# Toward an Understanding of the Role of Water-Soluble Oligomers in the Emulsion Polymerization of Styrene–Butadiene–Acrylic Acid. Function of Carboxylic Acid

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**ABSTRACT:** In a further effort to understand the role of water-soluble oligomers formed during the emulsion terpolymerization of styrene/butadiene/acrylic acid (St/Bu/AA), the reaction temperature, initiator concentration, and ionic strength were varied and the kinetics and resulting oligomers were characterized as a function of reaction time. The rate of polymerization ($R_p$) was observed to increase with increasing temperature and initiator concentration; the reasons for this vary. The increase in $R_p$ with increasing initiator concentration is mainly attributed to the increase in the number of oligomeric radicals formed and, subsequently, the resulting number of particles ($N_p$). Increasing the temperature increases the water solubility of both monomers and polymers, which results in changes in the composition and molecular weight of the oligomeric radicals being formed. The primary reaction locus in the St/Bu/AA system was noted to shift to the aqueous phase after most of the styrene and butadiene had reacted, based on the unreacted AA profile. The role of water-soluble oligomers (both oligomeric radicals and dead oligomers) during the emulsion polymerization of St/Bu with acrylic acid can be described by three periods: (1) particle generation and (2) before and (3) after the critical surface saturation concentration (CSSC) is reached during the particle growth period. The incorporation of AA monomer into the oligomer chains after the CSSC may cause destabilization of the latexes through a bridging flocculation mechanism. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1988–1999, 2003

**Key words:** oligomers; carboxylated styrene/butadiene latex; emulsion polymerization; kinetics (polym.); particle nucleation

## INTRODUCTION

An important class of industrial emulsion polymer systems involving water-soluble monomers is carboxylated latexes. They are widely used in paper coatings, textile coatings, and adhesives. The locations of the carboxyl groups in the latex system have been noted to significantly affect the final latex properties. The uncharged carboxyl groups can form hydrogen bond associations with each other or with water (water hydrate) in a latex system; therefore, they could stabilize or destabilize the particles, depending on which form of hydrogen bonding occurs. A number of publications discuss the effect of the incorporation of carboxylic monomers and their influence on particle stabilization, particle morphology, and partitioning of the carboxyl groups. These works are typically focused on the final latexes. The experimental characterization of the aqueous phase species during the polymerization was previously carried out for the styrene/acrylic acid copolymerization system by Wang and Poehlein.[1] However, questions remain, such as: What is the real role of the carboxylic acid monomer at the beginning of the reaction (i.e., the particle generation period)? How and where are these monomers incorporated into the latex particles? How they contribute to the hydrophilic–hydrophobic balance of the latex particle surface is still not truly understood.

A model industrial emulsion polymerization system containing styrene (St), butadiene (Bu), and acrylic acid (AA) monomers is being investigated in this research. The goal is to experimentally investigate the formation and characteristics of water-soluble oligomers produced during emulsion polymerization and their relevance to the kinetics and mechanisms of particle nucleation and growth by characterizing the low molecular weight species found in the aqueous phase throughout the reaction.

In the previous study,[2] the development of a series of techniques was described and used to quantitatively characterize the free water-soluble oligomers found in the aqueous phase. The formation of water-soluble oligomers and their relevance to the kinetic behavior of model systems with different AA concen-

trations were investigated. The formation and characteristics of the water-soluble oligomers produced during the emulsion polymerization process will be further examined in this study based on the experimental results obtained by varying the reaction temperature, initiator concentration, and ionic strength. Subsequently, the role of water-soluble oligomers in the aqueous phase for the St/Bu/AA emulsion polymerization system are discussed.

## EXPERIMENTAL

### Materials

Acrylic acid (AA) monomer ($CH_2$=$CHCOOH$, MW = 72.06 g/mol, 99% active) inhibited with 200 ppm 4-methylhydroquinone (MHQ; Aldrich, Milwaukee, WI) was distilled under vacuum at about 10 mmHg and 39°C vapor temperature to remove the inhibitor. The purified acrylic acid was stored at about 14°C under running tap water. Storage at a lower temperature (<13°C) would freeze the liquid. Styrene (St) monomer [$CH_2$=$CHC_6H_5$, inhibited with 55 ppm $p$-t-butyl catechol (Aldrich)] was passed through activated aluminum oxide (Brockmann I Standard grade, basic, ~ 150 mesh, 58 Å, 155 m²/g surface area, Aldrich) to remove the inhibitor. The purified styrene monomer was stored in a refrigerator at about −2°C until use. Butadiene (Bu) monomer ($CH_2$=$CH$—$CH$=$CH_2$; Air Products and Chemicals, Allentown, PA) was passed over Ascarite[e] II (sodium hydroxide–coated silica, Aldrich) to remove the inhibitor, followed by drying over Drierite (Fisher Scientific, Pittsburgh, PA). The butadiene monomer was then condensed in a cold trap immersed in a mixture of isopropanol (Aldrich) and liquid nitrogen just before use. Sodium lauryl sulfate [SLS, $CH_3(CH_2)_{11}SO_4Na$, MW = 288.4 g/mol; Texapon K-1296, Cognis Corp., Ambler, PA] was used as received. Potassium persulfate (KPS, $K_2S_2O_8$, MW = 270.33 g/mol; 99+%, A.C.S. reagent; Aldrich) was used as the initiator. 4-Methyl hydroquinone (MHQ, $CH_3OC_6H_4OH$, MW = 124 g/mol; 99%, purified grade; Aldrich) was used as received. Distilled-deion-

### TABLE I
### Model Recipe Used for the Synthesis of St/Bu/AA Latex[a]

| Component | Amount (g) |
|---|---|
| Distilled deionized water | 21.66 |
| Sodium lauryl sulfate (SLS) | 0.22 |
| Styrene (St) | 5.22 |
| Butadiene (Bu) | 3.90 |
| Acrylic acid (AA) | 0.38 |
| Potassium persulfate | 0.019[b] |

[a] Monomers (mol %): Bu/St/AA = 57/39/4; total solids (wt %) = 30; oil/water ratio (wt) = 1/2.4 [SLS] = 32 m$M$ (cmc = 9 m$M$ in pure water at 70°C).
[b] [I] = 3.17 m$M$, based on water.

### TABLE II
### Synthesis Conditions

| System | $T$ (°C) | [I] (m$M$) | [SLS] (m$M$) | [AA] (mole %) | Notes |
|---|---|---|---|---|---|
| 1 | 70 | 3.17 | 32 | 4 | [I] |
| 2 | 80 | 3.17 | 32 | 4 | |
| 3 | 70 | 6.34 | 32 | 4 | 2[I] |
| 4 | 70 | 3.17 | 32 | 4 | [I] + KCl (6.34 m$M$) |

ized (DDI) water was boiled for 15 min and cooled to room temperature while bubbling nitrogen gas to remove dissolved oxygen that might inhibit the reaction. High purity nitrogen gas ($N_2$, zero grade; JWS Technologies, Folsom, CA) was used throughout.

