

Semibatch Emulsion Copolymerization of Butyl Acrylate and Glycidyl Methacrylate: Effect of Operating Variables

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ABSTRACT: Semibatch emulsion copolymerization was carried out to prepare poly(butyl acrylate-co-glycidyl methacrylate) latexes at 75°C, using potassium persulfate as an initiator, sodium dodecylbenzene sulfonate as an emulsifier and sodium bicarbonate as a buffer. The reaction was conducted in three stages; a further stage (called the steady stage, 2 h) was added to the traditionally stages (i.e., feed and seed stages) to improve considerably the monomer conversion. The monomer conversion and particle size distribution were studied by gravimetric and laser light scattering methods, respectively. The effects of variables such as agitation speed, emulsifier concentration, initiator concentration, feeding rate and comonomers ratio were fully investigated based on the monomer conversion-time profiles and the particle size distribution to find the optimized copolymerization conditions. Increas-

ing the agitation speed had a negative effect on the monomer conversion, but reduced coagulation of polymer particles. Monomer conversion could be improved by increasing the initiator or emulsifier contents. Feeding rate increased the polymer particle size sharply; however, it showed no significant effect on conversion. The final conversions were as high as 97–99% and they were recognized to be independent of the comonomers ratios employed. Morphological studies by scanning electron microscopy showed nano-sized isolated particles which were partially aggregated. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2771–2780, 2010

Key words: emulsion copolymerization; glycidyl methacrylate; monomer conversion; particle size distribution; morphology

INTRODUCTION

Emulsion polymerization is a preferred process to industrial preparation of polymer latexes because it produces high molecular weight polymers and no or negligible volatile organic compounds.^{1,2} The reaction medium (usually water) facilitates agitation, heat and mass transfer and provides an inherently safe process.³

Three types of processes are commonly used in emulsion polymerization: batch, semibatch, and continuous. In a batch polymerization, all ingredients are added at the beginning of the reaction. Polymerization begins as soon as the initiator is added and the temperature is increased. It is commonly used in the laboratory to study reaction mechanisms and kinetics, but most commercial latex products are manufactured by semibatch or continuous systems.⁴

In the semibatch process, one or more of the ingredients are added continuously or incrementally. The monomers may be added neat or as preemulsion. The advantage of this process is the ability to

exercise precise control over the various aspects, which include the rate of polymerization and thus the rate of generation and removal of the polymerization heat, the particles number, colloid stability and coagulum formation, copolymer composition and particle morphology. In the continuous process, the polymerization ingredients are fed continuously into a stirred reactor, or several reactors connected continuously, while the latex product is simultaneously removed at the same rate.⁵

In the previous literatures, the effects of different variables on emulsion polymerization have been studied. They covers variables such as agitation speed,^{1,6–19} initiator type and concentration,^{1,2,6–8,15,16,18,20–32} emulsifier type and concentration,^{8,18,20,21,24,25,28–30,32–37} feeding rate,^{3,11,26,30} temperature,^{1,6,7,16,21–24,26,29,30,33} monomer/water phase ratio,^{8,15,18,20,29} electrolyte concentration,^{14,31} and pH.^{16,29}

Majority of the laboratory works have focused on the batch systems,^{2,8–10,12,14–23,25,29–34} and fewer works have been conducted via semibatch^{1,3,6–8,11,12,26,27,30,35,36,38} and continuous systems.^{24,28,39}

Monomers methyl methacrylate, butyl acrylate (BA), vinyl acetate, and styrene are conventionally used in the processes to produce acrylic latices either in laboratory or in industry. Meanwhile, glycidyl methacrylate (GMA) is an interesting monomer

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possessing an oxirane function of potential reactivity.⁴⁰ Copolymerizations of GMA with conventional monomers have been widely investigated for their potential applications (e.g., functionalization with amines, polymers, acids, cation-exchange adsorbent crown ethers).^{41,42} The interest in these copolymers is largely due to the ability of the pendant epoxy group to enter into a large number of chemical reactions.^{41,42} GMA-based polymers have recently gained special interest because of their superior performance in more specific applications such as drug and biomolecule binding.⁴³

Latex particles containing epoxy groups represent an important class of useful materials. Epoxy-functionalized latexes are used not only in adhesives⁴⁴ and waterborne coatings^{45–47} but also in other applications such as latex particles for medical diagnostic purposes⁴⁸ and the chemical modification of surfaces.⁴⁹ In coatings, the epoxy groups act as crosslinking sites and the chemical resistance, adhesion, hardness and heat and abrasion resistance of the final film can be improved.^{5,50} In spite of the advantages of GMA, it is yet too expensive to be used extensively in industrial production of coatings.

This work deals with GMA-BA latexes prepared via semibatch polymerization under various conditions. As the polymer quality can be controlled by adopting a suitable operating strategy, we investigated the influence of agitation speed, initiator and emulsifier concentration, comonomers ratio, and feeding rate on conversion and particle size distribution (PSD). For this purpose, several polymerizations were performed to obtain the conversion plots and polymer characteristics with an emphasis on practical aspects.

EXPERIMENTAL

Materials

Butyl acrylate (BA, Fluka) and glycidyl methacrylate (GMA, Merck) as monomers and potassium persulfate (KPS, Merck) as initiator were used as received. Sodium dodecylbenzene sulfonate (SDBS, reagent grade, Merck) as emulsifier, sodium bicarbonate as buffer, and hydroquinone as inhibitor were used without further purification. Distilled water (DW) was used as the continuous phase and chloroform (Merck) used as solvent of produced polymers.

