

Effect of Water-Soluble Monomers on Emulsifier-Minor Emulsion Polymerization of Butylacrylate–Methacrylic Acid–Styrene and Properties of the Latices

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Received 22 October 2004; accepted 17 April 2005

DOI 10.1002/app.22560

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The stability of emulsifier-minor emulsion polymerization and the final latices depends on whether water-soluble monomers can be bound to the particle after polymerization, which relies on the hydrophilicity of the water-soluble monomers. Less hydrophilic monomers are apt to be buried in the latex particle, but extremely hydrophilic monomers tend to homopolymerize in the water phase. The suitable hydrophilic index I/O of water-soluble monomers is preferably 3–5. The adhesion power and water resistance of emulsifier-minor latex films are better than that

of conventional latex film, but the impact resistance and gloss of the former are poorer. The gloss and water resistance of the emulsifier-minor latex films are relevant to the type of water-soluble monomers. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 796–801, 2006

Key words: emulsifier-minor emulsion polymerization; BA-MMA-St; carboxylic monomers; water-soluble monomers; effect

INTRODUCTION

Emulsifiers play a crucial role in emulsion polymerization. However, they have some adverse effects, as follows. First, they can cause foaming during application and processing of latices; Second, once the latices have been applied as films, the emulsifiers can migrate to the film–air surface, which affects the film gloss, and can also migrate to the film–substrate interface, which lowers film adhesion. Third, low-molecular-weight emulsifiers bring about poor water resistance. Besides, there can be further problems during processing of latices; for example, they may migrate to other phases or react with other ingredients when mixed with other ingredients, and they can desorb under the influence of the high shear, which causes destabilization. To avoid the above shortcomings, importance has been attached to emulsifier-free emulsion polymerization. Unfortunately, it is very difficult to obtain stable emulsifier-free latices with high solid contents, which is a requisite for coatings, adhesives, etc. In fact, the small amount of emulsifiers is very important for the production and application of coatings, adhesives, etc., for instance, for the wetting of substrates and dispersion of pigments. We studied a novel emulsion polymerization technique referred to as emulsifier-minor emulsion polymerization, where the dosage of

emulsifier is very small and slightly more than its cmc.¹ This work was undertaken to attempt to reveal the effect of the types of water-soluble carboxylic monomers and nonionic monomers on emulsifier-minor emulsion polymerization of butylacrylate–methacrylic acid–styrene and properties of the lattices.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), butylacrylate (BA), methacrylic acid (MAA), acrylic acid (AA), hydroxyethylacrylate (HEA), and hydroxypropylacrylate (HPA) were produced by Beijing Dongfang Chemical. Styrene (St) was produced by Qilu Petrochemical. Itaconic acid was produced by Qingdao Langyatai Group. Maleic anhydride (MA), *N*-hydroxymethyl acrylamide (*N*-MA), acrylamide (AM), ammonium persulfate (APS), and sodium bicarbonate were produced by Tianjin Institute of Chemical Reagent. All the above materials, sodium alkylated diphenyl ether disulfonate (France Rhodacal, abbreviated DSB), and TiO₂ R-930 were purchased from Qingzhou Pada Chemical. Various coating aids (Henkel aids) were supplied by Shenzhen Ocean Power Industrial. All materials were used as received.

Latices synthesis

The emulsifier-minor latices were synthesized by semicontinuous emulsion polymerization. The synthesis was performed in a four-neck 250-mL flask

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TABLE I
Recipe for Synthesis of the Latices

No.	Feed name	Weight (g)
I	Styrene (St)	15.5
	Methyl methacrylate (MMA)	40.5
	Butyl acrylate (BA)	42.5
II	Emulsifier (DSB; 50 wt %)	0.1–0.40
	Deionized water	100.0
	Water-soluble nonionic monomers	0–3.0
	Water-soluble carboxylic monomers	0–3.0
III	Ammonium persulfate	0.4
	Sodium bicarbonate	0.4
	Deionized water	30.0

