

Controlled Preparation of Nanocolorants via a Modified Miniemulsion Polymerization Process

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ABSTRACT: Nanocolorants were successfully prepared via a modified miniemulsion polymerization process into which styrene, a polar monomer, crosslinkers, a highly hydrophobic solvent, dyes, and so forth were introduced. The obtained nanocolorants were nanocomposite entities in which a fraction of dye molecules attached to the cross-linked macromolecular chains and more dye molecules formed clustering because of the phase separation between the dye and polymer during the polymerization process and were further embedded in the interior of the cross-linked polymer because of the high hydrophobicity of the

dyes. The effects of the polar monomers, the amounts of the dyes dissolved in styrene, and the polymer crosslinking, as well as the effects of the water-soluble and oil-soluble initiator, the amount of the surfactant, and the ultrasonic homogenization time, on the preserving fastness of the dyes in the polymeric matrix and the morphology and particle size distribution of the nanocolorants were studied. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3036–3041, 2007

Key words: dispersions; dyes/pigments; latices; nanoheterogeneity; phase separation

INTRODUCTION

Traditional water-soluble dyestuffs and ultrafine organic pigment particles have been largely applied to color ink-jet inks,¹ red–green–blue color layers² used in color filters of liquid-crystal displays, and dry and liquid color toners for electrophotography^{3,4} for many years. However, because of the respective inherent disadvantages of dyestuffs and pigments, they cannot meet the need for greater performance and lower cost for an increasing number of applications. Thus, nanocolorants have been developed as a new class of colorants that can achieve the advantages of both dyestuffs and organic pigments.^{5–7} In architecture, nanocolorants are a class of generally recombined nanocomposite dyes that act as essential ingredients and suitable matrix polymers by noncovalent interactions, and their performance targets are to integrate the excellent chromatic properties and good processibility of dyestuffs and the superior durability (e.g., high-temperature stability and light fastness) of organic pigments.

Two early approaches were briefly reported to prepare nanocolorants. Boehm and coworkers^{5,6} prepared colorants applied for the coloration of plastics, cosmetics, and so forth by miniemulsion polymerization, whereas Barashkov and Liu⁷ packaged a water-soluble, fluorescent dye into submicrometer polymer

particles by conventional emulsion polymerization; this was called dye-packaging technology. In recent years, quite a few nanohybrid particles have been prepared by miniemulsion polymerization because of its attractive advantages.^{8–13} For a highly stable miniemulsion, minidroplet nucleation is predominant, so the minidroplets containing the dispersed or dissolved essential ingredients for nanohybrid formation can be regarded as independent nanoreactors. Therefore, a situation very close to a 1 : 1 copying procedure from nanodroplets to nanoparticles will be generated, and the adjustment and control of the size and size distribution of the nanoparticles are conveniently realized by the adjustment of the amount and type of the surfactant, the parameters of ultrasonication or high-pressure homogenization, and the volume fraction of the disperse phase. Recently, Takasu et al.^{14,15} prepared nanosized, colored latices by miniemulsion polymerization, and colored latices with polyurea shells were prepared by the introduction of interfacial polycondensation to the miniemulsion polymerization process.¹⁶ Winnik and coworkers^{17,18} obtained fluorescent polymer particles containing covalently bound fluorescent dye comonomers by miniemulsion polymerization. However, to the best of our knowledge, their research was almost entirely focused on how to improve the migration fastness of a dye in a polymeric matrix, and very little work was systematically involved in the preserving fastness of dyes and the architecture and morphology control of nanocomposite particles by a one-step miniemulsion polymerization. In this

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article, we report a controlled preparation of nanocolorants via a modified miniemulsion polymerization process. Our method involves the miniemulsion polymerization of styrene in the presence of polar methyl methacrylate (MMA), crosslinkers, highly hydrophobic solvent dyes (also acting as effective costabilizers),¹⁹ polystyrene (PS) of an appropriate molecular weight (acting as a nucleating enhancer as well as a hydrophobe),^{20,21} a surfactant, oleic acid (OA), and so forth. The effects of the polar monomers, amounts of the dyes dissolved in styrene, and polymer crosslinking, as well as the effects of the water-soluble and oil-soluble initiator, amount of the surfactant, and ultrasonic homogenization time, on the preserving fastness of dyes in polymeric matrices and the morphology and particle size distribution of nanocolorants were studied.