Polymerization

Semibatch emulsion polymerization were carried out at 75°C ± 1°C in a 250-mL four-necked laboratory glass reactor fitted with reflux condenser, three-bladed stainless steel impeller stirrer, nitrogen inlet, and feeding tube. The reaction components are given in Table I. An initial charge of monomers (20% of

total monomers), water, emulsifier, and buffer (0.200 g) were added to the reactor. The reactor contents were brought to the 75°C and purged with nitrogen for 30 min to remove any dissolved oxygen prior to the start of reaction. The desired amount of initiator dissolved in 2.5 mL DW was added to the reactor. After a fixed period (seed stage, 1 h), the rest of monomers (as a previously emulsified mixture) was added in a certain feeding rate (18–28 mL/h) to the reactor via a metering pump (feed stage). Then, the reaction system maintains at the fixed bath temperature for 2 h to possibly increase the monomer conversion (steady stage).

Characterization

Instantaneous monomer conversion (X), is defined as the weight ratio of the polymer formed to the total monomer fed until the sampling time, t .¹³ Samples were directly taken from the reactor and polymerization was inhibited by hydroquinone. Then, they were dried in a vacuum oven and the conversion calculated as follows:

$$X = \frac{W_1 - W_{\text{inhibitor}}}{W_2 \times S_T} \quad (1)$$

where W_1 , W_2 , $W_{\text{inhibitor}}$ are, respectively, weights of taken sample, dried sample, and added inhibitor, and S_T (total solid content) is the mass fraction of monomer in the latex. It can be calculated at the moment of sampling using eq. (2).

$$S_T = \frac{(W_{\text{initial}} \times S_{\text{initial}}) + (W_{\text{preemulsified}} \times S_{\text{preemulsified}})}{W_{\text{initial}} + W_{\text{preemulsified}}} \quad (2)$$

where W_{initial} and $W_{\text{preemulsified}}$ are, respectively, weights of initial charge and added preemulsified mixture, and S_{initial} and $S_{\text{preemulsified}}$ are solid contents of initial charge and preemulsified mixture, respectively.

The PSD was measured by a laser light scattering (LLS) system (Sematech, model SEM-633). Particle size polydispersity index was calculated as follows³:

$$\text{PSDI} = \frac{\langle r^2 \rangle}{\langle r \rangle^2} \quad (3)$$

where r is the radius of latex particles and $\langle r \rangle$ is the number average radius of latex particles, computed from the eq. (4);

$$\langle r \rangle = \frac{\sum_i n_i r_i}{\sum_i n_i} \quad (4)$$

TABLE I
Recipes^a Used for Preparing the Latex Samples and Their Characteristics

Sample code	Preparative conditions				Product characteristics			
	Agitation speed (rpm)	SDBS in feed stage, (g)	KPS, (g)	Feeding rate, (mL/h)	BA/GMA, wt. ratio	Mean diameter, D_p , (nm)	Polydispersity index	Gel content, (%)
S1	75	0.980	0.050	18.8	80/20	41.6	0.235	32.9
S2	100	0.980	0.050	18.8	80/20	54.8	0.237	33.4
S3	150	0.980	0.050	18.8	80/20	34.7	0.234	33.0
S4	250	0.980	0.050	18.8	80/20	20.5	0.244	29.2
S5	100	0.735	0.050	18.8	80/20	65.4	0.237	35.7
S6	100	1.147	0.050	18.8	80/20	20.3	0.237	30.6
S7	100	0.980	0.025	18.8	80/20	124.0	0.103	34.3
S8	100	0.980	0.075	18.8	80/20	18.7	0.242	33.4
S9	100	0.980	0.075	28.2	80/20	121.0	0.241	34.1
S10	100	0.980	0.075	19.0	90/10	16.1	0.250	26.7
S11	100	0.980	0.075	18.6	70/30	168.3	0.257	38.8

^a Bath temperature $75^\circ\text{C} \pm 1^\circ\text{C}$. Initial charge (1 h): water 25.0 g, sum of monomers 8.0 g, SDBS 0.240 g, NaHCO_3 0.200 g. Charge of feed stage (2–3 h): water 21.0 g, sum of monomers 32.5 g.

The gel content of samples was determined using chloroform as an extraction solvent. A certain weight (50–100 mg) of the polymer was added to about 50 mL of chloroform and kept under stirring for 48 h. Then, the mixture filtered using 2- μm filter paper and dried at room temperature to reach a constant weight. The gel content was calculated by division of final weight to the initial sample weight.

All of the latex samples characteristics are given in Table I.

Infrared spectra were obtained on a FTIR spectrometer (Bruker Instruments, model Aquinox 55, Germany) in the $4000\text{--}400\text{ cm}^{-1}$ range at a resolution of 0.5 cm^{-1} . Samples were quenched in liquid nitrogen to come below their T_g and their pellets prepared with KBr (FTIR grade, Fluka).

Glass transition temperature (T_g) of copolymers was measured by a dynamic mechanical analyser (DMA, Triton, Model Tritec 2000, England).

Morphology of samples was characterized by a scanning electron microscope (SEM, TESCAN Vega II, Czech). Samples for SEM were prepared via freeze drying the latexes at -40°C and kept under their glass transition before the analysis.

