

Online Conductivity and Stability in the Emulsion Polymerization of *n*-Butyl Methacrylate: Nonreactive Versus Reactive Systems

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ABSTRACT: Two different types of conductivity probes, that is, a torroidal probe and a resistance probe, were used as online sensors to monitor conductivity during the course of emulsion polymerizations of *n*-butyl methacrylate (BMA). These measurements were first applied to a nonreactive system, but the results showed that this method cannot be used to monitor latex stability in this system. Batch emulsion polymerizations of BMA were then carried out using different concentrations (0.6, 1.2, 2.4, and 7.8 mM) of sodium lauryl sulfate (SLS) as surfactant. The profiles of the two conductivity curves changed with the variation of the SLS concentration. Because deposition of polymers on the surfaces of the electrodes of the resistance probe can reduce the measured conductivity

values obtained from this probe (R) such that they are lower than the true values, as measured by the torroidal probe (T), the final conductivity ratio (R/T) between the two conductivity curves was chosen as a parameter to correlate the conductivity measurements to latex stability, which was estimated using blender tests and turbidity measurements. A linear relationship between them was found, indicating that the online conductivity measurements could be used to predict latex stability in the BMA emulsion polymerization system. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

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INTRODUCTION

Latex stability is the property by which polymer particles remain dispersed as single entities for long periods of time.¹ It is one of the most important factors for all commercial emulsion polymers, because it can not only affect the cost and the yield of latexes in large reactors, but also affect the quality of the final products. During emulsion polymerization, the polymer particles must be dispersed in the medium without significant coagulation. After the polymerizations, the latexes must survive the subsequent processing, such as pumping under high pressure or shipping large distances during different seasons, which may expose the latexes to widely varying temperature fluctuations. Moreover, latex stability dictates the shelf-life time for the products. However, so far, there is no effective method or online sensor that can monitor latex stability with the ability to take correcting action, if needed, if the system begins to become unstable during polymerization.

There are three main types of latex stability: mechanical (shear), chemical, and thermal (freeze-thaw). Among these, the mechanical and chemical stabilities were investigated in this research. The mechanical stability of a latex has implications for the pumping, transportation, and processing of the latex, where the emulsion polymers must have sufficient stability to withstand shearing forces. There are two distinct types of mechanical stability tests. One is to determine the time when the first visible coagulum appears under defined experimental conditions, known as the mechanical stability time²; the other is to measure the weight of coagulum present in the latex after a given time of agitation.³ Because it is hard to judge the first signs of coagulum, a blender test is applied to shear the latex and the resulting amount of coagulum is then measured. Chemical stability means the ability of a latex to withstand destabilization influences with the further addition of chemical agents. In this research, the added chemical agent is a water-soluble electrolyte, and the stability to added electrolyte is termed electrolyte stability. The critical coagulation concentration (ccc), which is the critical concentration of added electrolyte which can cause rapid coagulation of a latex, is the most important parameter used to estimate the electrolyte stability. If the electrolyte concentration is

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higher than the ccc, the electrostatic repulsive forces between two particles are completely cancelled and rapid coagulation occurs as a result of Brownian motion. On the other hand, if the electrolyte concentration is below this point, coagulation is slow.⁴ Turbidity measurements are normally used to determine the ccc of a latex.

Conductivity probes are relatively inexpensive and easily accessible tools. They can serve as online sensors,⁵ which may provide added insight into an emulsion polymerization reaction. Conductivity can be used to monitor the mobility of ionic species present in the formulation and responds to changes in the concentrations of ionic species (e.g., surfactant, initiator, etc.), which are related to latex stability. Because the conductivity of a solution can also be affected by temperature, relative conductivity is normally used to eliminate the effect of temperature on conductivity. This means that if conductivity is measured at a given temperature, it should be normalized to a value corresponding to its conductivity at 25°C, which is defined as the relative conductivity. Relative conductivity can be calculated through the temperature compensation equation:

$$k_{25} = \frac{k_T}{[1 + 0.02(T - 25)]} \quad (1)$$

where k_{25} ($\mu\text{S}/\text{cm}$) is the relative conductivity at 25°C, and k_T is the measured conductivity at temperature T (°C). The value 0.02 present in eq. (1) is the typical temperature correction factor.⁶

Studies describing the application of online conductivity measurements have been reported, not claimed previously. For example, Santos et al.^{7,8} claimed that conductivity measurements corresponded to changes in the concentration of the ionic surfactant in emulsion polymerizations of styrene. In their research, conductivity measurements were used to determine the critical micelle concentration (CMC) of sodium lauryl sulfate (SLS) at different temperatures. Moreover, a conductivity meter was coupled to a calorimetric reactor to provide online conductivity measurements during the emulsion polymerizations of styrene. They also gave an explanation for the shape of the conductivity profiles. When the emulsion polymerization reaction starts, particles are formed, causing an increase in particle surface area. Surfactant is adsorbed from the aqueous phase onto the newly formed particle surfaces to stabilize them. The mobility of the adsorbed SLS molecules is much smaller compared with free SLS molecules, which results in a decrease in conductivity. After this point, the conductivity increases, which was considered to result from the consumption of the monomer, releasing small amounts of the surfactant into the continuous phase. This explanation estab-