EXPERIMENTAL

Materials

The dyes were anthraquinone-based red, yellow, blue, or green solvent dyes (technical-grade) and were used as received from Aolunda Co., Ltd. (Wuxi City, China); their molecular structures are shown in Figure 1. Styrene and MMA (Shanghai Chemistry Reagent Co., Shanghai, China) were purified upon distillation under reduced pressure and kept refrigerated until use. Divinylbenzene (DVB) was a technical-grade material containing 70 wt % divinyl monomer, with the remaining 30 wt % being styrene and ethylstyrene; glycol dimethacrylate (GDMA) was analytical-grade. Sodium dodecyl sulfate (SDS), sodium bicarbonate (NaHCO₃), OA, and potassium persulfate (KPS) were analytical-grade and were purchased from Shanghai Chemistry Reagent. PS (weight-average molecular weight = 50,000; Shanghai Chemistry Reagent) was the immobile liquid of gas chromatography, and the light stabilizer (HALS-13) was obtained from Clariant Corp. (Shanghai, China).

Preparation of the nanocolorants

The nanocolorants were prepared according to the following procedure with the typical recipes given in Table I. A deionized (DI) water solution of SDS and NaHCO₃ was added to a styrene solution com-

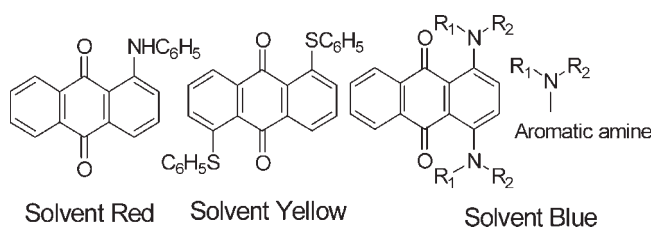


Figure 1 Molecular structures of the dyes.

TABLE I
Typical Recipes Used To Prepare Various Miniemulsions

Ingredient	Amount (g)	Concentration
Styrene	10	70–77 wt % ^a
MMA	0.5–2.0	4–15 wt % ^a
DVB and GDMA	1.0	8–9 wt % ^a
Dyes	0.7–2.0	5–14 wt % ^a
SDS	0.144–0.432	10–40 mM ^b
DI water	50	77–78 wt % ^c
KPS	0.1	0.8 wt % ^d

^a Based on the solid content.

^b Based on the aqueous phase.

^c Based on the total recipe.

^d Based on the monomers.

prising a polar monomer, crosslinkers, completely dissolved dyes, predissolved PS, a light stabilizer, and OA, and then the solution was quickly mechanically stirred at room temperature for 20 min. The resultant macroemulsion was miniemulsified with a JYD-650 ultrasonic homogenizer (ZhiSun Instrument Co., Shanghai, China) operated at 400–500 W for a set time under ice cooling; finally, a miniemulsion was obtained. The miniemulsion was transferred into a flask equipped with an agitator, a thermometer, a reflux condenser, and a nitrogen tube. The system was heated to 60°C, purged with a nitrogen flow for 10 min, and simultaneously stirred by a paddle stirrer at 200 rpm, and then the polyreaction was initiated by the injection of a water solution of KPS; the reaction was finally continued at 65°C for 4 h. The polymerization conversion was determined by gas chromatography (GC9790, Fuli Analytical Instrument Co., Wenling City, China) until no monomer could be detected.

Analysis and characterization

Samples dispersed in DI water were transferred to copper grids and left to dry for transmission electron microscopy (TEM; JEM-2010, JEOL, Japan) and field-emission TEM (JEM-2100F, JEOL). Samples appropriately diluted in DI water, spread onto silex wafer substrates, left to dry, and sputtered with a thin layer of Au were used for field-emission scanning electron microscopy (SEM; SIRION 200, FEI). Samples properly diluted in high-purity water were studied with photon correlation spectroscopy (PCS; Zetasizer 3000HSA, Malvern Instruments, Ltd., UK) to obtain the particle size and size distribution. The ultraviolet–visible (UV–vis) absorption was studied with a UV–vis spectrometer (Lambda-20, PerkinElmer). The ζ potential was measured with a Malvern Instruments Zetasizer 3000HSA, and the samples were prepared by the same procedure used for PCS. Before the test, the apparatus had to be calibrated with a standard sample, which was a ζ -poten-

tial transfer standard (-50 ± 5 mV) obtained from Malvern Instruments.

