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EMULSION POLYMERIZATION OF ACRYLIC MONOMERS STABILIZED BY POLY(ETHYLENE OXIDE)

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ABSTRACT

The stability of acrylic latices stabilized by poly(ethylene oxide) (PEO) is governed by the bridging flocculation process during polymerization. The final latex particle size increases with increasing concentration of initiator, PEO, or NaCl. The total scrap formed during the reaction increases rapidly with increasing NaCl concentration due to the ionic strength effect. It is shown that the final latex particle size decreases rapidly with an increase in the agitation speed. The amount of total scrap formed during polymerization is generally greater at a higher agitation speed. These results suggest that the fraction of the particle surface covered by PEO and the ratio of the thickness of the PEO adsorption layer to that of the electric double layer of the latex particles should play an important role in determining the final latex particle size and colloidal stability.

INTRODUCTION

Conventional emulsion polymerization [1] involves the dispersion of monomers in water by means of anionic surfactants (e.g., sodium lauryl sulfate) and heating of the monomer emulsion to the reaction temperature, followed by addition of the initiator solution to start the reaction. This heterogeneous polymerization

technique has been widely used to manufacture latices for such industrial applications as adhesives, coatings, binders, thermoplastics, etc. The resultant latex product involves a large number of polymer particles (ca. 50–1000 nm) dispersed in the aqueous phase. Stability of the reaction system can be achieved by the repulsive force among the interactive particles, provided by the adsorbed anionic surfactant molecules on the particle surface. Nevertheless, the latex product protected by the electrostatic repulsion mechanism is very sensitive to changes in the ionic strength of the aqueous phase. One approach to overcome this disadvantage is to use nonionic surfactants (e.g., nonyl phenol–40 mol ethylene oxide adduct) to impart steric stabilization to the latex particles [2, 3].

Both the anionic and nonionic surfactant molecules are generally small and mobile, and they can easily diffuse to the surface layer of the polymeric film. Thus the application properties of the latex products, such as adhesion and water resistance, can be greatly reduced. Water-soluble poly(ethylene oxide) (PEO) resembles the hydrophilic component of the nonionic surfactant, nonyl phenol–40 mol ethylene oxide adduct, and it can be chemically incorporated into the latex particles by grafting the hydrophobic polymer radicals onto PEO chains via the hydrogen abstraction mechanism [4, 5]. Thus the surface-active graft copolymer formed in situ is just like a nonionic surfactant, and it can help nucleate and stabilize the primary particles in the emulsion polymerization system. The water resistance of the latex product should not be impaired since the grafted PEO chains have become an integral part of the emulsion polymer. Furthermore, the polymeric coatings also show satisfactory film-formation properties.

Literature dealing with emulsion polymerization systems using PEO as the stabilizer has been scarce. Bromley [4] prepared PEO-stabilized polymer particles dispersed in methanol/water mixtures by means of a semibatch process. The minimum molecular weight of PEO required for appropriate steric stabilization was determined to be 1000–1500 g/mol. In addition, the level of free PEO was estimated to be less than 0.002% based on total polymer by thin-layer chromatography. The experimental data of Chang [6] showed that new primary particles were continuously nucleated before 20% conversion for the emulsion polymerization of methyl methacrylate in the presence of PEO. As a result of the long particle nucleation, the latex products generally exhibited a broad particle size distribution. Donners [7] pointed out that PEO was useful for modifying the particle size and particle size distribution of carboxylated latices. For latices incorporated with high levels of carboxylic monomers, it was postulated that complex formation between PEO and carboxyl-group-rich parts of the emulsion copolymer could have an influence on the particle nucleation process. Ødegard et al. [8] synthesized pyrrole latex particles stabilized by PEO as electron-conducting polymer electrodes. The amount of PEO used was quite high (pyrrole:PEO = 1:1). Recently, Brown et al. [5] studied the batch emulsion polymerization of styrene using PEO as the stabilizer. They postulated that significant secondary agglomeration of the latex particles took place during the reaction. Very little effort has been devoted to systematic studies of colloidal stability during polymerization and control of the final particle size.

