

Control of Particle Size and Carboxyl Group Distribution in Soap-Free Emulsion Copolymerization of Methyl Methacrylate–Ethyl Acrylate–Acrylic Acid

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ABSTRACT: Polymer microspheres with narrow size distribution and with carboxyl groups on their surfaces were synthesized by soap-free emulsion polymerization of methyl methacrylate (MMA), ethyl acrylate (EA), and acrylic acid (AA), and the distribution of –COOH in the latex was determined by conductometric titration. Effects of ingredients on polymerization, latex particle size (D_p), and its distribution, and the distribution of –COOH were investigated. Results showed that monomer conversion and the amount of embedded –COOH (E_a) decreased, and D_p increased with increasing amounts of NH_4HCO_3 . The amounts of surface –COOH (S_a) and water –COOH (F_a) and the number of

–COOH on each square centimeter of the particles' surface (S_d) increased with increasing amounts of NH_4HCO_3 and AA. With the increase of initiator (APS) and AA, D_p decreased. E_a increased with the increase of AA. F_a increased and then remained constant, and S_d decreased with the increase of initiator. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 433–438, 2004

Key words: particle size distribution; emulsion polymerization; distribution of carboxyl groups; conductometric titration; microstructure

INTRODUCTION

Functional polymer microspheres have been widely studied and used in biomedical and biochemical fields, material science, and information industries, to name but a few of their applications.^{1–3} Because many application properties of these particles are significantly influenced by the morphology and surface properties of the particles, interest has been increasingly focused on control of the particle size and its distribution and the control of the distribution of functional groups. In the 1980s, Ugelstad et al.⁴ invented a new process, designated two-step swelling method, to prepare monodisperse microspheres whose size larger than 1 μm . In the next decade, Okubo and coworkers⁵ synthesized monodisperse crosslinked polymer particles with vinyl groups by seeded emulsion polymerization of divinylbenzene using a dynamic swelling method, and submicron-sized polymer particles with multihollow morphology were also studied using the stepwise alkali/acid method.^{6,7} In our previous work, a series of monodisperse core/shell latex particles containing carboxyl groups were prepared by seeded emulsion copolymerization, and the influences of unsaturated acid, pH value, swelling agent, and crosslinking agent on the pore formation in seeded

latex particles were also studied. Results indicated that unsaturated carboxyl acid was necessary in the second step of polymerization to prepare porous latex particles in alkali/acid posttreatment.^{8–10} Recently, we found that the particle morphology and particle size distribution were also influenced by the type of initiator used in the second step and the swelling conditions in the two-stage emulsion polymerization.^{11–13}

In the field of functional latex particles, greater attention has been paid to microspheres with carboxyl groups because of their easy synthesis and functionalization. Shen et al.¹⁴ researched the effect of unsaturated acids with different degrees of water solubility on the distribution of carboxyl groups in latex. Guillaume and coworkers¹⁵ studied the influences of ingredients and conditions on the distribution of carboxyl groups in poly(styrene–butyl acrylate–methyl methacrylate) [P(St–BA–MAA)] and P(St–BA–potassium sulfo propyl methacrylate) latices. Using carboxyl groups-containing azoinitiator, Bastos et al.¹⁶ prepared carboxylated PSt latex to bind antibodies efficiently onto the surface of particles by chemical bond. Wang et al.¹⁷ characterized the distribution of carboxyl groups in P(St/AA) and P(St/MAA) latices using X-ray photoelectron spectroscopy and elemental analysis.

