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

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ARTICLE INFO

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.

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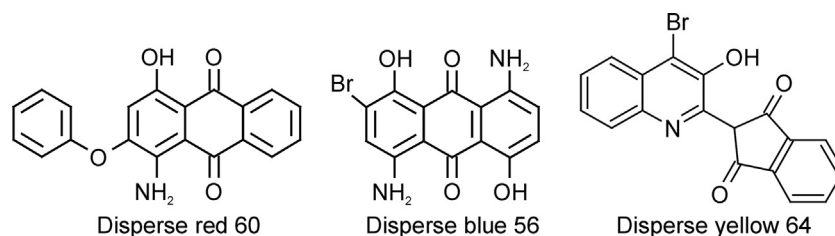
Fig. 1. Molecular structures of the disperse dyes used.

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
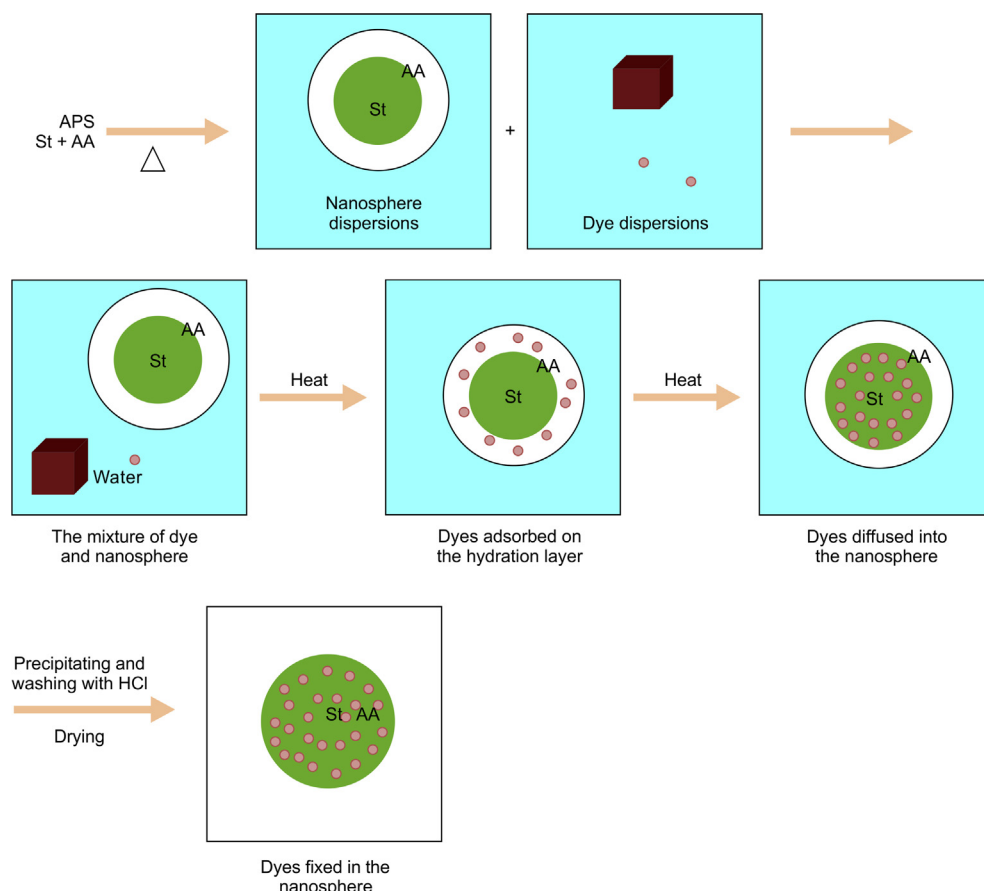

Fig. 2. Preparation of the colored nanospheres.

Yellow E-GL (C. I. disperse Yellow 64), were supplied by Hongda Chemical Industrial Co., Ltd, China, and used as received. The chemical structures of the dyes are shown in Fig. 1. Styrene (St), acrylic acid (AA), ammonium persulfate (APS) and tetrahydrofuran (THF) were all of analytical grade and were purchased from Qingdao Huadong Chemicals and Equipments Co., Ltd, China; these were used as received without further purification. Deionized water was used in all experiments.