The size distribution of the latex particles can have a significant effect on the quality of the products. For example, the primary functions of trade paints and industrial coatings are protection and decoration. The particle size and size distribution play an important role in the application properties of these latex products

(e.g., film formation, mechanical properties, chemical resistance, and optical properties). Removal of coagulum from the latex products by filtration is necessary since the coagulum produced by the loss of colloidal stability has a negative effect on the application properties. In addition, the reactor needs to be shut down for cleaning when polymer on the wall accumulates to an unacceptable level. Both factors will cause plant production problems and increase product cost. Thus, a knowledge of the effects of important reaction variables on the final latex particle size and the colloidal stability during polymerization is essential for successful product development and production.

The objective of this work was to systematically investigate the effects of various reaction parameters on the emulsion copolymerization of methyl methacrylate (MMA) and butyl acrylate (BA) in the presence of PEO. The parameters selected for study include the ratio of MMA to BA (MMA/BA), the number-averaged molecular weight of PEO (\bar{M}_n of PEO), the concentration of PEO based on total monomer ([PEO]), and the concentration of initiator based on total water ([I]). We will focus our attention on particle size control. Another goal of this project was to gain a better understanding of the key to achieving a satisfactory colloidal stability during the reaction.

EXPERIMENTAL

Materials

The chemicals used were methyl methacrylate (Kaohsiung Monomer Co.), butyl acrylate (Formosa Plastics Co.), poly(ethylene oxide) with various molecular weights (Aldrich), sodium persulfate (Riedel-de-Haen), nitrogen (Ching-Feng-Harnng Co.), and deionized water (Barnsted, Nanopure Ultrapure Water System, specific conductance $< 0.057 \mu\text{S}/\text{cm}$). The monomers, MMA and BA, were distilled under reduced pressure before use. All other chemicals were used as received.

Polymerization Process

Batch emulsion polymerization was carried out in a 250-mL glass reactor equipped with a 45° pitched 4-bladed agitator, a thermometer, and a condenser. The reactor has a diameter of 7.5 cm and the depth of liquid in the vessel is 2.8 cm. The diameter and width of the turbine impeller are 6 cm and 0.6 cm, respectively. The impeller is positioned 0.9 cm from the bottom of the vessel. The reactor is not baffled in this work, but the thermometer can provide some baffling effect. The principal flow patterns are radial and tangential, and the latter action can induce vortexing and swirling in the reaction system. A typical recipe can be found in Table 1. The reaction mixture (including water, PEO, and monomers) was purged with nitrogen for 10 minutes to remove dissolved oxygen while heated to 80°C , followed by addition of the initiator solution to start the reaction. The reaction temperature was kept at 80°C over 4 hours. The total solids content of the latex product is about 15% for complete conversion. The agitation speed was kept constant at 400 rpm throughout this work.

The latex product was filtered through a 40-mesh (0.42 mm) screen and a 200-mesh (0.074 mm) screen in series to collect the filterable solids. Scrap adhering

TABLE 1. A Typical Recipe of 3×3 Latin Square Design for the Batch Emulsion Polymerization of MMA and BA Stabilized with PEO: (A, a, I, 1)

A	a	B	a	C	a
I	1	II	3	III	2
A	b	B	b	C	b
II	2	III	1	I	3
A	c	B	c	C	c
III	3	I	2	II	1

(A, a, I, 1)	Chemicals	Weight, g
Reaction mixture	H ₂ O	80.00
	PEO (1500)	0.075
	BA	13.5
	MMA	1.5
Initiator solution	H ₂ O	5.0
	Na ₂ S ₂ O ₈	0.085
Total weight (g)		100.2
Total solids content (%)		15.1

to the agitator, thermometer, and reactor wall was also collected. Total solids content was determined by the gravimetric method. Particle size data were obtained from the dynamic light-scattering method (Otsuka, Photal LPA-3000/3100).

RESULTS AND DISCUSSION

First, a 3×3 Latin square design (4 variables, 3 levels, and 9 experiments, as shown in Table 1) was used to screen the four reaction parameters: MMA/BA (A = 10/90, B = 50/50, and C = 90/10), \bar{M}_n of PEO (a = 1500, b = 4600, and c = 8000 g/mol), [PEO] (I = 0.50%, II = 2.25%, and III = 5.00% based on total monomer), and [I] (1 = 0.10%, 2 = 0.15%, and 3 = 0.20% based on total water). For example, the reaction parameters for the experiment in the top left corner of the Latin square (A, a, I, 1) shown in Table 1 are: MMA/BA = 10/90, \bar{M}_n of PEO = 1500 g/mol, [PEO] = 0.5%, and [I] = 0.1%. The agitation speed was kept constant (i.e., 400 rpm) throughout this designed series. The purpose of a screening design is to identify the few important parameters from many possible candidates. These critical variables then can be investigated in more detail by using a full two-level factorial design, as will be shown below. It should be noted that the desired main effects can be confounded with any of the possible interactions in a

screening design. Thus, the Latin square design was only used to determine qualitatively the magnitude of the effect of each variable on the properties of the latex product. The experimental data are summarized in Table 2.