Until now, most of the functional polymer latex particles were usually prepared by traditional emulsion polymerization, in which the emulsifier could

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TABLE I
Emulsion Polymerization Recipe^a

MMA	EA	AA	APS	NH ₄ HCO ₃	H ₂ O
19	1	Variable	Variable	Variable	124

^a Unit: gram.

potentially confer a disadvantage to the application, and most of investigations focused primarily on the polymerization system of styrene (St). Compared to St, methyl methacrylate (MMA) is more hydrophilic, and it is supposed that PMMA particles with carboxyl groups on their surfaces may have many promising applications in the biomedical and biochemical fields. In this study, P(MMA-*EA-AA*) particles with narrow size distribution and with carboxyl groups on their surfaces were first synthesized by soap-free emulsion polymerization, and the effects of ingredients on the polymerization, particle size, and their distribution, as well as the distribution of carboxyl groups in the latex, were also investigated.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), ethyl acrylate (EA), and acrylic acid (AA) (all AP grade) (First Chemical Reagent Factory, Tianjin, China) were purified by distillation under reduced pressure and kept in the refrigerator. Ammonium persulfate (APS, AP grade) (Aijian Modern Reagent Factory, Shanghai, China) was purified by recrystallization twice in water before use. NH₄HCO₃, NaOH, and H₂SO₄ (all AP grade) (Beihua Fine Chemical Products Co., Ltd., Beijing, China) were used as received. Deionized water was distilled.

Soap-free emulsion polymerization

P(MMA-*EA-AA*) latices were synthesized in a 250-mL, four-neck, round-bottom flask equipped with a glass stirrer, thermometer, nitrogen/reagent inlet tube, and reflux condenser. At first, 100 mL deionized water was added to the reactor and the polymerization system was deoxygenated by bubbling with nitrogen for 15 min, then NH₄HCO₃ and the mixture of MMA, EA, and AA were added into the system according to Table I. The reactor was then immersed in the water bath in which the temperature was previously adjusted to 80°C, and stirring speed was controlled at around 300 rpm. APS dissolved in 24 mL deionized water was introduced in three steps at different polymerization times: 16 mL at the beginning, 4 mL at 4 h, and the last 4 mL at 6 h. After 7.5 h of polymerization, the polymerization was continued for an additional 0.5 h at 90°C.

Characterization

Monomer conversion was determined by gravimetry. The diameter (D_p) and morphology of latex particles were characterized on a Hitachi H-800 transmission electron microscope (TEM; Hitachi, Osaka, Japan) using phosphotungstic acid as a staining agent. The polydispersity of latex particles size was expressed as the quotient of the standard deviation (δ) of the particle diameter and D_p . The lesser the value of δ/D_p is, the narrower the size distribution will be. The number of particles per liter (N_p) was calculated based on D_p , monomer conversion, and polymer density.

The distribution of -COOH in the latex was determined by conductometric titration as follows: 4 mL of original latex was diluted with 24 mL of water and its solids content was measured by gravimetry method. The pH value of the diluted latex was first adjusted to 11.5 ± 0.02 using 0.385 mol/L NaOH solution, and then the latex was titrated with 0.0242 mol/L H₂SO₄ solution under the monitor of a DDS-307 conductometer (Leici, Shanghai, China). The amounts of surface -COOH (S_a) and water -COOH (F_a) corresponding to per gram polymer were calculated directly from conductometric titration curve, and the amount of embedded -COOH (E_a) inside the particles corresponding to per gram polymer was obtained from the difference between the initial charge of AA and the sum of S_a and F_a . The density of surface -COOH (S_d), defined as the average number of carboxyl groups on each square centimeter of particles' surface, was calculated as

$$S_d \text{ (cm}^{-2}\text{)} = \frac{S_a W_Y S_Y N_A}{V_Y N_p \pi D_p^2} \times 10^{14}$$

where W_Y , S_Y , and V_Y are the weight, solids content, and volume of the initial latex, respectively. N_A is the Avogadro constant.

RESULTS AND DISCUSSION

Influence of NH₄HCO₃ on the polymerization and latex properties

NH₄HCO₃ is a key material for the control of D_p and the distribution of -COOH in latex. The effect of NH₄HCO₃ on polymerization and latex properties is shown in Table II.

