

Statistical Experimental Strategies Approach to Emulsion Copolymerization of Styrene and *n*-Butyl Acrylate

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Received 24 July 1997; accepted 27 December 1997

ABSTRACT: A batch emulsion copolymerization for the preparation of styrene-*n*-butylacrylate (St/BA) copolymer latexes is investigated. A series of *n*-butylacrylate-styrene copolymer latexes were obtained by emulsion copolymerization in the presence of $K_2S_2O_8$ (KPS) as initiator and with/without emulsifier (sodium lauryl sulfate). The effect of such preparation conditions as initiator concentration, the St/BA ratio, reaction temperature, agitation rate, and emulsifier concentration on the polymerization rate, particle size of copolymer latex, and molecular weight distribution of the resulting copolymer ($\sim 80\%$ conversion), respectively, is systematically studied using fractional factorial design methodology. Fractional factorial analysis indicates that the effects of the St/BA ratio, reaction temperature, emulsifier concentration, as well as the two-factor interaction of temperature and emulsifier concentration, are the key variables influencing the polymerization rate. At $\sim 80\%$ monomer conversion, statistical analysis clearly isolates emulsifier concentration as the dominant factor affecting average particle size of copolymer latex; results also indicate that the effects of the St/BA ratio, reaction temperature, and emulsifier concentration are major effects influencing the polydispersity of polymer molecular-weight distribution. For 7.30 g KPS/100 g monomer and 500 rpm agitation rate, the conditions for minimizing molecular-weight distribution ($\sim 80\%$ conversion) occur for a reaction temperature, St/BA ratio, and surfactant concentration of 70°C , $\sim 3.59/1$, and ~ 2.08 g/100 g monomer, respectively, generating a minimum molecular-weight polydispersity of ~ 3.0 . © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 551–563, 1998

Key words: emulsion copolymerization; statistical experimental strategies; styrene; *n*-butylacrylate

INTRODUCTION

Since the successful development of emulsifier-free emulsion polymerization ~ 3 decades ago, this polymerization process has drawn the attention of researchers from the polymer field. Such a

polymerization process has been used in a variety of monomers/comonomers and demonstrated efficaciousness for producing monodispersity and “clean” latexes.^{1–7} In this polymerization system, polymer particles are stabilized by ionizable initiators or by ionic comonomers. Several mechanisms have been proposed for particle nucleation and growth during polymerization without emulsifier.^{8–10} Generally, these mechanisms are in agreement with the actual process, which depends on the water solubility of a monomer. In a study of the $K_2S_2O_8$ (KPS)/styrene (St)/ H_2O

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Contract grant sponsor: The National Science Council of the Republic of China; contract grant numbers: NSC-86-2214-E-168-001 and NSC-87-2218-E-168-006.

Journal of Applied Polymer Science, Vol. 69, 551–563 (1998)

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CCC 0021-8995/98/030551-13

system, Goodall and colleagues² and Goodwin and colleagues¹¹ found that the nucleation mechanism is the micellar type. St monomers polymerize in the aqueous phase to oligomeric radicals with the sulfate group, which are surface-active and form micelles in emulsion polymerization.⁸ On the other hand, for a more water-soluble monomer—like methyl methacrylate¹⁰—the particles are formed by the precipitation of a critical chain length. In the previous two cases, subsequent polymerization would occur in monomer swollen particles.¹²

St-butylacrylate (BA) emulsion copolymers have received considerable attention in the past few years due to their successful application in industry. The flexibility of obtaining a large number of polymer materials is usually used through the variation of the copolymer composition and the polymerization process. Owing to the differences in the physicochemical properties of monomers (polarity, water solubility) and of the corresponding homopolymers (T_g , solubility parameters), this copolymerization system is quite interesting and has been extensively studied. Kinetic study showed that the reactivity ratios determined in batch emulsion polymerization^{13–15} are close to those obtained in bulk or solution polymerization^{16,17}; there exist some differences in comparison with a semicontinuous condition.¹⁸ In addition, the formation of particles is significantly dominated by a homogeneous nucleation mechanism due to the relatively higher water solubility of BA,¹⁸ except when the emulsifier concentration exceeds its critical micelle concentration.

Recently, many papers^{19,20} and patents have described the preparation of structured latexes by emulsion polymerization and found that many parameters influence particle formation. Hearn and colleagues³ reported that the bimodal molecular weight distribution could not be explained by conventional theory and that the polymerization possibly proceeded at two sites. Arai and colleagues²¹ compared the polymerization rate of bulk polymerization, emulsion polymerization, and emulsifier-free emulsion polymerization, and also studied the effects of the mixing rate.²² However, there is still a lack of a systematical study for the effects of process parameters on kinetic behavior, emulsion particle size, and polymer molecular weight distribution.

In this study, fractional factorial design²³ was used in planning experiments that study the effects of such preparation variables as initiator

Table I Factors and Levels for the 2⁵⁻¹ Fractional Factorial Design

Factors ^a	Levels	
	+	-
A, KPS concentration (g)	5.838	1.946
B, St/BA ratio	8/72	72/8
C, Reaction temperature (°C)	70	60
D, Agitation rate (rpm)	500	250
E, SLS concentration (g)	1.664	0

^a The volume of aqueous solution of St/BA comonomer mixture is ~800 mL containing 80 g monomers and 720 g H₂O.

concentration, St/BA ratio, polymerization temperature, agitation rate and emulsifier concentration on polymerization kinetics, emulsion particle size, and polymer molecular weight distribution.

EXPERIMENTAL

Materials

The monomers, St (from Osaka Co., Osaka, Japan) and BA (from Osaka Co.), were stored at -5°C in nitrogen. Potassium persulfate (from Merck GR grade) was used as received. Sodium lauryl sulfate (SLS) (from Osaka Co.) was used as an emulsifier. Deionized water was purged with nitrogen 1 h before use.

Preparation of Latexes

Latexes were prepared according to the copolymerization process in one step. The device used was constituted of a 1000 mL, four-necked, round-bottomed reactor vessel equipped with a Teflon paddle-propeller stirrer, a nitrogen inlet and outlet, a temperature control, and a thermometer (thermocouple).

