

Emulsifier-Minor Emulsion Copolymerization of BA-MMA-St-MAA (or AA)-N-MA

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ABSTRACT: A novel emulsion polymerization technique referred to as emulsifier-minor emulsion polymerization was achieved by the copolymerization of methyl methacrylate, butyl acrylate, and styrene (MMA-BA-St) with a combination of water-soluble ionic monomers [methacrylic acid (MAA) or acrylic acid (AA)] and nonionic monomers (*N*-methylol acrylamide). In the technique, water-soluble monomers play a crucial role in the stabilization of the latex particles as they can be bound to the particle surface and form a hydrate protective layer, which exhibits steric and/or electrostatic effects to prevent particle coagulation. The minor but over its critical micelle concentration emulsifier so-

dium alkylated diphenyl ether disulfonate (DSB) results in the nucleation of particles mainly by the micelle nucleation mechanism and thus determines the polymerization rate, the particle size, and the number. The film water resistance of the latices can be improved, and the foaming capacity of can be lowered by using technique instead of conventional emulsion polymerization. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2923–2929, 2004

Key words: emulsifier-minor emulsion polymerization; MMA-BA-St; (meth)acrylic acid; *N*-methylol acrylamide; micelle nucleation mechanism

INTRODUCTION

Emulsifiers play a crucial role in emulsion polymerization. They are very important for the nucleation of the latex particles, the emulsification of the monomer droplets, and the stabilization of the polymer particles. However, they can have adverse effects as follows. First, they can cause foaming during application and processing of latices. Second, once the latices have been applied in films, the emulsifier can migrate to the film–air surface, which affects the film gloss, and can also migrate to the film–substrate interface, which reduces film adhesion. Third, small molecular weight emulsifiers bring about poor film water-resistance. Besides, there can be further problems during processing of the latex; 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 problems, 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. A way to obtain the latices is to use surfmers containing a polymerizable double bond.^{1–4} However, the structural

requirements for the optimal performance of surfmers are harsh; for example, the lower reactivity, suitable hydrophilicity, and better copolymerizability with main monomers are essential to make them fix to the surface of latex particles after polymerization.^{5–8} In addition, surfmers in general are very expensive, which limits their use. Another way is to copolymerize with water-soluble monomers. Some literature reported that the latices with over 40 wt % of solids can be prepared by using well-designed processes and suitable water-soluble monomers,^{9–14} but the polymerization rate is usually very slow and latex particles are very coarse, which adversely affects film formation. The stability of the latices is not good enough to meet the requirements for coatings, adhesives, etc. Macromolecular protective colloids are also used for stable emulsifier-free latices, but solid contents of the obtained latices are not high enough. In fact, minor surfactants are very important for the production and application of coatings, adhesives, etc., for instance, for the wetting of substrates and the dispersion of pigments. From the above considerations, the present work was undertaken to attempt to develop a novel emulsion polymerization technique referred to as an emulsifier-minor emulsion polymerization, where the dosage of emulsifiers is substantially reduced by using a combination of water-soluble ionic monomers and nonionic monomers; thus, the negative effects of emulsifiers in conventional emulsions can be avoid or alleviated, which represents a compromise between a conventional and an emulsifier-free emulsion polymerization.

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TABLE I
Recipe for Synthesis of the Latexes

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	70.0
III	N-MA	0–3.0
	MAA or AA	0–3.0
	Deionized water	30.0
IV	Ammonium persulfate	0.4
	Sodium bicarbonate	0.4
	Deionized water	30.0

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), butyl acrylate (BA), styrene (St), methacrylic acid (MAA), acrylic acid (AA), *N*-methylol acrylamide (*N*-MA), ammonium persulfate (APS), sodium bicarbonate (NaHCO₃), and sodium alkylated diphenyl ether disulfonate (RHODACAL DSB) were purchased from Qingzhou Pada Chemical Co., Ltd. Other materials were provided by Qingdao Chemical Co., Ltd. All materials were of commercial grade and used as received.

