

## Preparation and Properties of Covalently Colored Polymer Latex Based on a New Anthraquinone Monomer

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**ABSTRACT:** 1-(6-acrylamidohexylamino)-4-(methylamino)anthraquinone (AHMAQ), a blue polymerizable dye, was first synthesized from an anthraquinone derivative, and its chemical structure was confirmed by  $^1\text{H-NMR}$  and IR. Then, a series of covalently colored polymer latexes were prepared by semi-continuous emulsion copolymerization of styrene (St), butyl acrylate (BA), and AHMAQ using 4,4'-azobis(4-cyanovaleric acid) (ACVA) as initiator, and the influences of AHMAQ and ACVA on the emulsion polymerization as well as the properties of the resulted copolymer latexes were investigated. Results showed that both the conversion of the dye monomer and the molecular weight of the latex polymer decreased with the increase of AHMAQ amount from 0 to 0.3 wt %. Increasing the ACVA amount resulted in higher monomer conversion but larger gel ratio, and optimum amount of ACVA was 1.2 wt % to the total monomers. Comparing with the noncovalently blue latex film colored with the unreactive dye, the light fastness of the blue P(St-BA-MAA-AHMAQ) latex films was greatly promoted by the covalent incorporation of chromophores with polymer matrix.  
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**KEYWORDS:** emulsion polymerization; dyes/pigments; nanoparticles; nanowires and nanocrystals; properties and characterization

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### INTRODUCTION

Because of their advantages of broad color range, great color strength, tunable color depth, and wide applications in different areas such as ink, paint, coating and textile dyeing, the polymer latexes colored by diverse organic dyes have attracted more and more attention in the past decade.<sup>1–5</sup> Meanwhile, along with the development of the biomedical engineering and material engineering, they are also applied in enzyme immobilization,<sup>6</sup> cell markers,<sup>7,8</sup> and chemical/biochemical sensors.<sup>9,10</sup> However, some inherent defects of this kind of colored polymer latexes seriously hamper their utilization. For example, compared with the inorganic pigments, the organic dyes are easy to fade or change their color when exposed in sunlight; due to the poor compatibility between dye and polymer, the colored latex is not stable enough, and the aggregation of dyes and the fading of polymer latex could be observed in storage.

To solve these problems, the polymeric encapsulation of dyes has been developed, and a number of successful encapsulated dyes with different polymeric materials have been reported. For example, Wu et al.<sup>11,12</sup> fabricated the latex colored by hydrophobic and hydrophilic dyes using miniemulsion polymerization technique; Wicks et al.<sup>13</sup> prepared thermally responsive colored

nanoparticle by encapsulating a colored polymer core with a shell of poly(*N*-isopropylacrylamide); Hu et al.<sup>14</sup> obtained relatively stable colored latex by using different kinds of crosslinkers in encapsulation process. However, as pointed out by Takasu,<sup>15</sup> dye migration was still inevitable after long-term storage.

Another useful strategy, covalent incorporation of dye with polymer to obtain polymeric dye, has been greatly concerned in the field of dyeing and coloration. In polymerization, polymerizable dyes can be copolymerized with other monomers and the chromophore groups can be directly integrated into the polymer chains, and the resulted covalently colored polymer exhibits enhanced photo- and thermo-stability and good resistance to wet and solvent.<sup>16,17</sup> This technique has been introduced into the preparation of colored polymer latex. For instance, Winnik et al. synthesized several kinds of fluorescent monomers and prepared fluorescent latex particles by traditional emulsion polymerization and miniemulsion polymerization.<sup>18,19</sup> In our previous work, the polymerizable azo and anthraquinone dyes were synthesized and utilized to prepare the red and yellow covalently colored latexes by different emulsion polymerization processes, and the storage stability of the latexes and the light fastness of the latex films were proved to be much better than that of the noncovalently colored latex.<sup>20–22</sup> For the further application,

a kind of blue covalently colored latex with higher color strength was expected to complete the color species.

In this article, a novel blue polymerizable dye with anthraquinone chromophore (AQ), 1-(6-acrylamidohexylamino)-4-(methylamino)anthraquinone (AHMAQ), was first synthesized. Then the covalently colored polymer latexes were fabricated by semicontinuous emulsion copolymerization of AHMAQ, styrene (St), butyl acrylate (BA) and methacrylic acid (MAA) using water-soluble 4,4'-azobis(4-cyanovaleric acid) as initiator. Furthermore, the influences of the polymerizable dye and the initiator on the emulsion copolymerization and the resulted latex properties were investigated, and the light fastness of both the covalently and noncovalently colored latex films was studied.

