

STABILITY OF EMULSIFIER-FREE EMULSION COPOLYMERIZATION OF METHYL METHACRYLATE/ BUTYL ACRYLATE/SODIUM MONO(ETHYL POLYOXYETHYLENE) MALEATE

Mao-gen Zhang, Zhi-xue Weng, Zhi-ming Huang and Zu-ren Pan*
Institute of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

Abstract A series of new water-soluble bifunctional comonomers having both carboxyl and alkyl polyoxyethylene groups, such as sodium mono(ethyl polyoxyethylene) maleate (ZE series) with various molecular weights of polyoxyethylene ethyl ether, were synthesized and characterized. The effects of the structural factor, the amount and feeding mode of the comonomers, the initiator concentration and polymerization temperature on the stability of emulsifier-free emulsion copolymerization of methyl methacrylate (MMA) and butyl acrylate (BA) in the presence of a small amount of ZE with potassium persulfate as initiator were investigated. Stable, almost monodispersed MMA/BA/ZE emulsifier-free latex particles were prepared.

Keywords Emulsifier-free emulsion polymerization, Stability, Monodispersed particle

INTRODUCTION

Much attention has been paid to the emulsifier-free emulsion polymerization (EFEP) as a newer process of emulsion polymerization in recent years^[1, 2]. Academic and practical interests have prompted the study of the stability, nucleation mechanism, and the preparation of clean products having monodispersed latex particles. One of the key problems in EFEP is to select appropriate comonomers and polymerization techniques so as to enhance the stability of emulsifier-free latex (EFL).

It is known that ionic and polar nonionic comonomers can enhance the stability of EFL. However, few works were concerned with comonomers having both ionic and nonionic groups on a same comonomer molecule. It would be expected that such a comonomer would significantly enhance the stability of latex particles since both ionic and nonionic surfactants were usually used to protect the latex particles in the traditional emulsion polymerization.

When water-soluble comonomers (WSC) were used in EFEP, they often damaged the stability of EFL, because coagulation of the particles usually occurred^[3, 4]. Consequently, the uneasily homopolymerizable but easily copolymerizable double-bonded comonomer should be selected. Maleic anhydride (MAn) is difficult to homopolymerize (maximum degree of polymerization is only 29), but copolymerizes readily^[5]. Maleate has similar behavior as MAn. For example, monoethyl maleate (EM) which is analogous to ZE structurally, has the reactivity ratio of $r_{\text{MMA}} = 0.94$, $r_{\text{EM}} = 0.30$, and $r_{\text{BA}} = 0.59$, $r_{\text{EM}} = 0.64$ calculated from Q and e value of MMA ($e = 0.4$, $Q = 0.74$), BA ($e = 0.53$, $Q = 0.43$) and EM ($e = 1.52$, $Q = 1.23$)^[6], indicating that EM is less active

* Corresponding author: Zu-ren Pan (潘祖仁), E-mail: wengzx@public.hz.zj.cn
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in homopolymerization, but is higher active in copolymerization.

In this paper, a series of new water-soluble bifunctional comonomers (WSBC) having both carboxyl and alkyl polyoxyethylene groups, such as sodium mono(ethyl polyoxyethylene) maleate (ZE comonomer series) with various molecular weight of polyoxyethylene ethyl ether, were designed and synthesized based on the investigation of sodium mono(polyethylene glycol) maleate (I or ZA comonomers series)^[7], and were used in the EFEP of MMA/BA. ZE is a modification in structure of ZA. The effects of the structural factor, the amount and feeding mode of ZE, the initiator concentration and polymerization temperature on the stability of emulsifier-free emulsion copolymerization of MMA/BA in the presence of a small amount of ZE will be investigated.

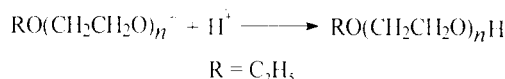
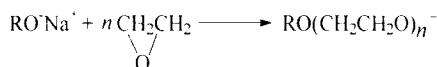
EXPERIMENTAL

Raw Materials

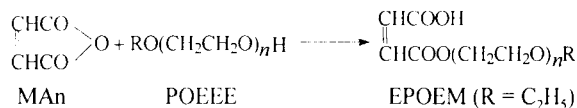
Methyl methacrylate (MMA) and butyl acrylate (BA) were of chemical pure grade and purified by distillation under reduced pressure before use. Ammonium persulfate (APS, analytically pure grade) used as initiator was recrystallized from water. Maleic anhydride (MAN) was of analytically pure grade.