### Polymerization procedures

Batch emulsion polymerizations were carried out in glass pressure bottles as described in the previous study.[2] The reaction was stopped by injection of MHQ solution. The synthesis process and the measurement of conversions (gravimetrically) are also described in detail in the preceding study.[2] The synthesis of latexes reported in this investigation was based on the model recipe shown in Table I, with certain adjustments in the recipe and the reaction conditions by varying the temperature (70 and 80°C), initiator concentration ([I] = 6.34 m$M$ and [I] = 3.17 m$M$ + 3.17 m$M$ KCl = 6.34 m$M$), and ionic strength ([I] = 3.17 m$M$ and [I] = 3.17 m$M$ + 3.17 m$M$ KCl = 6.34 m$M$). The four systems are listed in Table II.

### Particle size measurements

The average particle diameter was measured using transmission electron microscopy (TEM, Phillips 400). Before TEM examination, the unreacted monomers were removed from the latexes using a rotary evaporator, and the particles were negatively stained using uranyl acetate to enhance their contrast, especially at low conversions. A cold-stage sample holder, cooled by liquid $N_2$, was used to harden the particles during the measurements [$OsO_4$ staining could not be used in the very early stages of the polymerization (<5% conversions) because of some hindered access of the $OsO_4$ to the particles created by a high carboxylic group concentration at the particle surface]. Typically, 1000 to 1500 particles were measured on the micrographs with a Zeiss Mop-3 Analyzer. The volume-average diameter $D_v$ (nm) was determined from these measurements, which was then used to calculate the number of particles $N_p$ (per liter) as follows:

$$N_p = \frac{6X(M/W)}{\pi \rho D_v^3} \tag{1}$$

where $X$ is the fractional conversion, $(M/W)$ is the initial monomer-to-water weight ratio, and $\rho$ is the polymer density ($\rho = 0.98$ g cm$^{-3}$).

### Serum composition

As described in detail previously,[2] the aqueous phase was separated from the particle phase by ultracentrifugation at optimized separation conditions: 37,000 rpm and 4°C for 36 h. The clear serum was concentrated using a specially designed technique[2] and $^1$H-NMR spectra (500 MHz) were obtained by use of a Bruker AM-500 NMR spectrometer (Bruker Instruments, Billerica, MA). The $^1$H-NMR spectra were used to quantitatively measure the oligomer component concentrations, as well as the surfactant (SLS) concentration in the aqueous phase without further separation.

### Oligomer molecular weight

The molecular weight of the water-soluble oligomers in the serum was determined by aqueous phase gel permeation chromatography (GPC) as described previously.[2] The oligomer peak overlaps the peak of the neutralized AA because of the limitations in the column separation (see previous study[2]). The molecular weight at the beginning of the first peak is taken as the maximum molecular weight (MW$_{max}$), and the one at the first peak position can be taken as the molecular weight of the greatest amount of oligomeric material (MW$_{peak}$) in each serum sample.

### Unreacted acrylic acid monomer in latex

The amount of residual acrylic acid monomer in the latex was measured by a gas chromatography (GC) method as described previously.[2] Acrylic acid monomer must be preneutralized by using trimethyl phenyl ammonium hydroxide (in 0.1$M$ methanol solution) before injection into the GC instrument to avoid AA adsorption on the GC column. Dioxane was used as an internal standard. A GC chromatogram for a latex sample and the calibration curve for acrylic acid were shown in the previous study.[2]

## RESULTS AND DISCUSSION

### Influence of polymerization temperature

The rate of initiator decomposition in free-radical polymerization is a function of the reaction temperature.[3] In general, increasing the temperature of an emulsion polymerization increases the rate of initiator decomposition, which in turn increases the number of nucleated particles contributing to an increase in the overall rate of polymerization. Determining the effect
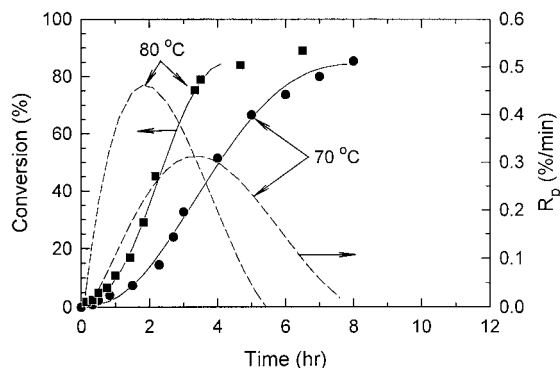


**Figure 1** Conversion (symbols, measured gravimetrically; solid lines: curve fit) and the rate of polymerization ($R_p$) versus time for the St/Bu/AA (39/57/4 mol %) emulsion polymerization system carried out for the model system: [SLS] = 32 m$M$, [I] = 3.17 m$M$, and [AA] = 4 mol % at 70 and 80°C.

of polymerization temperature on the formation and characteristics of water-soluble oligomers would be important for a better understanding of the role of water-soluble oligomers formed during the emulsion polymerization process.

### Conversion and $R_p$ versus time at 80°C

An emulsion polymerization was carried out at 80°C according to the same model recipe shown in Table I (System 2 in Table II). The kinetics and aqueous phase characterization results are compared with those obtained for the model system that was polymerized at 70°C (System 1 in Table II). The conversion and the rate of polymerization ($R_p$) versus time curves for these two systems (70 and 80°C) are presented in Figure 1. The symbols represent the percentage conversion measured experimentally, and the solid lines were obtained by polynomial curve fits. The $R_p$ curves (dashed lines) were obtained by taking the derivatives of the polynomials ($dX/dt$).

The conversion versus time curves are S-shaped, as found for many emulsion polymerizations. As expected, the reaction at 80°C proceeded at a higher rate than that at 70°C. The maximum rate of polymerization occurred at approximately 30% conversion for both reactions (the end of Interval II). Besides the increase in the propagation rate coefficients, one of the other possible reasons for the higher rate during Interval I is that more free radicals are generated by decomposition of the initiator in the aqueous phase with increasing temperature. This causes more primary particles to be formed, which results in the increase in the rate of polymerization.

In general, an increase in the rate of polymerization with temperature for systems employing monomers of low water solubility is considered to be attributable to both an increase in the rate of initiator decomposi-
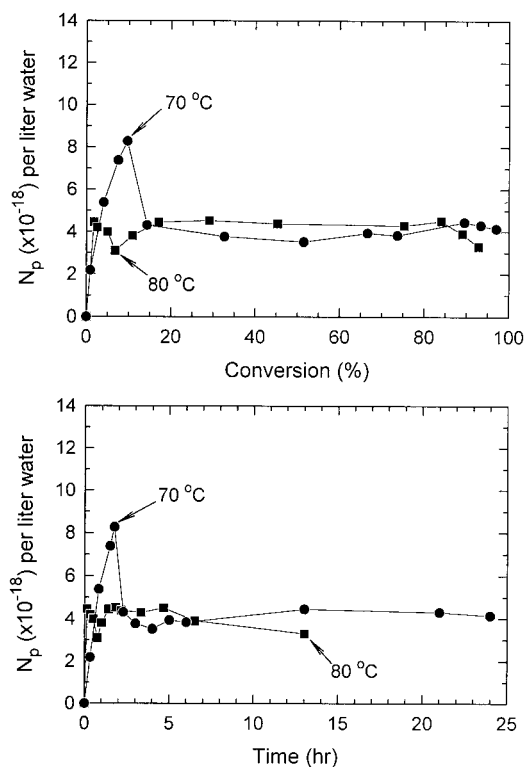
**Figure 2** Number of particles per liter of water ($N_p$) versus conversion (a, top) and time (b, bottom) for St/Bu/AA (39/57/4 mol %) emulsion polymerizations carried out at 70 and 80°C with [SLS] = 32 m$M$, [I] = 3.17 m$M$, and [AA] = 4 mol %.

tion ($k_d$) and the number of particles ($N_p$) as well as the propagation rate constants ($k_p$). However, for a system employing a high water solubility monomer (i.e., AA), the effect of temperature on $R_p$ would be more complicated because, in this case, the partitioning of monomers between the aqueous and particle phases will be changed, and the stabilization properties of the carboxyl groups must also be considered. In addition, according to Klein et al.,[4] the monomer concentration in the particle phase $[M]_p$ may be increased because of a decrease in the particle/water interfacial tension with increasing temperature. Therefore, a true understanding of the temperature dependency needs to combine all information, including the kinetics and evolution of the number of particles $N_p$, as well as the analysis of the water-soluble oligomers found in the aqueous phase.

