

Fluorescence visualization of interactions between surfactants and polymers

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Experimental section

Chemicals and Instruments

Chitosan (200–500 mpa·s, 85% deacetylation) was purchased from Tokyo Chemical Industry Co. Ltd (Tokyo, Japan). The PEO used in the experiment is $M_n = 375$ (polydispersity index (PDI) = 1.06), $M_n = 550$ (PDI = 1.06), $M_n = 1,430$ (PDI = 1.03), $M_n = 4,120$ (PDI = 1.03), $M_n = 5,500$ (PDI = 1.09), $M_n = 8,100$ (PDI = 1.03), $M_n = 21,200$ (PDI = 1.06) and $M_n = 89,200$ (PDI = 1.12), respectively. All the PEO reagents were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO). TPE-SDS was synthesized according to our previous work.¹ Acetic acid and sodium acetate were of analytical reagent grade. Milli-Q Academic A10 (Millipore, Bedford, MA) was used to prepare ultrapure water. AR2000 rheometer (T. A. Instruments, Waters Co., USA) was used for the viscosity experiments. Fluorescence spectra were measured with an F-7000 fluorescence spectrophotometer from Hitachi. The UV-visible absorption spectra were measured through Shimadzu UV-3600 spectrophotometer (Tokyo, Japan). Fluorescence microscope images were taken on a Leica TCS SP8 confocal microscope (Leica, Germany) with a 100× oil

immersion objective. Transmission electron microscopy (TEM) photographs were performed on a Tecnai G220 TEM (FEI Company, USA).-Conductivity measurements were performed with a EC 215 conductivity meter (Shanghai Jingmi Instrumental Co., China).

Samples preparation and experimental methods

Samples Preparation

0.1 g chitosan powder was dissolved in 50 mL acetate buffer solution (pH 4.0, 100 mM acetate buffer composed of acetic acid and sodium acetate) overnight at room temperature. The obtained 0.2% (w/v) chitosan solution was used as stock solution. All the samples were prepared on a dilute chitosan solutions (0.1% w/v) with different concentration of TPE-SDS (5–80 μ M). The mixing solutions were stirred for 12 hours to form homogeneous solutions. Similarly, 0.1 g PEO was dissolved completely in 50 mL ultrapure water to serve as stock solution. Then, the TPE-SDS-PEO complexes were prepared based on the same procedure.

Viscosity measurements

The viscosity properties of TPE-SDS and chitosan solutions were measured using an AR2000 rheometer (T. A. Instruments, Waters Co., USA) at 25 ± 0.1 °C. A 4-cm-diameter cone and plate geometry with a 2° angle was used. The viscosity of the samples were obtained from steady flow measurements with a low shear rate range of 0.07-140 s^{-1} , which was applicable for low-viscosity liquids. Rotational mapping was performed for calibration to ensure the accuracy of the measurements. Similarly, the viscosity of TPE-SDS-PEO solution was measured in the same way.

Fluorescence measurements

The fluorescence intensity was obtained with a 320 nm excitation wavelength for the emission located in the region from 390 nm to 600 nm. Samples containing a series of concentrations of TPE-SDS (5–80 μM) and constant concentration of chitosan/PEO were used to investigate the interactions between TPE-SDS and different kinds of polymers.

