Emulsion Polymerization of an Epoxy-Acrylate Emulsion Stabilized with Polyacrylate. I. Influence of Salt, Initiator, Neutralizing Amine, and Stirring Speed

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ABSTRACT: The past decade has seen the development of high-performance epoxyacrylate coatings. Some of these coatings are used exclusively as can coatings. To improve chemical resistance, emulsion polymerization in the presence of the dispersed epoxy resin can be conducted. Replicated factorial designs were designed to investigate some of the factors that contribute to the performance and stability of the epoxyacrylate coating. The factors investigated in this study were: the type and amount of neutralizing amine, the type of initiator, the presence or absence of salt, and the stirring speed of the impeller. The measured responses for the experimental design were particle size, particle size distribution, and conversion. It has been shown in this study that the type of amine used to neutralize the polyacrylic stabilizer significantly influenced the observed responses probably by acting as chain transfer agent during polymerization. The addition of salt significantly affected the observed responses by shielding the surface charges on the particle surface that impart stability to the latex through electrostatic repulsion. Stirring speed of the impeller and the type of initiator as factors in the range investigated do not influence the kinetics or the particle size and polydispersity to any great extent either on their own or in combination with other factors. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1347-1360, 1999

Key words: epoxy-acrylate; emulsion polymerization; can coating; statistically designed experiments; conversion; particle size; polydispersity

INTRODUCTION

During the past 10 years, legislation in the United States and Europe on the reduction of the volatile organic content of paints and coatings has resulted in the development of many new waterreducible coatings. Among these is the water-reducible epoxy coatings. $^{1-11}$

Research into these water-based epoxy coatings has resulted in the development of so-called transitional products, so named because they signified the transition of the traditional solventbased coatings to coatings dispersed in water. In these transitional water-based coating systems, low molecular weight diglycidyl ethers of bisphenol A were emulsified with combinations of an-

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ionic and nonionic surfactants.¹¹ The development of products with even lower volatile organic content contents than the previous transitional products and the use of acid-salted amine adducts to impart dispersion of the epoxy in water followed. These water-based epoxy coatings were termed "first-generation coating systems."

In these first-generation coating systems, hydrophilic molecules were incorporated into the chemical structure of the epoxy to make it waterdispersible.^{1-6,10} Grafting was extensively used to produce water-reducible epoxy graft copolymers.^{4,12}

In an example of a grafting reaction, addition polymerization of combinations of hydrophilic and hydrophobic monomers initiated by a standard initiator, such as benzoyl peroxide, was conducted in the presence of an epoxy resin.⁴ After polymerization, the grafted epoxy resin, along with a significant amount of ungrafted copolymer, was dispersed as micelles in the water phase by neutralizing the carboxylic acid groups with a suitable amine. The main problem associated with most of these first-generation products was the unsatisfactory chemical and water resistance, combined with their somewhat inferior film-forming ability and the inability to be applied to metallic substrates.

In the late 1980's and early 1990's, the following observations were made regarding high-performance coatings based on acrylic dispersants or polyelectrolytes. Much higher molecular mass epoxies, compared with previous water-based systems with a resultant increase in coating quality, could now be formulated. The resultant epoxyacrylate emulsion was also able to undergo selfcuring after application as a coating on a substrate.^{12–14} Many of these latest epoxy-acrylate water-based emulsions are used commercially as metal coatings with an improved film-forming ability and for high-gloss applications. There is also some epoxy-acrylate emulsions that are designed specifically to be applied as can coatings.¹⁴

Can coatings for alcoholic beverages are required to have superior film-formation ability, be durable, and exhibit high chemical and water resistance, as well as possess specific rheological properties.

In our laboratories, we are studying ways to increase the chemical and water-resistance of can coatings. This is achieved by adding combinations of suitable monomers, such as butyl acrylate and styrene to the predispersed epoxy-acrylate dispersion and initiating the polymerization with a suitable initiator, such as ammonium persulfate.

The aim of this article is to highlight the effects that various factors that contribute to a stable, high-performance epoxy-acrylate emulsion have on the overall conversion of monomers (such as butyl acrylate and styrene to the resultant copolymer, particle size, and polydispersity of the emulsion). Examples of these factors include stirring speed of the agitator, the presence of dissolved salt in the water, the type of initiator used for addition polymerization, and the amount and type of amine used to neutralize the polyacrylate.

