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ORIGINAL PAPER

Synthesis of nanocolorants with crosslinked shell by miniemulsion polymerization stabilized by waterborne polyurethane

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Abstract Nanocolorants were prepared by miniemulsion polymerization, in which waterborne polyurethane was used as surfactant for the first time. Transmission electron microscopy (TEM), atomic force microscopy (AFM), and dynamic light scattering (DLS) were utilized to confirm the particle diameters and particle size distributions (PSD). The results indicated that nanocolorants with relatively small particle size diameters and narrow particle size distributions could be easily prepared by this method. Simultaneously, the particle size could be controlled by adjusting the concentration of waterborne polyurethane surfactant (WPU), and the obtained nanocolorants exhibited high stability against electrolyte, lightness, and strong color depth owing to the nanoscale effects of the nanocolorant particles. Furthermore, the prepared nanocolorants achieved superior migration fastness and good thermal stability.

Keywords Miniemulsion polymerization · Nanocolorants · Waterborne polyurethane

Introduction

Nanocolorants have many potential applications fields such as aqueous ink-jet inks, electrophotographic toners and dye for polymers, [1–3]. Several techniques have

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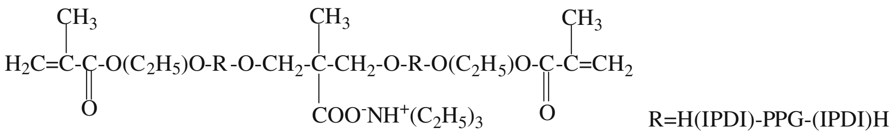
been devised for the synthesis of nanocolorants, such as conventional emulsion polymerization and miniemulsion polymerization [4–6]. Miniemulsion polymerization is a versatile and efficient technique for the formation of nanocolorants. During miniemulsion polymerization, micro-droplets containing monomer and dye are dispersed in continuous aqueous phase using a suitable surfactant under high shear. The particle shell is then formed by polycondensation because the growing polymer chains become immiscible and the new phase is separated from the dye phase [7]. The particle nucleation mainly occurs within the droplets that have typical diameters between 50 and 500 nm [8]. To prevent dye molecules from migrating into aqueous phase, some improved works have paid on polyurea shell in miniemulsion polymerization [4]. Polyurea shells were formed by interfacial polymerization first, in which diisocyanates were used as hydrophobic monomers and diamines were employed as hydrophilic monomers, and cores mainly composed of dye and polystyrene were formed by polymerization of styrene inside the miniemulsion globules afterward. However, properties of the nanocolorants can be manipulated by type and amount of surfactant, intensity and uniformity of energy input, and polarity of the monomer. Surfactants are required to facilitate the formation, prevent the coalescence of the liquid droplets, and enhance the stability of the latex particles later [9]. The conventional surfactants that have low molecular weight, such as sodium lauryl sulfate, often give bad effects on properties of the final polymer latex. Polymeric surfactants provide some unique advantages in miniemulsion polymerization, such as low foaming, and good chemical and mechanical stability of the latex [9–11]. Polymeric surfactants can also increase the latex stability against electrolytes acting as steric stabilizers and as emulsifiers simultaneously in miniemulsion polymerizations. Moreover, polymeric surfactant could undergo chain scission and react with other monomers during miniemulsion polymerization.

In this article, isocynate-glycol polyurethane (WPU) with the designed structural formula as shown in Fig. 1 was employed as polymeric surfactant to prepare nanocolorants by the method of miniemulsion polymerization. Dynamic light scattering (DLS) was utilized to assess the effect of surfactant concentration on the particle size and particle size distribution of the final nanocolorants. Transmission electron microscopy (TEM) and atomic force microscopy (AFM) were utilized to gain insight onto the effect of the surfactant on the size and morphology of the resulting nanoparticles. UV–vis spectrometer was employed to assess the effect of WPU' concentration on the migration fastness of dyes in the particle. Thermogravimetric analysis was utilized to investigate the thermal stability of the nanocolorants stabilized.



