Role of Three Different Carboxylic Monomers in Acrylate Emulsion Copolymerization in the Presence of Reactive Emulsifier

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ABSTRACT: In this article, a series of carboxylated acrylate copolymer latices were prepared based on the semicontinuous emulsion polymerization via the pure monomer dropwise manner with three different kinds of carboxylic monomers in presence of reactive emulsifier. The effects of the carboxylic monomers [acrylic acid, methacrylic acid, and monobutyl itaconate (MBI)] on the conversion and the properties of acrylate latices and films have been investigated. The carboxylic groups (—COOH) distribution of these three kinds of latices were investigated as well. The results show that the concentration of surface —COOH (C_S) and embedded —COOH (C_b) both increase with the increase of the amount of carboxylic monomers. It shows that MBI, the most hydrophobic of the three carboxylic monomers used, tends to be concentrated inside the particle core, and the latex particles have a narrow size distribution. The results of common stability test have demonstrated that the stability of the latex is satisfactory. Moreover, the water absorption and the acid and alkaline resistance of the latex depend on the kind of carboxylic monomer. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 2807–2813, 2012

Key words: latices; emulsion polymerization; monomers; distribution

INTRODUCTION

Functionalized latices that can be produced through the emulsion polymerization have been widely studied.[1–3] Among the functionalized latices, the latex prepared with main acrylate monomers and other functional carboxylic monomers has been used in many fields such as coatings, biochemical, adhesion, and printing ink. Carboxylic monomers, such as acrylic acid (AA), methacrylic acid (MAA), itaconic acid, and fumaric acid (FA),[4–6] copolymerize to form functional latex and can improve the polymerization and colloidal stability, enhance the adhesive characteristics of latex on different substrates, and improve the mechanical properties, aging resistance of the films.[7–9] A few investigations[10,11] show that the properties of carboxylated latex are influenced by the hydrophilic nature of carboxylic monomers, the method of introduction, and the widely used emulsifiers. The behaviors of carboxylic monomers in the emulsion polymerization have been widely investigated,[12–14] including both the application perform-

ance and the homogeneous nucleation theory. Oliveira[1] reported the effect of IAs and FAs on the emulsion copolymerization of other acrylate monomers. The results put forward the method to determine the distribution of the carboxylic groups throughout the three phases of the latex, which depending on the solubility of the corresponding monomers. Kang[15] used AA as the carboxylic monomer in soap-free emulsion polymerization with MMA and ethyl acrylate. The report showed that the amount of emulsifier, initiator, and buffering agent would influence the latex particle size and the distribution of —COOH. Thus, the carboxylic group distribution would have large effects on the emulsion polymerization and application. However, the carboxylic group distribution under a reactive emulsifier has not been concerned since then, and it is a development trend that using a reactive emulsifier to improve the latex application performance.

In most of the studies of carboxylic acrylate emulsion polymerization, usage of some traditional emulsifiers or excessive use of emulsifiers will bring objectionable influence for application properties of the latex and film, while the reactive emulsifier provide a way of solution. The reactive emulsifier ammonium sulfate allyloxy nonylphenoxy poly (ethyleneoxy) (10) ether (DNS-86) is an anionic emulsifier which has an excellent emulsifying ability and high reactivity in emulsion polymerization. As

the double bond of this emulsifier can copolymerize with the other monomer and become a part of polymeric material, the DNS-86 can improve the latex performance and the appearance of films. Xiao[16] synthesized emulsifier-free fluorinated polyacrylate latex with core-shell structure and a narrow particle size distribution by a seeded emulsion polymerization in the presence of DNS-86. Inorganic–organic hybrid latex containing fluoride has been prepared by Qu[17] in multistage emulsion polymerization in the presence of DNS-86 and OP-10, and the distribution of fluorine in different latex films has been measured. With the emulsifier DNS-86 and two other kinds of emulsifiers, Meng[18] prepared an ambient self-crosslinking polymer acrylic microemulsion via a modified microemulsion polymerization. The results showed that compared with conventional microemulsions, the soap-free microemulsions showed fast drying speed and their films presented better water resistance. However, until now, no report has been seen that investigated the carboxylic group's distribution under a reactive emulsifier. Hence, this article decided to carry a research on the carboxylic group's distribution under a reactive emulsifier.