BACKGROUND

The epoxy-acrylate dispersion (dispersed epoxy phase) and later the epoxy-acrylate emulsion (with added monomer) are stabilized mainly by the contribution of the neutralized carboxylic acid groups incorporated during the synthesis of the polyacrylate. The number of ionic groups on the surface of the particle influences the thickness of the diffuse electric layer around the particle. The thickness and therefore the stability of the dispersed particle are influenced by the thickness of this layer. The thickness is given in terms of the Debye length $1/\kappa$. κ is given by the following equation:

$$\kappa = \left(\frac{8\pi n Z^2 e^2}{\varepsilon k T}\right) \tag{1}$$

In this equation, the symbol n denotes the number of ionized groups, Z is the valence of the ionized groups, e is the elementary charge, ε is the dielectric constant, k is the Boltzmann constant, and T is the temperature in Kelvin.

An initiator, such as ammonium persulfate, can contribute to the latex stabilization through the ionic end-groups of the polymer chains. Apart from electrostatic stability, a degree of steric stabilization may also contribute to the overall stability of the latex. This may be possible through the extension of parts of the polyacrylate containing enough ionic carboxylic acid groups extending into the medium as long chains or loops. However, because these chains also contain ionized groups, they will be susceptible to the same factors that destabilize the charges on the surface of the particle. The difference between coagulation and flocculation needs to be qualified because these two terms are sometimes used synonymously. Coagulation occurs when the forces holding particles in suspension are overcome or neutralized. Flocculation on the other hand occurs when groups of particles aggregate into larger groups of particles or flocs.

Coagulation may be described as the result of two or more particles colliding with enough force to break through the electrostatic barrier and steric hindrance surrounding the latex particle to form a new larger particle: (1) by reducing the potential energy barrier due to the electrostatic and steric stabilization can accelerate coagulation and (2) by increasing the probability of a collision encounter between particles.

Simple electrolytes, such as NaCl in water, act by shielding the charges on the surface of the latex particle and compressing the electric double layer surrounding the particle.^{15–17} In this way, the thickness of the diffuse electric layer is reduced and, in so doing, the potential energy barrier to coagulation is lowered. Reduction of repulsive forces allows the attractive forces between particles to become dominant.

The kinetics of coagulation assume that the process is diffusion-driven.¹⁷ This means that a stable colloidal system of uniform primary particle size that is suddenly subjected to conditions that will enhance flocculation and coagulation will experience diffusion of particles toward a primary particle that will act as a center for further agglomeration. This theory also assumes that all particle collisions are effective in causing flocculation. However, the presence of a potential barrier surrounding the particles will have the effect that only a certain percentage of particle collisions will result in coagulation.

Agitation will promote the probability of collisions and therefore coagulation. This probability takes into account the velocity gradient that the particle is subjected to according to the following equation:

$$J = (\frac{4}{3}N(R_{ij})^3(du/dz)$$
(2)

The probability of collision of particle *i* with particle *j* is given by J. R_{ij} is the collision radius, and du/dz is the velocity gradient. The combination of an electrolyte and increased rate of agitation will enhance the probability of collision and eventual coagulation.

If the number of loci or particles change significantly with time during an emulsion polymerization, this will also affect the rate of polymerization and the extent of conversion of monomer to polymer. There is a direct dependence of the rate of emulsion polymerization on the number of loci for polymerization $(R_p \propto N_c)$. This becomes clear if one examines the rate equation for emulsion polymerization.¹⁸

$$R_p = \frac{dx}{dt} = \frac{C_p k_p \bar{n} N_c}{n_m^0 N_A}$$
(3)

In eq. (3), C_p is the monomer concentration inside the particle, k_p is the propagation rate constant, \tilde{n} is then the average number of radicals per particle, N_c is the number of latex particles per dm³, n_m^0 is the starting monomer concentration per dm³ latex, and N_A is Avogadro's number.

It is also well known that ionic strength of the medium affects the mass transfer of monomer and radicals in conventional emulsion polymerization. It is therefore important to understand the effects that the various factors discussed in this study will have on the stability and mechanism of polymerization.

