

Online Conductivity and Stability in the Emulsion Polymerization of *n*-Butyl Methacrylate: Batch versus Semibatch Systems

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ABSTRACT: A homemade resistance probe (*R*) and a torroidal probe (*T*), which work on different principles to measure conductivity, were used as online sensors to monitor conductivity during the course of emulsion polymerizations of *n*-butyl methacrylate (BMA). Six batch emulsion polymerizations of BMA (20% solids content) were carried out using sodium lauryl sulfate (SLS) as surfactant. To compare latex stability and conductivity profiles, the SLS concentration was varied (5, 6, 8, 10, 20, and 30 mM). Seven semibatch emulsion polymerizations of BMA (40% solids content) were also run. All semibatch polymerizations had the same seed stage, while different amounts of SLS were fed during the feed stage. During these reactions, the conductivity curves obtained from the two different probes overlapped if the SLS concentration was high enough (20 and 30 mM); on the other hand, the two curves diverged if the SLS concentration was low. Since the final conductivity values obtained from the two probes were not the same in most of the reactions, the ratio between them (*R/T*) was used to correlate conductivity to latex stability. A blender test and turbidity measurements were carried out to estimate the mechanical stability and the electrolyte stability of the prepared latexes, respectively. The results showed that *R/T* varied linearly with the latex stability. These results showed that latex stability could be predicted through online conductivity measurements. Moreover, the reason for an observed increase in conductivity during these emulsion polymerization reactions was also investigated. This increase was related to the disappearance of monomer droplets, which demonstrated that the conductivity measurements could also be used to aid in the study the kinetics of the emulsion polymerization process. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 4001–4013, 2013

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INTRODUCTION

Emulsion polymerization is a widely used process for the production of synthetic latexes since its first introduction on an industrial scale in the mid-1930s.¹ Latex particles need to remain stable during the polymerization process with minimal coagulum formed. Stability is also required for storing, pumping, and shipping the latex as well. Thus, the colloidal stability of latex to electrolyte, temperature and shear are critical.² At present, there is a need for the development of more accurate online conductivity sensors that may be inserted into a reactor to follow coagulum formation during the course of polymerization. If caught early enough, it may be possible to change some of the process conditions during polymerization (e.g., adding additional surfactant) to keep any coagulum formed at low levels. In this article, several types of conductivity probes are used to monitor colloidal stability during the course of the polymerization. The stability of the final latex after polymerization was determined using a standard blender test.

Conductivity probes have been used previously in industry to obtain additional information (e.g., changes in the amounts of ionic species such as initiator and surfactant in a reactor) during the emulsion polymerization process.³ In addition, there have been a number of studies that utilized conductivity measurements during emulsion polymerization.^{4–8} For example, Santos et al.^{4,5} investigated the changes in conductivity during the emulsion polymerizations of styrene using sodium lauryl sulfate (SLS) as surfactant. They established a model to predict the number of latex particles formed during the emulsion polymerization process using conductivity values. However, no latex stability information can be obtained from their model.

Ortiz Alba⁶ recorded conductivity changes using a resistance conductivity probe during emulsion polymerizations of styrene. He reported that the absorption of coagulum on the glass surfaces of the conductivity probe would affect the accuracy of conductivity values obtained using this probe. Therefore, he suggested that a different type of conductivity probe, i.e., a torroidal probe, which

operates on a different principle than the traditional resistance probe, was needed to compare the conductivity results obtained from the resistance probe during the reactions. Engisch⁷ investigated changes in conductivity using both resistance and torroidal conductivity probes during the emulsion polymerization of styrene. He found that the values obtained from the two conductivity probes diverged. His results showed that the resistance probe could not be relied upon to give accurate conductivity measurements during the polymerizations.

In our previous article,⁸ online conductivity measurements were applied to both non-reactive and reactive systems. In the non-reactive system, the two conductivity curves obtained by a resistance probe and a torroidal probe did not show major differences. On the other hand, the two conductivity curves exhibited significant differences during the emulsion polymerization of butyl methacrylate (BMA). Moreover, the mechanical and electrolyte stabilities of the prepared latexes were tested. The results showed that there was a linear relationship between latex stability and the final conductivity ratio (R/T) between the two conductivity curves. However, the solids content used in this reactive system was low (5%). Further studies of the relationship between latex stability and conductivity measurements were needed at higher solids contents or higher viscosity systems.

In this article, online conductivity measurements were carried out in batch (20% solids content) and semibatch (40% solids content) BMA emulsion polymerizations. The torroidal probe (manufactured by Invensys Foxboro) used was the same as that introduced previously,⁸ which measures conductivity through an induction mechanism. Because the surface area of the electrodes of the commercial resistance probe used in our previous studies was small and the gap between the two electrodes was narrow and easily clogged at high solids contents, a homemade resistance probe was built and used in this research as described below.

EXPERIMENTAL

Design and Construction of a Homemade Conductivity Probe

The homemade conductivity probe has two pieces of platinum ($10 \times 10 \times 0.1 \text{ mm}^3$ connected with platinum wires (Figure 1). The platinum pieces were fixed on a Teflon jacket, which was fixed to the head of the torroidal probe. In this manner, the two separate types of conductivity probes were combined into one probe. Moreover, the electrodes of this homemade resistance probe are totally exposed to the medium in which the probe is immersed. Compared to the commercial resistance probe used previously where the electrodes are located inside a glass channel, the benefit of this design is that the surfaces of the electrode are better exposed to the reaction mixture, providing greater sensitivity. On the other hand, the position of the two electrodes is back-to-back instead of face-to-face, as in the commercial resistance probe. In this case, the current lines in the aqueous phase are in an arc pattern and are longer in a face-to-face electrode configuration.⁸ A disadvantage of this back-to-back configuration is that the conductivity measurements can be affected by the presence of insulators, such as monomer droplets, which are dispersed in the aqueous phase. This effect will be discussed later. The homemade probe was connected to a commercial conductivity meter and the signals obtained from this probe were correlated to standard conductivity values using standard NaCl solutions. The results (Figure 2) showed that there was a linear relationship between the signal and conductivity values, indicating that this homemade probe could be used to measure conductivity. Using the homemade resistance and torroidal probes, conductivity profiles were obtained during the emulsion polymerization reactions and then correlated to latex stability. Additionally, kinetic information was obtained through conversion versus time curves and these were correlated to the conductivity data in terms of the mechanism of emulsion polymerization.

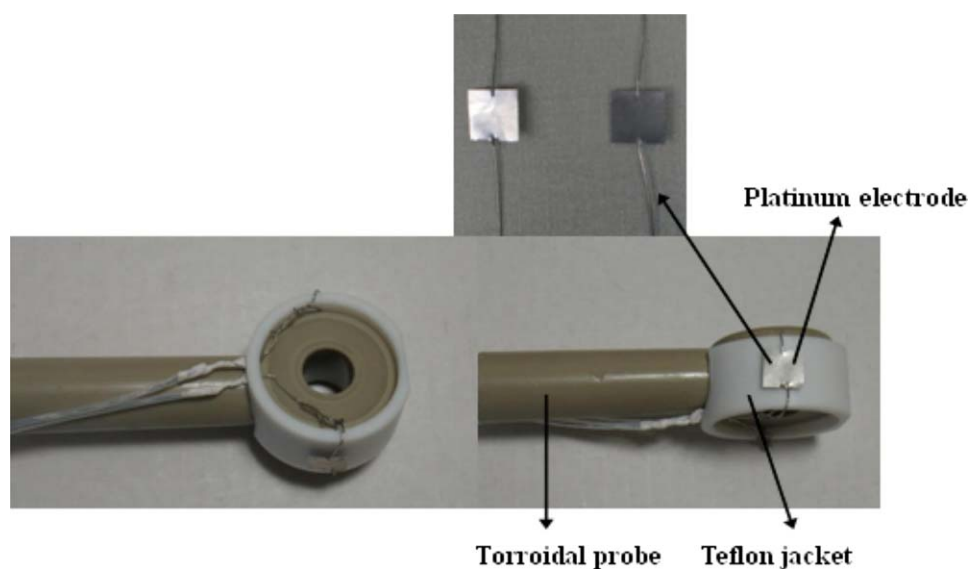


Figure 1. Torroidal probe modified by addition of Pt electrodes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