In this work, we use 2% of DNS-86 to the total amount of monomers to prepare acrylate latices with three different kinds of carboxylic monomers via polymerization technologies of pure monomer dropwise manner. The conversion of the monomers was studied to review the polymerization stability, and the influence of type and amount of different carboxylic monomers on the properties of latex and film such as the distribution of carboxylic group, particle size, stability of latex, and the resistance of water, acid, and alkaline were investigated.

EXPERIMENT

Materials

Methyl methacrylate (MMA; technical grade, Shanghai Gaoqiao Petrochemical, China), butyl acrylate (BA; technical grade, Beijing Dongfang Chemical, China), AA (reagent grade, Shanghai Enterprise Group Chemical Reagent, China), MAA (reagent grade), and monobutyl itaconate (MBI; reagent grade) were used as-received (from Qingxin Hanerchem Chemical Technology, China). Reagent grade ammonium persulfate (Shanghai Enterprise Group Chemical Reagent, China) and ammonium hydrogen carbonate (NH$_4$HCO$_3$; Shanghai Enterprise Group Chemical Reagent, China) were used as the initiator and the buffering agent, respectively. The emulsifier used in this work was the ammonium sulfate allyloxy nonylphenoxy poly(ethyleneoxy) (10) ether, abbreviated "DNS-86," was provided by Qingxin
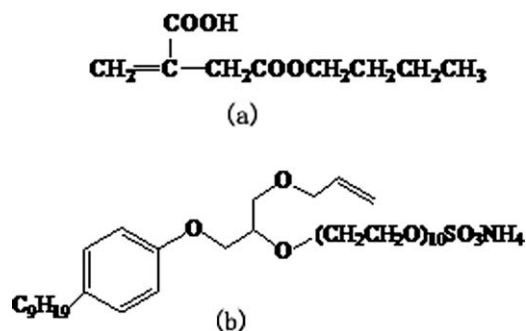
Scheme 1   The structures of (a) MBI and (b) DNS-86.

Hanerchem Chemical Technology, China, and used as-received. Deionized water (prepared by a special device in our college) was used in all the experiments. The scheme structure of DNS-86 and MBI is shown in Scheme 1.

Preparation of arcylate latices

Polymerization was carried out in a four-neck round-bottomed flask equipped with an electromotive stirrer, thermometer, addition funnel, and reflux condenser. A series of carboxylic acrylate latices with the theoretical solids content of 50% have been prepared based on semicontinuous emulsion polymerization via pure monomer dropwise manner.

A basic recipe can be found in Table I. The concentrations of carboxylic monomers in the polymer were varied from 1 to 5% based on the total amount of monomers. Here, all percent content means weight percent.

First, 30% of water was added into the flask. When the temperature reached to 82°C, a certain amount of emulsifier, 40% of initiator, and 30% of water, the entire buffering agent and a certain amount of mixed monomer solution were injected into the flask, respectively. All of the monomers (MMA, BA, and carboxylic monomers) based on the recipe were mixed and stirred uniformly in a cone-shaped bottle. The remaining mixed monomer solution and the rest of initiator solution were fed continuously over a period of 2.5 ~ 3 h. The mixed monomer solution was continuously stirred during the feeding stage. On completion of the feeding, polymerization was allowed to continue for an additional 1 h at 85 ± 1°C. At last, the emulsion was cooled down to room temperature. Coagulate-free and long-time stable latex with a particle diameter of about 110 nm was obtained.

Characterization

The solid content and conversion were measured by gravimetric analysis. A total of 1 ~ 2 g of latex was

TABLE I
Emulsion Polymerization Recipe

Component	Amount (g)
Monomers (the mass ratio of MMA/BA) (AA or MAA or MBI)	100 (45/53) (1 ~ 4; 1 ~ 4% of monomers)
DNS-86	2.0[a]
Ammonium persulfate	0.4[a]
NH$_4$HCO$_3$	0.006[a]
Deionized water	100

[a] Indicates the percent of total monomer weight.

casted onto a Petri dish and dried at 105°C to a constant weight. The solid content and the final conversion were calculated according to the normal way. Here, the conversion means the total conversion in a special carboxylic monomer, not for an individual monomer, but it contains the effect of the individual monomer on the conversion.