In Table 2 the numerical value corresponding to the variable represents the effect of the variable on the latex property. For example, the overall average of the particle size of the finished products in the Latin square design is 427 nm. The effect of the variables A, B, and C on d_p is +13, -54, and +40 nm, respectively. That is, the experiment with MMA/BA equal to 10/90, 50/50, or 90/10 (A, B, or C), on the average, can contribute +13, -54, or +40 nm to d_p with respect to the overall average value (427 nm). The greater the range of the numbers (e.g., -96 to +72 nm in this design), the stronger the effect of the variable (e.g., [PEO] in this design) on the final particle size (d_p). The d_p data show that the parameters in the decreasing order of importance are [PEO] > [I] > MMA/BA > \overline{M}_n of PEO. The parameter d_p decreases with an increase in [PEO] or [I], but these trends are not conclusive for the reasons discussed below.

Table 2 shows that both the total scrap and 200-mesh filterable solids are very high for the Latin square design. The total scrap represents the scrap collected by a 40-mesh screen and a 200-mesh screen in series plus those adhering to the agitator, thermometer, and reactor wall. The overall average of the total scrap data is 11.03% and that of the 200-mesh filterable solids data is 3.63%. Such a high level of

TABLE 2. Effect of Each Reaction Variable on Latex Properties in a 3 × 3 Latin Square Design^a

	d_p , nm	Total scrap, %	200-mesh, %
A	13	2.10	3.88
B	-54	-4.64	-0.98
C	40	2.53	-2.90
a	33	-9.57	-3.53
b	-18	-5.95	-2.65
c	-14	15.52	6.19
I	72	-4.54	-1.21
II	24	6.65	-2.35
III	-96	-2.11	3.56
1	42	3.15	-2.61
2	17	-0.96	-0.70
3	-60	-2.19	3.31
Overall average	427	11.03	3.63

^a d_p : The final latex particle size. Total scrap: The scrap collected by a 40-mesh screen and a 200-mesh screen in series plus those adhering to the agitator, thermometer, and reactor wall. 200-mesh: The filterable solids collected by a 200-mesh screen.

200-mesh coagulum can cause a serious filtration problem in plant production. For the total scrap data, the parameters in the decreasing order of importance are \bar{M}_n of PEO > [PEO] > MMA/BA > [I]. For the 200-mesh filterable solids data, the parameters in the decreasing order of importance are \bar{M}_n of PEO > MMA/BA > [I] > [PEO]. The parameter \bar{M}_n of PEO plays an important role in controlling latex stability during the reaction. Both the total scrap and 200-mesh filterable solids increase with an increase in the molecular weight of PEO because of the increased probability of interparticle bridging. These trends suggest that significant flocculation of the latex particles must have occurred during polymerization, most likely due to the bridging flocculation mechanism [3, 5]. Intensive bridging flocculation among the interactive particles can result in the formation of coagulum as shown by the total scrap data in Table 2. On the other hand, it is postulated that the lightly agglomerated and then coalesced polymer particles can still be stably dispersed in the aqueous phase, termed the "limited bridging flocculation process." Thus, such a complicated flocculation process can definitely make the task of particle size control almost impossible.