## $N_p$ versus conversion

The numbers of particles as a function of conversion and time for the polymerizations carried out at 70 and 80°C are shown in Figure 2. In general, it would be expected that with increasing temperature, an increase in $N_p$ would be observed,[3] given that more free radicals, and thus more particles, are generated. It does

not seem to be this simple for the system containing AA. The $N_p$ versus time curve shows that $N_p$ increased slightly faster at the higher temperature (80°C) in the very early stages of the polymerization. After reaching a maximum value at about 3% conversion, it decreased sharply, which indicates that limited aggregation appeared at a much earlier stage of the polymerization than the reaction carried out at a lower temperature (70°C). These results suggest that the newly formed particles at 80°C are not as stable as those formed at the lower temperature (70°C). Therefore, they must have increased in size and surface charge density through aggregation with each other until a new equilibrium state was reached, which results in the decrease in $N_p$.

Two possible reasons can explain the early-stage limited flocculation and the increase in the final particle size with increasing temperature. One is related to the stabilization properties of the carboxyl groups, whereas the other considers the composition of the oligomeric radicals formed in the early stages of the polymerization. As mentioned earlier, according to Napper,[5] the stabilization of particles by nonionized carboxyl groups is considered to be a form of steric stabilization, which is the generic term used to describe the stability against flocculation that nonionic macromolecules impart to a dispersion of colloidal particles (e.g., polymer latexes). It was also reported that the flocculation of sterically stabilized latexes could be induced by a change in temperature,[6] or by a change in pressure,[7] or also by the addition of a nonsolvent for the stabilizer molecules.[8,9] In general, dispersions that flocculate on heating are enthalpically stabilized, and those that flocculate on cooling are entropically stabilized.[10] Furthermore, it has been noted that entropic stabilization is more common in nonaqueous media, whereas enthalpic stabilization is more frequently encountered in aqueous media,[11–13] although the preparation of aqueous entropically stabilized latexes[14] and enthalpically stabilized latexes in nonaqueous media[15] under certain solvent conditions have also been reported.

Therefore, the observed decrease in the number of particles (increasing particle size) with increasing temperature in this study might indicate that the stabilization by carboxylic acid oligomers at the particle surface is an enthalpic stabilization because the particles flocculate on heating. Evans and Napper[15] explained that the enthalpic effect may arise mainly from the dehydration of the PAA chains in the aqueous phase with heating. This means that the hydrogen-bonded water molecules (water of hydration) of the stabilizing PAA chains may be released on close approach because of the energy supplied at higher temperatures, which can cause the breakage of hydrogen bonds. However, it has also been pointed out that dehydration of the PAA chains is not the only reason

for flocculation.[16] The effect of the solvent on the solubility of the polymer chains should also be important, and can be taken as a second reason for flocculation in the early stages of the polymerization.

At both reaction temperatures, there was a constant number of particles during the middle stages of the polymerizations (i.e., from ~ 20 to 80% conversion), and the $N_p$ values were slightly higher for the polymerization at 80°C. The reason for this higher $N_p$ is not truly understood. However, a coincident result was obtained in the unreacted AA versus conversion plots for these two systems (see Fig. 8), which is discussed later; the amount of AA monomer converted to polymer was lower at 80 than at 70°C during this period. It seems that as the amount of AA monomer incorporated into the polymer is increased, the degree of coagulation will also be increased. These results might indicate that there is a dependency of the flocculation of carboxyl group stabilized particles with heating on the concentration of the carboxyl groups at the particle surface and in the aqueous phase.

On the other hand, it was also noted at 80°C that $N_p$ increased again after the early limited flocculation until the end of Interval I, and then remained almost
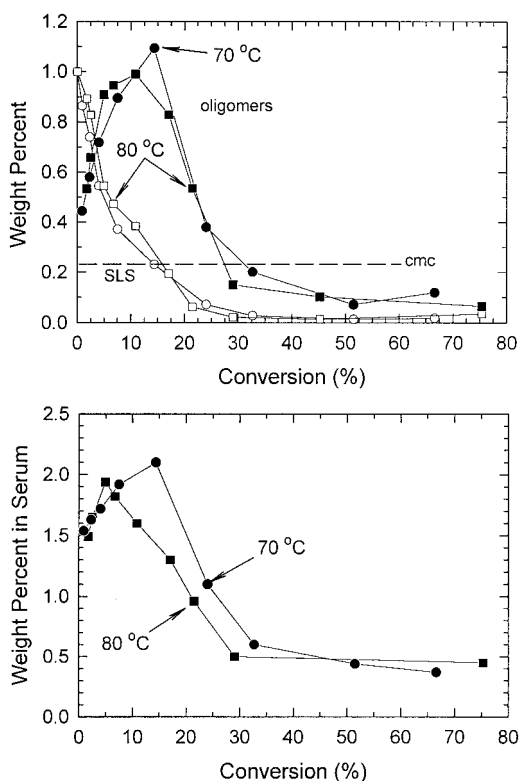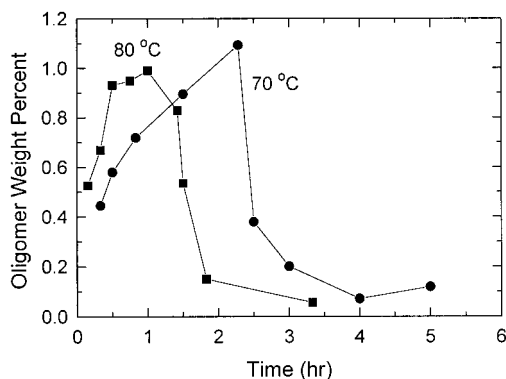


**Figure 4** Weight percentage of water-soluble oligomers in the aqueous phase (measured by ^{1}H-NMR) versus time for the St/Bu/AA (39/57/4 mol %) emulsion polymerization systems carried out at 70 and 80°C with [SLS] = 32 m$M$, [AA] = 4 mol %, and [I] = 3.17 m$M$.

constant until about 85% conversion. The reason for this second increase in $N_p$ may be explained as follows. At the higher temperature (80°C), the rate of formation of the overall particle surface area ($ds/dt$) must be rapid initially, whereas the rate of establishment of equilibrium adsorption of the surfactant on the newly formed particle surfaces ($d\Gamma/dt$) may be relatively slow, such that $d\Gamma/dt < K \, ds/dt$ (where $K$ is a constant). Therefore, a decrease in $N_p$ should occur until an equilibrium adsorption of emulsifier is established on the aggregated latex particles. More important, up to approximately 15% conversion the aqueous surfactant concentration is still above the critical micelle concentration (cmc), as shown in Figure 3(a), which indicates that micellar nucleation should continue in the system. Therefore, the rate of nucleation should still be high, thus accounting for the observed second increase in $N_p$.

