

# Preparation of Cationic Pigment Dispersions by Surface Grafting of Polystyrene-Maleic Anhydride with Glycidyltriethylammonium Chloride

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**ABSTRACT:** Novel cationic pigment dispersions, which have potential uses in inkjet inks and coloration of textile and paper, were prepared by grafting quarternary ammonium groups onto the surface of polystyrene-maleic anhydride encapsulated C. I. pigment yellow 14 (PY 14) powder. It is shown that the Zeta potentials greatly rely on the reaction time and temperature. And also, when the weight ratio of glycidyltriethylammonium chloride (GTA) to encapsulated PY 14 powder was 3 : 1, the Zeta potential of modified pigment dispersion reached to +

35.05 mV. Just due to the high Zeta potential of the prepared cationic pigment dispersions, the prepared cationic pigment dispersion shows good dispersion stability and a narrow size distribution with the average particle size of 202.9 nm. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1448–1453, 2009

**Key words:** cationic pigment dispersion; surface grafting; polystyrene-maleic anhydride; glycidyltriethylammonium chloride; preparation

## INTRODUCTION

The optimization of ultrafine pigments for the coloration of materials is critical to cost-effective product performance. The ability to efficiently utilize color properties relies on the preparation process of pigment dispersions. To achieve good pigment dispersions, mechanical and chemical approaches were adopted to stabilize the pigment dispersions. The use of anionic and nonionic dispersants including small-molecular and macromolecular compounds is one of the most common approaches to stabilize the pigment dispersions. Considering growing concern on the environmental problems, waterbased pigment dispersions become the trend of pigment dispersion manufacture. More over, the rapid development and application of inkjet technology give rise to the high performance pigment dispersions for ink formulation.<sup>1,2</sup>

For most pigment dispersions, the particle surfaces are usually negatively charged. While, in the case of waterbased pigment dispersions, the materials to be

colored such as fabrics, paper and walls are often surface-negatively-charged. Low color fastness, color bleeding and pigment migration often occur in these cases. Therefore the preparation and application of cationic pigment dispersion are of great interest for its distinguished properties compared with anionic pigment dispersions.<sup>3–6</sup>

In our previous study, pigments encapsulated by styrene-maleic acid copolymers were made into aqueous dispersions through hydrolysis of anhydride groups into carboxylic anion groups.<sup>7–9</sup> In present work we prepared stable cationic pigment dispersions by grafting glycidyltriethylammonium (GTA) chloride onto the surface of polystyrene-maleic anhydride (PSMA) copolymers encapsulated on pigment particles. And also, the particle size and the storage stability of the pigment dispersions were thoroughly investigated.

## EXPERIMENTAL

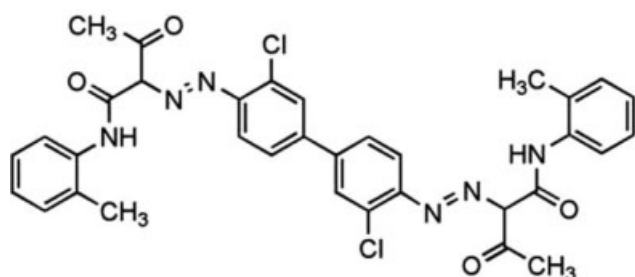
### Materials

Methanol, alcohol, acetone, *N,N*-dimethylformamide, monomers such as maleic anhydride and styrene, benzoyl peroxide (BPO) as initiator and other chemical reagents were all analytical grade supplied by Shanghai Lingfeng Chemical Reagents, Glycidyltriethylammonium chloride was a laboratory grade

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**Scheme 1** The chemical structure of PY 14.

product of Shandong Dongying Specialty Chemicals, C. I. Pigment Yellow 14 (PY 14). Scheme 1 was a press cake of Wuxi Xinguang Chemical. The pigment was purified before use. Put 5 g pigments into 100 g 5% HCl water solution and heat 20 min, then washed by deionized water and filtrated. HPLC analysis showed that the purity of purified pigment is 99.6%.