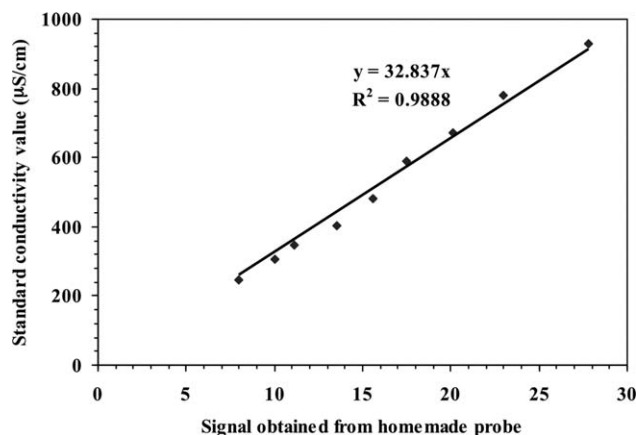


Figure 2. Calibration curve for the homemade resistance probe.

Materials

Inhibitor [10 ppm monomethyl ether of hydroquinone (MEHQ)] was removed from the *n*-BMA monomer (Sigma-Aldrich), by passing it through an inhibitor-removal column (Sigma-Aldrich). SLS (Fisher Scientific) and sodium bicarbonate (NaHCO₃, Sigma-Aldrich) were used as surfactant and buffer, respectively. Potassium persulfate (KPS, Sigma-Aldrich) was used as initiator. Potassium chloride (KCl, Sigma-Aldrich) was used for turbidity measurements. All chemicals, except for the monomer, were used as received. Deionized (DI) water was used for all experiments.

Batch Emulsion Polymerizations of *n*-BMA

Six batch emulsion polymerizations of BMA (Table I) were carried out to investigate the changes in conductivity during the polymerization process. All reactions were run in a 1 L reactor without baffles immersed in a 70°C constant temperature water bath and stirred at 250 rpm using a 7-cm diameter Rushton impeller with six blades. Both the homemade resistance and toroidal probes, which were fixed in a four-neck adapter, were used to measure the conductivity during the polymerizations. The reactor was blanketed with nitrogen during the polymerizations to prevent O₂ inhibition. The SLS concentration was varied from 5 to 6, 8, 10, 20, and 30 mM, while the amounts of the other components were the same. These six reactions are labeled as B-20%-5 mM (B stands for batch emulsion polymerization, 20% stands for the solids content, and 5 mM stands for the SLS concentration), B-20%-6 mM, B-20%-8 mM, B-20%-10

Table I. Recipes Used for the Batch Emulsion Polymerization of BMA (20% Solids Content) at 70°C

Ingredient	Amount
DI water	600 g
BMA	150 g
SLS	0.865–5.191 g (5–30 mM) ^a
KPS	0.280 g (1.7 mM) ^a
NaHCO ₃	0.084 g (1.7 mM) ^a

^aBased on the aqueous phase.

mM, B-20%-20 mM, and B-5%-30 mM, respectively. Since the critical micelle concentration (CMC) of SLS has been reported to be 7.8 mM,⁹ the SLS concentration in the recipes was varied from below the CMC to approximately the CMC and then above the CMC. KPS initiator was added as an aqueous solution to the reactor to start the polymerization. The reactions were run for 60 min. The conductivity values obtained from the two probes and the temperature in the reactor obtained from a sensor in the toroidal probe were recorded every minute until the temperature decreased during the reaction, and then were recorded every 5 min. Samples were taken at periodic intervals to measure the conversion by gravimetry.

Semibatch Emulsion Polymerizations

Seven semibatch emulsion polymerizations of BMA were run under the same conditions as described above. The recipes for all reactions are shown in Table II. The seed stage of each reaction was the same, with 20 mM SLS and 20% solids content, and was carried out for 30 min. The choice of this recipe was based on the consideration of online conductivity measurements and latex stability. First, the latex prepared during the seed stage should have good stability. If unstable latex was used as the seed, it would be hard to determine the reason for any instability of the final latex prepared by the semibatch process. Moreover, if the latex was not stable at the end of the seed stage, it would be difficult to interpret the changes in the conductivity curves obtained during the feed stage. Second, if the SLS concentration was too high in the seed stage, the final latex may have good stability even if no extra SLS was added during the feed stage. Therefore, it would be impossible to distinguish any differences in the stability of the final latexes prepared using the different recipes. Based on these considerations, recipe B-20%-20 mM was chosen as the recipe for the seed stage with the amount each component being scaled down.

The feed stage was run for 137 min, where the solids content was increased from 20 to 40%. The monomer and SLS solution were fed in two different streams using two syringe pumps during the feed stage. The monomer feed rate was 1.5 g/min (1.678 mL/min), which was chosen based on Krishnan's research.¹⁰ In

Table II. Recipes Used for the Semibatch Emulsion Polymerizations of BMA (40% Solids Content) at 70°C

	Ingredient	Amount
Seed stage	DI water	380 g
	BMA	95 g
	SLS	2.193 g (20.0 mM) ^a
	KPS	0.178 g (1.7 mM) ^a
	NaHCO ₃	0.178 g (5.5 mM) ^a
	Time	30 min
Feed stage	DI water	70 g
	BMA	205 g
	SLS	0–8.750 g
	Time	137 min

^aBased on the aqueous phase.

his research, monomer-starved conditions were achieved using this monomer feed rate. The SLS solution feed rate was 0.511 mL/min. The only difference in the seven reactions was the amount of SLS added during the feed stage. In the first reaction, no SLS was added. In the other six reactions, the amount of added SLS was increased from 0.807 to 8.750 g, such that the total weight ratio (including both the seed and feed stages) of SLS based on the monomer was varied: 0.7, 1.0, 1.4, 1.7, 2.0, 2.5, and 3.6%, respectively. In the following discussion, the semibatch reactions are labeled as semi-0.7% (semi stands for semibatch emulsion polymerization, 0.7% stands for the total weight ratio of SLS based on BMA), semi-1.0%, semi-1.4%, semi-1.7%, semi-2.0%, semi-2.5%, and semi-3.6%, respectively.

Characterization

The conversion of monomer to polymer of each sample was determined gravimetrically. Dynamic light scattering (Nicomp 370, Pacific Scientific) was used to determine the particle size. To estimate the surfactant (SLS) surface coverage of the PBMA particles, serum from each sample was obtained using a stirred filtration cell equipped with a size exclusion membrane (GE Water & Process Technologies, with a pore size of 0.1 μm and membrane diameter of 76 mm). The surface tension of each serum sample was measured using a tensiometer, which works on the DuNoüy Ring method (Autotensiomat, Fisher Scientific). A calibration curve (surface tension vs. SLS concentration) was established to calculate the free SLS concentration in the aqueous phase. Then, the difference between the SLS concentration in the recipe and in the aqueous phase could be calculated, which represents the amount of SLS adsorbed on the surfaces of the latex particles. 54 $\text{\AA}^2/\text{molecule}$ was used as the area covered per SLS surfactant molecule at surface saturation in the PBMA-SLS system^{10,11} and the surfactant surface coverage could be estimated.