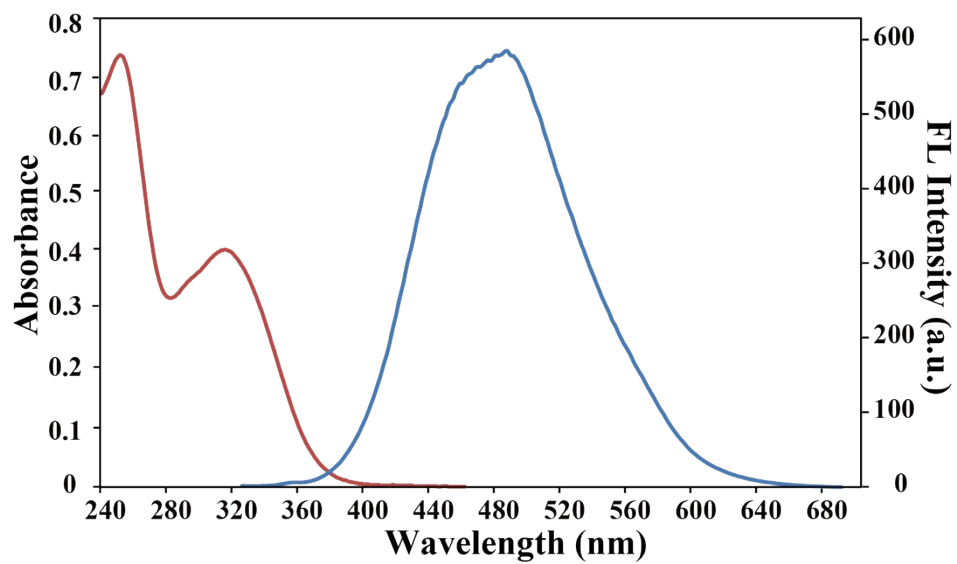


Fig. S1 Absorbance spectrum (red line) and fluorescence emission spectrum (blue line) of 40 μ M TPE-SDS in water.

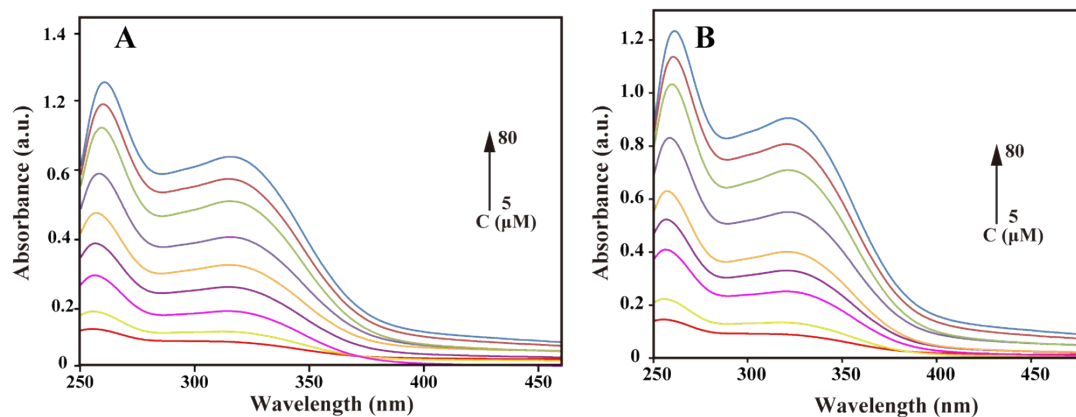


Fig. S2 Absorption spectra of different concentrations of TPE-SDS: (A) in the presence of 0.1% (w/v) chitosan and (B) in the absence of chitosan.

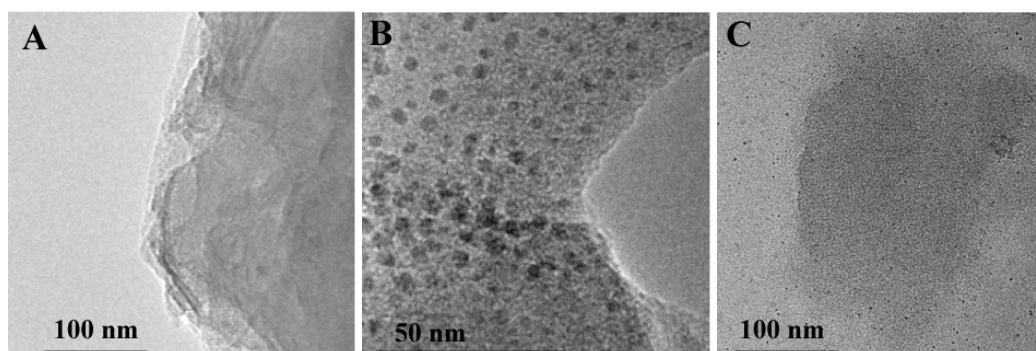


Fig. S3 TEM images of (A) chitosan; (B) the micellization of TPE-SDS in the chitosan backbone; (C) TPE-SDS-Chitosan complexes and free micelles.