### Characterization of water-soluble oligomers

Viewed from the standpoint of molecular structure, the composition and molecular weight of the oligomeric radicals formed in the early stages of polymerization should be another important factor affecting the nucleation of particles. The results obtained from aqueous phase characterization can help us better understand the problem.

Figure 3(a) shows the concentration (wt %) of water-soluble oligomers found (by ^{1}H-NMR) in the serum versus conversion for the polymerizations carried out at 70 and 80°C. It is apparent that the trend is similar for both reactions. The concentration of water-soluble oligomers increased with increasing conversion during Interval I. A faster increase can be clearly observed for the same data graphed versus time for the reaction carried out at the higher temperature, as shown in Figure 4. This indicates that the increased free-radical
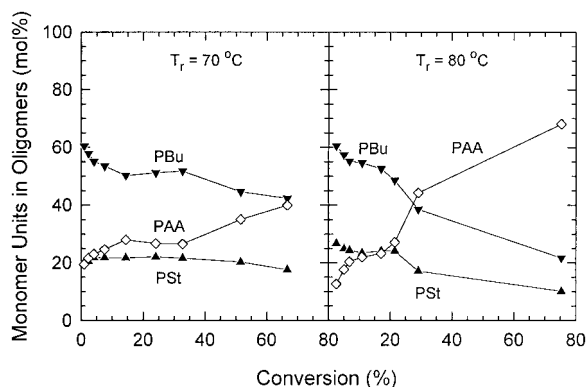




**Figure 3** Weight percentage of water-soluble oligomers (solid points) and surfactant (SLS, open points) in the aqueous phase (measured by ^{1}H-NMR) (a, top) and serum solids content (measured gravimetrically) (b, bottom) versus conversion for the St/Bu/AA (39/57/4 mol %) emulsion polymerization systems carried out at 70 and 80°C with [SLS] = 32 m$M$, [AA] = 4 mol %, and [I] = 3.17 m$M$.

**Figure 5** Mole percentage of styrene, butadiene, and acrylic acid monomer units in the water-soluble oligomers as a function of conversion for the St/Bu/AA (39/57/4 mol %) emulsion polymerizations carried out at (a) 70°C and (b) 80°C with [SLS] = 32 m$M$, [AA] = 4 mol %, and [I] = 3.17 m$M$.

production rate at 80°C results in an increase in the rate of oligomeric radicals being generated at the very early stages of the reaction. The maximum total concentration of oligomers found in the aqueous phase is similar for the two reactions; at 80°C, the maximum oligomer concentration was reached at a slightly lower value (i.e., ~ 1 g/100 g serum) and earlier in the polymerization (~ 15% conversion after ~ 1 h reaction at 80°C, and ~ 18% conversion after ~ 2.5 h polymerization at 70°C). A similar trend was also observed in the serum solids content (which represents the total amount of oligomers, surfactant, initiator, and inhibitor remaining in the serum phase) measured by the gravimetric method, as shown in Figure 3(b), which further confirms the results obtained by $^1$H-NMR analysis.

As mentioned earlier, one of the important effects of temperature in heterogeneous emulsion polymerization systems using a highly water-soluble monomer (e.g., AA) is that it changes the monomer concentration in the aqueous phase arising from changes in the water solubility of both monomers and polymers, therefore affecting the rate of polymerization. Generally, with increasing temperature, an increase in the water solubility of hydrophobic monomers, such as St and Bu, should be expected. As the total monomer concentration increases in the aqueous phase, the particle generation rate is likely to vary. Evidence for this can be found in the results obtained for the composition of the water-soluble oligomers (measured by $^1$H-NMR) for these two systems. Figure 5(a) and (b) present the mol % of styrene, butadiene, and acrylic acid monomer units in the water-soluble oligomers as a function of conversion for the polymerizations carried out at 70 and 80°C, respectively. It can be seen that, in the very early stages of the polymerizations (<5% conversion), the oligomers initially contain a

higher percentage of hydrophobic (St + Bu) monomeric units and a lower percentage of hydrophilic monomeric units (AA) at 80 than at 70°C (i.e., the mole ratios of the three monomeric units are St/Bu/AA = 27/61/12 at 80°C and 20/60/20 at 70°C). A similar trend is also noted in the plots of mole concentration of St, Bu, and AA present in the water-soluble oligomers versus conversion for these two systems, as shown in Figure 6(a) and (b). It can be seen that at 80°C the mole concentration of styrene and butadiene units increase during Interval I similarly for both reactions, with the reaction at 80°C producing oligomers with slightly higher levels of the hydrophobic monomers. The increase of styrene monomeric units is noted to be much more significant than that of butadiene in the oligomers with increasing temperature. This may be because butadiene has a low boiling point (−4°C at 1 atm); therefore, the increase in the evaporation of Bu into the gas phase may be more significant than its increase in water solubility with increasing temperature.

Furthermore, it was also observed that the molecular weights of the water-soluble oligomers (measured by aqueous phase GPC) vary with conversion. Figure 7 shows that both MW$_{max}$ and MW$_{peak}$ initially increase with conversion, and after reaching maximum values at around 2 to 3% conversion, decrease sharply at first and then more slowly with increasing conversion. The maximum values of both MW$_{max}$ and MW$_{peak}$ for the polymerization carried out at 80°C are higher than those at 70°C. Because of the increase in the water solubility of the hydrophobic monomers as well as their polymers at the higher temperature, the oligomeric radicals contain greater amounts of the hydrophobic monomer units and higher molecular weights are formed. These oligomeric radicals will
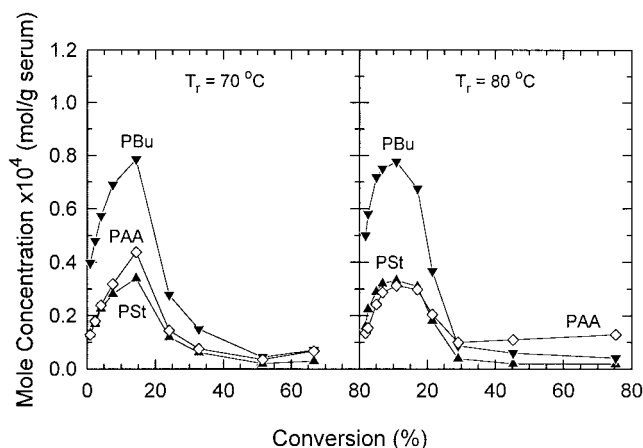


