

Honeycomb-patterned fluorescent films fabricated by self-assembly of surfactant-assisted porphyrin/polymer composites

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ABSTRACT

A novel honeycomb-patterned fluorescent film was fabricated by self-assembly of polystyrene (PS)/poly(ethylene glycol) (PEG)/meso-tetra (N-methyl-4-pyridyl) porphinetetratosylate (TMPyP) blend system, at the assistance of diisooctyl sodium sulfosuccinate (AOT). Ordered microporous PS/PEG/TMPyP/AOT blend films were prepared by the breath figure method. The condensed water droplets acted as the sacrificial templates, which were stabilized by strong hygroscopic PEG and amphiphilic surfactant AOT. Relative humidity and evaporation conditions considered as critical factors were investigated to control the morphologies of the films. The introduction of surfactant AOT greatly promoted the dissolution of the TMPyP in PS/PEG polymer solution according to the UV–vis spectra data, which led to the fluorescence enhancement of ordered porous blend films. The unique “internal ring” structures were formed during phase separation and confirmed by scanning electron microscopy images and fluorescence micrographs.

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1. Introduction

Since Francois et al. [1] successfully prepared honeycomb films by the breath figure method in 1994, great progress has been made in the method [2–5] and theory [6–8] and the fabrication of ordered porous films. Nowadays, the focus of the research has been gradually transferred from the formation mechanism of the films to the practical applications. It has great research significance of conducting functional films [9,10] with various materials (nanoparticles, precious metal, electrical materials, optical materials, biological materials) [9,11–17]. These functional films have greatly scientific value and important application prospect in the fields of photonic crystals [18,19], cell culture [20], solar cell [21], and so forth.

By reason of the unique amphiphilic structure, surfactant AOT can interact with various substances [22–24]. Many composite materials with controlled surface properties can be obtained by modification of AOT. And at the assistance of AOT, many aggregation structures can also be formed at the oil/water interface [25–28]. A variety of functional substances such as CNTs, nanoparticles, and biological materials can be assembled at the assistance of modified AOT [29–32]. As an important class of functional substances, porphyrin [33] and metalloporphyrin not only own good catalytic, optical, electrical, biological activity and other properties,

but also have a certain chemical and thermal stability. Therefore, the studies of self-assembled structures based on porphyrin [34] play an important role in the fields of chemistry, life science, materials science, medicine, and environmental science [35–38].

In the present study, blend of polystyrene (PS)/polyethylene glycol (PEG) was selected as the basic material of films [39–42]. At the assistance of AOT, functional TMPyP molecules were loaded on the porous films by self-assembly of PS/PEG blend polymeric system. Humidity and evaporation conditions (under high purity nitrogen flow or in the atmosphere) were studied and considered as critical factors during the formation of ordered porous films. Consequently, the ordered honeycomb-patterned films demonstrate good fluorescent properties due to the embedded TMPyP functional molecules.

2. Experimental section

2.1. Materials

Meso-tetra (N-methyl-4-pyridyl) porphinetetratosylate (TMPyP) was purchased from Frontier Scientific Inc. Polystyrene (average MW 250,000) was commercially obtained from Acros Organics. Polyethylene glycol 400 was supplied from Sinopharm Chemical Reagent Company. Diisooctyl sodium sulfosuccinate (AOT) was from Sigma. Water used in all experiments was deionized to 18.25 MΩ cm. All other reagents were of analytical grade. All the experiments were performed at room temperature.

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2.2. Film preparation

PS/PEG (70/30, w/w) toluene solution (5 wt%) was prepared for stock solution. Light purple red PS/PEG/TMPyP toluene solution can be obtained by adding 0.0002 g TMPyP to 20 mL PS/PEG toluene stock solution. Light green PS/PEG/TMPyP/AOT toluene solution was obtained by adding 0.0320 g AOT into 20 mL PS/PEG/TMPyP toluene solution.

The films were fabricated through casting the series of solutions onto the cleaned substrates by micro-injector. 6 μ L of a sample solution was dropped onto glass and single-crystal silicon slides under a flow of moist air with different humidity at room temperature. The glass and single-crystal silicon slides were cleaned by immersion in a series of ultrasonically agitated solvents (acetone, H₂O, ethanol, H₂O) for 20 min at 50 °C. The cleaned wafers were immersed in Piranha solution (30% H₂O₂/concentrated H₂SO₄ = 3/7, v/v) at 80 °C for 1 h, rinsed with deionized water, and dried under a nitrogen stream. The relative humidity was gained by perpendicularly blowing high purity nitrogen gas saturated with water vapor to the sample solution surface. Five minutes later, solvent and water evaporated completely and a flat thin film was obtained.

2.3. Characterization

UV–vis spectra were carried out with Shimadzu UV3101PC (Japan). Scanning electron microscopy (SEM) images were collected using Hitachi S-2500 field emission scanning electron microscopes (Japan). Atomic force microscopy (AFM) measurements were performed using a Veeco Nanoscope IIIa scanning probe microscope

operating in tapping mode. Fluorescence images of porous films were recorded by inverted fluorescence microscope Olympus IX51 (Japan) with excitation wavelengths (λ_{ex}) of 510–550 nm. The relative humidity (RH) was measured by hygrothermograph CEM DT-321S (China).

