EADP is shown in Scheme 1).

Rheological measurements

Rheological measurements were performed at 25 °C using the MCR302 (Anton Paar, Austria) rotational rheometer equipped with a Searle-type concentric cylinder geometry. All rheological measurements were carried out under the condition of a linear range of strains. All relaxation modes of the systems with certain temperature were determined in the same way, and a master curve could be obtained by means of time-temperature superposition.

Dynamic light scattering measurements

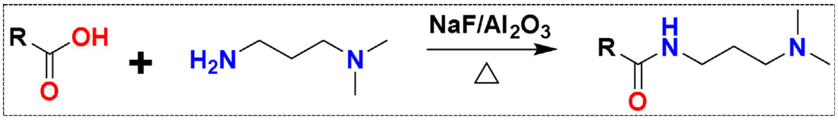
Dynamic light scattering (DLS) measurements were performed on the Zetasizer Nano ZS (Malvern, UK) with a laser light wavelength of 633 nm and a scattering angle of 90°. The sample was transferred to a square sample pool and the measurement was repeated three times to obtain more precise data. All measurements were conducted at 25 ± 0.1 °C.

^1H NMR

^1H NMR spectra were recorded on a MP-400 nuclear magnetic resonance spectrometer (Varian Company, US) at a proton resonance frequency of 400.15 MHz. The spectra were deter-mined in deuterium oxide and deuterochloroform (containing TMS as an internal reference).

Cryo-TEM observation

Loading 5 μL solution onto a TEM carbon grid using a micropipette. The TEM carbon grid was blotted with two pieces of filter paper in order to form a thin film suspended on the mesh hole. About 5 s later, samples were plunged into a reservoir of liquid enhance at −165 °C. The samples were stored in liquid nitrogen till they were transferred to a cryogenic sample holder



Scheme 1. Synthetic route of EADP.