The amount of coagulum was measured by collecting the grit on the reactor wall and stirrer, and by filtering the latex. It is expressed as the weight of coagulum per total weight of monomer added.

Latex particles sizes were determined by means of light scattering using the Zetasizer 3 of Malvern with a He–Ne laser (632.8 nm, 5 mW), a photomultiplier, and an angle of 90°.

The distribution of ─COOH in the latex was determined by conductometric titration using conductivity meter (DDSJ-308A, Shanghai, China) and platinum black electrode (Constant Measure of the Conductivity Electrode was 0.96). The latex was diluted with water until the solid content was 1.5%, and the pH value of the diluted latex was adjusted to 11.5 using 0.09436 mol/L NaOH solution. Then, the latex was titrated with 0.0197 mol/L HCl solution. The amount of ─COOH on the surface of latex particles (C_s) and in the aqueous phase (C_f) corresponding to per gram polymer was calculated directly from conductometric titration curve, and the amount of buried ─COOH (C_b) inside the particles corresponding to per gram polymer was obtained from the difference between the initial charge of carboxylic monomer and the sum of C_s and C_f.

The freeze-thaw stability was determined by placing the latex in a freezer at −5°C for 18 h, and then at 20°C for 6 h. After five freeze-thaw cycles, the state of latex was observed and recorded.

Dilution stability was measured as follows: firstly the latex was diluted with water until the solid content was 3%, and then 100 mL of the diluted latex was placed in a graduated flask covered with aluminum foil and kept at 25°C for 72 h. Finally, the state of latex was observed and recorded.

Centrifugal stability was tested via centrifugal machine. Placing the latex into a centrifuge tube,

and centrifugate for 1 h at the speed of 12,000 rpm, the state of the latex was observed and recorded. If the latex was not demulsification, the test results would be pass.

Water absorption ratio was determined according to ASTM D570-8. The latex films were prepared by casting the copolymer latices onto a Petri dish and making the water evaporate slowly at room temperature. The dry test samples were 2.0 ± 0.10 cm in length, 1.5 ± 0.10 cm in width, and 0.60 ± 0.10 mm in thickness, which were soaked in the deionized water for a certain time, and then taken out. The excess water at their surface was gently removed using filter papers and the samples were weighed.

The swelling ratio of acid and alkaline of latices was measured as follows: the latex films were prepared by casting the copolymer latices onto a Petri dish and immersion into NaOH solution (1%) and HCl solution (1%) for 48 h, and then taken out. The excess water at their surface was gently removed using filter papers and the samples were weighed.

RESULTS AND DISCUSSION

The monomers conversion of copolymer latices

The reactive emulsifier DNS-86 has an excellent emulsifying ability and high reactivity on the latex and can improve the latex performance and the film appearance. The conversion of monomers as a function of the amount of carboxylic monomer was shown in Table II. It can be seen that different carboxylic monomers present different monomers conversion. Conclusively, the monomers conversions were above 94% and the reaction could also be carried out steadily. For the latex prepared with AA, the monomers conversion was relatively high when the amount of AA was 2 ~ 3%. The reason is that small amount of AA could not maintain the stability of latex and large amount of AA would self-polymerization easily at high amounts. That is, larger amount of AA may have a tendency toward homogeneous nucleation as more AA would stay in aqueous phase. Thus, the monomers conversion was low at the 1% AA and 4% AA, respectively. Then for the

TABLE II
Conversion of Monomers as a Function of the Amount of Functional Monomers