equipped with a mechanical stirrer, a thermometer, a reflux condenser, and two dropping funnels. The stirring rate was kept constant at 150 rpm throughout the synthesis. The reaction temperature was controlled using a thermostatted water bath. According to the recipe listed in Table I, portion II composed of 0.1–0.4 g DSB, 100 g deionized water, 0–3 g water-soluble carboxylic monomers, and 0–3 g water-soluble nonionic monomers, and one third of portion I composed of 15.5 g St, 40.5 g MMA, and 42.5 g BA were added to the flask. The contents were pre-emulsified by stirring and heated. Upon heating to 80°C, one third of portion III composed of 0.4 g APS, 0.4 g sodium bicarbonate, and 30 g deionized water was then added and held for 30–90 min until monomer droplets on the flask wall disappeared. The remainder of portions I and III were then added dropwise from separate dropping funnels to the reactor at a temperature of 80 to 85 °C over a period of 1.5 h. After addition of all the ingredients, the reaction temperature of 80 to 85°C was maintained for an additional 2 h. Then, the contents were cooled to ambient temperature and neutralized with ammonia to pH 7.5–8.0. Finally the product was obtained by screening the coagula with 300-mesh screen. The coagula were dried until constant weight at 100–105°C in an oven for determining the stability during polymerization.

Analysis of the latex properties

Viscosity of latices was measured at 23 to 25°C by a NDJ-1 rotary viscometer (Shanghai Scale Instrument Manufacturer).

The total monomer conversion and the solid content of latices were determined gravimetrically.

The mechanical stability of latices (MS) was tested by a XR-14 latex high-speed mechanical stability testing machine (Chengde Testing Machine). A total of 50 g of latices passed through a 300-mesh screen was charged into the vessel and stirred at 14,000 rpm for 5 min and then passed through a 300-mesh screen to separate the coagula produced during stirring. The

coagula were dried until constant weight at 100 to 105 °C in an oven. The mechanical stability is represented by the weight percentages of the dry coagula based on the latices; higher value indicates poorer stability.

The stability of latices during polymerization (PS) is represented by the weight percentages of the dry coagula formed during polymerization based on all monomers.

The stability of latices against electrolytes (ES) was tested by the process as follows. A total of 5 mL of latices was discharged into a test tube, and then 1 mL of aqueous solution of 5 wt % anhydrous calcium chloride was added to the test tube under shaking. After the addition, the test tube was shaken for an additional 1 min and left standing for 48 h. If flocculation and phase separation of the contents during 48 h occurs, stability against the electrolytes is poor; if not, stability is good.

Particle size was measured by dynamic light scattering employing a Malven zetasizer 3000HS particle sizer.

The content of carboxyl group on the latex particle was measured by ion-exchange-conductimetric titration using a DDS-11A conductivity meter (Shanghai Analysis Instrument Manufacturer).

Preparation of latex coatings

The formulation of latex coatings is listed in Table II.

A total of 50 g of R-930 TiO₂, 2 g of the dispersant (SN-Dispersant 5040), and 50 mL of deionized water were charged into a 200-mL sand mill, ground for 1 h, and then filtered with a 300-mesh screen and thickened with SN-Thickener 612 to obtain a white pigment paste. A total of 16.5 g of the white pigment paste, 66 g of latices, and a small amount of defoamer (Nopco 8034) were added into a 150-mL beaker under stirring. The mixture was stirred for 15 min and filtered with a 300-mesh screen. Finally, the coating was obtained by thickening the mixture with SN-Thickener 612.

Measurement of the properties of coating films

Glass transition temperature (T_g) was measured with a Netzsch DSC204 differential scanning calorimeter

TABLE II
Formulation of Latex Coatings

Feed name	Weight percent (%)
White pigment paste (49 wt %)	33.0
Latices (50 wt %) ^a	66.0
Defoamer Nopco 8034	Little
Thickener SN-612(40 wt %)	Little

^a If solid content is lower than 50 wt %, the amounts of latices are increased based on equivalent solids.

TABLE III
I and O of Some Groups

Groups	—O—	—OH	—CH ₂ —or—CH ₃ —	C ₆ H ₅ —	—COO—	—COOH	—COONH ₄	—CONH—
I	20	100		15	60	150	400	250
O			20	100				

and heated from -50 to 100°C at a rate of $20.0^{\circ}\text{C}/\text{min}$ under N_2 atmosphere.

