Preparation of Styrene-Maleic Acid Copolymers and Its Application in Encapsulated Pigment Red 122 Dispersion

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ABSTRACT: Styrene-maleic acid copolymers were synthesized by free radical polymerization. Encapsulated pigment red 122 dispersions were prepared by sedimentation with these copolymers. Effects of copolymer structure such as molar content of maleic acid, molecular weight, and the amount of copolymers on stability and particle size of dispersion were investigated. The results showed that encapsulated pigment dispersion with higher stability, smaller particle size, and narrower particle distribution could be achieved when the molar content of maleic acid was at 0.43 and the intrinsic viscosity was at 79.65 ml/g with amount of copolymers 10%. The encapsulated layer was about 5 nm which could be observed by TEM. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 317–321, 2007

Key words: styrene-maleic acid copolymers; sedimentation; encapsulated pigment red 122 dispersion; copolymer structures; stability; particle size

INTRODUCTION

Ulrafine pigments with excellent properties have widely used in ink jet printing inks, dyeing of fibers, and other fields.[1] However, organic pigments always exist in aggregation or coagulation with low polarity, it is hard to be wetted and dispersed in aqueous media, thus the organic pigments must be modified before using.

Polymeric dispersants during the last years have proven good properties in stabilizing pigments in coating system. These good properties include higher stability, smaller particles size, lower viscosities, and less moisture sensitivity.[2,3] In aqueous media they build a voluminous shell around particles and intensify the charge on the surface. Both of these aspects help avoiding flocculation and coagulation.[4] Unlike low molecular dispersants, polymeric dispersants always stay on the surface even if some parts of chain are desorbed. In recent years, more and more copolymers have been synthesized and applied in pigment dispersions, Harry J. Spinelli prepared an AB diblock acrylic polymer which A was a hydrophobic block and B was a hydrophilic block,[5] Simms synthesized graft polymers whose backbone adsorbed on the surface of pigments and entropic arm stretched in the media.[6] Yu also prepared the pigment 122 dispersion using the styrene-maleic acid copolymers (PSMA) as dispersant, but in his research, the dispersants first dissolved in water and then absorbed onto the pigment surface.[7]

Encapsulated pigments that use pigments as core and polymeric materials as the shell facilitate to improve pigments processing and its qualities. A large number of successful encapsulations have been reported. For instance, Lelu et al. encapsulated organic phthalocyanine blue pigments into polystyrene latex particles by miniemulsion polymerization process,[8] Viala et al. encapsulated some inorganic pigments by emulsion polymerization.[9]

How to get ultrafine pigments dispersion with high stability is still the main obstacle to widen application pigments although there are lots of research reports about pigment modification. In this article, PSMA with different structures were synthesized and used as encapsulated layer for pigment dispersions. Effects of copolymer structure and amount of copolymers on stability and particles size were investigated. In the meanwhile, the shape of pigment particles was observed by Transmission electron microscope (TEM), the size distribution was measured by Dynamic light scattering (DLS).

METHODS

Preparation of styrene-maleic acid copolymers

All the agents used in these work were analytical grade, styrene was dried by calcium hydride and then distilled before use, 2, 2′-AZo-bisiso-butyloni-trile (AIBN) was purified by recrystallization with hot ethanol. The PSMA was prepared according to our team previous work.[10] Molar content of maleic acid in PSMA was determined by titration method and was calculated as formula (1). The PSMA with molar content of maleic acid 0.38, 0.39, 0.43, 0.45, 0.48 respectively, was prepared with 1.8% molar dosage of initiator to monomers.

$$F = \frac{104[C_{NaOH}V_0 - C_{HCl}(V - V_1)]}{2000W + 6[C_{NaOH}V_0 - C_{HCl}(V - V_1)]} \quad (1)$$

C_{NaOH}, concentration of titrated sodium hydroxide solution (mol/L); C_{HCl}, concentration of titrated hydrochloric acid solution (mol/L); V_0, volume of adding hydroxide solution (mL); V, volume of consuming hydrochloric acid (mL); V_1, volume of consuming hydrochloric acid in blank experiment (mL); W, weight of copolymers (g).

The intrinsic viscosity of PSMA was measured using Ubbelodhe Viscosimeter (0.6–0.8 µm, Shang-Hai) at 25°C ± 0.1°C by extrapolation, cyclohexanone used as solvent. The results show that the PSMA with intrinsic viscosity was at 23.40, 38.41, 79.65, 98.35, and 164.20 mL/g respectively, was prepared when the molar ratio of monomers was at 1.4 to 1 with the different dosage of initiator.