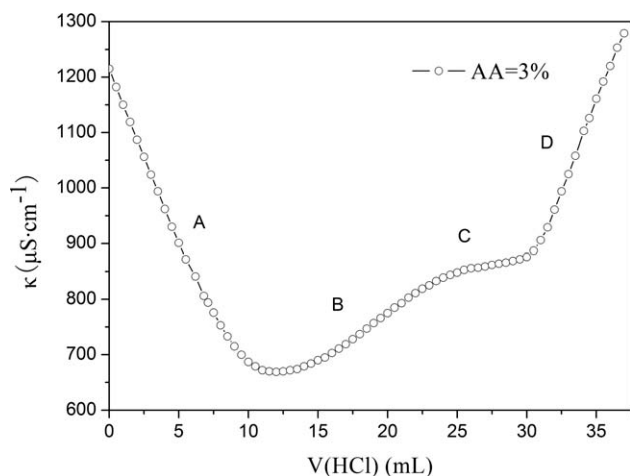| Functional monomers (%)	Conversion of monomers (%)		
	In AA presence	In MAA presence	In MBI presence
1	95.82	95.56	94.07
2	99.70	97.23	96.63
3	96.53	97.10	96.34
4	95.73	96.86	97.06

Figure 1 The typical conductometric titration curve of the latex.

latex prepared with MAA, the most adoptable amount of MAA was 2 ∼ 3%, the same as AA. In addition for the carboxylic monomer of MBI, the monomers conversions were increased as the monomer amount increased, which proved that the choose MBI as functional monomer can improve the stability of polymerization.

Carboxylic groups distribution in latices

The distribution of carboxylic groups in latices was important for the properties of latexes and films. Figure 1 shows the typical conductometric titration curve of the latex using 3% AA. The tendency of the curve conformed to other reports.[9,10] The curve can be distinguished into four parts: the decrease of conductance values in part A was attributed to neutralization of excess NaOH and the increase of part D was attributed to excess HCl, where part B and C were attributed to the neutralization of surface-bound carboxylate groups and free carboxylate groups in serum-phase, respectively.

According to the curve, C_s and C_f can be calculated directly. C_b can be calculated by materials balance of the total acid amount. Table III shows the distribution of acid of carboxylic group in the latices.

From the date list in Table III, we can see that the concentration of surface —COOH (C_s) and buried —COOH (C_b) increased with the increase of carboxylic monomers. At the same amount of three kinds of carboxylic monomers, the C_s of latex prepared with AA was higher than that of latex prepared with MBI, and the latex prepared with MBI got the lowest value of C_s. Increased the amount of AA from 1 to 5%, the C_s increased remarkably, in fact the value of C_s almost increased nine times.

Nevertheless the C_b of these three different latices presented the opposite tendency of C_s, which means that the C_b of latex prepared with AA was lowest, the C_b of latex prepared with MAA was higher than that of AA, and the latex prepared with MBI got the highest value. When the amount of carboxylic monomer was 1%, the C_b of the latices was about 15×10^{-5} (mol/g), while when the amount was increased to 5%, the C_b of the latices prepared with MAA and MBI were reach 51.93×10^{-5} (mol/g) and 58.66×10^{-5} (mol/g), which became two times than that of latex prepared with AA.

Concerning the C_f of the latex, we can see that the free acid in latex contained AA was slightly higher than the other two latices. With the increase of carboxylic monomer, the increasing extent of latex contained AA was larger than MAA and MBI, indicating that with the total amount of AA increased, the probability of homogeneous nucleus formation happened in aqueous phase increased as well, which brought out the higher free acid.

Conclusively, it can be known that the main factor for these phenomenons was the different degree of hydrophilicity among the carboxylic monomers. For these three kinds of carboxylic monomers, except for having carboxylic group and unsaturated double bond, the MBI also includes a butyl ester group, thus having the longer chain length than MAA and AA. From this point, we can know that the hydrophobic property of MBI was strongest, and the MAA was much more hydrophobic than AA analogical. During the polymerization process, carboxylic monomer with higher hydrophobic would get into the interior of particle, polymerized with other monomer, and become a part of particle. For the carboxylic monomers which have good

TABLE III
Effect of Acid Monomer on Carboxylic Groups Distribution in Acrylate Latexes

