

Nano-Encapsulation of Fluorescent Dyes in Diblock Copolymer Micelles

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Introduction

In a selective solvent that dissolves only one of the blocks, diblock copolymers self-associate into micelles with soluble coronas and insoluble cores.¹ These micelles can solubilize otherwise insoluble substances in the cores so that they can be suitable for colloidal stabilization, drug delivery, and so on. In this study, two different fluorescent dyes capable of electronic interaction via FRET (fluorescence resonance energy transfer) were solubilized in diblock copolymer micelles by selective encapsulation of dyes into the cores. When two dyes were intimately mixed in a common solvent, acceptor-only emission was observed due to FRET. In contrast, when independently-prepared solutions of micelle-encapsulated dyes were mixed together, simultaneous light emissions from both dyes were observed due to an effective isolation of dye molecules by the micellar structure.

Experimental

Polystyrene-poly(4-vinyl pyridine), PS-PVP, diblock copolymers were purchased from Polymer Source Inc. The number average molecular weights of diblock copolymers were 47,600 and 20,600 g/mol, respectively. The polydispersity index was 1.14.

To prepare PS-PVP micelles in toluene, a selective solvent for the PS block, a 2.0 wt% toluene solution of copolymers was prepared, and then stirred for 3 hr at 70 °C. Two different fluorescent dyes, 7-amino-4-methyl-3-coumarinylacetic acid (COU) and quinacrine dihydrochloride (QUI), were independently added to the individual micellar solution with molar ratios of $0.00025 < [\text{COU}]/[\text{VP}] < 0.0025$ and $0.001 < [\text{QUI}]/[\text{VP}] < 0.008$. These solutions were stirred for at least 2 weeks to ensure the complete encapsulation of dyes into the PVP cores. For a mixture solution, independently prepared solutions of micelle-encapsulated dyes were mixed together with the weight ratio of 1:1.

UV-vis absorption spectra were recorded on a Sinco (model S-3100) spectrophotometer. Photoluminescence spectra were recorded on an Acton (model Spectrapro-2300i) spectrometer.

Results and discussion

In toluene, a selective solvent for the PS block, PS-PVP diblock copolymers spontaneously associate into spherical micelles with soluble PS coronas and insoluble PVP cores.^{1,2} Since the PVP core can be served as energetically compatible environments for small functional molecules, which are not soluble in toluene, dye molecules of COU and QUI were selectively encapsulated into the PVP core.

In UV-vis and photoluminescence (PL) spectra of toluene solution of micelle-encapsulated dyes, the absorption maxima of COU and QUI were at 346 nm and 420, and their emission maxima at 421 nm and 482 nm, respectively. It should be noted that the emission spectra of micelle-encapsulated COU was overlapped with the absorption spectra of micelle-encapsulated QUI. PL intensities of micelle-encapsulated dyes increased with increasing the molar ratio of dyes to VP unit, and then decreased at the high molar ratios because of the self-quenching. The optimum molar ratios of COU and QUI to VP were 0.001 and 0.004, respectively.

To examine light emissions from a mixture of micelle-encapsulated dyes, we mixed independently-prepared toluene solutions of PS-PVP micelles containing COU and QUI individually. We also prepared ethanol solutions of dyes with the same concentrations for comparison.

Figure 1(a) shows typical PL spectra obtained from ethanol solutions of dyes. PL spectra from COU (dotted line) and QUI (dashed line) showed the maxima at 427 nm and 489 nm, respectively. The intensity of COU in ethanol was stronger than that of QUI, presumably due to a higher quantum yield and a lower molar extinction coefficient.

A mixture of COU and QUI in ethanol (solid line) resulted in the emission predominantly from QUI. The COU donor emission at 427 nm was almost disappeared, whereas the QUI acceptor emission at 489 nm was enhanced.

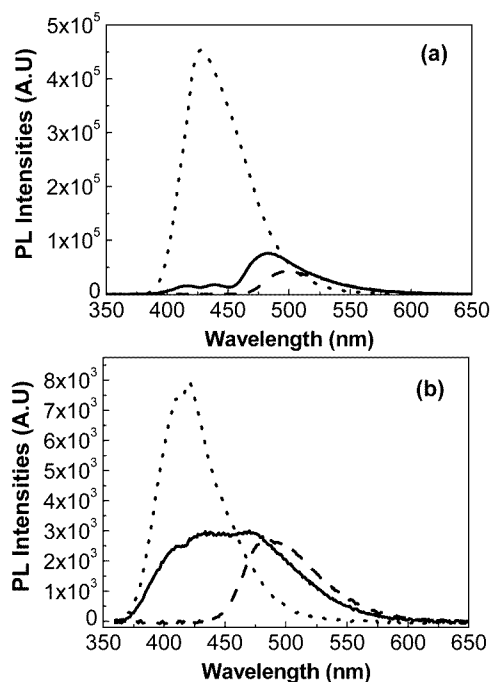


Figure 1. PL spectra of COU (dotted), QUI (dashed), and mixture (solid): (a) in ethanol; (b) in toluene with micelle encapsulation.

By encapsulating fluorescent dyes in PS-PVP micelles, the shape and peak position of PL spectra of micelles-encapsulated COU (dotted line) and QUI (dashed line) were almost unchanged, compared to those in ethanol as shown in Figure 1(b). However, the PL spectrum of a mixture of micelle-encapsulated COU and QUI (solid line) showed both emissions from COU and QUI.

When the emission spectrum of donor molecules is overlapped with the absorption spectrum of acceptor molecules, the excited-state energy of the donor can be transferred to the acceptor by the long-range dipole-dipole interactions, i.e., FRET.³ Therefore, it is normally difficult to observe light emissions from both donor and acceptor molecules because the FRET between the molecules leads to acceptor-only light emission. In contrast, if dye molecules are isolated beyond their Förster radius, simultaneous light emission from both donor and acceptor can be obtainable. The Förster radius is typically in the range of 10 ~ 100 Å. In ethanol, COU and QUI molecules could contact each other so that their mutual distance could be within their Förster radius, which resulted in the acceptor-only emission as shown in figure 1(a). For a mixture of COU and QUI in PS-PVP micelles, however, COU and QUI were effectively separated by the PS corona. Thus, the donor-acceptor distance could exceed their Förster radius, which resulted in simultaneous light emission from COU and QUI as shown in Figure 1(b).

Conclusions

Fluorescent dyes of COU and QUI were effectively isolated in PS-PVP micelles. From a mixture of micelle-encapsulated COU and QUI, simultaneous light emission from both COU and QUI was observed because the FRET was suppressed by the site isolation of dye molecules in the micelle.

References

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