RESULTS AND DISCUSSION

To achieve optimal conditions for practically preparing poly(BA-GMA) latexes with high conversion and low coagulation, the influence of some variables (i.e., agitation speed, initiator and emulsifier concentration, comonomers ratio and feeding rate) were investigated.

A FTIR spectrum from $400\text{ to }4000\text{ cm}^{-1}$ is typically given for sample S11 (Fig. 1). Indicative peaks are pointed in Figure 1 and can be referred as follows: stretching mode of C–H bond $2850\text{--}3000\text{ cm}^{-1}$, bending mode of C–H bond $1455\text{ and }1374\text{ cm}^{-1}$,

C=O bond 1737 cm^{-1} , C–O bond 1190 cm^{-1} , stretching mode of epoxy group 1230 (symmetric), $746\text{ and }848\text{ cm}^{-1}$ (asymmetric). Stretching mode of OH group formed via hydrolysis of epoxy groups are appeared at 3442 cm^{-1} .

As process variables (except comonomers ratio) has no significant effect on T_g , the T_g values of three samples having different comonomers ratio (i.e., samples S8, S10 and S11) were typically measured. The T_g values were -18.4 , -28.0 and -9.2°C for samples S8, S10 and S11, respectively. As GMA homopolymer possesses higher T_g value (94°C) comparing to that of BA homopolymer (-54°C), higher T_g value for the samples having more GMA content was expected.

Effect of agitation

In heterogeneous reaction systems, mass transfer is one of the important factors affecting the polymerization rate (R_p).¹⁵ Emulsion polymerization depends on agitation in several ways. It determines the emulsification of the monomers, affects the transport of the reactants to the polymerization loci (polymer particles) and mixing time for sufficient homogenous distribution.¹³ It can also have an undesirable effect as it can promote coagulation.^{17,51}

According to Evans et al.,¹⁹ the effects of the agitation on emulsion polymerization can be generally described in three steps. With increasing agitation speed, the rate of polymerization (monomer conversion) is firstly decreased (nucleation; interval I), then it is increased (interval II), and finally, it shows agitation speed independency (interval III). According to them, an increasing agitation rate during nucleation produced a better emulsification of monomers, causing a rise of the interfacial area of the monomer droplets and thus increasing the amount of

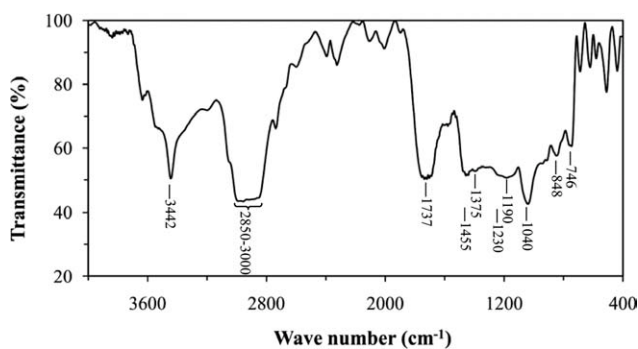


Figure 1 Representative FTIR spectrum for sample S11.

emulsifier adsorbed onto the monomer droplets. Therefore, less emulsifier will be available for the stabilization of the new polymer particles. During interval II, the emulsifier is desorbed from monomer droplets because of the increasing area of the growing particles. Therefore, monomer droplets are coalesced, rendering slower monomer diffusion due to a reduction of the monomer droplets-aqueous-phase interfacial area. An increasing agitation degree improved droplet dispersion and thus led to an increase in the polymerization rate. In interval III, all the monomer is in the polymer particles and diffusion is not affected by agitation.¹⁹

In this work, some experiments were carried out under fixed circumstances to optimize agitation speed (Table I, samples S1–S4).

Experimental results are presented in Figure 2 where the monomer conversions are plotted against reaction time at different agitation speeds. The seed, feed, and steady stages are distinguished by dashed lines. In these experiments, weight of initiator (I) was 0.050 g and emulsifier amounts in initial charge (E_{initial}) and in feed (E_{feed}) were 0.240 and 0.980 g, respectively. At the seed stage, monomer conversion and thus polymerization rate are increased with decreasing agitation speed from 250 to 100 rpm. At 75 rpm, however, the monomer conversion highly decreased (seed stage). This is due to insufficient agitation speed to well emulsify the monomer; as a result, part of the monomer is separated from the emulsion leading to a decrease in the rate of monomer transport to the particles where polymerization is taking place.¹² Such dissimilarities are also observed at feed and steady stages (Fig. 2).

According to Nomura et al.,⁵² the monomer diffusion from droplets to the aqueous phase represents a main resistance to monomer transport. Monomer diffusion from droplets to the aqueous phase depends on both the mass transfer coefficient and the total area of the monomer droplets. With increasing the agitation, the interfacial area will be increased, leading to high monomer diffusion from monomer droplets to the aqueous phase¹³ resulting

in increased polymerization rate and conversion. However, major divergences were experimentally monitored as observed in Figure 2, i.e., the agitation rate of more than 100 rpm disfavors the higher conversion.