### Instruments

An Ultra Turrax IKA T18 Basic (IKA Instruments) was used to disperse pigment powder to liquid. The ultrasound crusher used was a JY98-3D type from Ningbo Xinzhi Instruments. A Nano-ZS90 (Malvern Instruments) was used to measure the particle size distribution and Zeta potentials. We used an H-7000 type transmission electron microscope (Hitachi, Japan) to observe the morphology of pigment particles.

### Encapsulation of PY 14 with polystyrene-maleic anhydride

Using styrene and maleic anhydride as monomers we synthesized PSMA under nitrogen atmosphere with BPO as initiator.<sup>7</sup> A quantitative of PSMA was dissolved in acetone and, a corresponding amount of press cake of P.Y. 14 was added into the solution under stirring. The mixture was dispersed for 1 h with the Ultra Turrax IKA T18 Basic at 4000 rpm. Then a certain volume of methanol was slowly added into the suspension to accelerate the dissolved PSMA to deposit and encapsulate onto the pigment particle surface. The mixture was filtered under vacuum and dried at 45°C

for 24 h in an oven, and PSMA-encapsulated PY 14 powder is obtained. The preparation process of encapsulation of PY 14 with PSMA was shown in Figure 1.<sup>8</sup>

### Preparation of cationic PY 14 by grafting PSMA with glycidyltriethylammonium

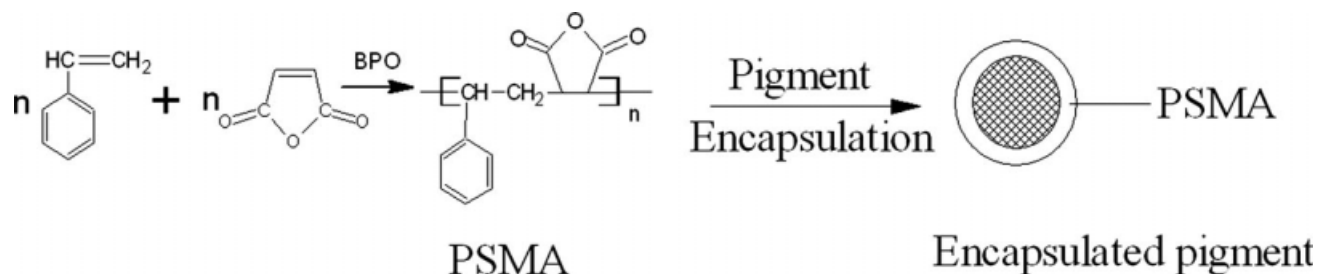
Encapsulated PY 14 powder (1.0 g) was added into 50 mL ethanol containing 0.1 g paratoluenesulfonic acid as catalyst and, the mixture was dispersed by the Ultra Turrax IKA T18 Basic at 10,000 rpm for 10 min. The mixture was transferred to a three-necked flask equipped with stirrer, thermometer, and reflux condenser. Under stirring a certain amount of GTA (epoxy content was 1.0 m mol/g) was added slowly into the flask, which was heated to boiling and kept refluxing for a certain time to end the reaction. Then the ethanol was distilled out completely. And some water was added into the system to make the modified pigments be dispersed into water. After the system was cooled the product was filtrated. The pigment cake was rinsed thoroughly with water to remove the impurities and dried in a vacuum oven, and cationic pigment powder could be obtained. This process was represented by Figure 2.<sup>10</sup>

### Preparation of waterbased pigment dispersions

Under the stirring of Ultra Turrax IKA T18 Basic a known amount of pigment powder was dispersed into a certain volume of water to make into 5% (w/w) pigment dispersion. The pH value of the dispersion was adjusted to 6–7 with a 0.1 mol/L HCl aqueous solution to make the surface of pigment particle positively charged and treated for 15 min by the JY98-3D type ultrasound crusher and, finally pigment dispersion was obtained.