$$H_2C{=}\overset{\overset{\large CH_3}{|}}{C}-\underset{\underset{\large O}{\|}}{C}-O(C_2H_5)O-R-O-CH_2-\underset{\underset{\large COO^-NH^+(C_2H_5)_3}{|}}{\overset{\overset{\large CH_3}{|}}{C}}-CH_2-O-R-O(C_2H_5)O-\underset{\underset{\large O}{\|}}{C}-\overset{\overset{\large CH_3}{|}}{C}{=}CH_2$$

R=H(IPDI)-PPG-(IPDI)H

Fig. 1 Designed structure of waterborne polyurethane surfactant

Experimental

Materials

Anthraquinone-based blue obtained from Aolunda Co. Ltd was used as received, and its molecular structure is shown in Fig. 2. Methyl methacrylate (MMA), 2,2-dimethylol propionic acid (DMPA), polypropylene glycol (PPG, Mn = 1,000), and N-methyl pyrrolidone (NMP) were purchased from Shanghai Gaoqiao Petrochemical Co., and purified by distillation under reduced pressure and kept refrigerated until use. Other chemicals including isophorone diisocyanate (IPDI) and triethylamine (TEA) from Shanghai Chemical Reagents Co., sodium bicarbonate ($NaHCO_3$), 2-hydroxyethyl methacrylate (HEMA), dibutyltin dilaurate (DBTL), sodiumdodecylsulfonate (SDS), and potassium persulfate (KPS) from Shanghai Changjiang Chemical Co., and hexadecane (HD) from Aldrich were utilized as received.

Synthesis of waterborne polyurethane surfactant (WPU)

The polyaddition reaction between IPDI and PPG was conducted in a 500 mL round bottom, four-necked flask, equipped with a mechanical stirrer, a nitrogen gas inlet and a condenser. 35.4 g PPG, 0.03 g DBTL, and 14.2 g IPDI were charged into the flask and heated to 80° for 2 h. And then 1.905 g DMPA dissolved in NMP solvent (0.127 g/mL) was added to the above mixture. When the NCO group content reached the calculated value that NCO groups consumed all hydroxyl groups, polyurethane was then endcapped with 3.7 g HEMA by the secondary polyaddition reaction and the sample was taken at given interval of time. Finally, 1.36 g TEA was added to neutralize the product to become aqueous soluble. IR spectra of the samples were measured by KBr method with Magna-IR550 (Niclet Japan Co.).

The IR spectra of the samples were illustrated in Fig. 3. The characteristic IR absorption band at 3,300 cm^{-1} demonstrates the NH stretching vibration of carbamate, and its bend band is observed at 1,537 cm^{-1}. The characteristic stretching vibration band of CH in DMPA, HEMA, and PPG is at 2,800–3,000 cm^{-1}. The characteristic stretching vibration band of C=O in carbamate is at 1,690 cm^{-1}. Band for C=O in DMPA at 1,715 cm^{-1}, C–O-C in HEMA at 1,240 cm^{-1} and C–O–C in PPG at 1,100 cm^{-1} are observed, respectively. The characteristic stretching vibration of isocyanate groups at 2,250 cm^{-1} fades away with increasing reaction time, which