2.2. Synthesis of poly (styrene-co-acrylic acid) nanosphere dispersions

An emulsifier-free emulsion polymerization was employed to prepare P(St-co-AA) nanospheres using St and AA as monomers, and APS as the initiator [12,13]. Typically, 0.1 g APS was dissolved in 200 mL H_2O, followed by the dropwise addition of 3.0 g AA with slow stirring. The mixture was transferred to a flask equipped with a Eurostar digital agitator (IKA Lab Technology, China), a reflux condenser, a N_2 tube, and a thermometer. The system was purged with N_2 for 30 min, followed by the dropwise addition of 20 g St over 1.5 h using a constant-pressure funnel. The system was heated to 70 °C and maintained at this temperature for 7 h with stirring at the rate of 400 rpm. After the reaction was complete, the product was filtered using a Buchner funnel to eliminate the larger particles. The solid content of the nanosphere dispersions and the conversion of the monomers were determined using a gravimetric method.

2.3. Preparation of colored P(St-co-AA) nanospheres

A 0.2 g sample of the disperse dye and 10 mL H_2O were added to a beaker, followed by the dropwise addition of 40 mL of the nanosphere dispersion under magnetic stirring. The pH of mixture was adjusted to 4 using 0.1 mol/L HCl. The prepared mixture was then transferred to an SW-12 dyeing machine (Laizhou Electronic Instrument Co., Ltd, China) and treated for 10 min at 50 °C. The system was subsequently heated to 90 °C at a rate of 1 °C per min and maintained at this temperature for 60 min. Subsequently, the colored sample was taken out of the machine and allowed to cool to room temperature.

Colored P(St-co-AA) nanospheres were obtained from the dispersion via a series of steps. First, 10 mL of HCl solution (1.0 mol/L) was added to 50 mL of the colored sample under magnetic stirring, and then, the colored nanospheres were separated by 3 cycles of centrifuging—washing with 0.1 mol/L HCl solution. Finally, the sample was dried at 50 °C, and the nanosphere powder was obtained.

2.4. Observation by transmission electron microscopy (TEM)

The colored nanosphere 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).

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

2.5. Differential scanning calorimetry (DSC) measurements

DSC analysis of the nanospheres was carried out using a Pyris Diamond DSC instrument (Perkin Elmer, USA). The heating and
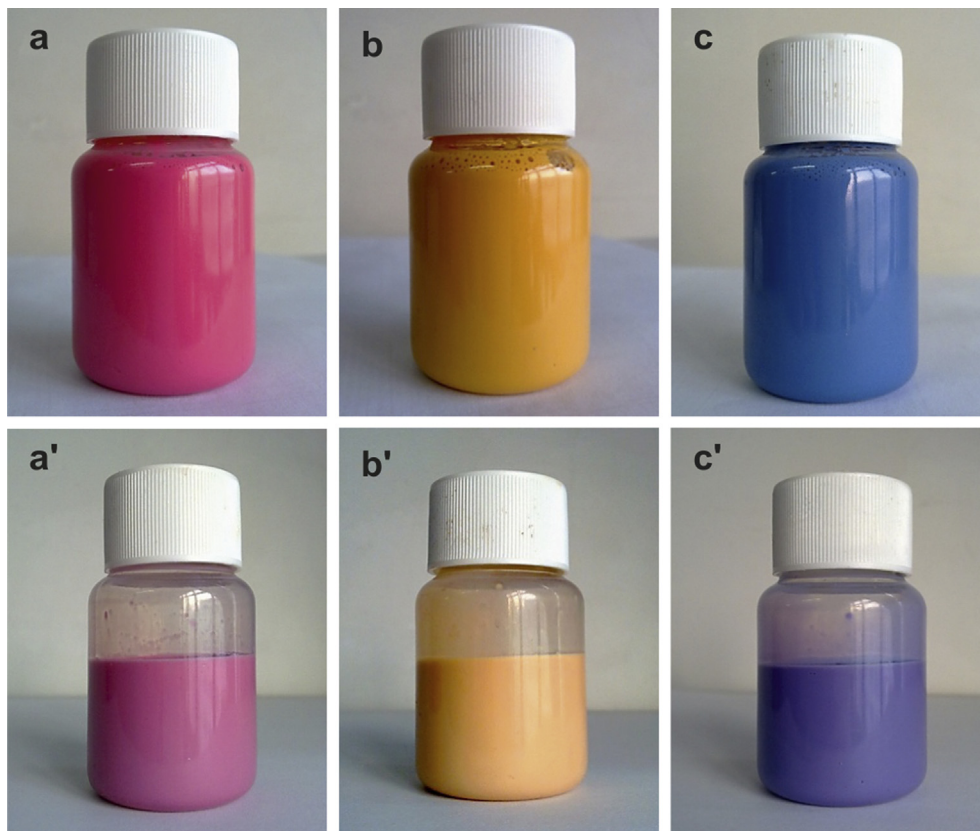

