

Stability of Nanoparticles During Semibatch Emulsion Polymerization of Butyl Methacrylate, in the Presence of Methacrylic Acid via RSM

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ABSTRACT: The size and stability of latex particles in the semibatch emulsion polymerization of butyl methacrylate (BMA), in the presence of 0–10% methacrylic acid (MAA), were investigated. Response surface methodology (RSM), as a design of experiment, was used to obtain a more systematic understanding of the role of emulsifier and MAA in the stability of the particles. The amount of coagulum can be greatly reduced by increasing the concentration of sodium lauryl sulfate (SLS) in the monomer emulsion feed (MEF) and initial reactor charge (IRC). On the other hand, increasing the concentration of SLS in the

IRC can result in a decrease of the particles size. According to the experimental data, the yield of reaction can be improved with incorporation of MAA into the emulsion polymers. The size and morphology of particles were obtained by scanning electron microscopy (SEM). FTIR and titration were used to determine the percentage of MAA in the copolymer. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1172–1180, 2007

Key words: stability; semibatch emulsion polymerization; response surface methodology

INTRODUCTION

Polymeric particles in the submicron and nanometer range can be prepared through miniemulsion,¹ microemulsion,² template and dendrimer polymerization,³ as well as via molecular assembly.⁴ Emulsions can be defined as systems formed by two liquids with reciprocal limited solubility, one of which is highly dispersed. The particle sizes of the dispersed phase are within the range 50–2000 nm.⁵ To obtain a stable emulsion, the presence of a third substance termed an emulsifier is required. Surface-active agents forming a surface-active film on the dispersed phase surface are the most often used emulsifiers. They render the coalescence of emulsion particles difficult by changing the interfacial tension at the liquid–liquid boundary. Various kinds of surface-active agents are used for emulsification. They can be distinguished into ionic and nonionic agents having hydrophilic groups and hydrophobic radicals. Carboxyl and sulfate compounds among others belong to the group of anionic surface-active agents.^{5–8}

Submicron particles can collide with one another by Brownian motion or mechanical agitation, and they tend to coagulate due to the attractive van der Waals force. The latex stability can be achieved by using an anionic surfactant, such as sodium lauryl sulfate, (SLS) which can provide a heterogeneous reaction system with a potential energy barrier against coagulation. The potential energy barrier is attributed to the repulsive force between the negatively charged electric double layers of the dispersed particles. Emulsion polymerization can be accomplished by using a batch, semibatch, or continuous process. Semibatch emulsion polymerization is an important process for the manufacturing of latex products. In addition to its operational flexibility for products with controlled polymer composition and particle morphology, the semibatch emulsion polymerization process can easily remove the enormous heat generated during the reaction. The most striking difference between the semibatch and batch emulsion polymerization processes is that reaction ingredients such as monomer, surfactant, initiator, or water can be added to the semibatch reaction system throughout the polymerization. Thus, the residence time distribution of particle nuclei is broader for semibatch emulsion polymerization.⁹ Novak¹⁰ studied the semibatch emulsion copolymerization of methyl methacrylate (MMA) and butyl acrylate (BA).

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Chern and Hsu¹¹ studied the effects of various reaction variables on the particle nucleation and growth processes for semibatch emulsion polymerization of acrylic monomers.

The objective of this work was to study the effect of various reaction parameters on the latex stability during the semibatch emulsion polymerization of butyl methacrylate (BMA) in combination with a small amount of MAA. The effects of three parameters are investigated within the context of RSM that incorporates design of experiments (DOE) and regression.^{12–14} This approach enables experimental investigation of the individual factors and the interactions of the factors simultaneously as opposed to one factor at-a-time approach. Both the percentage of the particle volume change and coagulum collection were used to quantify the effects of the parameters chosen for study. The results of colloid use for the preparation of the organic–inorganic nanocomposites with core-shell structures^{14,15} that have numerous applications include impact modifiers, nanocomposites and toughening agents, gloss enhancers for paper coatings, polymeric nanocapsules for controlled and sustained drug delivery,^{16,17} and encapsulation of volatile solvents or toxic substances.

EXPERIMENTAL

Materials

Butyl methacrylate (BMA) and methacrylic acid (MAA) were purchased from Merck Chemical (Whitehouse Station, NJ), and purified by distillation under reduced pressure and stored in a dark bottle at -5°C until requirement. Potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) as initiator (Cat. No. 105090) and sodium lauryl sulfate (SLS) as emulsifier (Cat. No. 817034) were supplied by Merck. $\text{K}_2\text{S}_2\text{O}_8$ was kept at -5°C and was used as received. The water used in all experiments was deionized and distilled in two stages.