Latexes synthesis

The emulsifier-minor latexes were synthesized by seeded semicontinuous emulsion polymerization. The synthesis was performed in a four-neck 250-mL flask 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 by using a thermostated water bath. Sodium alkylated diphenyl ether disulfonate (DSB) was used as an emulsifier. According to the recipe listed Table I, portion II, composed of 0.1–0.4 g DSB and 70 g deionized water; portion III, composed of 0–3 g MAA or AA, 0–3 g *N*-MA, and 30 g deionized water; 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 preemulsified by stirring and heated. When heated to 80°C, one-third of portion IV, 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 remainders of portion I and portion IV were then added dropwise from separate dropping funnels to the reactor under the temperature of 80–85°C over a period of 1.5 h. After the addition of all the ingredients, the reaction temperature of 80–85°C was maintained for an additional 2 h. Then, the contents were cooled to

ambient temperature and neutralized with ammonia to a pH of 7.5–8.0. Last, the product was obtained by screening the coagula with a 300-mesh screen. The coagula were dried until constant weight at 100–105°C in an oven for the calculation of the stability during the polymerization.

The conventional latexes were synthesized by the same scheme except for the following changes. The emulsifiers were composed of 3 g TX-10 (nonyl phenol ethoxylate) and 2 g DSB, and portion III consisted of 3 g AA and 20 g deionized water.

Analysis of the latex properties

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

The total monomer conversion was determined gravimetrically. To follow monomer conversions and the particle growths during the seeded polymerization stage, approximately 5 g of the samples was taken by a syringe at intervals and injected into vials containing a small amount of hydroquinone and chilled in an ice bath to inhibit further polymerization.

The mechanical stability of latexes (MS) was tested by an XR-14 latex high-speed mechanical stability testing machine (Chengde Testing Machine Co., Ltd.). Through a 300-mesh screen, 50 g of latexes was added to 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 the stirring. The coagula were dried until constant weight at 100–105°C in an oven. The mechanical stability is represented by the weight percentages of the dry coagula based on the latexes: the higher the value, the poorer the stability.

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

The stability of latexes against electrolytes (ES) was tested by the process as follows. Latexes (5 mL) were discharged into a test tube; then 1 mL of aqueous solution of 5 wt % anhydrous calcium chloride was added into the test tube while shaking. After addition, the test tube was shaken for an additional 1 min and left standing for 48 h. If the flocculation and phase separation of the contents during 48 h occur, the stability against electrolytes is poor; in other words, the stability is no pass, if not, pass.

The foaming behavior was tested by the following method. Latexes (2 g) were added to a test tube with 20 cm length and diluted with 10 mL deionized water. Then, the test tube was stoppered and shaken vigorously for 1 min and left to stand. After shaking, the foam height in the test tube versus time histories was recorded: the higher the foam, the stronger the foaming capacity. The same operation was done twice.

TABLE II
Effect of DSB Loading on the Polymerization

DSB (solids wt %)	0.0	0.05	0.10	0.20
E.S		Pass	Pass	Pass
PS (%)	Coagulation	0.51	0.40	0.33
MS (%)		0.05	0.04	0.05
Viscosity (mPa s)		60	1120	1160
Dv (nm)		301.4	176.1	119.9
Dz (nm)		263.4	178.3	120.0
PDI		0.03	0.01	0.02
Np (ml H ₂ O) × 10 ⁻¹⁴		0.47	2.41	7.64
Conversion (%)		98.1	98.2	98.5

ES: stability against electrolyte; PS: stability during polymerization; MS: mechanical stability; Dv: volume average diameter; Dz: z-average diameter; PDI: polydispersity index; Np: particle number.

Particle sizes and its distributions were measured by dynamic light scattering by employing a Malven zetalyzer 3000HS particle sizer. The number of polymer particles produced was determined from monomer conversion and volume-average diameter provided the density of the polymer was 1.12 g/cm³.

The morphology of the latices was determined by transmission electron microscopy (TEM) by using a JEM-2000EX.

The surface tension of the latices was measured at 24–25°C by a suspended platinum ring (Du Nouy method) by using a JYW-200B automatic tensiometer (Chengde Testing Machine Co., Ltd.).