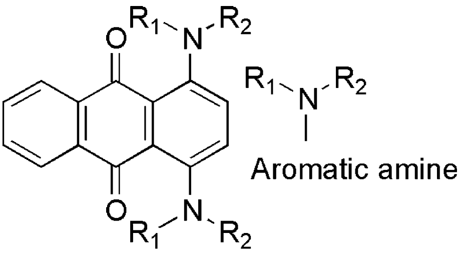


Fig. 2 Molecular structure of the employed dye

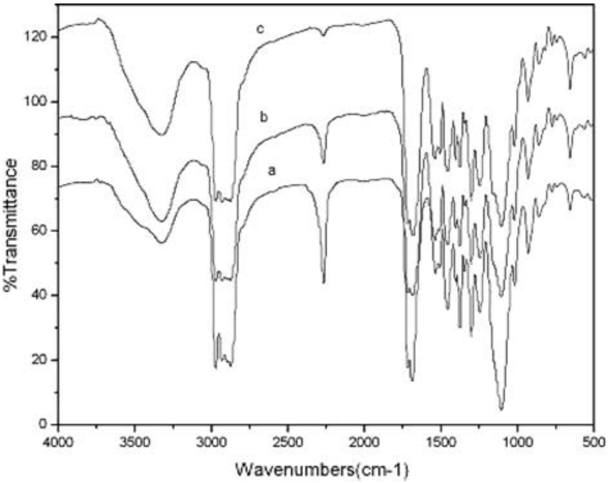


Fig. 3 IR spectra of samples at different times during the secondary polyaddition reaction. *a* 1 h, *b* 2 h, *c* 3 h

indicates the reaction did occur between OCN–NCO (IPDI) and HO–OH (PPG) gradually.

Synthesis of nanocolorants

Recipes for the various experiments are listed in Table 1. The aqueous solution of WPU (or SDS) and $NaHCO_3$ was added to organic solution containing MMA, dye and HD, and the mixture was quickly stirred at room temperature for 20 min. After that the resultant macroemulsion was miniemulsified with an ultrasonic homogenizer (JYD-650, Zhi Sun Instrument Co.) which was operated at 400–500 W for 20 min under ice cooling. Then the miniemulsion was transferred into a flask equipped with an agitator, a thermometer, a reflux condenser and a nitrogen tube. After being purged with nitrogen for 10 min and heated to 70 °C under nitrogen flowing, the miniemulsion was stirred by a paddle stirrer at 200 rpm and a water solution of KPS was injected to initiate the polymerization. The reaction was kept for 4 h at 70 °C.

Characterization

Latex stability tests

0.6 g electrolyte solution containing NaCl and $CaCl_2$, respectively, was mixed with 3.0 g latex in a test tube. The states of flocculation were observed visually after the given time.

For the freeze/thaw test, the sealed tube containing 20–30 mL latex was kept at −20 °C for 18 h and then kept at room temperature for 6 h. The states of flocculation of the latex sample were observed.

Table 1 Recipes used in the miniemulsion polymerization

Composition	Sample				
	S1	S2	S3	S4	S5
MMA (g)	10	10	10	10	10
Hexadecane (g)	0.15	0.15	0.15	0.015	0.15
PUS (g)	0.75[a]	1.5[b]	3.25[c]	5[d]	0
SDS	0	0	0	0	0.33
Sodium bicarbonate (g)	0.015	0.015	0.015	0.015	0.015
Potassium persulfate (g)	0.01	0.01	0.01	0.01	0.01
Anthraquinone-based blue (g)	1	1	1	1	1
DDI water (g)	25	25	25	25	25

[a] Concentration of PUS in water was 0.5 CMC

[b] Concentration of PUS in water was 1.0 CMC

[c] Concentration of PUS in water was 2.2 CMC

[d] Concentration of PUS in water was 3.3 CMC

Transmission electron microscopy (TEM)

A droplet of diluted aqueous suspension was deposited on copper grids and left to dry. TEM was performed on a JEOL JEM-2010 at 80 kV.

Atomic force microscopy (AFM)

One droplet of an undiluted latex solution was deposited on an angularly placed, flat silica surface to form a smooth polymeric film consisting of a few monolayers of latex particles. Excess water was removed by blotting with filter paper. AFM experiments were carried out using a Topometrix Explorer (Nanosensors GmbH) with silicon noncontact tips. AFM images were obtained at ambient conditions and the instrument was conducted in noncontact mode.

Droplet and particle size

The average size and size distribution of monomer droplets were obtained from dynamic light scattering (DLS), using Microtrac UPA (Honeywell Co.). The sample was diluted with water to adjust the intensity of the scattering light. The diluted water was a monomer saturated solution of 60 mM PUS.

UV–vis absorption

UV–vis absorption of the latex was studied by using a UV–vis spectrometer (HITACHI Spectrophotometer U-3500). Dye content in colored latex particles at t_0 (storage time $(t) = 0$) was measured immediately after the latex prepared. Then, the latex products were maintained in a thermostat at 25 °C, and dye contents in the particles were measured at storage time *t*. The measurement by absorptiometry was carried out by the method described in [4].