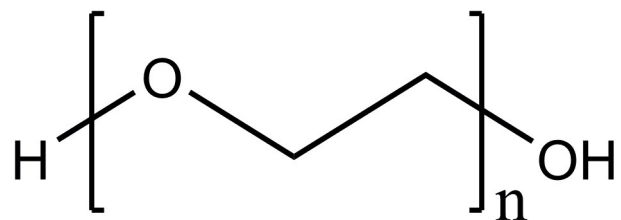


Fig. S4 Chemical structure of poly(ethylene oxide) (PEO).

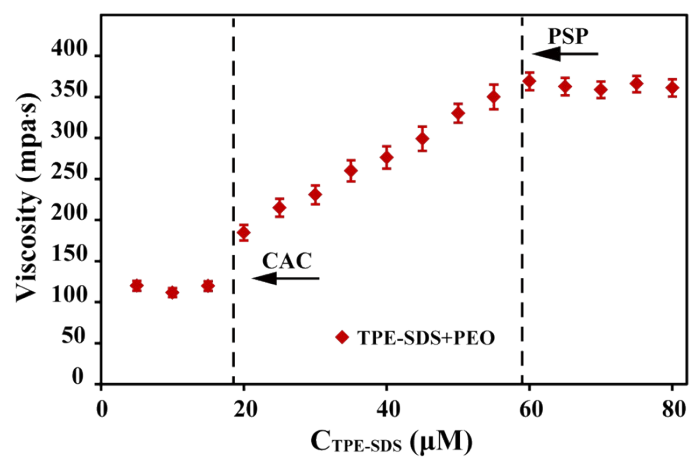


Fig. S5 Viscosity of PEO solution (0.1% w/v) as a function of TPE-SDS concentration.