**Figure 6** Mole concentration of St, Bu, and AA units present in the water-soluble oligomers in the serum versus conversion for the St/Bu/AA (39/57/4 mol %) emulsion polymerizations carried out at (a) 70°C and (b) 80°C with [SLS] = 32 m$M$, [AA] = 4 mol %, and [I] = 3.17 m$M$.
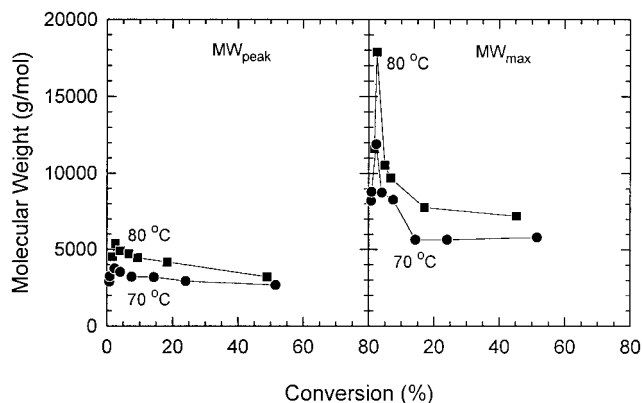
**Figure 7** Molecular weight of water-soluble oligomers (a) $MW_{peak}$ and (b) $MW_{max}$ versus conversion for the St/Bu/AA (39/57/4 mol %) emulsion polymerizations carried out at 70 and 80°C with [I] = 3.17 m$M$, [AA] = 4 mol %, and [SLS] = 32 m$M$.

also reach their critical degree of polymerization more rapidly compared with those formed in the polymerization carried out at the lower temperature (70°C). In the latter case, oligomer formation is slower and the AA composition in the oligomers is initially higher and the chain lengths shorter, which allows them to be more soluble in the aqueous phase. The oligomers formed at 80°C, which are higher in molecular weight and richer in Bu and St monomeric units, would precipitate earlier to form primary particles. Obviously, in this case, more surfactant should be required to stabilize these primary particles to avoid flocculation arising from the presence of more hydrophobic monomeric units (St and Bu). However, the surfactant concentration–conversion curves [see the open symbols in Fig. 3(a)] show that slightly more surfactant was found in the aqueous phase instead of at the particle surface by increasing the temperature to 80°C, which may be caused by the decreased adsorption of the surfactant at the solid/liquid interface with increasing temperature, resulting in limited flocculation occurring earlier than at 70°C.

Still, it can also be seen that in the early stages of the polymerizations the highest concentration of monomeric units in the oligomers is not AA, but rather Bu. The reason for this is related to the mechanism of water-soluble oligomer formation, which is discussed in detail in the next article in this series.

## Behavior of acrylic acid

As discussed previously, the concentration of acrylic acid units in the oligomers does not increase as the temperature increases from 70 to 80°C, based on the ^{1}H-NMR analysis. It is therefore necessary to further examine the reaction behavior of acrylic acid during the polymerization process. The unreacted acrylic acid

in the latex samples was determined by GC. Figure 8(a) gives the AA concentration profiles at 70 and 80°C. The data show that the concentration of AA decreases rapidly at the beginning of each reaction and then starts to slow down at around 10 to 13% overall conversion, depending on the curve. It then decreases at a relatively constant rate. The decrease in AA for the 80°C system does not appear to be significantly faster than that at 70°C. These results appear to indicate that much of the AA is converted to polymer by aqueous phase solution polymerization in the latter stage of the reaction.

If the unreacted AA in the latex is plotted as a function of conversion, as shown in Figure 8(b), it is noted that the amount of AA decreased rapidly during the early stages of the reaction (<15% conversion) and the later stages of the reaction (>80% conversion). Only around 10–15% of the AA was reacted between 20 and 70% conversion. By increasing the temperature to 80°C, a significant increase in the overall rate of polymerization was observed (see Fig. 1). However, this was not reflected in the rate of AA copolymerization. Furthermore, by comparing the overall conversion–time curves with the acrylic acid conversion–time curves at both 70 and 80°C, as shown in Figure 9(a) and (b), respectively, different conversion profiles
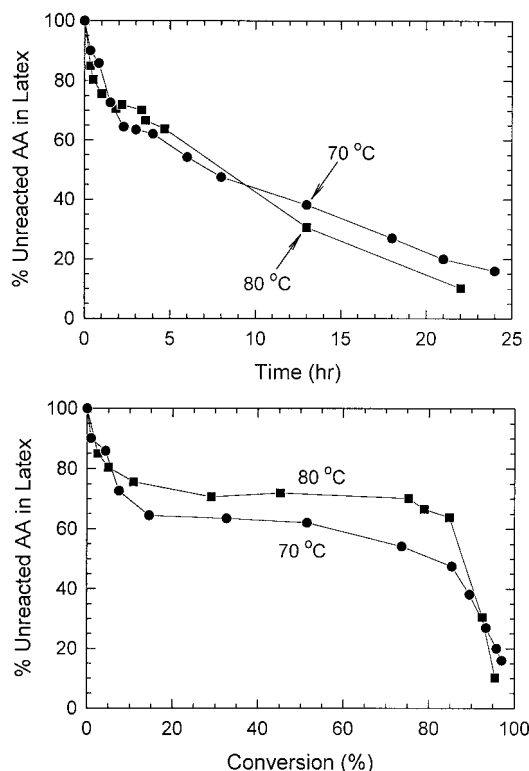


**Figure 8** Weight percentage of unreacted acrylic acid monomer in the latex (measured by GC) versus time (a, top) and overall conversion (b, bottom) for the St/Bu/AA (39/57/4 mol %) emulsion polymerization carried out at 70 and 80°C. [SLS] = 32 m$M$, [AA] = 4 mol %, and [I] = 3.17 m$M$.
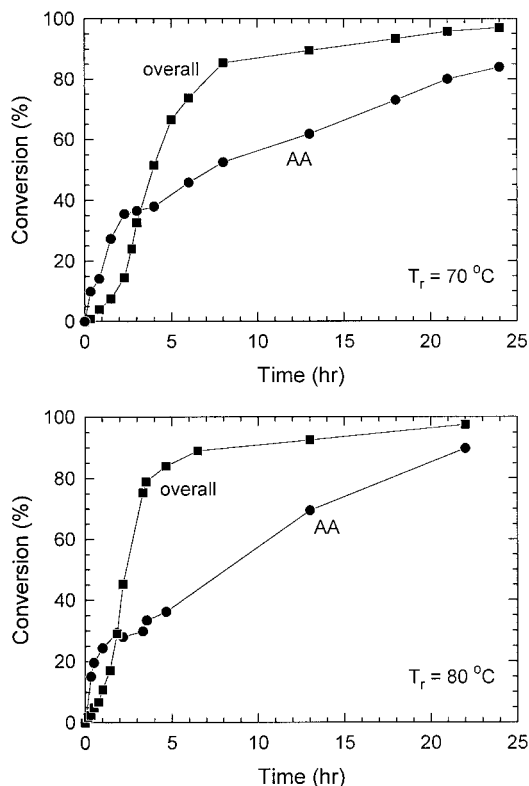
**Figure 9** Overall conversion (measured gravimetrically) and acrylic acid conversion in the latex (measured by GC) versus time for the St/Bu/AA (39/57/4 mol %) emulsion polymerization carried out at 70°C (a, top) and 80°C (b, bottom) with [SLS] = 32 m$M$, [AA] = 4 mol %, and [I] = 3.17 m$M$.

are noted. The results reveal that, except during Interval II, the conversion rates (the slopes of the curves) of acrylic acid were faster than the overall conversion rate, especially during Interval I ($X < 15\%$). The decrease in the polymerization rate of AA after Interval I may be explained by a shift in the overall polymerization site during the emulsion polymerization process, which was previously reported in the literature.