## EXPERIMENTAL

### Materials

St, BA, and MAA (First Chemical Reagent Factory, Tianjin) were purified by vacuum distillation. Dichloromethane and n-hexane (Beijing Chemicals) were dried with anhydrous  $\text{MgSO}_4$  and stored with 4A molecular sieve. Acryloyl chloride (Alfa Aesar) and 4,4'-azobis(4-cyanovaleric acid) (ACVA) (Shanghai Yuanye Co.) were used as received. Other reagents, including sodium dodecyl sulfate (SDS), octylphenol polyoxyethylene (10) ether (OP-10) (Beijing Chemicals), 1,6-diaminohexane, dimethyl sulfide (DMSO) (First Chemical Reagent Factory, Tianjin), and 1-bromo-4-(methylamino)anthraquinone (Chongqing Kuayue), were used without further purification.

### Synthesis of the Polymerizable Dye and the Unreactive Dye

**Synthesis of 1-(6-aminohexylamino)-4-(methylamino)anthraquinone (1).** To a suspension containing DMSO (80 mL), 1-bromo-4-(methylamino)anthraquinone (6.32 g, 20 mmol), anhydrous copper acetate (3.66 g, 20 mmol) and potassium acetate (1.96 g, 20 mmol), 9.28 g (80 mmol) of 1,6-diaminohexane was added, and the reaction was carried out with stirring at 90°C for 2 h. The mixture was cooled to room temperature and then poured into an aqueous NaOH solution (0.1 wt %). The precipitate was filtered and washed with deionized water for three times. After evaporation of water at reduced pressure, the product was purified by recrystallization from ethyl acetate to give 5.34 g dark blue solid (76% yield).

$^1\text{H-NMR}$  (600MHz, DMSO- $d_6$ , TMS,  $\delta$ /ppm): 8.22 (d  $\times$  d, 2H, AQ 5,8-*H*), 7.77 (d  $\times$  d, 2H, AQ 6,7-*H*), 7.55 (d, 1H, AQ 2-*H*), 7.50 (d, 1H, AQ 3-*H*), 3.40 (t, 2H,  $\text{CH}_2\text{NH-AQ}$ ), 3.04 (s, 3H,  $\text{CH}_3$ ), 1.71 (t, 2H,  $\text{CH}_2\text{NH}_2$ ), 1.28-1.50 (m, 8H, alkyl *H*).

FTIR (KBr,  $\text{cm}^{-1}$ ): 3000–3600 (primary amino  $\text{NH}_2$ ); 2926, 2852 (alkyl C–H); 1593, 1576 (AQ C=C); 1524 (amide N–H bend); 1261 (AQ C–N stretch and N–H bend).

**Synthesis of 1-(6-acrylamidohexylamino)-4-(methylamino)anthraquinone (AHMAQ)(2).** To a solution containing 1-(6-aminohexylamino)-4-(methylamino)anthraquinone (1) (3.51 g, 10 mmol), triethylamine (1.5 g, 15 mmol) and dichloromethane (50 mL), 1.09 g of acryloyl chloride (12 mmol), dissolved in dichloromethane (10 mL), was added slowly over 15 min. The round-bottom flask was cooled in an ice–water bath and stirred for 2 h. After removal of solvent by rotary evaporation, the

**Table I.** Recipes for the Preparation of Colored Polymer Latexes

Ingredients	Amount (g)
St	7.50
BA	7.50
MAA	0.06
AHMAQ	Variable <sup>a</sup>
ACVA	Variable <sup>b</sup>
SDS	0.30
OP-10	0.15
H <sub>2</sub> O	30

<sup>a</sup>0 ~ 0.3 wt % based on the total monomers.

<sup>b</sup>1 ~ 1.6 wt % based on the total monomers.

blue–violet solid was purified by silica column chromatography using a mixture of dichloromethane/ethyl acetate (3 : 1 by volume) as eluent to give 2.92 g of product (72% yield).