In order to study the effects of [PEO] and [I] on d_p with acceptable levels of coagulum, the parameters \bar{M}_n of PEO and MMA/BA were kept constant at 1500 g/mol and 50/50, respectively, in the remaining work based on the total scrap and 200-mesh filterable solids data in Table 2. We then chose [PEO] (0.5–5.0%) and [I] (0.1–0.2%) as the reaction variables of a two-level factorial design (5 points in a designed square, 1 midpoint included) to analyze quantitatively the effects of the variables on the final latex particle size. The numerical value in the above parentheses represents the minus level and the plus level of that variable in the factorial design. Each point (recipe) was carried out four times to test the batch-to-batch variations in this designed series. The experimental data are compiled in Table 3. The reproducibility of the experiments is reasonably good except the 200-mesh filterable solids data (see the experimental errors in Table 3). Furthermore, the overall average of the total scrap and 200-mesh filterable solids data is 1.91% and 0.54%, respectively. As expected, the degree of flocculation taking place during polymerization has been reduced greatly by selecting appropriate values for the

TABLE 3. Experimental Data of Two-Level Factorial Design^a

[PEO], [I], %	d_p , nm	d_w/d_n ^b	Total scrap, %	200-mesh, %
0.50, 0.10	350 ± 27	1.020 ± 0.008	0.73 ± 0.13	0.006 ± 0.004
5.00, 0.10	377 ± 28	1.015 ± 0.005	3.01 ± 1.36	0.885 ± 0.228
0.50, 0.20	384 ± 16	1.015 ± 0.004	1.17 ± 0.44	0.081 ± 0.074
5.00, 0.20	477 ± 27	1.015 ± 0.003	2.63 ± 0.45	1.342 ± 0.390
2.25, 0.15	367 ± 33	1.028 ± 0.012	1.99 ± 0.83	0.342 ± 0.224
Overall average	391	1.019	1.91	0.531

^aEach datum is an average of four experiments. The numerical value represents mean ± standard deviation.

^b d_w/d_n : Polydispersity index of the particle size distribution.

parameters \overline{M}_n of PEO and MMA/BA. The results of the factorial design are discussed below.

The experimental data show that both the parameters [I] (+66.6 nm) and [PEO] (+59.9 nm) are important in determining the final latex particle size. The numerical value in the above parentheses represents the standardized effect of the variable on the final particle size when the variable is changed from the minus level to the plus level. The overall average particle size of the finished products in the factorial design is 391 nm. In addition, the particle size distribution of the finished batches is relatively narrow as shown by the polydispersity index (d_w/d_n) data in Table 3. Please note that the factorial design shows that d_p will increase with an increase in either [I] or [PEO], which is in contradiction to the results of the Latin square design discussed above. The contradictory results are probably caused by the different degrees of flocculation occurring in the course of polymerization.

Based on the factorial design, an equation was derived to predict the final latex particle size, d_p . Figure 1 shows the contour plot of d_p constructed from the predictive equation. The abscissa represents the concentration of PEO and the ordinate represents the concentration of initiator. In considering the curve with d_p equal to 400 nm, for example, the parameter [I] required to maintain the same particle size will decrease with an increase in [PEO]. Another interesting point is that 1) lower levels of [I] and [PEO] can result in latex products with smaller d_p (see the bottom left corner of Fig. 1) and 2) higher levels of [I] and [PEO], on the other hand, can lead to latex products with larger d_p (see the top right corner of Fig. 1). It is

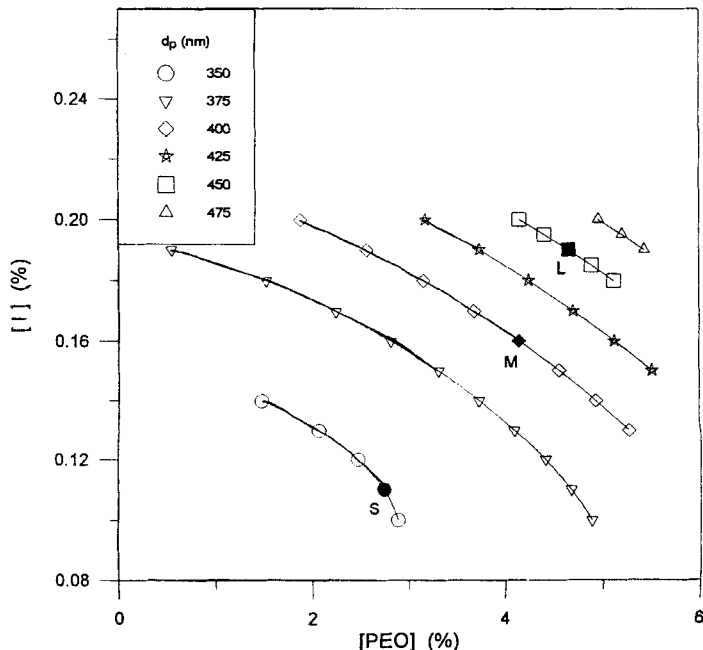


FIG. 1. Contour plot of final latex particle size; MMA/BA = 50/50, \overline{M}_n of PEO = 1500 g/mol, and agitation speed = 400 rpm.

