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Short communication

Hollow disperse dyes/copolymer composite nanospheres

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ABSTRACT

Due to the high refrangibility hollow polymer spheres have a strong opacity and covering power. Color hollow copolymer spheres for fiber coloration were prepared by using four commercial disperse dyes with different structures. TEM images show that the hollow size increased from 288.5 nm to 302.5 nm. The conductive titration tests indicate that the hydrophobic disperse dye molecules went into the shell copolymer part in the dyeing process and made the shell more compact and more hydrophobic. The dye content absorbed by the hollow spheres were different with increasing the pH value of the dye-bath from 2 to 12 for anthraquinone and azo disperse dyes. The DLS analysis indicates that the particle size distribution of the spheres dyed at pH 10 was narrower than the original spheres and the spheres dyed at pH 12. Increasing the dye concentration, dyeing temperature and time the dye content increased.

1. Introduction

Hollow polymer spheres have many advantageous properties, such as sustained release, low density, high specific surface area, and strong light scattering. Therefore, they are widely used in biomedicine, leather making, paper coating, cosmetics etc [1–6]. *N*-vinylpyrrolidone-co-polylactic acid polymer hollow spheres were prepared by solvent evaporation extraction to extend the drug release period [7]. Enzymes immobilized on the magnetic hollow composite particles exhibited high activity and good stability [8]. Leather embossed with voided polymer particles showed good pattern clarity and sharpness [9]. Paper coated with hollow polymer spheres obtained the advantages of high gloss, good smoothness and high stiffness [10]. Shampoo containing hollow particles could nourish human hair much better [11]. Personal care compositions containing voided polymer particles showed high effectiveness and good storage stability [12].

The polymer shell and the air inside the hollow nanospheres have different refractive indexes, resulting in a big refractive difference. Therefore, when the light shines on the hollow polymer nanospheres, the incident light can be scattered effectively [13,14]. That endows the hollow nanospheres with good opacity and covering power [15]. Paper coated with hollow polymer spheres exhibited extinguishing opacity [16]. Generally, it is difficult to print bright patterns on colored fabrics. However, using hollow spheres in pigment printing could produce glossy and vivid textiles with good handle [15]. Therefore, colored hollow polymer spheres are expected to produce much better color effect than the white ones on fabrics [17].

The objective of the present study was to prepare hollow disperse dyes/copolymer nanoscale spheres, hollow copolymer spheres with ideal colors, which could be used for fiber coloration. Poly (styrene-co-acrylic acid) (P (St-co-AA)) hollow nanospheres dispersions were directly dyed with commercial disperse dyes. The morphology and sizes of the disperse dyes/copolymer nanoscale spheres were analyzed using TEM and DLS. Dye contents adsorbed on the spheres were measured, and the factors influencing the dye adsorption were investigated. Such results have never been reported up to date.

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2. Experimental

2.1. Materials

Hydrochloric acid, sodium hydroxide and N *N*-dimethylformamide (DMF) were all of analytical grade and were purchased from Qingdao Huadong chemicals and Equipments Co., Ltd, China Four commercial disperse dyes, disperse Red FB (C. I. disperse Red 60), disperse Blue 2BLN (C. I. disperse Blue 56), disperse Blue HGL (C.I. disperse Blue 79) and disperse Yellow 6 GS (C. I. disperse Yellow 114), were supplied by Hongda Chemical Industrial Co., Ltd, China, and used as received. The chemical structures of the dyes are shown in Fig. 1. Hollow P (St-co-AA) spheres dispersions were kindly supplied by Dow Chemical. The solid content of the copolymer spheres dispersions was 29% measured by drying.

2.2. Preparation of hollow disperse dyes/P (St-co-AA) composite spheres

A 3.5 g P (St-co-AA) hollow spheres dispersions and 99.6 ml H_2O were added to a beaker, followed by the addition of disperse dye suspension under magnetic stirring. The pH value of the mixture was adjusted with (1.0 mol/L) HCl and (1.0 g/L) NaOH aqueous solutions. The prepared mixture was then transferred to an SHB constant-temperature shaker dyeing machine (Changzhou Guohua Electronic Instrument Co., Ltd, China) for 3 h at 90 °C. Subsequently, the colored sample was taken out of the machine and allowed to cool to room temperature [18].

Colored P (St-co-AA) hollow spheres were obtained from the dispersion via a series of steps. First, the color sample was transferred to a high-speed centrifuge which rotating speed was 1000, and then the rotating speed was increased to 5000. Finally, the sample was dried at 50 °C, and the nanospheres powder was obtained [18].

