Emulsion Polymerization of an Epoxy–Acrylate Emulsion Stabilized with Polyacrylate. II. Using the Results of Statistically Designed Experiments to Deduce a Possible Polymerization Mechanism

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ABSTRACT: Epoxy–acrylate composite emulsions such as the one in this study can be used as metal coatings, etc. Many factors can influence the final quality of the product, and it is the aim of this study to highlight some of these factors. Statistically designed experiments were performed to investigate the influence of monomer level, the polymeric dispersant level, epoxy level, and the initiator level on particle size (light scattering), particle size distribution, and fractional conversion. It was found that the monomer level significantly influenced particle size and particle size distribution. The epoxy level and the monomer level influenced fractional conversion significantly. A qualitative model based on these observations is put forward to describe the mechanism of particle formation and polymerization. This model states that the high internal viscosity of the initial dispersed epoxy phase inhibits the formation of smaller particles and accelerates the polymerization rate during the first few minutes of polymerization by inducing a gel effect that inhibits termination and chain transfers of radical species. The addition of a monomer lowers the internal viscosity of the particles and causes them to break up into droplets containing dissolved epoxy, polyacrylate, and monomer. At the same time, radical species inside the smaller droplets can now undergo termination and chain transfer reactions. To confirm this model, polyacrylates of varying molecular masses were synthesized. Variation of the molecular masses of these polyacrylates resulted in variation in the viscosity of the dispersed phase. Polymerizations conducted with the polyacrylates confirmed the model observations. A dispersed phase with a high viscosity results in an increased polymerization rate, larger overall particle size, and a higher mass average molecular mass copolymer compared to lower molecular mass polyacrylates. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 368–381, 2000

Key words: epoxy–acrylate; composite emulsion; factorial design; particle size; conversion; model; polyacrylate

INTRODUCTION

Recently we have reported on a number of factors that influence the stability of an epoxy-acrylate emulsion.[1] This article is a continuation of that work, and will consider the effects of monomer, epoxy, and polyacrylate levels on particle size, polydispersity, and conversion of an epoxy–acrylate emulsion. To study the first-order interactions of the listed factors, all experiments were designed as replicated factorial designs.

BACKGROUND

To understand some of the results of this study, it is prudent to list those factors that influence or can influence particle size, particle size distribution, and conversion.

Factors That Influence Particle Size and Particle Size Distribution

Wu[2] developed an equation that accounts for most of the variables that can influence particle size and particle size distribution.

$$d = \frac{\sigma_i}{\dot{\gamma}\eta_{\text{cont}}} f\left(\frac{\eta_{\text{disp}}}{\eta_{\text{cont}}}\right) \qquad (1)$$

It is clear from this equation that those factors that can lower the viscosity of the dispersed phase can also serve to reduce the ultimate particle size that can be achieved. In the present study this is achieved by addition of monomer to the oil-in-water emulsion containing the dispersed epoxy phase and the polymeric dispersant.[1] A smaller particle size reduces the Gibbs free energy of the system and contributes to the ability of the epoxy–acrylate to remain emulsified.

Factors That Can Influence Conversion

Changes in particle size and particle size distribution should also affect conversion. Apart from changes in the number of particles available for polymerization, radical entry and exit rates into and out of particles will also be influenced. The rates of entry, exit, and emulsion polymerization are given in eqs. (2) and (3).[3]

Rate of entry of radical species into particles

$$\eta_{\text{initiator}}\,(100\%) = \frac{2k_d[I]N_A}{N_c} \qquad (2)$$

The rate of emulsion polymerization.

$$R_p = k_p\frac{N_c}{N_A}\bar{n}C_p \qquad (3)$$

The rate of radical exit.

$$k(\text{exit}) = \frac{3D_w}{r_s^2}\frac{k_{tr}}{k_p}\frac{C_w}{C_p} \qquad (4)$$

The concentration of particles in the latex (N_c) features in both the equations determining the entry rate of radicals as well as the rate of emulsion polymerization. Consequently, those factors that influence particle size will also influence the concentration of particles in this study.[1] Equation 4 shows the relationship between the exit rate and the radius of the particle. It is, therefore, clear that particle size will significantly influence the rate of exit of radicals out of the particles.

Effect of Electrosteric Stabilization on the Kinetics of Polymerization

Recently, Gilbert et al.[4] noted that latices stabilized by an *in situ* polymerized poly-acid stabilizer poses an additional barrier to the entry and exit of radical species. Electrosteric stabilization is imparted to the latices through the neutralization of the carboxylic acid groups, and steric stabilization is the result of the extension into the water medium of the neutralized carboxylic acid polymeric chains.

Water-soluble initiators such as ammonium persulphate produce negatively charged radical species on decomposition that have to traverse not only the electrosteric barrier but also the steric barrier created by the poly-acid. In this study, the effect of the polymeric dispersant that contains neutralized carboxylic acid groups, which in all probability also extends into the water medium as chains and/or trains, will most likely also influence the rate of emulsion polymerization. This influence may also derive from the ability of the polymeric dispersant to hinder entry and exit of radical species.

Effect of Interfacial Viscosity on the Kinetics of Polymerization

Miller et al.[5–7] have highlighted the effect of interfacial viscosity on the rate of miniemulsion polymerization. By dissolving a small quantity of polystyrene in styrene monomer prior to polymerization, an increase in the rate of miniemulsion polymerization was observed. The addition of polystyrene to the monomer resulted in an increase in the interfacial and internal viscosity of the dispersed monomer droplets. A higher internal particle viscosity may reduce the rate of diffusion of oligomeric radical species inside the particles.[3] Because of this, the exit rate of radicals may be reduced and the rate of propagation increased. However, these observations were made

Table I Recipe for Polyacrylate of Variable Molecular Mass

Solvent (butoxy ethanol)	438 g
Methacrylic acid	187 g
Styrene	95 g
Methyl acrylate	32 g
Benzoyl peroxide	Variable

with regard to miniemulsion droplets with added polymer, which ranged in diameter from 67 to 171 nm, and consequently, would contain only one propagating radical per particle.[5–7] In the present study, particle diameters at the beginning of the polymerization process were in the region of 1 μm or greater. Only when monomer is added to the system does the particle size change to well below 1 μm. The effect of this is that many radicals per particle may be present at the beginning of polymerization. In effect, the mechanism of polymerization in the initial stage of polymerization for the present study may be related more to dispersion polymerization. Each droplet may act as a small bulk polymerization reactor in which the effect of the polyacrylate as well as the dissolved epoxy phase on the internal viscosity may lead to an increase with regard to propagation at the expense of termination, thus resulting in an induced gel effect.