Coating films were prepared by casting latex coatings on standardized galvanized iron sheets and dried in ambient temperature for 7 days. The coating films were used to evaluate the properties of the coating films.

Adhesion power was evaluated with a QFZ adhesion testing machine (Tianjin Weida Testing Machine Manufacturer). Impact resistance was evaluated with a QCJ film impact testing machine (Tianjin Weida Testing Machine Manufacturer). Gloss was measured at 45° reflectance with a KJI-1B glossmeter (Tianjin Weida Testing Machine Manufacturer).

The clear film of latices for water absorption test was cast on a glass panel and allowed to dry and age in air under 20 to 25°C and about 50% relative humidity for 7 days and then removed from the substrate using a razor blade. The thickness of the film was about 0.5 mm. The water absorption test was carried out by immersing the film specimen (dimensions: $20 \times 20 \times 0.5\text{mm}$) in deionized water at 24 to 25°C . The film specimen was carefully removed from the water at different time intervals, and the water on the surface was absorbed by touching it with a filter paper. The swollen films were immediately weighed and then immersed in the same water again and again. Water absorption was calculated from the increase in film weight during the soaking period.

Hydrophilic index (I/O) of the water-soluble monomers

Japanese scholars put forward the concept of inorganic value (abbreviated I) and organic value (abbreviated O).² They claimed that the characteristics of all organic compounds are between pure inorganic and pure organic property, and this property may be represented by I and O. The larger the I/O of a compound is, the stronger its inorganic property is, that is, the more water-soluble and more hydrophilic.² The concept was used to evaluate the water solubility and hydrophilicity of the water-soluble monomers. The I and O of relevant groups and monomers are listed in Tables III and IV, respectively.³ The data in parentheses are after neutralization with ammonia. Maleic anhydride is hydrolyzed to be maleic acid in hot water; therefore, the I and O of MA was that of maleic acid.

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RESULTS AND DISCUSSION

Effect of water-soluble monomers on stability

In emulsifier-minor emulsion polymerization, stability of the latex particle depends on whether water-soluble monomers can be bound to the particle after polymerization, which relies on the type and dosage of water-soluble monomers.

Effect of carboxylic monomers

The effect of carboxylic monomers AA, MAA, IA, and MA loading on emulsifier-minor emulsion polymerization was investigated in the presence of 2.0 wt % N-MA and 0.1 wt % of DSB based on all monomers. As seen in Tables V to VIII, the levels of carboxylic monomers have a great effect on emulsifier-minor emulsion polymerization, and both the lower and the higher lead to destabilization and even complete coagulation. The level of AA and MAA is preferably 1.0 – 1.5 wt %, and that of IA and MA is preferably 0.5 – 0.75 wt % on the basis of all monomers. During the above levels, the

TABLE IV
I and O of Relevant Water-Soluble Monomers

Water-soluble monomer	I	O	I/O
AA	150 (400)	40	3.75 (10.00)
MAA	150 (400)	60	2.50 (6.67)
IA	300 (800)	60	5.00 (13.33)
MA	300 (800)	40	7.50 (20.00)
N-MA	300	60	5.00
AM	200	40	5.00
HEA	160	80	2.00
HPA	160	100	1.60

Note. Data in parentheses are after neutralization with ammonia.

TABLE V
Effect of AA Loading on Polymerization

AA (wt %)	0.5	1.0	1.5	2.0
ES	Good	Good	Good	
PS (%)	3.4	0.8	0.9	Coagulation
MS (%)	< 0.05	< 0.05	< 0.05	
Viscosity (mPa · s)	200	240	1660	
Conversion (%)	96.1	98.4	98.2	
Particle size (dp/nm)	145.3	132.1	137.1	

Note. ES, stability against electrolyte; PS, stability during polymerization; MS, mechanical stability.