$^1\text{H-NMR}$  (600MHz, DMSO- $d_6$ , TMS,  $\delta$ /ppm): 8.25 (d  $\times$  d, 2H, AQ 5,8-*H*), 7.80 (d  $\times$  d, 2H, AQ 6,7-*H*), 7.51 (d, 1H, AQ 2-*H*), 7.46 (d, 1H, AQ 3-*H*), 6.20 (d  $\times$  d, 1H, 2-acryloyl *H*), 6.09 (d, 1H, 3-acryloyl cis *H*), 5.59 (d, 1H, 3-acryloyl trans *H*), 3.44 (t, 2H,  $\text{CH}_2\text{NH-AQ}$ ), 3.14 (t, 2H,  $\text{CH}_2\text{NHCO}$ ), 3.08 (s, 3H,  $\text{CH}_3$ ), 1.32-1.70 (m, 8H, alkyl *H*).

FTIR (KBr,  $\text{cm}^{-1}$ ): 3290 (N–H stretch); 2929, 2852 (alkyl C–H); 1655 (acryloyl C=O); 1591, 1579, 1558 (AQ C=C); 1525 (amide N–H bend); 1259 (AQ C–N stretch and N–H bend).

### Synthesis of 1-(6-acetamidohexylamino)-4-(methylamino)anthraquinone (3).

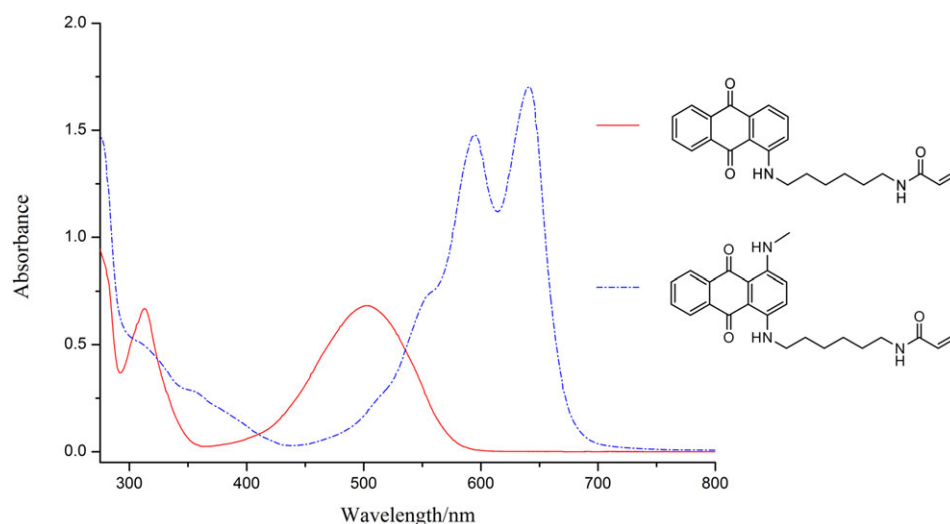
A mixture of 1-(6-aminohexylamino)-4-(methylamino)anthraquinone (1) (1.17 g, 3.3 mmol), acetic anhydride (15 mL), and pyridine (15 mL) was stirred and heated at 100°C for 1 h. It was cooled to room temperature and then dropped slowly into water. The precipitate was filtered and washed with deionized water for three times. After evaporation of water in vacuum, the product was purified by silica column chromatography using a mixture of dichloromethane/ethyl acetate (3 : 1 by volume) as eluent to give 1.01 g of product (78% yield).

$^1\text{H-NMR}$  (600MHz, DMSO- $d_6$ , TMS,  $\delta$ /ppm): 8.24 (d  $\times$  d, 2H, AQ 5,8-*H*), 7.79 (d  $\times$  d, 2H, AQ 6,7-*H*), 7.49 (d, 1H, AQ 2-*H*), 7.45 (d, 1H, AQ 3-*H*), 3.43 (t, 2H,  $\text{CH}_2\text{NH-AQ}$ ), 3.08 (s, 3H,  $\text{CH}_3\text{NH-AQ}$ ), 3.03 (t, 2H,  $\text{CH}_2\text{NHCO}$ ), 1.79 (s, 3H,  $\text{CH}_3\text{CO}$ ), 1.30–1.70 (m, 8H, alkyl *H*).

FTIR (KBr,  $\text{cm}^{-1}$ ): 3302 (N–H stretch); 2927, 2852 (alkyl C–H); 1647 (acryloyl C=O); 1579, 1558 (AQ C=C); 1525 (amide N–H bend); 1257 (AQ C–N stretch and N–H bend).