Effect of Polyacrylate Molecular Mass on Conversion and Particle Size

The effect that the polyacrylate has on the properties of epoxy–acrylic composite latex has not received much attention in the literature. An exception to this is the work by Kojima et al.[8] on the development of can coatings. In their publication, an acrylic polymer is used that is composed of methacrylic acid, methyl acrylate, ethyl acrylate, and styrene in the ratio of 40/20/20/20. The effect of the amount of acrylic polymer on particle size as well as the effect of varying the acrylic polymer composition has on particle size was studied. It was found that lower amounts of acrylic resin produced larger particles, and changing the composition to incorporate more styrene and acrylic monomers relative to the amount of methacrylic acid also produced larger particles. This was attributed to a reduction in the ability of the acrylic polymer to stabilize the latex particle effectively because of a reduction of the carboxylic acid functionality that provides electrostatic stabilization.

In work by Woo and Eley[9] the particle size of an epoxy–acrylate graft copolymer was inversely related to the amount of initiator used. They interpreted these results by ascribing the smaller particle size of the latices made with larger amount of initiator to more grafts and shorter grafted side chains. Shorter grafted side chains have a folded conformation that reduces the internal viscosity of the particle, thus enabling the achievement of smaller particle sizes. Longer side chains can aggregate, leading to higher internal viscosity and larger ultimate particle size. However, no study to date has investigated the effect of the polyacrylic stabiliser on particle size development and conversion of monomer to polymer.

EXPERIMENTAL

Synthesis of Polyacrylate of Varying Molecular Mass

To the study of the effect of the polyacrylate molecular mass on conversion and particle size, polyacrylates of varying molecular mass were synthesized based on styrene, methacrylic acid, and methyl acrylate. The mass percentage composition of the polymer consisted of 60% methacrylic acid and 20% each of styrene and methyl acrylate. The recipe for the polyacrylate is given in Table I.

The amount of peroxide initiator was varied from 2 g for the highest molecular mass polyacrylate to 9.77 g for the intermediate molecular mass and 19 g for the lowest molecular mass polymer. The molecular masses of these polymers were determined using GPC, and they are reported relative to styrene standards in Table II.

The procedure of making these polyacrylates consisted of feeding a mixture of the monomers over a period of 3 h to a reactor equipped with a dropping funnel, thermal probe, heating jacket, reflux condensor, stirrer, and an inlet for nitrogen gas. The solvent was added to the reactor at the start before heating the reactor to 130°C. After having reached the temperature of 130°C the

Table II Molecular Masses of Polyacrylates

Identification Code	M_n	M_w
PA4	9967	25193
PA3	1849	4026
PA1	3264	7293

Table III Upper and Lower Levels of Factors for Factorial Designed Experiments

Factor	Lower Level	Upper Level
Monomer level	5 g	40 g
Polyacrylate level	70 g	90 g
Initiator level	0.25 g	1 g
Epoxy level	10 g	40 g

monomer feed was started. The initiator, benzoyl peroxide, was dissolved in the monomer mixture prior to the reaction.

After addition of all the monomers, the reaction was continued for a further 30 min before the mixture was allowed to cool. Depending on the amount of initiator used, a clear straw-colored viscous solution was obtained. The solids content of these solutions were determined with a Mettler moisture analyzer housed near an extractor hood. The solids content varied from 60 mass % for PA4, 52.26 mass % for PA1, to 46.22 mass % for PA3. The sample handling procedure as well as the actual emulsion polymerization has been described previously.[1]

Determination of Water-in-Oil Latex Viscosities

To study the effect of increased polyacrylate molecular mass on the viscosity of the dispersed epoxy phase, an experiment was designed to highlight and compare the differences in viscosities. In these experiments, a water-in-oil emulsion was prepared by adding to 35 g of the polyacrylate 10 g epoxy solution (73 mass % solids), 5 g dimethyl aminoethanol, and 5 g water. The resultant clear emulsions were analyzed using a Brookfield LV viscometer. The spindle used was a No. 4 spindle and the instrument was operated at 12 min^{-1} for PA1, 30 min^{-1} for PA3 and 6 min^{-1} for PA4. The readings were converted to mPa · s using the converter chart accompanying the instrument.

Determination of Molecular Mass

To get an idea of the effect of the polyacrylate molecular mass on the styrene/butyl acrylate copolymer molecular mass, samples taken during polymerization (4-mL vials) were dried for 2 days at 80°C in a vacuum oven. After drying, 2 mL THF was added to each sample, and all samples were left for 2 days with intermittent stirring to dissolve any polymer. After 2 days, samples were filtered and analyzed on a GPC equipped with four columns fitted together in series. The pore sizes of the individual columns were 10^5, 10^4, 10^3, and 10^2 Å. Eight polystyrene standards were used to calibrate the GPC. These standards had number average molecular masses of 1.54 million; 892,000; 392,000; 200,000; 41,000; 31,010; 16,700; and 3978.

Experimental Design

In this study experiments were designed as two-level factorial designs with center points. The number of factors studied are listed in Table I. The factorial experiments consisted of a fractionally 2^{4-1} replicated design as well as 2^4 designs. The reason for the replicated design was to gain information about the reproducibility and variance of the experiments.

In the following treatment, references to low- and high-factor levels will refer to the levels listed in Table III. The multiple linear regression models on which the response surface graphs are based have the following general formula for a design in b replicated blocks:

$$Y_u = \beta_0 + \sum_{i=1}^{k} \beta_i x_{ui} + \sum_{i=1}^{k} \beta_{ii} x_i^2$$

$$+ \sum_{i<j}^{k} \beta_{ij} x_{ui} x_{uj} + \sum_{l=1}^{b} \delta_l z_{ul} + \varepsilon \quad (5)$$

Table IV contains the ingredients for a typical polymerization run. As was discussed previously,[1] the emulsification of the epoxy phase by

Table IV Standard Recipe Used for Epoxy-Acrylate Emulsion Polymerisation

Ingredients	Quantities
Polymeric dispersant batch number	Apr1
Polymeric dispersant level	Variable
Styrene level	Variable
Butyl acrylate level	Variable
Epoxy level	Variable
Initiator level	Variable
Dimethyl aminoethanol amount	25 g
Distilled de-ionized water	450 g
Temperature	70° Celsius
Stirspeed	250 min^{-1}

means of the polymeric dispersant or polyacrylate occurs through an inversion process.