The effects of the following parameters on the polymerization rate, particle size of copolymer latexes, and molecular weight distribution of the resulting copolymer, respectively, were investigated: (1) initiator (potassium persulfate) concentration; (2) St/BA ratio; (3) reaction temperature (°C); (4) agitation rate (rpm); and (5) surfactant (SLS) concentration. Experiments were conventionally conducted by varying 1 factor at a time, with the remaining factors held constant. In this study, fractional factorial design was uti-

Table II Design Matrix and Experimental Data from the 2⁵⁻¹ Fractional Factorial Design with the Defining Relation I = ABCDE

Run	Factors					Responses					Remark (~80% conversion)
	A	B	C	D	E	$t_{80\%}^*$ ^a (min)	ΔT_{\max}^* ^b (°C)	D_p^* ^c (nm)	\bar{M}_n^* ^d (10 ⁵)	\bar{M}_w^*/\bar{M}_n ^e	
1	-	-	-	-	+	33.5	1.8	66	3.76	3.53	82.5
2	+	-	-	-	-	435	0.9	593	0.29	4.25	81.0
3	-	+	-	-	-	270	1.2	643	1.09	9.80	82.5
4	+	+	-	-	+	13	4.9	57	3.42	5.19	83.7
5	-	-	+	-	-	334	0.8	543	0.30	4.51	77.3
6	+	-	+	-	+	14.5	3.6	48	0.98	2.77	80.5
7	-	+	+	-	+	7.5	6.2	48	3.44	4.34	83.8
8	+	+	+	-	-	50	3.3	445	0.61	4.63	81.7
9	-	-	-	+	-	1500	0.6	366	0.45	5.15	77.1
10	+	-	-	+	+	27	2.2	52	2.25	3.20	80.0
11	-	+	-	+	+	78	5.2	51	6.24	4.65	81.7
12	+	+	-	+	-	230	1.6	584	0.80	7.03	79.1
13	-	-	+	+	+	16	2.5	61	3.11	2.73	80.9
14	+	-	+	+	-	162	2.0	363	0.15	3.12	76.6
15	-	+	+	+	-	90	1.7	479	1.01	5.38	81.2
16	+	+	+	+	+	9.5	7.3	60	2.61	4.32	83.7

^a Reaction time for ~80% conversion.

^b Maximum temperature rise during polymerization.

^c Hydraulic-average particle size for ~80% conversion.

^d Number-average molecular weight corresponding to the polymer with ~80% monomer conversion.

^e Polydispersity of polymer molecular weight.

lized in designing the experiments. A total of 16 experiments were performed. Fixed levels and design levels for the previous five parameters are given in Tables I and II respectively.

To a 1000-mL, four-necked, round-bottomed flask, water (720 g) was charged under a nitrogen gas atmosphere, and a solution of 80 g monomer mixtures (St/BA) and KPS with or without SLS surfactant—depending on the reaction in question (refer to Tables I and II)—was then added immediately and kept over a period of 1 h while stirring. Depending on the reaction in question, the resulting mixture was then heated at a reaction temperature of either 60 or 70°C under an agitation rate of either 250 or 500 rpm until ~80% conversion of the monomer was reached, as determined by the gravimetric method. A latex of ~10% solids was obtained.

Polymerization Rate

Monomer conversion was determined by the gravimetric method of solid product precipitated and dried from the reaction mixture.

Particle Size and Particle Size Distribution

The particle size and particle size distribution were determined by a laser scattering spectrophotometer (Otsuka, LPA 3000/3100). This procedure involved diluting a few drops of the emulsion in distilled water before spectrophotometric measurement.

Molecular Weights

The molecular weight distribution and the average molecular weight of the polymer were determined by gel permeation chromatography (Shimadzu R-7A data module, LC-10AS pump). The separation columns were two linear columns in the series. The flow rate for tetrahydrofuran was 1 mL min⁻¹ at 40°C using polystyrene standards.

Glass Transition Temperatures

The T_g 's of copolymers were determined with differential scanning calorimetry equipment (Du-

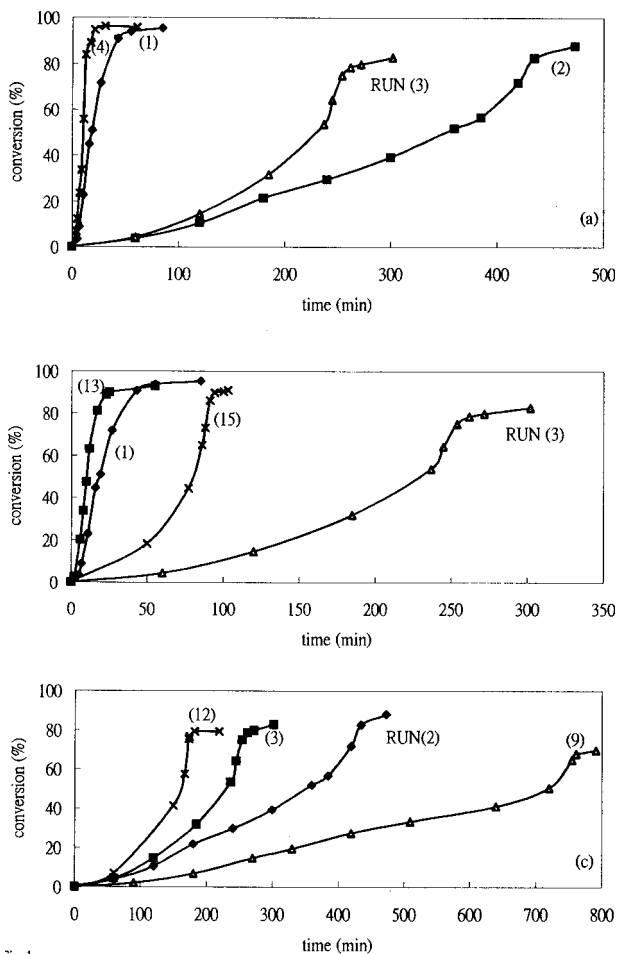


Figure 1 Conversion vs. reaction time. The recipe of experimental run refers to Table II.

Pont 2910 MDSC) between -60°C and 120°C , using a heating rate of $10^{\circ}\text{C}/\text{min}$.

Copolymer Composition

The copolymer composition of the various samples at different conversions was deduced from the T_g data of these copolymers.