### Particle size distribution and Zeta potentials

The size distribution of cationic pigment particles and Zeta potentials were measured by the Nano-ZS90 particle size and Zeta potential analyzer. The sample to be measured was prepared by diluting



**Figure 1** Polymerization and encapsulation of PSMA.

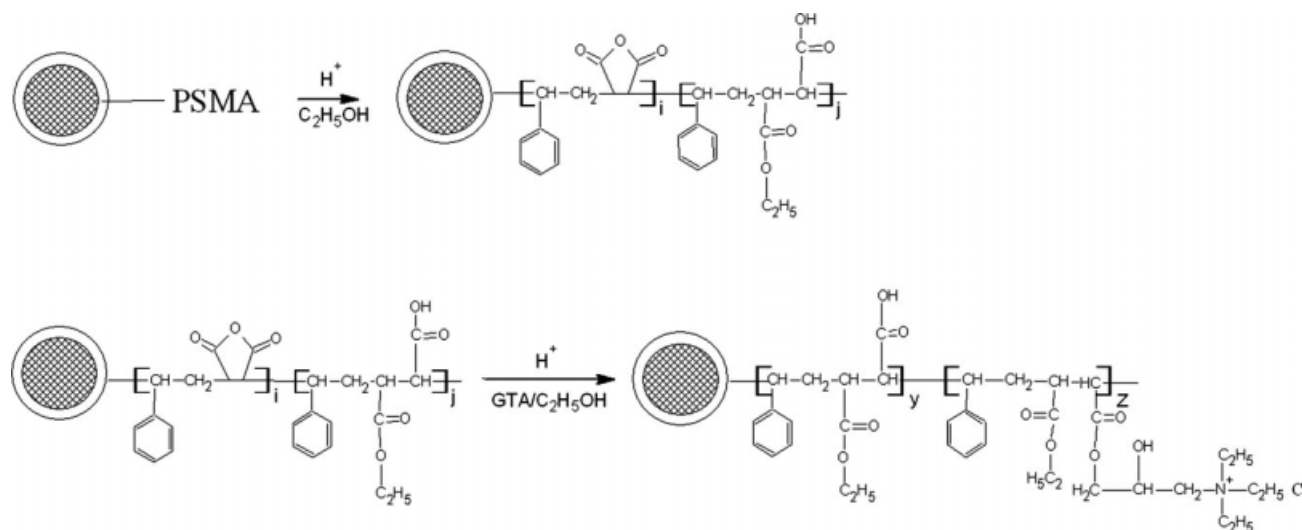


Figure 2 Alcoholysis and grafting of PSMA with GTA.

the pigment dispersion into 0.1% (w/w) solution using deionized water.

### Transmission electron microscopy (TEM)

The morphology of pigment particles was observed by the H-7000 type transmission electron microscope.

## RESULTS AND DISCUSSION

### The reaction medium

The solvent used as reaction medium for grafting PSMA with GTA is very important. The principle for choosing solvent is that GTA can be dissolved in it but PSMA cannot and the solvent should induce solubilization of the PSMA layer on the surface so that the reaction can be promoted. So the reaction of PSMA and GTA can only take place on the surface of encapsulated pigment particles. Table I gives the solubility of PSMA and GTA in some solvents. From Table I we see that water, methanol and ethanol can be used as reaction medium. In this research we chose ethanol as reaction medium because we used GTA (glycidyltrimethylammonium chloride) as grafting agent.

TABLE I  
The Solubility of PSMA and GTA in Some Solvents<sup>a</sup>

Solvents	PSMA	GTA
Water	×	✓
Methanol	×	✓
Ethanol	×	✓
Acetone	✓	×
DMF	✓	✓

<sup>a</sup> × Represents insoluble and ✓ represents soluble. The measured temperature was 20°C.

### GTA amount on zeta potentials of pigment particles

As shown in Figure 2, GTA could make the surface of pigment particles cationized through the esterification reaction with the carboxyl groups produced by alcoholysis of anhydride groups of PSMA with ethanol. Table II shows the variation of Zeta potentials of modified pigment particles with the increase of GTA amount after refluxing for 4 h. When the amount of GTA was 1.0 g the Zeta potential was -17.83 mV, which indicates that the number of ionized carboxyl groups overpasses the number of GTA groups. As the amount of GTA increased to 2.0 g the Zeta potential changed to +12.7, which means that the surface of pigment particles became positively charged. Further increasing GTA amount led to much higher Zeta potential as +35.05 mV. But from 3.0 g GTA to 4.0 g GTA there is a little variation of Zeta potential, which indicates that the surface of pigment particles may reach to a saturated positive state.