At first, a small amount of water and the neutralizing amine is added to a mixture of the polyacrylate and the epoxy. Once a clear water-in-oil emulsion is formed, this emulsion is inverted to yield an oil-in-water emulsion through the addition of the remainder of the water to the total amount in Table III.

The polymeric dispersant solution used in this study had a solids content of 65%. The epoxy used was Shell's EPIKOTE 3001. The solid epoxy was dissolved in butoxyethanol to yield a solution with a total solids content of 73%. Monomer purification was discussed previously.[1]

RESULTS AND DISCUSSION

Particle Size as a Response

The particle size was measured by means of a Malvern Zetasizer operated in the "multiangle" mode. This means that the dispersed light was detected at more than one angle. Consequently, the occurrence of secondary nucleation could be observed. The response surfaces for particle size are given in Figure 1(a)–(f). Table VI presents the coefficients used in the multiple linear regression fits of the data.

It is immediately evident from the F-ratios in Table V that the factor that exercises the greatest amount of control over particle size is the level of monomer. This observation has been explained[1] as the drive of the system to decrease the unfavorable interfacial tension between the hydrophobic monomer–solvent–epoxy mixture and the water phase to lower the Gibbs free-energy of the system. Figure 1(a)–(f) provides the response surface graphs for particle size as a response. Figure 1(a) shows that particle size increases with increased amount of polyacrylate and decreasing level of epoxy. A decrease in the level of epoxy results in a decrease in the amount of dispersed polymer phase. Consequently, the total surface area for stabilization decreases. The larger particle size may be a result of greater association between hydrophobic polyacrylate chain segments that may result in bridging between small particles to form larger particles or agglomerates of smaller particles.

Figure 1(b), (d), and (f) illustrates the influence of the level of monomer on the particle size. As the level of monomer increases, the particle size

drops. Of interest is the effect of the initiator level illustrated in Figure 1(c) and (e). As the polyacrylate level increases along with the initiator level, the particle size drops. This may be because of the additional electrostatic stabilization imparted by the persulfate end groups brought about by the decomposition of the initiator.[1] This effect is highlighted in Figure 1(e).

Polydispersity as a Response

The distribution of the particle size relative to the mean z-average particle size was also measured as a response. The Malvern Zetasizer uses the Mie-theory in combination with dynamic light scattering to estimate the particle size and particle size distribution. This instrument fits a correlation function to the measured light intensity signals.

$$g_i(\tau) = \sum_{i=1}^{n} c_i \exp(-T_i \tau) \qquad (6)$$

Equation (6) can be rewritten as a logarithm, and when it is plotted against time it usually shows an exponential decrease for the logarithmic correlation function. By fitting a fifth-order power series to the exponential decay of the correlator signal, the polydispersity index, which is an indication of the variance of the distribution, can be obtained.

$$\log(g_i) = a + b\tau + c\tau^2 + d\tau^3 + e\tau^4 + f\tau^5 \quad (7)$$

$$\text{Polydispersity index} = 2c/b^2 \approx \sigma^2 \qquad (8)$$

This index indicates the spread in particle size relative to the z-average mean particle size. A value of 1 indicates that the particle size distribution is widely distributed around the average particle size with a standard deviation as large as the average particle size or even larger. A value for the polydispersity index close to zero indicates that the particle size distribution has a small standard deviation compared to the average particle size. For example, if a latex sample has an average particle size of 98 nm and a polydispersity of 0.126, the standard deviation amounts to roughly 34 nm for that sample.

In Table V, the factor that stands out in relative magnitude of importance is the level of the monomer. As in the case of the particle size as a
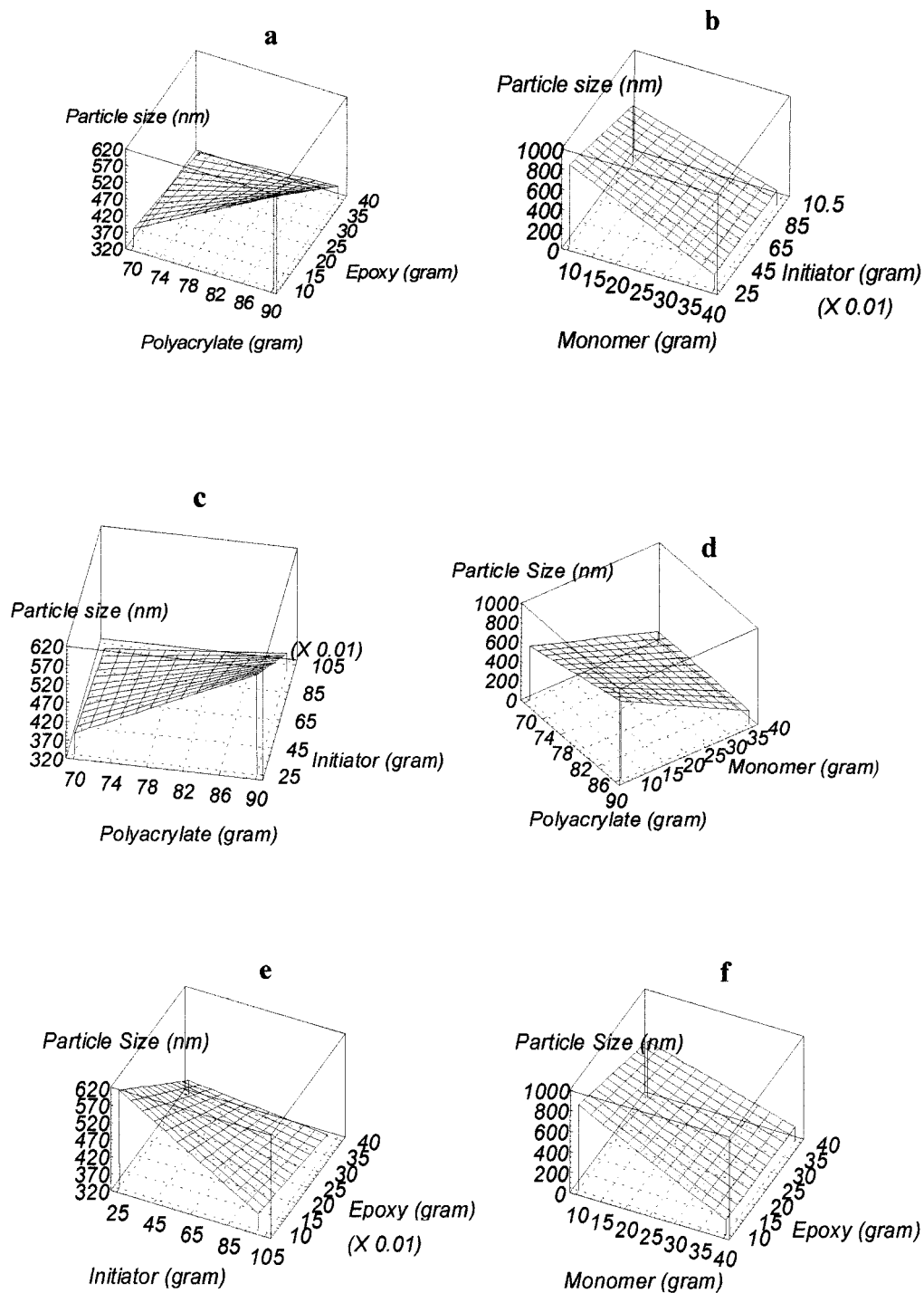
Figure 1 Estimated response surfaces for particle size.

