Factorial Experimental Design Approach in Semicontinuous Emulsion Polymerization of Methyl Methacrylate to Study the Effect of Process Variables

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ABSTRACT: This article describes the effect of various process variables in the semicontinuous emulsion polymerization of methyl methacrylate. A series of poly(methyl methacrylate) (PMMA) emulsions were prepared using ammonium persulphate as initiator in absence and presence of Dowfax 2AI as surfactant. The effect of process variables such as initiator concentration, monomer concentration (solid content), surfactant concentration, reaction temperature, monomer feeding time, and holding time were systematically studied on monomer conversion, particle size, gel content, and molecular weight using a two-level fractional factorial experimental method. Analysis of fractional factorial design revealed that surfactant concentration, monomer concentration, initiator concentration, and monomer feeding time affect all the properties. However, the surfactant concentration and the interaction effect of initiator and monomer feeding time are the key variables influencing the properties of PMMA latex. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3742–3749, 2009

Key words: emulsion polymerization; fractional factorial design; methyl methacrylate

INTRODUCTION

Emulsion polymerization is a complex heterogeneous process in which lot of components such as monomers, surfactant, initiator, buffer, and chain transfer agents are present in the formulation. These components affect the rate of polymerization as well as the final properties of latex. In addition, the reaction variables such as temperature, reaction system design, and polymerization process, i.e., batch, semicontinuous, and continuous methods also affect the polymerization. In industry, the end-use applications mainly depend upon the final properties of the emulsion. Hence, a systematic study on emulsion polymerization to optimize the reaction variables, i.e., solid content, particle size, molecular weight, and its distribution that can produce polymer with predetermined properties is of greater industrial importance. So design of experiments to achieve these properties is very important. The statistical method in designing the experiments is very useful.

In this case, poly(methyl methacrylate) (PMMA) latex was taken for study because it can be used as a seed material in the synthesis of a seeded emulsion polymerization of acrylic copolymers. To investigate the effect of seed properties on the final latex properties, the synthesis of the seed latex is very important. A factorial experimental design was used to synthesize PMMA latex by varying the reaction variables such as initiator, surfactant, monomer concentration, temperature, feeding time, and holding time. The variation of one factor at a time keeping the others at a constant level is a tedious process when a large number of factors have to be investigated. But statistically based experimental designs provide a more efficient approach to deal with a large number of variables.[1] A two-level factorial design was used here, as the factorial design with more than three variables significantly increases the complexity of the experiment. Again a two-level full factorial design requires 2^N experiments where N factors have to be investigated. So the full factorial design of six variables with two levels requires at least 64 experiments. The number of experiments can be reduced by using fractional factorial design without loss of information about the main effect. So the number of experiments reduced to 16 using a quarter factorial designs (1/4) with two levels and six variables. The analysis of responses leads us to identify their influences. Thus, the optimal values of these variables can be established to obtain the required response, diminishing the variability of the response, and the effects of the number of controlled variables.

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The application of statistical design of experiments in emulsion polymerization is reported in the literature, i.e., (i) the Placket-Burman design was used to investigate the effect of 12 variables in making the core-shell latexes using 16 experiments,[2] (ii) Chern and Hsu studied the effect of various reaction parameters on the particle nucleation and growth in butyl acrylate (BA)/ methyl methacrylate (MMA) copolymers[3], (iii) Yang and Yang[4] applied statistical experimental strategies in emulsion copolymerization of styrene and *n*-butyl acrylate, (iv) Wen et al.[5] also used the statistical design strategy to optimize properties in emulsion copolymerization of MMA and acrylonitrile, (v) Rempel et al. studied the effect of process variables on the grafting reaction of styrene and MMA onto natural rubber and styrene-butadiene rubber,[6,7] (vi) use of factorial experiments for improved process understanding in ethylene-vinyl acetate semibatch emulsion copolymerization was studied by Penlidis and coworkers,[8] (vii) Saldivar et al.[9] studied the effect of initiator, surfactant, water-to-monomer ratio, and monomer composition in emulsion copolymerization of acrylic monomer by fractional factorial method, (viii) Wet-Roos et al.[10] also studied the influence of salt, initiator, amine, and stirring speed in emulsion polymerization of an epoxy–acrylate emulsion stabilized with polyacrylates. However, no reports are available regarding the synthesis of PMMA latex using factorial design of experiments.

