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pH-switchable wormlike micelle formation by *N*-alkyl-*N*-methylpyrrolidinium bromide-based cationic surfactant

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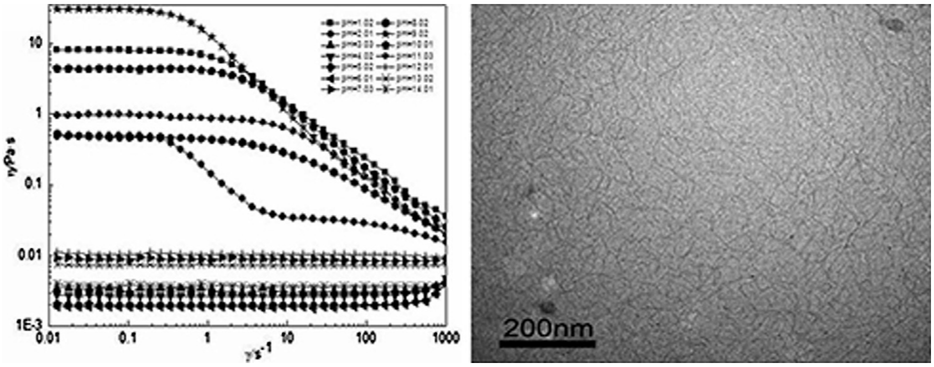
HIGHLIGHTS

- A non-covalent bonding method is utilized for the formation of pH-switchable wormlike micelles.
- The microstructure transition was the fundamental reason for the pH-switchable rheological properties.
- The unusual rheological and micellar responses are caused by the changing binding capacity of a hydrotrope to C_{16}MPBr as the pH varies.

GRAPHICAL ABSTRACT



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ABSTRACT

A non-covalent bonding method is utilized for forming pH-switchable wormlike micelles system by mixing *N*-hexadecyl-*N*-methylpyrrolidinium bromide-based cationic surfactant and pyrocatechol. The peculiarity of this system is that it has high viscoelasticity at acidic conditions and alkaline conditions, while it shows water-like behaviors at neutral conditions. Rheology, dynamic light scattering, and cryogenic-transmission electron microscopy results revealed that the microstructure transition between spherical micelles and wormlike micelles was the fundamental cause of the pH-switchable rheological properties. The unusual rheological and micellar responses of this system to pH are caused by different binding capacity of hydrotrope to C_{16}MPBr as pH varies. Fluorescence analysis and nuclear magnetic resonance result support this hypothesis.

1. Introduction

Molecular self-assembly is composed of molecules that spontaneously associate into structurally well-defined entities, which include spherical micelles, rod-like micelles, vesicles, lamellar micelles, inverted micelles, etc [1–5]. Among the polymorphous self-assembly structures, wormlike micelles (WLMs) have shown excellent viscoelastic properties similar to polymer solutions [6]. Nevertheless, the difference between polymer entanglements and WLMs is the latter could break and recombine dynamically within an equilibrium process. Thus, WLMs is also called “living” polymers [7]. Over the past decades, due mainly to their unique aggregate microstructures and rheological responses, considerable attention from both a theoretical viewpoint and industrial applications has been focused on WLMs. Up to now, WLMs have made great influence upon various aspects of society, e.g., oil well drilling, cleaning

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fracturing fluid, tertiary oil recovery, biomedicine, drag reduction and personal care to name a few [8–12].

The design of stimuli-responsive wormlike micelles (SWLMs) that dynamically alter their structures and properties in response to external stimulus (electric current, UV–vis, temperature, redox reaction, and pH) has been one of the hot research topics in the past decade [13]. Compared with electric current, UV–vis, redox reaction, and temperature stimulus, pH is an uncomplicated and reversible measure for regulating WLMs [14]. There are one or more stimuli-responsive functional groups on the hydrophilic headgroup or the hydrophobic tail of the traditional stimuli-responsive surfactant. Maeda et al. achieved reversible transformation of WLMs solutions by adjusting the ionization degree of oleyldimethylamine oxide [15]. Hamachi et al. described two kinds of small amphiphilic molecules formed a pH-sensitive supramolecular hydrogel [16]. Engberts group surveyed pH-responsive properties of carbohydrate-based gemini surfactants. The results showed that vesicles were formed by most of the gemini surfactants when verge on the neutral pH and the vesicles transformed to WLMs when lowering pH of the solutions [17]. These studies are all using organic synthesis to associate pH-responsive moieties with amphiphiles covalently to achieve control the viscoelastic of fluids through pH. This method is not only time-consuming and low yield, while the range of pH-sensitive is fixed simultaneously. Through the use of the hydrophobic and electrostatic interaction between amphiphiles and organic functional additives to forming pH-sensitive assemblies can avoid the above-mentioned disadvantages brought by organic synthesis. It inspires us to study the properties of pH-sensitive WLMs induced by amphiphiles and organic functional additives.