It has been well established that the thermal decomposition rate of APS decreases with the increase of pH and ionic strength of the polymerization system in acidic medium.¹⁸ The introduction of NH₄HCO₃ will certainly increase the pH value and enhance the ionic strength of the system. Thus, the thermal decomposition rate of APS will decrease with increasing amounts of NH₄HCO₃, thus leading to a decrease of monomer conversion when temperature and time of polymerization are given. From Table II it may be seen that the

TABLE II
Influence of NH_4HCO_3 Amount on Polymerization and Latex Properties^a

NH_4HCO_3 (g)	Conv. (wt %)	D_p (nm)	δ/D_p	N_p (10^{-15}L^{-1})	S_a (10^5mol/g)	F_a (10^5mol/g)	E_a (10^5mol/g)	S_d (10^{-15}cm^{-2})
0	97.51	306	0.009	9.80	32.74	25.01	8.04	1.01
0.10	96.70	317	0.011	8.34	36.90	23.42	8.79	1.17
0.20	97.23	367	0.014	5.53	39.15	25.53	3.65	1.45
0.30	95.22	383	0.015	4.79	41.96	26.66	2.85	1.62
0.40	95.77	391	0.008	4.51	43.07	27.38	2.63	1.71
0.50	94.66	420	0.006	3.38	45.58	29.27	1.94	2.08
0.60	91.40	461	0.017	2.55	47.82	34.11	1.52	2.34
0.70	90.68	517	0.012	1.85	48.47	34.69	0.78	2.54
0.80	89.30	525	0.017	1.77	51.34	35.26	0.33	2.79
0.90	83.37	585	0.019	1.18	52.14	36.99	0.12	3.16

^a AA: 1.00 g; APS: 0.285 g.

monomer conversion has a decreasing trend with increasing amounts of NH_4HCO_3 . When the amount of NH_4HCO_3 was more than 0.7 g, the monomer conversion was less than 90% and some coagulation appeared in the polymerization, and the resulting latices separated into two layers after a 2-week period of storage at room temperature.

The size of latex particles was also clearly affected by the amount of NH_4HCO_3 . One can see, from Figure 1, that D_p increased with increasing amounts of NH_4HCO_3 , and that a good linear relationship between D_p and the amount of NH_4HCO_3 may be observed. The experiment showed that the pH value of latex was less than 3 in the absence of NH_4HCO_3 , and most of the carboxyl groups existed in the form of $-\text{COOH}$. When NH_4HCO_3 was used in the system, the number of $-\text{COO}^- \text{NH}_4^+$ increased with the increase of NH_4HCO_3 . When APS was introduced, unsaturated monomers in aqueous phase were first initiated to form polymer radicals. Because the hydrophilicity of polymer chain radicals with $-\text{COO}^-$ is better than that of polymer radicals with $-\text{COOH}$, the length of the critical chain of polymer radicals with $-\text{COO}^-$ in-

creased, which led to the decrease of the number of primary particles. Moreover, because of the decrease of thermal decomposition rate of APS, the nucleation rate in the aqueous phase decreased, which resulted in the concomitant decrease of N_p and increase of D_p .

By combining TEM images (Fig. 2) with the value of δ/D_p (Table II), one can see that the latex particles with narrow size distribution were synthesized with different amounts of NH_4HCO_3 .

Influence of NH_4HCO_3 on the distribution of carboxyl groups

The distribution of carboxyl groups in the latex was also obviously influenced by the amount of NH_4HCO_3 (Table II). With increasing amounts of NH_4HCO_3 , S_a , F_a , and S_d increased and E_a decreased.

As mentioned earlier, because the length of the critical chain of polymer radicals with $-\text{COO}^-$ increased when the amount of NH_4HCO_3 increased, the amount of "dead" polymer molecules containing more AA units dissolved in water increased accordingly, which resulted in the increase of F_a . Furthermore, because the hydro-

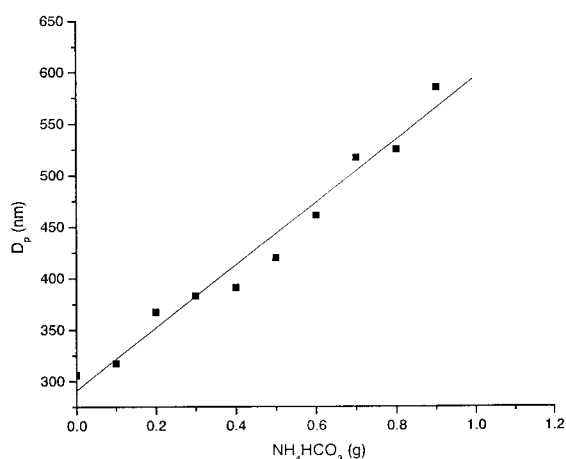


Figure 1 Relationship between D_p and amount of NH_4HCO_3 .