Ultracentrifuge sedimentation velocity run (S-run)

Aqueous dispersions (5 mL) of the nanocolorants were taken and diluted with 25 mL of absolute ethyl alcohol, and then 25 mL was put in the tube of an ultracentrifuge (Optima L-80XP, Beckman-Coulter Co.). The S-run was carried out for 30 min at 50,000 rpm at 25°C, and then the supernatant was extracted for UV-vis absorption analysis. The remains were diluted five times with absolute ethyl alcohol to implement the UV-vis analysis.

RESULTS

Typical morphology of the nanocolorants

According to the architecture of the nanocolorants, the dyes should be completely incorporated into the polymeric matrix. Otherwise, some of the unincorporated dye will flocculate and sedimentate, and the other part will be adsorbed onto the surface of the polymer nanoparticle because of the high water insolubility of the dyes. To add a suitable diluent (a nonsolvent for the polymer and dissoluble for the dyes) to a dilute nanocolorant aqueous dispersion, the unincorporated dyes will be dissolved in the diluent and be un-sedimentable after an S-run. Therefore, according to the S-run described in the Experimental section and subsequent UV-vis absorption analysis, we can determine the existent state of the dyes in the polymeric matrix by observing the absorption spectrum difference before and after an S-run. Figure 2 shows that the absorption peaks of the supernatant are equivalent to zero after an S-run,

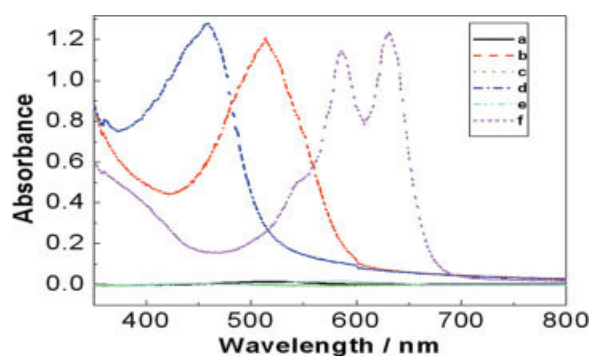


Figure 2 UV-vis absorption spectra of the nanocolorant dispersions before and after an S-run: (b) red, (d) yellow, and (f) blue samples before an S-run and (a) red, (c) yellow, and (e) blue samples after an S-run. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

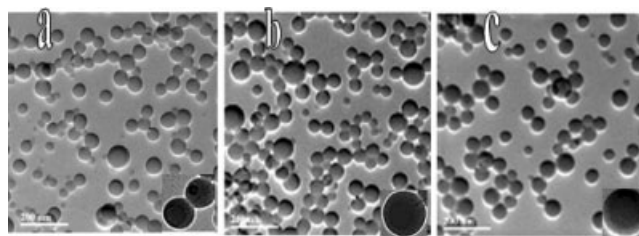


Figure 3 TEM images of the nanocolorants: (a) the red nanocolorant, (b) the yellow nanocolorant, and (c) the blue nanocolorant (scale bar = 200 nm). The inserts show enlarged images from field-emission TEM. Dye/polymer ratios of 0.9 g/12.5 g, 1.2 g/12.5 g, and 1.5 g/12.5 g represent the loadings of the red, yellow, and blue dyes, respectively.

and so it is proved that the dyes are completely incorporated into the polymeric matrix.

Typical TEM and SEM images, shown in Figures 3 and 4, respectively, demonstrate that the morphology of the nanocolorants is a homogeneous and spherical nanoparticle with a uniform surface. Under the condition of a sufficient dye loading, phase separation between the polymer and dye will be generated during the polymerization process. By field-emission TEM, we can see that the separated dye phase, that is, the darker domain, is embedded in the crosslinked polymeric matrix.

Size distribution and basic characteristics of the nanocolorants

From PCS observations, we could exactly obtain the particle size distribution of the nanocolorants. As shown in Table II, the average particle size is less than 100 nm, and the polydispersity index (PDI) indicates that the size distributions of the nanocolorants are straightly unimodal. Each of the obtained nanocolorant aqueous dispersions has a high ζ potential, excellent storage stability, high surface tension, and very low rotary viscosity, which are very desirable for aqueous ink-jet ink applications.