EXPERIMENTAL

Synthesis of Polyelectrolyte

The polyfunctional acrylic polymer (polyacrylate) was synthesized by charging 1,755 g of butyl cellosolve to a 10 L stainless steel Buchi batch reactor. The reactor was heated to a temperature of 130°C and then 545 g of methacrylic acid, 563.8 g of 2-hydroxyethyl acrylate, and 2,112 g of butyl acrylate were fed to the reactor, according to a fixed monomer feed regime. At the same time, benzoyl peroxide, dissolved in 550 mL butyl cellosolve, was added to the reactor at a prescribed rate. Changing the initiator concentration, as well as the addition rates of monomer and initiator, could vary the molecular mass of the resultant acrylic polymer. The polyacrylate was used, as it was prepared without further purification. The solids content of the solution was determined by drying a weighed sample for 2 h at 150°C in an oven equipped with a fan.

Experimental Design

Two types of initiator were investigated for the emulsion copolymerization of styrene and butyl ac-

Factor	Lower Level	Upper Level
DMEA level Stirspeed	10 g 100 rpm	40 g 600 rpm
Sodium chloride level	0 g	5 g

Table IUpper and Lower Levels of Factors forFactorial Designed Experiments

rylate, namely 2,2'-azo-iso*bis*-butyronitrile (AIBN), recrystallized from methanol, and ammonium persulfate purchased from Fluka (Ronkonkoma, NY) and used as received.

The emulsion polymerization experiments for the determination of the effects of agitator stirring speed, initiator type, neutralizing amine type, and concentration, as well as the effect of dissolved salt on fractional conversion, particle size, and polydispersity of the emulsions, were designed as center-point replicated factorial designs, with the factors and levels investigated for each initiator type given in Table I. Polydispersity in the context of this study is an estimate of the variance of distribution. This is a dimensionless index of the broadness of the particle size distribution.

The responses measured were Z-average particle size and polydispersity at the end of emulsion polymerization and fractional conversion after 6,000 s of the total monomer concentration. The standard recipe for emulsion polymerization is summarized in Table II.

In the future, references to low- and high-factor levels will refer to the amounts given in Table I. The results of the factorial designed experiments will be illustrated in terms of response surface graphs. These graphs are the product of multiple regression models of the main factors and their interactions.^{19,20} The multiple linear regression models have the following general formula for a design in *b* replicated blocks:

$$Y_{u} = \beta_{0} + \sum_{i=1}^{k} \beta_{i} x_{ui} + \sum_{i=1}^{k} \beta_{ii} x_{i}^{2}$$
$$+ \sum_{i$$

In eq. (4), Y_u denotes the observed response value of the *u*th experimental run, x_{ui} is the corresponding *i*th input variable, δ_l denotes the effect of the *l*th block, z_{ul} is a dummy variable having the value of 1 if the *u*th trial is conducted in the *l*th block. If this is not the case, z_{ul} is 0. In eq. (1), $\beta_0, \beta_1, \ldots, \beta_k$ are the unknown parameters for which estimates are sought to fit a model to the physical data.

The molecular mass of the electrosteric polyacrylate used to disperse the epoxy in the water phase was kept constant throughout. The polyacrylate solution had a solids content of 58%. The epoxy used was SHELL's EPIKOTE 3001. The solid epoxy was dissolved in butoxy ethanol to yield a solution with a total solids content of 73%. Monomers were washed with 0.3M NaOH to remove as much inhibitor as possible and then distilled under reduced pressure. In all instances, the middle fraction of the distillate was kept. Monomers were stored at -10° C and were used within 1 week after distillation.

Emulsion Polymerization

In a typical emulsion polymerization experiment, the correct amounts of epoxy resin solution and polyacrylate solution were weighed off and mixed together. Dimethyl aminoethanol (DMEA) and a small amount of water were then added to the epoxy/polyacrylate mixture to yield a water-in-oil emulsion. This water-in-oil emulsion was inverted to give an oil-in-water emulsion by the addition of the remainder of the water as stated in Table II. Depending on the requirements of the experimental design, salt was added (see Table I). The pH was measured with a pH meter both before and after polymerization.