Equipment

The diameter of the gold-sputtered nanoparticles were determined and examined by scanning electron microscopy (ZEISS DSM 960A, Oberkochen, Germany). About 100 random particles were measured to determine average diameter and distribution. SemAfore software, ver. 4, from JEOL (Skandinaviska, Sollentuna, Sweden) has been used to process the SEM images. Uniformity and average particle diameter can be calculated by this software. To set an idea about the MAA contents in copolymers, SHI-MADZU FTIR has been used and compared with each other.

Polymerization process

Polymerization was carried out in a 250-mL glass reactor equipped with a tree-bladed agitator, a thermometer, and a condenser. The reactor was charged with water, the initial surfactant, and monomers at room temperature. The initial reactor charge (IRC) was purged with nitrogen for 10 min to remove the dissolved oxygen. The reactor was heated to 80°C . The reaction was then initiated by adding the initiator solution (IS) to the reactor. After 15 min, the monomer emulsion was fed dropwise into the system for 3 h. Then, the reaction was maintained at 80°C for 1 h to reduce the level of the residual monomer. In the designed experiments, all the reaction variables were held constant except the levels of MAA and SLS. A typical recipe for the semibatch emulsion polymerization of MBA with various levels of MAA is shown in Table I. All the reaction steps are shown in Figure 1.

Characterization

To determine the stability of latex particles during polymerization, the filterable solids, which were collected by filtering the final latex product through 40-mesh (0.42 mm) screens, was used. Scrap adhering to the agitator, thermometer, and reactor wall was also collected. Total solid contents were determined by the gravimetric method. For SEM analysis, the emulsion samples were diluted in water 1 : 1000 (v/v). A drop of diluted emulsion was placed on the sample holder and dried under freeze-drying. Then the samples were placed under vacuum, flushed by Argon, evacuated, and coated by powdered gold.

A supersaturated NaCl solution was used to precipitate the final latex sample. For purification and calculating the reaction yield, the copolymer was

TABLE I
A Typical Recipe for the Semibatch Emulsion
Polymerization of MBA with Various Levels of MAA

Components	MAA%		
	0.5%	5%	10%
IRC			
H ₂ O (ml)	60.5	60.5	60.5
SLS (g)	x_1	x_1	x_1
BMA (ml)	3	3	3
MAA (ml)	0.05	0.15	0.3
IS			
H ₂ O (ml)	4	4	4
$\text{K}_2\text{S}_2\text{O}_8$ (g)	0.17	0.17	0.17
MEF			
H ₂ O (ml)	20	20	20
SLS (g)	x_2	x_2	x_2
BMA (ml)	52	52	52
MAA (ml)	0.2	2.3	4.5

x indicates the amount of SLS used in the reactions.

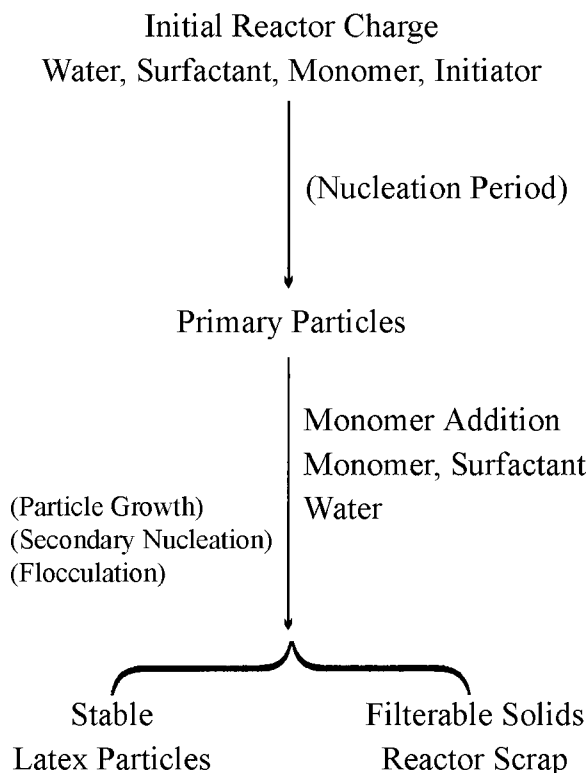


Figure 1 The steps in semibatch emulsion polymerization.

dissolved in 10 vol % THF : DMSO (20 : 80) and the solution was added dropwise into 500 vol % methanol. The polymer was precipitated, separated from methanol, and dried at 70°C to constant weight. After that the weight of the obtained purified polymer was determined and the reaction yield was calculated. To determine the value of the acid in the copolymers, the titration procedure was investigated. For this purpose, the purified copolymer was dissolved in THF : DMSO (20 : 80). The solution was titrated with a solution of 0.1N NaOH.