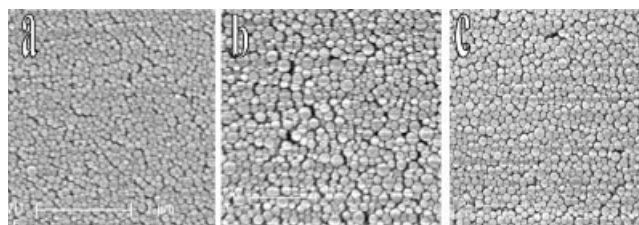


Figure 4 SEM images of the nanocolorants: (a) the red nanocolorant, (b) the yellow nanocolorant, and (c) the blue nanocolorant. Dye/polymer ratios of 0.9 g/12.5 g, 1.2 g/12.5 g, and 1.5 g/12.5 g represent the loadings of the red, yellow, and blue dyes, respectively.

TABLE II
Typical Characteristics of the Nanocolorants and Their Aqueous Dispersions with Solid Contents Greater Than 20 wt %

Nanocolorant sample	Particle size (nm)	PDI	ζ potential (mV)	Storage stability	Surface tension at 30°C (mN/m)	Rotary viscosity at 30°C (cp)
Red	69.8	0.0915	-55.1	E	54.1	1.1
Yellow	85.8	0.0513	-53.9	E	54.3	1.0
Blue	89.2	0.0275	-57.8	E	60.2	1.2

Dye/polymer ratios of 0.9 g/12.5 g, 1.2 g/12.5 g, and 1.5 g/12.5 g represent the loadings of the red, yellow, and blue dyes, respectively, and miniemulsions with 20 mM SDS and 15-min ultrasonic times were used. The storage stability was evaluated as E; that is, the samples dispersed very well without agglomeration for 60 days at 30°C.

DISCUSSION

Effects of the polar monomers

To acquire a satisfying preserving fastness of a dye in a polymeric matrix as well as a modified surface polarity of nanoparticles, which not only can reinforce the nanoparticle–water hydration to enhance the stability of a nanocolorant aqueous dispersion but also can facilitate the integration of nanocolorants with applied media. The proper amounts of polar and hydrophilic MMA and GDMA, also acting as crosslinkers, are introduced into nonpolar, water-insoluble styrene. In addition, a small amount of OA can be used as a cosurfactant and can promote the stability of minidroplets; the unsaturated bond of the OA molecule may react with polar and hydrophilic monomers concentrated in the oil/water interface region during the polymerization process.

The difference in the morphologies of nanocolorants with and without polar monomers can be observed in the TEM images in Figure 5; that is, the surface of the nanoparticles without polar monomers is not as even as that of the former. For the sample with polar monomers, because of the incomplete surfactant molecule coverage for minidroplets,²¹ the polar monomers with higher hydrophilicity tend to concentrate in the oil/water interface region, whereas the more highly hydrophobic dyes tend to be impelled into the inner region of minidroplets to further lower the interfacial energy. Along with the ongoing polymerization, the polar polymer layer becomes mainly located at the exterior of nanoparticles, whereas dyes become embedded in the interior of nanoparticles. As a result, after polymerization by the introduction of polar and hydrophilic MMA and GDMA, the nanoparticles are basically packaged by the outer polar polymer shell for inhibiting dye migration. A similar phenomenon has been observed in PS/poly(methyl methacrylate) (PMMA) composite particles.^{22,23} PS, which is more hydrophobic than PMMA, shows a tendency to locate in the interior of core/shell nanospheres in an oil/water emulsion system fed simultaneously with the two monomers. With respect to the uneven surface of a nanocolorant without polar monomers, we think that a fraction of

the dye is expelled onto the exterior of the nanoparticles and absorbed onto the surface of the latex particle because of the competitive placement between the hydrophobic dye and hydrophobic polymer during the polymerization process, which induces the unordered layout of the morphology of the nanoparticles.