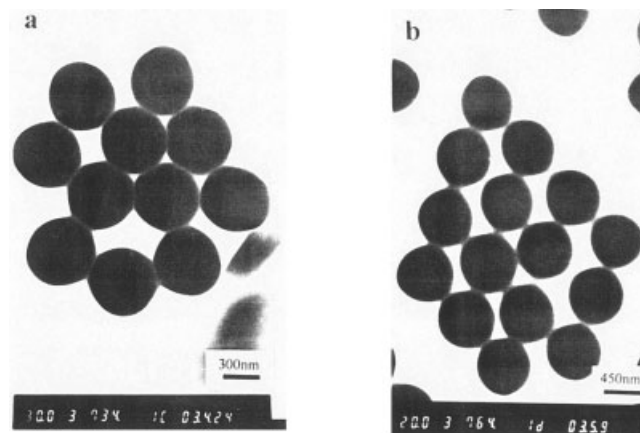


Figure 2 TEM micrographs of P(MMA-EA-AA) latex particles with different amounts of NH_4HCO_3 : (a) 0.50 g; (b) 0.80 g.

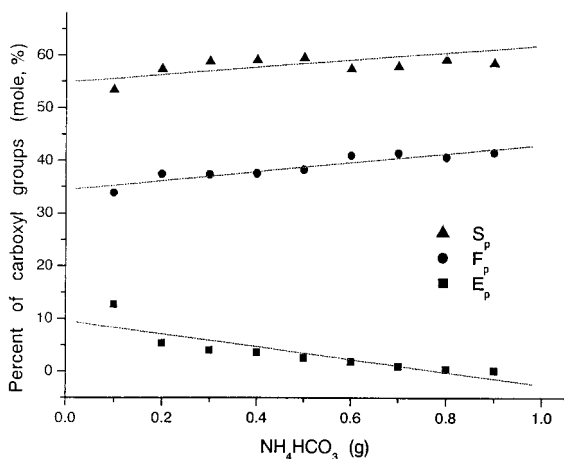


Figure 3 Distribution of carboxyl groups in MMA-EA-AA latex with different amounts of NH_4HCO_3 . S_p , F_p , and E_p represent, respectively, the percentage of carboxyl groups on the particles' surface, in the aqueous phase, and embedded inside particles.

philicity of $-\text{COO}^-$ is better than that of $-\text{COOH}$, the polymer chains containing $-\text{COO}^-$ had a higher ability of movement toward the surface of particles from inside of the particles based on the principle of thermodynamics, and so S_a and the density of surface functional groups (S_d) increased and E_a decreased.

The relationship between the percentage of $-\text{COOH}$ in different parts of the latex and amount of NH_4HCO_3 is shown in Figure 3. One can see that the percentage of surface $-\text{COOH}$ (S_p) and water $-\text{COOH}$ (F_p) showed an increasing trend, but the percentage of embedded $-\text{COOH}$ (E_p) decreased significantly with the increase of NH_4HCO_3 . Considering the value S_a , it may be one of the best methods to increase the surface $-\text{COOH}$ by adjusting the amount of NH_4HCO_3 used.

Influence of AA on the polymerization and latex properties

It has been found that the use of unsaturated monomer in emulsion polymerization can improve some properties of the resulting latex such as colloidal stability, mechanical and freeze-thaw stability, and affini-