Design of experiments and optimization by RSM

Response surface methodology refers not simply to the use of a response surface as a multivariate function but also to the process for determining the polynomial coefficients themselves. A response surface equation is simply a polynomial regression to a data set. The process is straightforward if a sufficiently large data set is available, that is if the number of members in the data set is at least as large as the number of coefficients in the polynomial. On the other hand, if the data set must be determined and if the process is time-consuming and computationally expensive, then the overall usefulness of the method will depend on the use of an efficient method for selecting the fewest possible members.¹⁸ Designs of experiments (DOE) techniques provide

the needed basis for this critical step in the methodology. In this study, regression analysis is performed using statistical software JMP IN 5.1 (SAS Institute). The software also conducts appropriate statistical test of hypotheses concerning the parameters in the mathematical model.

RESULTS AND DISCUSSION

A latex product consists of innumerable submicron polymer particles dispersed in water. These particles are generally stabilized by anionic surfactants. Nevertheless, the surfactant molecules remaining in the latex product can have a negative effect on the application properties such as adhesion of the pressure-sensitive adhesives and film formation and water resistance of the coating materials, because the small and mobile surfactant molecules tend to migrate to the surface layer of the polymeric film. One approach to overcome the surfactant migration problem is to reduce the level of surfactant used in the recipe, or emulsifier-free emulsion polymerization.^{19,20} However, latex stability can be greatly reduced, and a significant amount of coagulum can form during the monomer addition period. Snuparek^{21,22} studied semibatch emulsion polymerization of acrylic monomers. Their experimental data showed that the incorporation of a small amount of acrylic acid (AA) into the emulsion polymers increased the latex stability, significantly. The carboxylate group ($-\text{COO}^-$) that is chemically incorporated into the emulsion polymer can increase the particle surface charge density and, therefore, enhance the repulsive force among the interactive particles.

It is established that the carboxyl containing species, such as acrylics or derivatives of methacrylic acid (MAA), affect numerous properties when it was incorporated onto surfaces. As one of the traditional functions of these entities is to provide additional crosslinking sites, there are other relatively unexplored opportunities for these groups to perform. However, when the latex particles contain MAA groups, they store the energy by the electrostatic repulsion between the charged particle surfaces, and an introduction of neutralizing ions may result in the release of surface ionic species. As a result, the potential energy is released during the conformational changes resulting from certain bonds cleavage, and the mechanical motion of molecular segments is anticipated. Four reaction variables have an effect on the latex stability:

1. The concentration of SLS in the IRC (0.15–0.80%, based on the weight of water in the IRC);

- The concentration of SLS in the MEF (0.4–1.6%, based on the total monomer);
- The weight percentage of MAA in the MEF and IRC (0.1–10% of the total monomer);
- The initiator concentration and the agitation speed were constant throughout this work (0.2%, based on the weight of water in the IRC and 300 rpm, respectively).

Effect of reaction variables on stability of the latex particles and optimization by RSM

Selection of the experimental design

Choosing meaningful ranges for the input variables must be done with great care. On the one hand, the ranges should be large enough to include all possible parameter spaces. On the other hand, the ranges cannot be so large that they reduce the prospect of a good regression fit of the response surfaces to the actual response. For this reason, a preliminary screening study was first carried out to rank the significance of three major parameters on the percentage of scrap. Selected ranges and levels for the input variables are shown in Table II.

Response surface model fitting

After performing a set of experiments or computer runs to obtain outputs according to the experimental designs, the next step is to take the vectors of inputs (x) and corresponding outputs (y) for fitting an appropriate model. These experiments were planned according to the modified central composite design. This type of design defines the fewer number of experimental combinations in the experimental domain to be explored to obtain the maximum information for adjusting the proposed model. For a quadratic model, experiments must be performed for at least three levels of each factor. Central composite design matrix of three variables in coded and natural units along with the observed responses are shown in Table III. The most widely used response surface function is a mathematical polynomial function. Typical response surface model limits the order of polynomial to one or two, since low-degree models contain fewer terms than higher-degree models and thus require fewer experiments to be performed. A

TABLE II
Experimental Range and Levels of Independent Variables

Variables	Range and levels		
	-1	0	+1
SLS% in IRC	0.15	0.48	0.8
SLS% in MEF	0.4	0.85	1.3
MAA%	0.1	5.05	10

TABLE III
Central Composite Design Matrix of Three Variables in Coded and Natural Units Along with the Observed Responses (Scrap%)