### Preparation of Colored Latex

The covalently colored latexes were prepared via semicontinuous emulsion copolymerization, and the typical recipes were listed in Table I. AHMAQ was first dissolved in a mixture of St, BA, and MAA, then 20 wt % of the monomer solution, 40 wt % of the surfactants (SDS and OP-10), and 25 mL of water were added into a 100 mL four-necked round-bottom flask equipped



**Figure 1.** Absorption spectra of the polymerizable dyes (0.1 mmol/L in ethyl acetate solution). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

with a  $N_2$  inlet, a feeding inlet, a reflux condenser and a mechanical stirrer. The initiator ACVA and the other 60 wt % of surfactants were dissolved in 5 mL of water prior to use. The flask was thoroughly charged with  $N_2$  for 15 min, and then heated in a water bath. When the temperature stabilized at  $80^\circ\text{C}$ , 40 wt % of ACVA and surfactant solution was injected to initiate polymerization, and the residual monomer solution was drop-wise added into the flask in 2 h. In the monomer feeding process, the residual ACVA and surfactant solution was introduced into the flask in six steps with the interval of 20 min, in each step 10 wt % of ACVA solution was injected. After that, the system was maintained at  $80^\circ\text{C}$  for an additional 1 h, and cooled down to room temperature to obtain the colored latex.

In a control experiment, 0.2 wt % of unreactive dye (**3**) based on the total monomers was employed using the same method to produce noncovalently colored latex.

### Characterization

Fourier-transform infrared (FTIR) spectroscopy measurements were performed using a Nicolet 560 instrument.  $^1\text{H-NMR}$  spectra were obtained on a JEOL JNM-ECA600 spectrometer. UV-Vis absorption was studied using a UV-Vis spectrometer (T6, Pgeneral). The morphology and the average size ( $D_p$ ) of the latex particles were measured by transmission electron microscopy (TEM, Hitachi H-7650B). The hydrodynamic diameter ( $D_h$ ), size polydispersity (polydis.) and zeta potential of the latex particles were characterized on Zetasizer 3000HS (Malvern). Gel permeation chromatography (GPC, Shimadzu) was used to measure the molecular weight and its distribution. The GPC instrument was equipped with a refractive index (RI) detector (Wyatt Optilab rEX) and fitted with a PLGel 5  $\mu\text{m}$  mixed-D column, which was calibrated using polystyrene standard. THF was used as the eluent.

### Monomer Conversion

Solid content ( $S$ , wt %) and gel ratio ( $C_g$ , wt %) were measured by gravimetric analysis, and the total monomer conversion of polymerization was calculated as below:

$$\text{Conv. wt\%} = S/S_t \times 100\% + C_g$$

where  $S_t$  denotes the theoretical solid content assuming all of the monomers were consumed in polymerization.

The characterization of the dye monomer conversion was carried out as follows: The colored latex was coated on a glass plate and dried in an oven at  $65^\circ\text{C}$  to obtain a latex film, and then the colored latex film was treated by Soxhlet extraction extractor for 5 h. Since methanol was good solvent for AHMAQ, the unreacted monomer was extracted in methanol solution, and then quantified by UV-Vis absorption method. The conversion of dye monomer ( $\text{Conv}_{\text{dye}}$ , wt %) was calculated as below:

$$\text{Conv}_{\text{dye}} \cdot \text{wt\%} = (1 - M_E/M) \times 100\%$$

where,  $M_E$  and  $M$  denote the mass of the extracted dye and the dye used in the recipe, respectively.