lished a relationship between conductivity and the location of the surfactant. Based on these results, Santos et al. established a model to predict the number of particles generated during the emulsion polymerization. However, more work needs to be done to prove this relationship. Moreover, this explanation did not correlate conductivity and surfactant concentration to latex stability during the emulsion polymerization process. Ortiz Alba⁹ reported widely varying conductivity profiles using a resistance conductivity probe during emulsion polymerizations of styrene with varying surfactant (Abex EP-110) concentration. He found that the conductivity values dropped to very low values during the reactions if the surfactant concentration was low. He also reported that some coagulum was found on the surfaces of the resistance probe and mentioned that deposited coagulum might influence the conductivity measurements using this probe, which meant that the conductivity values measured by this probe were not correct. Therefore, he suggested that another probe, which works on a different principle compared with the conventional resistance probe, needed to be used to measure conductivity during the reactions to overcome the shortcomings of the resistance probe. Engisch¹⁰ used both resistance and toroidal conductivity probes to investigate changes in conductivity during styrene emulsion polymerizations. He found that the values obtained from the two probes were not the same and the differences between them were not constant. The reason for the differences was that there was some plating of polymers on the electrodes of the resistance probe, which decreased the measured conductivity values of the resistance probe. Therefore, there may be a relationship between these conductivity differences and latex stability or the amount of coagulum formed on the surfaces of the probes. However, further investigation needs to be carried out to establish this relationship.

In this article, a resistance probe (manufactured by Control Company) and a toroidal probe (manufactured by Invensys Foxboro; Fig. 1) were used to measure conductivity changes in a nonreactive latex and *n*-butyl methacrylate (BMA) emulsion polymerizations. These two conductivity measurements are based on different principles as shown in Figure 2. The resistance probe works by applying a potential difference between two electrodes [Fig. 2 (top)], so the surface areas exposed to the measured solution will strongly influence the measurements obtained from this probe, which means that deposited coagulum on the electrodes will affect the measurements obtained from this probe. On the other hand, the toroidal probe measures conductivity through induction [Fig. 2 (bottom)]. Any adsorbed coagulum present on the surfaces of this probe does not affect the

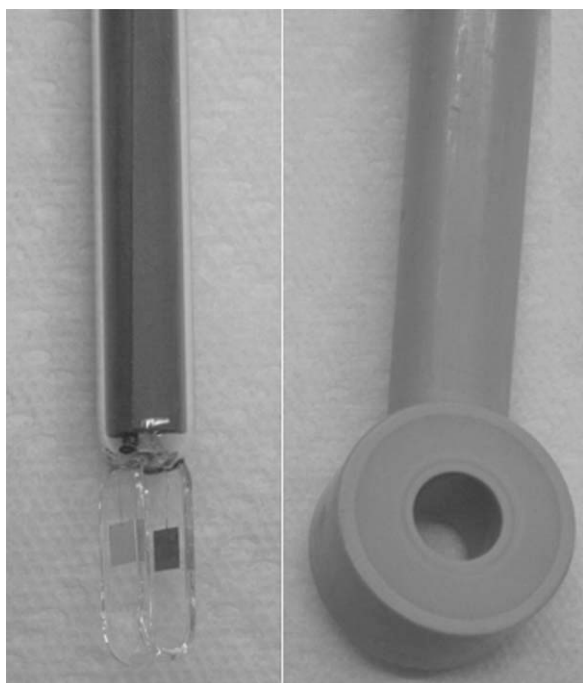


Figure 1 Resistance conductivity probe (left) and toroidal probe (right).

measurements. The purpose of using these two probes together is to determine the feasibility of predicting latex stability through online conductivity measurements. If a relationship between the conductivity measurements and latex stability can be established, this method can potentially be used as an

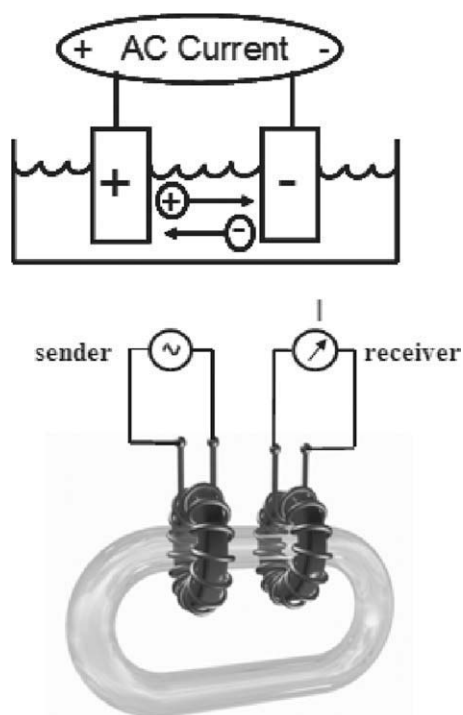


Figure 2 Principle of operation of the resistance (top) and toroidal (bottom) conductivity probes.

TABLE I
Recipes Used for the Batch Emulsion Polymerizations of BMA at 70°C

Ingredient	Amount
DI water	725 g
BMA	37.5 g
SLS	0.125–1.625 g (0.6–7.8 mM) ^a
KPS	0.375 g (1.9 mM) ^a
NaHCO ₃	0.375 g (6.1 mM) ^a

^a Based on the aqueous phase.

online technique to predict latex stability during an emulsion polymerization. This could have significant commercial implications.