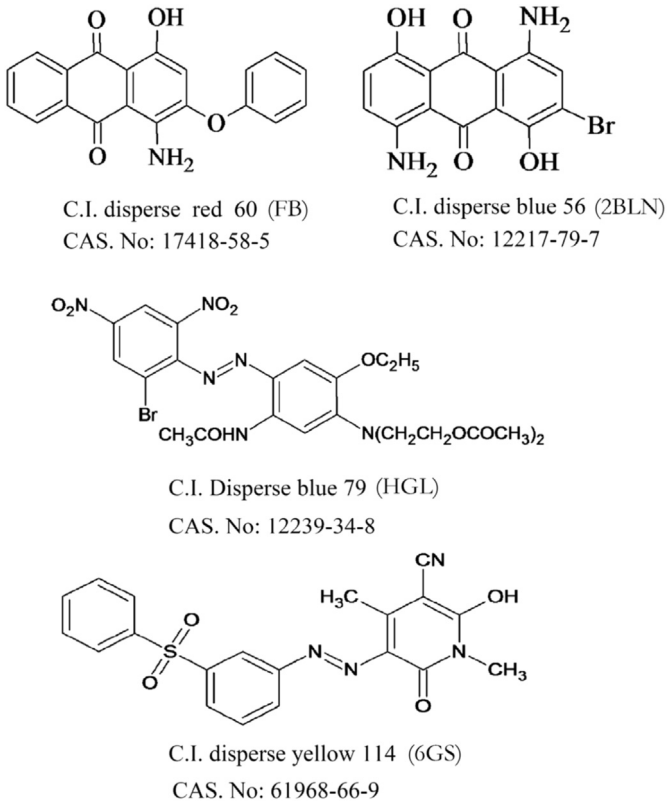

Fig. 1. Molecular structures of the disperse dyes used.

2.3. Observation by transmission electron microscopy (TEM)

The colored hollow nanospheres samples were ultrasonically diluted 25 times with deionized water and dropped onto Cu meshes. After drying under an infrared lamp, the size and morphology of the P (St-co-AA) nanospheres were observed using a JEM-1200 EX transmission electron microscope (JEOL, Japan) [18].

The diameters of 100 different hollow spheres on the TEM images were measured. The average diameter D of the hollow spheres was calculated according to the formula, $D = \sum_{i=1}^{n} di/n$, where n equals 100, and d_i is the diameter of hollow nanospheres i.

2.4. Sizes and distributions of the disperse dyes/copolymer spheres

The sizes and distributions of the nanospheres were measured by using a Nano-ZS90 instrument (Malvern, UK) at 25 °C. All samples were diluted with deionized water before test.

2.5. Dye content measurements

A known weight of disperse dye was dissolved in DMF and the concentration was adjusted to 0.01 mg/ml. The colored hollow nanospheres powder was also dissolved in DMF to achieve a dye concentration of approximately 0.1 mg/ml. The visible absorption spectrum of the DMF solution was measured using a double-beam UV–vis spectrophotometer (TU-1901, Beijing Purkinje General Instrument Co., Ltd, China). The absorbance of the DMF solution was then measured at the maximum absorption wavelength of the dye. The dye content of the colored hollow spheres was calculated using Lambert-Beer's law [19].

2.6. Conductivity titration

The pH value of known weight P (St-co-AA) dispersion was adjusted to 11 using a 0.5 g/L NaOH solution. Then, it was placed at room temperature for 30 min. A 0.25 moL/L H_2SO_4 solution was slowly added into the P (St-co-AA) dispersion under magnetic stirring. Simultaneously, the conductivity of the dispersion was recorded using a Mettler Toledo laboratory conductivity instrument. Finally draw conductance - sulfuric acid curve [20,21].

3. Results and discussion

3.1. Morphology of the disperse dyes/copolymer composite nanoscale spheres

TEM images in Fig. 2a show that the P (St-co-AA) spheres have obvious hollow structure. The average particle size of the hollow spheres was 407.8 nm, and the diameter of the hollow part was 288.5 nm. As shown in Fig. 2b, after coloration the size of the spheres increased to 411.5 nm while the hollow size increased to 302.5 nm, i.e., the obtained disperse dyes/copolymer composite spheres have an average diameter of 411.5 nm with the hollow diameter of 302.5 nm.

3.2. Interaction between the dyes and the hollow spheres

In order to reveal the interaction between the dye molecules and the hollow nanospheres macromolecules, we adjusted the pH value of the P (St-co-AA) dispersion to 11 using a 0.5 g/L NaOH solution. Then, a 0.25 mol/L H_2SO_4 solution was slowly added into the P (St-co-AA) dispersion. Simultaneously, the conductivity of the