The objective of this study was to investigate systematically the effect of reaction variables using fractional factorial design to determine the significant variables and optimize conditions for the preparation of PMMA seed having desired characteristics.

EXPERIMENTAL

Materials

MMA of commercial grade (GSFC: India); ammonium persulphate (APS: CDH) were used as received. Dowfax-2AI (a sodium salt of dodecyl disulphonate diphenyl ether; Dow Chemical) was used as surfactant in the polymerization. Deionized water was used throughout the reaction.

Synthesis of PMMA seed latex

Experimental designs

A set of PMMA latexes were prepared using fractional factorial designs of experiment by varying the reaction variables such as initiator concentration, monomer concentration (solid content), surfactant concentration, reaction temperature, monomer feeding time, and holding time. In this case, a two-level fractional factorial design (1/4) was chosen, since

TABLE I
Factor and Levels for 2_{IV}^{6-2} Fractional Factorial Design

Designation	Factors	Levels	
		−1	+1
I	Initiator (g)	0.25	0.5
M	Monomer (g)	10	30
S	Surfactant (g)	0.0	6.9
T	Temperature (°C)	70	80
Ft	Feeding time (h)	3	4
Ht	Holding time (h)	3	12

−1 = Lower level and +1 = higher level of reaction variables taken for study.

the higher order interaction is expected to be negligible. Process variables were varied according to a 2_{IV}^{6-2} design, resolution R = (IV). For each process variable, low and high levels were chosen, and they were coded as (–1) and (+ 1). The values of the variables for the two levels of the factors were chosen after performing a series of trial experiments. Table I shows the independent variables as well as the values assigned to both levels considered in this study.

All the reactions were carried out in a 2 L four-necked glass reaction flask fitted with a nitrogen inlet, a reflux condenser, thermometer, and the stirrer was inserted through the middle neck. To the reaction flask, 260 mL of water along with or without the surfactant (as given in the recipe) were charged. The mixture was thoroughly stirred under nitrogen purging for 1 h and then heated to the desired reaction temperature. The reaction was initiated by addition of 10% of initiator solution, prepared in 30 mL of water. After attaining the reaction temperature, both monomer and initiator solution were fed continuously. After complete addition, the mixture was further stirred for 1 h to reduce the residual monomer followed by cooling to room temperature. Then the latex was filtered through 200 μ mesh screen to remove the coarse or coagulum particles. The details of experiments (16 experiments) are given in Table II.

CHARACTERIZATION

Solid content

The monomer conversion was calculated gravimetrically. Samples were withdrawn during the polymerization to a preweighed aluminum foil and dried at 105°C in oven till a constant weight.

Particle size determination

The latexes were characterized for its particle size by dynamic light scattering (Malvernizer: 2000). For DLS analysis, the samples were diluted with deionized water.

Sample designation	Factors						Characteristic properties		
	I	M	S	T	Ft	Ht	% NVS	$M_w \times 10^{-4}$	dp (nm)
S-1	−1	−1	−1	−1	−1	−1	5.4	7.31	743.2
S-2	+1	−1	−1	−1	+1	−1	9.96	17.79	107.2
S-3	−1	+1	−1	−1	+1	+1	—	—	—
S-4	+1	+1	−1	−1	−1	+1	—	—	—
S-5	−1	−1	+1	−1	+1	+1	9.78	9.87	34.0
S-6	+1	−1	+1	−1	−1	+1	9.62	10.85	27.2
S-7	−1	+1	+1	−1	−1	−1	31.3	60.85	55.5
S-8	+1	+1	+1	−1	+1	−1	32.6	33.83	53.9
S-9	−1	−1	−1	+1	−1	+1	11.1	16.85	531.4
S-10	+1	−1	−1	+1	+1	+1	11.5	3.51	313.8
S-11	−1	+1	−1	+1	+1	−1	—	—	—
S-12	+1	+1	−1	+1	−1	−1	—	—	—
S-13	−1	−1	+1	+1	+1	−1	9.69	14.14	28.2
S-14	+1	−1	+1	+1	−1	−1	9.12	10.49	25.6
S-15	−1	+1	+1	+1	−1	+1	31.7	33.71	55.9
S-16	+1	+1	+1	+1	+1	+1	32.6	14.22	54.0