TABLE VI
Effect of MAA Loading on Polymerization

MAA (wt %)	0.5	1.0	1.5	2.0
ES	Good	Good	Good	Good
PS (%)	3.4	0.7	0.4	2.1
MS (%)	< 0.05	< 0.05	< 0.05	< 0.05
Viscosity (mPa · s)	200	265	1120	1160
Conversion (%)	96.5	98.8	98.0	96.6
Particle size (dp/nm)	145.3	145.3	142.0	141.1

stability during polymerization and the mechanical and electrolytic stability of the final latices are good. By copolymerizing with the main monomers, the hydrophilic carboxylic monomers can be located on the particle surface, which can form a hydrate layer that exhibits a steric effect to prevent particle coagulation. In addition, after neutralization with ammonia, the ionized carboxyl groups on the particle surface also provide an electrostatic repulsion to further enhance the stability of the final latices. The lower levels of carboxylic monomers contribute to insufficient stabilization. However, the carboxylic monomers tend to homopolymerize in water phase and form water-soluble oligomers, which result in increased viscosity of the contents. The higher the dosage of the carboxylic monomers, the larger the viscosity of the contents, which affects adversely the mass and heat transfer of the contents, which, in turn, leads to destabilization. This is confirmed by the data as shown in Table IX where the contents of carboxylic groups on the particle surface increase with increasing dosage of carboxylic monomers, but the ratio of the calculated contents of carboxylic groups/determined on the particle surface decreased rapidly with increasing dosage of carboxy-

TABLE VII
Effect of IA Loading on Polymerization

IA (wt %)	0.25	0.5	0.75	1.0
ES	Good	Good	Good	Good
PS (%)	2.3	1.4	1.3	2.2
MS (%)	< 0.05	< 0.05	< 0.05	< 0.05
Viscosity (mPa · s)	75	78	88	75
Conversion (%)	93.0	94.3	94.3	93.7
Particle size (dp/nm)	163.4	163.9	171.1	168.0

TABLE VIII
Effect of MA Loading on Polymerization

MA(wt %)	0.25	0.5	0.75	1.0
ES		Good	Good	Good
PS (%)	Coagulation	1.6	1.9	2.5
MS (%)		< 0.05	< 0.05	< 0.05
Viscosity (mPa · s)		50	50	50
Conversion (%)		94.9	94.7	93.9
Particle size (dp/nm)		193.2	210.9	211.10

TABLE IX
Effect of Dosages of Carboxylic Monomers on the Contents of Carboxylic Groups on the Latex Particles

—COOH-monomers (wt.%)	Calc.content (mol/g×10 ⁵)	Deter.content (mol/g×10 ⁵)	Deter:Calc (%)
MAA			
1.0 wt %	11.83	2.57	21.72
1.5 wt %	17.64	3.89	22.05
AA			
1.0 wt %	14.13	2.50	17.69
1.5 wt %	21.09	2.96	14.04
MA			
0.5 wt %	10.44	1.78	17.05
0.75 wt %	15.61	1.83	11.72
1.0 wt %	20.76	1.73	8.33
IA			
0.25 wt %	4.58	1.11	24.24
0.50 wt %	9.13	1.43	15.66
0.75 wt %	13.66	1.72	12.59
1.0 wt %	18.17	1.77	9.74

lic monomers, which reveals that more carboxylic monomers are homopolymerized in water phase (provided the amount of carboxylic monomers buried in the latex particle is unchanged). The optimal dosage of AA and MAA is larger than that of IA and MA; this may be because the molecules of AA and MAA contain only one carboxylic group, but IA and MA contain two carboxylic groups. The stability during polymerization using AA or MAA was better and the particle size was smaller than when MA and IA were used, which may be attributed to the greater hydrophilicity of IA and MA as shown in Table IV, which results in a greater tendency to homopolymerize in the water phase. This is also confirmed by the results that the contents of carboxylic groups on the particle surface with IA and MA are lower than that with AA and MAA, as shown in Table IX.