Fig. 3. Photographs of mixtures of 40 mL P(St-co-AA) nanosphere dispersions and 0.2 g disperse dyes: a, b, and c are samples treated at 90 °C for 60 min; a′, b′, and c′ are untreated samples; a and a′ are samples of disperse Red 60, b and b′ are Yellow 64, c and c′ are Blue 56. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. Pure colored P(St-co-AA) nanosphere powders: a is the sample colored by 3.06% disperse Red 60, b is the sample colored by 3.18% disperse Yellow 64, and c is the sample colored by 3.25% disperse Blue 56. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

cooling rates were both 10 °C/min. The temperature scanning range was 50 °C–200 °C.

2.6. Visible absorption spectrum measurements

A known weight of disperse dye was dissolved in THF and the concentration was adjusted to 0.01 mg/mL. The colored nanosphere powder was also dissolved in THF to achieve a dye concentration of approximately 0.1 mg/mL. The visible absorption spectrum of the THF solution was measured using a double-beam UV–vis spectrophotometer (TU-1901, Beijing Purkinje General Instrument Co., Ltd, China).

2.7. Dye contents of colored nanospheres

A known weight of colored nanosphere powder was dissolved in THF. The absorbance of the THF solution was then measured at the maximum absorption wavelength of the dye. The dye content of the colored nanospheres was calculated using Lambert–Beer's law [33].

3. Results and discussion

3.1. Preparation of colored P(St-co-AA) nanospheres

Emulsifier-free emulsion polymerization is known to produce nanospheres with superior purity [18,19,24,25,28]. The outer layer of a nanosphere formed using this methodology for the copolymerization of St and AA is composed of carboxyl groups, with the interior made up of the chain segments of St. The surface carboxyl groups form a hydration layer that provides suspension stability [25]. Owing to the hydrophobic characteristic of the internal St segments, P(St-co-AA) nanospheres interact strongly with disperse dyes, which are also hydrophobic. These dyes have extremely poor solubility in water, forming a finely dispersed state, with particles in the size range of approximately 0.5–1 μm [35]. When a P(St-co-AA) nanosphere dispersion was mixed with a dye dispersion, a new system with two solid–liquid interfaces was formed. One of these was the interface between the dye particle and the dye solution, and the other was that between the nanosphere and the dye solution.

As shown in Fig. 2, increasing the temperature of the mixed system improved the solubility of the dye, resulting in a higher dye concentration in the aqueous solution. At the same time, the increase in temperature enhanced the mobility of the AA chain segments on the nanosphere surface, producing more free volume and promoting interaction between the dye molecules in solution and the nanospheres [35]. Once the dye molecules were in sufficient contact with the nanosphere surface, they formed hydrogen bonds with the carboxyl groups of AA, increasing the amount of dye adsorbed on the outer hydration layer. This then produced a dye concentration gradient between the surface and the interior of the nanosphere. Because of the strong hydrophobic interaction between the disperse dye and the St chain segments, the dye molecules diffused from the nanosphere surface into the interior, which decreased the dye concentration in the aqueous phase [36]. In order to maintain equilibrium, more dye from the suspended dye particles dissolved in the water, until all molecules were absorbed by the nanospheres. At the end of the preparation process, the system was cooled down to room temperature, so that the motion of the P(St-co-AA) chain segments was frozen and the dye molecules were fixed within the nanospheres.