3. Results and discussion

3.1. UV–vis absorption spectroscopy characterization

To obtain films, 200 μ L of sample solutions was cast onto 0.17 mm glass substrates under high purity nitrogen flow (RH 67%) at room temperature. Fig. 1 shows the UV–vis spectra of films prepared from PS/PEG (a), PS/PEG/TMPyP (b), and PS/PEG/TMPyP/AOT (c) toluene solution, respectively. It can be seen that the films fabricated from self-assembly of PS/PEG/TMPyP/AOT toluene solution (c) have distinctly higher absorbance around 440 nm (Soret band) characteristic of porphyrin ring than of PS/PEG/TMPyP film (b). The results indicate that only a small amount of TMPyP dissolved in PS/PEG toluene solution. However, the introduction of AOT significantly enhanced the dissolution of TMPyP in PS/PEG toluene solution (as seen in Fig. 1c). In fact, TMPyP and AOT dissolved and ionized in toluene polar organic solvent. A TMPyP cation carried four positive charges and AOT dissolved in solvent with a negative charge. There was electrostatic interaction between AOT and TMPyP molecules. Four AOT anions gathered around a TMPyP cation to form TMPyP/AOT composite structure, which contributed to higher dissolution of TMPyP molecules in PS/PEG toluene solution.

3.2. Effect of AOT on the pore size of self-assembled films

Scanning electron microscopy was employed to observe the morphologies of the films. Fig. 2 shows the SEM images of PS/PEG (a), PS/PEG/TMPyP (b), and PS/PEG/TMPyP/AOT (c) honeycomb-patterned films under high purity nitrogen flow with RH 67%. In Fig. 2a, the average pore diameter of PS/PEG blend films is about 5 μ m. There are no obvious changes in pore size of PS/PEG/TMPyP porous films prepared from adding TMPyP to PS/PEG toluene solution (Fig. 2b). As a result, the introduction of AOT significantly improved the dissolution of TMPyP in PS/PEG toluene solution according to UV–vis spectra data. Meanwhile, the average pore size of PS/PEG/TMPyP/AOT honeycomb films increases dramatically to 12 μ m. In the solution of PS/PEG/TMPyP/AOT (c), AOT anions interacted with TMPyP cations to form TMPyP/AOT composites, which resulted in the higher dissolution of TMPyP in the blend polymer solution. The excessive AOT molecules adsorbed at the interface of condensed water droplets and the toluene solution, which was beneficial to the stability and growth of condensed water droplets. Moreover, the adsorption of AOT anions at the

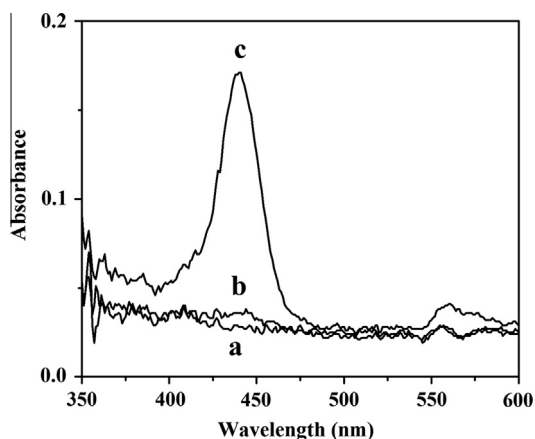


Fig. 1. UV–vis spectra of PS/PEG (a), PS/PEG/TMPyP (b), and PS/PEG/TMPyP/AOT (c) honeycomb-patterned films under high purity nitrogen flow with RH 67%.

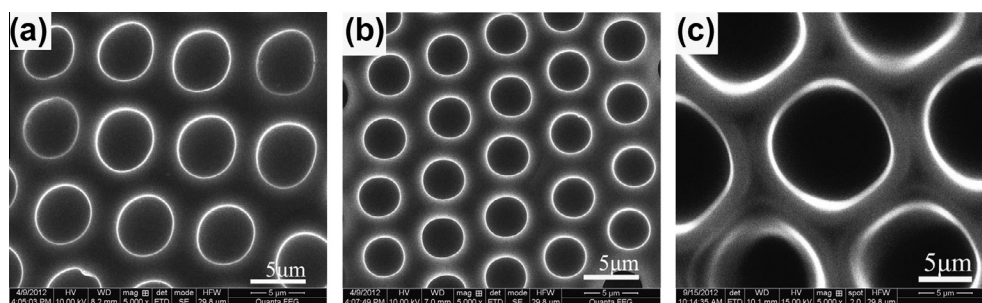


Fig. 2. The SEM images of PS/PEG (a), PS/PEG/TMPyP (b), and PS/PEG/TMPyP/AOT (c) honeycomb-patterned films under high purity nitrogen flow with relative humidity: 67%.

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