However, the amount of MMA also affects the particle size distribution of nanocolorants. We carried out experiments with 0, 0.5, 1.0, 1.5, or 2.0 g of MMA added (based on 10 g of styrene and 0.9 g of solvent red dye), and the corresponding PDIs were 0.0395, 0.0486, 0.0651, 0.0915, and 0.1317. The particle size distribution of the nanocolorants widens along with an increasing amount of MMA. There are likely two causes, that is, the higher solubility of MMA in water and the weaker solubility of the dye in MMA. An increasing amount of MMA will tend to separate from styrene and self-form osmotically instable droplets only containing a small amount of the dye, and more MMA in the miniemulsion augments the probability of homogeneous nucleation in the aqueous phase. Therefore, to ensure an appropriate polar polymeric layer, the feed amount of MMA should be controlled.

Effects of the amounts of the dyes dissolved in styrene

The amount of the hydrophobic dye dissolved in styrene plays an important role in the phase separation between the polymer and dye during the polymerization process. For a small dye loading, the intermolecular interaction of the dye is weak because

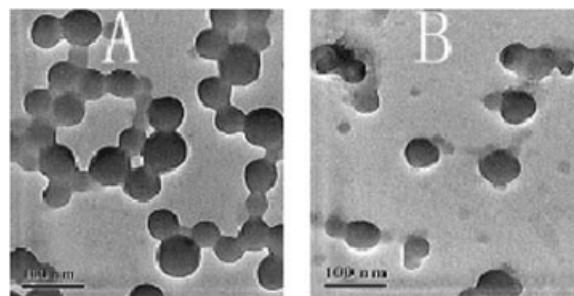


Figure 5 TEM images of the nanocolorants (A) with and (B) without polar monomers.

of the relatively large intermolecular distance, and the rate of polymerization of monomers is thought to be higher than the clustering rate of dye molecules. Thus, it is difficult to obtain complete phase separation, but the dye molecules basically attach to the macromolecular chains. Along with an increasing feed amount of the dye, the enhanced intermolecular interaction of the dye molecules and reinforced hydrophobic action of the dye promote phase separation when monomers originally acting as solvents turn into polymers. Consequently, besides a fraction of the dye attached to the macromolecular chain, more dye forms a separated dye phase and tends to be embedded in the polymeric interior.

In addition, the amount of the dye dissolved in styrene also influences the stability of the polyreaction and the preserving fastness of the dye in a polymeric matrix. If the feed amount of the dye is too small, the suppressed Ostwald ripening²¹ from the hydrophobic dye will not likely be enough to generate a highly stable miniemulsion and also will lead to inadequate color depth for products. However, if the dye overloads, when the monomer droplets turn into polymer particles with a smaller volume, the excessive dye will likely be expelled from the polymeric layer by phase separation and form an agglomerate to settle down. Moreover, overloaded dye makes a thinner polymer layer and weakens the packaging ability of the polymer; thus, the migration of the dye incorporated into the polymer will be accelerated.

Effect of the polymer crosslinking

Nanocolorants obtain a protective shell for inhibiting dye migration in the presence of polar monomers, but to further enhance the preserving fastness of a dye in a polymeric matrix, moderate crosslinking of the polymer is indispensable. Polymer crosslinking, especially derived from polar GDMA between MMA concentrated in the oil/water interface region of minidroplets, leads to a more compact and rigid polymeric exterior and greatly reduces the free volume of the polymer; accordingly, the dye molecular migration from the polymeric matrix is sharply restrained. Our experiments have shown that the crosslinked nanocolorants possess excellent storage stability after settling for 60 days at 30°C, whereas the uncrosslinked color latex dispersions yield some agglomeration under the same conditions. Furthermore, crosslinking will improve the high-temperature stability of the matrix polymer and thus will result in superior heat durability for the obtained nanocolorants. However, because of the tendency toward self-polymerization, which will lead to inhomogeneity of the polymeric matrix, the total crosslinker content should be limited to 10 wt % with respect to the monomers.

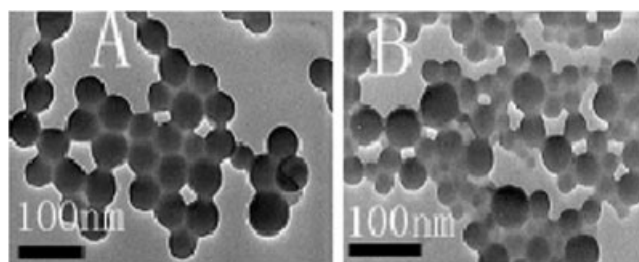


Figure 6 TEM images of nanocolorants initiated with (A) KPS and (B) AIBN.

