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Pyranine-induced self-assembly of colloidal structures using poly(allylamine-hydrochloride)

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ABSTRACT

Complexes of dyes and polyelectrolytes have found widespread use in a variety of functional materials and interfaces. Here it is found that upon mixing the anionic dye pyranine and a cationic polyelectrolyte, poly(allylamine-hydrochloride), two different colloidal structures may form. Above a certain concentration of anionic dye, crosslinking of the polyelectrolyte is initiated, and the formation of sheet-like colloidal structures was observed. Addition of hydroxyl ions resulted in the formation of micron-sized spherical colloids. It was also found that the colloidal shape transition was accompanied by a significant red-shift in the fluorescence emission. Combining fluorescence measurements with studies of the particle size with time, it was found that red-shift was related to the crosslinking of the dye and the polyelectrolyte, and was not influenced significantly by the aggregation and particle growth. Further information about the colloidal behavior and stability was obtained by letting droplets dry and follow the kinetics of this process. It was found that the particles collapsed near the contact line and formed a ring deposit, in agreement with previous studies. However, unlike previous studies, the thickness of the ring deposit did not grow significantly with time, due to the peculiar process of formation found here.

1. Introduction

Polyelectrolytes tend to form aggregates with themselves and a wide variety of molecules. It has been shown that the complexation of polyelectrolytes and surfactants may lead to interfacial gels depending on factors such as surfactant/polymer molar ratio and molecular weight [1,2]. Cations or anions with multiply charged sites may allow crosslinking of polyelectrolytes through coulombic interactions, thus creating well-defined functional materials [3–8]. Pyrene-derivatives, such as pyrenetetrasulfonate, have found widespread use due to their strong negative charge and useful optical characteristics, and the crosslinking of this anionic dye with polyelectrolytes has been studied with the aim of creating new fluorescent colloidal structures [9–11].

Additional functionality using such pyrene-derivatives can be obtained by substituting a sulfonate with a hydroxyl group. The trisulfonate molecule, often called pyranine, is a water–soluble cationic dye with well-known photophysical properties, and has traditionally been used to monitor pH in vesicles and biological systems [12–14]. The fluorescence properties of this photoacid have been studied in detail in presence of salts, surfactants or a number of organic molecules [15–18]. Moreover, research has revealed a photoexcited state with pK_a much smaller than the ground state and a proton transfer of the order of picoseconds [19,20]. A number of recent studies have revealed that due to its multiple charged sites the anion may also be used to generate and functionalize colloidal micro or nanoparticles [21–23]. Rana and coworkers have shown that such particles could further be functionalized to obtain magnetic properties which allow arrangement into chains or other magnetically assembled structures [23].

Although studies have been undertaken to create new functional materials using pyranine-induced crosslinking between cationic polyelectrolytes, studies relating the optical properties to the corresponding colloidal structure appear to be lacking. In the light of the recent advances in functionalizing such particles for use in advanced materials, it would therefore be of interest to obtain a better understanding of how optical properties correlate with structure. Of particular interest here is the application of pyranine in the crosslinking of the polyelectrolyte poly(allylamine-hydrochloride) (PAH). PAH was chosen due to its structural simplicity and the fact that it has been carefully studied in solution [24]. It has positively charged side chains (NH_3^+) along the polymer chain, which can be used as linking sites for the anionic dye pyranine. Once the electrostatic bond between the anionic dye and the cationic polymer side chain has been formed, the local environment has a major impact on the fluorescence properties of the dye. Fluorescence probes have been widely used to investigate the microscopic environment and reactions in polymeric systems

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[25,26]. A number of studies by Yilmaz and coworkers have revealed that pyranine is an efficient probe for studying phase transitions, monomer conversion, and particle aggregation [27–31]. We will here use pyranine as both a crosslinking agent and to probe the local environment through its fluorescence. Together with optical microscopy, the fluorescence spectrum allows us to follow the formation of colloidal structures formed at different ambient conditions.

2. Experimental methods

The anionic dye 8-Hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HPTS), also named pyranine, was purchased from Sigma Aldrich, see Fig. 1.

Standard 1 M NaOH solution and poly(allyl-hydrochloride), PAH, of molecular weight M_w = 15 kDa, was also purchased from Sigma Aldrich. All chemicals were used as received, and all solutions were prepared using ultrapure (>18.2 MΩ cm) water from a Millipore system. The fluorescence spectra of the solutions were measured in a 2 mL cuvette using an USB 2000 + Ocean Optics fiber spectrometer using a violet (404 nm) 5 mW diode laser as excitation source. The colloidal structures formed were visualized with an Olympus BX51 polarization microscope. The particle size was determined using optical microscopy and a Nanosight LM10 light scattering instrument using a 635 nm laser to probe the Brownian motion. The diffusion coefficient thus measured can be used to estimate the size using the Stokes–Einstein relationship [32].

