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Hydrophobic structural color films with bright color and tunable stop-bands

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ABSTRACT

Hydrophobic structural color films have attracted a special attention due to the great advantages in application, which currently become a research hot-spot. This study presents a convenient approach to fabricate hydrophobic structural color films by modifying self-assembled polymer opal from cross-linked polystyrene microspheres and polydimethylsiloxane. The obtained films exhibited several unique characteristics, such as a high water contact angle of 137°, bright structural color, and tunable stop-bands. Additionally, the combination of hydrophobicity and tunable stop-bands was significant for potential application in paint and external decoration of architectures. The present result opens new vistas for the research of functional films, using thermal-assisted self-assembly as a simple method that is cheap and commonly available.

1. Introduction

Structural color originates from interference, diffraction, or scattering of visible light, which results from well-ordered arrangement of a periodic microstructure [1–6]. Its coloration mechanism is relatively different from that of traditional colorants (dyes, pigments, etc.). Artificial structural color has a unique anti-photobleaching characteristic that has made it a topic of interest for a broad range of applications, such as full-color display, ink, optoelectronics, and chemical sensors [7–11]. In contrast to expensive and unscalable technologies of dielectric layer stacking and direct lithographic patterning, colloidal particle self-assembly is most frequently used to generate a photonic crystal because raw materials are easily obtained and the self-assembly method is controllable, simple, and inexpensive [12,13]. Although some reported films show structural color, they do not possess hydrophobicity because of the charge characteristics of colloidal particles. For outdoor applications, they may be limited by pollution caused by dust particles, snow, and fog, among others. Therefore, research on films with both structural color and hydrophobicity is of great practical significance. However, this field involves various challenges. Based on the popular Wenzel [6] and Cassie–Baxter models [14,15], the combination of suitable surface roughness and low-surface-energy materials contributes to enhancing hydrophobicity. In spite of the difficulties, some researchers have successfully obtained dual function films that exhibit both structural color and hydrophobicity. Gu et al. [3] fabricated inverse opal films with a contact angle (CA) of 155°. However, the self-assembly approach to inverse opal films involves infiltration of colloidal crystal in the voids of another colloidal crystal (template) followed by removal of the template. Every step is extremely important, and control over the surface morphology is very difficult [12]. Thus, the fabrication process is time consuming and requires rigorous conditions, including calcination at 450 °C. Jiang et al. [16] used polystyrene (PS) spheres to form two-dimensional colloidal crystals with high reflection and a CA of only 125°. Sun and his co-workers [17] reported a simple one-step method to generate hydrophobic graphene surfaces with bright structural color. In this method, two-beam laser interference was utilized to fabricate periodic grating structures and to simultaneously remove the oxygen groups on the film, which contributes to the hydrophobic and colorful features. Considering these factors, a simple and practical method to fabricate films with both bright structural color and hydrophobicity is essential to researchers.

In this article, we developed a convenient method to form hydrophobic structural color films with bright color from cross-linked PS microspheres and polydimethylsiloxane (PDMS) by using the thermal-assisted self-assembly method. PDMS is a typical

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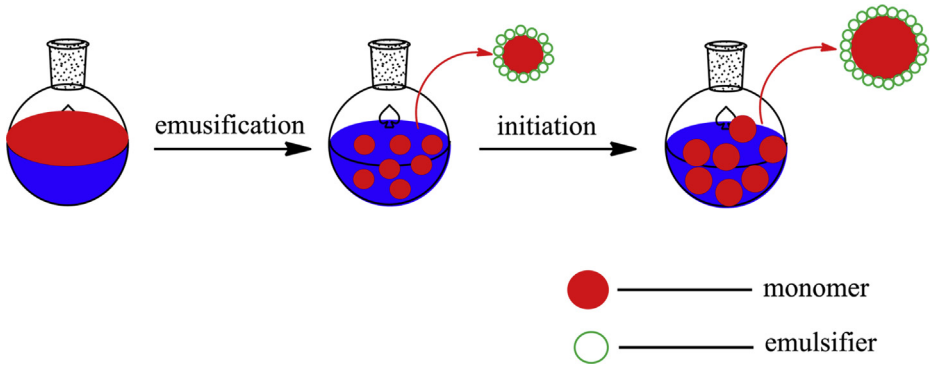

Fig. 1. Schematic illustration of cross-linked PS emulsion polymerization.

elastomeric material with low surface energy of about 20 mN/m [18]. Its excellent properties, such as hydrophobicity, low toxicity, long-term endurance, and transparency [19–22], make it an attractive material for outdoor applications. The fabricating process was very simple because the mixture of cross-linked PS suspension and PDMS solution was directly used to assemble structural color films. And the stop-bands were easily tuned by changing the cross-linked PS microspheres sizes, which was essential for actual application in paint and external decoration of architectural structures.