As a carboxylic acid is a very weak organic acid, HCl could suppress the ionization degree of the AA segments, decreasing the thickness of the hydration layer, reducing the negative charge, and destabilizing the P(St-co-AA) nanosphere dispersion. As a result, the nanospheres precipitated out from the dispersion. They were then repeatedly washed with dilute HCl and dried to afford the final nanosphere powder. The obtained material could be re-dissolved in water by adjusting the solution pH to afford a new stable nanosphere dispersion.

3.2. Colors of P(St-co-AA) nanospheres

Fig. 3 shows photographs of the mixtures of the P(St-co-AA) nanospheres and the disperse dyes. The mixtures heat-treated at 90 °C for 60 min (Fig. 3a–c) had a more intense color than did the untreated samples (Fig. 3a′–c′), which indicated that the dye molecules were successfully transferred into the nanospheres. The colors observed in photographs a, b, and c were mainly produced by the colored nanospheres suspended in solution [35], whilst for the untreated mixtures (a′, b′, and c′) the color resulted from the dye particles dispersed in solution.
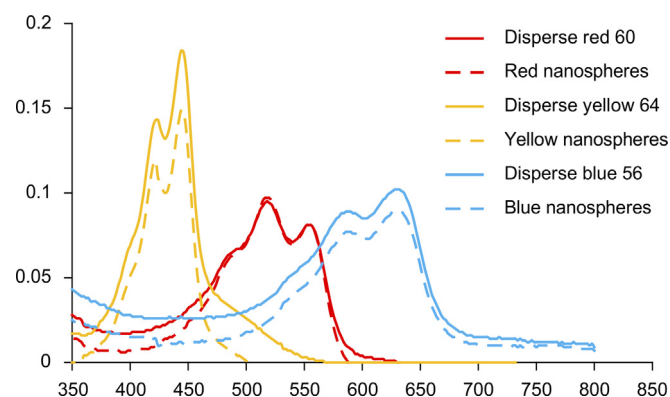

Fig. 5. Visible absorption spectra of the colored nanospheres and the disperse dyes in THF solution, with dye concentrations of approximately 0.01 mg/mL. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
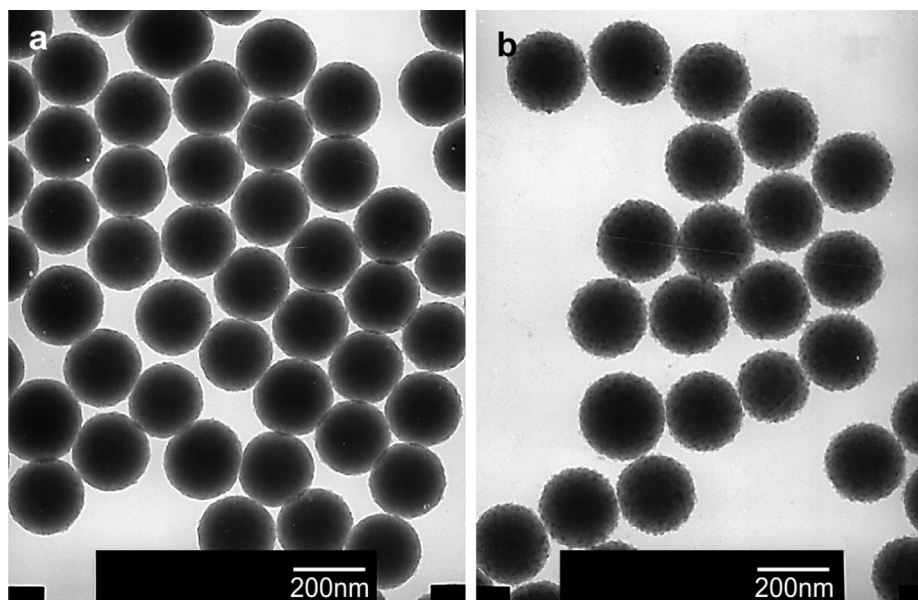
Fig. 6. TEM images of the nanospheres: a, the unmodified P(St-co-AA) nanospheres and b, the nanospheres colored by disperse Red 60 with a dye content of 3.06%.