quite difficult to produce latex products with d_p less than 300 nm within the range of experimental conditions investigated. This result is consistent with the work of Brown et al. [5] in which the particle size of the polystyrene particles stabilized with 5–15% PEO ranges from 500 to 350 nm. Future research is required in order to be able to synthesize small particle size latices using PEO as the sole stabilizer.

Three formulas (L, M, and S corresponding to the closed square, diamond, and circular data points, respectively, in Fig. 1) were then selected to verify the predictive equation of the final latex particle size. The recipes and experimental data are listed in Table 4. The experimental d_p data agree reasonably well with the predictions. These experimental results again support the above conclusion that lower levels of [I] and [PEO] can produce latex products with smaller d_p , whereas higher levels of [I] and [PEO] can produce latex products with larger d_p . It is interesting to note that both the total scrap and 200-mesh filterable solids increase with an increase in the product of [PEO] and [I] in this series of experiments. The amount of coagulum (i.e., large flocs) formed during polymerization is presumably controlled by the fraction of the particle surface covered by PEO (θ) and the ratio of the thickness of the PEO adsorption layer to that of the electric double layer of the latex particles ($\kappa\delta$) [9, 10]. The parameter δ is the thickness of the PEO adsorption layer and $1/\kappa$ is that of the electric double layer of the latex particles. The electric double layer around the particles originates from the sulfate group ($-\text{SO}_4^-$) on the particle surface derived from the persulfate initiator. The parameter θ and the ratio $\kappa\delta$ can play an important role in the bridging flocculation process. According to De Witt and van de Ven [10], at lower values of $\kappa\delta$ the electrostatic repulsion force predominates the interparticle interaction process, leading to a relatively stable colloidal system. The system becomes unstable due to the bridging flocculation mechanism when the ratio $\kappa\delta$ is equal to unity. Under the condition of $\theta \rightarrow 1$ and $\kappa\delta > 1$, the system is stable as a result of steric stabilization. Nevertheless, this subject is beyond the scope of this study because both the parameters [PEO] and [I] were varied in this series of experiments.

Figure 2 shows the $\log(d_p)$ vs $\log[\text{I}]$ curves at various levels of [PEO], calculated according to the predictive equation obtained from the factorial design. At a constant [PEO], d_p increases concavely with an increase in [I]. Based on the micellar nucleation mechanism [11], Smith-Ewart theory [12, 13] predicts a 0.4 power de-

TABLE 4. Experiments Designed to Verify the Prediction Equation of Final Latex Particle Size

	L	M	S
[I] (%)	0.19	0.16	0.11
[PEO] (%)	4.66	4.15	2.74
Predicted d_p (nm)	450	400	350
Experimental data (nm)	464	387	307
Error (%)	3	3	12
d_w/d_n	1.04	1.04	1.04
Total scrap (%)	4.32	1.30	0.95
200-mesh (%)	2.41	1.08	0.20