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

RESULTS AND DISCUSSION

Effect of DSB loading on the polymerization

The effect of emulsifier DSB loading on the emulsion polymerization was investigated in the presence of 2.0 wt % of *N*-MA and 1.5 wt % of MAA on the basis of all monomers. Complete coagulation during the polymerization occurred in the absence of emulsifier DSB. When DSB loading was 0.05 wt % or more (based on its solids) based on all monomers, the stability during the polymerization and the mechanical and electro-

lytic stability of the final latices were good, the coagula produced during the polymerization was about 0.5%, and the monomer conversions were also higher than 98%. As can be seen in Table II and Figure 1, DSB dosage had a significant effect on the particle size, the particle number of the latices, and the polymerization rate. The particle size decreased drastically, but the particle number and polymerization rate during the seeded stage increased markedly with increasing DSB loading. The polymerization rate was very slow in the absence of DSB; the monomer conversion during the seeded stage was below 1% for 10 min reaction time and about 50% for 60 min. However, when DSB dosage was 0.20%, it took only 30 min for the seeded polymerization to end upward of about 90% conversion. The results are in line with the phenomena in a conventional emulsion polymerization; that is, generally in a conventional emulsion polymerization, an increase in surfactant concentration leads to a smaller particle size, a large number of particles, and a faster polymerization rate. The data obtained by surface tension measurement reveal that the critical micelle concentration (CMC) of DSB is 0.1 g/L water. A 0.05 wt % DSB loading based on all monomers corresponds to the concentration of 0.45 g/L water based on the added water in the seeded polymerization stage, which largely exceeds the CMC of DSB. Therefore, as the dosage of DSB is 0.05 wt % or more, it is very

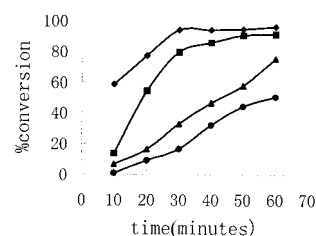


Figure 1 Effect of DSB loading on the conversion-time behavior for the seeded stage DSB loading (solids wt % based on all monomers): ●, 0.00; ▲, 0.05; ■, 0.10; ◆, 0.20.

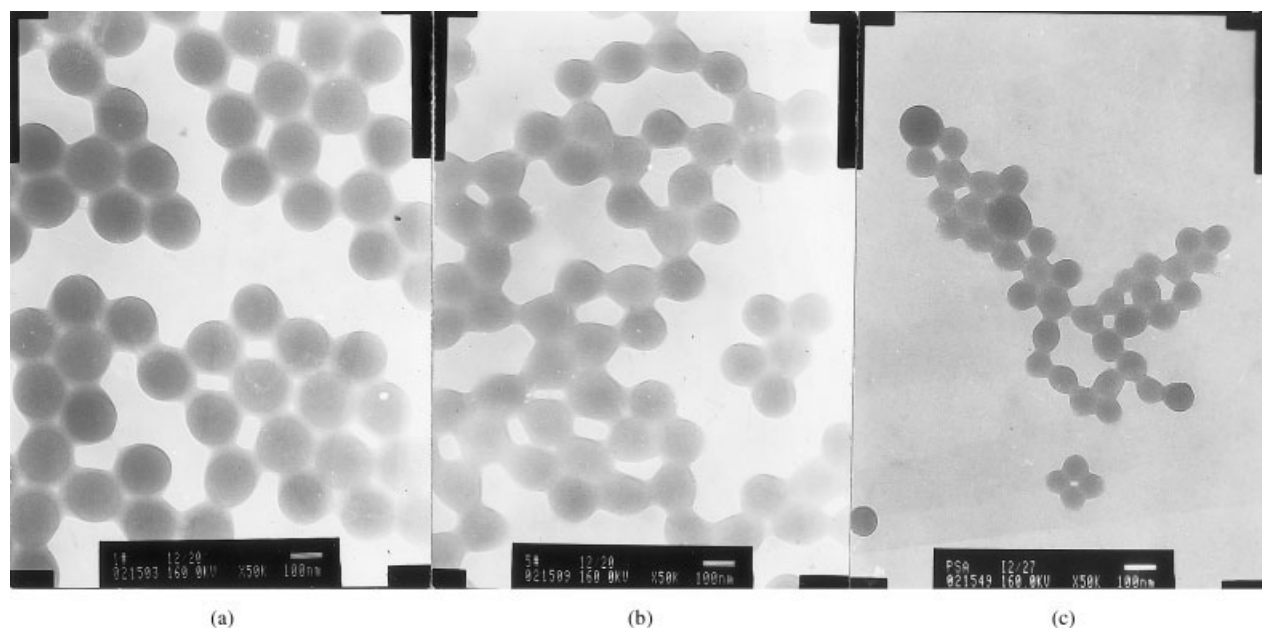


Figure 2 TEM images of the latex particles with different DSB levels (a) 0.05 wt %; (b) 0.10 wt %; (c) 0.20 wt %.