The emulsion was degassed for 1 h before polymerization and also during polymerization,

Table IIStandard Recipe Used for Epoxy-Acrylate Emulsion Polymerization

Ingredients	Quantities	
Surfactant batch no.	Apt4r1/Apr1	
Surfactant amount	70 g	
Styrene amount	20 g	
Butyl acrylate amount	20 g	
Epoxy amount	20 g	
Initiator amount	4.3821 E-03 mol	
DMEA amount	Variable	
Sodium chloride amount	Variable	
Distilled deionized water	$350 \mathrm{~g}$	
Temperature	70°Č	
Stir speed	Variable	

		Observed Response		
Input Variables		Particle Size	Polydispersity	Conversion
A.	Stirring Speed	0.104	-3.62E-04	1.04E-4
B.	DMEA	5.28	-0.016	-0.016
C.	Salt	100.38	-0.168	-0.168
AB		-0.0037	1.8E-7	1.8E-7
AC		-0.00431	2.7E-5	2.7 E-5
BC		-2.339	3.2E-3	3.2E-3
Blo	ck	37.11	-0.035	-0.0093
Coi	nstant	72.61	0.40	0.887

Table III Estimates of Coefficients for Multiple Regression Model

by bubbling nitrogen gas through the emulsion. Before it was decided to bubble nitrogen through the emulsion, experiments were done to ensure that this did not cause surface coagulation. After the initial degassing period, monomer as well as initiator were added to the reactor. The time when the monomer was added to the emulsion was taken as the beginning of the experiment. All emulsion copolymerizations were conducted over a period of 5 h (18,000 s) in a water bath regulated to a temperature of 70°C.

Samples of the emulsion were taken at regular intervals and analyzed by means of gas chromatography (GC) for monomer conversion. Particle sizes (Z-average) and polydispersity measurements were obtained with a Malvern Zetasizer 4S. The GC used was a Perkin-Elmer Autosystem GC (Perkin-Elmer, Norwalk, CT). The GC was equipped with a capillary column of 45 m in length and 0.32 mm in diameter. The stationary phase was 2 μ m thick and was based on poly(methyl silicone). The detector was a FID detector.

Chromatograms were obtained and integrated by means of EZCHROM software on a personal computer linked to the GC.

Sample Handling

Samples for GC analysis were withdrawn from the reactor during runs with a 1-mL syringe at regular intervals. All samples were quickly added to a vile containing a solution of hydroquinone, acetic acid, and butoxy ethanol. The reason for the acetic acid was to adjust the pH for the hydroquinone to be effective as inhibitor. Directly after addition of the withdrawn sample to the quenching solution, the vial was cooled down in ice. Dimethylformamide was added as internal standard to every sample taken.

Samples for analysis by the Malvern particle size analyzer were withdrawn at regular intervals during emulsion polymerization. Sampling consisted of adding 2–5 drops of the emulsion to a vial containing a solution of deionized water con-



Figure 1 Response surface graphs showing the effects of stirring speed, DMEA concentration, and the addition of salt on particle size of the emulsion after 5 h of emulsion polymerization.



Figure 2 Effect of salt in combination with a low level of DMEA on particle size and polydispersity during emulsion polymerization.

taining 1 m*M* NaCl. The exact amount of latex added to the vial was adjusted to give a reading of 1,000 kiloCounts on the Malvern. Before use, distilled deionized water was filtered twice through a filter with an average pore size of 0.45 μ m.

To validate the particle sizes as determined by the Malvern, transmission electron micrographs (TEMs) were obtained for some of the latexes. The particular method used was a negative staining technique using uranyl acetate as masking agent. Particles were deposited onto copper grids covered with a thin carbon film before treatment with the masking agent. The particle sizes obtained with the Malvern compared well with the TEM results, although some shrinkage of the particles occurred during the time the particles were left on the copper grid to dry.

RESULTS

The results will be discussed under two major headings, namely "Water-Soluble Initiator: Am-



Figure 4 Effect of DMEA levels with salt on polydispersity during emulsion copolymerization.

monium Persulfate" and "Water-Insoluble Initiator: AIBN." Each of these two sections will be subdivided into discussions of the responses for the factorial experiments, namely particle size, polydispersity, and conversion.