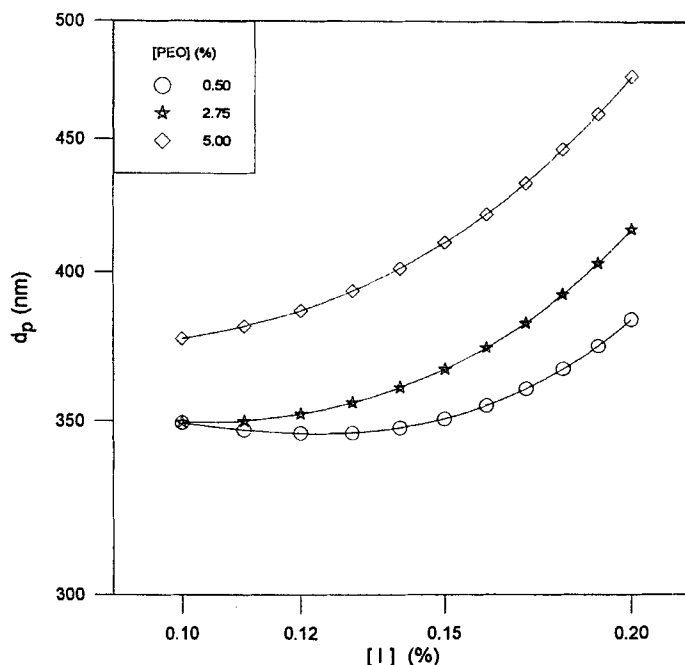


FIG. 2. Final latex particle size vs concentration of initiator curves; MMA/BA = 50/50, \bar{M}_n of PEO = 1500 g/mol, and agitation speed = 400 rpm.

pendence of the total number of latex particles (N_p) on [I] or a -0.133 power dependence of d_p on [I] for the polymerization system stabilized by an anionic surfactant because $(\pi/6d_p^3) \rho_p N_p$ is equal to a constant in this series of runs. The parameter ρ_p is the density of a polymer. It is shown in Fig. 2 that the polymerization system stabilized by the water-soluble polymer PEO does not follow the simple relationship ($d_p \sim [I]^{-0.133}$) predicted by Smith-Ewart theory, and the relationship between d_p and [I] is strongly dependent on [PEO]. Furthermore, the slope of the $\log(d_p)$ vs $\log[I]$ curve is positive over a wide range of [PEO] and [I], which is opposite to the Smith-Ewart theory. Again, it is postulated that the final latex particle size is closely related to the parameters θ and $\kappa\delta$. At a constant [PEO], the parameter δ should remain relatively constant during the particle nucleation period. Nucleation of the polymer particles is most likely governed by the homogeneous nucleation mechanism [14-16] because there is no surface-active materials present in the reaction system at the very beginning of polymerization. In this case, increasing the initiator concentration will enhance the ionic strength of the solution, which can compress the electric double layer around the particles and then reduce the thickness of the electric double layer $1/\kappa$ (or increase κ). On the other hand, increasing the initiator concentration can possibly increase the particle surface charge density and, thus, increase $1/\kappa$ (or decrease κ). It is postulated that the former effect can override the latter during the particle nucleation period based on the experimental data. This action can cause the ratio $\kappa\delta$ to approach unity when the initiator concentration is increased from 0.1 to 0.2%. As mentioned above, the

interactive primary particles can become relatively unstable as a result of the bridging flocculation mechanism when the ratio $\kappa\delta$ is close to unity. Thus, the higher the initiator concentration, the greater the extent of the secondary agglomeration (i.e., the larger the primary particles nucleated). Such a secondary agglomeration (or limited bridging flocculation) process will cease when the ratio $\kappa\delta$ associated with the coalesced particles becomes greater than unity. Thus, the resultant latex particles can still be stably dispersed in the aqueous phase.

One of the recipes used in the factorial design was selected to further study the effect of the electrolyte concentration on the final latex particle size. In this series of experiments the ionic strength was adjusted by using various levels of NaCl ([NaCl] = 0–0.6% based on total water) and the other parameters were kept constant (i.e., [PEO] = 0.5%, [I] = 0.1%, and agitation speed = 400 rpm). The parameter [NaCl] represents the concentration of sodium chloride in water. The experimental data are summarized in Table 5. The final latex particle size, d_p , increases from 350 to 574 nm when [NaCl] is increased from 0.0 to 0.6%. This trend supports the above postulation that the ratio $\kappa\delta$ plays an important role in the particle nucleation process. It is also interesting to note that the total scrap increases rapidly with increasing [NaCl]. This result can serve as supporting evidence for the postulation that the ratio $\kappa\delta$ can have a significant influence on the bridging flocculation process. To the best of the authors' knowledge, bridging flocculation has not been reported in the literature for the PEO molecular weight range investigated here. Future research is required to verify the postulated bridging flocculation mechanism.

The dispersed latex particles, under mechanical agitation, may coagulate with one another by the attractive van der Waals force during polymerization. The shear

TABLE 5. Experiments Designed to Study the Effects of Ionic Strength and Agitation Speed

	d_p , nm	d_w/d_n	Total scrap, %	200-mesh, %
[NaCl], %: ^a				
0.0	350	1.02	3.59	0.03
0.3	462	1.02	9.32	0.92
0.6	574	1.01	21.85	0.17
Agitation speed, rpm: ^b				
200	429	1.01	0.60	0.01
400	350	1.02	3.59	0.03
600	229	1.06	2.41	0.01
[PEO], %: ^c				
0.5	384	1.02	1.17	0.08
5.0	477	1.02	2.63	1.34
15.0	508	1.02	3.54	3.12

^a[PEO] = 0.5%, [I] = 0.1%, and agitation speed = 400 rpm.

