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A facile method for preparing colored nanospheres of poly (styrene-co-acrylic acid)

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ABSTRACT

Colored nanospheres are widely used in paints, inks, food, electronic displays, textiles, and medicine. In the present study, we describe an emulsifier-free emulsion polymerization process for the synthesis of poly(styrene-co-acrylic acid) nanospheres, such that the influence of surfactants is eliminated. The obtained nanosphere dispersions were mixed with three commercial disperse dye solutions. After heat treatment, pure and brightly colored nanosphere powders were obtained by a simple purification procedure. Transmission electron microscopy images showed that the average particle size of the nanospheres increased by 23 nm after coloration, and differential scanning calorimetry revealed a decrease of 2.98 °C in the glass transition temperature. The amounts of dyes fixed within the nanospheres depended on the dye concentration of solution. The three different dyes were incorporated to varying levels, corresponding to their ability to form hydrogen bonds with the polymer nanospheres.

1. Introduction

Colored particles containing both visible and fluorescent colorants integrate the excellent chromatic properties and processability of synthetic dyes and the superior durability of organic pigments. They therefore have great potential in a wide variety of applications, for example, in paints, inks, food, electronic displays, textiles, and biomedicine [1–13].

Surface modification of pigments is an easy method to produce nanoscale colored particles [10,13–16]. For instance, Phthalocyanine Green nanoparticles with a size of 120 nm have been obtained using anti-solvent recrystallization combined with in situ modification [10], and microcapsules with Benzidine Yellow pigment as a core material have been synthesized by in situ polymerization for use in electrophoretic image displays [13]. However, it is difficult to obtain monosized spherical colored particles using this technique, as the crystal structure of the pigment cannot be changed in the grinding process [14–16]. In addition, the encapsulation of pigment particles with polymers usually reduces their color gamut [11].

Dispersion, emulsion, and miniemulsion polymerizations are well established methods for preparing polymer particles [17–28]. Colorants can be incorporated into these particles during their synthesis. For example, poly(methyl methacrylate-co-ethylene glycol dimethacrylate) (P(MMA-co-EGDMA)) particles with Oil Blue N as a colorant were prepared by emulsifier-free emulsion polymerization [8], and negatively charged ultrafine black particles of the same copolymer, but with Sudan Black B as a colorant, were prepared by dispersion polymerization [9]. Polymer particles containing oil-soluble dyes have been prepared by miniemulsion polymerizations [29–31]; however, the color of these particles can fade spontaneously because of dye leakage [31,32]. Therefore, dyes with polymerizable double bonds in their structure were used as an alternative for using miniemulsion polymerization to prepare colored nanoparticles [32]. Although the chemical synthesis techniques are effective for incorporating colorants into polymer particles, it is difficult to obtain pure products in most cases owing to the simultaneous reaction between the monomers themselves, resulting in phase separation. In addition, these methods are time-consuming and complex, requiring control over numerous parameters such as monomer composition, reaction conditions, and emulsifier type [33].

Abbreviations: (P(MMA-co-EGDMA)), poly(methyl methacrylate-co-ethylene glycol dimethacrylate); PS, polystyrene; (P(St-co-AA)), poly(styrene-co-acrylic acid); St, styrene; AA, acrylic acid; APS, ammonium persulfate; THF, tetrahydrofuran; DSC, differential scanning calorimetry; TEM, transmission electron microscopy.

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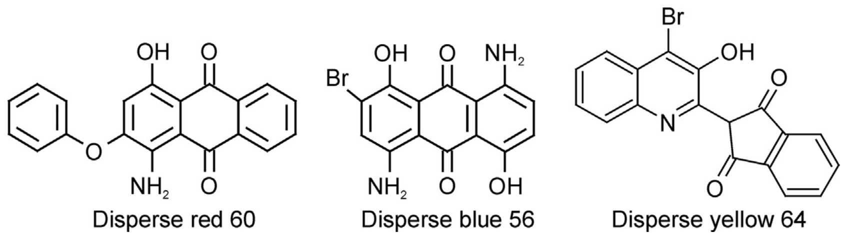

Fig. 1. Molecular structures of the disperse dyes used.