response, it is obvious from the response surface graphs in Figure 2(b), (e), and (f) that the level of the monomer exercises the greatest effect on particle size distribution (PD). In Figure 2(d) it is shown that the PD increases as the amount of

polyacrylate increases and the amount of initiator decreases. The additional stability imparted by the persulfate end groups may contribute to a narrower particle size distribution by increasing the electrostatic repulsion be-

Table V *F*-Ratios of Main Factors and Their First-Order Interactions

Factor	Particle Size (PS)	Particle Size Distribution (PD)	Fractional Conversion
A: Polyacrylate level	1.56	0.14	7.68
B: Monomer level	29.78	24.21	41.18
C: Initiator level	1.88	0.04	0.71
D: Epoxy level	2.01	0.96	63.74
AB	1.54	0.49	0.02
AC	0.7	0.09	0.93
AD	0.94	0.15	0.27
BC	1.51	0.14	0.28
BD	1.98	2.85	2.99
CD	1.00	0.19	1.25

tween particles and thereby reducing coalescence, which contributes to a greater variation in particle sizes.

Conversion as a Response

The third response measured in this the study was the conversion after 6000 s. The reason for this choice to report conversion is because the differences between individual experiments are more clearly defined. When one looks at Table V it is immediately clear that the level of monomer, the levels of epoxy and polyacrylate, as well as the interaction between monomer and initiator and monomer and epoxy is of significance. The level of monomer and epoxy affect the total number of loci available for polymerization through eq. (3). What is not immediately clear is how the amount of epoxy can influence the conversion. We can see in Figures 3(a), (b), and (c) that the conversion increases as the amount of epoxy decreases. Figure 3(b) shows that conversion increases as the level of monomer and epoxy decreases. This effect may be related to the increased interfacial viscosity and its effect on the rate of the reaction as observed by Miller et al.[7]

At low monomer and high epoxy levels, the internal viscosity of the droplets is much higher than at high levels of epoxy and monomer. This results in an induced Tromsdorff effect. As in the case of miniemulsion droplets with added polystyrene, the added epoxy and polyacrylate in this case increases the droplet internal viscosity, thereby increasing the radical capture efficiency as well as localizing the captured radical in the initial stages of polymerization. This should result in a reduction in the termination rate as well

as a decrease in the exit rate and an overall increase in polymerization rate.

In many of the experiments conducted in this study the conversion profiles showed a large increase in the polymerization rate initially (within the first 5 min), followed by a sudden decrease in the reaction rate. Figure 4 illustrates this observation.

Consequently, the following qualitative mechanism is proposed to explain this. Just before the monomer is added, the particle sizes in most cases are in the region of 1 μm (see Fig. 5). Particle size measurements with the Malvern Zetasizer just before the addition of monomer and initiator confirmed this. As soon as monomer and initiator are added, the particle size drops, depending on the amount of monomer added. At the start of the reaction the internal viscosity of the dispersed epoxy phase is still high. As monomer and initiator are added, oligomeric radicals are captured very effectively through the previously discussed mechanism. This results in a large increase in the initial polymerization rate. To illustrate the change in viscosity of the epoxy phase when water is added, consider Figure 6.