After purification and drying, colored nanosphere powders were obtained, as shown in Fig. 4. The separated and purified P(St-co-AA) nanospheres colored with the three disperse dyes, Red 60, Yellow 64, and Blue 56, were then dissolved in THF and the visible absorption spectra were measured (Fig. 5). It can be seen that the spectra of the colored nanospheres were very similar to those of the disperse dyes alone [37]. All the spectra showed two absorption peaks, and the λ_{max} values of the colored nanospheres were the same as those of the corresponding disperse dye: 518 nm for disperse Red 60, 444 nm for disperse Yellow 64, and 630 nm for disperse Blue 56.

3.3. Morphology of the colored P(St-co-AA) nanospheres

The morphologies of the purified P(St-co-AA) nanospheres, as visualized by TEM, are shown in Fig. 6. The unmodified P(St-co-AA) nanospheres appear spherical and uniform with an average diameter of 375 nm and a relatively smooth surface. The colored P(St-co-AA) nanospheres have a rough surface and a diameter around 23 nm larger than that of the unmodified P(St-co-AA). The contact between the disperse dye molecules and the nanosphere surface would have disrupted the interactions between the P(St-co-AA) macromolecules and increased their mobility, thus promoting rearrangement of the macromolecular chains to form the salient points that are visible in the TEM images, and increasing the particle size [35].

3.4. Dye contents of the colored P(St-co-AA) nanospheres

Since the colored nanospheres in THF solution had the same λ_{max} values as the corresponding disperse dyes in visible region, the amount of dye fixed on the nanospheres could be calculated by measuring the absorbance of the colored nanospheres in THF solution and employing Lambert–Beer's law [33]. Table 1 shows the obtained results for the dye contents of the colored nanospheres vs. the dye concentrations. It can be seen that with an increase in dye concentration, the amount of dye fixed on the nanospheres increased. At the same dye concentration, the dye contents of the colored nanospheres followed the order blue dye > red dye > yellow dye. This sequence was consistent with the hydrogen-bond formation ability of the dye.

The stronger the ability of the dye to form hydrogen bonds with water and the carboxyl groups of AA, the greater is the amount of dye dissolved in the aqueous phase, adsorbed on the hydration layer and diffused into the nanospheres [35,36].

3.5. Coloration mechanism of the P(St-co-AA) nanospheres

DSC measurement is an effective method for determining the glass transition temperature (T_g) of polymers. The DSC curves of the uncolored and the colored nanosphere powders are shown in Fig. 7. It can be seen that T_g of the P(St-co-AA) nanospheres decreased from 110.69 °C to 107.71 °C, i.e., T_g decreased by 2.98 °C after the coloration. This result indicated that the dye molecules fixed within the nanospheres increased the mobility of the P(St-co-AA) chains by breaking the hydrophobic interactions between the macromolecules.

During the coloration process, increasing the temperature of the mixed system resulted in more dye molecules dissolving in the aqueous phase and more free volume in the nanospheres [35]. The dye molecules in the aqueous phase adsorbed easily onto the nanosphere surface and formed hydrogen bonds with the carboxylic acid groups of AA, which increased the thickness of the nanosphere hydration layer. As a result, the distance between the dye molecules and the hydrophobic segments was shortened. The affinity of the dye molecules for the nanosphere macromolecules was enhanced through increasing π-electron interactions, dispersion forces, and hydrophobic attraction. Therefore, more dye molecules

Table 1
Dye contents of the colored nanospheres at various dye concentrations.[a]

Dye concentration (%)	Dye contents of the nanospheres (%)		
	Red dye	Yellow dye	Blue dye
1	0.83	0.87	0.87
2	1.43	1.55	1.63
3	2.01	2.09	2.29
4	2.51	2.57	2.66
5	3.06	3.18	3.25