NVS, nonvolatile solid content; dp, particle size; M_w, Weight average molecular weight; +1, higher levels of variables and −1, lower levels of variables taken.

Molecular weight determination

The molecular weight and molecular weight distribution of the soluble fraction of the polymer was determined using Waters size exclusion chromatography. A differential refractive index detector was used. Three columns with pore sizes of 10^2, 10^4, and 10^6 A° (Waters HR$_2$, HR$_4$, and HR$_6$) and tetrahydrofuran (THF) at a flow rate of 1 mL min^{-1} were used. Narrow polystyrene standards having molecular weight ranging from 4×10^2 to 10×10^6 were used for calibration.

RESULTS AND DISCUSSION

The statistical method of fractional factorial design (two levels/six variables) was used to screen the reaction variables that mostly affect the properties of PMMA latexes. The process variables include the amount of initiator, monomer concentration (solid content), surfactant concentration, reaction temperature, feeding time, and holding time and are given in Table II. MINITAB statistical software (version 14) was used to design and analyze the fractional factorial experiments.[11] The properties were analyzed using the estimation of the effect, analysis of variance (ANOVA) such as residual plot, the correlation coefficient (R^2), the significance F by performing a lack-of-fit test with $\alpha = 0.05$.

The combination of the observations used in estimating the main effect and the interaction effect of factors is identical to that used in estimating the other interaction factors. Hence estimating factor I and the interaction factors of M, S, T, Ft, and Ht are said to be confounded. According to Box et al.,[1] the defining relationship $I = I \times M \times S \times T \times$ Ft $\times$ Ht was established to identify those relationships which exist between the effects. Estimation of the experimental variable effect is the mean of the difference between the values at high level (+1) and the values at low level (−1). In this study, the effect of main variable and a two-way interaction effects were discussed whereas higher order interaction effects (three and higher factors interaction in this study) were ignored.

In ANOVA analysis, the total sum of squares (SS$_{total}$) is calculated as

$$SS_{Total} = \sum_{i=1}^{n} Y_i^2 - \sum_{i=1}^{n} \frac{Y_i^2}{n}$$

Where Y_i is the response and n is the number of experiments. The sum of the square (SS) for any main and interaction effect is SS$_{total} = 2^{N-2-2}$(effect)^2, where N is known as the number of effects. The error sum of the square (SS$_{error}$) is the result of the difference between the total sum of square and the sum over all the SS$_{main\ effect}$ and SS$_{interaction\ effect}$. The degree of freedom for the main effects is the total number of levels minus one. Therefore, in the present case, there are 16 (total number of experiments) − 13 (the sum over all the number of main and interaction effects) − 1 = 2 degree of freedom for error. The adjusted mean square (MS) for the effect, interaction and the error can be calculated by dividing each of the sums of square by the degree of freedom for error. The test statistics F and R^2 are defined as $F = $ MS/ MS$_{error}$ and $R^2 = 1 - $ SS$_{error}$ /

SS_{total}. According to F-statistics, if F-calculated is greater than F-tabulated, then that variable has a significant effect on the corresponding properties.[12] R^2 ($0 \leq R^2 \leq 1$) is the multiple correlation coefficients. A value close to 1 for R^2 signifies the perfect fit to the experimental data. In this section, the experimental designs thta were analyzed by the above model are given. Measured response were conversion by gravimetric, average particle diameter (DLS), molecular weight of soluble parts (GPC), and gel content (immiscible fraction) of the latexes.