Latex Stability Tests

Based on ASTM (American Standard Test Methods) D1417-03D,¹² a blender test was used to determine the mechanical stability of the final latexes. A Hamilton Beach blender was used and the agitation speed was ~ 8000 rpm. The prepared latexes (200 g) were directly used for this test without any dilution. For the latexes prepared by batch emulsion polymerization, the blender test was run for 20 min. The blender was stopped every 5 min and a sample was taken through a long plastic pipette from the liquid phase present at the bottom of the blender. The solids content of each sample was measured gravimetrically and the percent coagulum was calculated. Owing to the high solids content and viscosity of the latexes prepared in the semibatch emulsion polymerizations, the blender test was run for only 5 min. Because water was trapped in the coagulum, it was difficult to isolate the water phase from the samples after this test was complete. Under this condition, the samples obtained after the blender test was complete were washed using DI water with agitation (magnetic stir bar) to remove the entrapped and uncoagulated particles that were adsorbed on the surfaces or inside of the coagulum. Then, a 100- μm mesh screen was used to filter out the coagulum. The mesh holding the coagulum was dried in an oven at 90°C for 24 h to remove any entrapped

water. The percent coagulum was calculated based on the dried coagulum weight.

Turbidity measurements were carried out at room temperature to evaluate the electrolyte stability of the synthesized latexes. The kinetics of coagulation was established based on the measurement of the slope of the optical density (OD) versus time curves obtained using a Shimadzu UV-2101PC spectrophotometer at a wavelength of 600 nm after adding varying amounts of KCl electrolyte. The stability ratio (W), which is defined as the ratio of the rate of rapid to slow coagulation, as well as the critical coagulation concentration (ccc), can be calculated as described in our previous article.⁸

RESULTS AND DISCUSSION

Batch Emulsion Polymerizations of BMA

The conversion-time curves for the batch emulsion polymerizations of BMA are shown in Figure 3, where the expected increase in overall polymerization rate is observed with increasing surfactant concentration. Corresponding to these curves, the particle size (Table III) decreased as the SLS concentration increased, as expected, based on the classical theory of emulsion polymerization (Smith–Ewart theory).¹³ The particle size distributions (PDI) were narrow for all of the latexes no matter whether the SLS concentration was below, equal to, or above the CMC. The polymerization rates of reactions B-20%-30 mM and B-20%-20 mM were fast and finished within 10 min. On the other hand, the reactions (B-20%-5 mM and B-20%-6 mM) carried out with the SLS concentration below the CMC were relatively slow, especially in the early stages of the reactions. For all reactions, no coagulum was found in the latexes, and the amount of coagulum adsorbed on the surfaces of the reactor, probes, and impeller was negligible. These reactions can be considered to be successful stable reactions.

The evolution of conductivity during all reactions was measured using both the homemade resistance and torroidal probes. The

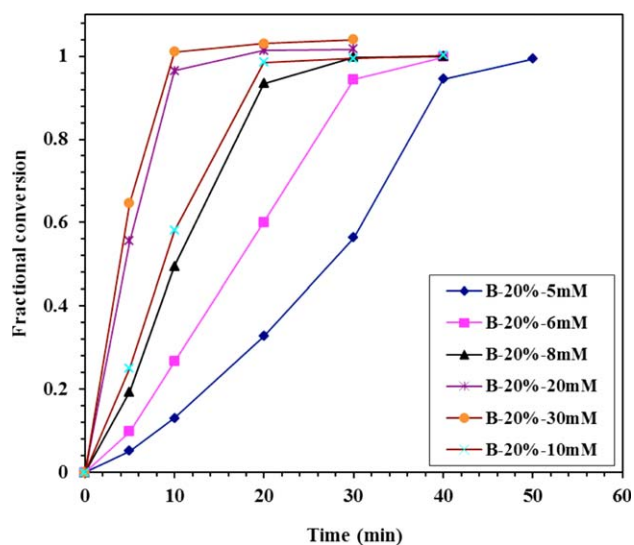


Figure 3. Fractional conversion versus time curves for the batch emulsion polymerizations of BMA at 70°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Particle Size Obtained from the Batch Emulsion Polymerizations (20% Solids Content) of BMA

	D_N (nm) ^a	D_W (nm) ^a	PDI ^a
B-20%-5 mM	212	212	1.00
B-20%-6 mM	162	174	1.07
B-20%-8 mM	138	153	1.11
B-20%-10 mM	120	124	1.03
B-20%-20 mM	92	103	1.12
B-20%-30 mM	85	93	1.09

^a D_N = number-average particle size; D_W = weight-average particle size; PDI = polydispersity index = D_W/D_N .

profiles are shown in Figure 4 along with the corresponding conversion-time curves. It can be seen that there is little agreement between the two conductivity curves for each reaction except near the ends (high conversion) of reactions B-20%-20 mM and B-20%-30 mM [Figure 4(e,f)], which employed the two highest surfactant concentrations. The conductivity values measured with the torroidal probe were higher (with the exception of reaction B-20%-30 mM) than those measured with the homemade conductivity probe. In the case of the homemade conductivity probe, the conductivity increased in the first minutes of reaction, then decreased quickly. A second increase then occurred, which is apparently related to the conversion rather than time, followed by a plateau at high conversion.

The results obtained in this study differ from those shown in our previous article,⁸ in which the conductivity was measured with a commercial resistance probe. The conductivity values obtained from the homemade resistance and torroidal probes were not the same at time = 0 (before initiating the reactions) and the values obtained from the homemade resistance probe were lower than those obtained from the torroidal probe. This was not caused by any coagulum that was deposited on the surfaces of the electrodes because the reaction had not yet begun, but by the presence of the monomer droplets. Since the monomer (BMA) itself has no electrical conductivity, the monomer droplets dispersed in the continuous aqueous phase act as insulators. These dispersed insulators can interrupt the movement of the ionic species present in the emulsion system, which can affect the current lines passing between the two electrodes. As mentioned previously, the homemade resistance probe has a back-to-back configuration and works with relatively long current lines, which is different from the commercial resistance probe used previously, which had a face-to-face configuration and a short pathway between the two electrodes. The effect of the monomer droplets on the conductivity measurements obtained from the homemade probe are much more significant compared with the commercial probe. To illustrate this phenomenon, a simple experiment was run and the results are presented in Figure 5. In this experiment, the torroidal, commercial, and homemade resistance probes were used to measure conductivity simultaneously. Five hundred grams of DI water, 20.28 g of 0.24M NaCl solution, 81.73 g of 0.07M SLS solution, and 150 g BMA monomer were charged into the reactor at

70°C and stirred at 250 rpm. Before adding monomer, the homemade resistance probe exhibited the same conductivity values as the other two probes. However, after the addition of 35 g of the monomer, the values obtained from the homemade resistance probe decreased and were slightly lower than the other two probes. As more monomer was added, the curve obtained from the homemade resistance probe showed a significant decrease and was much lower than the other two curves. This resulted from the insulating behavior of the monomer.

From the conductivity results in Figure 4, it can be seen that there were obvious differences between the two conductivity curves at the end of the reactions for reactions B-20%-5 mM, B-20%-6 mM, B-20%-8 mM, and B-20%-10 mM. On the other hand, the final conductivities obtained from the two probes were not significantly different for reactions B-20%-20 mM and B-20%-30 mM. Because the divergence occurred during reactions B-20%-8 mM and B-20%-10 mM, in which the SLS concentrations (8 and 10 mM) were in the vicinity of the CMC of SLS, these results prove that the differences between the two conductivity curves are not related to the CMC, but are caused by polymer deposited on the surfaces of the electrodes, which may be related to the stability of the latexes. Since the difference between the final conductivities obtained from the two probes changed with the variation of the SLS concentration, this experiment shows that the homemade resistance probe has good sensitivity. Moreover, all reactions were run at least three times and the conductivity results showed good repeatability. These results prove that this homemade resistance probe can be used to measure conductivity changes that occur during the emulsion polymerization process.

