Supporting Information for

Encapsulated dye/polymer nanoparticles prepared via miniemulsion polymerization for inkjet printing

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Catalogue

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The particle size and polydispersity of the polymer and encapsulated dye/polymer nanoparticles were analyzed using DLS. As shown in Figure S2, as the reaction proceeds, the particle size gradually increases, whereas the PDI first decreases and then increases, before finally stabilizing. It is noteworthy that all of the PDI values were <0.1. The minimum PDI value was obtained at the reaction time of 1 h because, at this time, the polymerization reached a steady state, and the polymer nanoparticles exhibited excellent polydispersity with uniform diameters. During the first 2 h of the reaction, the monomer conversion rate was relatively high (90%), so the particles grew faster. During the last 5 h, the degree of polymerization tended to be stable, so the particles enlarged slowly and remained almost unchanged. Although PDI got almost invariable at 2 hours, the particle size was still increasing, indicating that the polymerization was not completely finished. At 7 hours, the particle size and PDI remained unchanged. Therefore, a total of 7 h were required to complete the reaction.

Figure S1 Chemical structure of the different dyes
Figure S2 Dependence of the particle size and PDI of St-BA copolymer nanoparticles on reaction time.

The surfactant SDS significantly influences the miniemulsion polymerization process. As shown in Figure S3, with increasing SDS amount from 0.1 to 0.5 g, the particle size of the encapsulated dye/polymer nanoparticles decreased from 150 to 55 nm (Figure S3A), PDI decreased and then increased (Figure S3B), and both the zeta potential and surface tension decreased (Figure S3C and S3D). According to the droplet nucleation mechanism of miniemulsion polymerization, the amount of surfactant should not exceed its critical micelle concentration, otherwise either micellar nucleation or homogeneous nucleation will occur resulting in poor polydispersity. SDS is an anionic surfactant. If the amount of SDS is too high, the surface potential is low and the electronegativity is high, which will affect the printing process. Therefore, the amount of SDS should be lower than 0.3 g. In order to achieve smaller size and PDI, and the appropriate surface tension, in this study, 0.2 g SDS was chosen as the most appropriate amount for droplet nucleation and inkjet printing.
Figure S3 Effect of SDS on the diameter (A), PDI (B), zeta potential (C), and surface tension (D) of encapsulated Solvent Yellow 163 dye/polymer nanoparticles.

Miniemulsion polymerization is different from conventional emulsion polymerization because it employs a miniemulsification process achieved via ultrasonic or high-shear treatment. The effect of the ultrasound power was investigated herein. As shown in Figure S4, the particle size of polymers decreased but PDI decreased and then increased with increasing sonication power. PDI showed an opposite tendency when the sonication power reached 90%; this phenomenon can be explained by Ostwald ripening and Brownian motion: small droplets will accumulate to reduce the surface area and energy of the droplets.
**Figure S4** Effect of sonication power on particle diameter and PDI.

Styrene and butyl acrylate form a block polymer via addition polymerization ($n \neq m$). The structural formula of the copolymer was listed in Figure S5. Degree of polymerization of the copolymer is low owing to the droplet nucleation mechanism of miniemulsion polymerization.

**Figure S5** Structural formula of the copolymer

Tg curves of St-BA copolymer latex with a monomer ratio of 8/2 (St/BA) were shown in Figure S6 (A) and (B), the Tg value of St-BA copolymer latex was about 68 °C. However, the Tg value of encapsulated Solvent Yellow 163 with St-BA copolymer is 52.71 °C (St/BA=8/2). This result can be explained that dye molecule has an effect on thermal properties of copolymer in spite of same monomer ratio. From Figure S6 (C), (D), (E) and (F), we can draw a conclusion that Tg value decreases with butyl acrylate increases.
Figure S6 Tg curves of St-BA copolymer latex with a monomer ratio of 8/2 (St/BA) miniemulsion polymerization (A) ordinary emulsion polymerization (B) and encapsulated dye/polymer nanoparticle (Solvent Yellow 163) with different monomer ratio St/BA=9/1(C) St/BA=8/2(D) St/BA=7/3 (E) St/BA=6/4(F)
TEM pictures of St-BA copolymer latex (80nm) was depicted in Figure S7. The morphology of pure copolymer is spherical with regular shape.

![Figure S7](image)

**Figure S7** TEM pictures of St-BA copolymer latex with a monomer ratio of 8/2 (St/BA)

Inkjet printing images on paper with encapsulated dye/polymer nanoparticles are shown in Figure S8. Moisturizer and surfactant were added into the ink dispersion to adjust the ink parameters to those required for use in the inkjet printer. The colors on paper were lighter than on cotton fabrics because the cotton fabrics were completely soaked with the inks, whereas the inks were sprayed onto paper via the nozzles of the inkjet printer.

![Figure S8](image)

**Figure S8** Inkjet printing images on paper with Disperse Red 60 (A), Solvent Blue 36 (B) and Solvent Yellow 43 (C).