Synthesis and Characterization of New Comonomers

Polyoxyethylene ethyl ether (POEEE) was synthesized as follows:



Mono(ethyl polyoxyethylene) maleate (EPOEM) was synthesized from MAN and POEEE:



Sodium mono(ethyl polyoxyethylene) maleate (ZE comonomers series) were prepared from the neutralization of EPOEM as follows:



POEEE was synthesized from the polymerization of ethylene oxide with sodium ethoxide/ethanol as initiator by the chemical factory affiliated to Zhejiang University. The product was neutralized, then made slightly acidic with glacial acetic acid, and then purified. The acid value, hydroxide value J and water content etc. of the purified product were measured. The number average molecular weight M_n of POEEE was calculated from J :

$$M_n = m \times 56.1 \times 1000/J \quad (1)$$

where m is the functional degree of polyether, and $m = 1$. The results are shown in Table 1, where n is the average degree of polymerization of polyoxyethylene.

Table 1. Parameters of POEEE

POEEE	Acid value	Hydroxyl value	Water content (wt%)	M_n	n
POEEE200	6.71	227	0.09	247	4.6
POEEE400	3.23	132.6	0.06	423	8.6
POEEE600	5.57	93.0	0.06	603	12.7
POEEE1300	0.51	42.15	0.05	1331	29.2

EPOEM can be synthesized from MAn and POEEE at moderate temperature, such as below 100°C, wherein the molar ratio of MAn to POEEE should be controlled precisely to decrease side products. In order to avoid the sublimation of MAn, a small amount of tetrahydrofuran that can be removed afterwards can be added into the reaction.

The EPOEMs prepared from POEEE200, POEEE400, POEEE600 and POEEE1300 (the number approximately denotes the average molecular weight of the polyether) were designated as EPOEM-2, EPOEM-4, EPOEM-6 and EPOEM-13, respectively.

The ZEs prepared from EPOEM-2, EPOEM-4, EPOEM-6 and EPOEM-13 were designated as ZE-2, ZE-4, ZE-6 and ZE-13, respectively, and were made into solutions with certain concentration.

The structure of ZEs were characterized by IR and ¹H-NMR and identified to be the target macromolecular monomers.

Polymerization

The EFEP of MMA/BA/ZE was carried out in a batch or semicontinuous process. The reactor was a 500 mL, double walled and four-necked glass kettle equipped with a stirrer, condenser, nitrogen inlet and thermometer. All of the monomers, comonomer solution and de-ionized water were added into the flask at the beginning, then the APS solution was added to initiate the polymerization in the batch process. In the semicontinuous process, the ZE solution was added dropwise just after the addition of the initiator solution. The reaction product in the kettle was filtrated to separate the coagulum from the latex after the reaction was completed.

Characterization

The average particle diameter and particle size distribution (PSD) of the latex products were measured by Coulter LS230 laser particle size analyzer which was calibrated with several standard latexes and powder samples of different sizes, and also by transmission electron microscopy

(TEM). The average particle diameter was characterized by $D(4, 3) = \frac{\sum_{i=1}^k n_i D_i^4}{\sum_{i=1}^k n_i D_i^3}$,

where n_i is the number of the particles having particle diameter D_i . The PSD can be observed directly by the PSD scheme given by the computer linked to the analyzer, or be characterized by

the monodispersity index, $U = D(4, 3) / D(1, 0)^{[8]}$, wherein $D(1, 0) = \frac{\sum_{i=1}^k n_i D_i}{\sum_{i=1}^k n_i}$. The

smaller the U value (tends to 1.000), the narrower the PSD, the better is the monodispersity of the latex particles.