possible that the nucleation of the latex particles is mainly via micelle nucleation mechanism. The micelle number formed in aqueous solution increases with an increase in the concentration of DSB, which contributes to an increase of the polymerization rate and the number of particles, and a decrease of the particle size. The TEM micrographs (Fig. 2) suggest that the latex particles are basically spherical and have a narrow size distribution. It was found that the particle size data values obtained from dynamic light scattering were generally somewhat larger than those obtained by TEM, which might be caused by some shrinkage of the dried particles under the electron beam.

Effect of MAA or AA loading on the polymerization

The effect of the levels of MAA or AA on the polymerization was tested when DSB and *N*-MA represented 0.1 and 2.0 wt % of all monomers, respectively.

Tables III and IV show that the levels of MAA and AA have a great effect on the stability during polymerization, and both the lower and the higher bring about more coagula. By copolymerizing with the main monomers, the hydrophilic carboxyl groups of MAA or AA 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 would also provide an electrostatic repulsion to further enhance the stability of the final latices such as the mechanical stability. The lower levels of MAA or AA contribute to an insufficient stabilization. However, MAA and AA tend to homopolymerize in water phase and form water-soluble oligomers which result in an increase of the viscosity of the contents. The increase of the viscosity may also be correlated with the ability of $-\text{COOH}$ groups to form strong hydrogen bonds with water molecules. The higher the dosage of MAA or AA, the larger the

TABLE III
Effect of AA Loading on the Polymerization

AA (wt %)	0.5	1.0	1.5	2.0
ES	Pass	Pass	Pass	
PS (%)	3.37	0.81	0.89	Coagulation
MS (%)	0.12	0.08	0.04	
Viscosity (mPa s)	200	240	1660	
Dv (nm)	176.9	172.3	170.7	
Dz (nm)	180.4	176.1	178.5	
PDI	0.02	0.02	0.03	
Np (mlH ₂ O) × 10 ⁻¹⁴	2.29	2.54	2.63	
Conversion(%)	95.5	97.6	97.9	

TABLE IV
Effect of MAA Loading on the Polymerization

MAA (wt %)	0.5	1.0	1.5	2.0
ES	Pass	Pass	Pass	Pass
PS (%)	2.3	0.71	0.40	2.1
MS (%)	0.11	0.07	0.04	0.05
Viscosity (mPa s)	850	965	1120	1160
Dv (nm)	173.9	175.3	176.1	173.2
Dz (nm)	180.1	178.9	178.3	176.5
PDI	0.03	0.02	0.01	0.02
Np (ml H ₂ O) × 10 ⁻¹⁴	2.43	2.41	2.41	2.50
Conversion (%)	96.5	97.5	98.2	96.6

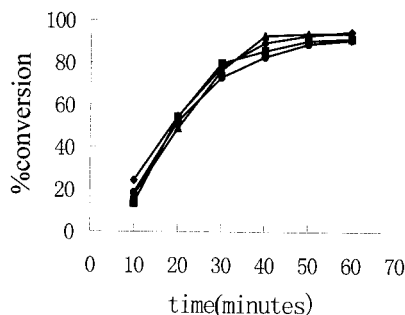


Figure 3 Effect of MAA loading on the conversion-time behavior for the seeded stage MMA loading (wt % based on all monomers): ●, 0.5; ▲, 1.0; ■, 1.5; ◆, 2.0.

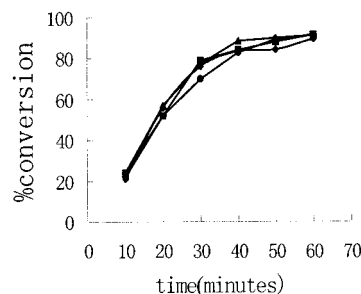


Figure 4 Effect of *N*-MA loading on the conversion-time behavior for the seeded stage *N*-MA loading (wt % based on all monomers): ●, 0.0; ▲, 1.0; ■, 2.0; ◆, 3.0.