During these batch emulsion polymerizations, the conductivity curves obtained using the homemade resistance probe exhibited two increases as noted previously. The first increase in conductivity occurred at the very beginning of each reaction and was caused by the addition of KPS initiator, an electrolyte. The second increase occurred in the middle of the reactions. The exact reason for this phenomenon is not certain. Some explanations have been given in prior research. For example, Santos et al.⁴ mentioned that this increase was probably caused by the monomer consumption in the medium, which could release small amounts of the surfactant back into the continuous phase. Schork and Fontenot¹⁴ also gave an explanation for this phenomenon based on a comparison of the emulsion and miniemulsion polymerizations of methyl methacrylate (MMA) using SLS as the surfactant under the same conditions. In the emulsion polymerization, the conductivity curve showed a significant increase. On the other hand, no increase was observed in the miniemulsion polymerization. They claimed that the increase corresponded to the disappearance of excess monomer (droplets) and a desaturation of the aqueous phase in the emulsion polymerization. In the miniemulsion polymerization, the monomer droplets become the polymer particles and there is no corresponding disappearance of monomer droplets. The explanations for the second increase in conductivity from these two research groups are not the same, but both groups mentioned that this increase was related to the consumption of the monomer droplets during the reactions. In our research, a

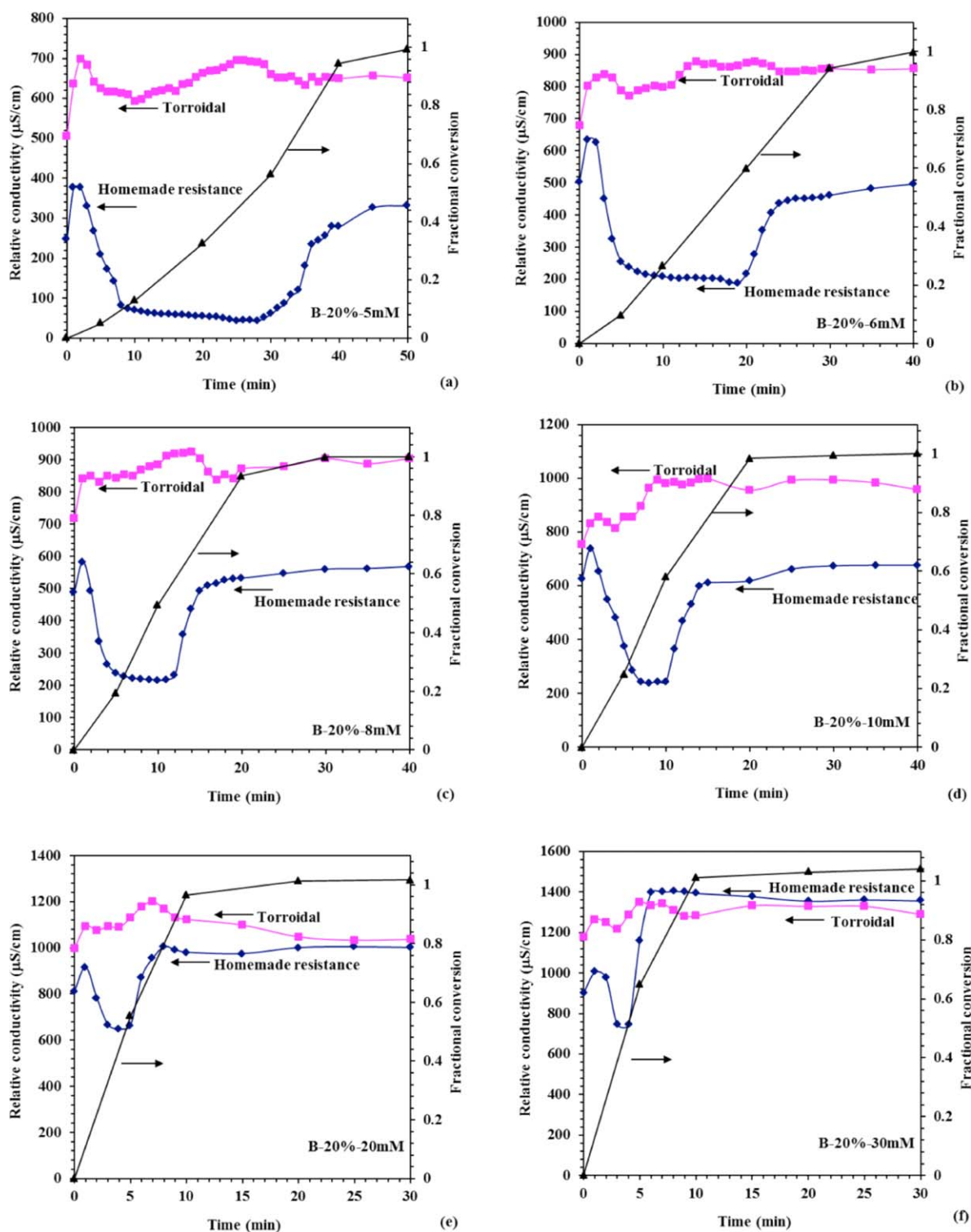


Figure 4. Relative conductivity and fractional conversion versus time curves for the batch emulsion polymerizations at 70°C: (a) B-20%-5 mM; (b) B-20%-6 mM; (c) B-20%-8 mM; (d) B-20%-10 mM; (e) B-20%-20 mM; and (f) B-20%-30 mM. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

comparison of the conductivity and kinetic curves was carried out to analyze the second increase. All of the conductivity curves obtained from the homemade resistance probe and the fractional conversion curves are combined in Figure 6. It can be

seen that all of the second increases in conductivity occurred in the same range of the fractional conversion, which was between 50 and 60%, no matter what SLS concentration was used. Based on the classical theory of emulsion polymerization, Interval II

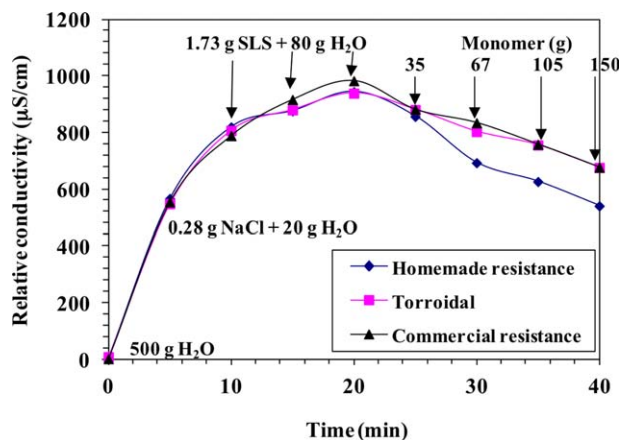


Figure 5. Effect of the presence of monomer droplets on the conductivity measurements obtained using the homemade resistance probe. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ends around 40% conversion, which corresponds to the disappearance of monomer droplets. The experimental results indicate that the second increase occurs at a conversion higher than 40% where monomer droplets are no longer expected to exist. However, if the fast reaction rate in this range and the time lag of sampling and stopping the reaction are taken into account, the real conversion at the beginning of the second increase should be very close to the conversion at the end of the second interval. Therefore, the disappearance of the monomer droplets is the most likely reason for the second increase in conductivity. Because the disappearance of the monomer droplets implies that “insulator material” is removed from the continuous aqueous phase, the interruption to the movement of the charged ionic species disappears, which causes the increase in conductivity as measured by the homemade resistance probe. As shown in Figure 4, the conductivity curves obtained from the homemade resistance probe are lower than those obtained from the torroidal probe before the second increase, which is caused by the presence of the monomer droplets as discussed previously. However, the two conductivity curves converge after this increase if the SLS concentration is high enough (20 and 30 mM) to stabilize the particles. This confirms that the disappearance of the monomer droplets is the reason for the second increase.