The polymerization stability in EFEP is characterized by the weight percent of coagulum in terms of theoretical copolymers or total monomers, m_c . The smaller the m_c , the better the polymerization stability:

$$m_c(\text{wt}\%) = \frac{W_{\text{coagulum}}}{W_{\text{monomers}}} \times 100\% \quad (2)$$

The latex electrolyte resistance stability (LERS) is characterized by the volume of 1.0 wt% CaCl₂ aqueous solution needed to get coagulum from 20 mL of latex with 10% of solid content. Thus, 20 mL of latex with 10% of solid content was put into a 100 mL beaker, then a 1.0 wt% CaCl₂ solution was added dropwise at a certain rate under electromagnetic agitation until creamy coagulum appeared. The greater the volume of the CaCl₂ solution consumed, the better the LERS of the latex.

The latex storage stability (LSS) is characterized by the state of the latex after storage for a month at room temperature and is classified as AA-excellent, A-good, B-fair, C-little precipitate,

easy to redisperse, D-a few precipitate but can be redispersed and E-much precipitate and difficult to redisperse.

The latex centrifugal stability (LCS) is characterized by the volume of clear liquid obtained from 5 mL latex after centrifugation at 4000 rpm for 3 min. The smaller the volume of the clear liquid, the better the LCS.

RESULTS AND DISCUSSION

Effect of Structural Factor of Comonomer on Latex Stability

Latex stability can be enhanced by the addition of water-soluble polymers and/or oligomers (WSO) in EFEP owing to the formation of solvated layers of water-soluble components on the surface of the polymer particle^[2]. However, there is a possibility of decreasing latex stability by the addition of WSO, which can be attributed to the interaction between WSO and the surface of the polymer particles, as a result of the interaction of water-soluble macromolecule with some particles by forming a globule-resin-globule type bond^[2]. This indicates that there are two incompatible aspects for the effect of WSO on latex stability.

Therefore, the chain length of polyether in water-soluble ZE comonomer should be considered. The effect of the chain length of polyether in ZE comonomers on the stability of MMA/BA/ZE EFL is shown in Table 2.

Table 2. Effects of polymerization degree of polyethylene glycol in ZE on the stability of MMA/BA/ZE batch EFEP*

Comonomer	m_c (wt%)	D (4, 3) (nm)	U	LSS	LCS (mL)	LEERS (mL) (1% CaCl ₂)
ZE-2	0.76	474	1.065	B	0.40	15.93
ZE-4	9.86	747	1.061	D	1.0	7.48
ZE-6	2.09	534	1.053	C	0.50	14.52
ZE-13	8.77	702	1.065	D	0.95	10.18

* MMA, 20 g; BA, 20 g; H₂O, 160 g; the amount of ZE, w (ZE), and the amount of initiator APS, w (APS), being 1.0 wt% and 0.68 wt%, respectively, based on monomers; 70°C; 250 rpm; these are the general conditions used in this work

There seems no pattern for the effect of the chain length of polyether in ZE comonomers on the stability of MMA/BA/ZE EFL, similar to that for the ZA series^[7]. However, it can be found that the polymerization stability, LSS, LCS and LEERS are better, and the average particle diameter D (4, 3) are smaller for the latexes with ZE-2 and ZE-6 comonomers than those for other systems, also similar to the ZA series in which ZA-2 and ZA-6 are better for the stabilization of the latex^[7].

This can be explained as follows. The spatial effect of carboxyl-nonionic comonomers (CNIC) increase with an increase in the chain length of polyether in CNIC molecule. Consequently they are more favorable to copolymerization than to homopolymerization, and are in favor of increasing hydrophilic protective layers on particle surface so as to increase the latex stability. On the other hand, the molecular weight of the water-soluble homopolymers or copolymers enriched with the comonomers increases simultaneously with increasing the chain length of polyether in CNIC molecule, and they are easy to cause chain tangle and bridging coagulation. In a word, an appropriate chain length of polyether in CNIC molecule is needed for the stabilization of latex particles.

Effect of Comonomer Concentration on Latex Stability

The effect of the amount of ZE comonomers on the stability of MMA/BA/ZE-2 EFL is shown in Table 3.

The polymerization stability, LSS, LCS and LEERS of the latexes are first increased and then decreased, while D (4, 3) are first decreased and then increased with an increase in the amount of

ZE comonomers. The participation of ZE comonomers in the copolymerization can cause the formation of hydrophilic protective layers on the particle surface. The protection of the hydrophilic layers increases with an increase in the amount of ZE comonomers, resulting in an increase of latex stability. However, ZE homopolymers or WSO enriched with ZE will simultaneously be increased with an increase in the amount of ZE comonomers, which favors chain tangle and bridging coagulation, leading to worse stability and larger average particle size.