Water-Soluble Initiator: Ammonium Persulfate

Table III contains the coefficients used to produce the response surface graphs in this section for the water-soluble initiator, ammonium persulfate.

The effects of the individual factors and their combinations are discussed in the next section. Initially, before monomer is added, most samples of the epoxy-acrylate emulsion for both initiator types have a large polydispersity (between a value of 0.6 and 1) and large average particle size (in the region of 1 μ m and larger). As soon as monomer is added, these large particles decrease in size and measured average particle sizes fall



Figure 3 Response surface graphs of the effects of stirring speed, DMEA level, and the addition of salt on polydispersity of the emulsion polymerization after 5 h of polymerization.



Figure 5 Effect of DMEA level and no added salt on the particle size of the emulsion polymerization.

into the region of 120–300 nm, depending on the amount of dimethylaminoethanol DMEA used to neutralize the polyacrylate.

The only exception to this observation of initial particle size before the addition of monomer is when a high DMEA level is combined with the addition of salt. In such cases, measured particle sizes initially have a diameter of ± 30 nm.

Particle Size and Polydispersity

The response of the factorial experiment for the water-soluble initiator, ammonium persulfate on particle size, is given in Figure 1. Unless otherwise stated, all figures will be of experiments in which the stirring speed was held constant at 100 revolutions per minute (rpm). A "system" in the context of this study will be defined as an emulsion polymerization consisting of the ingredients in Table II and conducted with a specific type of initiator.

From the response surface graphs shown in Figure 1, it is clear that the greatest influence on particle size is represented by those graphs in which salt is an added factor. Particle size and polydispersity both influence the latex rheology and film formation of the endproduct. The greatest interaction is seen when salt is added in combination with variations in the level of DMEA.

The addition of salt causes agglomeration and eventual coagulation of the emulsion. This is most pronounced when salt is added at a low level of DMEA. Figure 2 illustrates the effect of this particular combination on the particle size.

The combination of salt and a high DMEA level affects the particle size to a lesser extent than

does the combination of salt and a low DMEA level (refer to Fig. 2).

The effect of stirring speed, added salt, and variation in the level of DMEA on the polydispersity of the emulsion can be seen in Figure 3. The prominent effect of salt is evident from these response surface graphs.

Figure 4 shows the changes in polydispersity when salt is added to a system with a low DMEA level and a system with a high level of DMEA, respectively.

The effect on particle size and polydispersity with constant stirring speed, no salt, and only the level of DMEA varied can be seen in Figure 5. Figure 6 shows the effect of this combination on polydispersity.

In both cases, it can be seen that the change in particle size (Fig. 5) and the polydispersity (Fig. 6) remain virtually constant over time.

Of great interest is the virtual doubling in particle size for the system in which a high level of DMEA is used relative to a low level of DMEA (refer to Fig. 5).

Conversion

Figure 7 shows overall fractional conversion of butyl acrylate and styrene monomers to polymer as a response to the three factors investigated.

The significant effect on conversion exhibited by the combination of DMEA and added salt, as well as the effect of DMEA and salt individually on conversion can be seen in these response surface graphs (Fig. 7). Stirring speed alone has less of an effect on conversion than in combination



Figure 6 Effect of DMEA levels and no added salt on the polydispersity during emulsion polymerization.



Figure 7 Response surface graphs of the effects of DMEA level, the addition of salt, and stirring speed on overall fractional conversion of styrene and butyl acrylate to the polymer after 6,000 s.

with DMEA and added salt. Figure 8 shows the effect that combinations of DMEA and salt have on fractional conversion.

From Figure 8, it appears that addition of salt to the system is accompanied by low conversion. This is in contrast to the high conversion found when no salt is added and the level of DMEA is low. The reason for this behavior should be sought in the particular emulsion polymerization mechanism operating under these conditions rather than concluding that the addition of salt is the reason for the observed reduction in conversion.