RESULTS AND DISCUSSION

Polymerization Rate

Figure 1 shows plots of conversion against time. In Figure 1(a), it is clear that the surfactant concentration can enhance the reaction rate (*cf.* run 1 and run 2). But, the increase in monomer ratio of St/BA retards the reaction rate (*cf.* run 3 and

run 4). The former result is possible because more particles are generated by increasing surfactant concentration. The latter result is attributable to the lower reactivity of the St monomer. In Figure 1(b), it is obvious that the increase of temperature (*cf.* run 1 and run 13) and agitation rate (*cf.* run 3 and run 15) can enhance the reaction rate. The reaction rate increases with increasing temperature due to the increase of reaction energy. In Figure 1(c), it is noted that the reaction rate significantly decreases with decreasing initiator concentration (*cf.* run 2 and run 9, and run 3 and run 12) in soap-free polymerization at a high agitation rate. The result can be attributed that less free radicals are generated by decreasing initiator concentration under this experimental condition.

To identify the key variables influencing the polymerization rate of St/BA copolymerization from the following process variables [(A) KPS concentration, (B) St/BA ratio, (C) reaction temperature, (D) agitation rate, and (E) surfactant concentration], the fractional factorial method and response surface procedure were first established. This experimental design allows the influence on each process variable to be observed at a variety of other variable levels, as well as allowing observations of the interaction effects among the variables.

The design factors and levels for the 2^{5-1} fractional factorial experiments are listed in Table I, and the results of these experiments are given in Table II. The level of each variable during a run is indicated in columns 2 to 6 of Table II, with the time of $\sim 80\%$ monomeric conversion ($t_{80\%}$) corresponding to each set of conditions shown in column 7. Note that the combination of observations used in estimating the main effect of factor *E* (surfactant concentration) is identical to that used estimating the 4-factor interaction effect of factors *A* (initiator concentration), *B* (St/BA ratio), *C* (reaction temperature), and *D* (agitation rate); hence, estimates of factor *E* and the interaction effect of factors *A*, *B*, *C*, and *D* are said to be "confounded."²³ Accordingly, the defining relation $I = ABCDE$, suggested by Box and colleagues,²³ was established to identify those relationships that exist between the effects.

Estimates of the experimental variable effects were algebraically calculated following the procedure recommended by Box and colleagues²³ and are given in Table III. Note that if the basic assumption of Box and colleagues²³ is employed,

Table III $t_{80\%}$ Estimates of the Effects from the 2^{5-1} Fractional Factorial Design with the Defining Relation I = ABCDE

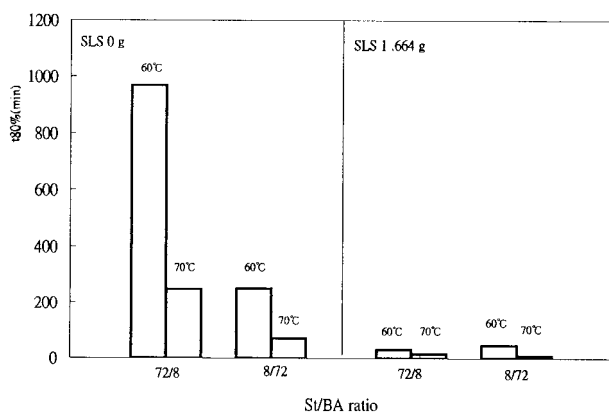
Effect	Estimate
A + BCDE	-173.5
*B + ACDE	-221.7
*C + ABDE	-237.8
D + ABCE	119.3
*E + ABCD	-359.0
AB + CDE	136.6
AC + BDE	120.6
AD + BCE	-140.3
AE + BCD	180.8
BC + ADE	129.3
BD + ACE	-102.6
*BE + ACD	226.0
CD + ABE	-151.5
*CE + ABD	211.8
DE + ABC	-103.8

where higher order interaction effects (3- and 4-factor interactions in this study) are often negligible and can be ignored, the main and 2-factor interaction effects can be obtained without confusion with higher order interaction effects.

An examination of Table III reveals that the effects of the St/BA ratio (B), reaction temperature (C), and surfactant concentration (E) are the key variables influencing the $t_{80\%}$, and that the 2-factor interactions on the $t_{80\%}$ of the St/BA ratio and surfactant concentration (BE), and of reaction temperature and surfactant concentration (CE) are significant and require further interpretation. These effects are indicated with an asterisk in Table III, and represent the relatively larger positive and negative estimated values. The effects of the St/BA ratio (B), reaction temperature (C), and surfactant concentration (E) cannot be discussed separately due to the significant interactions on the $t_{80\%}$ between the St/BA ratio and surfactant concentration (BE), as well as reaction temperature and surfactant concentration (CE). Hence, the $t_{80\%}$ is depicted as a function of St/BA ratio (B), reaction temperature (C), and surfactant concentration (E) in Figure 2. An examination of Figure 2 reveals that the combination of these effects clearly isolates surfactant concentration as the dominating factor affecting the $t_{80\%}$. The $t_{80\%}$ decreases after the addition of 1.664 g of SLS surfactant into the reaction mixture. This result can be ascribable to many uniform emulsion particles (micelles) easily generating in the

reaction mixtures, leading to a decrease in reaction time. At 0 g SLS surfactant, decreasing the St/BA ratio from 72/8 to 8/72 and increasing reaction temperature from 60 to 70°C results in a decrease in the $t_{80\%}$. This situation is thought to arise from the fact that St/BA comonomers devoid of SLS surfactant with high St/BA ratios and low temperature are able to form uniform emulsion particles and results in a significant increase in the $t_{80\%}$. On the other hand, at 1.664 g SLS surfactant, the $t_{80\%}$ decreases after an increase in temperature from 60 to 70°C. This result is similar to that of 0 g SLS surfactant. At the same reaction temperature, it is noteworthy that the changes of $t_{80\%}$ for the 1.664 g SLS system are relatively insignificant to the variations of the St/BA ratio.