Carboxylic monomer (%)	C_s (10^5 mol/g)			C_b (10^5 mol/g)			C_f (10^5 mol/g)		
	AA	MAA	MBI	AA	MAA	MBI	AA	MAA	MBI
1	5.36	3.24	3.06	14.04	15.26	15.57	1.83	2.29	3.41
2	11.13	9.88	3.80	23.73	28.03	32.56	6.65	3.36	5.42
3	31.79	18.34	10.60	27.60	30.45	47.62	13.29	3.43	7.54
4	48.84	19.20	14.39	28.83	51.93	58.66	14.33	7.45	9.80

TABLE IV
The Particle Size and Polydispersity Index of Latex Particles

Carboxylic monomer (%)	Particle size (nm)			Polydispersity index		
	AA	MAA	MBI	AA	MAA	MBI
1	106.0	108.5	110.0	0.020	0.032	0.007
2	111.5	108.5	107.0	0.032	0.021	0.011
3	109.0	108.0	108.0	0.030	0.008	0.020
4	108.5	106.0	110.5	0.023	0.032	0.046

hydrophilicity, they would inclined to homogeneous nucleation in the aqueous phase. Therefore, the carboxylic groups of AA tend to stay into particle surface and in aqueous phase, the carboxylic groups of MBI tend to get into the interior of particle, and the carboxylic groups of MAA tend to stay between AA and MBI.

Latex particle size

The particle size data of the latexes prepared with three different carboxylic monomers are shown in Table IV. From the particle size data listed in Table IV, we can see that the particle size of all latices was ranged from 106 to 112 nm, and the polydispersity indexes were all less than 0.1, indicating that the particles exhibit a narrow distribution. The nearly homogeneous particle size was evidential for the good polymerization stability of the reactive emulsifier DNS-86. From these phenomena, we also can propose the polymerization technology, which can be prepared by the latex with controllable particle size.

Stability test

Excellent stability for latex is very important and necessary. Stability tests were carried out according to the methods described in the experimental, and

Table V shows the amount of carboxylic monomer on the stability of latex. As we know, the use of emulsifier and the distribution of carboxylic groups would influence the stability of latex. For the polymerization stability, as the amount of carboxylic monomer increased, the amount of coagulum was decreased, which indicated that the introducing of carboxylic groups can enhance the stability of polymerization. In the dilution stability test, all of the latices have no laminate; while some of them have a few macroparticles appeared. These phenomenon maybe attributed to the depressed concentration of emulsifiers could not maintain the stability between particles after dilution. Furthermore, the freeze-thaw and centrifugal stability of most latices were excellent, no flocculated and laminate were observed during the test except the latex contained MAA at the 3 ∼ 4% amount, which occurred to water and oil layers after the first cycle of freeze-thaw.

From Table V results, it can be found that the carboxylic monomers effects on the polymerization, dilution, freeze-thaw, and centrifugal stability are different. The reason might be that the different stability has different stable mechanism. To understand these thoroughly, further studies will be carried out later on.

Water absorption

Table VI shows the influence of different types and amount of carboxylic monomers on the water absorption of the latex films. We can see that the carboxylic group distributed on the surface of particle was the main factor of the water absorption. The latex films would get a poor water resistance when the carboxylic monomers were import excessive. For the latices prepared with AA, the water absorption was about 5% when the amount of AA was lower than 3%, then the water absorption increased as the AA amount increased. Then, for the latex prepared

TABLE V
The Stabilities of Latexes as a Function of the Levels of Carboxylic Monomers

Carboxylic monomer (%)		Polymerization stability (%)	Dilution stability	Freeze-thaw stability	Centrifugal stability
AA	1	1.22	No laminate and no insoluble matter	5	Pass
	2	0.76	No laminate and no insoluble matter	5	Pass
	3	0.35	No laminate, few macroparticles	5	Pass
	4	0.33	No laminate, few macroparticles	5	Pass
MAA	1	1.04	No laminate, few macroparticles	5	Pass
	2	0.51	No laminate, few macroparticles	5	Pass
	3	0.37	No laminate, few macroparticles	2	Pass
	4	0.35	No laminate, few macroparticles	2	Pass
MBI	1	2.21	No laminate and no insoluble matter	5	Pass
	2	0.5	No laminate and no insoluble matter	5	Pass
	3	0.69	No laminate, few macroparticles	5	Pass
	4	0.53	No laminate, few macroparticles	5	Pass

with MAA and MBI, the water absorption was about 7 ∼ 8%, and when the carboxylic monomer increased, the value was changed in a small range.