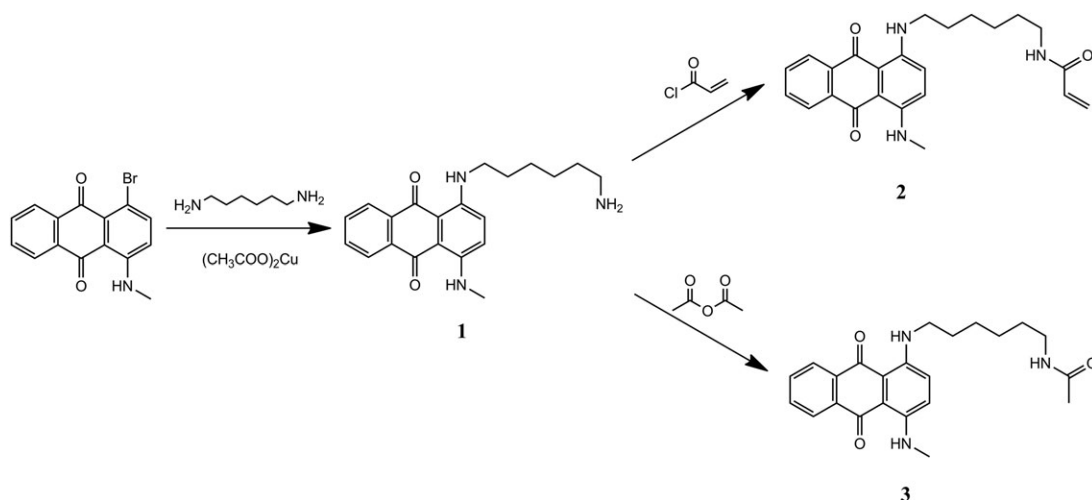
### Measurement of the Light Fastness

The colored latex films produced as above were treated by Xenon lamp irradiation at  $40^\circ\text{C}$  for 7 days. The irradiation intensity was  $180 \text{ W/m}^2$ , and the relative humidity was 50%. The color difference ( $\Delta E$ ) before and after light irradiation was measured by a colorimeter (HP-200, Chinaspec) on white printing paper.

## RESULTS AND DISCUSSION

### Synthesis of the Polymerizable Dye AHMAQ

The anthraquinone dyes, being famous for their beautiful color brilliance and prominent fastness, have been widely used in dyestuff and colorant industry. A series of polymerizable dyes containing anthraquinone chromophore have been synthesized and used to fabricate the covalently colored polymer latex in our previous research,<sup>21,22</sup> but the color strength of these synthetic dyes are still not very satisfactory. Since the



**Figure 2.** Synthesis of the polymerizable dye AHMAQ (2) and the unreactive dye (3).

molar absorptivity of the dye is determined by the electron donating substituent of the anthraquinone structure, it is believed that the introduction of amino group on AQ will cause both bathochromic effect and hyperchromic effect.<sup>23</sup> As expected, the color strength of 1,4-bis(alkylamino)anthraquinone was greatly improved in comparison with that of 1-alkylaminoanthraquinone as shown in Figure 1, and the new polymerizable dye AHMAQ consisted of 1,4-bis(alkylamino)anthraquinone chromophore, alkyl chain and polymerizable acrylamide group. The alkyl spacer between AQ and acrylamide group was designed to improve the dye solubility in monomer mixture, meanwhile it would decrease the steric hindrance of AQ structure on the propagating chain radical. AHMAQ is dark violet–blue solid, the maximum absorption peaks of its UV–Vis spectrum are 594.8 nm and 641.2 nm, it can be calculated that the  $\epsilon$  of AHMAQ is  $1.70 \times 10^4$  L/mol.cm (641.4 nm), while the  $\epsilon$  of the red polymerizable dye, 1-(6-acrylamido-hexylamino)anthraquinone reported in Ref. 20, is only  $6.82 \times 10^3$  L/mol.cm (503.0 nm). The melting point of AHMAQ is 160.5–161.5°C.

The anthraquinone chromophore of AHMAQ was synthesized in analogy to commercial C.I. Disperse Blue 14. First, aminolysis of 1-bromo-4-(methylamino) anthraquinone was carried out with excessive 1,6-diaminohexane in the presence of copper(II) catalyst to produce a dark blue dye (1), then acryloyl chloride was employed for amidation reaction to obtain monomer

AHMAQ (2) as illustrated in Figure 2. Meanwhile, a blue unreactive dye (3) was synthesized for control experiment. The chemical structure of AHMAQ and blue unreactive dye (3) were confirmed by <sup>1</sup>H-NMR and FTIR.

### Semicontinuous Emulsion Polymerization

In semicontinuous emulsion polymerization, dye monomer was copolymerized with St, BA, and MAA to produce blue polymer latex, in which AQ chromophore was covalently bonded to the polymer chain. To maintain the latex stability in the later stage of polymerization, a part of surfactants SDS and OP-10 were added in feeding process together with ACVA.

Ammonium persulfate (APS) is a very common initiator in emulsion polymerization, and has been widely used in the preparation of polymer latexes. However, when APS was employed to initiate the polymerization in this work, the latex color resulted from the polymerizable dye AHMAQ quickly faded. This phenomenon should be related to the ease of electrophilic attack at the N-atom of alkylamino-substituted AQ dye.<sup>24</sup> Since N-atom is a comparatively electron-rich center, alkylamino-substituted AQ can be easily oxidized into hydroxyl-substituted AQ by oxidant APS, causing the fading of the colored latex. Therefore, a water-soluble azo initiator ACVA, which has been used in emulsion polymerization,<sup>25</sup> was selected to replace persulfate initiator in this work. The influences of AHMAQ and ACVA on the emulsion copolymerization and the latex properties were investigated.