EXPERIMENTAL

Materials

A total of 10 ppm monomethyl ether of hydroquinone inhibitor was removed from BMA monomer (Sigma-Aldrich) by passing it through an inhibitor-removal column (Sigma-Aldrich). SLS (Fisher Scientific), sodium bicarbonate (NaHCO₃, Sigma-Aldrich), and potassium persulfate (K₂S₂O₈, Sigma-Aldrich) were used as surfactant, buffer, and initiator, respectively. All of these chemicals were used as received. Deionized (DI) water was used for all experiments.

Polymerizations

Bottle emulsion polymerizations were carried out to prepare the poly(*n*-butyl methacrylate) (PBMA) latexes that were tested in a nonreactive system. The recipe used was based on the one developed by Hong.¹¹ The solids content of this recipe is low (5%) as it was originally used to prepare the seed stage in a semibatch reaction. Moreover, the SLS concentration used is 0.6 mM, which is much lower than the CMC of SLS (7.8 mM).¹² The concentrations of initiator (KPS) and buffer (NaHCO₃) were 1.9 and 6.1 mM based on the aqueous phase. All components were charged into 480 mL bottles and then nitrogen was bubbled into the solution for 15 min in order to remove O₂, which could inhibit the polymerization. The bottle polymerizations were run in a tumbler reactor at 70°C for 4 h by end-over-end rotation at 40 rpm.

Four batch emulsion polymerizations of BMA were run to investigate the changes in conductivity during the polymerization process. Because the surfactant concentration can affect latex stability, the SLS concentration was varied from 0.6 to 1.2, 2.4, and 7.8 mM (Table I), whereas the concentrations of the other components were the same. In the following discussion, these four reactions are labeled as B-5%-0.6 mM (B stands for batch emulsion

polymerization, 5% stands for the solids content, and 0.6 mM stands for the SLS concentration), B-5%-1.2 mM, B-5%-2.4 mM, and B-5%-7.8 mM, respectively. All reactions were run in a 1 L reactor without baffles at 70°C and stirred at 250 rpm using a 7-cm diameter Rushton impeller with 6 blades. Both the commercial resistance and toroidal probes were used to measure conductivity during the polymerizations. The reactor was flushed with nitrogen through a needle during the polymerizations to prevent O₂ inhibition. The reactions were run for 90 min. The conductivity values measured by the two probes were recorded every minute for the first 10 min of each reaction, and then were recorded every 5 min.

Characterization

The solids content of each sample was measured by gravimetry from which the conversion was calculated. A Nicomp 370 instrument (Pacific Scientific) was used to determine the particle size based on dynamic light scattering. To estimate the surface coverage of the PBMA particles by the adsorbed SLS molecules, the serum of each sample was obtained using a stirred filtration cell using a size exclusion membrane (GE Water and Process Technologies, 0.1 μm, 76 mm). The surface tension of each serum was measured by an Autotensiomat (Fisher Scientific) using the DuNoüy Ring method. The free SLS concentration in the aqueous phase could be obtained using a calibration curve (surface tension vs. SLS concentration). Then, the amount of SLS adsorbed on the surfaces of the latex particles could be calculated based on a mass balance. Assuming the area covered per surfactant molecule at surface saturation was around 54 Å²/molecule in the PBMA-SLS system,^{13,14} the fractional surface coverage could be estimated.

Latex stability tests

To determine the latex stability in the nonreactive system, the latex prepared by bottle polymerizations was charged into a 2 L reactor without baffles and stirred at 170 rpm using a 7-cm diameter Rushton impeller with 6 blades. Both the resistance and toroidal probes were used to measure conductivity during the experiments (and act as baffles to some degree). The reactor was covered with aluminum foil to minimize evaporation and lowered into a water bath set at 70°C.

A standard test used to determine the mechanical stability of a latex is given in American Standard Test Methods (ASTM, D1417-03D)¹⁵: "A sample of latex is subjected to mechanical shear by the use of a high-speed stirrer. The amount of coagulum formed after a given time of agitation is considered a mea-

sure of latex stability". Based on this principle, a blender test was used to determine the mechanical stability of the latex samples. A Hamilton Beach blender was used for this test. The rotational speed was around 8000 rpm at the highest setting. A total of 200 g of latex was used for this test without any dilution. At the beginning of blending (shearing), the temperature of the latex was 25°C. After 20 min of the blender test, the temperature rose to 60°C. According to the ASTM (D1417-03D),¹⁵ the temperature should not exceed 60°C, so it was reasonable to run the blender test for 20 min. During this process, a great deal of foam was formed, so the blender was stopped every 5 min to take a sample from the liquid phase present at the bottom of the blender. After the experiment was stopped, a 100 μm nylon mesh was used to filter the coagulum from the latex. DI water was used to wash the foam and the blender during the filtration process. The mesh supporting the coagulum was placed in an oven (90°C) for 24 h to dry and remove entrapped water, and the weight of the coagulum was measured. Moreover, the solids content of each sample obtained during the test was measured. The percent coagulum of these samples was calculated based on the solids content of the sample before and after the blender test.