The above observation may be discussed by the competition between radical entry of micells and droplets. Breaking the monomer up into more droplets by using higher agitating rate will result in more radical entry of droplets. Therefore, contribution of bulk polymerization in the droplets, which is slower than that of emulsion polymerization in polymer particles, will be increased and led to decreased conversion.⁵³

Other reasoning can be based on the trace air entrance into the reaction. The transfer rate of oxygen from the reactor headspace into the emulsion is lower at the lower agitation speeds, thus it causes a lower number of termination events, a higher concentration of growing free radicals and an overall higher reaction rate.^{1,10} Nomura et al.⁵² observed a similar phenomenon induced by the oxygen impurities of the nitrogen gas blanket used.

According to Ramirez et al.,⁹ an additional interpretation can be given as well. The undesired effects of high agitation speed may be originated from the increment of frequency of the free radical re-entry to the polymer particles. Above a certain agitation speed range, polymer latex particles tend to undergo limited coagulation leading to a decrease in the polymer molecular weight.

In our experiments, at the feed stage, monomers are continuously added to the reactor as a preemulsified mixture (Fig. 2). As monomer/water weight ratio was much higher in the preemulsified mixture (i.e., 32.5/21) than that of the initial charge (i.e., 8/25), number of monomer droplets was increased during feed stage, leading to more radical entry to droplets and free radical re-entry effect. Consequently, a loss of conversion is observed in feed

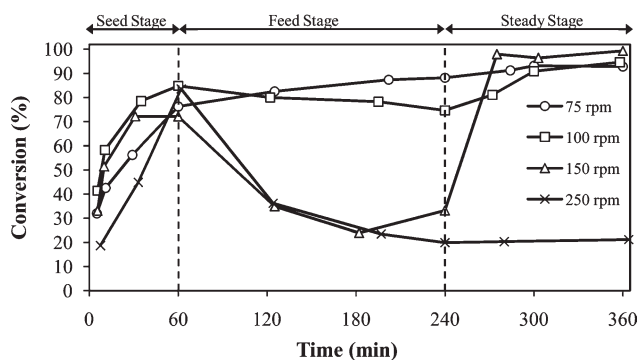


Figure 2 Conversion versus time in different agitation speed. Seed stage: KPS 0.050 g, SDBS 0.240 g. Feed stage: SDBS 0.980 g, feeding rate 18.8 mL/h.

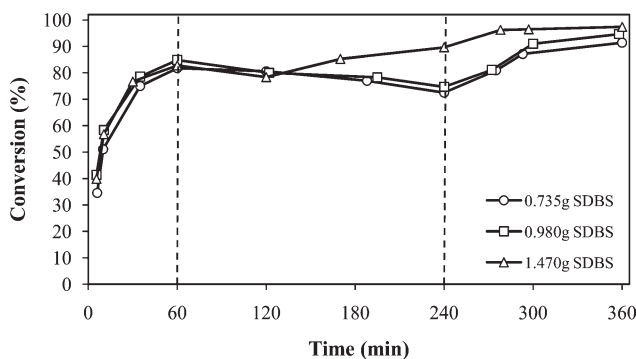


Figure 3 Conversion versus time at different SDBS concentration in preemulsion. Seed stage: KPS 0.050 g, SDBS 0.240 g, agitation speed 100 rpm. Feed stage: feeding rate 18.8 mL/h.

stage especially for 150 and 250 rpm where number of monomer droplets is higher.

To ensure completion of the monomer conversion, the polymerization time was extended to 2 h at the same temperature and agitation speed with no reactant addition (Fig. 2, Steady stage). This approach had a considerable improving effect on the conversion, particularly for 150 rpm. Here, the monomers concentration (and so number of monomer droplets) is reduced because it is consumed with time. Therefore, with decreasing radical entry to droplets, the conversion will be increased significantly. Such conversion improvement was recorded for moderate agitation speed, 75 and 100 rpm. At very high agitation speed (i.e., 250 rpm), however, no conversion change was observed. This can be due to no change in monomer droplets quantity (very low monomer was consumed because of low conversion).

Overall, 100 rpm was taken as an optimum agitation speed because it caused no conversion loss in the feed stage and it resulted in over 90% conversion. Although agitation speed of 75 rpm had similar effectiveness, this low rpm led to higher level of coagulated polymer particles.

Table I exhibits the effect of agitating speed on the polymer particle size (Samples S1–S4). As expected, higher agitation speed led to smaller particles. Nevertheless, mean diameter in 75 rpm is lower than that of 100 rpm. This is, as mentioned previously, is due to inefficient emulsification of mixture and deviation from a normal emulsion polymerization. The polydispersity index showed no remarkable changes because coagulated particles formed mainly in lower agitation speed are too larger to be able to measure by the LLS instrument.

Effect of emulsifier concentration

Increasing the emulsifier concentration led to more micelles and nucleation.⁴ According to eqs. (5) and

(6), number of polymer particles per volume (N_T) increased by the emulsifier concentration and R_p (and therefore conversion) will be increased by increasing N_T .^{54,55} Therefore, a higher conversion was expected when higher concentration of emulsifier was used.

$$N_T = k(R_i/\mu)^{0.4}[a_s(E_0 - E_M)]^{0.6} \quad (5)$$

$$R_p = k_p[M_p]\bar{n}N_T \quad (6)$$

where k is between 0.37 and 0.53, R_i is rate of radical generation in the water phase, μ is volumetric growth rate per polymer particle, a_s is the surface area of polymer particles covered by a unite mole emulsifier, E_0 is initial emulsifier concentration in water phase, E_M is concentration of the emulsifier adsorbed on the monomers droplets at initial step of reaction, k_p is the propagation rate constant, $[M_p]$ is the monomer concentration in the monomer-swollen polymer particles, and \bar{n} is the average number of radicals per particle.