**Table II.** Influence of AHMAQ on the Emulsion Polymerization and the Latex Properties<sup>a</sup>

Sample	AHMAQ (wt %)	Conv. (wt %)	Conv <sub>dye</sub> . (wt %)	C <sub>g</sub> (wt %)	D <sub>h</sub> (nm)	Polydis.	ζ (mV)	M <sub>n</sub> (10 <sup>4</sup> g/mol)	PDI (M <sub>w</sub> /M <sub>n</sub> )
A1	0	97.8	–	3.6	68.3	0.0548	–74.8	7.808	2.258
A2	0.1	97.2	93.9	4.3	60.2	0.100	–70.2	7.334	3.039
A3	0.2	96.5	90.8	4.6	60.9	0.0891	–69.3	6.194	2.573
A4	0.3	96.2	88.3	6.8	65.3	0.103	–76.5	4.721	2.850

<sup>a</sup>1.2 wt % ACVA to the total monomers was used.

**Table III.** Influence of ACVA on the Emulsion Polymerization and the Latex Properties<sup>a</sup>

Sample	ACVA (wt %)	Conv. (wt %)	Conv <sub>dye</sub> (wt %)	C <sub>g</sub> (wt %)	D <sub>h</sub> (nm)	Polydis.	ζ (mV)	M <sub>n</sub> (10 <sup>4</sup> g/mol)	PDI (M <sub>w</sub> /M <sub>n</sub> )
<b>B1</b>	1.0	88.4	84.1	0	65.2	0.101	-75.4	8.893	2.273
<b>B2/A3</b>	1.2	96.5	90.8	3.6	60.9	0.0891	-69.3	6.194	2.573
<b>B3</b>	1.4	95.3	92.5	7.7	65.6	0.0975	-74.8	4.761	2.558
<b>B4</b>	1.6	97.0	93.1	11.1	65.8	0.0850	-72.6	3.739	2.755

<sup>a</sup>0.2 wt % AHMAQ to the total monomers was used.