The locus of polymer formation in most conventional emulsion polymerization systems is predominantly inside the polymer particles. Systems containing both hydrophobic and hydrophilic monomers may exhibit significant reactions in both the aqueous and particle phases. Some polymerization may also occur in the monomer droplets; however, because of the small number of droplets relative to the number of polymer particles, reaction in the droplet phase is usually considered to be negligible (except in the case of miniemulsion polymerizations). A shift in the reaction locus in the styrene–acrylamide system was previously reported by Kawaguchi et al.[17] They showed that the reaction locus was initially in the aqueous phase (where almost 99% of the acrylamide was located), moved to the polymer particles as styrene became incorporated into the oligomeric radicals, and then

moved back into the aqueous phase after the styrene was depleted. Based on experimental evidence, Shoaf and Poehlein[18] also suggested that the primary reaction locus in the acrylic acid–styrene system may shift into the aqueous phase after the styrene has been consumed; they called this period Interval IV. In fact, the reaction site for the water-soluble monomer (such as acrylic acid) must be mainly in the aqueous phase because of its hydrophilicity, whereas the primary polymerization site for the other monomers will shift to the particle phase after particle nucleation. The primary polymerization site may shift back to the aqueous phase when most of the hydrophobic monomers are consumed.

Possible reasons for the shift of the reaction site from the particle phase back to the aqueous phase were given by Shoaf and Poehlein[18] as being attributed to the following: (1) the increase in the hydrophilicity of the oligomeric radicals arising from the depletion of styrene, which decreases the driving force for the radicals to penetrate into the hydrophobic particle core; and (2) the presence of a hydrophilic polymer surface layer, which surrounds the polymer particles and inhibits the penetration of hydrophilic oligomeric radicals into the particle where additional reaction would occur. Both of these would result in an overall decrease in the rate of diffusion of oligomeric radicals into the polymer particles and shift the primary reaction locus to the aqueous phase.

Furthermore, Greene and Saunders[19] investigated the electrolyte stability of styrene/butadiene latexes containing copolymerized AA and pointed out that a surface saturation condition of the stabilizing ions can exist in this system. The stability of the latexes was found to increase with the concentration of stabilizing ions on the surface of the latex particles at concentrations below this saturation level and remained practically unchanged at concentrations above saturation. They also reported that the surface of the latex particles became saturated with carboxyl groups when the concentration of AA used was greater than or equal to 1.25% for St/Bu (60/40) latexes prepared by a seeded and continuous polymerization process.

Based on this previous work in the literature and the experimental results observed in this study, it can be assumed that, during the particle growth period in the emulsion polymerization of St/Bu/AA, the particle surface will be covered by an increasing amount of hydrophilic groups that could be both ionic and nonionic, such as $SO_4^-$ end groups from the initiator, $SO_4^-$ from the emulsifier, and COOH and $COO^-$ (if AA is neutralized) from the acrylic acid comonomer. The total concentration of these hydrophilic groups at the particle surface will finally reach a maximum (i.e., saturation), which can be referred to as the critical saturation surface coverage (CSSC). This will lead to the buildup of a potential energy barrier at the particle
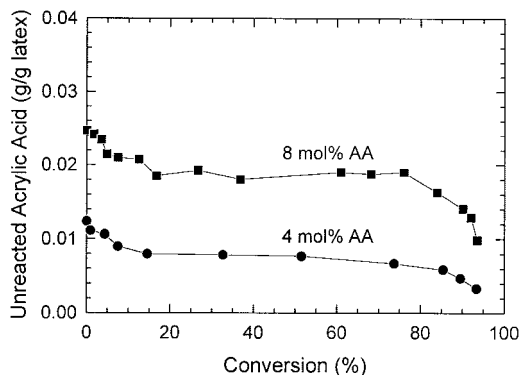
**Figure 10** Weight percentage of unreacted acrylic acid monomer in the latex (measured by GC) versus conversion for the St/Bu/AA (39/57/4 mol %) emulsion polymerizations carried out at 4 and 8 mol % AA with [SLS] = 32 m$M$ and [I] = 3.17 m$M$ at 70°C.

surface, which may limit the penetration of the oligomeric radicals into the particles and shift the polymerization site more toward the aqueous phase. Therefore, after the particle surfaces are fully covered by this hydrophilic layer sometime in Interval III, the penetration of the hydrophilic oligomeric radicals into the particles would be more difficult. Further aqueous phase reactions will lead to the formation of water-soluble oligomers containing large fractions of AA monomer units.

The existence of these newly formed, high carboxylic acid containing oligomers can increase the chance of flocculation of the particles by the formation of hydrogen bonds between carboxylic acid groups located between the particle surfaces or in a particle/oligomer/particle (P/O/P) interphase. Increasing the amount of carboxylic acid groups in the system (e.g., on the particle surface by both chemical bonding or adsorption and in the water-soluble oligomer chains) would increase the chances of forming hydrogen bonds in the P/O/P interphase, which would lead to the flocculation of the latex. This can result in a decrease in the number of particles, as reported previously for an AA concentration of 8 mol %.[2] In that case, the particle number decreased when the conversion exceeded 80%, with the latex containing about 15% (of the total latex volume) coagulum at about 85% conversion. Further evidence can also be observed from the plot of the concentration of unreacted AA monomer in the latex versus conversion for both the 4 and 8 mol % AA systems, as shown in Figure 10. The results show that almost 50% of the initial AA (~ 0.19 g) in the 4 mol % AA system and 25% of the AA (~ 0.27 g) in the 8 mol % AA system reacted in these latex systems by the time the polymerizations reached 85 and 75% conversion, respectively. The concentration of unreacted AA monomer increased with increasing AA concentration. This means that, after

reaching the CSSC, it would be expected that much AA monomer would remain in the aqueous phase, particularly for the system containing 8 mol % AA, so that more water-phase polymer would be formed, which would thus increase the chances of flocculation of the latex particles. This may be the reason that only a limited amount of AA (<6% according to Maistrovich[20]) could reportedly be used to obtain stable latexes without coagulation in other systems.

**Influence of initiator concentration**

In general, increasing the initiator concentration (at a constant reaction temperature) increases the rate of generation of radicals in the system, thereby increasing the number of nucleated particles and consequently the rate of polymerization. The major difference in the cause of the increase in $R_p$ brought about by increasing the temperature, compared to increasing the initiator concentration, is that the monomer water solubility and partitioning in each phase changes in the former case, as discussed earlier, but not in the latter case. Therefore, it might be expected that more water-soluble oligomers should be found in the aqueous phase initially for the case where the polymerization was carried out at a higher initiator concentration. According to the results obtained previously, it seems that if more AA monomer can be converted to polymer during the early stages of a polymerization, then obviously less AA would be left to form water-phase polymers during the later stages of the polymerization. Therefore, the possibility of coagulating the latex should be reduced.