Meanwhile, a probable secondary nucleation (originated from increased emulsifier concentration) may be also contributed in the reaction rate increase.

In Figure 3, conversion for three levels of emulsifier in preemulsified feed is plotted against time (Table I, samples S2, S5, and S6). In these experiments, agitation speed and the initiator level was 100 rpm and 0.050 g, respectively. Only the highest level of the used SBDS (1.470 g) showed distinguished conversion improvement at the feed stage. No appreciable difference was observed when lower amounts of the emulsifier were used. Again, the steady stage induced an improving effect on the conversion. The reasons for these observations were discussed in last section. Decreased particle mean diameter (D_p) at higher amounts of emulsifier was also observed (Table I, samples S2, S5, and S6). This emphasizes N_T was increased due to reverse relation between N_T and D_p (eq. 7).

$$N_T = \frac{6M_0X}{\pi d_p \sum_i n_i D_i^3} \quad (7)$$

where M_0 is the initial monomer concentration (g/mL water), n_i is the number fraction of particles with unswollen diameter D_i , X is the fractional total conversion of monomers, and d_p is the average copolymer density.

It should be pointed out that the highest level of SBDS was not selected as a favorable content of emulsifier because the great amounts of hydrophilic emulsifier are reported to be disfavored with desirable properties such as weather ability and water resistant of the finally formulated coatings.⁴

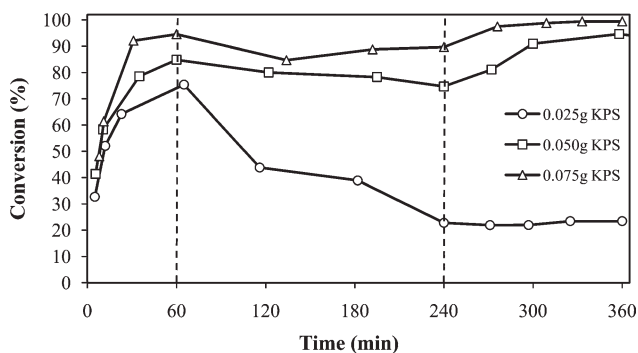


Figure 4 Conversion versus time in different KPS concentration. Seed stage: SDBS 0.240 g, agitation speed 100 rpm. Feed stage: SDBS 0.980 g, feeding rate 18.8 mL/h.

Effect of initiator concentration

Figure 4 shows the variation of conversion with time at three initiator levels (Table I, Samples S2, S7, and S8). In these experiments, agitation speed was 100 rpm and E_{initial} and E_{feed} were 0.240 and 0.980 g, respectively. As expected, monomer conversion was increased in all stages by increasing the KPS concentration.

This behavior can be explained as follows. When the concentration of initiator is increased, the rate of initiation reaction and, thus, the concentration of the free radicals will be raised.⁵⁶ Therefore, the number of polymerization loci will be increased leading to higher conversion. It can also be confirmed by the increasing number of polymer particles due to decreased D_p (Table I, D_p values). The reason is due to the rate of polymerization (and thus, conversion) which is proportionally changed with N_T (eq. 6).

The reason of decreasing D_p comes back to both the rate of initiation and the nature of the initiator. According to eqs. (5) and (8), number of polymer particles (and therefore D_p) is proportional to rate of radical generation in the water phase (R_i) and, therefore, initiator concentration, $[I_0]$.

$$R_i = 2k_d f [I_0] \quad (8)$$

where k_d is the rate constant for initiator decomposition, f is the initiator efficiency, and $[I_0]$ is initial initiator concentration.

In addition, when an ionic initiator such as potassium or ammonium persulfate is used, variation of the initiator concentration inevitably changes the ionic strength of the aqueous phase. With increasing the ionic strength, the cmc (critical micelle concentration) of the emulsifier is decreased, which results in decreased size of polymer particles.⁵⁶ However, it seems to have no major effect on the ionic strength increase because of the amount of initiator looks trivial in comparison to the amount of emulsifier and buffer.

Nevertheless, a higher coagulation was observed with increasing the persulfate concentration. It has been attributed to highly increasing the HSO_4^- in the system [eqs. (9) and (10)].²⁷



At the feed stage, as the low amount initiator (0.025 g) was not enough to continue the polymerization, conversion was reduced. The higher amounts of initiator (0.050 and 0.075 g) caused a nearly unchanged conversion level. At these initiator concentrations, the steady stage caused a conversion enhancement of ~ 10 – 15% due to the foresaid reasons (See section of effect of agitation).

Effect of feeding rate

The polymerization rate will be increased proportionally with the monomer feeding rate if feeding rate is lower than the rate of monomer diffusion to the polymer particle. However, when feeding rate is higher than the monomer diffusion rate, the latter will determine the overall rate of reaction.²⁶ This is why the monomer conversion was almost unchanged with the monomer feeding rate increase, as exhibited in Figure 5. This figure shows conversion versus time at two feeding rates (Table I, samples S8 and S9). The samples were prepared at fixed amount of initiator (0.075 g), emulsifier ($E_{\text{initial}} = 0.240$ and $E_{\text{feed}} = 0.980$) and agitation speed (100 rpm).