Figure 6 illustrates the viscous behavior of the epoxy solution as water is added. Initially, there is little change in the viscosity, but as more water is added, the viscosity in the low-shear region starts to increase. This means that a large amount of water relative to a small amount of dispersed epoxy will result in a significant increase in the viscosity of the epoxy phase as the butoxyethanol partitions between the epoxy and water phase, respectively. This partitioning of the solvent will lead to the observed gel effect by
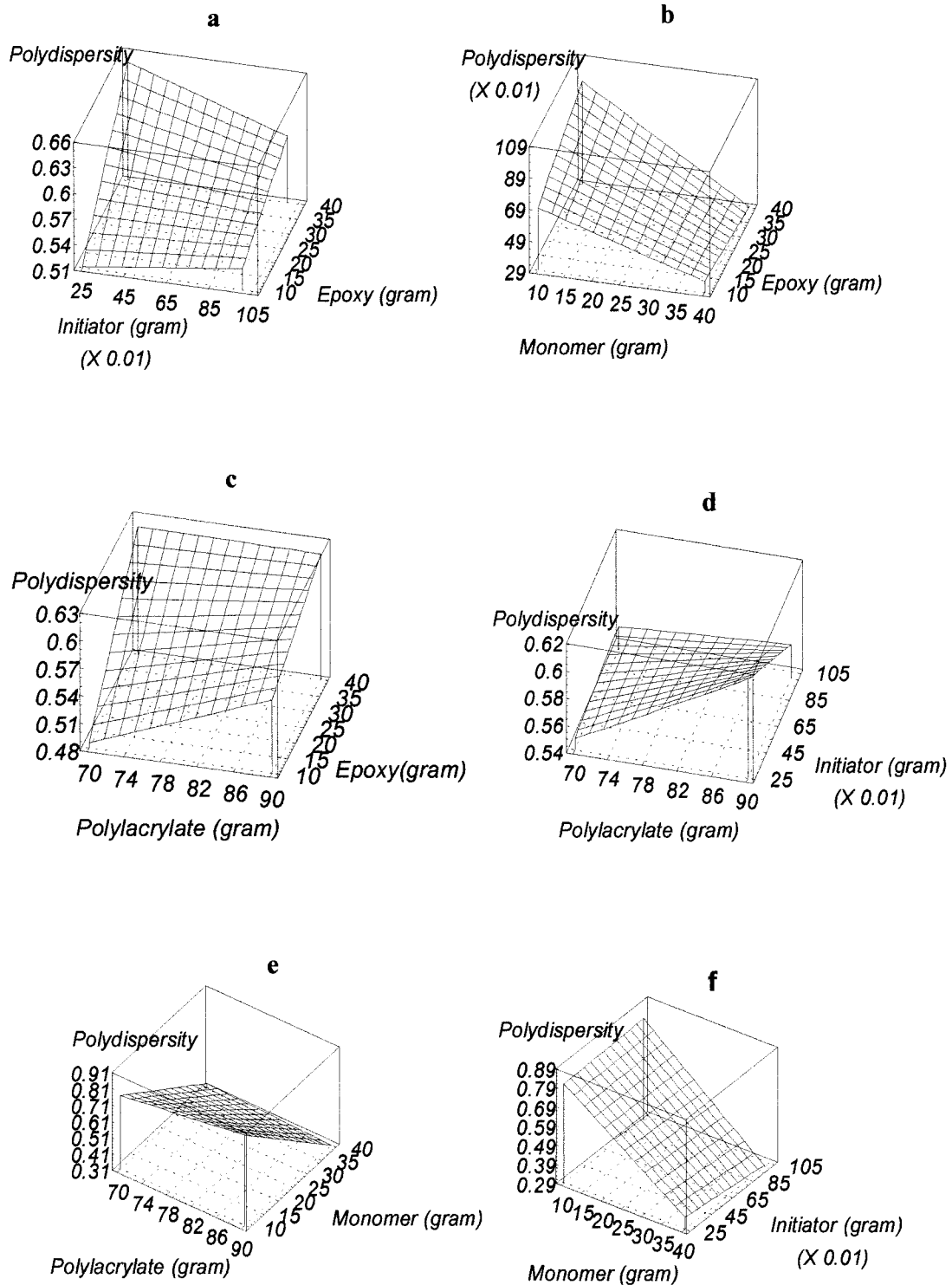
Figure 2 Estimated response surfaces for polydispersity.

reducing the internal viscosity of the particle. This is also the reason why the particle size is large compared to the smaller particle size later when the monomer is added.

When the monomer is added, it is captured by the dispersed epoxy particles through mixing (physical interaction with droplets) and by diffusion to form droplets containing a mixture of monomer and
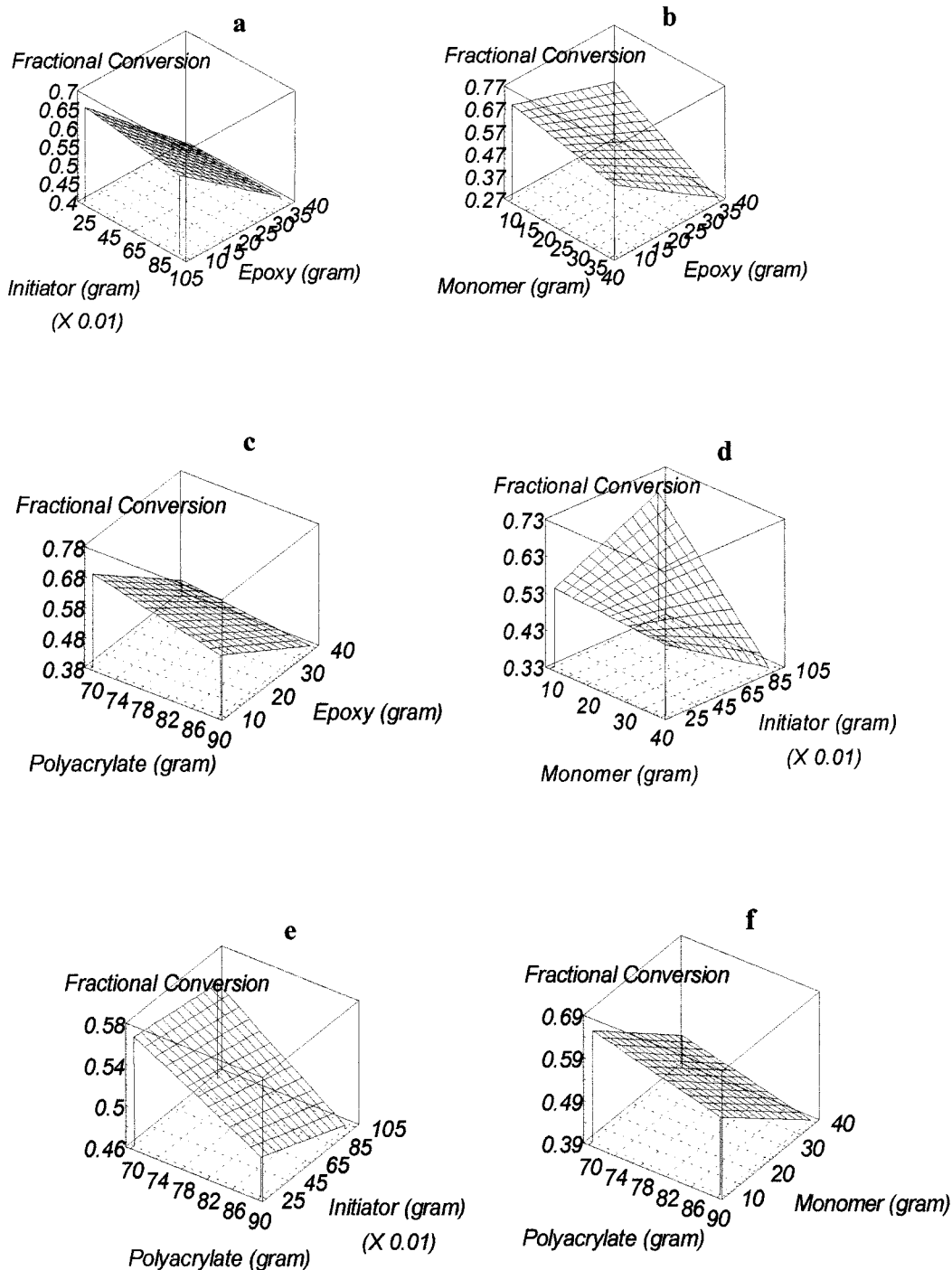
Figure 3 Estimated response surfaces for fractional conversion measured after 6000 s.