It assumes that no main effect is alias of either another main effect or of some interaction of two variables. Besides, the interactions of two variables are aliases to each other ($I * M = S *$ Ft, $I * S = M *$ Ft, $I * T =$ Ft $*$ Ht, $I *$ Ft $= M * S$, $I *$ Ht $= T *$ Ft, $M * T = S *$ Ht, $M *$ Ht $= S * T$). As can be seen, half of the experiments of each variable are made at high level and other half at low level.

Nonvolatile solid content

The nonvolatile solid content (%) of all the PMMA latexes is given in Table II. Gravimetric results showed $\geq 95\%$ conversion in all the experiments except S-1, irrespective of the solid content. A lot of coagulum was produced in S-1 latex during the end of the reaction. Surfactant-based latexes are more stable than surfactant-free latexes. The surfactant-free latexes are found to be stable with solid content up to $\sim 10\%$, therefore samples such as S-3, S-4, S-11, and S-12 prepared at a solid content of $\sim 30\%$ were unstable in surfactant- free recipe. The instability in surfactant-free latex may be due to the decrease in surface charge density with increase of polymer particles, which might increase the ease of coalescences.

The estimate of the effect of factors from the fractional factorial design on solid content was given in Table III. It can be seen that monomer (M) and surfactant (S) concentration has a profound effect on the final solid content as the main variables, where as the interaction effect of initiator and feed time ($I *$ Ft) had a significant contribution. This may be attributed to the fact that surfactant was responsible for the stability of particles. At high level of surfactant, more micelles present in the water phase which in turn, responsible for the formation of a number of new particles leaving behind very little free monomer during polymerization. So with increase in monomer content and surfactant concentration, the rate of monomer conversion increased. Latexes prepared in the absence of surfactant are less stable as the negatively charged radical concentration is not sufficient for emulsion prepared using higher monomer content. On the other hand, the combined effect of initiator concentration and feeding time together

TABLE III
Monomer Conversion Estimates of the Effects from the 2^{6-2} Fractional Factorial Design

Effects	Estimate
Mean	0.7106
I	0.0412
M	-0.4213
S	0.5263
T	0.0438
Ft	0.0638
Ht	0.0612
$I * M$	-0.0412
$I * S$	-0.0637
$I * T$	-0.0562
$I *$ Ft	0.4738
$I *$ Ht	-0.0487
$M * T$	-0.0438
$M *$ Ht	-0.0613

have a profound effect as the radical flux increases with increase in initiator concentration.

Particle size

The results of particle size (dp) of all PMMA latexes prepared under different conditions are given in Table II. The surfactant concentration is found to be the most influencing factor on the particle size of the polymer. In surfactant-based latexes, smaller particles were formed. All the surfactant-based latexes having 30% solid content showed the particle size value around 55 ± 1 nm. The latexes having 10% solid content showed a lower value of particle size, i.e., between 23 and 34 nm. This could be due to increase in the surfactant/monomer ratio in emulsions prepared having lower solid content.

Larger particle size was observed in surfactant-free latexes. Initiator concentration was found to be the main parameter affecting the particle size in surfactant-free latexes. The latexes with low amount of initiator concentration (0.25 g) have large particle size in comparison with that prepared using higher initiator concentration (0.5 g). At lower initiator concentration, higher solid content latexes were unstable due to decrease in surface charge density and increased ease of coalescence. Low temperature, low initiator concentration, increasing feed time, and holding time were favorable for large particle size in surfactant-free latexes. Similar behavior has been reported by Goodwin et al.[13] in polystyrene system.