Blender tests were carried out to test the mechanical stability of the latexes prepared by the batch emulsion polymerizations of BMA (Table I) and the results are shown in Figure 7. Latex B-20%-30 mM had the best stability. The solids content of this latex did not decrease during the blender test, which meant that no coagulation occurred under the applied shear forces imposed by the blender blades. Latex B-20%-20 mM was stable within the first 5 min and then lost solids at a slow rate. This latex can be considered as stable even though it is not as good as latex B-20%-30 mM. The positions of latexes B-20%-10 mM and B-20%-8 mM were switched and the results were similar. The results for latexes B-20%-6 mM and B-20%-5 mM were close. All four of these latexes lost more than 30% of their solids content within 5 min and lost more than 40% solids content after this test. Therefore, they are not considered to be stable.

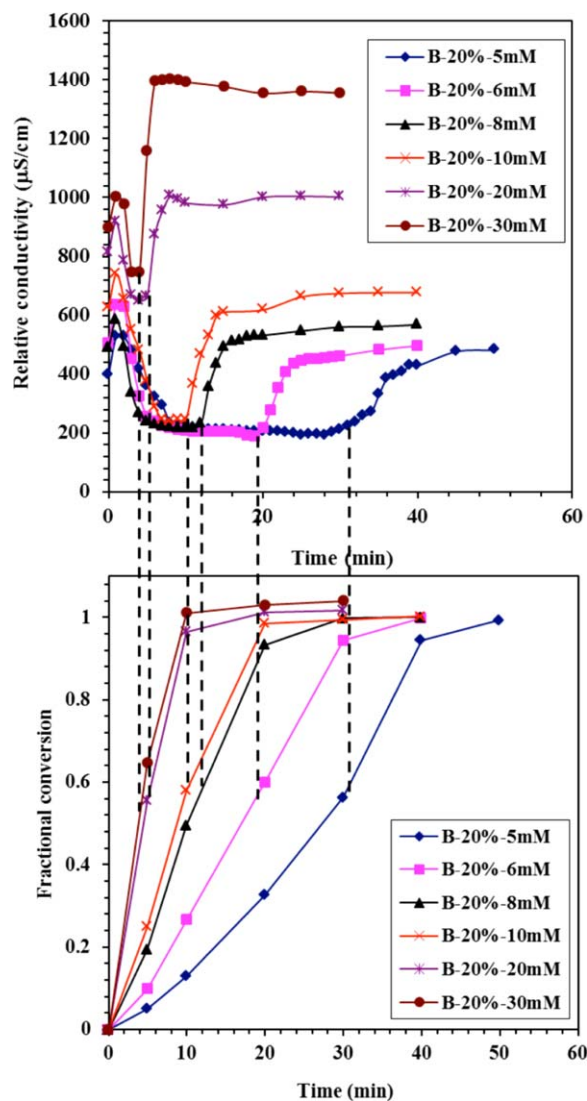


Figure 6. Summary of the conductivity curves obtained from the homemade resistance probe (top) and the fractional conversion curves (bottom) of the batch emulsion polymerizations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The ccc of the prepared latexes, estimated through turbidity measurements, are shown in Table IV. The ccc’s of latexes B-20%-5 mM and B-20%-6 mM are close. Except for these two samples, the ccc increased with the increase in the SLS concentration in the recipe. However, the differences among these results are not as significant as those obtained from the blender tests. This is most likely caused by the dilution of the latexes necessary to carry out the turbidity measurements. Some SLS molecules are released to the aqueous phase from the particle surfaces during dilution, which reduces the differences in stability among these latexes. However, the ccc values change with the variation in the SLS concentration, so the latexes still have different degrees of stability after dilution and the ccc values can be used to represent the degree of the electrolyte stability of these latexes, even though the stability of the diluted and original latexes is not exactly the same.

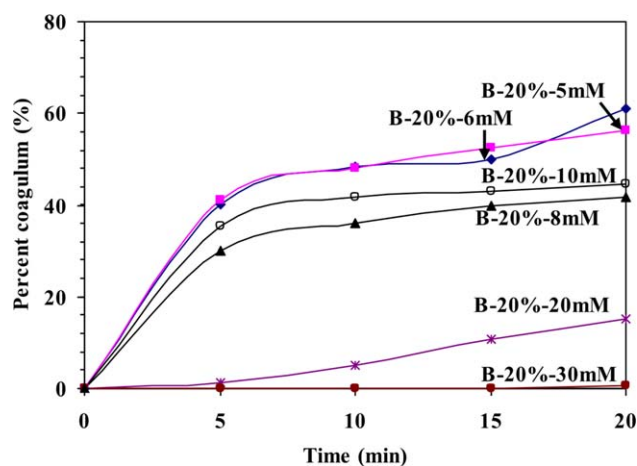


Figure 7. Percent coagulum versus time curves obtained in blender tests of the latexes prepared in the batch emulsion polymerizations of BMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Because the conductivity values obtained from the resistance probe are proportional to the surface area of the electrodes if all other parameters are fixed, the ratio of the measured conductivity value to the true conductivity value can be used to represent the degree of fouling (percent coverage) of the surfaces of the electrodes. Since plating does not affect the measurements obtained from the torroidal probe, the conductivity values measured by the torroidal probe during the emulsion polymerizations can be considered to be the true conductivity values. As discussed in our previous article,⁸ the final conductivity ratio (R/T), which is defined as the ratio between the final conductivity values obtained by the two probes (R stands for resistance probe and T stands for torroidal probe) is used to correlate the conductivity data to latex stability. Moreover, the surfactant surface coverage of each latex, which is an important parameter that affects the degree of latex stability, was also estimated based on surface tension measurements. The surface coverages of the prepared latexes from B-20%-5 mM to B-20%-30 mM were 21.3, 19.1, 23.8, 24.1, 36.5, and 48.6%, respectively.

R/T is correlated to the percent coagulum obtained in the blender test and the surface surfactant coverage as shown in Figure 8. Because both latexes B-20%-20 mM and B-20%-30 mM are stable with the R/T values close to 1, Latex B-20%-20 mM was used to represent the results. The percent coagulum

Table IV. Critical Coagulum Concentration (ccc) of the Latexes Obtained from the Batch Emulsion Polymerizations of BMA Shown in Table I

Latex	ccc (M, KCl)
B-20%-5 mM	0.527
B-20%-6 mM	0.522
B-20%-8 mM	0.550
B-20%-10 mM	0.560
B-20%-20 mM	0.616
B-20%-30 mM	0.699

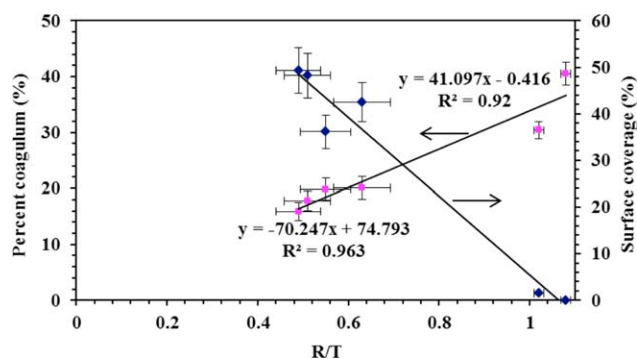


Figure 8. Correlation between the percent coagulum obtained in the blender test (5 min) and the final conductivity ratio (R/T), and the surfactant surface coverage and R/T . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

after 5 min in the blender test (Figure 7) was used in the correlation. The results show that there is a linear relationship between the percent coagulum and R/T , and the surface coverage and R/T . This indicates that online conductivity measurements can be used to predict the mechanical stability of the final latexes. Figure 9 shows the relationship between R/T and critical coagulum concentration (ccc) estimated based on the turbidity measurements (Table IV). A linear relationship is also obtained, which indicates that this method can be used to predict the electrolyte stability of the final latexes.