Obs. no.	x_1	x_2	x_3	SLS% in IRC	SLS% in MEF	MAA%	y scrap %
1	-1	-1	-1	0.15	0.4	0.1	8.9
2	-1	-1	+1	0.15	0.4	10	13
3	-1	0	0	0.15	0.85	5.05	3.1
4	-1	+1	-1	0.15	1.3	0.1	3.5
5	-1	+1	+1	0.15	1.3	10	4.9
6	0	-1	0	0.475	0.4	5.05	2.3
7	0	0	-1	0.475	0.85	0.1	2.9
8	0	0	0	0.475	0.85	5.05	1.7
9	0	0	0	0.475	0.85	5.05	1.6
10	0	0	+1	0.475	0.85	10	3.9
11	0	+1	0	0.475	1.3	5.05	1.4
12	+1	-1	-1	0.8	0.4	0.1	2.4
13	+1	-1	+1	0.8	0.4	10	3.0
14	+1	0	0	0.8	0.85	5.05	0.7
15	+1	+1	-1	0.8	1.3	0.1	1.8
16	+1	+1	+1	0.8	1.3	10	2.1

typical response surface function for three input variables is in the form of:

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2$$

The results of the second order response surface model fitting in the form of Analysis of Variance are given in Table IV. The Fisher F -test [$F = 22.3$] with a very low probability value ($\text{Prob}(p) > F = 0.0001$) demonstrates a very high significance for the regression model.²³ The goodness of fit of the model was checked by the determination coefficient (R^2). In this case, the value of the determination coefficient ($R^2 = 0.934$) indicates that only 6.6% of the total variations are not explained by the model. The value of the adjusted determination coefficient ($\text{Adj. } R^2 = 0.892$) is also very high to advocate for a high significance of the model. A higher value of the correlation coefficient, ($R = 0.980$), justifies an excellent correlation between the independent variables. Table IV shows the result of analysis of variance for this model.

The significance of each coefficient was determined by t -test and p -values. The larger the magni-

TABLE IV
Analysis of Variance for the Model

Sources of variations	Sum of squares	Mean square	F ratio	$\text{Prob}(p) > F$
Model	150.171	21.45	22.318	<0.0001
Error	10.573	0.96		
COR. Total	160.745			

Mean of response = 3.31; RMSE = 0.98; $R^2 = 0.934$; $R = 0.980$; $\text{Adj. } R^2 = 0.892$.

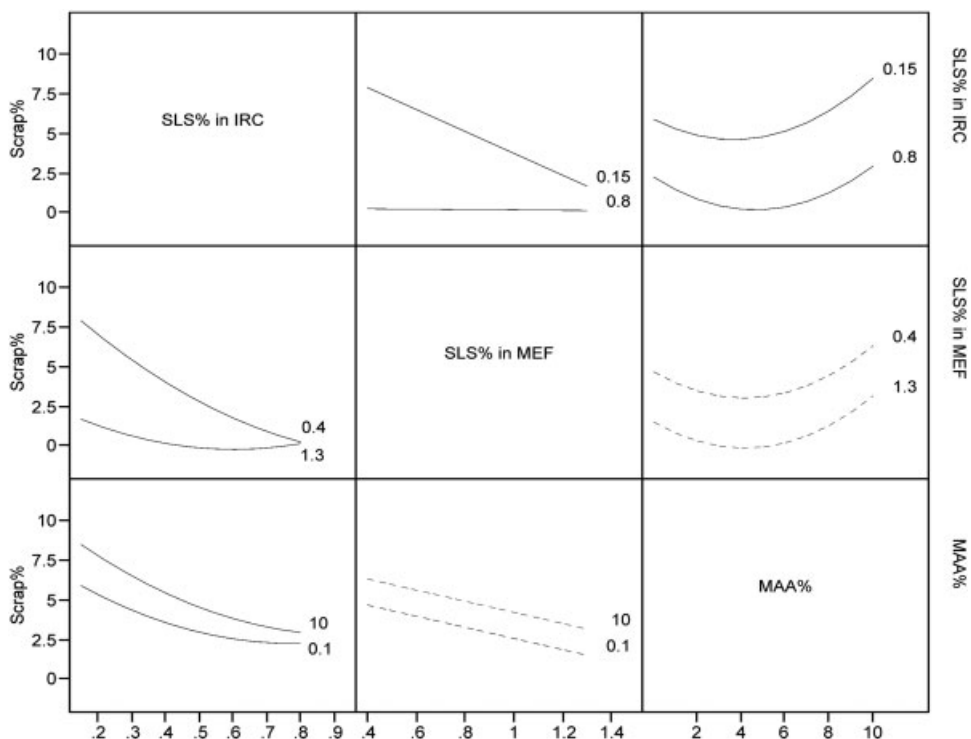


Figure 2 The interaction plots of the effect of the deferent parameters on the scarp percentage.