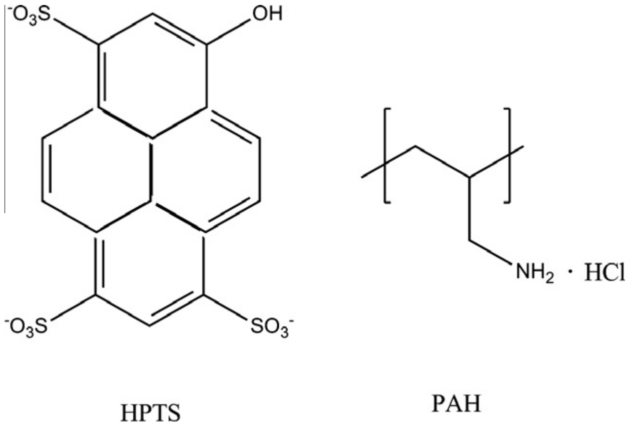

Fig. 1. The structures of 8-Hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HPTS) and poly(allylamine hydrochloride).

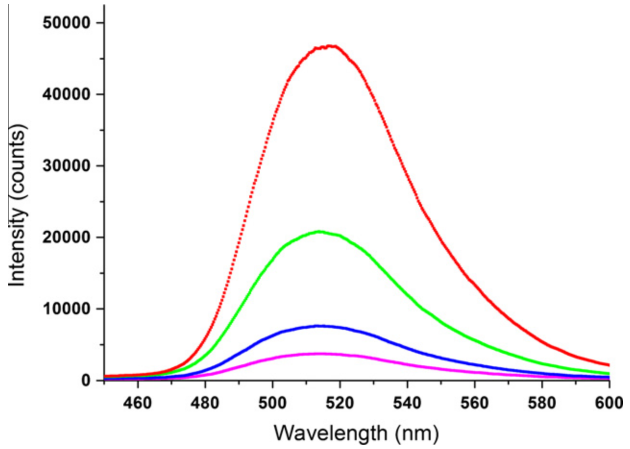

Fig. 2. The fluorescence spectrum of HPTS is shown for HPTS concentrations 5 μM (magenta), 15 μM (blue), 45 μM (green) and 4.54 mM (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

3. Results

The spectrum of HPTS is shown in Fig. 2 for HPTS concentrations 5 μM (magenta), 15 μM (blue), 45 μM (green) and 4.54 mM (red). At concentrations in the mM range the fluorescence emission reached saturation. The emission peak is located at about 517 nm for all the concentrations.

In a typical experiment creating a colloidal complex, 1 mL 667 μM (10 g/L) PAH was mixed with a corresponding solution of HPTS. The concentration of HPTS was systematically adjusted by gradually adding more of the anionic dye while observing the fluorescence spectrum. In Fig. 3 the fluorescence spectra for HPTS concentrations 5.5 μM (magenta), 11 μM (red), 16 μM (green), 21 μM (blue), 45 μM (yellow) and 87 μM (black) are shown. Note that the fluorescence spectra also here have peaks at approximately 517 nm, and do not shift for the small HPTS concentrations seen in the figure. It should be noted that the intensity is different from that of HPTS alone (Fig. 2), but this is believed to be due to the fact that PAH changes the pH (to be weakly acidic) and thus the spectrum of the pyranine.

We did however observe a blue-shift to 514 nm when the HPTS concentration increased above 1 mM (not shown). Moreover, upon increasing the HPTS concentration above 500 μM we observed that a precipitate became visible in the cuvette, and the corresponding spectral intensity maximum started to decrease. This trend is more clearly displayed in Fig. 4, where the spectral intensity maximum is reported as a function of the HPTS concentration.

Once the ratio between the number of HPTS and PAH molecules approached 1:1, the precipitate was observed. However, it was not until the HPTS concentration reached 10 mM or above, corresponding to a HPTS to PAH ratio >15, we clearly could observe colloidal structure in the microscope. The precipitates were inspected in an optical microscope; see Fig. 5a. The HPTS-PAH complexes consist of rather irregularly formed flakes. By gently pouring HPTS over a thin liquid film of PAH we could generate a nearly uniform thin film of the HPTS-PAH complex. If NaOH solution was added to the system to increase the pH > 11, we found that the complex dissolved and started to form small spherical colloid. A snapshot of the spheres is shown in Fig. 5b.

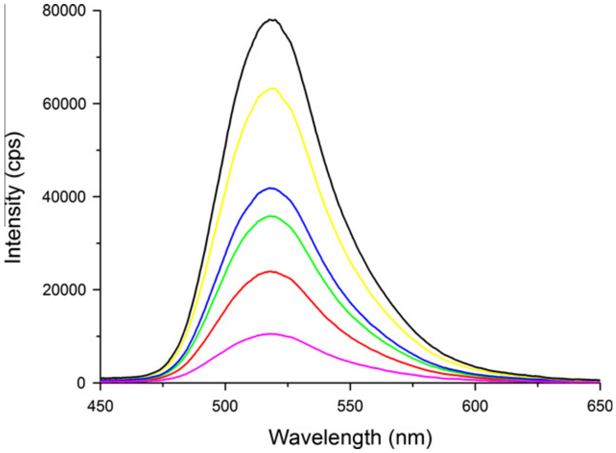

Fig. 3. The fluorescence spectrum of HPTS mixed with PAH at HPTS concentrations 0.0055 mM (magenta), 0.011 mM (red), 0.016 mM (green), 0.021 mM (blue), 0.045 mM (yellow) and 0.0872 mM (black). The integration time was 0.4 s for all but the largest HPTS concentrations, where it was 0.8 s. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).