The combination of a high level of DMEA with the addition of salt at any stirring speed level showed a less severe change in stability (change in particle size and polydispersity over time). The stability of the emulsion containing added salt and a high level of DMEA did show a dependence on agitation to remain emulsified. As soon as agitation was stopped after polymerization, the emulsion flocculated. The floc was reemulsified when agitation was again applied later. Although the exact mechanism still needs to be investigated, flocculation in this case is probably due to a bridging mechanism between the particles, giving rise to a three-dimensional floc. When samples were taken for particle size analysis, no flocculation occurred because of a dilution effect both in particle concentration and ionic strength of the medium.

The observed difference in rate of conversion between a system containing a high level of



Figure 8 Effects of combinations of DMEA and salt levels on conversion. Stirring speed had no real effect on the fractional conversion.

	Observed Response		
Input Variables	Particle Size	Polydispersity	Conversion
A. Salt	414.54	0.07	-0.065
B. DMEA	42.85	0.029	-0.0064
C. Stirring speed	3.07	0.00039	0.0002
AB	-14.16	-0.0025	0.000066
AC	0.46	0.00017	-0.000025
BC	-0.103	-0.000014	-1.67E-6
Block	-167.8	-0.064	-0.032
Constant	-1077.72	-0.057	0.848

Table IV Estimates of Coefficients for Multiple Regression Model

DMEA with added salt (Fig. 8) and one containing no salt was not as pronounced as in the case of experiments in which low levels of DMEA were used.

The reason for these differences will be examined in terms of differences in mechanisms operating in the various emulsion polymerization systems and will be reported on in a future publication.²¹

Water-Insoluble Initiator: AIBN

The reason for choosing a water-insoluble initiator, such as AIBN, was to determine whether there are marked differences in the behavior of emulsion copolymerization in terms of conversion, particle size, and polydispersity, compared with a system in which a water-soluble initiator was used. The coefficients describing the multiple linear regression models for the various responses are given in Table IV.

Particle Size and Polydispersity

In Figures 9 and 10, the effect of stirring speed in conjunction with added salt and variation in DMEA level shows a much greater effect on particle size and polydispersity than was observed for similar responses in the water-soluble initiator system.

Figure 11 shows the effect of combinations of DMEA and salt levels on particle size for the AIBN initiated system. For the sake of comparison, stirring speed is kept constant at 100 rpm.

Figure 12 shows the effect of the combinations of DMEA and salt levels on the polydispersity for the same experiments.

It can be seen from Figure 11 that the particle size increases with time for the system in which the DMEA level is low and salt is added. The emulsion eventually coagulates after a period of 3 h. This behavior is similar to that observed for the water-soluble initiator system. It is clear from



Figure 9 Response surface graphs showing the effects of salt and DMEA levels and stirring speed on the particle size of an epoxy-acrylate emulsion after polymerization with a water-insoluble initiator system.



Figure 10 Response surface graphs of the effects of stirring speed, DMEA level and salt on the polydispersity of an epoxy-acrylate emulsion after polymerization with a water-insoluble initiator.

Figure 11 that a high level of DMEA increases the average particle size, compared with the system in which a low level of DMEA was used. It is also evident from Figure 11 that a high level of DMEA in combination with added salt does not suffer the same fate, namely coagulation, compared with the system with a low level of DMEA.

Figure 12 compares the polydispersity for the various combinations of DMEA and salt levels at a constant stirring speed of 100 rpm. Of interest herein is the observation that a high DMEA level without added salt yields the lowest polydispersity. It is also evident from Figure 12 that the polydispersity of the system with a low level of DMEA and added salt increases in time in the same way as particle size. This would suggest that the particle size and polydispersity of the system depend on the same factors for changes to be observed.

An increase in particle size is seen when the stirring speed is increased from 100 rpm to 600 rpm (see Fig. 13).



Figure 11 Effect of DMEA and salt levels on the particle size of emulsion polymerization initiated by AIBN.

Figure 13 illustrates how the absence of additional electrostatic stabilization combined with changes in the velocity gradient and radius of interaction can influence the particle size.

Conversion

Figure 14 shows the effect of the various factors on conversion as a response for the AIBN initialized system.

Compared with the previous response surface graphs in Figures 9 and 10 for particle size and polydispersity, the effect of stirring speed on conversion is much reduced.