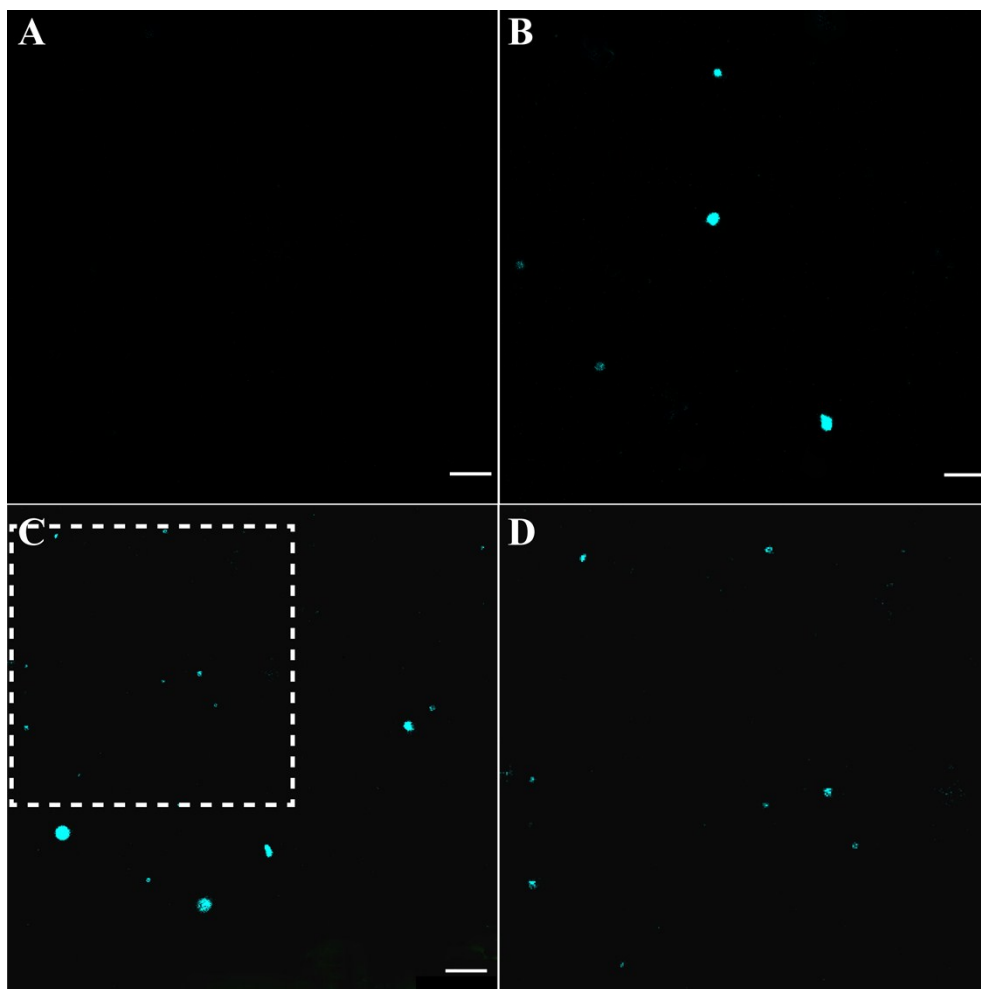


Fig. S6 Confocal fluorescence microscopy images of three stages process during the interactions between of TPE-SDS and PEO: (A) Low concentration of TPE-SDS (5 μM); (B) Medium concentration of TPE-SDS (40 μM). (C) High concentration of TPE-SDS (80 μM). (D) Magnification of the indicated region in (C). Scale bars: 5 μm . The concentration of PEO solution was 0.1% (w/v). All images were taken with a 405 nm laser.

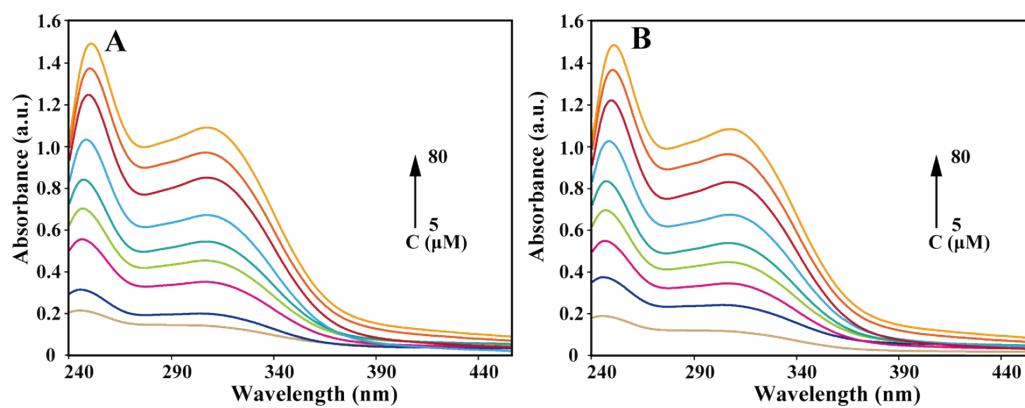


Fig. S7 Absorption spectra of different concentrations of TPE-SDS: (A) in the presence of 0.1% (w/v) PEO and (B) in the absence of 0.1% (w/v) PEO.