Semibatch Emulsion Polymerizations of BMA

Seven semibatch emulsion polymerizations of BMA were run, where only the amount of SLS was varied during the feed stage (Table II). The fractional instantaneous and overall conversions for reaction semi-0.7% are shown in Figure 10 as a function of the feed time. It can be seen that the fractional instantaneous conversions were greater than 0.95, indicating that monomer-starved conditions were achieved. A high overall conversion was reached indicating that the reaction proceeded as designed. The particle size data is reported in Table V. Because the only difference among these reactions is the variation of the added SLS amount during the feed stage, the particle size of these latexes should theoretically be the same. The results show that the particle size of these latexes varied over a small range. Furthermore,

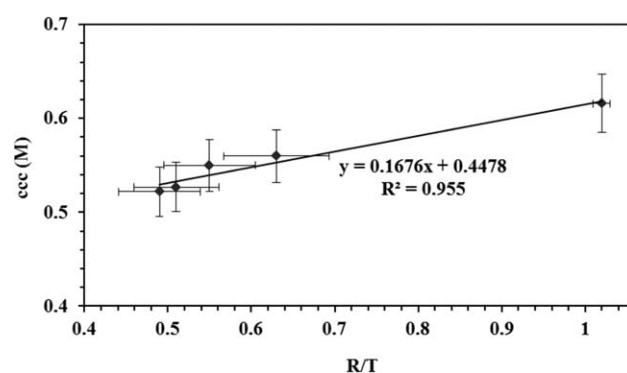


Figure 9. Correlation between the critical coagulum concentration (ccc) estimated from turbidity measurements and the final conductivity ratio (R/T).

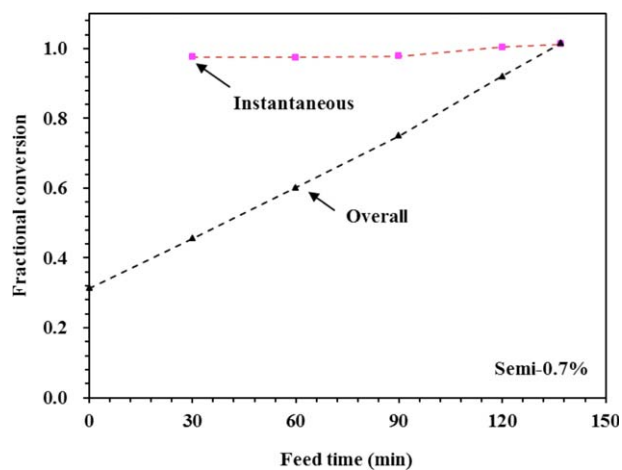


Figure 10. Fractional instantaneous and overall conversions versus feed time for reaction semi-0.7%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the PDI's indicate that the distributions were relatively narrow. These results demonstrate that no secondary nucleation occurred during the feed stage, which means that the added amounts of SLS were not excessive. After these reactions were complete, no coagulum was observed in any of the latexes. The amount of coagulum adsorbed on the surfaces of the probes, impeller, and reactor was negligible.

Figure 11 shows the conductivity recorded during reaction semi-0.7%. It can be seen that the two conductivity curves almost overlap at the end of the seed stage, as in batch Reaction B-20%-20 mM [Figure 4(e)]. At the very beginning of the feed stage, the conductivity curve obtained using the homemade resistance probe exhibited an obvious decrease in conductivity and the curve obtained from the torroidal probe exhibited a small increase. These phenomena resulted from two different causes. The former should be related to the processes of diffusion and swelling of monomer in the polymer particles, while the latter is related to the change in liquid volume. At the end of the seed stage, there was no monomer remaining; at the beginning of the feed stage, monomer was introduced into the system and the presence of the monomer droplets influenced the measurements from the homemade resistance probe as discussed previously since the monomer droplets act as insulators. As the monomer diffused through the aqueous phase, swelling

Table V. Particle Size Obtained from the Latexes Produced in Semibatch Emulsion Polymerizations of BMA (Table II)

	D_N (nm)	D_W (nm)	PDI
Semi-0.7%	95	107	1.13
Semi-1.0%	110	117	1.06
Semi-1.4%	95	107	1.12
Semi-1.7%	111	118	1.06
Semi-2.0%	102	111	1.09
Semi-2.5%	97	109	1.12
Semi-3.6%	96	108	1.12

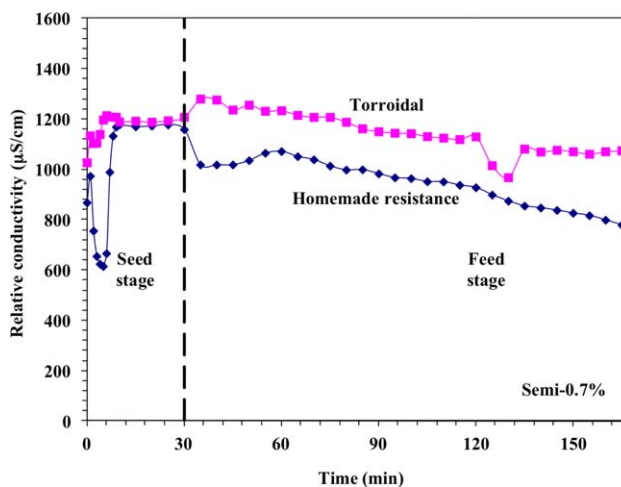


Figure 11. Relative conductivity versus time curves for reaction semi-0.7%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the latex particles, and was subsequently consumed in the polymerization reactions, the effect on the measurements of the homemade resistance probe was decreased because the monomer feed rate was slower than the monomer reaction rate. Therefore, the conductivity curve obtained from the homemade resistance probe exhibited an increase in conductivity following the first decrease (40–60 min in Figure 11).

Another experiment was carried out to illustrate these processes. Ten grams of BMA monomer was added to 500 g of latex B-20%-30 mM under agitation at room temperature. As shown in Figure 12, the conductivity values obtained from the two probes were similar before the addition of monomer. Both curves showed a decrease in conductivity after monomer addition. However, the curve obtained from the torroidal probe only decreased slightly while a sharp decrease occurred for the one obtained from the homemade resistance probe. Because the torroidal probe works on an induction principle, the monomer droplets do not significantly affect the measurements obtained

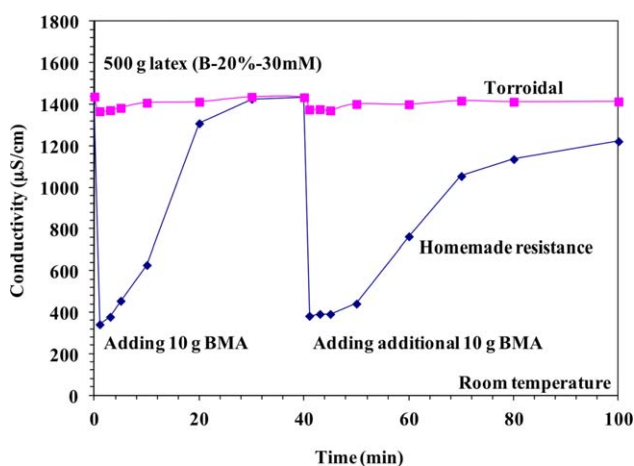


Figure 12. Effect of monomer addition on the conductivity measurements. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

using this probe, which means that the slight decrease obtained from this probe reflected the true decrease in conductivity by the addition of monomer. However, the conductivity curve obtained from the homemade probe decreased to a low value and then increased gradually as time passed. This showed the effect of the transfer of monomer from the droplets to the polymer particles. During this process, the number and size of monomer droplets decreased as the monomer swelled the particles, so the effect on the measurements of the homemade resistance probe decreased and the measured values increased. When the added monomer was totally absorbed by the particles, the monomer droplets disappeared from the aqueous phase, which caused the two conductivity curves to overlap. This process took 40 min. When 10 g of additional BMA monomer was added, a similar process occurred. Because the monomer concentration reached saturation in the particles, some monomer droplets remained after 100 min and the conductivity values obtained from the homemade resistance probe were lower than the true values.