Compared with the system in which a watersoluble initiator was used, we are now able to see more clearly how the addition of salt affects the conversion of monomer to polymer with time (Fig. 15). As in the case of reactions conducted with a water-soluble initiator, there is a major difference in the rate of conversion when the level of salt is



Figure 12 Effect of DMEA and salt levels on the polydispersity during emulsion polymerization initiated by AIBN.



Figure 13 Effect of stirring speed on particle size for systems in which the DMEA level was varied.

varied from low to high for a system with a low level of DMEA. The same change in the rate of reaction is also observed for the system in which a high level of DMEA was used with variation in the level of salt. A reduction in the rate of reaction is observed (refer to Fig. 15). However, this reduction in reaction rate is much less, compared to the case in which a low level of DMEA is used.

DISCUSSION

To summarize the results of the various experiments conducted with the different initiators, the effects of the various factors on the measured responses are given in terms of tables of F-ratios for the different initiators. This statistic is obtained by dividing the sample variance by the pooled variance obtained for all responses. As long as the observations are normally distributed, the F-ratio provides a test to decide whether the variance due to an observed response is significant or not. If the F-ratio is equal or smaller than 1, the variance due to the observed response is not significant and the observation is probably due to random variation. If the observed F-ratio is larger than 1, the observed response is probably significant.

It is well known that tertiary amines act as radical scavengers.^{22,23} The ability of these amines to react with radical sources present during polymer degradation make them excellent



Figure 14 Response surface graphs of the effects of stirring speed, DMEA level, and the addition of salt on the conversion as a response for the water-insoluble initiator system.



Figure 15 Effects of DMEA and salt levels on the conversion profile during emulsion polymerization initiated by AIBN.

stabilizers. However, in the context of epoxy-acrylates, tertiary amines are used as catalysts for the reaction of the epoxy groups and carboxylic acid groups during heat curing.¹³ They also decrease the problem of odor associated with ammonia and other primary amines and yield a clear film upon heat curing. They may also aid in the eventual application viscosity of the emulsion and play a part in the film formation process.

The use of a tertiary amine as a neutralizing agent for the carboxylic acid groups in the epoxyacrylate system under investigation has caused significant changes in the conversion profiles obtained. This may be because of chain transfer reactions occurring between monomeric free radicals and tertiary amines in the water phase and between growing polymer segments and tertiary amines in the particles.

To clarify this observation, additional emulsion polymerizations were conducted in which the tertiary amine was substituted with ammonium hydroxide. The pH of the system neutralized by the ammonium hydroxide was adjusted to reflect that of a system with a low DMEA level (10 g) and that of a high level of DMEA (40 g). The starting pH for the lower level DMEA was 9.1. For the higher DMEA level, the starting pH was 11.

For the system in which the DMEA level was adjusted, as in the previous experiments, without added salt, particle size increased as before and the same influence on conversion was observed as in previous experiments. The results of these experiments, in terms of average figures of particle size and polydispersity are given in Table V. Conversion is taken after 6,000 s, one-third of the total time of polymerization.

It is evident from the results shown in Tables V and VI that it is not the pH as such that affects

Table V Summary of Averaged Results Obtained for Additional Epoxy-Acrylate Emulsion Polymerizations Using Low (10 g) and High (40 g) Levels of DMEA with No Added Salt and Stirring Speed Held Constant at 350 rpm

Factors	Low DMEA Concentration	High DMEA Concentration
Particle size (nm)	144.67	248.055
Polydispersity	0.453	0.278
Conversion	0.76	0.36

Ammonium persulfate was used as initiator.

the reaction kinetics, but rather the type of amine used in neutralizing the polyelectrolyte. Of considerable interest is the effect that a high DMEA level (as in Table V) has on the particle size, compared with the use of ammonium hydroxide as a neutralizing amine (as in Table VI). It would seem that the type of counterion used in the neutralization of the polyacrylate influences the particle size significantly.

From the results on particle sizes (Table V) and the stability of latexes with high DMEA and salt levels compared with those with low DMEA and salt levels, it may be that the overriding mechanism of stabilization for such systems is steric stabilization.