dissolved epoxy. During this time the internal viscosity of the particles is lowered and the droplets break up into smaller particles because of the drive towards lower free energy (see Fig. 7). Now the polymerization mechanism changes, the captured radicals should now be able to exit and enter the particles, as in a conventional emulsion polymerization. However, the effect of the polyacrylate in creating a barrier to the entry of oligomeric radicals may become an impediment to polymerization.
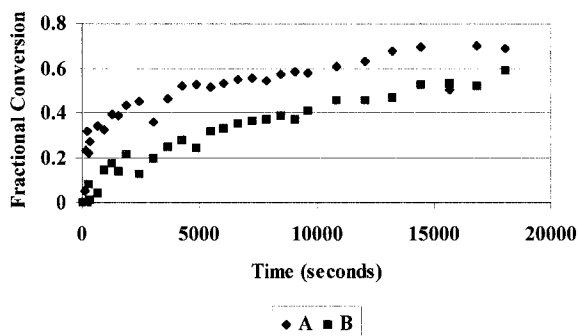
Figure 4 The levels of polyacrylate and initiator were high in both experiments. However, experiment A had a low level of monomer and a high level of epoxy. Experiment B had a high level of monomer and a high level of epoxy. Note the increase in the conversion of A relative to B at the beginning of the experiments.

Figure 6 shows the effect of added polyacrylate and epoxy to the experiments in which the initiator concentration was kept at the minimum level and the monomer level was high. In conventional emulsion polymerization, an increase in the level of surfactant increases the number of loci for polymerization because more micelles are generated to act as loci for polymerization. The same observation is made in the case of the epoxy–acrylate system. The difference is that an increase in surfactant concentration generally leads to an increase in the rate of reaction in conventional emulsion polymerization, while the opposite effect is observed in the epoxy–acrylate emulsion.
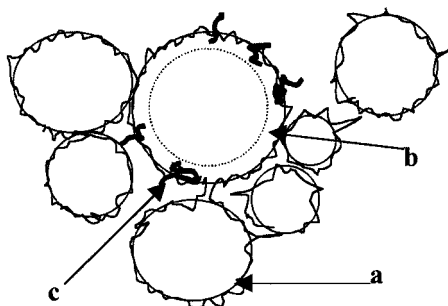

Figure 5 The system as it appears a few seconds after the addition of a monomer and an initiator. The particle size is still relatively large, as the mass transfer is still taking place. (a) Denotes a particle surrounded by polyacrylate as a stabilizer. (b) Showing interfacial zone of the highest viscosity. (c) Oligomeric/polymeric radicals trapped at interface, unable to move because of high interfacial viscosity, gives rise to a gel effect.
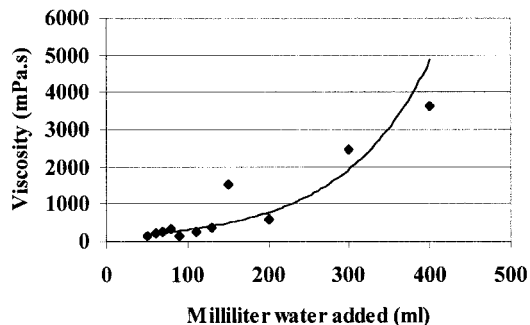

Figure 6 Change in the low-shear rheology profile of an epoxy solution with addition of water.

The observed decrease in the rate of polymerization in the present study can possibly be ascribed to the barrier presented to the entry of oligomeric radicals by the additional polyacrylate and epoxy at the interface of the particle and the aqueous phase. This barrier may consist of two parts. In the first instance, the higher viscosity at the particle interface results in the slow diffusion of oligomeric radicals into the particle. Second, the polyacrylate may also present a steric barrier because of an increase in the number of loops of the water-soluble portions of the molecule in the aqueous phase. This may cause a decrease in the number of oligomeric radicals actually entering the particle.

Figure 7 illustrates the same tendencies observed in Figure 6, even at higher initiator levels. Schematically the qualitative mechanism may be represented as follows.

The Effect of Polyacrylate Molecular Mass on Particle Size

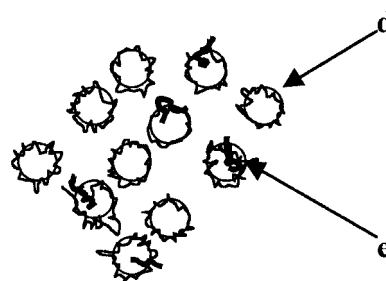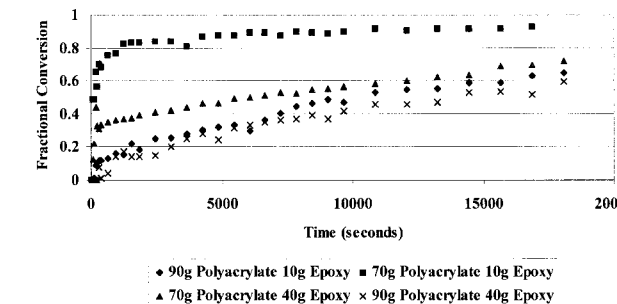To verify the quantitative model of the preceding section, it was felt that further confirmation of the