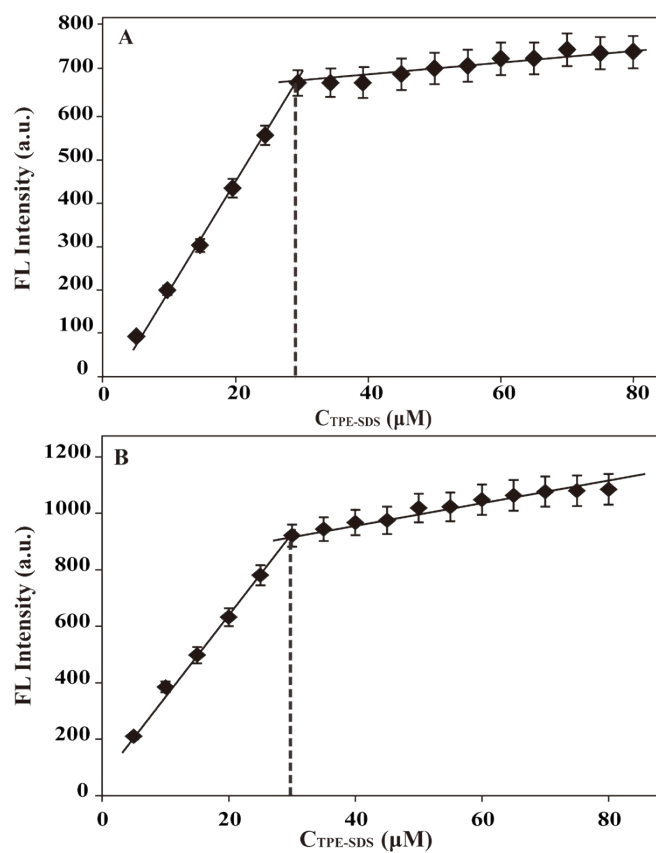


Fig. S8 Fluorescence intensity curves of TPE-SDS with PEO of low molecular weight: (A) $M_n = 375$; (B) $M_n = 550$.

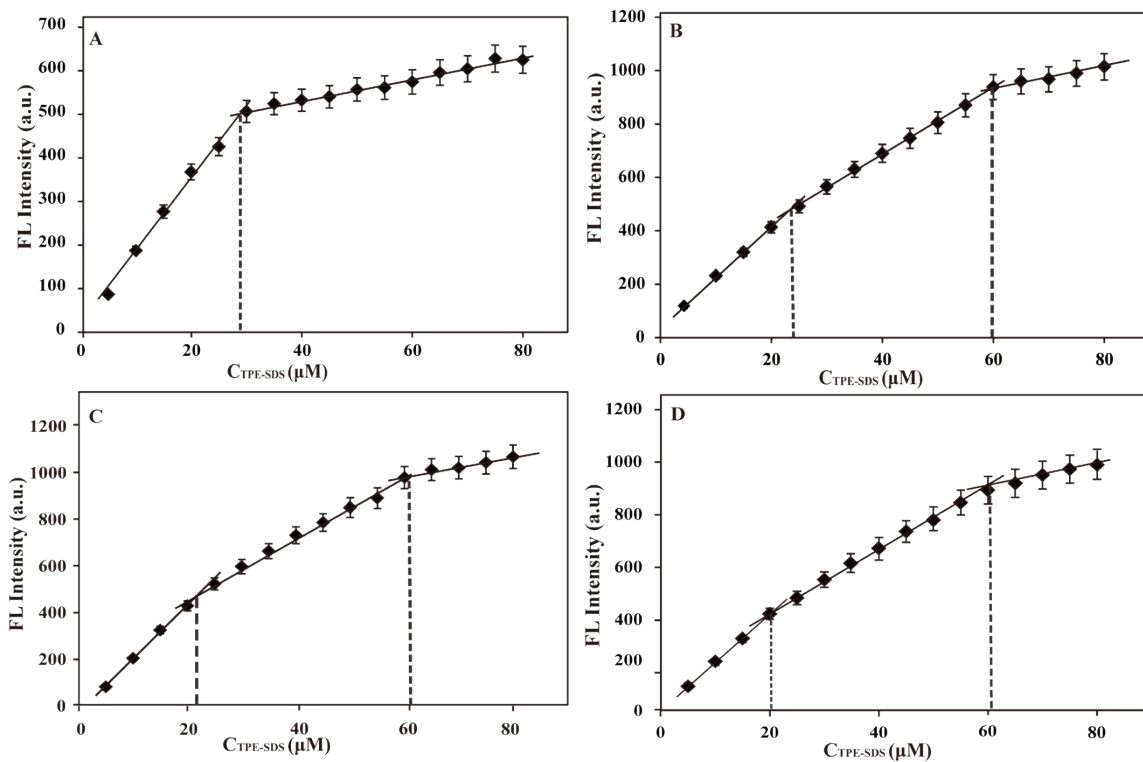


Fig. S9 Fluorescence intensity curves of TPE-SDS with PEO of moderate molecular weight:

(A) $M_n = 1,430$; (B) $M_n = 4,120$; (C) $M_n = 5,500$; (D) $M_n = 8,100$.