The effect of salt on the outcome of the factorial experiments seems to be especially important for the experiments in which combinations of low DMEA levels were used with added salt. The effect was less clear with combinations of higher DMEA levels and added salt. The decrease in polymerization rate observed with low DMEA levels and added salt seems to be linked to the fact

Table VI Summary of Results Obtained for an Epoxy-Acrylate Emulsion Polymerization in Which pH Was Adjusted to Correspond to the pH of a Low Level of DMEA and a High Level of DMEA, Respectively, While Containing No Added Salt and Keeping the Stirring Speed Constant at 350 rpm

Factors	Low pH System	Higher pH System
Particle size (nm)	143.0	171.52
Polydispersity	0.319	0.279
Conversion	0.96	0.94

Ammonium persulfate was used as initiator.

Factor	Particle Size	Polydispersity	Conversion
A. Stirring speed	0.00	0.87	4.2
B. [DMEA]	2.9	7.3	34
C. [Salt]	36	2.1	100
AB	0.69	1.5	0.13
AC + block	0.03	2.2	1.6
BC + block	27	0.43	38
Block	2.5	0.37	0.34

Table VII F-Ratios for Individual Factors and Their Interactions Up to First Order

 for the System Initiated by the Water-Soluble Initiator, Ammonium Persulfate

that significant coagulation occurred over time during polymerizations conducted under these combinations. This is seen in terms of observed changes in the size of particles with time.

Reduction of the number of loci available for polymerization should significantly affect the kinetics of emulsion polymerization. Nomura²⁴ discussed the effect of particle size on the exit of radicals from particles, as well as the contribution of termination to the overall kinetics of the polymerization. Similar studies by Casey and colleagues,²⁵ Asua and colleagues^{26,27} and Nomura²⁸ corroborate the idea that changes in the size and number of particles affect the mechanism of emulsion polymerization in terms of exit and termination of radicals, and are therefore the main reasons for the observed decrease in conversion rate observed with variation in DMEA and salt levels.

From Tables VII and VIII, it is evident that certain factors are more pronounced when they are compared for the two initiator types. The greater effect of stirring speed on the particle size and polydispersity for the AIBN-initiated system probably stems from the absence of additional stabilization imparted by the ionic end groups of the ammonium persulfate-initiated system as previously discussed. In the case of the AIBN- initiated system, this additional electrostatic stability is not present, and therefore we see the greater effect of stirring speed on particle size and polydispersity (Table VIII).

The effect of DMEA as an individual factor on conversion can be seen in the magnitude of the F-ratios for conversion in Tables VII and VIII. DMEA may also affect the mechanism of emulsion polymerization by acting as chain transfer agent.

CONCLUSIONS

Based on the results of replicated factorial designed experiments conducted with a water-soluble initiator and a water-insoluble initiator, it can be concluded that the type and concentration of neutralizing amine influences the rate of monomer conversion probably through chain transfer, as well as the particle size. The combination of salt and a low level of tertiary amine as neutralizing agent for the polyacrylate used to emulsify the epoxy resin results in low conversion through coagulation of the emulsion that effectively reduces the number of loci for polymerization.

Table VIII F-Ratios for Individual Factors and Their Interactions Up to FirstOrder for the System Initiated by the Water-Insoluble Initiator, AIBN

	Factor	Particle Size	Polydispersity	Conversion
A.	Stirring speed	1.6	6.7	1.2
В.	DMEA	3.8	7.8	28
С.	Salt	6.1	14	88
AB		5.5	4.4	2.6
AC		0.8	2.7	0.5
BC		1.5	0.7	0.08
Blo	ck	0.6	2.1	4.5

Combinations of high DMEA levels and added salt show less pronounced effects on particle size, polydispersity, and conversion, compared with systems with a low level of DMEA. When comparing the effect of neutralizing amine type on particle size and conversion, it is seen that the type of amine plays a significant role. This observation is illustrated by the fact that a primary amine, such as ammonium hydroxide, does not affect the rate of the reactions at pH values adjusted to correspond to those of the tertiary amine, dimethylathanolamine, used in the factorial designs.

Although slight differences in the responses are seen between the water-soluble initiator, ammonium persulfate, and the water-insoluble initiator, AIBN, the basic trends in particle size development, polydispersity, and conversion profiles are similar for both systems.

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