Preparation of encapsulated pigment red 122 dispersion

Encapsulated quinacridone red pigment 122 dispersions were prepared according to reference.[11] A quantitative of PSMA was dissolved in a solvent, and then corresponding amount of press cake of C.I.P.R122 (WuXi Xingguang provided) was added into the solution under stirring. The mixed slurry was transferred to an Ultra Turrax IKA T18 Basic (IKA Instruments) and dispersed for 1 h at 4000 rpm, adsorption accelerants which could reduce the solubility of PSMA in the solvent were added into the slurry, PSMA was slowly deposited and encapsulate onto the pigment surface. The mixture was filtered under vacuum and dried at 45°C for 24 h in an oven, and then encapsulated pigment was obtained.

The dispersions were prepared with 5 g encapsulated pigments and 95 g distilled water, adjusted pH value to 8 using solution of sodium hydroxide, heated at 45°C and stirred by Ultra Turrax IKA T18 Basic for 30 min.

Particles size and stability of encapsulated pigment red 122 dispersion

The stability of encapsulated pigment dispersion was determined by centrifuging method and freeze-thaw method. Centrifuging method was done as reference.[12] Encapsulated pigment dispersion was centrifuged at 4000 rpm for 60 min, and then 0.03 g supernatant in the centrifugal tube was taken out and diluted into 2000 times with distilled water. Then absorbency A_{60} of the supernatant was measured by a spectrophotometer. A relativity absorbency r_{60} was calculated according to the following formula (2).

$$r_{60} = \frac{A_{60}}{A_0} \times 100\% \quad (2)$$

where A_0 is the absorbency of the dispersion before centrifuged, r_{60} can reveal the stability of dispersion which caused by weight, the larger r_{60}, the higher stability of dispersion is.

The pigment dispersion was sealed and placed at −5°C for 24 h and then put into oven at 50°C for another 24 h, the changing rate of particle size (T_d) was calculated according to the following formula (3).

$$T_d = \frac{|d_0 - d_T|}{d_0} \times 100\% \quad (3)$$

where d_0 is the starting particle size of dispersion, d_T is particle size of pigment dispersion after freeze-thaw treatment, the smaller T_d, the higher stability of dispersion is.

Encapsulated pigment dispersion was diluted 2000 times, adjusted pH = 8′ and then Z average particles size (particle size) and ξ-potentials were measured by Nano-ZS90 (Malvern Instruments).

Shape and size distribution of encapsulated pigment red 122 dispersion

The shape of pigment particle was observed by TEM (H-7000, Japan). The dispersion was diluted to 2000 times and then the size distribution of encapsulated pigment dispersion was measured by Nano-ZS90 (Malvern Instruments, England).

RESULTS AND DISCUSSION

Effect of copolymer structures on particle size and stability of encapsulated pigment dispersion

Molar content of maleic acid in PSMA could greatly affect on the particle size and stability of encapsulated pigment dispersion. Table I indicates that particle size decreased first and then increased with increasing molar content of maleic acid, r_{60} reached its maximum and d_T reached its minimum when molar content of maleic acid was at 0.43.

TABLE I
Effect of Molar Content of Maleic Acid on Pigment Particle Size and Stability of Encapsulated Pigment Dispersion[a]

Molar content of maleic acid (%)	Particle size (nm)	ξ–potentials (mv)	Stability	
			r60	dT
0.36	121.0	−25.5	95.6	8.0
0.39	114.1	−26.8	99.7	1.3
0.43	104.6	−30.2	100.0	0.7
0.45	106.0	−30.3	100.0	5.9
0.48	112.9	−30.0	99.2	21.2

[a] The weight ratio of PSMA to pigment was 10%.

When molar content of maleic acid in PSMA was lower than that of 0.43, the forces of electric repulsion and steric repulsion which produced by encapsulated layer was so small that some pigment particles could overcome the repulsive forces to reunite, thus led to large particle size and poor stability of pigment dispersion. On the other hand, when molar content of maleic acid was high enough, the forces between the PSMA and media would also be increased and then some PSAM would be easily peeled off from the pigment surfaces which also result in large particle size of pigment and poor stability of pigment dispersion. These phenomena could also be proved by changing of the ξ-potentials on pigment surface.

Moreover, molecular weight of PSMA was another important factor that would influence the pigment particle size and stability of encapsulated pigment dispersion. Encapsulated pigment dispersion used different intrinsic viscosity of PSMA as encapsulated layer were prepared. The particle size and stability of encapsulated pigment dispersion were shown in Table II.

Table II reveals that particle size of encapsulated pigment dispersion reduced first and then increased, and stability increased first and then decreased with increase intrinsic viscosity of PSMA. Particle size seemed to reach its minimum, and stability seemed to reach maximum when intrinsic viscosity of PSMA was at 79.65 mL/g. When intrinsic viscosity was

TABLE II
Effect of Intrinsic Viscosity of Copolymer on Pigment Particle Size and Stability of Encapsulated Pigment Dispersion[a]

Intrinsic viscosity [η] (mL/g)	Particle size (nm)	ξ–potentials (mv)	Stability	
			r60	dT
23.50	138.6	−25.3	97.8	5.8
38.41	132.1	−27.9	98.8	5.7
79.65	104.6	−30.2	100.0	0.7
98.35	120.5	−30.0	100.0	3.2
120.36	124.5	−30.2	98.0	8.7
164.20	128.6	−30.6	97.8	15.6

[a] The weight ratio of PSMA to pigment was 10%.