2. Experimental

2.1. Materials

Styrene, divinyl benzene, potassium peroxydisulfate, and sodium dodecyl benzene sulfonate were purchased from Sinopharm Chemical Agent Company (Shanghai, P.R. China). Styrene was alternately washed in a separatory funnel four times with 0.1 M NaOH to remove polymerization inhibitors and then washed with deionized water until neutrality. PDMS obtained from Dow Corning (Midland, MI) was used with a 10:1 base to curing agent mixing ratio. Deionized water was used in all polymerizations. All other chemical reagents were used without further purification.

2.2. Preparation of monodispersed, cross-linked PS suspension

Monodispersed, cross-linked PS spheres with different sizes were prepared by emulsion polymerization. The typical process was performed as follows: 120 mL deionized water, 10.0 g styrene, 0.5 g divinyl benzene, and an appropriate amount of sodium dodecyl benzene sulfonate were added to a 250 mL three-necked flask equipped with a temperature indicator, mechanical stirrer, and reflux condenser. The system was kept at 85 °C by using a water bath under N_2. Then, 0.100 g potassium peroxydisulfate was added when the temperature was stable. The cross-linked PS microsphere emulsion formed after 5 h.

Table 1
Zeta-Sizer of four kinds of cross-linked polystyrene emulsion.

Sample	Amount of emulsifier (g)	Size (nm)[a]		PDI	Zeta potential (mV)
		D_h	D_a		
(a)	0.065	307	269	0.03	−45.0
(b)	0.073	294	251	0.06	−43.3
(c)	0.084	264	230	0.07	−44.0
(d)	0.115	224	191	0.01	−41.4

[a] D_h: Hydrodynamic size of these microspheres measured by Nanoparticle size measurement. D_a: Actual measured diameters from the SEM.

2.3. Preparation of hydrophobic structural color films

For high viscosity of 3500 mPa s, PDMS was used in the form of solution, which contained 2.0 g PDMS in 4.0 mL tetrahydrofuran (THF). Cross-linked PS emulsion was modified by adding an appropriate amount of PDMS solution. The modified suspension was dipped on a glass substrate. After carefully spreading the suspension to fully cover the surface, the substrate was placed on a hot plate at 50 °C to assist self-assembly. An ordered structure with a large area was fabricated within several minutes as a result of rapid water evaporation.

2.4. Characterization

The average hydrodynamic sizes of the particles were measured by using a particle size analyzer (Zetasizer 1000, Malvern, UK). The microstructures of bright structural color films were observed via scanning eletron microscopy (SEM; Nova NanoSEM 450, FEI, USA). All samples were coated with gold before observation. CAs were measured on a Phoenix-300 contact-angle system (SurfaceTech, Korea). Topographical images were obtained by using atomic force microscopy (AFM; Nanoscope IIIA+, Veeco Instruments, USA). The reflection spectra of the films were measured at a scan speed of 300 nm/min by using a Hitachi U-4100 spectrophotometer with a slit width of 8.00 nm. Optical photos of cross-linked PS structural color films before and after modification were taken with a Nikon digital camera.

3. Results and discussion

3.1. Preparation and characterization of emulsion

The synthesis strategy of cross-linked PS emulsion is shown in Fig. 1. The effects of sodium dodecyl benzene sulfonate on the sizes and polydispersity index (PDI) of cross-linked PS microspheres are summarized in Table 1.

As shown in Table 1, the hydrodynamic particle size of the emulsions obviously decreased from 307 nm to 224 nm when sodium dodecyl benzene sulfonate increased from 0.62% to 1.10% of the monomer weight. The actual measured diameters from the SEM results were 269, 251, 230, and 191 nm. This illustrated that particle size could be easily controlled by changing the amount of emulsifier. Moreover, PDI was <0.1 and zeta potential was <−40 mV, demonstrating that the obtained emulsion was monodispersed and stable [23].

3.2. Fabrication and characterization of microstructure

We fabricated high quantities of polymer structural color films by using a previously reported thermal-assisted self-assembly