A batch emulsion copolymerization was conducted in which the reactor was initially charged with all the water, monomers, initiator, and with/without surfactant. Figure 3 presents the temperature variation (ΔT) and conversion of reaction system against reaction time. The points were experimental values measured by the thermocouple. In Figure 3(a), it can be seen that a continuous increase of the polymerization rate was observed from $\sim 20\%$ conversion to 80%. This increase is attributable to the more BA generating the higher copolymerization rate, reflecting the fact that the fraction of St decreases consecutively in the St/BA comonomer mixture as the conversion increases. In Figure 3(b), as explained previously, there was obviously a similar tendency of experimental results. To confirm this explanation, run 15 was conducted using the recipe of Table II and the plot of glass transition temperature (T_g , dif-

**Figure 2** Model predictions for the time of $\sim 80\%$ monomeric conversion as a function of SLS concentration, St/BA ratio, and reaction temperature.

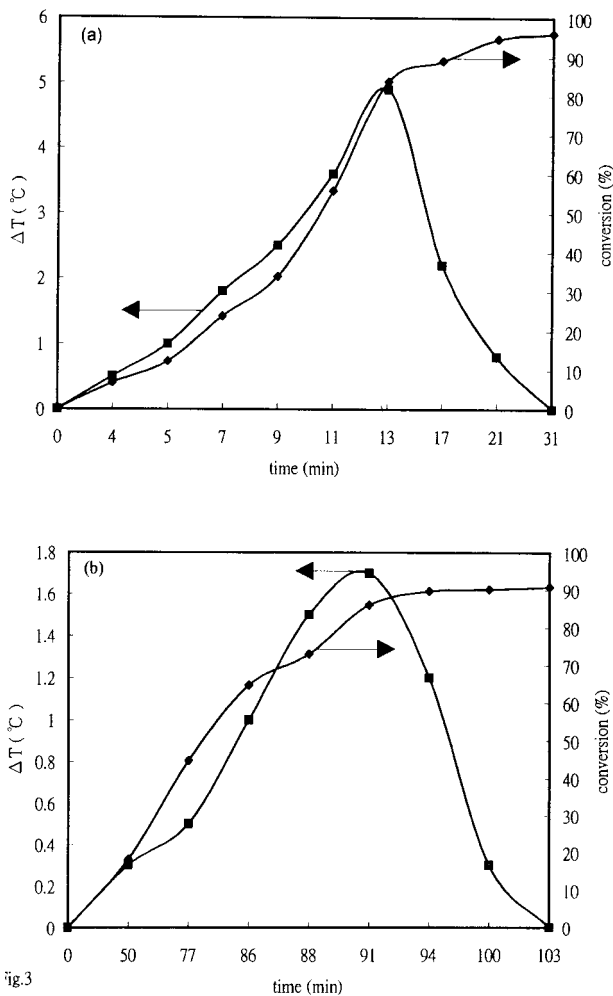


Figure 3 Temperature variation (ΔT) and conversion of reaction system *vs.* reaction time. (a) Run 4. (b) Run 15.

ferential scanning calorimetry results) of copolymer against conversion is presented in Figure 4. An examination of Figure 4 reveals that T_g decreases with increasing conversion. This result reflects the fact that St is enriched in the early stage of polymerization and then gradually decreased in the later stage.

The quantity of ΔT_{\max} corresponds to the most significant existence in the autoacceleration process of polymerization. To clarify the effects of process variables on ΔT_{\max} , the results of 2^{5-1} fractional factorial experiments are given in Table II (column 8); and estimates of the experimental variable effects are given in Table IV. An examination of Table IV reveals that the effects of the St/BA ratio (B), reaction temperature (C), and surfactant concentration (E) are the key variables

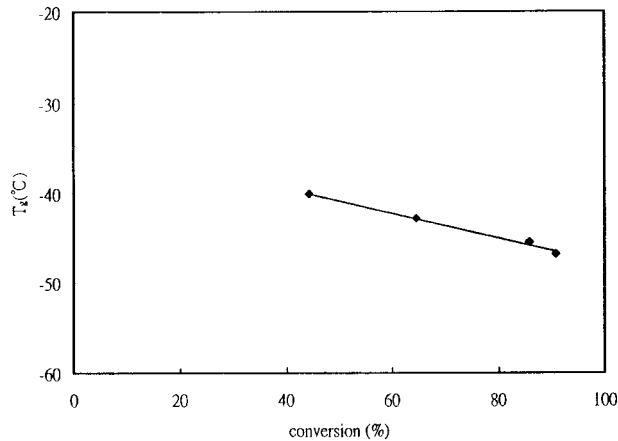


Figure 4 Plot of glass transition temperature (T_g) against conversion for run 15.

influencing the ΔT_{\max} , and that the 2-factor interactions on ΔT_{\max} of the St/BA ratio and surfactant concentration (BE) are significant. The main effect of a variable can be individually interpreted, if and only if its effects are not confused with those of other variables. Because interaction of the reaction temperature (C) with the other factors is insignificant—their estimated values are relatively small (see Table IV)—the effect of reaction temperature on ΔT_{\max} will be discussed separately. The ΔT_{\max} *versus* reaction temperature is plotted in Figure 5, and reveals that an increase in the former corresponds to an increase in the latter. This situation is thought to arise from the

Table IV ΔT_{\max} Estimates of the Effects from the 2^{5-1} Fractional Factorial Design with the Defining Relation I = ABCDE

Effects	Estimate
A + BCDE	0.72
*B + ACDE	2.12
*C + ABDE	1.12
D + ABCE	0.05
*E + ABCD	2.7
AB + CDE	-0.02
AC + BDE	0.52
AD + BCE	0.05
AE + BCD	-0.15
BC + ADE	0.27
BD + ACE	0.00
*BE + ACD	1.12
CD + ABE	-0.42
CE + ABD	0.25
DE + ABC	0.12

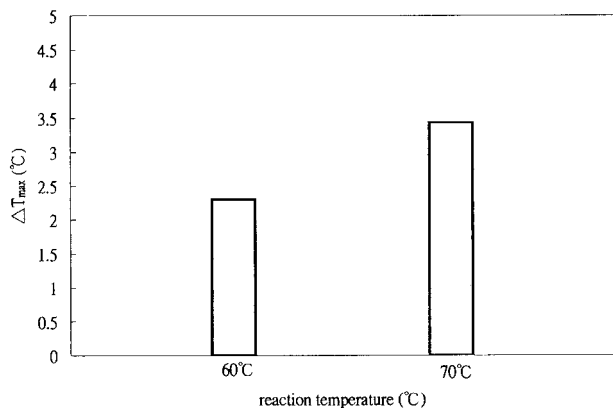


Figure 5 Effect of reaction temperature on the maximum temperature variation (ΔT_{\max}).