Thermal stability

The thermogravimetric analyses of nanocolorants were performed on Netzsch TG 209 thermogravimetric analyzer. The measurement was performed at heating rate of 10°/min in nitrogen atmosphere.

Result and discussion

Latex stability

Two latex samples were compared for electrolyte addition and freeze/thaw testing as illustrated in Table 2. It can be found that the latex stabilized with WPU had better stability against electrolytes than that stabilized with SDS. The latex stabilized with SDS did not resist a high concentration of monovalent salt (0.5–1.0 M NaCl) or a low concentration of bivalent salt (0.1–1.0 M $CaCl_2$), whereas the latex stabilized with WPU just did not resist a high concentration of bivalent salt (0.5–1.0 M $CaCl_2$). It demonstrates that WPU can improve the latex stability against electrolytes. After one freeze/thaw cycle, both the latex stabilized with SDS and latex stabilized with WPU totally flocculated, because there was no steric stabilization in the experiments.

Typical morphology of nanocolorants

The TEM images in Fig. 4 show the morphology and particle size distribution of the prepared nanocolorants. In every case, particles composed of dark domain of dyes surrounded by light polymer edge can be observed, which means the phase separation between dye and polymer. However, when the concentration of WPU reached to a certain extent (200 mM), there were spherical polymethylmethacrylate (PMMA) particles with a mean diameter of 30 nm, (as illustrated on Fig. 4d for sample S4). It is assumed that an excessive increase in surfactant concentration will lead to the presence of free surfactant micelles in the miniemulsion, which will lead to secondary nucleation and thus secondary particle formation due to the presence of free micelles.

Table 2 Latex stability against the electrolytes

Sample	Surfactant	0.1 M NaCl	0.5 M NaCl	1.0 M NaCl	0.1 M $CaCl_2$	0.5 M $CaCl_2$	1.0 M $CaCl_2$
S5	SDS	+	++	++	+++	+++	+++
S3	WPU	+	+	+	+	+++	+++

+, stable after 1 month; ++, flocculation in time (10–30 days); +++, immediate flocculation

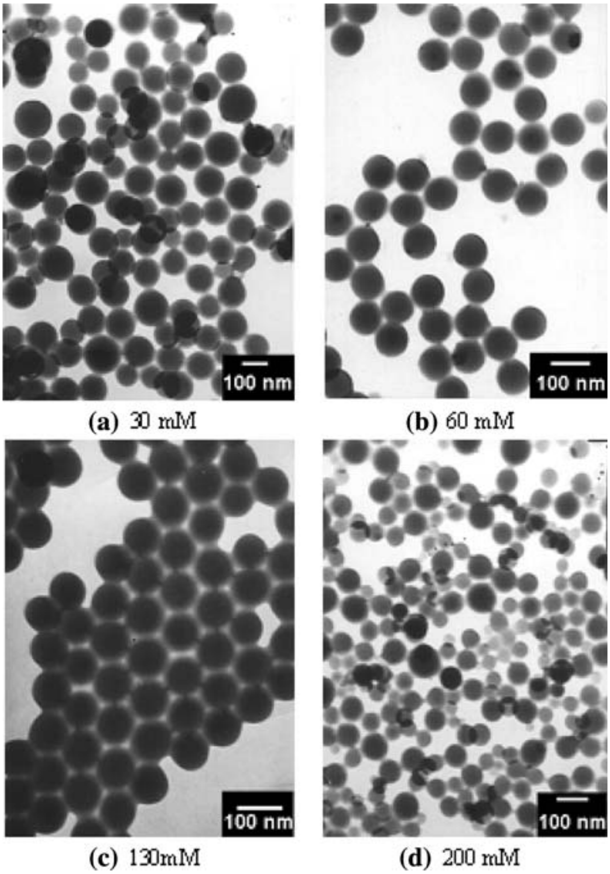


Fig. 4 TEM image of nanocolorants with different concentrations of WPU

Typical AFM image as shown in Fig. 5 also demonstrated that the morphology of nanocolorants is homogeneous spherical nanoparticle with a uniform surface.