Figure 1 shows the particle size distribution curve for S-8, S-15 (surfactant based), S-9, and S-10 (surfactant free) sample. S-8, S-9, S-10, and S-15 showed a uniform distribution of particles which suggest that the nucleation time is too short in comparison with reaction time. A narrow particle size distribution
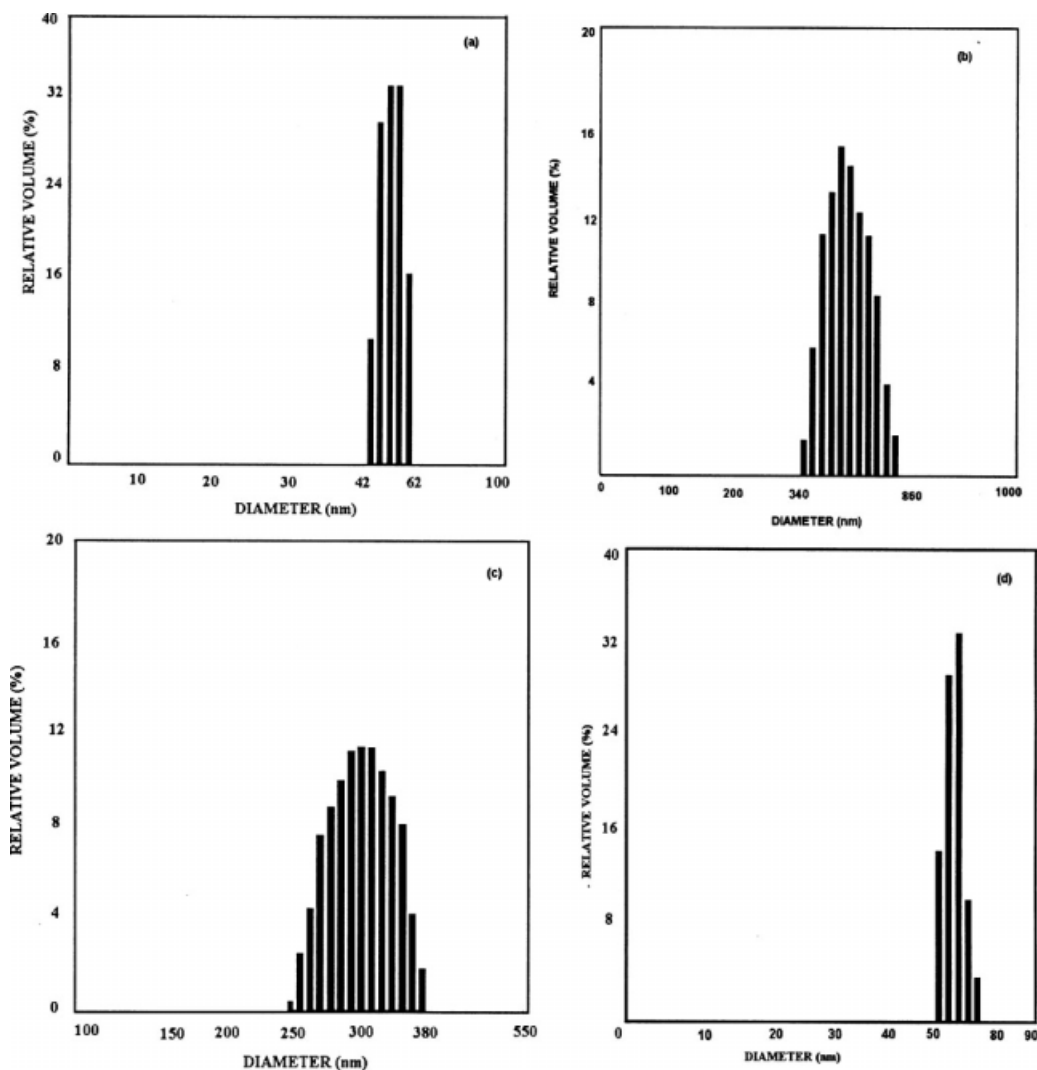
Figure 1   Particle size distribution curve of samples (a) S-8, (b) S-9, (c) S-10, and (d) S-15.

was observed in S-8 and S-15 latexes whereas it was broad in S-9 and S-10. But in S-1 polymer, broad and bimodal particle size distribution was observed with large particle size in comparison with other surfactant-free latexes. Decrease in temperature and the initiator concentration might cause a long nucleation time and formation of shear-induced coagulation which result in bimodal distribution with large particle size.