The electrolyte stability of a latex was evaluated using turbidity measurements, where the kinetics of coagulation was followed by the measurement of the slope of the optical density (OD) vs. time curve. All measurements were performed at a constant temperature, which was ~ 25°C. The OD was measured using a Shimadzu UV-2101PC spectrophotometer set at a wavelength of 600 nm. All latex samples were diluted to 0.13 wt % before the measurement. One milliliter of the diluted sample was charged into both the reference and sample cells. Different volumes of 4M KCl solution were added to the sample cell and the OD was recorded automatically after quick shaking. The stability ratio (*W*) is defined as the ratio of the rate of rapid to slow coagulation and is calculated using eq. (2):

$$W = \frac{(d\tau/dt)_{0,C_E > ccc}}{(d\tau/dt)_{0,C_E}} \quad (2)$$

where τ is the OD and C_E is the electrolyte concentration. The ccc can be estimated from the log(*W*) versus log(C_E) curve.

RESULTS AND DISCUSSION

Nonreactive system

Fully converted latex (99.4%) was prepared by bottle emulsion polymerization at 70°C for 4 h as previously described. The volume-average particle

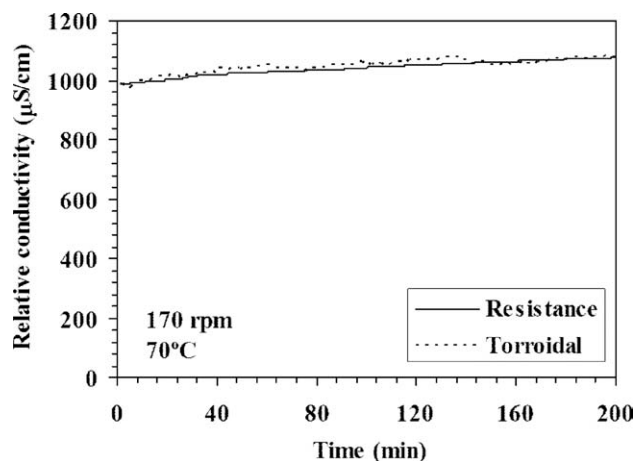


Figure 3 Relative conductivity versus time curves for the PBMA latex in the nonreactive system at 70°C and 170 rpm.

diameter (D_V) was 269 nm. The latex was charged into a 2 L reactor to check its stability (70°C, 170 rpm, and 200 min). Both the resistance and torroidal probes were used to measure conductivity during this process and the results are shown in Figure 3. It can be seen that the conductivity curves obtained from the two probes overlap, which indicates that the resistance probe gives the correct results (as compared with the values obtained from the torroidal probe). This demonstrates that there is no plating on the surfaces of the electrodes of the resistance probe during the test. The conductivity curves show a slight increase with time. This was caused by some evaporative loss of water during this test. On the other hand, some coagulum was found on the surfaces of the reactor and the conductivity probes after this test, which indicates that the latex had some degree of instability. Because the conductivity curves do not show any significant changes despite the formation of some coagulum, this shows that the online conductivity measurements cannot be used as sensors to predict latex stability in this nonreactive system, which is in contrast to the reactive system as reported below. The reason is unclear so far. It may be caused by the nature of the system. Because no

TABLE II
Latex Particle Size Obtained from the Batch Emulsion Polymerizations (5% Solids Content) of BMA

	D_N (nm)	D_V (nm)	D_W (nm)	PDI
B-5%-0.6 mM	205	214	218	1.06
B-5%-1.2 mM	184	186	187	1.02
B-5%-2.4 mM	159	160	161	1.01
B-5%-7.8 mM	73	75	77	1.05

D_N , number-average particle diameter; D_V , volume-average particle diameter; D_W , weight-average particle diameter; PDI, polydispersity index ($= D_W/D_N$).

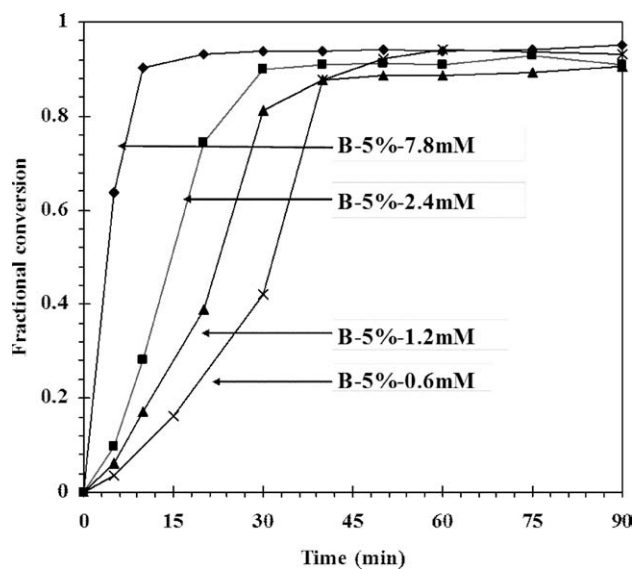


Figure 4 Fractional conversion versus time curves for the batch emulsion polymerizations of BMA shown in Table I at 70°C and 250 rpm.

polymerization reaction is occurring in the reactor, the coagulum formed under the given temperature and shear conditions prefers to adsorb onto surfaces other than the platinum electrodes of the resistance probe.