Effects of water-soluble nonionic monomers

The effect of the levels of water-soluble nonionic monomers *N*-MA, HEA, HPA, and AM on emulsifier-minor emulsion polymerization was tested in the presence of 0.1 wt % of DSB and 1.5 wt % of MAA based on all monomers. As can be seen in Tables X to

TABLE X
Effect of *N*-MA Dosage on Polymerization

<i>N</i> -MA (wt %)	0.5	1.0	1.5	2.0	3.0
ES	Poor	Poor	Good	Good	Good
PS (%)	1.6	0.8	0.5	0.2	2.4
MS (%)	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Viscosity (mPa · s)	75	240	650	885	1400
Conversion (%)	97.2	98.0	98.8	98.3	95.7
Particle size (dp/nm)	142.4	135.6	136.1	140.1	133.8

TABLE XI
Effect of HEA Dosage on Polymerization

HEA(wt %)	1.0	2.0	2.5
ES	Poor	Poor	Poor
PS (%)	7.2	11.4	7.2
MS (%)	< 0.05	< 0.05	< 0.05
Viscosity (mPa · s)	60	200	240
Conversion (%)	90.3	94.5	94.7
Particle size (dp/nm)	167.5	163.2	173.3

XII, stability during polymerization and electrolytic stability of the final latices using HEA and HPA are poorer and the latex particle size is coarser than when *N*-MA and AM were used. The water-soluble nonionic monomers are bound to the particle surface after polymerization, which form a hydrate protective layer to exhibit steric stabilization. A steric stabilization caused by the hydrate protective layers are almost unaffected by electrolytes, and this is responsible for the better electrolytic stability of the latex with water-soluble nonionic monomers. Table IV shows that the I/O of HEA and HPA is less than that of *N*-MA and AM; that is, the hydrophilicity of the former is less than that of the latter. Therefore, the HEA and HPA are apt to be buried in the latex particle and have difficulty binding to the particle surface, which leads to poorer stability and coarser particle size.

The levels of *N*-MA and AM have also a great effect on stabilization (Table 13). The hydrate protective layer is not full with a lower amount of *N*-MA and AM, which leads to decreased electrolytic stability and stability during polymerization. As with AA and MAA, *N*-MA and AM tend also to homopolymerize in the water phase, which adversely affects stabilization, so that the higher dosage brings about poor stability during polymerization.

The above results show that water-soluble monomers must have suitable hydrophilicity to obtain good stabilization. Less hydrophilic monomers tend to be buried in the latex particle, and extremely hydrophilic monomers tend to homopolymerize in the water phase, which brings about poor stabilization. The hydrophilic index I/O of water-soluble monomers should be preferably 3–5.

TABLE XII
Effect of HPA Dosage on Polymerization

HPA (wt %)	1.0	2.0	2.5	3.0
ES	Poor	Poor	Poor	Poor
PS (%)	8.1	8.9	5.5	4.3
MS (%)	< 0.05	< 0.05	< 0.05	< 0.05
Viscosity (mPa · s)	105	60	60	60
Conversion (%)	91.2	90.3	91.5	93.2
Particle size (dp/nm)	156.3	162.9	173.2	158.0

TABLE XIII
Effect of AM Amount on EM Polymerization

AM (wt %)	0.5	1.0	1.5	2.0
ES	Poor	Poor	Good	Good
PS (%)	0.2	0.4	0.2	0.5
MS (%)	< 0.05	< 0.05	< 0.05	< 0.05
Viscosity (mPa · s)	50.0	88	1013	1400
Conversion (%)	98.3	98.2	98.5	98.3
Particle size (dp/nm)	132.6	133.0	135.8	144.3

Effect of types of water-soluble monomers on the properties of emulsifier-minor latices

Effects on the water resistance of latex film

The water resistance of latex film is represented by the water absorption of latex film. The higher the water absorption, the poorer the water resistance. The effect of the types of carboxylic monomers on the water resistance of the latex film was tested in the presence of 0.1 wt % of DSB and 2.0 wt % of *N*-MA based on all monomers. The results are listed in Figure 1, which shows that the water resistance of the emulsifier-minor latex film is relevant to the types of carboxylic monomers. By comparison of the I/O of the carboxylic monomers shown in Table IV and the results of the water absorption tests, it is found that the water absorption of the film is related to the hydrophilicity of carboxylic monomers used, the larger the I/O of the carboxylic monomers; that is, the greater their hydrophilicity, the poorer the water resistance of the film. The water resistance of the film is unchanged obviously using AM instead of *N*-MA.