autoacceleration process promoted by higher temperature that provides more reaction energy to initiate the free-radical polymerization. This promotion of autoacceleration process leads to more evolution of heat with the net result of higher ΔT_{\max} being formed. Due to the significant interaction on ΔT_{\max} between the St/BA ratio and surfactant concentration (BE), the ΔT_{\max} is depicted as a function of St/BA ratio and surfactant concentration in Figure 6. An examination of Figure 6 reveals that the combination of these effects clearly isolates St/BA ratio as the dominating factor affecting ΔT_{\max} . At a St/BA ratio of 8/72, the ΔT_{\max} for a specific SLS surfactant is relatively sensitive, while increasing the SLS surfactant from 0 to 1.664 g results in a significant increase in the ΔT_{\max} . Decreasing the St/BA ratio from 72/8 to 8/72 results in an increase in the ΔT_{\max} .

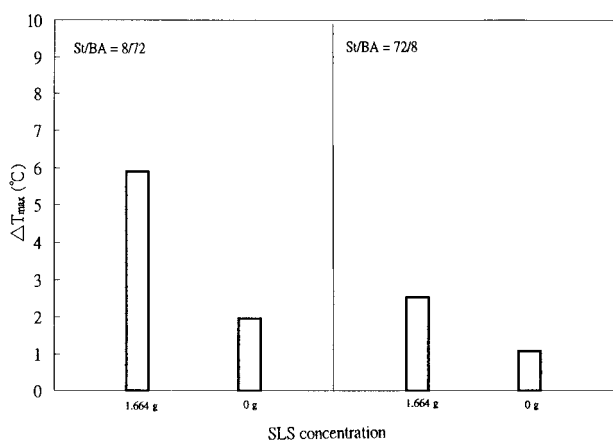


Figure 6 Model predictions for ΔT_{\max} as a function of SLS concentration and St/BA ratio.

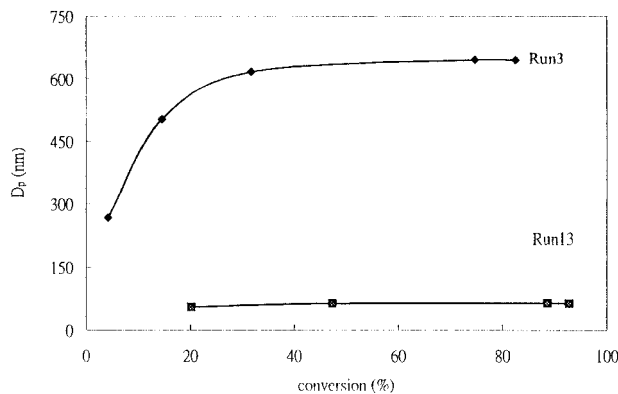


Figure 7 Hydraulic-average particle size (D_p) vs. conversion.

This result is thought to arise from the fact that more particles can be easily generated with the addition of (1.664 g) surfactant; whereas at relatively higher St/BA ratios, reactivity decreases, which results in a significant decrease in the ΔT_{\max} .

Particle Size

The particle size (D_p , hydraulic-average size) obtained from laser scattering spectroscopy as a function of conversion is shown in Figure 7. Particle size increases with increasing conversion for both with (run 13) and without (run 3) surfactants. The particle size gradually approaches a constant when monomers are used up. This figure also shows that smaller particles are obtained with the addition of surfactant (run 13). The similar phenomena have been observed in Chiu and

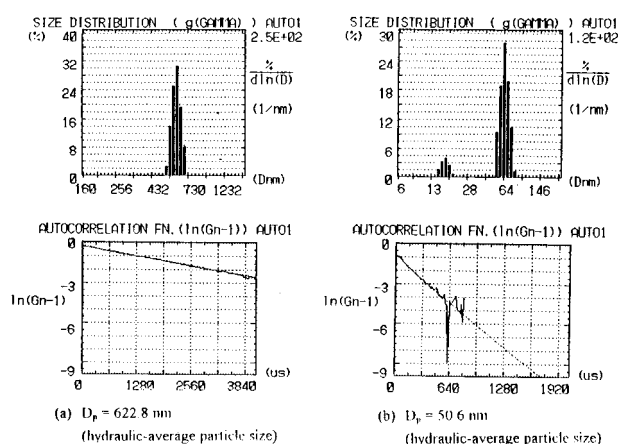
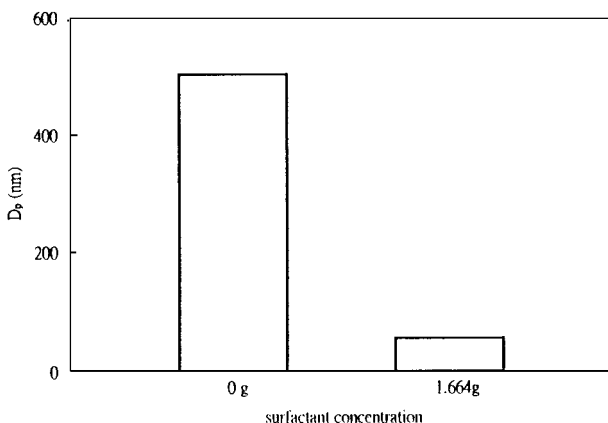
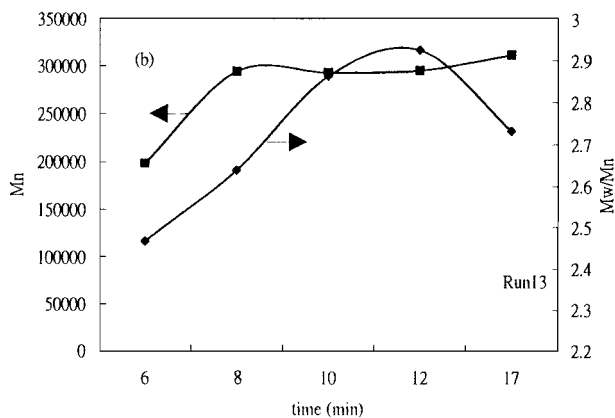
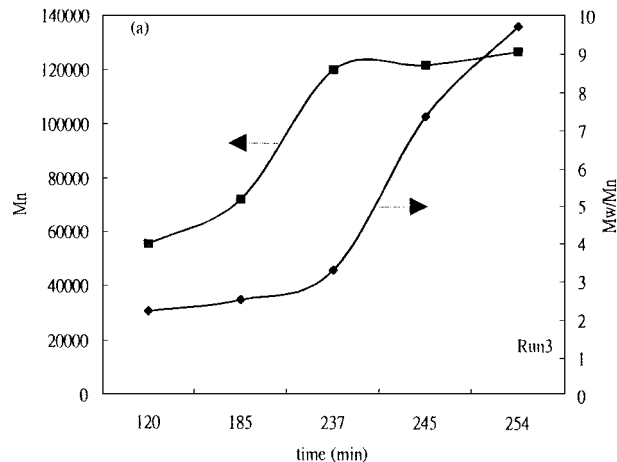