[a] The dye concentration and dye content were calculated on basis of the weight of the nanospheres. All samples were treated at 90° for 60 min, purified, and dried.
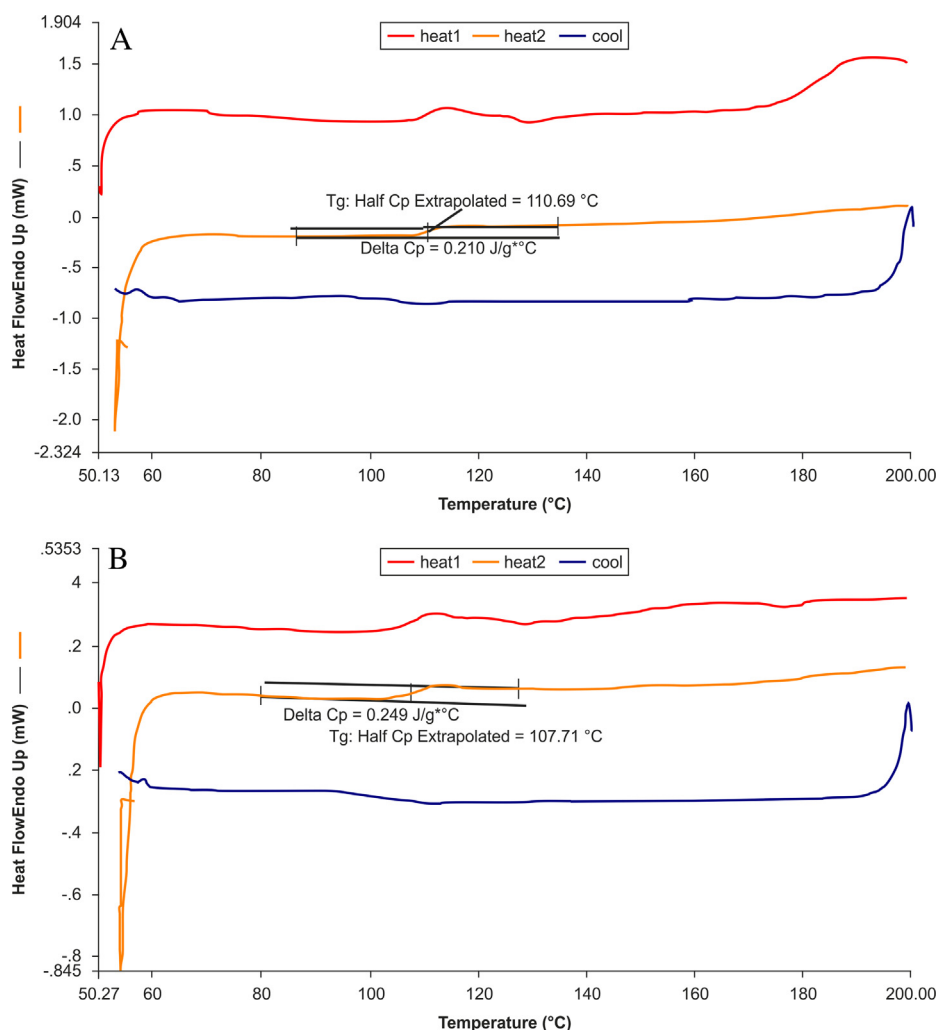
Fig. 7. DSC curves of the purified P(St-co-AA) nanospheres: (a) uncolored, (b) colored by disperse Red 60 with a dye content of 3.06%. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

diffused into the nanospheres, the nanosphere size increased, and T_g of the polymer decreased.

4. Conclusions

Monosized P(St-co-AA) nanosphere dispersions synthesized by an emulsifier-free emulsion polymerization process could be directly colored with commercial dyes by simply mixing the two solutions and heating. The colored nanospheres were easily separated from the mixed dispersions by decreasing the solution pH with HCl. The obtained pure colored nanosphere powders could be re-dispersed in water by controlling the pH. The average particle size of the nanospheres was seen to increase by approximately 23 nm after coloration, and the T_g value decreased by 2.98 °C. The amount of dye fixed on the nanospheres increased with increasing concentration of dye in solution, with different dyes being incorporated in the order disperse Blue 56 > disperse Yellow 64 > disperse Red 60. These results demonstrate the great potential of this methodology for preparing highly uniform, intensely colored nanospheres that have a wide range of applications.

Conflict of interest

The authors do not have any conflict of interest to declare.

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