The influence of process variables on particle size was also identified by a systematic application of the statistical design. The results of 2_{IV}^{6-2} fractional factorial experiments are given in Table IV. The estimation of the experimental variables showed that the monomer (M) and surfactant (S) concentration are the key independent variables that affect the particle size. With increase in these parameters, the particle size decreases. This may be due to the formation of more number of particles. The two-way interaction effect between initiator-feed time (I*Ft) and mono-

mer-surfactant concentration (M*S) also had profound effect on particle size.

The particle sizes were also analyzed by ANOVA. To ensure that the assumption of normality and constant variance were met the response variable particle size was calculated. The 95% confidence intervals ($F_{1,2} = 18.5$) provide a test to decide whether the variance due to an observed response is significant or not. If Fc value is greater than or equal to 18.5, the observed response is probably significant. The results from Table IV showed the Fc value of monomer (M) and surfactant concentration (S) were close to theoretical value. However, the interaction effect between initiator-feed time (I*Ft) and monomer-surfactant concentration (M*S) had significant effect on the particle size. All other factors did not show any significant effect on the particle size.

Figure 2 shows the variation of mean particle size as a response of the levels (high and low) of all six variables. Surfactant and monomer concentration are

TABLE IV
Results of Main Effect and Two-Factor Interaction for Response and the Analysis of
Variance of Particle Size (dp) for PMMA Latexes

Effects	dp estimate	SS	DF	MS	P	Fc
Mean	126.87					
Initiator (I)	−108.31	46,926	1	46,926	0.334	4.28
Monomer (M)	−198.91	158,265	1	158,265	0.063	14.44
Surfactant (S)	−170.16	115,821	1	115,821	0.119	10.57
Temperature (T)	−1.51	9	1	9.2	0.989	0.00
Feed time (Ft)	−105.96	44,912	1	44,912	0.345	4.10
Hold Time (Ht)	0.34	0	1	0.5	0.998	0.00
I * M	107.44	46,171	1	46,171	0.290	4.21
I * S	105.09	44,174	1	44,174	0.333	4.03
I * T	52.79	11,146	1	11,146	0.657	1.02
I * Ft	224.99	202,478	1	202,478	0.031	18.48
I * Ht	51.74	10,707	1	10,707	0.663	0.98
M * S	224.99	202,478	1	202,478	0.007	18.48
M * T	1.64	11	1	10.7	0.988	0.00
M * Ht	−0.21	0	1	0.2	0.998	0.00
Error		119.5	2	10,958		
$R^2 = 0.97$						

DF, degree of freedom; SS, sum of squares; MS, mean square. Significant difference exists, if F-calculate $> F$-tabulated ($F_{1,2} = 18.5$) or if $P < 0.05$.

two main factors that affect the particle size where the significant effects are coming from the interaction of initiator and feed time. Temperature and holding time have no effect on the particle size. Hence, the factors affecting the particle sizes are the surfactant concentration, monomer concentration, and the interaction effect of initiator concentration and monomer feed time. The particle size decreases with increase in surfactant concentration (from 0.0 to 6.9 g) and monomer concentration (from 10% to 30%). Similar trend was observed with initiator con-