Returning to Figure 11, the increase in the conductivity curve obtained using the toroidal probe at the very beginning of the feed stage was caused by a change in the liquid volume. Because the liquid level in the seed stage just covered the head of the toroidal probe, as required to obtain correct measurements with this probe, at the beginning of the feed stage, a small change in the liquid volume would affect the magnetic field, which would result in a change in the conductivity measurements of the toroidal probe. Therefore, the divergence, which occurred at the very beginning of the feed stage, was caused by the effect of the changes in the reactive system on the measurements obtained from the probes and was not related to plating or latex stability.

The results of the other six semibatch reactions are shown in Figure 13. From these figures, it can be seen that the changes in the amount of SLS used in these reactions affected the shapes of the conductivity curves. At the end of the reactions, the differences between the two conductivity curves became smaller as the SLS concentration increased. With increased amounts of surfactant added during the feed stage, the stability of the latex increased. The gaps between the two conductivity curves are related to latex stability. However, during these reactions it was hard to judge when the divergence occurred owing to the interruptions in the measurements at the beginning of the feed stage, which was discussed previously.

The final conductivity ratios (R/T) were calculated to investigate the relationship between the conductivity data and latex stability. However, the degree of divergence shown in Figure 13 was not as significant as those found in the batch emulsion polymerization system (Figure 4). The R/T values were greater than 0.9 in the four cases having the highest surfactant concentration, which implied that only a small portion of the electrodes was covered by polymer during the semibatch polymerizations. This was caused by the higher viscosity of the latexes brought about by the high solids content (40%). As shown in Figure 14 (left), viscous latex was found on the surfaces of the combined conductivity probes at the end of reaction

semi-0.7%. However, most of the material on the electrodes is not a result of plating or coagulated particles. It can be removed easily by rinsing and the degree of the actual plating is not high [Figure 14 (right)]. Because the adsorbed viscous latex may act as a membrane and prevent the further deposition on the surfaces of the electrodes, the differences in divergence among these reactions are not as significant as those shown for the batch polymerization systems.

Since the R/T values are relatively high as discussed above, it is possible that the small divergence is caused by experimental errors instead of plating. To test this, another conductivity ratio was also determined. After each semibatch reaction, the combined probes were rinsed with DI water and put into a standard KCl solution. The conductivity was then recorded using the homemade resistance probe. After soaking in toluene and followed by acetone and DI water, the homemade resistance probe was again used to measure the conductivity in the same standard electrolyte solution. The ratio between the measured conductivity values before and after cleaning was calculated. To distinguish between the two types of conductivity ratios, the one between the final values of the two probes at the end of the semibatch reactions was termed the “dynamic ratio”; the other between the conductivity values of the same solution measured using the “dirty” and “clean” homemade resistance probe is called the “static ratio.” The results are listed in Table VI. It can be seen that the values are close, indicating that plating is indeed the cause of the R/T values being lower than unity.

The 5-min blender test was applied to all the final semibatch latexes (40% solids content). The percent coagulum for each sample is reported in Table VII. For the two samples having the lowest amounts of fed SLS (semi-0.7% and semi-1.0%), the results were 32.7% and 29.5% coagulum, indicating that these latexes were not stable. For the samples having the highest amounts of fed SLS (semi-2.5% and semi-3.6%), a great deal of foam formed during the tests. Little coagulum was found attached to the surfaces of the blade and no coagulum was evident in these latexes indicating that these latexes were stable. Figure 15 shows a comparison of the blender blade before and after the blender test for samples semi-1.0% and semi-2.5%. The obvious difference in the amount of coagulum on the blades can be seen, which illustrates the difference in the stability between these two samples. The other three samples (semi-1.4%, semi-1.7%, and semi-2.0%) exhibited intermediate levels of coagulum.

Turbidity measurements were again used to estimate the electrolyte stability of these latexes and the surface coverages of these latexes were also estimated. These results are summarized in Table VII. As expected, the latex stability increases with the increase in the surfactant surface coverage. These results are consistent with the blender test results.

The correlation between the conductivity data and latex stability was investigated. Because the conductivity ratio (R/T) measured statically (static ratio shown in Table VI) is more reliable, this data was used to represent the degree of plating on the surfaces of the electrodes of the homemade resistance probe. The correlations are shown in Figures 16 and 17. Similar to the previous

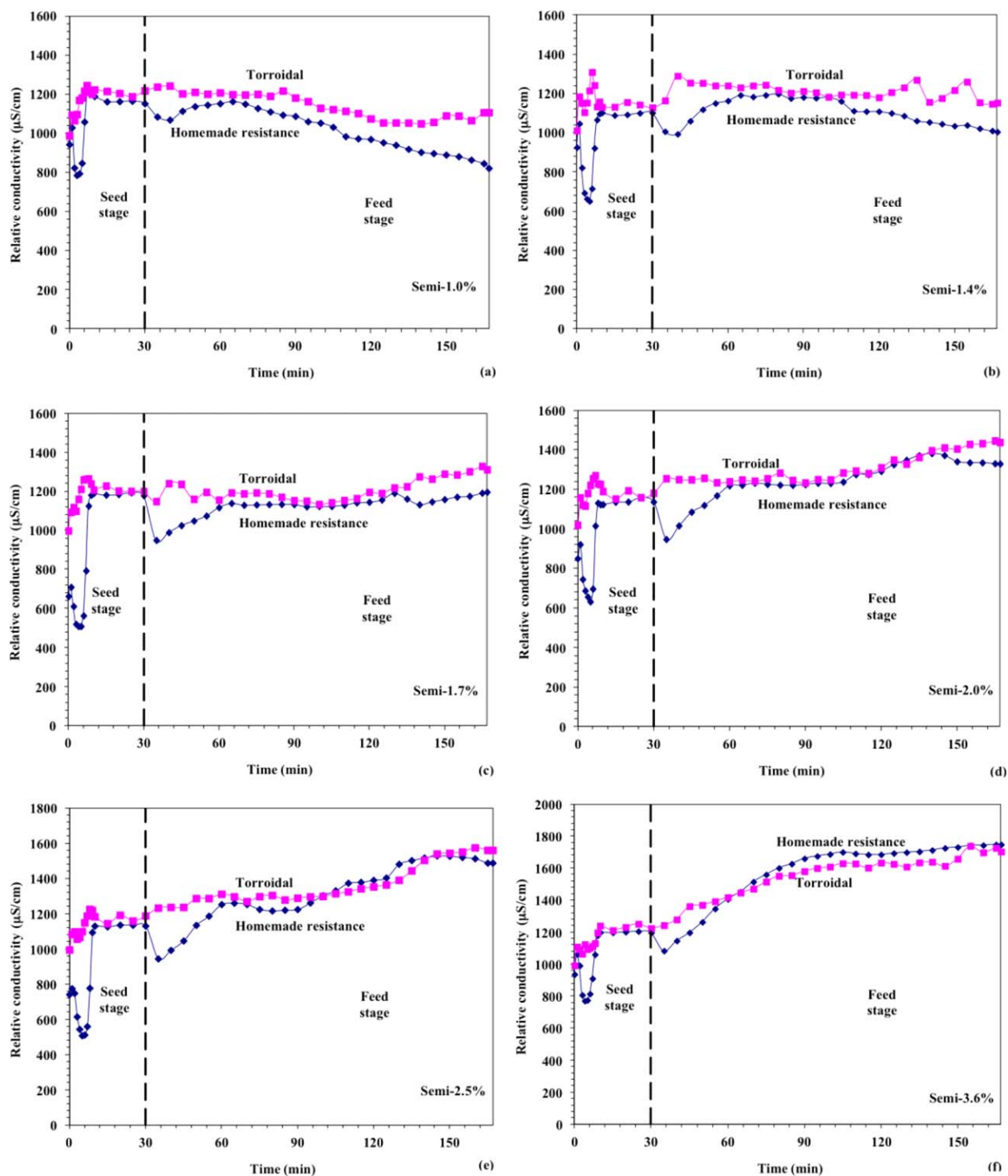


Figure 13. Relative conductivity versus time curves for the other six semibatch reactions: (a) semi-1.0%; (b) semi-1.4%; (c) semi-1.7%; (d) semi-2.0%; (e) semi-2.5%; and (f) semi-3.6%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

results (Figures 8 and 9), there is a linear relationship between the mechanical stability and static R/T , and the electrolyte stability and static R/T . These results indicate that the online conductivity measurements can be used to predict latex stability. Since semibatch emulsion polymerizations are widely used in industry, the results show that it is possible for this method to be applied in industrial processes.