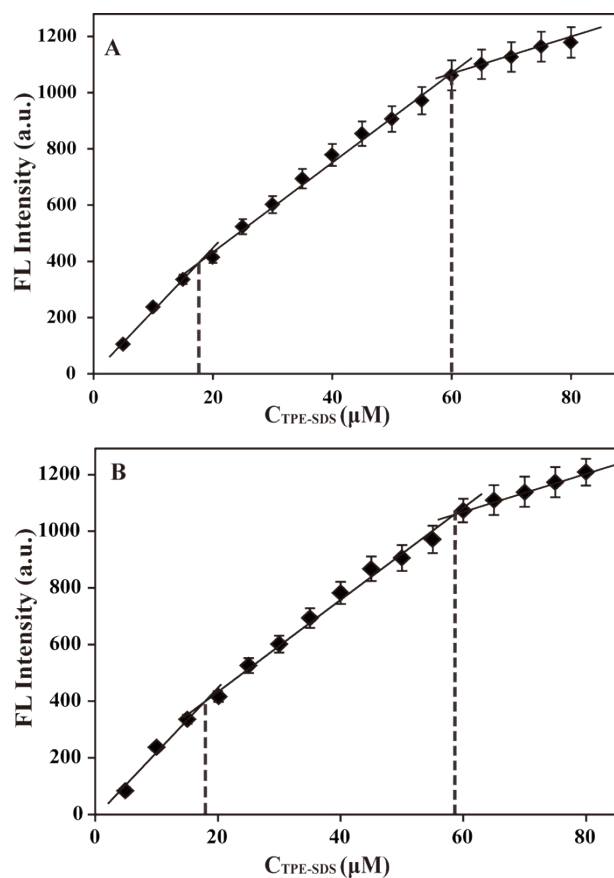


Fig. S10 Fluorescence intensity curves of TPE-SDS with PEO of high molecular weight: (A) $M_n = 21,200$; (B) $M_n = 89,200$.

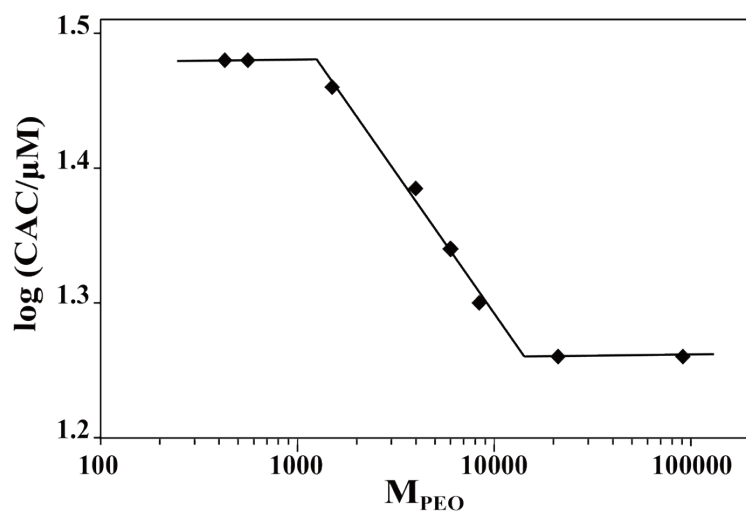


Fig. S11 Critical aggregation concentration (CAC) as a function of PEO molecular weight.

Reference

1. W. J. Guan, W. J. Zhou, C. Lu and B. Z. Tang, *Angew. Chem. Int. Ed.*, 2015, **54**, 15160.