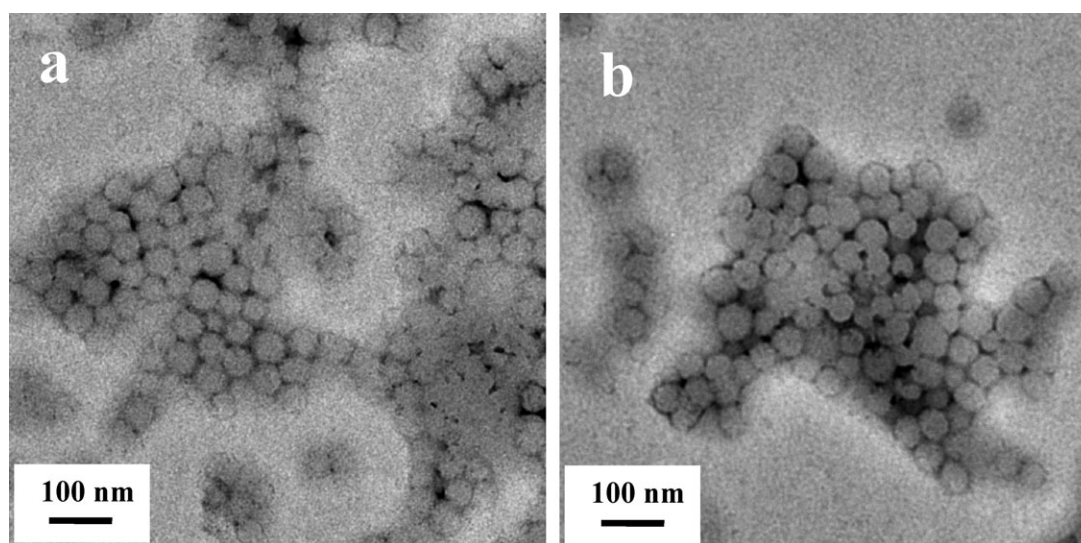
### Dye Concentration

Because of the solubility limitation in monomer mixture, the amount of AHMAQ employed was in the range of 0.1–0.3 wt % based on the total monomer in this work. Using 1.2 wt % ACVA as initiator, a series of covalently colored latexes were prepared and the results were listed in Table II. Although the polymerization process can be completely finished with a high monomer conversion, the conversion of the dye monomer decreased when increasing AHMAQ amount from 0 wt % to 0.3 wt %, meanwhile, the gel ratio (C<sub>g</sub>) of the emulsion polymerization evidently increased if AHMAQ was higher than 0.2 wt %. These phenomena can be ascribed to the low water solubility and the large molar weight of AHMAQ, which hindered the migration of AHMAQ molecule from the monomer droplet to the latex particles in emulsion polymerization.<sup>8</sup> In this case, the aggregation and precipitation of the dye would be increased with increasing AHMAQ concentration, which considerably reduced the conversion of dye monomer and induced the coagulation of latex particles. GPC analysis showed that the M<sub>n</sub> of covalently colored polymer was significantly decreased with the increase of AHMAQ, and this tendency was considered as the result of chain transfer reaction, in which process the propagating chain radical changed into anthraquinone radical and lost its reactivity.<sup>26,27</sup> The obtained colored polymer latex exhibited

excellent colloidal stability, and no dye leakage from the polymer latex was observed during the storage of 6 months.

### Initiator Concentration

Because of the inhibition effect of AQ structure on radical polymerization,<sup>26,27</sup> the initiator played an important role in the preparation of the colored latex. The blue P(St-BA-MAA-AHMAQ) latexes with different amount of ACVA in recipe were fabricated using the same amount of 0.2 wt % AHMAQ. As shown in Table III, both the total monomer conversion and the conversion of dye monomer increased with the increase of ACVA amount. When 1 wt % ACVA was used in emulsion polymerization, the monomers cannot be polymerized completely, with the total conversion only 88.4%, and the dye monomer conversion was as low as 84.1%, whereas, the colorless latex without using AHMAQ could be easily prepared in the same condition with monomer conversion higher than 97%. Therefore, it could be concluded that the polymerizable dye AHMAQ acted as a weak inhibitor, and additional initiator must be utilized to promote the monomer conversion. On the other hand, the excessive ACVA resulted in higher C<sub>g</sub>. When the amount of ACVA rose to 1.6 wt %, 1.66 g gel was generated in the system, accounting for 11.1% of the total monomer weight (sample **B4**). In contrast, the emulsion polymerization under the same condition using equimolar APS as initiator went smoothly, and its C<sub>g</sub> is lower



**Figure 3.** TEM images of latex particles: (a) the colorless P(St-BA-MAA) latex (sample **A1**), and (b) the blue P(St-BA-MAA-AHMAQ) latex (sample **A3**).

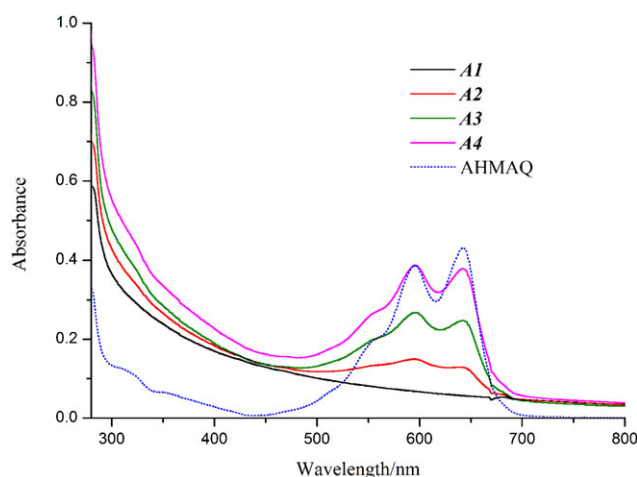
than 2.0 wt %. It is well known that not only the surfactant but also the initiator residues of polymer chain provide stability of polymer latex in conventional emulsion polymerization. In this study, the terminal group of polymer chain, cyanovaleric acid, was decomposed from ACVA. On account of its ionization degree, the carboxyl group was inferior to the sulfate group decomposed from APS in stabilizing the latex, so that the coagulation of particles occurred when too much ACVA was introduced. In addition, the molecular weight of the resulted polymer also declined with the increasing ACVA amount as expected. Thus, the optimized amount of ACVA is 1.2 wt % based on the total monomers.