centration and feed time of monomer. This could be explained by the fact that with increase in initiator concentration the radical flux in the water phase increases thus producing a number of growing radicals. With increase in surfactant, more free micelles present in the water phase increases the number of particles, thus decreasing the particle size. The effect of monomer concentration in surfactant-free experiments was not clear as higher solid content (30%) emulsions without surfactant were unstable. The synthesis used for surfactant-free recipe here found
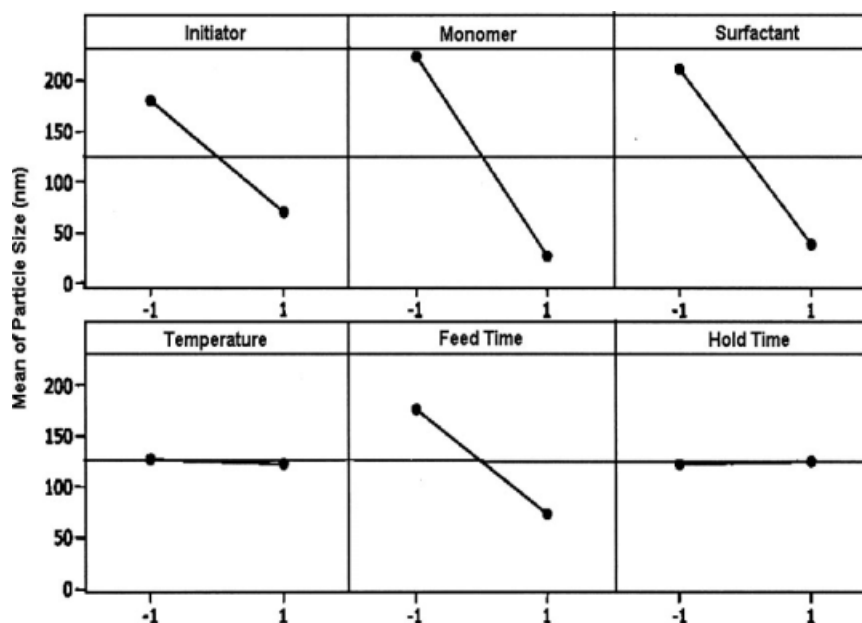

Figure 2 Effect of main reaction variables on particle size of PMMA latexes. The y axis represents mean particle size (nm).

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TABLE V
Results of M_n, M_w, and PDI from Estimation of the Effect

Effect name	Estimate		
	$M_n * 10^{-4}$	$M_w * 10^{-4}$	PDI
Mean	23.576	14.588	4.355
I	−9.003	−6.504	0.452
M	10.264	6.474	−2.028
S	29.370	17.811	1.893
T	−6.832	−5.946	0.915
Ft	−10.340	−5.836	−0.842
Ht	−11.408	−6.924	−0.350
I * M	−13.428	−5.121	0.425
I * S	−12.091	−5.789	1.720
I * T	−10.211	−2.616	−0.007
I * Ft	28.045	17.839	4.790
I * Ht	−5.666	−1.459	1.353
M * T	−6.424	−5.739	−0.843
M * Ht	−1.848	−4.761	0.423

TABLE VI
Analysis of Variance of M_w for PMMA Latexes

Effect Name	SS	DF	MS	F-calculated
I	169.20	1	169.2	2.70
M	167.60	1	167.6	2.67
S	1268.96	1	1269.0	20.23
T	141.40	1	141.4	2.25
Ft	136.20	1	136.2	2.17
Ht	191.75	1	191.8	3.06
I * M	104.91	1	104.9	1.67
I * S	134.00	1	134.0	2.14
I * T	27.38	1	27.4	0.44
I * Ft	1272.90	1	1272.9	20.29
I * Ht	8.51	1	8.5	0.14
M * T	131.73	1	131.7	2.10
M * Ht	90.68	1	90.7	1.44
Error	125.5	2	62.73	
$R^2 = 0.97$				

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to give colloidal stability with solid content up to 10%. But particle size increases with increase in monomer content as observed in surfactant-based latexes. Again, with increase in feed time, the monomer concentration at a given time during polymerization decreases.

Molecular weight

The molecular weight (M_w) of all the samples is given in Table II. The surfactant-based latexes had high molecular weight in comparison with the surfactant-free latexes. The surfactant-based latexes with higher solid content had exceptionally high molecular weight (M_w) in comparison with lower solid content latexes. In surfactant-free latexes, lower initiator concentration gives high molecular weight.