To test the influence of initiator concentration, two emulsion terpolymerizations were carried out at different $K_2S_2O_8$ concentrations. Based on the model recipe, the initiator concentration was doubled to 6.34 m$M$ (System 3 in Table II). Considering that there is a general dependency of both the particle size and also the rate of polymerization on ionic strength,[22] 3.17 m$M$ of potassium chloride (KCl) was added to the low initiator concentration system (System 4 with [I] = 3.17 m$M$ + KCl = 6.34 m$M$) described in Table II as [I] + KCl, to create similar ionic strength conditions as those in the 2[I] system.

The conversion and the rate of polymerization ($R_p$) versus time curves for both the 2[I] and [I] + KCl systems are shown in Figure 11. Again, the rate curves were obtained by differentiation of a polynomial fit of the conversion–time data. The conversion–time curves are both S-shaped. As expected, the rate of polymerization increased with increasing initiator concentration.

Figure 12 shows the weight percentage of water-soluble oligomers and surfactant (open symbols) as a function of conversion for these two systems. In contrast to increasing the temperature, a significant in-
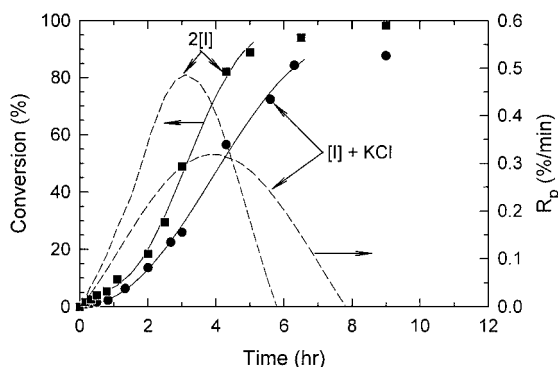
**Figure 11** Conversion (symbols, measured gravimetrically; solid line is curve fit) and $R_p$ (dashed lines) versus time for the St/Bu/AA (39/57/4 mol %) emulsion polymerizations carried out at 2[I] = 6.34 m$M$ and [I] = 3.17 m$M$ + KCl = 6.34 m$M$. [SLS] = 32 m$M$, [AA] = 4 mol %, and 70°C.

crease in the concentration of water-soluble oligomers formed during Interval I was observed as the initiator concentration was increased at a constant temperature and adjusted ionic strength. This can be simply understood as follows: increasing the initiator concentration (without changing the water solubility of the monomers) increases the amount of free radicals produced, which results in the generation of more water-soluble oligomers in the aqueous phase. Therefore, increasing the incorporation of acrylic acid into the copolymer in the early stages of the polymerization can be carried out by increasing the initiator concentration.

The evolution of the number of particles ($N_p$) with conversion is shown in Figure 13. The results indicate that the increase in the rate of polymerization with increasing initiator concentration is caused by an increase in the number of particles brought about by the increase in the number of free radicals produced. The
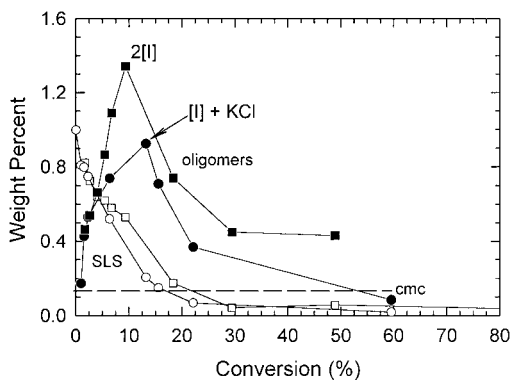


**Figure 12** Weight percentage of water-soluble oligomers (closed points) and surfactant (open points) as a function of conversion for the St/Bu/AA (39/57/4 mol %) emulsion polymerizations carried out at 2[I] = 6.34 m$M$ and [I] = 3.17 m$M$ + KCl = 6.34 m$M$. [SLS] = 32 m$M$, [AA] = 4 mol %, and 70°C.
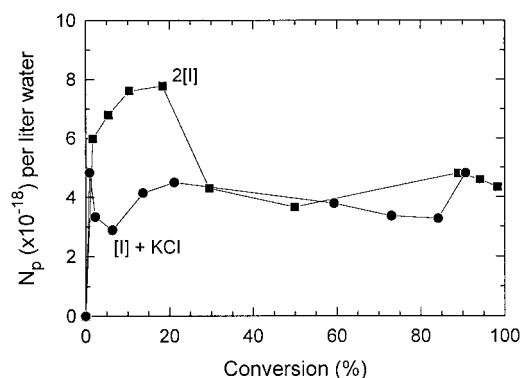


**Figure 13** Number of particles per liter ($N_p$) versus conversion for the St/Bu/AA (39/57/4 mol %) emulsion polymerizations carried out at 2[I] = 6.34 m$M$ and [I] = 3.17 m$M$ + KCl = 6.34 m$M$. [SLS] = 32 m$M$, [AA] = 4 mol %, and 70°C.

formation of increased numbers of particles resulted in a higher rate of polymerization in Interval I.

At the higher initiator concentration (2[I]), increased amounts of free radicals and primary particles were generated. In this case, a greater number of sulfate end groups (from the initiator) stabilized these particles. Thus, the number of particles increased until a maximum value was reached. Limited aggregation occurred at the beginning of the Interval II (~ 20% conversion), resulting in a near constant $N_p$ during Intervals II and III.

For the polymerization conducted at the lower initiator concentration and constant ionic strength, a much different evolution in the number of particles was noted in Interval I. Limited aggregation was observed much earlier in the polymerization. This seems to indicate that decreasing the initiator concentration decreases the rate of polymerization mainly attributable to the formation of fewer particles. The decreased $N_p$ results from the production of fewer radicals, and the particles that are formed may be less stable than in the case of the higher initiator concentration arising from the presence of fewer sulfate end groups to help stabilize them. As noted before, $N_p$ increased after the early limited aggregation until the end of Interval I, and then remained nearly constant. This decrease in $N_p$ at the very beginning of the polymerization is considered to occur because the rate of increase in the surface area of the newly formed particles is greater than the rate of establishment of equilibrium adsorption of the emulsifier on these surfaces. In this case, with the cmc at around 4.5 m$M$ (0.129 g/100 g serum), the SLS concentration falls below the cmc at about 16% conversion, as shown in Figure 12. Therefore, the increase of $N_p$ could be observed when the limited aggregation ended far before the end of Interval I.