tude of the t -value and smaller the p -value, the more significant is the corresponding coefficient. The application of response surface methodology yielded the following regression equation which is an empirical relationship between the scrap% and the test variables in coded unit:

$$y = 1.5 - 2.29x_1 - 1.57x_2 + 0.82x_3 + 1.52x_1x_2 - 0.47x_1x_3 + 0.97x_1^2 + 2.39x_3^2$$

where y is the response, that is, the scrap% and x_1 , x_2 , and x_3 are the coded values of the test variables that have been shown in Table III. This equation suggests that the amount of SLS in IRC and MEF have got an indirect relationship with the scrap%. This is in good accordance with the observations made by the previous workers. These observations are also substantiated by the fact that the amount of the SLS in IRC is the most significant (scaled estimate = -2.29) parameter in the stability of the particles in the reaction. In the interaction plots, evidence of interaction is shown as nonparallel lines. Figure 2 shows the interaction plots that indicate the effect of deferent parameters on the scarp percentage produced in the presence of various amounts of emulsifier with different levels of MAA. For example, in the (SLS in IRC)*(SLS in MEF) plot, the effect of SLS in MEF is very small at the high values of SLS in IRC, but it diverges widely for the low values

of SLS in IRC. These plots can be explained in the next three sections.

A: Influence of the concentration of SLS in the IRC. As shown in all levels of MAA, the amount of coagulum formed during polymerization will decrease when the concentration of SLS increases from 0.15% to 0.80%. It was found that the concentration of sodium lauryl sulfate (SLS) in the initial reactor charge was the most important parameter in determining the final latex stability. Growth of the particles via conversion of the imbedded monomer to polymer in the particles will cause an increase in the particle surface area during the monomer addition period. The newly created particle surfaces require more surfactant to maintain an adequate colloidal stability.

B: Influence of the concentration of SLS in the MEF. The amount of scrap can be reduced significantly, when the concentration of SLS in the MEF increases. It is due to the fact that the surfactant added to the reaction medium will cause to increase the surface charge density on the growing particles and, thus to improve the latex stability.

C: Influence of different levels of MAA. The effect of different amount of MAA on the latex stability was investigated. It is found that the amount of scrap formed during the reaction decreases with increasing the amount of MAA from 0.1 to about 5%. This kind of behavior suggests that less surfactant (both in the IRC and MEF) is required to maintain the same latex stability when a higher weight percentage of MAA

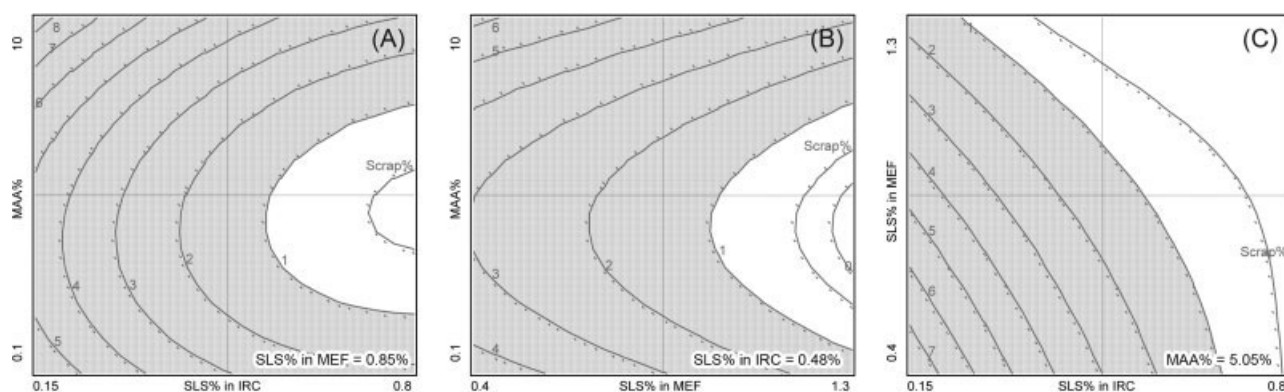


Figure 3 Contour plots of the effect of (A) SLS% in IRC and MAA%, (B) SLS% in MEF and MAA%, and (C) SLS% in IRC and SLS% in MEF in the amount of scrap%.

in the monomer mixture is used. As mentioned earlier, the carboxylic monomer MAA has been shown to be the most efficient one to help nucleate and stabilize the latex particles during the semibatch emulsion polymerization.²⁴ Increasing the quantity of MAA can increase the particle surface charge density and, therefore, increases the repulsive force among the interactive particles. On the other hand, the scrape percentage increases as the weight percentage of MAA in the monomer mixture increases from 5 to 10%. In this manner, more surfactant is required to maintain the same latex stability at a very high MAA concentration, which is probably due to the increased concentration of polyelectrolyte in the aqueous phase. It is postulated that the abundant and ionized polyelectrolyte in water can compress the electric double layer of the particles and, conse-

quently, decrease the potential energy barrier against coagulation. Another possible explanation is that the higher the concentration of hydrophilic MAA unit on the particle surface, the less the amount of SLS adsorbed on the particle surface. Thus, the latex stability can be greatly reduced as a result of decreased repulsive force among the interactive particles.