Figure 7 Some minutes after the addition of the monomer and the initiator. The particles (d) are now droplets of dissolved epoxy and monomer. Most particles contain only one oligomeric/polymeric radical (e).
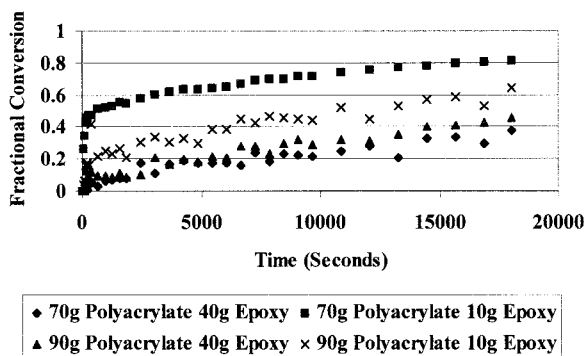
Figure 8   Effect of increasing the levels of polyacrylate and epoxy on fractional conversion. Increasing the polyacrylate level.

model was necessary. To this end three polyacrylate polymers were synthesized with different molecular masses. The idea behind this is to show how an increase in the internal viscosity of the dispersed phase affects the particle size and conversion (see Table VII for details of polymerization conditions).

In this aspect of the study it can be seen from Figure 10 that the particle size of the higher molecular mass polyacrylate remains high compared to the low and intermediate molecular mass polyacrylates throughout the duration of the reaction. The correlation between particle size and internal viscosity of the dispersed phase holds in each case with regard to the polyacrylates used in this study. Interestingly, the particle size of the lower molecular mass polyacrylate

Figure 9   Effect of increasing the levels of polyacrylate and epoxy on fractional conversion. Increasing the epoxy level.
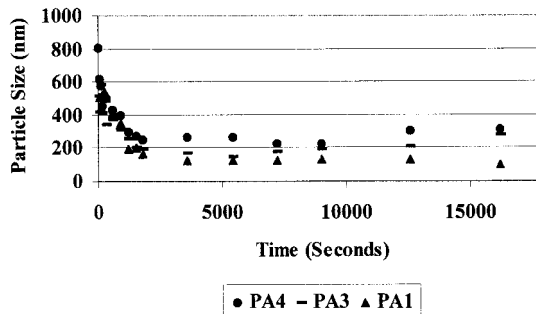

Figure 10   Effect of polyacrylate molecular mass on particle size.

starts to increase near the end of the reaction. A similar trend is observed for the high molecular mass polyacrylate.

The Effect of Polyacrylate Molecular Mass on Conversion

In Figure 11 the rate of polymerization increases significantly early in the reaction in the case of the high molecular mass polyacrylate. This is especially evident in the initial phase of polymerization. As the molecular mass of the polyacrylate drops, the initial rate of reaction also drops, as does the overall conversion. It is also evident from Figure 11 that the lowest molecular mass polyacrylate PA3, shows a slightly higher overall conversion even though the initial rate of reaction is slower compared to the intermediate molecular mass polyacrylate, PA1.

The reason for the observed conversion profiles can be directly related to the viscosities of the dispersed epoxy/acrylate phase. Table VIII gives the viscosities of the water-in-oil phases of the epoxy–acrylates.
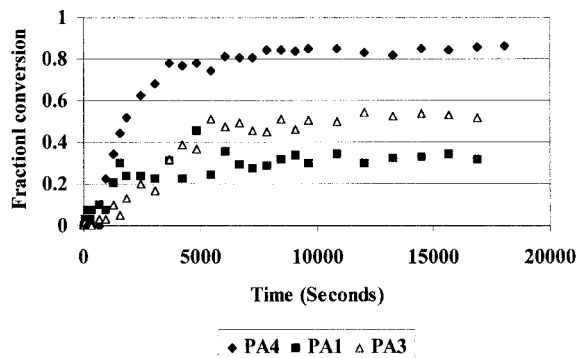

Figure 11   The effect of polyacrylate molecular mass on conversion.

Table VI   Coefficients for Multiple Linear Regression Models

Factors	Particle Size	Particle Size Distribution	Fractional Conversion
A: Polyacrylate	31.91	0.013	−0.0054
B: Monomer	0.26	0.013	0.0065
C: Initiator	214.58	0.45	0.40
D: Epoxy	7.83	0.024	−0.011
AB	−0.42	−0.00023	8.6E-6
AC	−11.25	−0.0038	−0.0014
AD	−0.33	−0.00013	8.7E-5
BC	11.02	−0.0032	−0.014
BD	0.32	−0.00037	−1.7E-4
CD	8.98	−0.0037	0.0017
Constant	−934.56	−0.46	1
R^2	0.90	0.86	0.97

It is clear that a correlation exists between the rate of polymerization given in Figure 11 and the viscosity of the dispersed phase. Higher internal viscosity of the dispersed phase induces a gel effect that remains operative in the case of the high molecular mass polyacrylate. In the case of the lower molecular mass polyacrylates, the reduced rate of reaction can probably be ascribed to the increased barrier to entry presented by the polyacrylate to oligomeric water-borne radicals and the comparatively lower internal viscosity of the dispersed phase. This is highlighted by the reduction in the initial rate of reaction.

Even though the conversion profile of the intermediate molecular mass polyacrylate shows an initial high rate of reaction, the overall conversion is lower than in the case of the conversion profile of the lowest molecular mass polyacrylate. It may be that the limit is reached in this case for the induced gel effect. As the molecular mass of the

Table VII   Conditions for Emulsion Polymerization Using Polyacrylates of Various Molecular Masses

Level of epoxy	20 g
Level of styrene	20 g
Level of butyl acrylate	20 g
Level of polyacrylate	70 g
Level of dimethylaminoethanol	10 g
Amount of water	350 g
Amount of initiator	0.1 g
Stirring speed	250 min^{-1}
Temperature	70°C

Table VIII   Viscosities of Polyacrylate Water-in-Oil Emulsions

| Polyacrylate	Viscosity (MPA · S)
PA1	7500
PA4	93,000
PA3	4500

polyacrylate falls, the internal viscosity of the particles lowers comparatively faster as monomer starts to diffuse into the particles. As such, termination, transfer, and exit processes can take place more readily.

In the case of the high molecular mass polyacrylate, the few radicals that manage to enter the particles in the beginning are trapped because of the high interfacial and internal viscosity of the dispersed phase. Even though the number of radicals that are able to enter the particles are low due to the barrier presented by the polyacrylate in terms of steric hindrance and interfacial viscosity effects, the rate of polymerization is high because the probability of termination becomes lower. From Figure 11 it seems that the probability of termination is inversely related to the viscosity of the dispersed phase.