Effect on the film properties

As can be seen in Table XIV, the adhesion power of the emulsifier-minor latex films is better than that of the

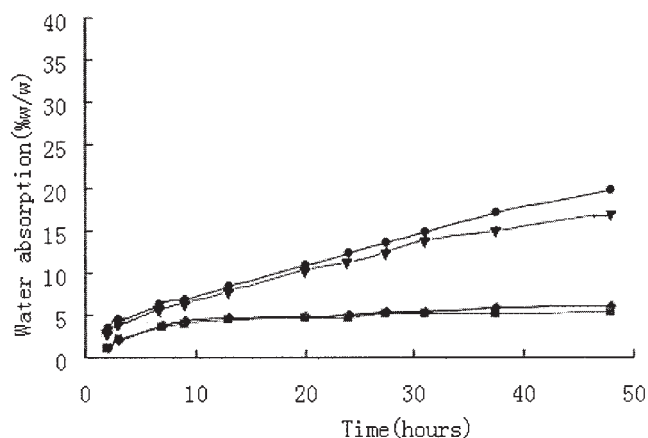


Figure 1 Effect of the type of carboxylic monomer on water resistance of emulsifier-minor latex films. (▼) IA, 0.7%; (■) MAA, 1.5%; (▲) AA, 1.5%; (●) MA, 0.75%.

TABLE XIV
Property Comparison between the Emulsifier-Minor and Conventional Films

Latex type	Water-soluble monomers (wt %)	Particle size (nm)	Impact resistance (N · cm)	Gloss (45°)	Adhesion (grade)	T_g (°C)
EML ^a	AA1.0, N-MA2.0	132.1	>440	54–55	1–2	13.4
	MAA1.5, N-MA2.0	142.0	>440	54–56	1–2	17.8
	IA0.75, N-MA2.0	171.1	>440	50–52	1–2	15.4
	MA0.75, N-MA2.0	210.9	>440	40–41	1–2	15.8
	MAA1.5, AM2.0	144.3	>440	48–49	1–2	12.5
CL ^b	AA3.0	122.0	>490	57–58	2–3	14.7

^a Emulsifier-minor latex.

^b Conventional latex.

conventional latex film, which is attributed to a very small amount of emulsifier in the emulsifier-minor latex, but the impact resistance and gloss of the former are poorer than that of the latter. The gloss of the emulsifier-minor latex films is relevant to the type of water-soluble monomers. By comparison of the film gloss and latex particle size, it is found that the film gloss depends on latex particle size; that is, the smaller the latex particle size, the better the film gloss. The particle size of the conventional latex is smaller than that of the emulsifier-minor latices, which results in higher film gloss of the former. The particle size of the emulsifier-minor latices with a combination of MA (or IA) and N-MA is coarser than that of the latex with a combination of AA (or MAA) and N-MA, which brings about the poor film gloss of the former. This may be because a latex with smaller particle size forms a film with smaller vacancy among latex particles. Although the particle size of the emulsifier-minor latex using AM instead of N-MA was small, the film gloss was poor too. Experimental phenomena showed that this was because some grit formed during the latex coatings.

CONCLUSIONS

The types of water-soluble carboxylic monomers and nonionic monomers have great effects on the stabilization of emulsifier-minor emulsion polymerization

and properties of latex films. To fix water-soluble monomers on the particle surface, which results in stabilization, the monomer must have suitable hydrophilicity. Less hydrophilic monomers are apt to be buried in the latex particle, but extremely hydrophilic monomers tend to homopolymerize in the water phase, which brings about destabilization. The suitable hydrophilic index I/O of water-soluble monomers is preferably 3–5. The adhesion power and water resistance of the emulsifier-minor latex films is better than that of conventional latex film, but the impact resistance and gloss of the former is poorer than that of the latter. The gloss and water resistance of the emulsifier-minor latex films are relevant to the type of water-soluble monomers. The particle size of the emulsifier-minor latices using a combination of AA (or MAA) and N-MA is close to that of conventional latex, which makes the film gloss as good as that of conventional latex film. Using excessively hydrophilic water-soluble monomers will result in latex film with poor water resistance.

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