Effects of the water-soluble and oil-soluble initiators

We expect that nanoparticle formation will be faster with an oil-soluble initiator [2,2'-azobisisobutyronitrile (AIBN)] because the initiator is predissolved in the monomers and the radicals are supposed to be directly generated in the minidroplets to initiate polymerization. However, for the same miniemulsion polymerization at 65°C for 4 h, the conversion of the polymerization initiated by AIBN was approximately 65–85%, as determined by gas chromatography, whereas for the polymerization initiated by an equal amount of KPS, no monomer could be detected. As shown in Figure 6, a better morphology of the nanocolorants was also not expected to be obtained by AIBN initiation, but the morphology is more heterogeneous. This is identical to Capek's²⁴ explanation: even with an oil-soluble initiator dissolved in droplets, the nucleation is still dependent on the entry of radicals from the aqueous phase.²⁴ We also speculate that AIBN primary radicals located in a cage of minidroplets will be transformed into stable molecules by a coupled reaction because they are too late to diffuse toward the aqueous phase from the cage. Therefore, to initiate a miniemulsion system containing a high concentration of hydrophobic dyes, a water-soluble initiator (KPS) is more suitable than an oil-soluble initiator (AIBN).

Effects of the amount of the surfactant and ultrasonic homogenization time

The nanocolorant particle size can be varied over a wide range by changes in the amount of the surfactant (SDS). As shown in Table III, with an increasing amount of SDS, the particle size decreases but the PDI first decreases and then rises. The change in the size of the nanoparticles reflects the variation of the minidroplets because the nanoparticles almost derive from the minidroplets by a close to 1 : 1 copying procedure, and the smaller minidroplets with a larger total interfacial area must be covered by more surfactant molecules. However, the amount of SDS should be limited under the concentration that yields free micelles, which likely lead to micellar nucleation

TABLE III
Effects of the Surfactant Concentration and Ultrasonication
Time on the Particle Size and PDI

SDS (mM) ^a	Particle size (nm)	PDI	Ultrasonic time (min) ^b	Particle size (nm)	PDI
10	179.3	0.0663	5	115.4	0.0936
20	89.2	0.0275	10	97.8	0.0665
30	83.3	0.0376	15	89.2	0.0275
40	79.1	0.0789	20	90.1	0.0554

The results are based on a blue dye/polymer ratio of 1.5 g/12.5 g.

^a With an ultrasonic time of 15 min.

^b With 20 mM SDS.

during the polymerization. The variation of PDI reflects that the nucleation in the polymerization process tends to become more complicated when the SDS concentration exceeds 40 mM with respect to the aqueous phase. Both the particle size and PDI first decrease and then rise with an increasing ultrasonic homogenization time. This is similar to a typical miniemulsion polymerization; that is, the polydispersity of a droplet decreases with constant fusion and fission processes, and then the miniemulsion reaches a steady state,²¹ but the excessive, intense shearing unfavorably makes surfactant molecules desorb from minidroplets, and this lowers the stability of the miniemulsion. In general, employing 20–30 mM SDS and a 10–15-min ultrasonic homogenization time will produce higher quality nanocolorants.

CONCLUSIONS

Red, yellow (or green), and blue nanocolorants with a monodispersive particle size and controlled morphology were successfully prepared via a modified miniemulsion polymerization process. The polar monomers greatly affected the morphology of the nanocolorants, which impelled the highly hydrophobic dyes into the interior of the polymeric matrix during the polymerization process, but the feed amount of the polar monomers should be controlled. The amounts of the hydrophobic dyes dissolved in styrene influenced the phase-separation process and the morphology of the nanocolorants: an underload of dyes did not induce phase separation, whereas an overload resulted in weaker preserving fastness of the dyes in the polymeric matrix. Moderate crosslinking of the polymer highly contributed to the enhancement of the preserving fastness of the dyes in the polymeric matrix and the heat durability of the matrix polymer. In addition, the water-soluble initiator possessed more advantages than the oil-soluble initiator for initiating this miniemulsion system, and the size and size distribution of the nanocolorants could be controlled by the adjustment of the amount of the surfactant and the parameters of homogenization.

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