Generally speaking, the more of the C_s in the latices particles, the larger the water absorption of latex films would be. From the distribution of carboxylic groups listed in above paragraphs, the C_s of latex prepared with AA was increased significant, while the water absorption data listed here were not increased remarkably as expected. The reason is that the emulsifier DNS-86 is a reactive emulsifier, and it can copolymerize with the main monomer and become covalently bound to form an integral copolymeric material. Therefore, there is nearly no emulsifier DNS-86 to migrate to the film surface, resulting the latex film containing more AA in surface adsorbs less water and the water resistance is quite well. Moreover, the low water absorption is an indirect evidence that the reactive emulsifier DNS-86 has been copolymerized into the acrylate copolymer. From this point of view, we can know that besides the amount of carboxylic monomer, the characteristic of emulsifier was another impotent factor to determine the water resistant of latex film.

Absorption of acid and alkaline

The data of swelling ratio to acid and alkaline of latices were listed in Table VII. From Table VII, we can see that the latex films having good acid resistance could be prepared using these different kinds of carboxylic monomers. With the amount of carboxylic monomer changed, the swelling ratio of latex varied within 5% and could maintain at low level.

Nevertheless, for the swelling ratio of alkaline, the different kind of carboxylic monomer using in the polymerization brought different degree of resistance. In the range of carboxylic monomer amount, the latex film prepared with MBI presented the best resistance to alkaline and the latex prepared with AA was the poorest. For latex film prepared with AA, when the amount of AA was increased from 2 to 3%, and for latex film prepared with MAA, when the amount of MAA was increased from 3 to 4%, the swelling ratio both increased very significant.

TABLE VI
Water Absorption of Latexes as a Function of the Levels of Carboxylic Monomers

Carboxylic monomer (%)	Water absorption (%)		
	AA	MAA	MBI
1	5.98	8.07	5.99
2	5.31	7.08	7.12
3	7.14	8.13	6.90
4	8.24	7.47	8.52

TABLE VII
The Swelling Ratio of Latexes as a Function of the Levels of Carboxylic Monomers

Carboxylic monomer (%)	The swelling ratio of acid (%)			The swelling ratio to alkaline (%)		
	AA	MAA	MBI	AA	MAA	MBI
1	4.73	4.53	4.88	5.45	5.16	4.64
2	5.13	4.72	5.26	6.06	4.91	5.24
3	5.43	5.41	4.56	59.14	8.95	4.89
4	5.38	4.58	4.56	96.74	55.75	5.41

This phenomenon illustrated that for AA and MAA system, the excessive carboxylic groups would lead poor resistance of latex film to alkaline, but for the carboxylic monomer of MBI, use of it can lead latex film with good resistance to acid and alkaline.

CONCLUSIONS

In this work, a series of carboxylic acrylate latices with the theoretical solids of 50% have been prepared based on semicontinuous technique via pure monomer dropwise manner by using the reactive emulsifier DNS-86. The emulsion polymerization has been carried out smoothly with the conversions all above 94%, and the latex prepared with different kinds of carboxylic monomers present discrepant characteristics. Conductometric titration shows that C_s and C_b increase continuously with the increase of the amount of carboxylic monomers. The degree of carboxylic monomer hydrophobicity was ordered as MBI > MAA > AA. In addition, the particle size has a nearly narrow distribution. The freeze-thaw, centrifugal, and dilution stability of most latex were excellent. Moreover, the latex prepared with MBI and MAA has relatively satisfied water resistance and the latex contained AA was relatively worse. All of the films presented excellent acid resistance. For the resistance to alkaline, the film contain MBI presented the best while the film contain AA was the poorest. Overall, both the types of carboxylic monomer and reactive emulsifiers play an important role in determining of particle size, carboxylic distribution, and many other properties of latices and films.

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