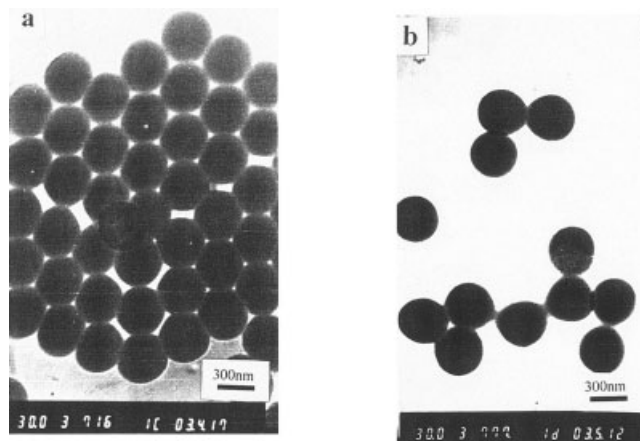


Figure 4 TEM micrographs of P(MMA-EA-AA) latex particles with different amounts of AA: (a) 0.8 g; (b) 1.2 g.

ty to biologically active molecules, for example.^{19,20} The results in this work are shown in Table III.

From Table III it may be seen that all the monomer conversions were more than 93% with different amounts of AA. When the amount of AA was less than 1.2 g, the monomer conversion increased with increasing amounts of AA, and the polymerization could proceed at a steady rate. When the amount of AA reached 1.2 g, a small amount of coagulation was produced in the polymerization, although the reaction could also be carried out steadily.

Because AA is a soluble monomer in water, aqueous nucleation was a dominant nucleation process in the MMA-EA-AA emulsion polymerization system. With increasing amounts of AA, the rate of nucleation and the number of polymerization sites increased, which certainly caused an increase in monomer conversion and a decrease in D_p . Table III indicates that δ/D_p values of all particles were very small, and Figure 4 confirms that the particles were spherical and had a narrow size distribution.

Influence of AA on the distribution of carboxyl groups

It may be observed from Table III that S_a , F_a , E_a , and S_d increased with increasing amounts of AA.

TABLE III
Influence of AA Amount on Polymerization and Latex Properties^a

AA (g)	Conv. (wt %)	D_p (nm)	δ/D_p	N_p (10^{-15} L^{-1})	S_a (10^5 mol/g)	F_a (10^5 mol/g)	E_a (10^5 mol/g)	S_d (10^{-15} cm^{-2})
0.60	93.79	333	0.010	7.19	24.17	20.58	1.26	0.81
0.70	94.89	321	0.011	8.13	24.61	20.62	4.85	0.88
0.80	95.35	316	0.009	8.67	27.67	23.50	6.22	0.92
0.90	96.48	310	0.011	9.15	29.52	24.81	7.71	0.96
1.00	97.51	306	0.009	9.80	32.04	25.89	8.92	1.01
1.20	96.85	298	0.013	10.50	36.27	26.84	10.48	1.07
1.40	96.81	283	0.016	12.02	52.25	39.06	16.98	1.51

^a APS: 0.285 g; NH_4HCO_3 : 0 g.

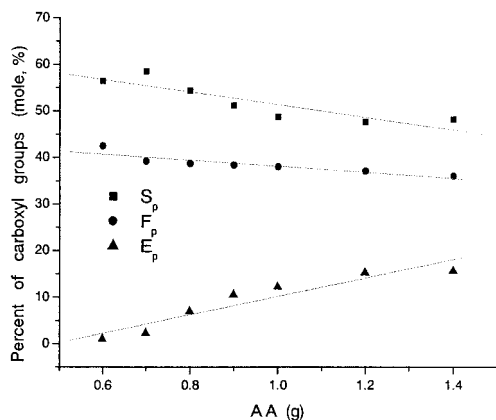


Figure 5 Distribution of carboxyl groups in MMA-EA-AA latex with different amounts of AA.

Because the generation rate of polymer radicals increased when the amount of AA in the aqueous phase increased, the monomer conversion increased and D_p decreased. Also, because the small D_p corresponds to large areas of the particles' surface, the probability of radicals entering into particles increased, thus causing S_a and E_a to increase. Although S_d increased with the increase of AA, the increment was smaller compared to that with NH_4HCO_3 because S_a and the area of per gram polymer increased at the same time.