Table 3. Effect of the concentration of ZE-2 on the stability of MMA/BA/ZE-2 batch emulsifier-free emulsion copolymerization

w (ZE-2) (wt%)	m_c (wt%)	D (4, 3) (nm)	U	LSS	LCS (mL)	LEERS (mL) (1% CaCl_2)
0	2.32	497	1.069	D	0.45	15.18
0.5	0.98	481	1.062	B	0.44	15.80
1	0.76	474	1.065	B	0.40	15.93
2	6.64	555	1.133	D	0.52	14.75
4	13.49	858	1.457	E	1.10	13.58

Effect of Feeding Mode of Comonomer on Latex Stability

The comonomers with double bond of maleate type are still homopolymerizable in aqueous solution^[7] though they are difficult to homopolymerize. If a semicontinuous feeding mode is used for ZE comonomers so as to decrease its instantaneous concentration in aqueous solution, the latex stability would be increased by increasing the uniformity of ZE in copolymer and its surface fraction on latex particles.

Table 4. Effect of feeding mode of comonomer on the properties of P(MMA/BA/ZE) EFL^{a)}

ZE	Feeding mode of ZE	m_c (wt%)	D (4, 3) (nm)	U	LSS	LCS (mL)	LEERS (mL) (1% CaCl_2)
ZE-4	Batch	9.86	747	1.061	D	1.0	7.48
ZE-4	41.38 mL/h ^{b)}	2.45	498	1.060	B	0.45	16.40
ZE-6	Batch	2.09	534	1.053	C	0.50	14.52
ZE-6	40.68 mL/h ^{b)}	3.72	498	1.057	B	0.45	31.50
ZE-13	Batch	8.77	702	1.065	D	0.95	10.18
ZE-13	40.68 mL/h ^{b)}	4.74	514	1.058	C	0.47	58.60

a) w (ZE), 1.0 wt% based on monomers; b) ZE was fed dropwise in 1.0 wt% aqueous solution

This is determined by experimental results. The effect of feeding mode of ZE comonomers on the polymerization stability, LSS, LCS and LEERS of the latexes is shown in Table 4, in which ZE is added once in the batch process and added dropwise in the semicontinuous process. It can be found that the latex prepared from the semicontinuous process has better polymerization stability, LSS, LCS and LEERS, smaller D (4, 3) and narrower PSD.

Comparison of the Effect of ZE and ZA on Latex Stability

The structure of ZE is a modification of ZA. The comparison of the effect of ZE and ZA with similar chain length of polyether on the stability of MMA/BA/CNIC EFL is shown in Table 5.

Table 5. Stability of MMA/BA/ZE and MMA/BA/ZA batch EFEP^{*}

Comonomer	m_c (wt%)	D (4, 3) (nm)	U	LSS	LCS (mL)
ZA-2	0.65	492	1.783	B	0.45
ZE-2	0.76	474	1.065	B	0.40
ZA-4	15.17	801	2.308	D	1.05
ZE-4	9.86	747	1.061	D	1.0

* w (comonomer), 1.0 wt% based on monomers

The polymerization stability are both very good for the EFL with ZA-2 and ZE-2 comonomers. The other properties for the EFL with ZE comonomers are better than those with ZA comonomers, indicating that the modification for ZA has some expected effects.

Effect of Initiator Concentration on Latex Stability

The effect of the amount of initiator, APS, on the stability and particle size of MMA/BA/ZE EFL is shown in Table 6.

Table 6. Effect of the amount of initiator on the properties of P(MMA/BA/ZE-2) EFL*

w (APS) (wt%)	m _c (wt%)	D (4, 3) (nm)	U	LSS	LCS (mL)	LERs (mL) (1% CaCl ₂)
0.51	1.62	495	1.120	B	0.45	15.58
0.68	0.76	474	1.065	B	0.40	15.93
0.86	2.52	492	1.058	B	0.45	15.50
1.03	5.88	501	1.146	C	0.46	14.88

* w (ZE-2), 1.0 wt% based on monomers

It can be found that the polymerization stability, LCS and LERS of the latex are increased and then decreased, and D (4, 3) is decreased and then increased with an increase in the amount of initiator.