### Latex Particle Morphology

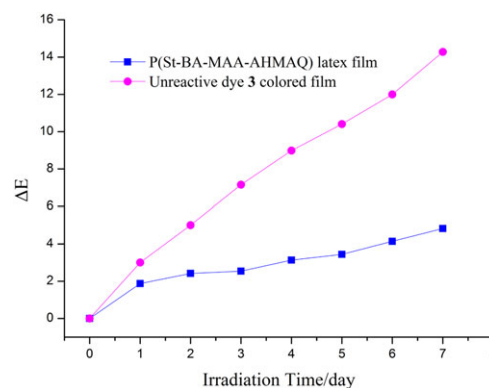
The morphology of latex nanoparticles was studied by TEM observation. Both the colorless nanoparticles (a) and the colored nanoparticles (b) were homogeneous sphere as shown in Figure 3, whereas the colorless latex particles in Figure 3(a) exhibited more uniform than that of the colored latex particles in Figure 3(b), which is consistent with the size polydispersity data in Table II. The average diameter of the dried particles from TEM was 40–50 nm, a little smaller than the hydrodynamic diameter  $D_{h}$ , which were in the range of 60–70 nm.

### UV–Vis Spectra of the Polymerizable Dye and the Colored Latex Polymer

UV–Vis absorption spectra were obtained from the ethyl acetate solution of the colored latex polymer and dye monomer AHMAQ. As shown in Figure 4, the maximum absorption wavelength ( $\lambda_{\max}$ ) of AHMAQ and the colored latex polymer exhibited at 593.4 nm and 641.2 nm, and the color strength of the blue P(St-BA-MAA-AHMAQ) latex was principally determined by the amount of AHMAQ unit on polymer chain. No noticeable batho- or hypsochromic shift of  $\lambda_{\max}$  was observed between the dye monomer and the colored latex polymer, indicating that the AQ chromophores did not change before and after the covalently bonding to the polymer chain.<sup>28</sup> Also, it can be concluded that the AQ chromophores were distributed uniformly on the polymer chain, both the dye aggregation and the



**Figure 4.** UV–Vis spectra of AHMAQ and the colored latex polymers prepared with different AHMAQ amount (A1 0 wt%; A2 0.1 wt%; A3 0.2 wt%; and A4 0.3 wt%). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 5.**  $\Delta E$  of the blue latex films versus irradiation time: (■) the blue P(St-BA-MAA-AHMAQ) latex film (sample A3), (●) the latex film colored with the unreactive dye 3. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

$\pi$ - $\pi$  stacking interaction were excluded from the results, since those would generate the bathochromic shift of  $\lambda_{\max}$ <sup>29</sup>

### Light Fastness of the Latex Films

To investigate the light fastness of the covalently colored latex polymer, the blue P(St-BA-MAA-AHMAQ) latex film was prepared by drying the colored latex, and an irradiation test of both covalently and noncovalently colored latex film was carried out. Color difference ( $\Delta E$ ) was used to evaluate the light fastness of the film, and the larger  $\Delta E$  indicated the weaker light fastness. The  $\Delta E$  of the colorless latex film (sample A1) was deducted from the data of each colored film. As shown in Figure 5, the light fastness of covalently colored polymer film was greatly improved in comparison with the film colored by the unreactive dye 3, demonstrating that the chemical bonding between AQ chromophores and the polymer matrix played an important role in the improvement of the fastness of dyes. The enhancement of photostability could be ascribed to an electron transfer from covalently bound dye to the polymer matrix during the transfer from its excited state  $S_1$  to ground state  $S_0$ , and this process can prevent the photodegradation of dye structure.<sup>30</sup>

### CONCLUSIONS

A blue polymerizable dye (AHMAQ) based on anthraquinone derivative was synthesized, and the covalently colored latex was fabricated by semicontinuous emulsion copolymerization of St, BA, MAA, and AHMAQ using water soluble 4,4'-azobis(4-cyanovaleic acid) (ACVA) as initiator. It was found that both the conversion of the dye monomer and the molecular weight of the latex polymer decreased when increasing AHMAQ amount, and increasing the ACVA amount resulted in higher monomer conversion and larger gel ratio. After polymerization, most of the chromophores were chemically bonded to the polymer chain with unchanged UV–Vis spectrum. The colored latex maintained excellent colloidal stability, and the light fastness of the covalently colored latex film was much better than that of the noncovalently colored film. Accordingly, the covalently colored polymer latex might have prospective application in waterborne coating, waterborne ink, hydrophilic nanoscale colorant, and so on.

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