Reactive emulsion polymerization system

Four batch emulsion polymerizations were carried out using the recipes shown in Table I. The particle sizes of these four latexes are shown in Table II. As expected, the particle size becomes smaller as the surfactant concentration increases. The particle size of latex B-5%-7.8 mM is much smaller than the others. This is caused by the relatively high SLS concentration used in this recipe compared with the other recipes. Moreover, the particle size distributions (PSD) are narrow as seen by the polydispersity index (weight-average diameter divided by number-average diameter) values, because the SLS concentrations are lower than the CMC of SLS (7.8 mM¹¹) in the first 3 recipes, which enables homogeneous nucleation to take place, which often leads to narrow PSDs. In the last recipe, the SLS concentration is approximately equal to the CMC. The number of micelles is relatively low and homogeneous nucleation may still dominate the nucleation phase compared with micellar nucleation, which again can result in a narrow PSD.

The fractional conversion versus time curves for the four reactions are compared in Figure 4. It can be seen that the higher the SLS concentration, the faster the reaction rate, as expected based on the classical emulsion polymerization Smith-Ewart theory.¹⁶ Especially for reaction B-5%-7.8 mM, the

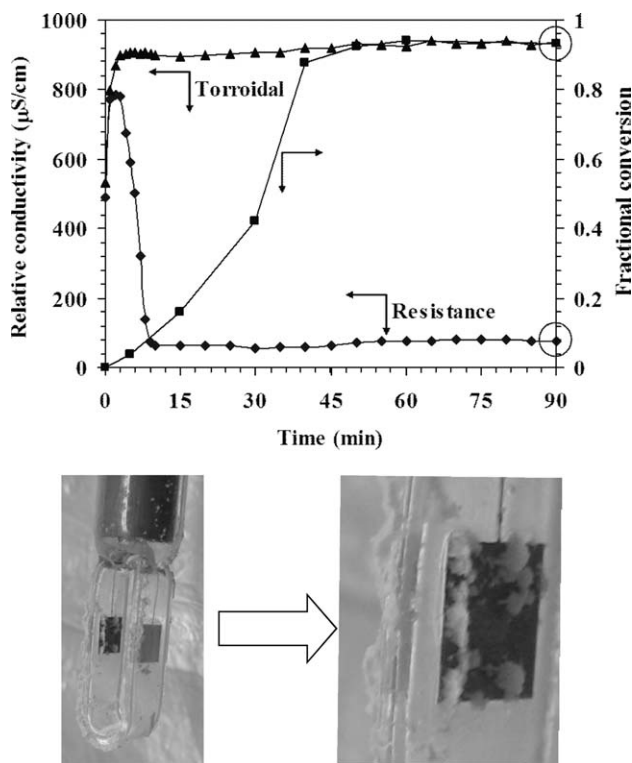


Figure 5 Relative conductivity and fractional conversion versus time curves for reaction B-5%-0.6 mM (Table I) at 70°C and 250 rpm (top); photograph of the resistance probe with plating on the surface of the electrodes (bottom).

reaction rate was very fast with the reaction being complete in 10 min because of the high SLS concentration. The first 3 reactions were completed at 45, 40, and 30 min, respectively.

No coagulum was found in any of the latexes. The weight of coagulum adsorbed on the surfaces of the impeller and reactor was considered to be negligible (less than 1%). These results show that the degree of coagulum was low and all of the four batch emulsion polymerizations could be considered as successful reactions.

Figure 5 (top) shows the fractional conversion and relative conductivity curves for reaction B-5%-0.6 mM. At the very beginning of the reaction, the conductivity values measured by the resistance and torroidal probes increased after the addition of initiator (KPS), an electrolyte. However, the values obtained from the two probes showed significant divergence after this initial rise in conductivity. The conductivity values obtained from the torroidal probe appeared almost constant after 5 min. On the other hand, the conductivity values measured by the resistance probe decreased dramatically after 3 min. This phenomenon did not occur in the nonreactive system, so it should be related to the emulsion polymerization process. This is caused by some plating of polymer (adsorbed coagulum) on the surfaces of

the electrodes of the resistance probe [Fig. 5 (bottom)]. The reason for the formation of plating is related to the stability of polymer particles. As polymer particles grow, the surfactant coverage on the particle surface will decrease if surfactant concentration is not high enough. In this case, some particle may be not stable under agitation and will deposit onto the surfaces of the electrodes. The accumulation of the deposition results in plating, which represents an insulating layer. Thus, the actual conductivity values measured by the resistance probe were smaller than the true values during this time period. This indicates that the difference in conductivity values obtained from the two probes might be used to predict latex stability in the reactive emulsion polymerization system.

The resistance probe was rinsed and dried in air after the reaction. The conductivity of a standard sodium chloride solution was measured using this resistance probe. The measured value was 132 $\mu\text{S}/\text{cm}$, whereas the standard value was 987 $\mu\text{S}/\text{cm}$. The resistance probe was then cleaned using toluene, acetone, and DI water. After cleaning, the resistance probe was again used to measure the standard solution and the measured value became normal (987 $\mu\text{S}/\text{cm}$). These results prove that the plating on the surfaces of the resistance probe decreased the measured conductivity values during the reaction.