## Influence of ionic strength

The ionic strength is known to strongly affect colloidal stability as well as particle size and number.[22] This is
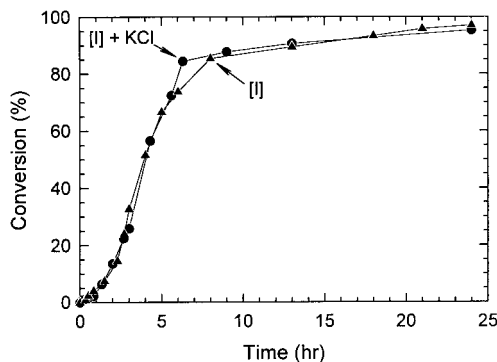
**Figure 14** Conversion (measured gravimetrically) versus time for the St/Bu/AA (39/57/4 mol %) emulsion polymerizations carried out at [I] = 3.17 mM and [I] = 3.17 mM + KCl = 6.34 mM. [SLS] = 32 mM, [AA] = 4 mol %, and 70°C.

because an increase in ionic strength will compress the electrical double layer at the surface of the particles, thus decreasing their stability, which in turn results in an increased particle size and decreased $N_p$, because of the occurrence of limited aggregation in the early stages of the reaction. By comparing the model system ([I] = 3.17 mM) with the system with KCl added ([I] = 3.17 mM + KCl = 6.34 mM), the effect of ionic strength can be observed. The conversion versus time curves for these two systems are shown in Figure 14. The corresponding particle number versus conversion curves are given in Figure 15. The conversion–time profiles are almost identical, which indicates that there is no significant effect of ionic strength on the rate of polymerization under these conditions, despite the difference in the evolution of the number of particles. In addition, the water-soluble oligomers formed in the aqueous phase for these two systems were noted to be only slightly affected by the changing ionic strength. Figure 16 presents the change in the oligomer concentration as a function of conversion at the two ionic strengths. The maximum oligomer concentration
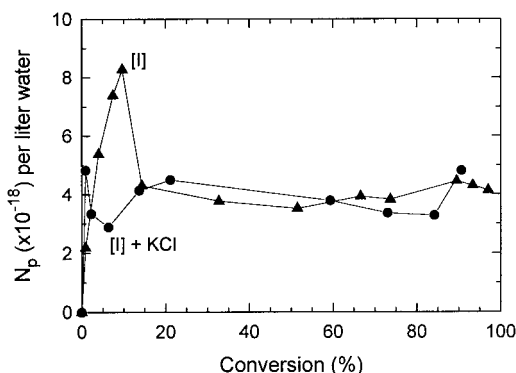


**Figure 15** Number of particles per liter ($N_p$) versus conversion for the St/Bu/AA (39/57/4 mol %) emulsion polymerizations carried out at [I] = 3.17 mM and [I] = 3.17 mM + KCl = 6.34 mM. [SLS] = 32 mM, [AA] = 4 mol %, and 70°C.
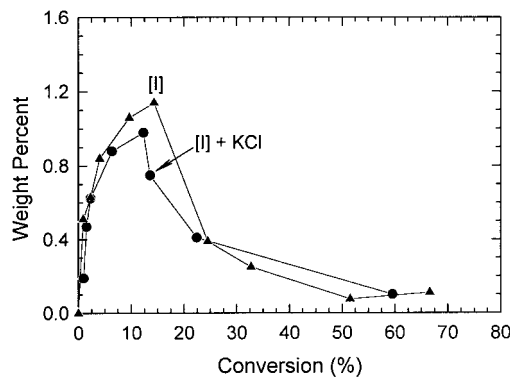


**Figure 16** Weight percentage of water-soluble oligomers as a function of conversion for the St/Bu/AA (39/57/4 mol %) emulsion polymerizations carried out at [I] = 3.17 mM and [I] = 3.17 mM + KCl = 6.34 mM. [SLS] = 32 mM, [AA] = 4 mol %, and 70°C.

found in the aqueous phase decreased slightly with increasing ionic strength, which may have been caused by a decrease in the water solubility of the oligomers as a result of a salting-out effect, which in turn leads to more oligomers being precipitated out of the water to form particles. On the other hand, according to Klein et al.,[4] increasing the ionic strength decreases the interfacial tension at the particle/aqueous interface, which would result in an increase in the adsorption of the oligomers on the particle surface, further resulting in fewer oligomers in the aqueous phase.

## Role of the water-soluble oligomers

Based on the experimental results and the discussions in this and the previous study,[2] the role of water-soluble oligomers in the emulsion copolymerization of St/Bu with acrylic acid varies throughout the course of the emulsion polymerization, and may be described according to three separate periods: (1) particle nucleation; and (2) particle growth before and (3) after the CSSC is achieved. These will be explained as follows and as depicted in Figure 17.

### Particle nucleation period

During this period, particle generation by both homogeneous-coagulative and micellar entry mechanisms begins in the aqueous phase when a water-soluble initiator is used. These growing oligomeric radicals will either form primary particles by entering micelles and polymerizing therein or precipitating after reaching their critical degree of polymerization ($j_{crit}$), or become a dead polymer as a result of aqueous phase termination. The formation of more water-soluble oligomeric radicals during this period will lead to the generation of more particles, thus increasing the rate
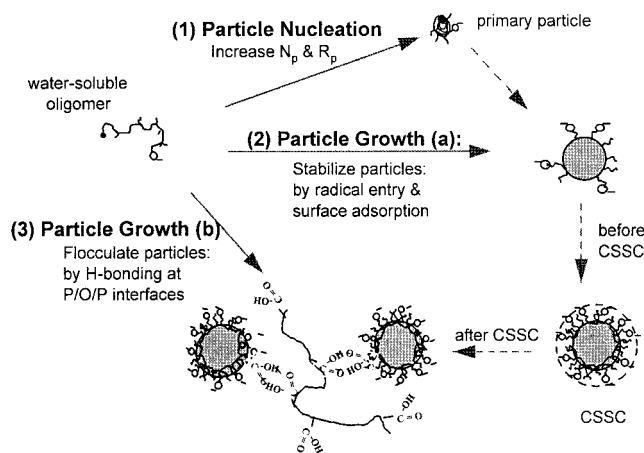
**Figure 17** Schematic representation of the role of the water-soluble oligomers formed during the emulsion polymerization of the St/Bu/AA termonomer system.

of polymerization. Therefore, any efforts to increase the concentration of acrylic acid monomeric units in the oligomers in this stage would help to increase the incorporation of carboxyl groups into the polymer phase through chemical bonding. Those carboxyl groups (nonionized) chemically bonded at the particle surface will stabilize the latex particles by steric stabilization, and will also decrease the surface coverage of the surfactant at the particle surface. Because of this, more particles will be stabilized by the surfactant than without acrylic acid in the system.

It was noted that, under the conditions investigated, the acrylic acid incorporated into the oligomers can be increased by increasing the initiator concentration and the initial acrylic acid concentration, but not the temperature and the ionic strength.

Particle growth

During the particle growth period, the growing particle surface will be covered by increasing amounts of carboxyl and sulfate groups (by adsorption of the oligomeric radicals). For a given system, this hydrophilic polymer coverage may finally reach a maximum, with further penetration of the water-soluble oligomeric radicals into the particles being more difficult. This is called the critical saturation surface coverage (CSSC). Therefore, during the particle growth period, the function of the water-soluble oligomers in the system may differ before and after the CSSC is reached.

Before the CSSC is reached, the water-soluble oligomeric radicals will help to grow the particles through propagation after adsorption (i.e., entry) and the dead

water-soluble oligomers will help to stabilize the particles by adsorption. Some dead oligomers will remain in solution in the aqueous phase or adsorb onto the particle surfaces with a decreased desorption rate compared to that in the micelles. These can have an increased adsorption rate as the composition of the hydrophobic monomeric units and chain lengths increase. The carboxyl groups present at the particle surface as adsorbed or bonded chains can prevent later limited aggregation, which occurs in the system without acrylic acid.

After the CSSC is reached, further polymerization in the aqueous phase will cause the formation of water-soluble polymers with high acrylic acid content. These water-phase oligomers might flocculate the latex particles by the formation of hydrogen bonds between the particles [particle/oligomer/particle (P/O/P)], thereby destabilizing the latex system.

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