Modification of preformed particles with colorants is a relatively facile method for the preparation of colored particles, owing to the wide range of monomers that can be polymerized [17–28,33]. Using dyes to modify polymer particles enables larger colored microspheres to be obtained [5–7]. Electrostatic and hydrophobic interactions have been utilized to drive the adsorption of a positively charged dye such as the cationic dye, Malachite Green, onto polystyrene (PS) microsphere surfaces carrying the opposite charge [34]. The preparation of colored polymer particles through surface modification usually changes the surface structure of the particles and affects the stability of their dispersions. Therefore, a swelling–diffusion technique was used to prepare fluorescent dye-labeled PS microspheres with sulfonate groups [33]. However, it was necessary to add a block copolymer surfactant to the suspension in order to prevent particle aggregation, which made it difficult to obtain pure colored microspheres.

Although there are many publications dealing with the preparation of microsized colored particles, the production of pure and uniform colored nanospheres is not often reported. The aim of the present study was to develop a facile preparation method for colored polymer nanospheres. By using emulsion polymerization, uniform poly(styrene-co-acrylic acid) (P(St-co-AA)) nanospheres were synthesized in the absence of an emulsifier in order to eliminate its influence on the subsequent purification. The synthesized nanosphere dispersions were directly colored with commercial disperse dyes utilizing the hydrophobic nature of the polymer chains of the synthesized particles. Pure, colored nanospheres were obtained after a simple purification procedure and subsequent drying. In contrast to the previously reported techniques, the present method is relatively simpler, avoids the use of toxic solvents, and broadens the spectrum of colored nanospheres to a great extent.

2. Experimental

2.1. Materials

Three commercial disperse dyes, disperse Red FB (C. I. disperse Red 60), disperse Blue 2BLN (C. I. disperse Blue 56), and disperse

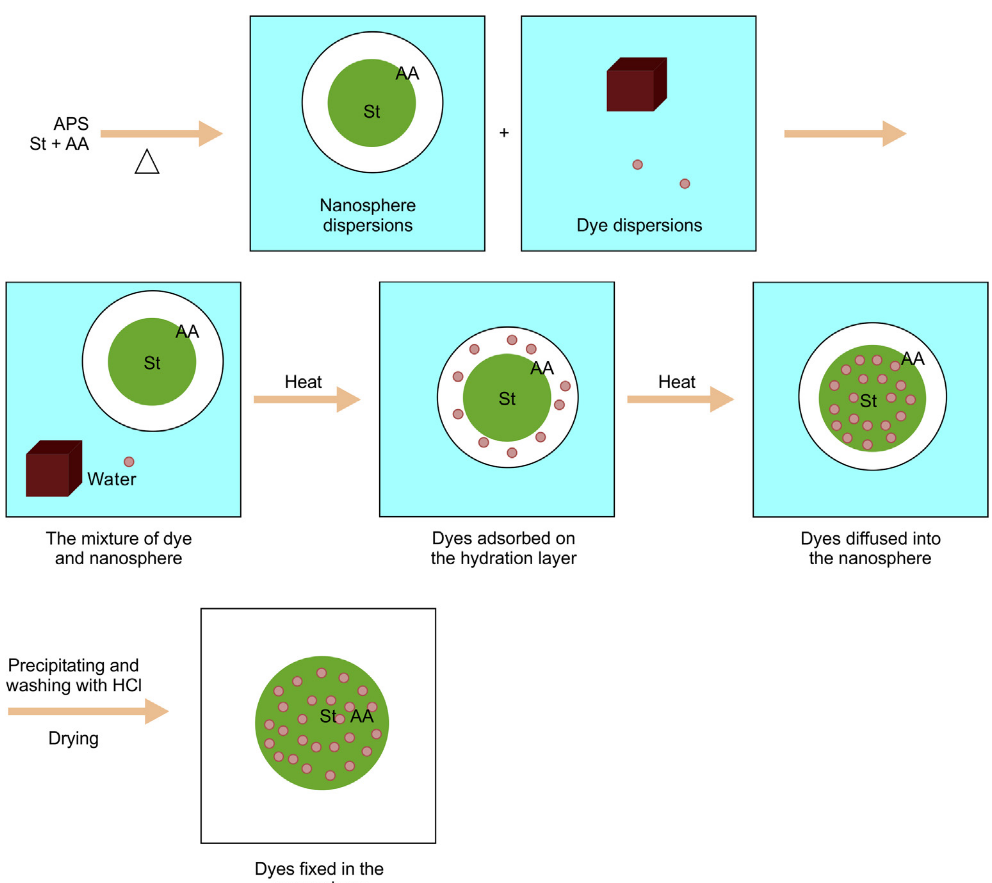

Fig. 2. Preparation of the colored nanospheres.