The effect of the initiator concentration, C_{in}, on the stability of EFL is related to the electrostatic factor, and is important for the stability. The ionic groups from initiator fragments are bonded to the end of macromolecules and most of them lie on the particle surface. The surface charge density (SCD) of the latex particles is in direct ratio to C_{in}^[9]. The critical coagulative concentration of latex particles is significantly related to its SCD^[10]. The persulfate initiator is itself an electrolyte of low molecular weight, which will affect the stability and size of latex particles. The average particle size is usually decreased and then increased with increasing C_{in}^[11]

In conclusion, the EFL has the best polymerization stability and LERS, smallest particle size and narrowest PSD in an appropriate initiator concentration.

Effect of Polymerization Temperature on Latex Stability

The effect of polymerization temperature on the stability and size of MMA/BA/ZE emulsifier-free latex particles is shown in Table 7.

Table 7. Effect of polymerization temperature on the properties of (MMA/BA/ZE-2) EFL*

T (°C)	m _c (wt%)	D (4, 3) (nm)	U	LSS	LCS (mL)	LERs (mL.) (1% CaCl ₂)
70	0.76	474	1.065	B	0.40	15.93
75	0.43	461	1.064	B	0.35	16.28
80	0.26	428	1.062	A	0.30	16.66

* w (ZE-2), 1.0 wt% based on monomers

It can be found that the polymerization stability, LSS, LCS and LERS of the latex are increased, and D (4, 3) is decreased with increasing polymerization temperature.

The effect of the polymerization temperature on the stability of EFL is also related to the electrostatic factor, and is important for the LERS. Generally, an increase in polymerization temperature results in an increase in decomposition rate of initiator, number of free radicals and active chains, particle number density, SCD, and latex stability, and an decrease in the particle size^[12]. Its effect on the stability of EFL is similar to that of increasing initiator concentration without increasing the concentration of electrolyte.

Preparation of Monodispersed Latex Particles

To sum up, stable, almost monodispersed particles of MMA/BA/ZE EFL can be prepared under

certain polymerization conditions with ZE in the appropriate structure, concentration and feeding mode. Some of the examples of MMA/BA/ZE EFL with good properties are shown in Table 8.

Table 8. Preparation of monodispersed particles of P(MMA/BA/ZE) EFL ^{a)}

Comonomer	Feeding mode of ZE	m_c (wt%)	$D(4, 3)$ (nm)	U	LSS	LCS (mL)	LEERS (mL) (1% $CaCl_2$)
ZE-2 ^{b)}	Batch	0.43	461	1.064	B	0.35	16.28
ZE-2 ^{c)}	Batch	0.26	428	1.062	A	0.25	16.66
ZE-4	Semicontinuous ^{d)}	2.45	498	1.060	B	0.45	16.40
ZE-6	Batch	2.09	534	1.053	C	0.50	14.52
ZE-6	Semicontinuous ^{d)}	3.72	498	1.057	B	0.45	31.50
ZE-13	Semicontinuous ^{d)}	4.74	514	1.058	C	0.47	58.60

a) w (ZE), 1.0 wt% based on monomers; b) 75°C; c) 80°C; d) ZE was fed dropwise in 1.0 wt% aqueous solution in the rate of 41 mL/h

CONCLUSIONS

A series of new water-soluble bifunctional comonomers containing both carboxyl and polar nonionic groups, such as sodium mono(ethyl polyoxyethylene) maleate (ZE series), were synthesized and characterized. The investigation of the emulsifier-free emulsion copolymerization of MMA/BA in the presence of a small amount of ZE showed that the polymerization stability, storage stability, centrifugal stability, electrolyte resistance stability and the particle size of the latexes were affected significantly by the structural factor, concentration and feeding mode of ZE comonomers. The concentration of persulfate initiator and polymerization temperature has an important effect on the latex stability and particle size of the system. Stable, almost monodispersed particles of MMA/BA/ZE emulsifier-free latexes can be prepared under certain polymerization conditions with ZE in the appropriate structure, concentration and feeding mode.

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