The relative conductivity profiles of reactions B-5%-1.2 mM, B-5%-2.4 mM, and B-5%-7.8 mM are shown in Figures 6–8, respectively. Divergence between the two conductivity curves occurred in reactions B-5%-1.2 mM and B-5%-2.4 mM. On the other hand, the two conductivity curves did not diverge and almost overlapped for reaction B-5%-7.8 mM. This was caused by the relatively high SLS concentration present in this recipe, which was significantly higher than that used in the other reactions. It is well known that latex stability can be improved

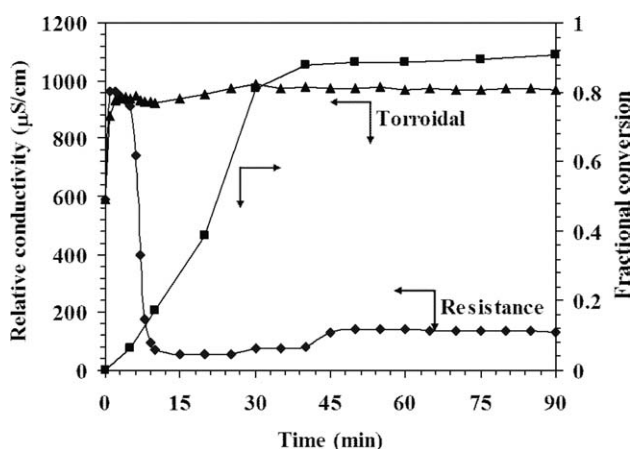


Figure 6 Relative conductivity and fractional conversion versus time curves for reaction B-5%-1.2 mM (Table I) at 70°C and 250 rpm.

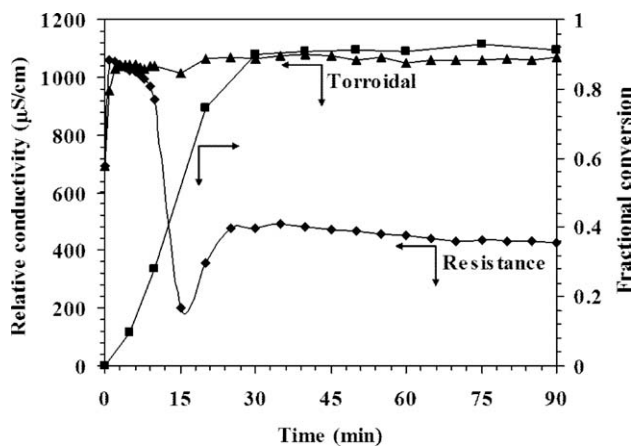


Figure 7 Relative conductivity and fractional conversion versus time curves for reaction B-5%-2.4 mM (Table I) at 70°C and 250 rpm.

by an increase in the surfactant concentration. During this reaction, the polymer particles may be stabilized sufficiently such that no plating occurred, and thus, the resistance probe correctly measured the conductivity with the two conductivity curves remaining similar during the period of this reaction. Therefore, these results prove that the SLS concentration can affect latex stability as well as the shapes of the conductivity curves, which indicates that there may be some relationship between latex stability and the conductivity curves.

Because SLS is an ionic surfactant, as the SLS concentration increases, the total conductivity of the system will increase, and the relative conductivity values measured by the torroidal probe will also increase. However, the shapes of the relative conductivity profiles obtained by this probe in these reactions were similar. However, the shapes of the relative conductivity curves obtained by the resistance probe are significantly different for each reac-

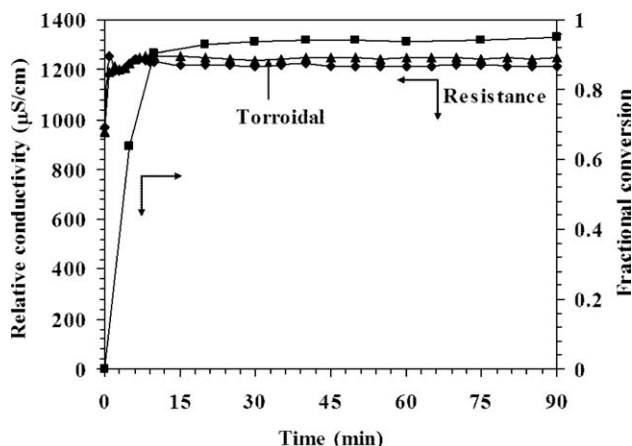


Figure 8 Relative conductivity and fractional conversion versus time curves for reaction B-5%-7.8 mM (Table I) at 70°C and 250 rpm.

tion and the four curves are plotted together for comparison in Figure 9. The curves of the first 3 reactions exhibited sharp decreases at 3, 5, and 10 min, and the conversions at these times were 2, 6, and 28%, respectively. In the first 2 reactions (B-5%-0.6 mM and B-5%-1.2 mM), the sharp decreases in conductivity occurred at an early stage of the emulsion polymerizations, so the formation of plating on the electrodes may be related to particle nucleation. In the third reaction (B-5%-2.4 mM), the sharp decrease occurred later in the polymerization and may be related to particle growth. This indicates that the time necessary to reach the sharp decrease in conductivity is delayed and the conversion becomes higher because of the increase in the SLS concentration. It can also be seen that as the SLS concentration increases, the final conductivity value measured by the resistance probe increases. Because the measurement of the resistance probe is proportional to the surface area of the electrodes if other parameters are fixed, the ratio of the measured conductivity value to the true value can be used to represent the degree of plating (percent coverage) on the surfaces of the electrodes. Because plating does not affect the measurements obtained from the torroidal probe, the measured conductivity values by the torroidal probe can be considered to be the true conductivity values. Therefore, the final conductivity ratio (R/T) can be defined as the ratio between the final conductivity values obtained by the two probes (the values circled in Fig. 5) as shown in eq. (3).