On the other hand, monomer concentration is increased and accumulated in the polymer particles. The monomer accumulation decreases the viscosity of particle interiors and increases the possibility of radical transport into the particles.⁵⁷

Feeding rate is the major parameter for controlling the polymer particle size.³ There are two mechanisms for continuing the reaction here. First, particle

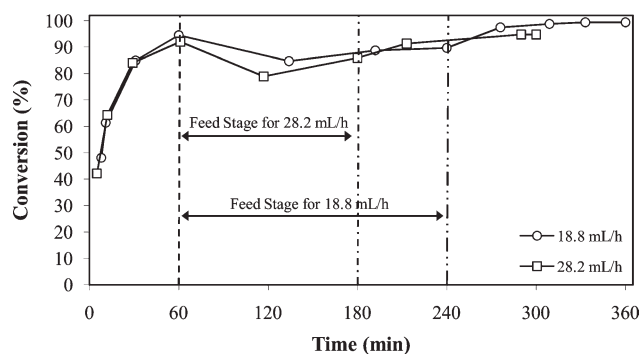


Figure 5 Conversion versus time for different feeding rate. Seed stage: KPS 0.075 g, SDBS 0.240 g, agitation speed 100 rpm. Feed stage: SDBS 0.940 g.

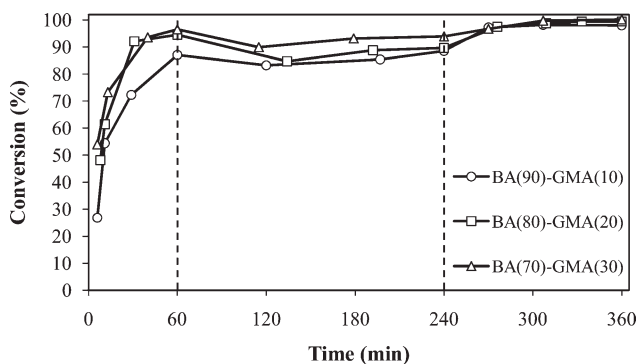


Figure 6 Conversion versus time for different comonomers ratio. Seed stage: KPS 0.075 g, SDBS 0.240 g, agitation speed 100 rpm. Feed stage: SDBS 0.940 g, feeding rate 19.0, 18.8, and 18.6 mL/h.

growth that means monomers entry to polymer particles from seed stage so that the number of these particles in the feed stage will be equal to the num-

ber of particles in seed stage but particle size will be increased. Second, secondary nucleation occurs to form new particles, thus the number of particles at feed stage will be raised comparing to the seed stage and particle size will be decreased. A bimodal PSD may even be attained.³ Both the above mechanisms work simultaneously and their contribution will determine the polymer particle size and their distribution.

As mentioned in Table I (samples S8 and S9), the polymer particle mean diameter was increased by increasing feeding rate. Therefore, it can be concluded that the secondary nucleation was suppressed and particle growth will be conquered.

Effect of comonomers ratio

For investigating the effects of comonomers ratio on the monomer conversion, three comonomers ratios were used (Table I, samples S8, S10, and S11). The