The results of effects of process variables on the molecular weights (M_n, M_w, and PDI) are given in Table V. An examination of the estimate results shows that the effect of surfactant is the key factor influencing both M_n and M_w of the latexes. Apart from surfactant concentration, the two-way interactions between initiator concentration and feed time of monomer (I*Ft) was more significant. Table VI summarizes the ANOVA of M_w. The F-test reveals the same factors responsible for M_w of the experiments as F-calculated is greater than F-tabulated (= 18.5 at $\alpha = 0.05$).
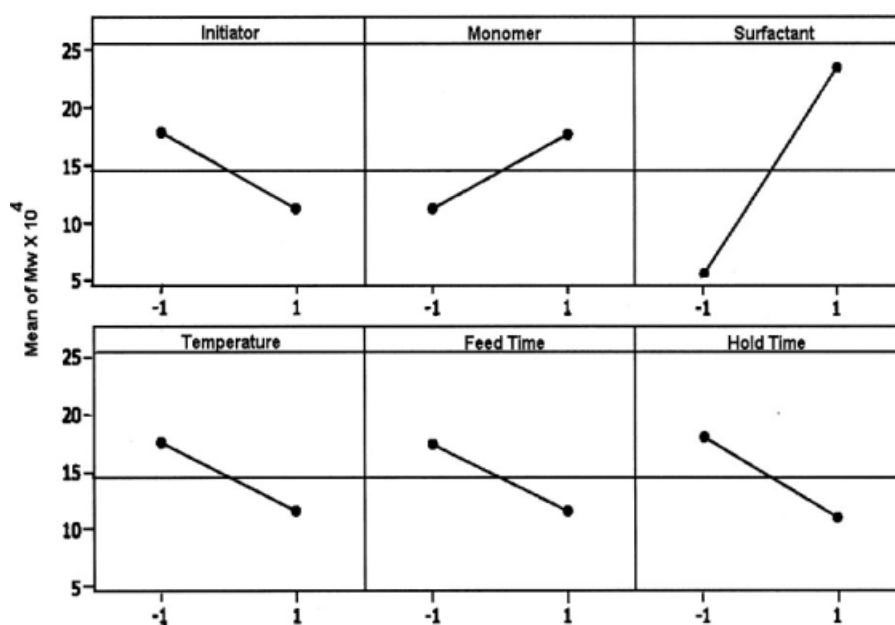

Figure 3 Effect of main reaction variables on molecular weight ($M_w * 10^4$). The y axis represents mean molecular weight ($M_w * 10^4$).

The surfactant is found to be the key independent factor affecting the molecular weight. Increase in molecular weight (M_n and M_w) with surfactant concentration was due to the generation of more number of polymer particles at higher concentration of surfactant. In emulsion polymerization, it is well known that with increase in polymer particle, the rate and degree of polymerization increases thus increasing the molecular weight. In this study, decreasing the initiator concentration from 0.5 to 0.25 g and increasing the monomer feed time from 3 to 4 h result in an increase in molecular weight. Lowering the initiator concentration decreases the number of growing radicals, but increase in feed time increases the chain length which increases the particle size thus increasing the molecular weight during propagation. Although the propagation rate decreases with increase in monomer ratio, but increased number of particles balance up the polymerization rate thus producing the high molecular weight. The reaction temperature and holding time have no significances. Figure 3 showed the effect of main variables on M_w of the latexes designed by fractional factorial design of experiments. Surfactant (S) is the major factor affecting the M_w value whereas the other factor has less effect on it. The two-way interaction effect of initiator and feed time (I*Ft) also had a significant effect on the molecular weight.

CONCLUSIONS

Emulsion polymerization of PMMA was carried out on the basis of fractional factorial design to study the effect of process variables such as initiator (APS), surfactant (Dowfax 2AI), monomer concentration, temperature, monomer feed rate, and holding time of the reaction after completion of monomer feeding. The experimental results were analyzed by means of ANOVA. From the results, it could be concluded that surfactant concentration is the key independent variable to affect the stability, final solid content (monomer conversion), particle size and also the molecular weight of the polymers. The two-way interaction effect of initiator concentration and monomer feed time had a significant effect on monomer conversion, molecular weight, and particle size of polymer.

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