$$\frac{R}{T} = \frac{\text{Final conductivity value measured by the resistance probe}}{\text{Final conductivity value measured by the torroidal probe}} \quad (3)$$

If there is no plating on the surfaces of the electrodes, the measured conductivity values obtained by

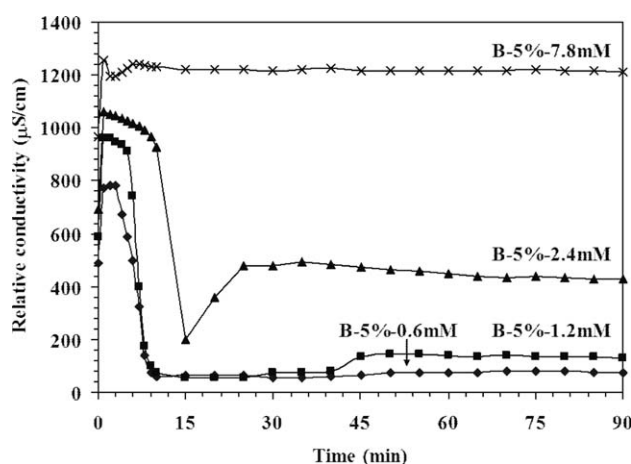


Figure 9 Comparison of relative conductivity curves obtained by the resistance probe for the four reactions (Table I).



Agitation Time 5 min 10 min 15 min 20 min
Percent Coagulum 62.9% 94.1% 96.4% 97.1%

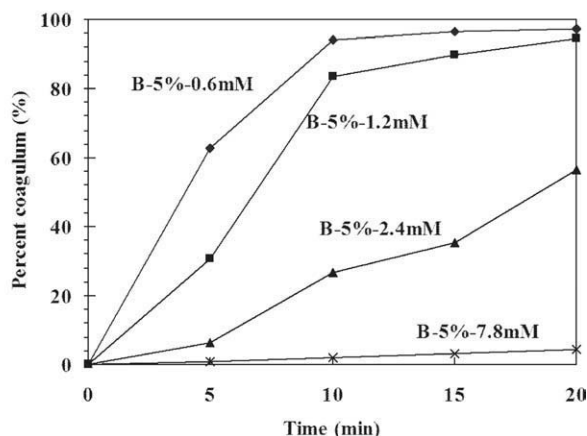


Figure 10 Photograph of the latex samples (B-5%-0.6 mM) obtained after shearing in the blender for varying amounts of time (top) and percent coagulum versus time curves for the four latex samples (bottom).

the two probes should theoretically be the same, and R/T would have a maximum value, which would equal 1; if the surfaces of the electrodes are fully covered by adsorbed coagulum, the R/T would have a minimum value, which is theoretically equal to 0. Because the degree of plating formed during the reactions may be related to latex stability, R/T can be used as a parameter to correlate the conductivity curves to latex stability.

In reaction B-5%-2.4 mM, the relative conductivity profile obtained by the resistance probe showed a significant increase in the middle of this reaction, which was termed as the second increase. The reason for this increase will be explained and discussed in a subsequent article.

Blender tests were carried out to investigate the mechanical stability of the prepared latexes. Figure 10 (top) shows a photograph of the latex samples removed from the bottom of the blender container during the blender test of latex B-5%-0.6 mM. Because polymer particles were dispersed in the water phase, the original latex was white. However, in this photograph, it can be seen that the samples became clearer as time passes. Especially in samples 3 and 4 (taken at 15 and 20 min), the samples con-

tain almost no polymer particles, so the solution is nearly transparent. This photograph illustrates that the latex becomes unstable and that coagulum is formed during this test. Obviously, the latexes with greater stability should have higher solids content in the samples and less coagulum present.

The solids contents of these samples taken during the blender test were measured and the percent coagulum was calculated based on a mass balance. The results are shown in Figure 10 (bottom). From this figure, it can be seen that the percent coagulum of each latex increased with time. Moreover, by comparing the curves of the four latexes, the degree of their mechanical stability can be compared. Latex B-5%-0.6 mM had poor stability and lost almost all solids during the blender test. Latexes B-5%-1.2 mM and B-5%-2.4 mM had better stabilities, but they were still unstable (94.5 and 56.6% coagulum). Latex B-5%-7.8 mM was stable and only lost a slight amount of solids during the 20 minutes. The percent coagulum obtained after the blender test was complete is summarized in Table III. These results show that the four latexes have different degrees of stability, even though they were prepared by successful batch emulsion polymerizations.

The SLS surface coverage of these latexes were estimated following the procedure described previously and were found to increase with initial SLS concentration: 0.8, 1.1, 6.7, and 41.9%, respectively (Table III). The adsorbed SLS molecules generate the electrostatic repulsive forces to stabilize the polymer particles, so the particles with higher surface coverage exhibit better stability. These surface coverage results explain why the latexes exhibited different stabilities during the blender tests.