### Reaction temperature on zeta potentials of pigment particles

Table III gives the result of reaction temperature on the Zeta potentials of encapsulated pigment particles using 1.0 g pigment powder and 3.0 g GTA after 4 h

TABLE II  
Effect of GTA Amounts on Zeta Potentials of Encapsulated Pigment Particles<sup>a</sup>

GTA (g)	1.0	2.0	3.0	4.0
Zeta potentials (Mv)	-17.83	12.7	35.04	36.48

<sup>a</sup> The cationizing reaction time was 4 h at boiling.

TABLE III  
Reaction Temperature on the Zeta Potentials  
of Pigment Particles<sup>a</sup>

Temperature/°C	Zeta potentials/Mv
20	-29.17
40	-10.73
60	+1.011
80 (refluxing)	+35.04

<sup>a</sup> The reaction time was 4 h using 1.0 g pigment and 3.0 g GTA.

reaction. From this table we can see that when temperature was below 40°C the Zeta potentials were negative data indicating that the cationizing reaction was slow and, a few cationic groups were grafted onto the surface of pigment particles. When the temperature reached to 60°C the Zeta potentials became positive and, dramatically increased to +35.04 mV at 80°C. This result shows that the esterification process depends largely on the reaction temperature.

#### Reaction time on zeta potentials of pigment particles

When PSMA-modified pigment powder was dispersed to ethanol to form a solid-liquid two phase suspension, the outmost layer of PSMA in the solid phase was first wetted and alcoholized by ethanol to produce carboxyl groups. The GTA molecules in the liquid phase should diffuse to the PSMA surface of pigment particles to seek carboxyl groups to react with. Therefore the esterification reaction of PSMA with GTA is the reaction of a solid surface with a liquid reactant. The reaction speed is very slow as described above. So reaction time has much more influence on the reaction process. Figure 3 shows the result of the effect of reaction time on the Zeta potentials of pigment particles.

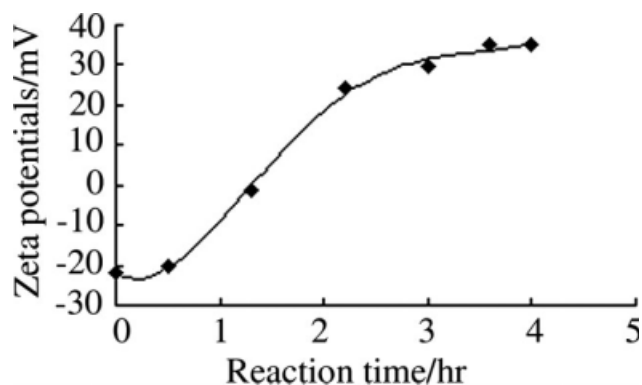


Figure 3 Influence of reaction time on the Zeta potentials of modified pigment particles, using 1.0 g encapsulated pigment and 3.0 g GTA at boiling temperature.

From Figure 3 we could see that the Zeta potentials increased markedly in the first 3 h and changed a little when the reaction time was over 3 h. When the reaction time was 1.3 h the Zeta potential was -1.283 mV, indicating that the epoxy groups reacted with very fewer carboxyl groups. This is because anhydride groups should be first esterified by hydroxyl groups of ethanol to release carboxyl groups, which makes the process lasts after longer time. When the reaction time reached to 2.2 h the Zeta potentials changed to +24.07 mV, implying that most anhydride groups of PSMA had been alcoholized. While the reaction time increased to 3 h the Zeta potential reached to +29.74 mV. Further increasing of reaction time the Zeta potentials increased slowly and, the Zeta potential was +35.04 mV after 4 h, indicating that most of carboxyl groups of PSMA alcoholized had been reacted with GTA molecules. There were some carboxyl groups still unreacted because of the electrostatic repulsion of cationic groups to GTA molecules. New carboxyl groups were not easily produced because the alcoholysis of inner anhydride groups of PSMA was hindered by