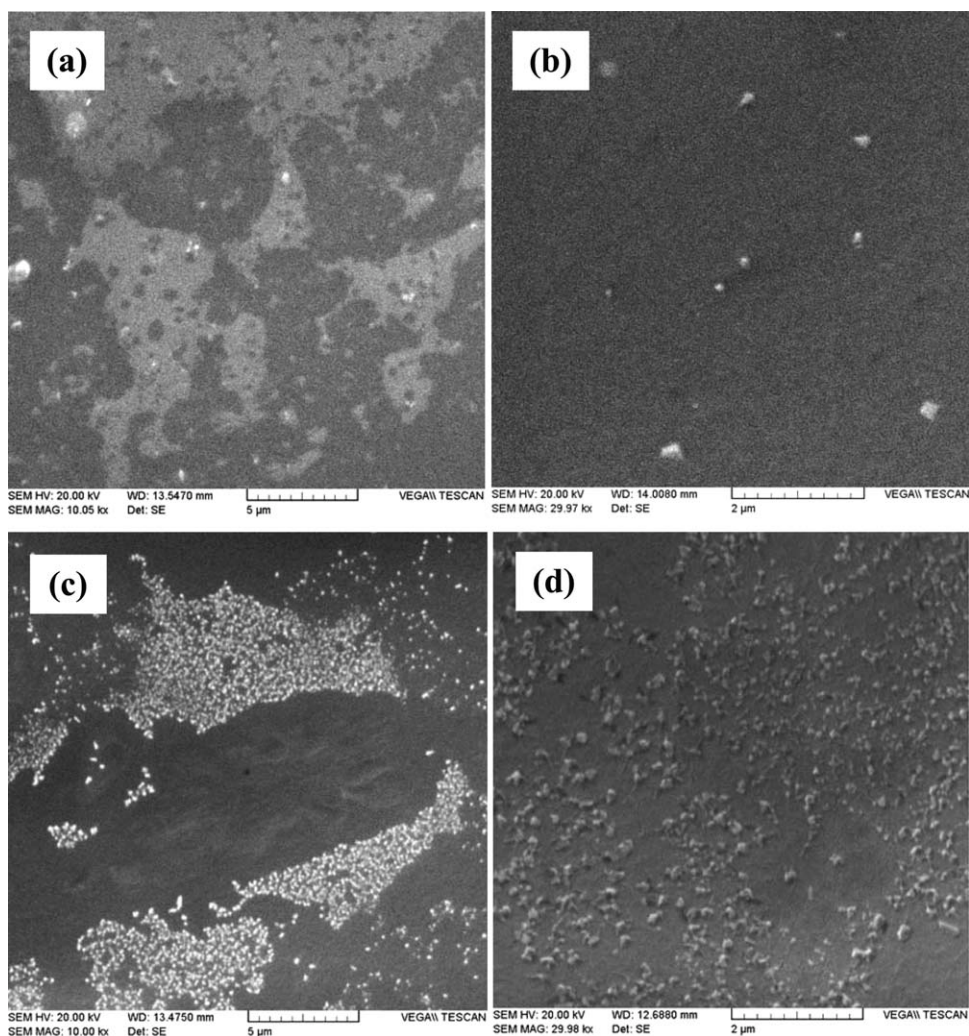


Figure 7 SEM pictures of samples S10 (a, b) and S11 (c, d). The right pictures ($\times 30,000$) are threefold larger than the left ones ($\times 10,000$).

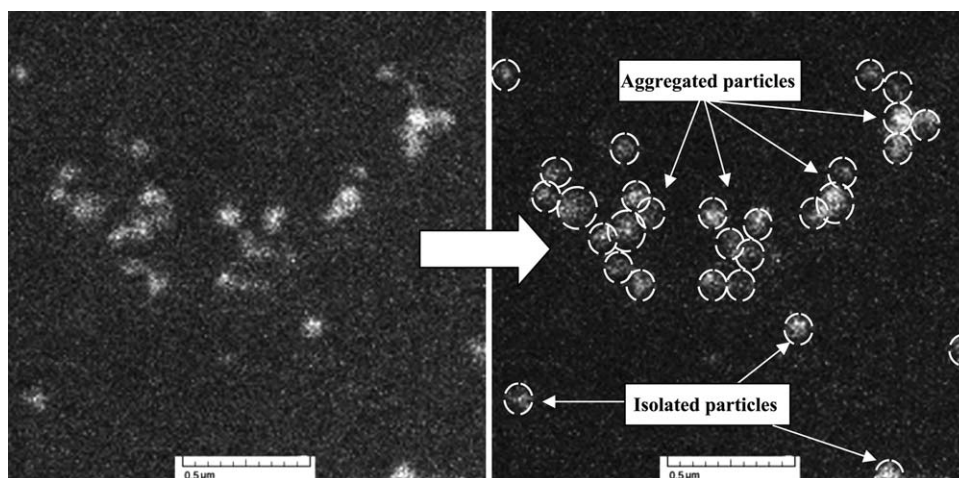
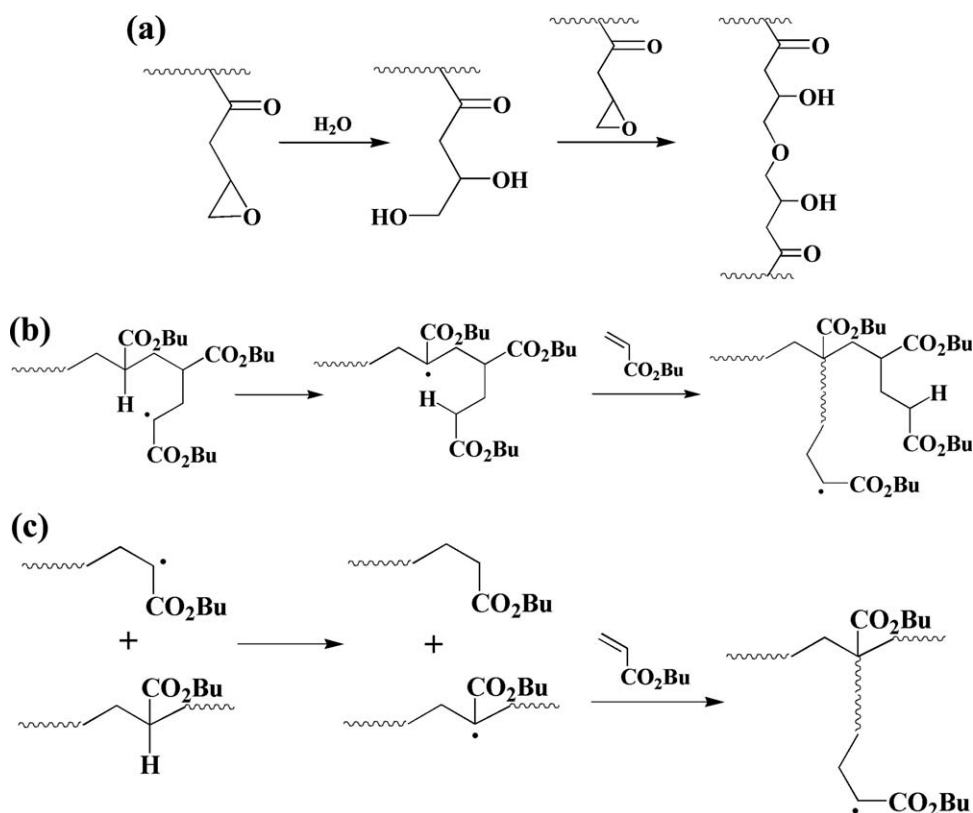


Figure 8 SEM picture of sample S11 (left) and illustration of isolated and aggregated particles (right). Magnification $\times 120,000$.

samples were prepared using initiator quantity of 0.075 g, while the mixture was agitated at 100 rpm. Figure 6 shows conversion against time for these samples. Increased monomer conversions were measured for two early stages with increasing GMA because of its higher reactivity ratio.⁵⁸ According to Figure 6, the final conversions were as high as 97–99% and they were recognized to be independent of

the used comonomers ratios (BA/GMA weight ratio from 90/10 to 70/30).