TABLE III
Effect of Amount of PSMA on Pigment Particle Size and Stability of Encapsulated Pigment Dispersion[a]

| Dosage of PSMA (wt %)	Particle size (nm)	ξ–potentials (mv)	Stability	
			r60	dT
4	183.7	−23.7	88.7	21.8
8	140.0	−28.2	98.7	6.8
10	104.6	−30.2	100.0	0.7
14	125.2	−32.6	100.0	0.9
18	149.0	−32.1	100.0	0.8

[a] The weight ratio of initiator dosage to monomers was 1.8%.

small, attractive forces among PSMA and pigment was low that some PSMA would be easily peeled off from pigment surface, which result in large particle size and poor stability, but when intrinsic viscosity of PSMA was higher than 79.65 mL/g, the viscosity of encapsulated pigment dispersion would increase greatly, which would reduce the wetting ability of encapsulated pigment, it could reduce the dispersing efficiency of encapsulated pigment, on the other hand, the long molecular chain might bridge two or more particles, all of these reason could lead to large particle size and poor stability.

Furthermore, amount of PSMA which encapsulated on the surface of pigment determines particle size and stability to a considerable degree. Table III indicates that particle size reduced first and then increased with increase amount of PSMA, stability were increased with increase the amount of PSMA at the range of 4–10%, and reached to 100% when the amount of PSMA was higher than that of 10%. The smaller particle size of quantitative pigment, the larger pigment surface area was which require more copolymer to encapsulation. On the other hand, when the amount of PSMA was high enough, a part of PSMA would disperse in the media which could increase the viscosity of dispersion rapidly, thus led to low dispersing efficiency. The data of ξ-potentials also reveal that the more amount of PSMA, the more
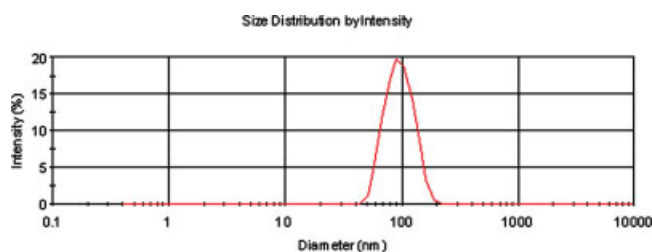
Figure 1 Particle size distribution of pigment dispersion used PSMA as encapsulated layer (the pigment was encapsulated by the copolymer which molar content of maleic acid was 0.43 and intrinsic viscosity was 79.65 mL/g with amount of copolymers 10%). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
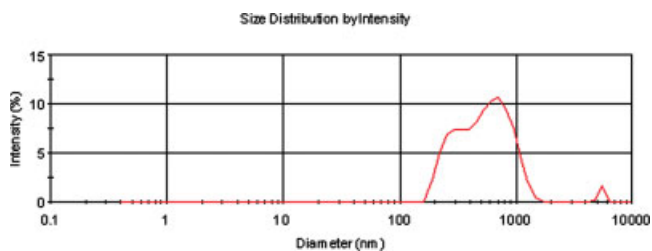
Figure 2 Particle sizes distribution of pigment dispersion used PSMA as dispersant (the pigment was dispersed using copolymer as dispersant which molar content of maleic acid was 0.43 and intrinsic viscosity was 79.65 mL/g with amount of copolymers 10%). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

PSMA encapsulated onto the pigment surface. The stability of dispersion can be explained by stokes formula, the larger particle size, the smaller viscosity of dispersion, the poorer stability was.

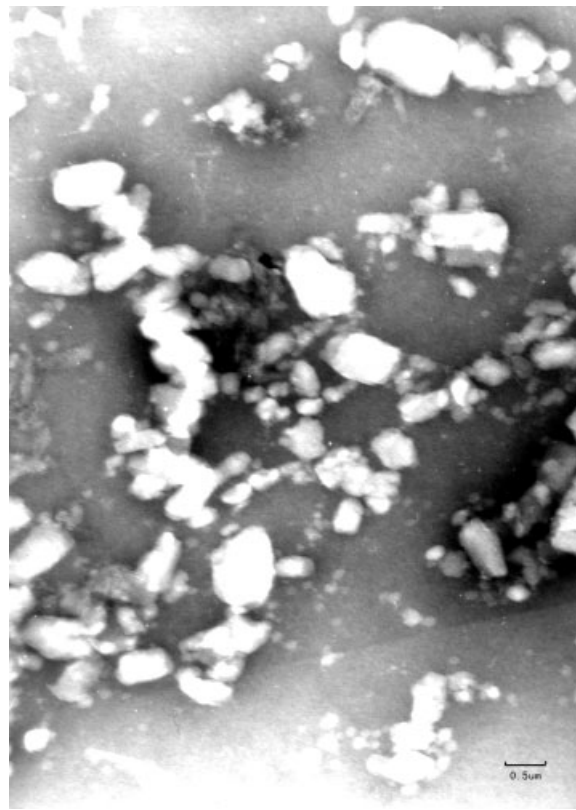### The shape and size distribution of encapsulated pigment particles