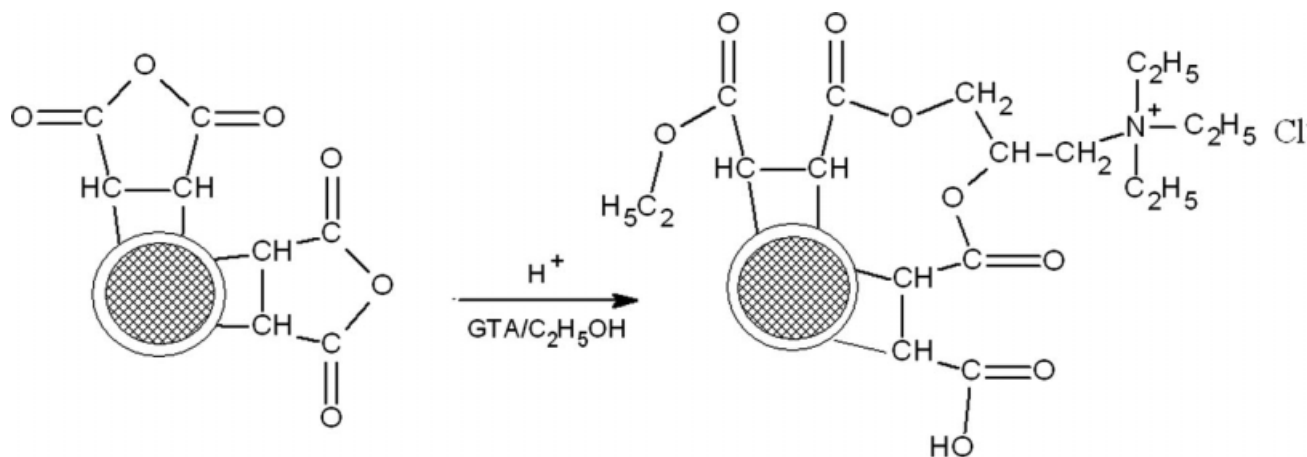
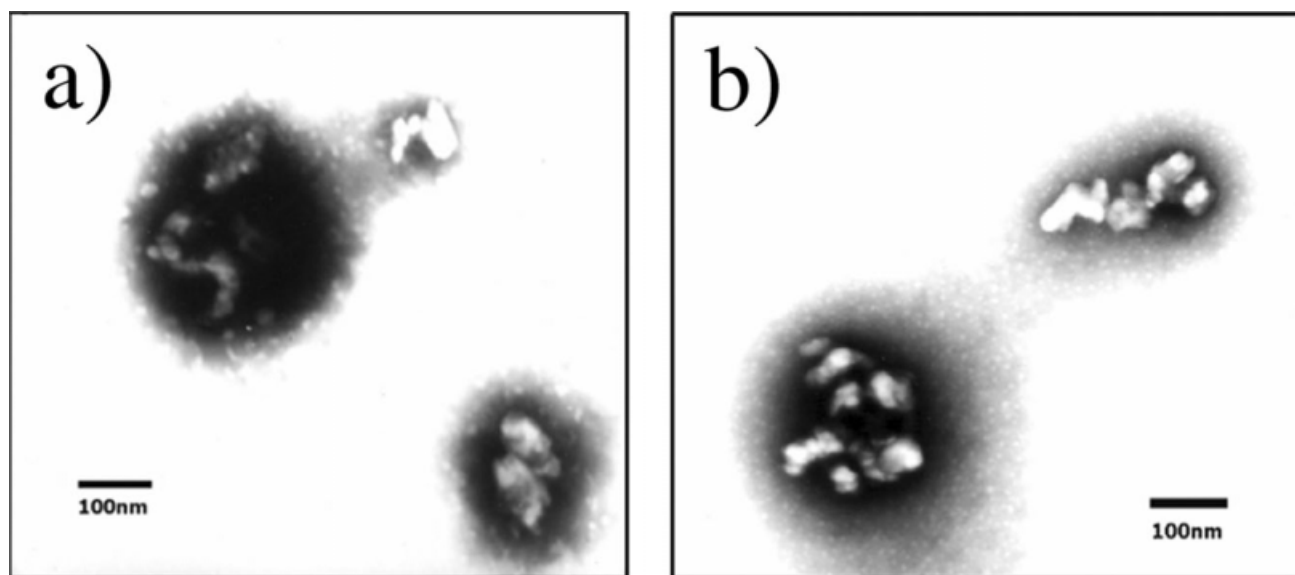


Figure 4 Esterification of two near carboxyl groups with a GTA molecule.