Graphical presentation of the model equation and determination of optimal operating conditions

The visualization of the predicted model equation can be obtained by the response surface plot and contour plot. The response surface plot is the theoretical three-dimensional plot showing the relationship between the response and the independent variables. The two-dimensional display of the surface

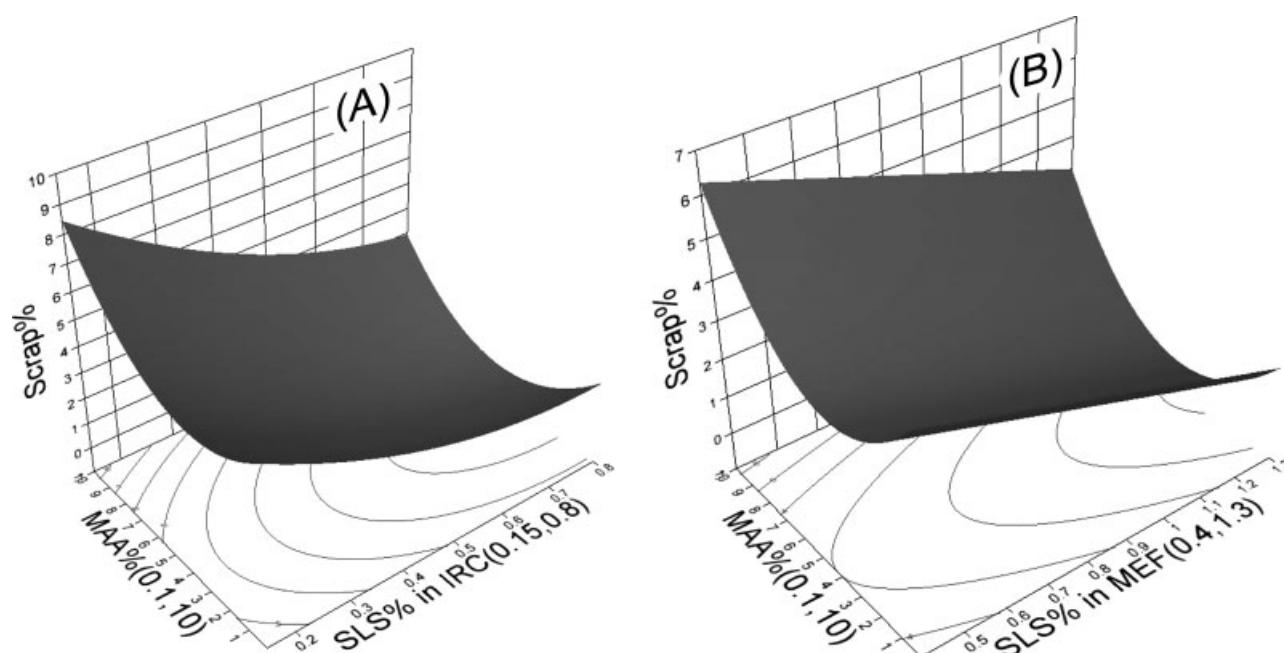


Figure 4 Response surface plots of (A) SLS% in IRC and MAA% and their interaction, and (B) SLS% in MEF and MAA% and their interaction on the amount of scrap%.

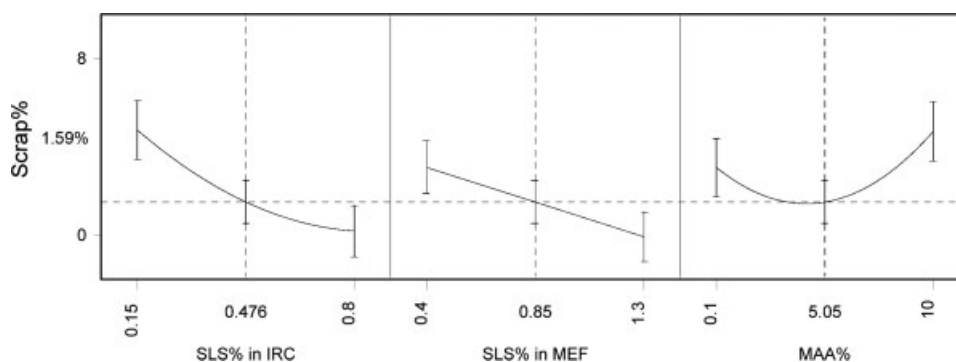


Figure 5 Prediction profiler and desired condition emulsion polymerization.