Figure 8 Particle size distribution. (a) Run 3 (conversion 80%). (b) Run 11 (conversion 87%).

Table V D_p Estimates of the Effects from the 2^{5-1} Fractional Factorial Design with the Defining Relation I = ABCDE

Effects	Estimate
A + BCDE	-6.8
B + ACDE	34.3
C + ABDE	-45.6
D + ABCE	-53.3
*E + ABCD	-446.6
AB + CDE	-12.0
AC + BDE	-47
AD + BCE	32.0
AE + BCD	5.0
BC + ADE	-30.0
BD + ACE	49.00
BE + ACD	-37.0
CD + ABE	23.0
CE + ABD	43.05
DE + ABC	55.0

colleagues.²⁴ This could be explained by the effect of surfactant on the increase of particle number. Figure 8 shows the particle size distribution. A comparison of Figure 8(a, b) reveals that the unimodal distribution exists in surfactant-free copolymerization system (run 3), and that the bimodal distribution exists in with-surfactant copolymerization system (run 11). These results suggest that the nucleation time is short relative to reaction time in the surfactant-free system, which leads to a uniform size of particles and that the nucleation time is long in with-surfactant system, which results in a bimodal size distribution of particles.²⁵

**Figure 9** Effect of SLS concentration on the average particle size.**Figure 10** Number-average molecular weight (M_n) and polydispersity (M_w/M_n) of polymer vs. reaction time. (a) Run 3. (b) Run 13.

To identify the effects of process variables on D_p corresponding to 80% monomeric conversion, the results of 2^{5-1} fractional factorial experiments are also given in Table II (column 9). Estimates of the experimental variable effects are given in Table V. An examination of Table 5 reveals that the effect of surfactant concentration (E) is the key variable influencing particle size. Particle size *versus* surfactant concentration is plotted in Figure 9 and indicates that an increase in the former corresponds to a decrease in the latter. This result is attributable to less particles being generated in surfactant-free emulsion polymerization.

Molecular Weight

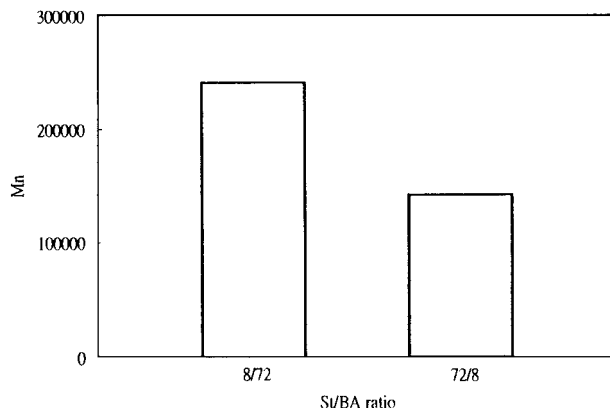
The molecular weight changes with time are shown in Figure 10. It is clear that the molecular

Table VI M_n Estimates of the Effects from the 2^{5-1} Fractional Factorial Design with the Defining Relation I = ABCDE

Effects	Estimate
*A + BCDE	-1.034
*B + ACDE	0.993
*C + ABDE	-0.760
D + ABCE	0.339
*E + ABCD	2.639
AB + CDE	-0.049
AC + BDE	0.158
AD + BCE	-0.215
*AE + BCD	-0.787
BC + ADE	-0.209
BD + ACE	0.181
BE + ACD	0.409
CD + ABE	0.046
*CE + ABD	-0.619
DE + ABC	0.309

weights increase with increasing polymerization time for both cases of surfactant-free and with-surfactant systems. These results are similar to those of the previous works.^{27,28} Similarly, the polydispersity of molecular weight increases with increasing polymerization time, and the polydispersity of the surfactant-free system is larger than that of the with-surfactant system. These results reflect that many molecules of different molecular weight generated in the later stage of polymerization (BA rich in this period) and that the larger polydispersity exists in the system of larger particle size.

To identify the effects of process variables on M_n corresponding to $\sim 80\%$ monomeric conversion, the results of 2^{5-1} fractional factorial experiments are also given in Table II (column 10). Estimates of the experimental variable effects are given in Table VI. An examination of Table VI reveals that the effects of initiator concentration (A), St/BA ratio (B), reaction temperature (C), and surfactant concentration (E) are the key variables influencing molecular weight (M_n). The 2-factor interactions on M_n of initiator concentration and surfactant concentration (AE), and reaction temperature and surfactant concentration (CE) are significant. The M_n versus the St/BA ratio is plotted in Figure 11 and reveals that an increase in the former corresponds to a decrease in the latter. One possible explanation for this result is that the monomers

**Figure 11** Effect of St/BA ratio on the number-average molecular weight of polymer.

of low St/BA ratio are easily propagated to obtain the polymer of higher molecular weight. Owing to the significant interactions on M_n between initiator concentration and surfactant concentration (AE), as well as reaction temperature and surfactant concentration (CE), the M_n is depicted as a function of initiator concentration (A), reaction temperature (C), and surfactant concentration (E) in Figure 12. An examination of Figure 12 reveals that the combination of these effects clearly isolated a surfactant concentration as the dominating factor affecting the M_n . The M_n is quite sensitive to the addition of SLS surfactant, while increasing SLS surfactant concentration from 0 to 1.664 g results in a significant increase in M_n . This re-

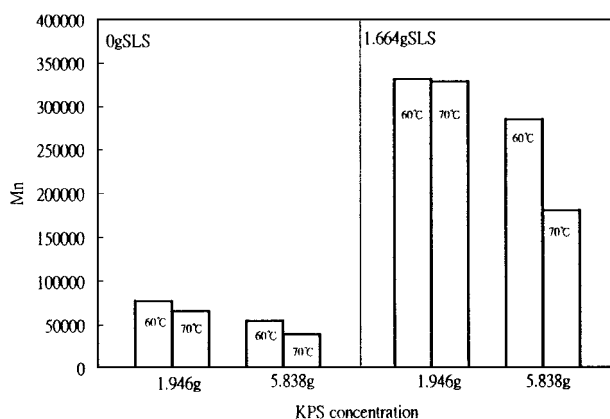
**Figure 12** Model predictions for M_n as a function of SLS concentration, reaction temperature, and KPS concentration.