To acquire the pigment particle distribution of encapsulated pigment dispersion, particle size distri-bution was tested by DLS (as shown in Fig. 1). Particle size distribution of unencapsulated pigment dispersion was shown in Figure 2. Compared with Figures 1 and 2, it is obviously that the pigment particle size of encapsulated pigment dispersion was smaller than that of unencapsulated pigment dispersion; the average particle size was 98.4 and 680.2 nm respectively. Size distribution of encapsulated pigment dispersion was narrower than that of unencapsulated pigment dispersion, which indicated that the pigment particle distribution of encapsulated pigment dispersion was more uniform dispersed in aqueous media than that of unencapsulated pigment dispersion.

To full obtain information about the pigment particle of encapsulated pigment dispersion, the shape and the encapsulated layer of encapsulated pigment were observed by TEM (as shown in Fig. 3). Compared with unencapsulated pigment (as shown in Fig. 4), it can be seen that the particles of encapsulated pigment dispersion was uniformly dispersed with little aggregation or coagulation, on the contrary, the unencapsulated pigment was combined with each other. It was also obviously that every particles of encapsulated pigment dispersion was
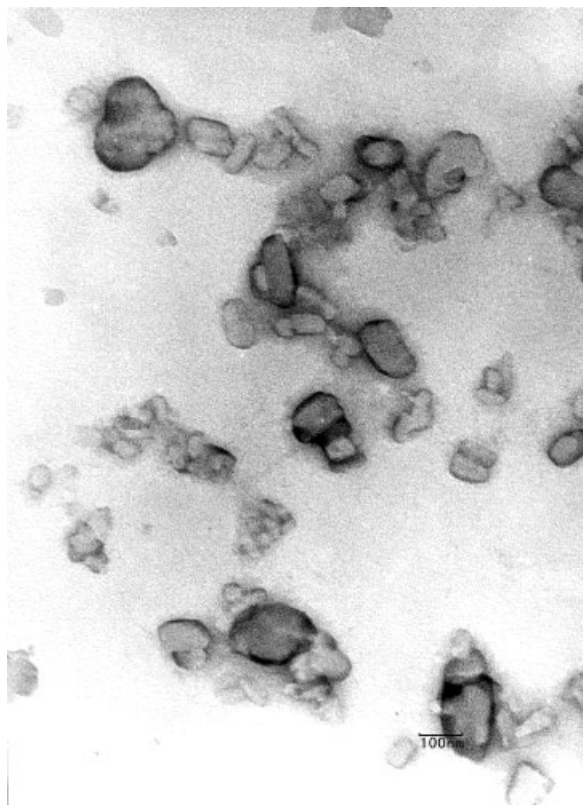
Figure 3 TEM photo of pigment dispersion used PSMA as encapsulated layer (the pigment was encapsulated by the copolymer which molar content of maleic acid was 0.43 and intrinsic viscosity was 79.65 mL/g with amount of copolymers 10%).

Figure 4 TEM picture of pigment dispersion used PSMA as dispersant (the pigment was dispersed using copolymer as dispersant which molar content of maleic acid was 0.43 and intrinsic viscosity was 79.65 mL/g with amount of copolymers 10%).

encapsulated by copolymers, the encapsulated layer was about 5 nm.

CONCLUSIONS

Copolymers of styrene and maleic acid were synthesized by free radical polymerization. The elliptoid shape of encapsulated pigment particles and narrow size distribution of pigment particles could be obtained with this copolymer by sedimentation.

Pigment particle size and stability of encapsulated pigment dispersion had closely related to the structure of copolymers and amount of copolymers. With increasing molar content of maleic acid, particle size decreased first and then increased and on the contrary, the stability of dispersion was increased first and then decreased. Moreover, particle size of encapsulated pigment dispersion reduced first and then increased, and stability increased first and then decreased with increase intrinsic viscosity of PSMA. Furthermore, particle size reduced first and then increased with increase amount of PSMA, stability were increased with increase the amount of PSMA at the range of 4–10%, and reached to 100% when the amount of PSMA was higher than that of 10%.

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