plot is called contour plot and in the contour plot, lines of constant response are drawn in the plane of the independent variables. The contour plots help to visualize the shape of a response surface. The predicted values of y (scrap%) based on the range of x_1 , x_2 , and x_3 in RSM were estimated as illustrated in Figures 3 and 4 as contour and response surface plots. In all of the contour and response surface plots, the effect of two variables on scrap% has been shown and the third variable is held constant at the mid point. The amount of this variable has been shown in the bottom right side of the plots.

The contour plot for MAA displays ellipses or circles. The center of this system refers to a maximum or minimum response. Sometimes, contour plot may display hyperbolic or parabolic system of the contours. In this case, the stationary point is called a saddle point and it is neither a maximum nor a minimum point. These plots give useful information about the model fitted, but they may not represent the true behavior of the system. The white areas in the plots are related to the condition of maximum stability. In this area, the scrap is below 1%. In plot (A), the lines are closer than the lines in plot (B) that shows SLS% in IRC is more effective on preventing of scrap formation during emulsion polymerization.

The two-dimensional illustrations of response surface function can also be shown in Figure 5. In this plot, the response (y) is plotted against each of the

input variables (x 's) while the other input variables are held constant. The plot shows how the response computation can change with the input variables over its range. From these prediction profiles, the operating conditions necessary to emulsion polymerization with the desired scrap% and the amount of needed emulsifier and MAA have been predicted. This figure shows the prediction profile and desired condition of semibatch emulsion. As shown, setting the condition in SLS in IRC = 0.47%, SLS in MEF = 0.85%, and MAA = 5.05%, leads to about 1.6% scrap.

Effect of the concentration of SLS in the IRC and MEF on the latex particles size

Figure 6 shows the SEM photomicrographs of copolymer particles in various amount of SLS in IRC. According to the observed results in Table V, the particles size are decreased with increasing the amount of surfactant in the IRC. It can be explained by the fact that the number of primary particles nucleated increase with increasing the concentration of SLS in the IRC. On the other hand, increasing the amount of SLS in the MEF causes lesser decrease on the particles size, and that causes particles size distribution to broaden. This can be explained by the fact that the number of secondary particles nucleated are increased with increasing the concentration of SLS in the MEF. Thus, the primary function of SLS

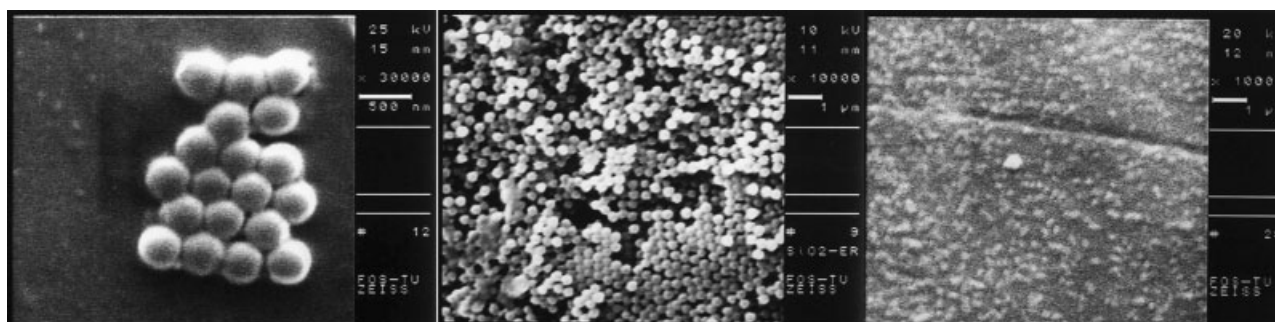


Figure 6 SEM photomicrograph of copolymer particles; left, SLS% = 0.15; middle, SLS% = 0.48, and right, SLS% = 0.80.

TABLE V
Effect of SLS Concentration in IRC on the Particles Size

	Obs. no.		
	3	8	14
SLS% in the IRC	0.15	0.48	0.80
Particles size (nm)	390	333	200

in the monomer emulsion feed is to stabilize the growing particles. Adding extra SLS to the reaction system during the monomer feed also can lead to formation of a second crop of primary particles (secondary nucleation). Secondary nucleation can reduce the average particle size and broaden the size distribution. Therefore, more polymer–water interfacial area is generated, and the more the particles need surfactant to prevent them from coagulation.