viscosity of the contents, which adversely affects the mass and heat transfer of the contents, and in turn, leads to destabilization and even complete coagulation. It was also found that the stability during polymerization by using MAA was better than by using AA, which may be because the solubility and homopolymerizing tendency of the former in water are less than that of the latter. This viewpoint was supported by the undesired results by using more water-soluble carboxyl monomers such as itaconic acid and maleic acid instead of MAA or AA. As can be seen in Figure 3, Table III, and Table IV, the dosage of carboxyl monomers during the range tested has a minimal effect on the particle size and number of the final latices and the initial rate during the seeded stage, which is not in agreement with the phenomena in an emulsifier-free emulsion polymerization where initial rate and particle number increase, and particle size decreases with increasing the amount of water-soluble monomers.¹⁵ This indicates that the nucleation in the homogeneous phase is negligible in the presence of a minor amount of emulsifiers, but over their CMC.

Effect of *N*-MA loading on the polymerization

Table V and Figure 4 show that *N*-MA has the same effect on the polymerization as MAA and AA with the following exception. The stability of the latices against

the electrolyte depends on the level of *N*-MA. The hydrophilic protective coatings on the particle surface formed by nonionic water-soluble monomers such as *N*-MA are almost not affected by electrolytes, which is different from that by ionic water-soluble monomers such as MAA and AA. This is responsible for better stability of the latices with a higher amount of *N*-MA against the electrolytes.

Effect of the addition mode of the water-soluble monomers

It was found that the addition mode of the water-soluble monomers was very important for the stabilization during the polymerization: the less the added fraction of the water-soluble monomers during the seeded stage, the poorer the stabilization during the polymerization, and even caused the complete coagulation of the latices. It is preferable that all the water-soluble monomers are discharged into the seeded stage.

Effect of the solid contents of the latices

As mentioned before, a high solid-content latex is necessary for industrial purposes and is difficult to be obtained by an emulsifier-free emulsion polymerization. Therefore, the effect of the solid content of latices,

TABLE V
Effect of *N*-MA Loading on the Polymerization (1.5 wt % MAA)

<i>N</i> -MA (wt %)	0.0	1.0	1.5	2.0	3.0
ES	No pass	No pass	Pass	Pass	Pass
PS (%)	2.5	0.75	0.54	0.40	1.51
MS (%)	0.06	0.05	0.04	0.04	0.05
Viscosity(mPa s)	62.5	112.5	462.5	1120	1930
Dv (nm)	162.1	177.3	175.2	176.1	166.9
Dz (nm)	171.3	180.5	179.8	178.3	173.4
PDI	0.04	0.02	0.02	0.01	0.03
Np (ml H ₂ O) × 10 ⁻¹⁴	2.96	2.32	2.42	2.41	2.83
Conversion(%)	96.1	97.7	97.8	98.2	97.5

TABLE VI
Effect of the Solid Contents of the Latexes

Solids (wt %)	42.9	43.1	44.0	46.5
ES	Pass	Pass	Pass	
PS (%)	0.81	0.86	0.91	Coagulation
MS (%)	0.05	0.05	0.05	
Viscosity (mPa s)	240	2020	2860	
Conversion (%)	98.2	97.9	97.4	

that is, the added water amount, was tested when DSB, *N*-MA, and AA were fixed at 0.1, 2.0, and 1.0 wt % on the basis of all monomers, respectively. Table VI shows that the latexes with about 45 wt % of solids can be obtained, and a further rise would bring about complete coagulation because of the high viscosity of the contents.

Effect of the neutralization of the seeded latexes

Some literature reported that stable, highly concentrated latexes were obtained by two-stage polymerization processes where the seeded latexes were neutralized. By neutralizing the seeded latexes, the carboxyl groups of the polymer are ionized, and the higher charged particles obtained here are a zone of further copolymerization of the monomers in the second stage. The significant hydrophilicity of the carboxyl ions causes their localization on the particle surface and creates good stability of the final latexes. The scheme was also tested in the present work. The results indicate that the type of neutralizing agents has an important effect on the stabilization during the polymerization. The use of amines and ammonia brought about complete coagulation of the latexes, but the same result as without neutralizing the seeded latexes was obtained by using the aqueous solution of NaOH. It was also found that the neutralization of the seeded latexes would cause a rise of the viscosity of the contents; then, more care should be taken to prevent the latexes from stabilization.