The final conductivity ratio between the two probes (R/T) is correlated to latex stability. The percent coagulum and surface coverage versus R/T curves are plotted in Figure 11. The results show that there is a linear relationship between them, which means that the percent coagulum can be predicted using the R/T value obtained at the end of the emulsion polymerization. The results also indicate that the online conductivity measurements can be used to predict the mechanical stability of the latexes in this system, which is obviously different from the nonreactive system.

TABLE III
Summary of the Results of the Conductivity Ratio (R/T), Percent Coagulum, Surface Coverage, and Critical Coagulation Concentration (ccc) for the Prepared Latexes

Latex	R/T	Percent coagulum (%)	Surface coverage (%)	ccc (M)
B-5%-0.6 mM	0.08	97.1	0.8	0.445
B-5%-1.2 mM	0.14	94.5	1.1	0.531
B-5%-2.4 mM	0.40	56.6	6.7	0.581
B-5%-7.8 mM	0.97	4.5	41.9	0.682

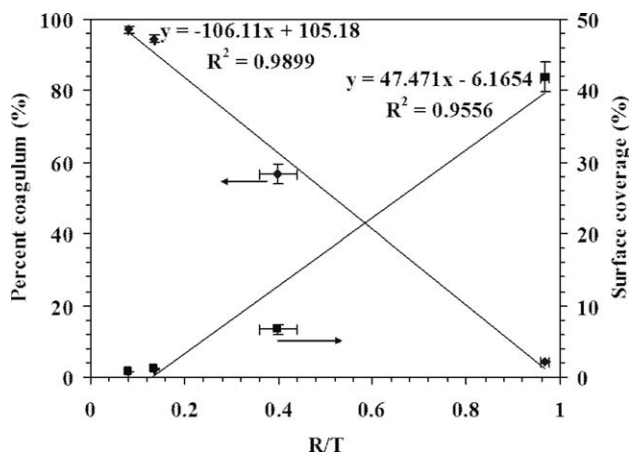


Figure 11 Percent coagulum and SLS surface coverage as a function of the final conductivity ratio (R/T).

The critical coagulation concentration (ccc) of these four latexes was estimated using the turbidity measurements as described previously. The ccc's of these latexes were 0.445, 0.531, 0.581, and 0.682M, respectively, and increased with SLS concentration (Table III). The correlation between the ccc and R/T is shown in Figure 12. The results show that there is a linear relationship, which means that the online conductivity measurements can be used as a tool to predict the electrolyte stability of the latexes in this system.

CONCLUSIONS

The investigation of latex stability and conductivity in nonreactive and reactive emulsion polymerization systems was carried out using resistance and torroidal conductivity probes. In the nonreactive system, some

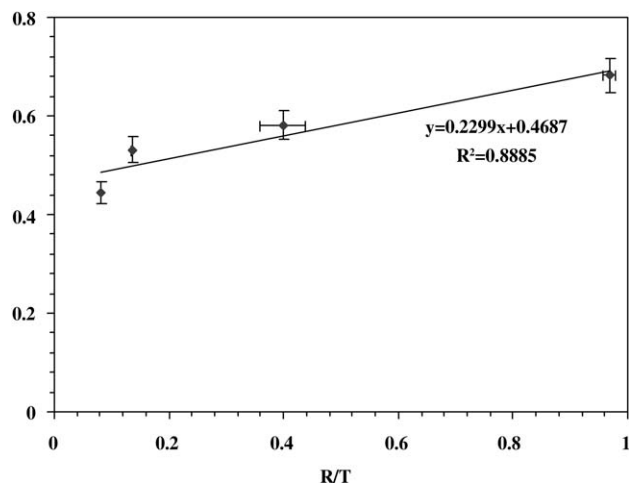


Figure 12 Correlation between the critical coagulation concentration (ccc) estimated by the turbidity measurements and the final conductivity ratio (R/T).

coagulum was found on the surfaces of the reactor, the shaft, and the conductivity probes after the experiments, but the conductivity curves obtained from the two conductivity probes did not show any significant differences. These results indicated that there was no obvious relationship between the conductivity curves and latex stability in this system. Therefore, these online conductivity measurements cannot be used as a tool to predict latex stability if there is no polymerization reaction occurring.

In the batch emulsion polymerization system, four reactions were carried out using different SLS concentrations. The relative conductivity curves obtained from the torroidal probe exhibited similar behavior. On the other hand, the conductivity curves obtained from the resistance probe showed significant differences. Moreover, the relative conductivity values between the two probes diverged early in some reactions, which differ from the profiles obtained in the nonreactive system. This was caused by some coagulum plating on the surfaces of the electrodes of the resistance probe. Blender tests and turbidity measurements were carried out to check the mechanical and electrolyte stability of the prepared latexes. The percent coagulum and the ccc are used to represent latex stability. The final conductivity ratio (R/T) between the two probes is used as a parameter to correlate the conductivity curves to latex stability. The results indicate that there exists a linear relationship between them, which means that the online conductivity measurements can be used to predict the mechanical and electrolyte stability of the final latexes in this system. Therefore, the conductivity measurements can be used as an online tool to monitor latex stability during emulsion polymerizations and to predict the mechanical and electrolyte stability of the final latexes in this system. Some actions can be taken, such as adding more surfactant, to prevent further instability based on the appearance of the divergence between the two relative conductivity curves. Therefore, this method has potential applications in industry.

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