Effect of different amount of MAA in the reaction yield

The reaction yield data that are given in Table VI indicate the highest yield of the reactions for the copolymer with about 5% MAA. As shown, the reaction yield increases with increasing the acid concentration to 5%. It can be explained that the MAA reactivity is greater than BMA, and the amount of scrap% decreases with increasing the acid concentration to this value. But with increasing the amount of MAA more than 5%, the reaction yield remains constant and even slightly decreases. It can be concluded that the amount of scrap% increases with increasing the acid concentration from 5 to 10%. The other probable reason is related to more solubility of the copolymer in methanol and water, and an amount of copolymer can be dissolved in methanol during the purification process.

To determine the value of the acid in the copolymers, the titration procedure was investigated.²⁵ The values of the used and calculated acid are given in Table V. As shown, the value of the used acid is higher than the calculated acid. It can be due to more solubility of MAA in comparison with BMA. The probable reason is that the oligomers containing the acid are more soluble in methanol and an

TABLE VI
Yield of Reactions and Percentage of MAA in the Reaction and Copolymer

Sample no.	Incorporated BMA (%)	Incorporated MAA (%)	Calculated MAA (%)	Yield (%)
A	100	0	0	60
B	99.5	0.5	0.4	62.2
C	99	1	0.8	75
D	95	5	4.7	78.1
E	91	9	8.2	77
F	90	10	8.8	76.8

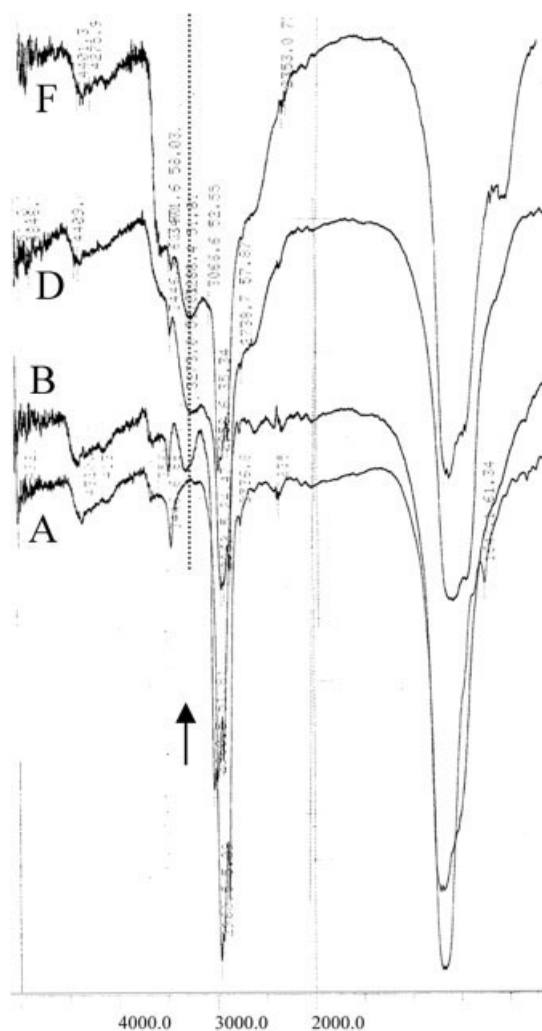


Figure 7 FTIR spectra of copolymers (labeled in Table VI).

amount of them remain in methanol during purification.

The given FTIR spectra in Figure 7 indicate an absorption at 3250 cm^{-1} (stretching vibration) for OH of carboxyl group in the copolymers. The absorbance is increased by increasing the acid concentration in the copolymers. As shown in Table VI, A is the spectrum of homo butyl methacrylate, and B, D, and F are the spectra of BMA–MAA copolymers with 0.5%, 5%, and 10% MAA, respectively. The spectra of samples C and E are very similar to the spectra of samples B and F, and so the samples C and E's spectra have not been shown in Figure 7.

CONCLUSIONS

The amount of scrap produced during the semibatch emulsion polymerization process was used to investigate the effect of number of reaction parameter on the latex stability. As a result, the amount of scrap

reduced greatly when the concentration of SLS in the MEF or IRC was increased. The designed experiments also show that the amount of scarp decreased significantly, when the amount of MAA increased from 0 to about 5%. But increasing the amount of MAA from 5% causes an increase in the amount of scarp. FTIR spectroscopy and titration procedure show that the amount of MAA in the copolymer was less than he incorporated MAA in the reaction. The observed results show that the particles size decreases with an increase in the amount of surfactant in the IRC.

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