Effect of Polyacrylate Molecular Mass on Molecular Mass of the Styrene–Butyl Acrylate Copolymer

The change in mass average molecular mass of the styrene/butyl acrylate copolymer is displayed in Figure 12.

The high molecular mass polyacrylate shows a large increase in molecular mass of the copolymer early in the polymerization. This trend continues
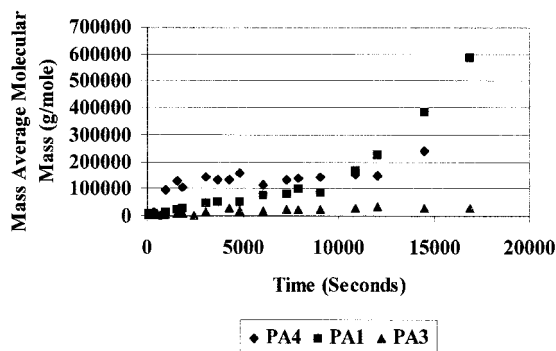
Figure 12   Effect of polyacrylate molecular mass on the mass average molecular mass of the copolymer.

as a function of polyacrylate molecular mass with regard to the other polyacrylates. Both the high molecular mass polyacrylate PA4 and the intermediate molecular mass polyacrylate PA1 show an increase in molecular mass near the end of the polymerization runs. In the case of the high molecular mass polyacrylate, significant amounts of undissolved polymer remained, and towards the end of the samples (starting from 4000 s onwards to the end of the reaction) only swollen insoluble polymer fractions remained. This was also observed for the intermediate molecular mass polyacrylate, although not to the same extent.

Each sample also contained an amount of epoxy that overlapped in some instances with the molecular mass distributions of the styrene/butyl acrylate copolymer. Because of this, it was difficult to use the number-average molecular mass to follow any trend because of a lot of scatter in the data. The mass average molecular masses showed the best trends with regard to the evolution of molecular mass with time and the differences in molecular masses between individual polyacrylates.

CONCLUSION

This study has shown that the epoxy and monomer levels significantly affect particle size, particle size distribution, and fractional conversion. The thermodynamic drive to decrease particle size for an epoxy–acrylate artificial emulsion is controlled mainly by the level of added monomer. According to eq. (1), the internal viscosity of the initial larger particles is lowered, interparticle association due to bridging, etc., is removed, and droplets of dissolved epoxy in the monomer phase are the end result. The major factor that seems to controls particle size also controls the particle size distribution or polydispersity. The level of monomer in this case is of importance as well as the interaction between monomer and the level of epoxy. Physically, large particles in the initial phases before monomer addition may be the result of a combination of interparticle association and the high viscosity of the dispersed epoxy phase.

The initial high conversion profiles during the first 5 min of some reactions are probably due to an induced gel effect. This effect has its origin in the fact that the high interfacial viscosity of the dispersed particles traps the incoming oligomeric radicals that originates in the water phase,

thereby increasing the average number of radicals per particle. The increased number of radicals plus the fact that the high interfacial and internal particle viscosity decreases the diffusion rate of these oligomeric/polymeric radicals result in an increase in propagation relative to termination and exit of radicals.

A few minutes later after monomer mass transfer into the particles has taken place, the large particles have been reduced in size to form droplets containing dissolved epoxy, monomer, and polyacrylate. With a lower internal viscosity, oligomeric radicals originating from the water phase can propagate, terminate, and exit the particles as in a conventional emulsion polymerization. However, the fact that a polyacrylate is used to provide stabilization to the emulsion may effect the entry and exit rates of oligomeric radicals compared to conventional emulsion polymerization. In addition, the number of droplets/particles produced when the monomer is added may also affect the rate of polymerization.

It is clear that the molecular mass of the polyacrylate significantly influences conversion, particle size, and molecular mass of the resultant styrene/butyl acrylate copolymer. Higher molecular mass polyacrylates may serve to increase the internal and interfacial viscosity of the latex particles. A higher internal particle viscosity results in fewer termination and exit events taking place, as explained previously. This effect is accounted for in the high initial mass average molecular mass of the high molecular mass polyacrylate.

A further consequence of the molecular mass of the polyacrylate is the control it exercises over latex particle size. A high molecular mass polyacrylate leads to a composite latex with a larger average particle diameter compared to that of a much lower molecular mass polyacrylate.

NOMENCLATURE

c_i Intensity weight of particle
C_p Monomer concentration within particles $(\mathrm{mol} \cdot \mathrm{dm}^{-3})$
C_w Monomer concentration in water phase $(\mathrm{mol} \cdot \mathrm{dm}^{-3})$
d particle size (diameter) (nm)
D Translational diffusion coefficient
f System-dependent function
gi Correlation function
[I]   Initiator concentration $(\mathrm{mol} \cdot \mathrm{dm}^{-3})$
k_d Initiator dissociation rate constant (s^{-1})

k_p Propagation rate constant $(dm^3 \cdot mol^{-1} \cdot s^{-1})$

k_{tr} Monomer transfer to monomer rate constant $(dm^3 \cdot mol^{-1} \cdot s^{-1})$

m_1 Refractive index of solution

$\bar{n}$ Average number of radicals per particle

N_A Avogadro constant

N_c Number of latex particles per dm^{-3} latex

q $= (4\pi \, m_1/\lambda_0)\sin \theta/2$

R_p Rate of polymerization

r_s Radius of swollen particle (nm)

T $= Dq^2$

x_{ui} ith import variable

Y_u Observed response of uth experimental run

z_{ul} Dummy variable

Greek Symbols

β_i Unknown parameter for which estimate is sought

γ Shear rate (s^{-1})

δ_l Effect of lth block

ε Residual error

η_{con} Viscosity of continuous phase $(kg \cdot m^{-1} \cdot s^{-1})$

η_{disp} Viscosity of dispersed phase $(kg \cdot m^{-1} \cdot s^{-1})$

θ Scattering angle

λ_0 Wavelength of laser

$\rho_{initiator}$ Rate of radical entry due to initiator decomposition (s^{-1})

σ_i Interfacial tension

τ Correlator time delay

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