Size distribution and basic characteristics of nanocolorants

The average size and size distribution of monomer droplets and latex particles with different concentrations of WPU are summarized in Table 3. From Table 3, we can see that the average size and the polydispersity index (PDI) of latex are nearly consistent with those of monomer droplets. The size of monomer droplets and latex particles decreased with increasing amounts of WPU used in the miniemulsions, which means that WPU could mainly play as surfactant and tend to form the surface shell of the minidroplets during miniemulsion. Therefore, there is the optimal concentration range of WPU to make the size distribution narrow.

When the concentration of WPU in water is higher than the CMC (as illustrated in Table 3 for Sample S3), the polymeric surfactant could generally form micelle in

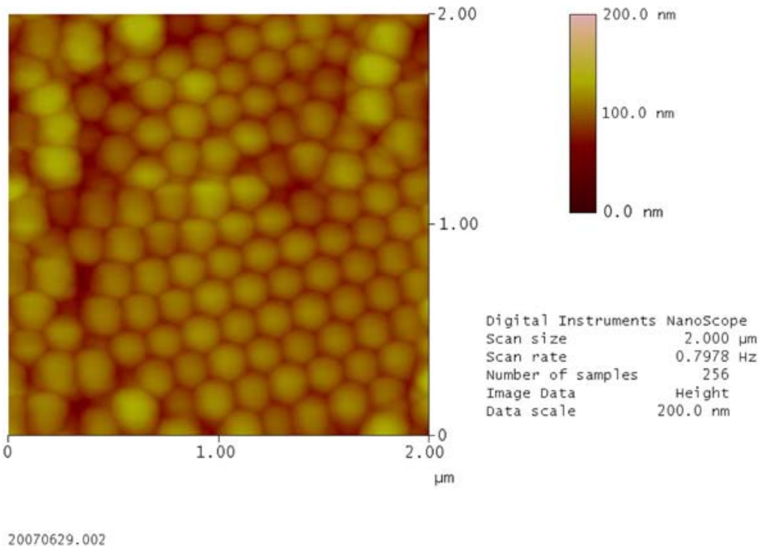


Fig. 5 AFM image of nanocolorant prepared by miniemulsion polymerization stabilized with WPU (sample S3)

Table 3 Effects of the surfactant concentration on the particle size and PDI

Sample	PUS (mM)	Before polymerization		After polymerization	
		Droplet size (nm)	PDI	Particle size (nm)	PDI
S1	30	135.1	0.066	134.3	0.087
S2	60	89.5	0.047	78.6	0.036
S3	130	69.4	0.035	73	0.039
S4	200	34.7	0.073	46.8	0.098

aqueous phase. In this case, the concentration of WPU is double CMC which is equal to 60 mM in neutral aqueous solution. However, from the TEM image of latexes (as illustrated on Fig. 4c for sample S3), no obvious secondary population of particles can be found, because some WPU molecules may exist in the monomer phase. On the other hand, a far excessive increase in surfactant concentration (as illustrated on Table 3 for Sample S4) will lead to the presence of free surfactant micelles in the miniemulsion, which will lead to secondary nucleation and thus secondary particle formation due to the presence of free micelles.

Nanocolorants with brilliant color could not be prepared at the WPU concentrations less than CMC. If the particle size is too large, latex will show a dull color due to the scattering of light. From the measurements of DLS, we could exactly obtain nanocolorants with narrow size distribution and with brilliant color. As shown in Table 3 nanocolorants with the average particle size below 100 nm could be prepared when the concentration of WPU was more than CMC.