Table VII M_w/M_n Estimates of the Effects from the 2^{5-1} Fractional Factorial Design with the Defining Relation I = ABCDE

Effects	Estimate
A + BCDE	-0.70
*B + ACDE	2.01
*C + ABDE	-1.37
D + ABCE	-0.39
*E + ABCD	-1.64
AB + CDE	-0.05
AC + BDE	0.17
AD + BCE	0.64
AE + BCD	0.76
*BC + ADE	-0.62
BD + ACE	-0.22
BE + ACD	0.44
CD + ABE	0.26
*CE + ABD	0.77
DE + ABC	0.20

sult implies that more particles are generated in the 1.664 g surfactant reaction mixtures, leading to an easy increase of the molecular weight of molecules in these smaller particles. On the other hand, decreasing reaction temperature from 70°C to 60°C and decreasing initiator concentration from 5.838 to 1.946 g result in an increase in the M_n . This result reflects the fact that the St/BA reaction comonomers with lower initiator concentration at lower reaction temperature are able to easily induce polymer chain propagation.

To identify the effects of process variables on M_w/M_n (polydispersity) corresponding to ~ 80% monomeric conversion, the results of 2^{5-1} fractional factorial experiments are also given in Table II (column 11); estimates of the experimental variable effects are given in Table VII. An examination of Table VII reveals that the effects of the St/BA ratio (B), reaction temperature (C), and surfactant concentration (E) are the key variables influencing the polydispersity of molecular-weight distribution. Decreasing the St/BA ratio from 72/8 to 8/72 results in an increase of polydispersity. This result is ascribable that a more significant gel (autoacceleration) effect exists in BA-riched comonomers, leading to a wider distribution of molecular weight. On the other hand, increasing surfactant concentration from 0 to 1.664 g results in a significant decrease of polydispersity. This re-

sult is thought to arise from the decrease of particle size induced by the addition of surfactant, which can be regarded as case II of the Smith-Ewart²⁶ theory. Such a decrease of particle size leads to the result that r_t (termination rate) is much higher than r_p (propagation rate). Although the polydispersity decreases with increasing reaction temperature (C), the interactions between reaction temperature and surfactant concentration (CE), and the ratio of St/BA and reaction temperature (BC) are also significant. Thus, the key variables influencing the polydispersity of molecular weight have been determined. Further verification of these results, as well as an investigation of the molecular-weight polydispersity dependence of St/BA ratio, reaction temperature, and surfactant concentration, were undertaken.

Distribution of Molecular-Weight Polydispersity

Because a smaller molecular-weight polydispersity was obtained in the presence of higher initiator level (5.838 g KPS) [see column 1 (A) in Table VII] and the effect of agitation rate [see column 1 (D) in Table VII] on molecular-weight polydispersity was insignificant, these parameters were held constant at 5.838 g and 500 rpm, respectively. The designed factors and levels for the 16 central composite design experiments are listed in Table VIII. The results of the molecular-weight polydispersity of St/BA copolymers are shown in Table IX. These results were subjected to regression analysis and consequently generated the following regression equation:

Table VIII Factors and Levels for the Central Composite Design

Levels	Factors		
	St/BA Ratio	Reaction Temperature (°C)	Surfactant Concentration (g)
-1.6818	72/8	56.6	0.000
-1	62.6/17.4	60.0	0.423
0	40/40	65.0	1.043
+1	17.4/62.6	70.0	1.664
+1.6818	2/72	73.4	2.087

Table IX The Design Matrix and Experimental Data of M_w/M_n from the Central Composite Design for the Quadratic Form Fit

Run	Factors			\bar{M}_n (10^5)	\bar{M}_w/\bar{M}_n	Remark (~80% conversion)
	B	C	E			
1	-1	-1	-1	1.538	3.11	88.9
2	-1	-1	+1	2.250	3.20	81.0
3	-1	+1	-1	0.551	4.17	88.9
4	-1	+1	+1	0.910	3.59	88.0
5	+1	-1	-1	1.919	3.27	81.7
6	+1	-1	+1	1.623	4.41	89.8
7	+1	+1	-1	1.074	3.81	79.0
8	+1	+1	+1	2.611	4.33	81.7
9	0	0	0	0.6828	6.10	80.4
10	0	0	0	0.678	6.12	80.4
11	0	0	-1.6818	0.228	6.29	79.2
12	0	0	+1.6818	1.674	3.51	78.5
13	0	-1.6818	0	4.020	2.64	76.3
14	0	+1.6818	0	0.568	4.72	78.1
15	-1.6818	0	0	1.297	3.41	81.6
16	+1.6818	0	0	1.276	4.23	86.3

$$\begin{aligned}
Y = & 0.14 + 0.23B + 0.40C - 0.25E \\
& (0.55) \quad (0.21) \quad (0.21) \quad (0.21) \\
& - 0.85B^2 - 0.98C^2 - 0.51E^2 \\
& \quad (0.25) \quad (0.27) \quad (0.27) \\
& - 0.12BC + 0.27BE - 0.16CE \quad (1) \\
& \quad (0.28) \quad (0.28) \quad (0.28)
\end{aligned}$$

where the Y , B , C , and E terms, respectively, represent polydispersity of molecular weight, the St/BA ratio, polymerization reaction temperature, and surfactant concentration. The number in parentheses below the coefficients are their standard errors based on error variance estimates ($s^2 = \text{mean square of error} = 0.63$). The analysis of variance is summarized in Table X. The test statistics, F and R^2 , are defined as $F = \text{MSR}/\text{MSE}$ and $R^2 = 1 - \text{SSE}/\text{SST}$, where MSR is the mean

Table X Analysis of Variance for the Quadratic Form Fit of M_w/M_n

Source	Sum of Squares	Degrees of Freedom	Mean Square	F
Model	15.30	9	1.70	2.687
Error	3.79	6	0.63	
Total	19.09	15		

$R^2 = 0.81$

square of regression obtained by dividing the sum of squares of regression with the degrees of freedom. MSE represents the mean square error from the analysis of variance. R^2 is the multiple correlation coefficient, with a value close to 1 meaning a perfect fit to the experimental data.