CONCLUSIONS

Online conductivity measurements were carried out during the batch and semibatch emulsion polymerizations of BMA using both a homemade resistance probe as well as a torroidal probe. The conductivity profiles obtained from the two conductivity probes changed with the variation of the SLS concentration. A

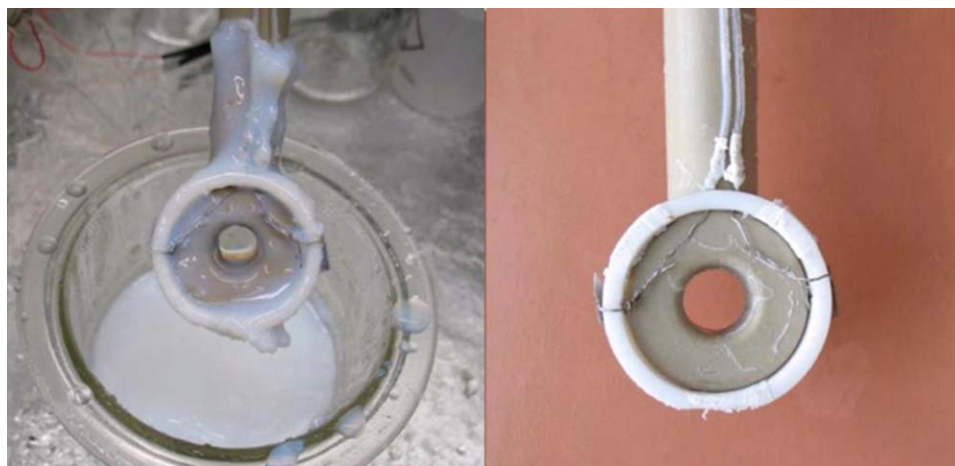


Figure 14. Photographs of the combined conductivity probes taken right after reaction semi-0.7% (left) and after rinsing and drying (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table VI. Dynamic Ratio and Static Ratio of the Conductivity Measurements (R/T)

Reaction	Dynamic ratio	Static ratio
Semi-0.7%	0.715	0.689
Semi-1.0%	0.742	0.711
Semi-1.4%	0.871	0.857
Semi-1.7%	0.912	0.914
Semi-2.0%	0.924	0.916
Semi-2.5%	0.954	0.952
Semi-3.6%	1.026	0.964

Table VII. Percent Coagulum, Critical Coagulation Concentration (ccc), and Surface Coverage of the Latexes Prepared by Semibatch Emulsion Polymerization (Table II)

Latex	Percent coagulum (%)	ccc (M, KCl)	Surface coverage (%)
Semi-0.7%	32.7	0.471	14.0
Semi-1.0%	29.5	0.566	20.5
Semi-1.4%	12.7	0.590	27.3
Semi-1.7%	11.2	0.675	36.6
Semi-2.0%	4.9	0.741	40.9
Semi-2.5%	0.5	0.777	50.9
Semi-3.6%	0.2	0.787	73.3

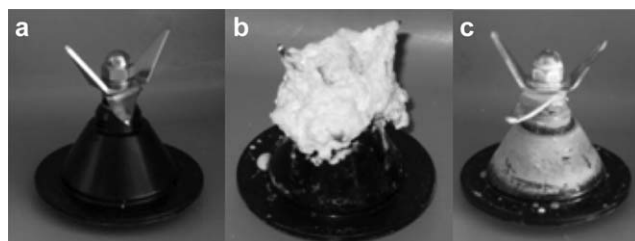


Figure 15. Comparison of the blender blade before (a) and after the blender test: latex semi-1.0% (b) and latex semi-2.5% (c).

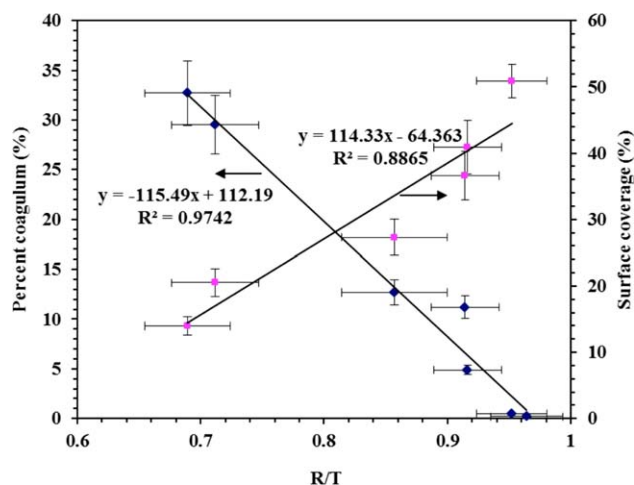


Figure 16. Correlation between the percent coagulum obtained after the blender test and the static conductivity ratio (R/T), and the surface coverage and R/T . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

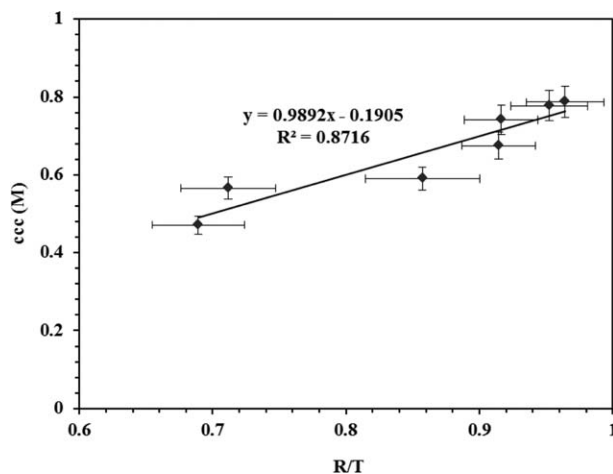


Figure 17. Correlation between the critical coagulation concentration (ccc) estimated by the turbidity measurements and the static conductivity ratio (R/T).

divergence between the two conductivity curves occurred in most of the reactions. This was caused by some coagulum plating on the surfaces of the electrodes of the homemade resistance probe, which decreased the exposed surface area of the electrodes and lowered the measured conductivity values. Therefore, the inaccuracy of the data obtained from the homemade resistance probe was considered to be related to the latex stability. Blender tests and turbidity measurements were applied to check the mechanical and electrolyte stability of the prepared latexes. The percent coagulum and the ccc were used to represent the degree of latex stability, which was correlated to the final conductivity ratio (R/T) between the two conductivity curves. The results indicate that a linear relationship between R/T and latex stability exists, which means that the conductivity measurements can be used as an online tool to monitor latex stability during the batch and semibatch emulsion polymerizations and predict the mechanical and electrolyte stability of the final latexes. In the batch emulsion polymerizations, the reason for the second increase in the conductivity obtained from the homemade resistance probe was also investigated. The results show that this increase is related to the disappearance of the monomer droplets. This means that the online conductivity measurements can also provide additional information to study the kinetics of emulsion polymerization process.

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