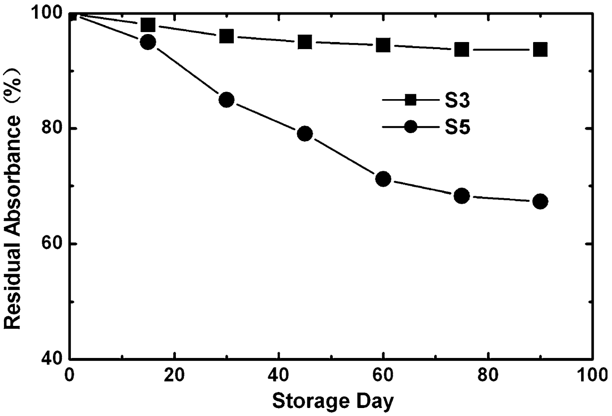


Fig. 6 Dye migration properties of nanocolorants stabilized with WPU and SDS

Migration fastness of nanocolorants

Nanocolorants are required to exhibit good dye preservation property for a long storage time. But, in some cases, dyes inside latex particles migrate to aqueous phase and precipitate as dyestuff aggregates. Dye migration from the polymeric matrix must be minimized as far as possible. In this study, WPU is also used as one kind of cross-linking agent for interfacial polycondensation to enhance the preserving fastness of dye in polymeric matrix.

It is clearly shown in Fig. 6 that the crosslinked nanocolorants exhibited excellent storage stability after settling for 90 days at 25 °C, whereas the uncrosslinked color latex yields some agglomerate in the same condition. With the addition of WPU, crosslinked polymer chains can be produced at the droplet/water interface. As a result, the mobility of crosslinked polymer chains will be less than that of straight polymer chains. Therefore, these crosslinked polymer chains could anchored, reacted, and separated at the interface, so it is difficult for dye molecules to pass through polymer shell and migrate to aqueous phase. Moreover, the miscibility between dye molecules and polymer is low. It is supposed that a polymer shell which is less miscible with the dye molecule is more effective against dye migration.

Thermal stability of nanocolorants

The TGA curves of the obtained nanocolorants are shown in Fig. 7, the nanocolorants show a two-stage decomposition process. The initial decomposition of nanocolorants could be due to that the dye molecule affinitied with macromolecular chain and the clustered dye-phase embedded in interior of polymer gradually escaped and sublimated. The second stage of decomposition was due to the decomposition of stable crosslinked PMMA.

As shown in Fig. 7, when WPU is introduced to the system, the degradation temperature of nanocolorant is significantly shifted to higher temperatures. It was supported that WPU can improve crosslinking density of PMMA, so the clustered

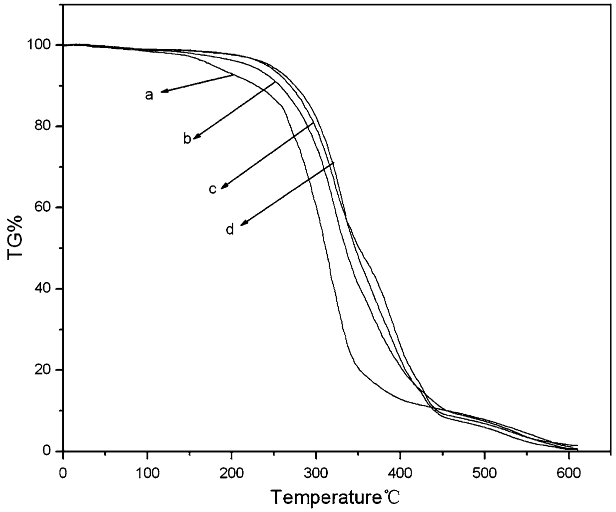


Fig. 7 The thermogravimetry curves of nanocolorants: *a* sample S1; *b* sample S2; *c* sample S3; *d* sample S4

dye-phase embedded in interior of crosslinked polymer can not move easily. Therefore, the thermal stability of nanocolorants was improved.

Conclusion

In summary, we have reported a route to production of nanoclorants with particle size less than 100 nm latexes via miniemulsion polymerization using waterborne polyurethane as surfactant. By varying the amounts of WPU at an excess of CMC, we achieved control over the particle size diameters below 100 nm with a core (dye)/shell (polymer) morphology. The obtained nanocolorants exhibited high stability, excellent color saturation, lightness, and strong color depth compared with nanocolorants prepared by conventional surfactant. They really achieved superior migration fastness and good thermal stability.

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