Figure 5 indicates that the percentage of surface -COOH (S_p) and water -COOH (F_p) decreased slowly, but the percentage of embedded -COOH (E_p) noticeably increased with increasing amounts of AA. By comparing Figure 3 and Figure 5, it may be observed that the tendency of S_d was inverse, although S_a increased with increases of NH_4HCO_3 and AA, and the addition of AA would cause E_a to increase. Therefore, it is not an efficient way to increase the surface -COOH only by increasing the amount of AA.

Influence of initiator (APS) on the polymerization and latex properties

The initiator is of vital importance in soap-free emulsion polymerization because it not only initiates the polymerization but also stabilizes the latex. The effect

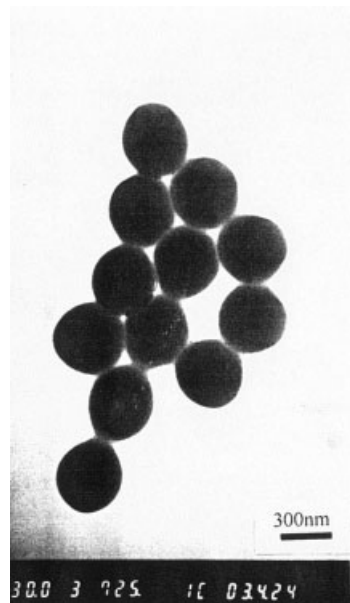


Figure 6 TEM micrograph of P(MMA-EA-AA) latex particles using 0.320 g APS.

of APS on polymerization and latex properties is shown in Table IV.

It is common knowledge that the increase of APS will increase the polymerization rate and monomer conversion. Given that APS is also an electrolyte, its excess would render latex unstable. When the amount of APS was greater than 0.528 g, the monomer conversion decreased and a small amount of coagulation appeared on the flask wall. Because the generation rate of free radicals and the concentration of polymer radicals in aqueous phase increased concomitantly with the increase of APS, the number of primary particles increased, which then led to an increase of N_p and a decrease of D_p .

The amount of APS had only a slight effect on the polydispersity of particle size. All the particles obtained were spheres and monodispersed (Fig. 6).

Influence of APS on the distribution of carboxyl groups

S_a showed a slight change with different amounts of APS, and F_a showed an increasing trend, after which it

TABLE IV
Influence of APS Amount on Polymerization and Latex Properties^a

APS (g)	Conv. (wt %)	D_p (nm)	δ/D_p	N_p (10^{-15} L^{-1})	S_a (10^5 mol/g)	F_a (10^5 mol/g)	E_a (10^5 mol/g)	S_d (10^{-15} cm^{-2})
0.208	91.36	321	0.014	7.44	30.58	26.86	10.21	1.02
0.285	97.51	306	0.012	9.80	32.74	25.01	8.04	0.98
0.320	97.61	302	0.009	9.92	31.80	29.09	5.90	0.95
0.425	99.65	296	0.010	10.85	32.26	30.68	5.93	0.92
0.528	98.63	293	0.011	11.04	33.49	30.56	6.00	0.89

^a AA: 1.00 g; NH_4HCO_3 : 0 g.

remained constant, whereas S_d decreased slowly as the amount of APS increased.

AA is more soluble than either MMA or EA in water. Because the generation rate of radicals in the aqueous phase increased with increasing amounts of APS, the polymer chain radicals containing AA segments and the probability of their collision increased; thus the "dead" polymers with carboxyl groups in water increased, causing an increase in F_a . Because D_p decreased with increasing amounts of APS (i.e., the total areas of latex particles increased), the probability increased that radicals would enter into the particles. As a result of the two reversed effects, F_a increased to a certain value when the amounts of APS reached >0.425 g. The decrease of S_d is mainly attributed to the increase of the areas corresponding to per gram polymer.

CONCLUSIONS

In this study, monodispersed latex particles with a "clean" surface were synthesized by soap-free emulsion polymerization of MMA, EA, and AA. The particle size can be well controlled in the range from 300 to 600 nm by adjusting the amount of NH_4HCO_3 used. The average number of carboxyl groups on the particles' surface can be adjusted in the range from 0.8 to $3.2 \times 10^{15}/\text{cm}^2$ by controlling the amounts of APS, NH_4HCO_3 , or AA used.

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