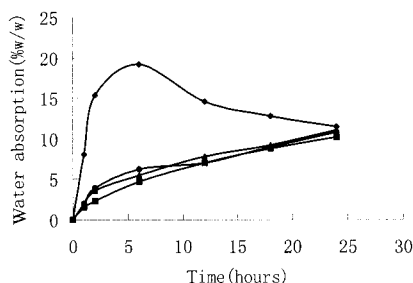


Figure 5 Water absorption versus time for the different latexes: \blacklozenge , the conventional latex; \blacksquare , emulsifier-minor latex with 0.05 wt % DSB; \bullet , emulsifier-minor latex with 0.10 wt % DSB; \blacktriangle , emulsifier-minor latex with 0.20 wt % DSB.

TABLE VII
Surface Tension of Latexes

Technique	Emulsifier-minor			Conventional		
Emulsifier (wt %)	0.05	0.10	0.20	2.7	3.2	3.6
$\gamma/\text{mN m}^{-1}$	53.9	55.3	55.3	39.3	37.6	36.9

Property comparison between the emulsifier-minor and the conventional latexes

Water-resistance

As shown in Figure 5, the film water absorption of the emulsifier-minor latexes (*N*-MA 2.0 wt %, MAA 1.5 wt %) is far less than that of the conventional latex; in other words, the water resistance of the former is far better than that of the latter. The film water absorption of the conventional latex versus time histories is abnormal, increases first with increasing immersing time, but decreases after 6 h, which can be attributed to the migration of the surfactants into water phase. During the 0.05–0.20 wt % range tested, the dosage of DSB has a minimal effect on the film water absorption of the emulsifier-minor latexes. A key parameter governing the success of latexes in almost every end-use application is the water resistance. Taking this into account, the emulsifier-minor emulsion polymerization shows real promise.

Surface tension and foaming behavior

Table VII and Figure 6 show that the surface tensions of the emulsifier-minor latexes are higher than that of the conventional latexes, correspondingly, and the foaming capacity of the former is weaker than that of the latter. The characteristics of the emulsifier-minor latexes are very important for the application of end-products such as latex coatings, adhesives, etc.

CONCLUSION

By copolymerizing with a combination of MAA or AA and *N*-MA, the dosage of the emulsifier DSB for the

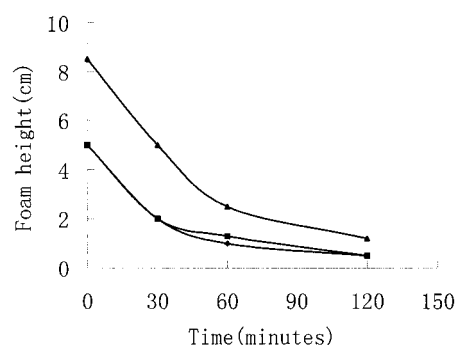


Figure 6 Foam height versus time for the different latexes: \blacklozenge , the conventional latex; \blacksquare , emulsifier-minor latex with 0.05 wt % DSB; \bullet , emulsifier-minor latex with 0.10 wt % DSB; \blacktriangle , emulsifier-minor latex with 0.20 wt % DSB.

emulsion copolymerization of BA-MAA-St can be reduced drastically from 3.0–3.6 to 0.05–0.20 wt % on the basis of all monomers. After polymerization, water-soluble monomers are bound to the particle surface and form a hydrate protective layer, which provides a steric effect to prevent particle coagulation and then improve the stability of the final latices. In addition, by neutralization, ionized carboxyl groups also provide an electrostatic repulsion to further improve the stability. As water-soluble monomers tend to homopolymerize in water phase, which affects adversely on the polymerization, the added amount of the monomers is very crucial, and the suitable amounts of MAA or AA and *N*-MA are 1.0–1.5 and 1.5–2.0 wt %, respectively. The polymerization rate, the particle size, and the number depend on the dosage of the emulsifier DSB, but are almost not relevant to MAA, AA, and *N*-MA, which reveals that the nucleation of the particles is mainly via micelle nucleation mechanism, not by homogeneous nucleation mechanism. The addition mode of water-soluble monomers is also very important, and the monomers are preferably added into the seeded stage. The water resistance of the latex films can be improved, and the foaming capacity of the latices can be lowered by using the emulsifier-minor

emulsion polymerization instead of a conventional emulsion polymerization.

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