Mean particle diameter was sharply increased by an increased GMA incorporated in the copolymer (Table I; S8, S10, and S11). Figure 7 shows typical SEM pictures of samples S10 and S11. Particles with micro- and nano-size dimensions are obvious from the pictures. GMA content of $>20\%$ resulted in



Scheme 1 Possible crosslinking reactions via (a) hydrolysis of GMA epoxy groups, (b) intramolecular, and (c) intermolecular hydrogen abstraction reaction of buthyl acrylate backbone.

TABLE II
Conclusive Summary of the Effects of Operation Variables on the Semibatch Emulsion Copolymerization of BA and GMA

Operation variable	Property		
	Conversion	Particle size	Polydispersity index
Agitation speed	Decreased ^a	Decreased ^a	Unchanged
Emulsifier concentration (feed stage)	Increased ^b	Decreased	Unchanged
Initiator concentration	Increased	Decreased	Increased
Feeding rate	Unchanged	Increased	Unchanged
GMA/BA ratio	Increased	Increased	Unchanged

^a At 75 rpm due to insufficient monomer emulsification, conversion and particle size were lower than 100 rpm.

^b Only at very high SDBS concentration (i.e., 1.470 g).

significant increase in the polymer particle diameter. It can possibly be attributed to particle adhesion leading to partial aggregations [Fig. 7(b,d)] which can be related to the GMA characteristics by some means. Water solubility of GMA is much higher than that of BA (50 versus 2 g/L water at 25°C⁵⁹). In addition, according to Geurts et al.,⁶⁰ the product of hydrolytic ring opening of the GMA epoxy group, 2,3-dihydroxypropyl methacrylate (glyceryl methacrylate), is a water soluble monomer. In our work, the hydrolysis can be catalyzed by the slightly alkaline media caused by sodium bicarbonate.⁶⁰ Besides, as noticed by Refojo,⁶¹ GMA has a higher solubility in water/glyceryl methacrylate mixture. Consequently, GMA can probably be (homo)polymerized in the aqueous phase to yield a polymer which will be insoluble in this phase. The presence of glyceryl methacrylate in the emulsion polymerization may also lead to water-soluble polymer or incorporation of glyceryl methacrylate in the particles (mainly at or near the surface). The aforementioned phenomena can cause a tendency of the particle surface to be adhered to each other. Figure 8 exhibited some aggregated particles with nonspherical morphologies. A good agreement was observed in the SEM and LLS data for sample S11 particle size (168.3 nm). In the case of S10, no clear picture was obtained due to tiny polymer particle (16.1 nm).

Finally, it should be pointed out that, it was not possible to measure the molecular weight or intrinsic viscosity of samples. In fact, they were swelled but not dissolved in common solvents such as acetone, methylethyl ketone, tetrahydrofurane, toluene, chloroform, and dimethylsulfoxide. The insolubility was attributed to some sort of undesirable crosslinking (gelation) during copolymerization resulted in the gel content around 30% (Table I) so that higher GMA content led to more gel fraction. This is because of the aforementioned tendency of GMA toward ring opening hydrolysis and crosslinking leading to insolubility [Scheme 1(a)]. Moreover, chain transfer to polymer

occurs extensively in emulsion copolymerizations of BA. In this regard, Lovell et al.⁶²⁻⁶⁶ reported that chain transfer to polymer occurs extensively in emulsion copolymerizations of BA and involved abstraction of hydrogen atoms from backbone tertiary C-H bonds [Scheme 1(b,c)]. They spectroscopically established formation of long-chain branches and potential crosslinking due to propagating branches terminated by coupling. Plessis et al.⁶⁷⁻⁷² also studied the seeded semibatch emulsion polymerization of BA and reported that, under starved conditions, a highly branched polymer (% branches = 0.9–3.4) containing 50–60% gel was formed.⁷²

CONCLUSIONS

BA-GMA latexes were prepared via semibatch emulsion copolymerization. Due to some practical purposes, the BA/GMA weight ratio of 80/20 was used for the majority of the polymerization recipes. The reaction was conducted in three stages; seed, feed, and steady stages. Frequently, the steady stage (2 h) caused considerable improvement of the monomer conversion. The conclusive remarks are summarized in Table II.

High agitation speed had a negative effect on the monomer conversion; however it reduced coagulation of polymer particles. Monomer conversion could be improved by using higher quantities of the initiator KPS or emulsifier SDBS. Our experiments showed that feeding rate increased the polymer particle size sharply, whereas no significant effect on conversion was observed. The final conversions were recognized to be independent of the used comonomers ratios (BA/GMA weight ratio from 90/10 to 70/30), but enhancing the GMA content caused to a tendency of the particle surface to be adhered.

Overall, we could conclude optimized conditions for the emulsion copolymerization as follows; agitation speed 100 rpm, SDBS 0.980 g, KPS 0.075 g, and feeding rate 18.8 mL/h. The latexes are now being

used to formulate and evaluate some modified acrylic coatings in our laboratory.

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