The magnitudes of the regression equation coefficients, compared with their estimated standard errors, are used as a basis for judging statistical significance and illustrate the relative effects of linear, quadratic, and cross-product interaction between the parameters and molecular-weight polydispersity. Accordingly, to examine the distribution of molecular-weight polydispersity, the reaction temperature was held at an arbitrary value (70°C), thereby illustrating the relationship between expected molecular-weight polydispersity, St/BA ratio, and surfactant concentration. Thus, the substitution of $C = 1$ (the reaction temperature at 70°C) into eq. (1) gives the following equation:

$$\begin{aligned}
Y = & 5.56 + 0.11B - 0.41E - 0.85B^2 \\
& - 0.51E^2 + 0.27BE \quad (2)
\end{aligned}$$

Since the sign of the coefficients associated with the quadratic terms (B^2 and E^2) are negative, the

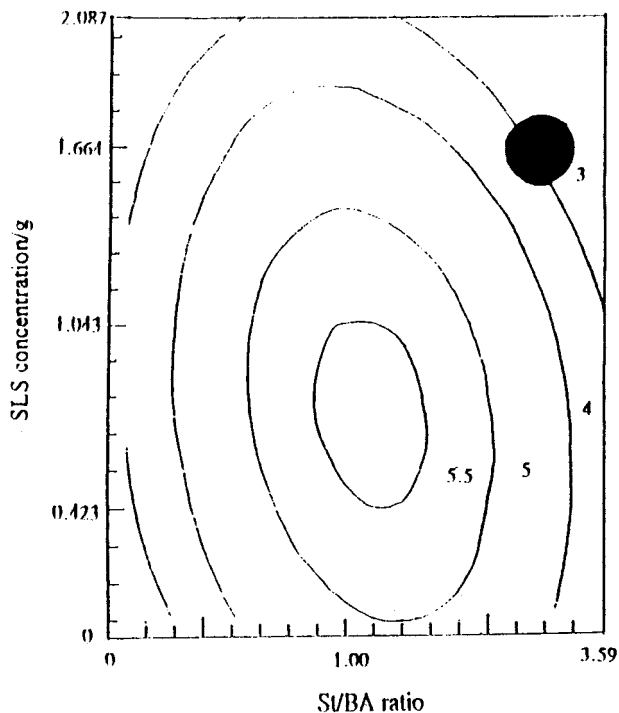


Figure 13 Constant polymer polydispersity contour lines against St/BA ratio and SLS concentration at a 70°C reaction temperature, 5.838 g KPS, and 500 rpm agitation rate. (●) Experimental check point.

distribution of molecular-weight polydispersity exists a maximum.

Equation (2) was used in constructing the contour plot shown in Figure 13 for the distribution of molecular-weight polydispersity against St/BA ratio and surfactant concentration for a reaction temperature of 70°C. An examination of Figure 13 reveals that the minimum molecular-weight polydispersity of ~ 3.0 occurs in the outside surrounding region of the St/BA ratio and surfactant concentration. Under these conditions, the minimum molecular weight distribution is thought to arise from the interactions between the St/BA ratio and surfactant concentration. The statistically

determined relationship between the distribution of molecular-weight polydispersity, St/BA ratio, and surfactant concentration at a 60 and 50°C reaction temperature was similar to that at 70°C. To confirm the validity of the statistical experimental strategies, an additional experiment was performed under the conditions of minimum molecular-weight distribution. The results are listed in Table XI. An examination of Table XI indicates that fractional factorial design and regression analysis are in good agreement with the experimental results.

CONCLUSIONS

Emulsion copolymers of St and n-BA were prepared and the effects of the following operating parameters (KPS concentration, St/BA ratio, reaction temperature, agitation rate, and surfactant concentration on the polymerization rate, particle size of the St/BA copolymer, and molecular-weight distribution of these copolymers) experimentally investigated. Fractional factorial design was shown to be a useful tool in reducing the number of trial runs and in reaching the unconfounded result. The experimental results from the response surface method, subjected to regression analysis and plotted as contour diagrams, were extremely useful in studying the effects of the key variables (St/BA ratio, reaction temperature, and surfactant concentration) on the polydispersity of molecular-weight. Polymerization rate was predominantly influenced by the single factor effects of St/BA ratio (B), reaction temperature (C), and surfactant concentration (E), in addition to the 2-factor interactions of St/BA ratio and surfactant concentration (BE) and reaction temperature and surfactant concentration (CE). The effect of surfactant concentration was the key variable influencing the particle size of copolymer latexes. The effects of St/BA ratio, reaction temperature, and surfactant concentration were the key vari-

Table XI Typical Experimental Data of M_n , M_w , and M_w/M_n for the Conditions Corresponding to the Check Point on Figure 13

Sample, 10^5 (St/BA)	\bar{M}_n (10^5)	\bar{M}_w (10^5)	\bar{M}_w/\bar{M}_n	Remark ($\sim 80\%$ conversion)
62.6/17.4	0.921	2.912	3.2	80.5

ables influencing the polydispersity of molecular-weight distribution, whereas the interactions between reaction temperature and surfactant concentration (CE), and the ratio of St/BA and reaction temperature were also significant. For 7.30 g KPS/100 g monomer and 500 rpm agitation rate, the conditions for minimizing molecular-weight occurred for a reaction temperature, St/BA ratio, and a surfactant concentration of 70°C, $\sim 3.59/1$, and ~ 2.08 g/100 g monomer, respectively, generating a minimum molecular-weight polydispersity of ~ 3.0 .

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