^b[PEO] = 0.5%, [I] = 0.1%, and [NaCl] = 0%.

^c[I] = 0.2%, [NaCl] = 0%, and agitation speed = 400 rpm.

force generated by intensive agitation can cause significant turbulence in a stirred-tank reactor. This action can increase both the force and frequency of collisions among the interactive particles. Such a shear-induced coagulation process may change the particle size distribution of the latex product and result in the formation of coagulum. In this work the recipe with $[\text{PEO}] = 0.5\%$ and $[\text{I}] = 0.1\%$ was chosen to investigate the effect of the agitation speed (200–600 rpm) on the emulsion polymerization of acrylic monomers stabilized by PEO. The experimental data listed in Table 5 show that d_p decreases rapidly with an increase in the agitation speed. The reason for this observation is not clear at present. In addition, the amount of total scrap formed during polymerization is generally greater at a higher agitation speed (see the total scrap data in Table 5).

Based on the predictive equation obtained from the factorial design, the calculated $\log(d_p)$ vs $\log[\text{PEO}]$ profiles at various concentrations of initiator are shown in Fig. 3. Smith-Ewart theory [12, 13] predicts a 0.6 power dependence of N_p on the surfactant concentration or a -0.2 power dependence of d_p on the surfactant concentration for the polymerization system stabilized by an anionic surfactant. The $\log(d_p)$ vs $\log[\text{PEO}]$ curves indicate that the system stabilized by PEO does not follow the relationship ($d_p \sim [\text{PEO}]^{-0.2}$) predicted by Smith-Ewart theory, and that the relationship between d_p and $[\text{PEO}]$ is strongly dependent on $[\text{I}]$. The slope of the $\log(d_p)$ vs $\log[\text{I}]$ curve is positive over a wide range of $[\text{PEO}]$ and $[\text{I}]$, which is opposite to the Smith-Ewart theory. At a constant $[\text{I}]$ (e.g., 0.2%), the parameter d_p first remains relatively constant and then increases with an increase in $[\text{PEO}]$

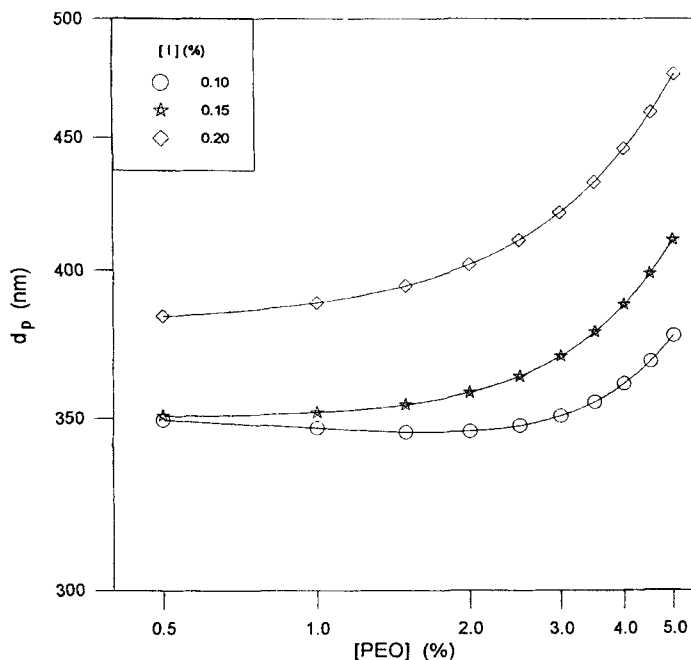


FIG. 3. Final latex particle size vs concentration of PEO curves; MMA/BA = 50/50, \bar{M}_n of PEO = 1500 g/mol, and agitation speed = 400 rpm.

because the ratio $\kappa\delta$ may approach unity when [PEO] is increased from 0.5 to 5% during the particle nucleation period. In addition, the recipe with [PEO] = 15.0% and [I] = 0.2% was carried out, and the trend of the increased d_p with [PEO] was further confirmed (see the d_p data in Table 5). This trend is in contradiction to the work of Brown et al. [5]. For emulsion polymerization of styrene stabilized by PEO, they showed that d_p decreased from ca. 500 to 350 nm when [PEO] was increased from 5 to 15%.