Herein, we report the use of a hydrophobic mimic, pyrocatechol, to form pH-switchable WLMs with a cationic surfactant *N*-hexadecyl-*N*-methylpyrrolidinium bromide (C_{16}MPBr). This system was created by incorporating pH-switchable moieties based on a common commercial compound to amphiphile non-covalently. It's a simple and promising strategy which does not rely on cumbersome and toxic organic synthesis to fabricate SWLMs that can be conversed reversibly between the high and low-viscosity fluid. Micellar aggregation behavior under different pH conditions are investigated by rheological measurements, nuclear magnetic resonance spectroscopy, fluorescence measurements, dynamic light scattering measurements, and cryogenic-transmission electron microscopy. In addition, the mechanism of pH-switchable WLMs was discussed in detail.

2. Experimental

2.1. Materials

Cationic surfactant *N*-hexadecyl-*N*-methylpyrrolidinium bromide (C_{16}MPBr) was synthesized and purified as described previously [18]. Pyrocatechol was purchased from Aladdin Chemistry Company. Potassium hydroxide (KOH) and hydrochloric acid (HCl), diluted as needed, were used to adjust pH of all solutions. KOH and HCl were GR grade products of Sinopharm Chemical Reagent Company. Pyrocatechol and KOH were used without further purification. The pH of the samples was determined by a Sartorius PB-10 pH meter. All of the samples were prepared by ultrapure water (Millipore).

2.2. Sample preparation

The samples were gained by mixing C_{16}MPBr with pyrocatechol in ultrapure water. The initial pH value of the solution is equal to 6.01. Afterwards, different volumes of KOH solution with certain concentration or HCl solution were added to the samples for adjusting pH to a certain value. In order to ensure that the surfactants completely dissolved, after fully sealing, the samples were mixed at 60 °C for about 2 h. The samples need to equilibrate at 25 °C for three days prior to any measurements. For reversibility experiments, NaOH or HCl were added alternately to 20 mL solution. Since it is difficult to reach exactly the same pH every time, only approximate pH values were obtained. But this does not compromise the reversibility of the rheological responses to pH changes.

2.3. Rheological measurements

Rheological properties of samples were performed on conducted with HAAKE MARS III rotational rheometer equipped with a cylindrical rotor of CC26Ti at 25.0 ± 0.1 °C. For the steady shear experiments, the shearing rate was set to a range of 0.01–1000 s^{-1}. In the dynamic oscillatory measurements, the frequency region ranged from 0.01 to 100 rad s^{-1}. The linear viscoelastic region was set as 1.0 Hz according to a dynamic strain sweep test.

Modulis of WLMs that follows the Maxwell model versus oscillatory frequency and relaxation time are given by the following equations [19]:

$$G' = \frac{(\omega\tau_R)^2}{1+(\omega\tau_R)^2}G_0 \qquad (1)$$

$$G' = \frac{\omega\tau_R}{1+(\omega\tau_R)^2}G_0 \qquad (2)$$

Here, G_0 is the plateau modulus, which can be obtained from the plateau value of G'. ω is the oscillatory frequency. τ_R is relaxation time, which is equal to the reciprocal of ω_c and relates to the average length of WLMs. At low frequencies, the Maxwell fluid behaves like a simple liquid and G' and G'' become proportional to ω^2 and ω; at high frequencies, the Maxwell fluid behaves like an elastic body and G' approaches the plateau modulus G_0, respectively.

2.4. Nuclear magnetic resonance (NMR) spectroscopy

^{1}H NMR spectra were recorded on a Bruker AVANCE III 600 MHz spectrometer (Bruker Inc., Rhinstetten, Germany) at 25 °C. The samples were analyzed in D_2O. Also, the water signal was suppressed by presaturation method.

2.5. Dynamic light scattering (DLS) measurements

A Malvern Zetasizer Nano ZS instrument with a 22 mW solid-state He–Ne laser was use to carried out DLS analyses. The wavelength of the incident beam was equal to 632.8 nm and the scattering angle was equal to 90 °C. To ensure temperature homogeneity of the samples, each sample required to equilibrate at 25 °C for 15 min. The CONTIN method was used to fitting the intensity autocorrelation functions.

2.6. Steady-state fluorescence measurements

Fluorescence anisotropy were measured on a Fluoromax-4 spectrofluorimeter (Horiba Jobin Yvon) with fluorescence polarization device at 25 ± 1 °C. A transparent quartz cuvette was used to hold the pyrene-containing samples. The slit width of excitation and emission was fixed at 5 nm and 10 nm, respectively. Emission spectrum monitoring range was from 350 to 450 nm. To avoid excimer formation, pyrene concentration for all samples were equal to 1×10^{-7} mol L^{-1}.