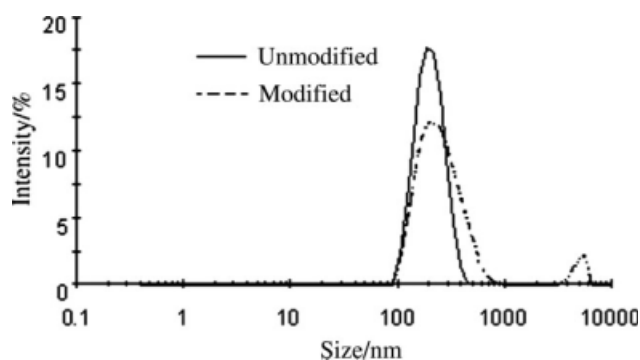


**Figure 5** TEM photos of pigments: (a) PSMA-encapsulated pigments and (b) GTA-modified pigments.

the network formed through the esterification of two neighboring carboxyl groups with a GTA molecule (shown in Fig. 4).

#### TEM observation

Figure 5 gives the TEM photos of unmodified pigments and GTA-modified pigments. It is clear that PSMA-encapsulated pigment particles (a) have much less gray layer around the outside of particles than GTA-grafted PSMA-encapsulated pigment particles (b). This difference indicates that the esterification reaction of GTA with surface PSMA made the out layer of PSMA-encapsulated pigment particles become more thickness and lower density. In a large particle there are many small pigment particles, which formed the cores of the cationic pigment particle. The overall shape of pigment particles had not changed during the cationic modification. The GTA-grafting just took place on the surface of encapsulated pigment particles.



**Figure 6** Particle size distribution of cationically modified and unmodified pigments.

#### Particle size distribution

Samples for particle size distribution were prepared by dispersing a known weight pigment powder in water using an ultrasound crusher under the same conditions. The particle size distribution of both samples of GTA-grafted and the contrast were measured with a Malvern's Nano-ZS90. The result is shown in Figure 6, which indicates that encapsulated pigment dispersion had a larger particle size distribution range from 100 nm to 10,000 nm and there were large particles at 5,000 nm and, the modified pigment dispersion had a more narrow size distribution and mainly concentrated in the range from 100 to 500 nm. The Z average particle size from 278.3 nm for the unmodified sample reduced to 202.9 nm for the GTA-modified. These particle size measurements inferred that GTA-modified pigments are more hydrophilic and are more easily dispersed in water than those unmodified pigments.

#### Dispersion stability

To evaluate the dispersion stability of the prepared cationic pigment dispersion, we compared the Zeta

**TABLE IV**  
Dispersion Stability of Pigment Dispersions  
by Storage Time

Storage time (days)	Unmodified		Modified	
	Zeta potentials (mV)	Average sizes (nm)	Zeta potentials (mV)	Average sizes (nm)
0	-19.14	278.3	+35.04	202.9
60	-20.15	1019.0	+35.52	206.9

potentials and average particle sizes of both dispersions of GTA-modified and unmodified pigments after 60 days storage. The results are shown in Table IV. It is clear that GTA-modified pigment dispersion had good storage stability with very few changes of Zeta potential and particle size after 60 days. But the unmodified pigment dispersion had poor dispersion stability with dramatic increase of particle size from 278.3 to 1019.0 nm and exhibited a little variation of Zeta potential from  $-19.14$  to  $-20.15$  mV. This means that the grafted cationic groups on the surface of pigment particles by GTA can effectively enhance the dispersion stability of PSMA-encapsulated pigment dispersion due to electrostatic repulsion.

### CONCLUSIONS

Cationic pigment dispersions were prepared by grafting on partially esterified PSMA encapsulated pigment particles with GTA through the surface of carboxyl groups. The Zeta potentials of the prepared pigment particles greatly rely on the GTA amount

used, reaction time and temperature. When the weight ratio of GTA to PSMA encapsulated PY 14 powder was 3 : 1, the Zeta potential of modified pigment dispersion reached to  $+35.05$  mV, achieving the best storage stability for prepared pigment dispersions. Also, the cationic pigment dispersion has a much narrower particle size distribution and much smaller particle size than the PSMA-encapsulated pigment dispersions.

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