Finally, it should be pointed out that the total solids content (15%) of the finished batch is quite low. The latex product should have a total solids content of at least 40% in order to be commercially viable. This can be achieved by using a semibatch emulsion polymerization process.

CONCLUSIONS

For batch emulsion polymerization of acrylic monomers stabilized by the water-soluble polymer PEO, the reaction parameters in the decreasing order of importance in determining the latex stability are \overline{M}_n of PEO > [PEO] > MMA/BA > [I]. During polymerization, the latex stability is governed by the bridging flocculation process. The final latex particle size d_p will increase with an increase in either [I] or [PEO]. These results indicate that the polymerization system does not follow the conventional Smith-Ewart theory. Within the range of experimental conditions investigated, it is difficult to produce latex products with d_p less than 300 nm. Based on a two-level factorial design, a predictive equation for d_p has been developed. Three formulations (designated as L, M, and S), which cover a wide range of d_p , were carried out to verify the predictive equation. Agreement between the experimental data and the predictions is satisfactory.

The final latex particle size d_p increases significantly with an increase in [NaCl] due to the ionic strength effect. This trend suggests that the fraction of the particle surface covered by PEO (θ) and the ratio of the thickness of the PEO adsorption layer to that of the electric double layer of the latex particles ($\kappa\delta$) should play an important role in the particle nucleation process. The total scrap, presumably caused by the bridging flocculation process, also increases rapidly with an increase in [NaCl]. Thus, the ratio $\kappa\delta$ can have an influence on the formation of coagulum. It is shown that d_p decreases rapidly with an increase in the agitation speed. Furthermore, the amount of total scrap formed during polymerization is generally greater at a higher agitation speed.

It can be concluded that the particle nucleation and growth processes for the emulsion polymerization system stabilized by PEO are dominated by the bridging flocculation mechanism. This can explain why the reaction kinetics are not in agreement with the conventional mechanisms.

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REFERENCES

- [1] D. C. Blackley, *Emulsion Polymerization, Theory and Practice*, Applied Science Publishers, London, 1975.
- [2] T. Sato and R. Ruch, *Stabilization of Colloidal Dispersions by Polymer Adsorption*, Dekker, New York, 1980.
- [3] D. H. Napper, *Polymeric Stabilization of Colloidal Dispersions*, Academic Press, London, 1983.
- [4] C. W. A. Bromley, *Colloids Surf.*, **17**, 1 (1986).
- [5] R. Brown, B. Stutzel, and T. Sauer, *Macromol. Chem. Phys.*, **196**, 2047 (1995).
- [6] M. C. Chang, "Emulsion Polymerization in the Presence of Non-Ionic Surfactant," Ph.D. Dissertation, University of Akron, Akron, Ohio, 1980.
- [7] W. A. B. Donners, *J. Polym. Sci., Polym. Lett. Ed.*, **25**, 29 (1987).
- [8] R. Ødegard, T. A. Skotheim, and H. S. Lee, *J. Electrochem. Soc.*, **138**, 2930 (1991).
- [9] E. G. M. Pelssers, M. A. Cohen Stuart, and G. J. Fleer, *J. Chem. Soc., Faraday Trans.*, **86**, 1355 (1990).
- [10] J. A. De Witt and T. G. M. van de Ven, *Adv. Colloid Interface Sci.*, **42**, 41 (1992).
- [11] W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 1428 (1947).
- [12] W. V. Smith and R. W. Ewart, *J. Chem. Phys.*, **16**, 592 (1948).
- [13] W. V. Smith, *J. Am. Chem. Soc.*, **70**, 3695 (1948).
- [14] R. M. Fitch, M. B. Prenosil, and K. J. Sprick, *J. Polym. Sci., Part C*, **27**, 95 (1969).
- [15] F. K. Hansen and J. Ugelstad, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 1953 (1978).
- [16] C. P. Roe, *Ind. Eng. Chem.*, **60**, 20 (1968).

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