Toward an Understanding of the Role of Water-Soluble Oligomers in the Emulsion Polymerization of Styrene−Butadiene−Acrylic Acid. Mechanisms of Water-Soluble Oligomer Formation

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ABSTRACT: The mechanism of water-soluble oligomer formation during the emulsion terpolymerization of styrene/butadiene/acrylic acid differs depending on whether the surfactant concentration is above or below the cmc. A growth mechanism for the water-soluble oligomers involving reactions in both the aqueous and organic phases for polymerizations carried out above the cmc of SLS is proposed. This is used to explain why the fraction of butadiene (Bu) units in the water-soluble oligomer chains is the highest compared to the styrene or even the acrylic acid (AA), despite the low water solubility of Bu monomer relative to AA. The supporting evidence for this mechanism includes (1) the increase in the oligomer molecular weight with increasing initiator concentration, as in the case of polymerization occurring in micelles, indicating that the oligomers had grown in an isolated organic phase, and (2) the much higher fraction of AA homodyads found in the oligomers formed at an SLS concentration below the cmc compared to that above the cmc. These results indicate that, in the absence of micelles, the oligomers will grow in the aqueous phase and result in more AA block dyad sequence units in the oligomer chains, owing to the higher AA monomer concentration there. When micelles exist, the water-soluble oligomers will grow in both the aqueous phase and the organic phase. In this case, fewer AA dyads will be noted.

Introduction

Studies on the kinetics and mechanisms of conventional emulsion polymerization often use monomers that are relatively water-insoluble, such as styrene and butadiene. The primary reaction locus is usually considered to be inside the polymer particles, and aqueous phase polymerization is usually considered to be negligible. However, many industrial reaction systems employ one or more monomers that have significant water solubility (e.g., carboxylic acids). The concentration and extent of reaction of these water-soluble monomers in the aqueous phase may be significant, and conventional emulsion polymerization kinetics do not apply directly to these systems. Carboxylic acid monomers, such as acrylic acid, are often completely soluble in water. They will still, however, partition to varying extents into the organic phase depending on their relative hydrophobicity. In this case, significant amounts of polymerization can occur in both the particle and aqueous phases.

Most of the research in emulsion polymerization involving water-soluble monomers described in the literature has focused on the overall kinetics scheme in order to predict reaction rates, copolymer compositions, particle compositions, particle concentrations, and particle sizes. Wang and Poehlein[1] reported the experimentally determined aqueous phase species formed during the polymerization of the styrene−acrylic acid comonomer system. Charmot et al. proposed a kinetic model to predict the rates of incorporation of acrylic acid on the surface and in the core (buried) as well as in the latex serum of styrene/butadiene or styrene/butyl acrylate copolymer particles.[2] However, questions, such as how the oligomers are formed in the very early stages of the polymerization and what are the behaviors of these water-soluble oligomers during the polymerization process, still remain unanswered to a large extent. The study of aqueous phase events can lead to a better understanding of the aqueous phase polymerization and the formation of oligomeric radicals during the particle nucleation period, which in turn leads to a better understanding of the particle nucleation mechanisms.

An industrial emulsion polymerization system employing styrene (St), butadiene (Bu), and acrylic acid (AA) monomers is being investigated in this study. The goal is to experimentally study the kinetics and mechanism of the formation of the water-soluble oligomers and their relevance to particle nucleation and growth by characterizing the low molecular weight species found in the aqueous phase during the reaction.

In the previous papers,[3,4] methods were developed to characterize the water-soluble oligomers found in the aqueous phase, such as their concentration, composition, and molecular weight, and the relevance of these characteristics to particle nucleation and particle growth was investigated. Emulsion polymerizations, based on the model recipe shown in Table 1, were carried out at different temperatures, initiator concentrations, acrylic acid concentrations, and ionic strengths with a surfactant concentration above the cmc ([SLS] = 32 mM). An unexpected result was found with respect to the concentration of each monomer unit in the oligomers as a function of conversion. The water-soluble oligomers were composed of significantly more butadiene monomeric units than acrylic acid units during interval I and the beginning of interval II, even for the system in which the concentration of acrylic acid was increased to 8 mol %.[3] This phenomenon was found in all systems studied where the surfactant concentration was initially above

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Table 1. 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 mM (cmc = 9 mM in pure water at 70 °C). [b] [I] = 3.17 mM, based on water.

the cmc. According to the nucleation mechanisms typically described for emulsion polymerizations (homogeneous-coagulative and micellar-entry), one would expect that, for a system containing both hydrophilic and hydrophobic monomers such as those used in this study, the oligomer radicals formed in the aqueous phase in the early stages of the polymerization would be comprised primarily of the more water-soluble monomer (AA). In particular, this should be the case for the system with the higher water-soluble monomer concentration (8 mol % AA), since the acrylic acid concentration in the aqueous phase exceeds that of the other monomers. In this study, to better understand the mechanism of water-soluble oligomer formation, an emulsion polymerization was carried out at a lower surfactant concentration of 6 mM SLS (< cmc) in addition to another experiment carried out at of 32 mM SLS (> cmc). The partitioning of acrylic acid and styrene monomers between the organic and aqueous phases was determined under these experimental conditions. The acrylic acid monomer sequence distributions in terms of the homodyad and the random dyad were determined by ^{13}C NMR, and subsequently a two-phase formation and growth mechanism for the water-soluble oligomers was proposed.

Experimental Section

Materials. Acrylic acid (AA) monomer ($CH_2{=}CHCOOH$, MW = 72.06 g/mol, 99% active) inhibited with 200 ppm of 4-methylhydroquinone (MHQ) (Aldrich) was distilled under vacuum at ~10 mmHg and 39 °C vapor temperature to remove the inhibitor. The purified acrylic acid was stored at ~14 °C under running tap water. Storage at a lower temperature (<13 °C) will freeze the liquid. Styrene (St) monomer ($CH_2{=}CHC_6H_5$; inhibited with 55 ppm of *p-tert*-butylcatechol (Aldrich)) was passed through activated aluminum oxide (Brockmann I Standard grade, basic, ~150 mesh, 58 Å, 155 m^2/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, Inc.) was passed over Ascarite[e] II (sodium hydroxide-coated silica, Aldrich) to remove the inhibitor, followed by drying over Drierite (Fisher). The butadiene monomer was then condensed in a cold trap immersed in a mixture of 2-propanol (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, Henkel) 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 initiator. 4-Methylhydroquinone (MHQ, $CH_3OC_6H_4OH$, MW = 124 g/mol, 99% purified grade, Aldrich) was used as received. Distilled−deionized (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) was used throughout.

Polymerization Procedures. Batch emulsion polymerizations were carried out in glass pressure bottles as described in the previous paper.[3] The reaction was stopped by injecting a methylhydroquinone (MHQ) solution. Conversions of the latex samples were measured gravimetrically.[3] The synthesis of latexes reported in this paper was based on the model recipe shown in Table 1 (6 mM SLS was also used in one case).

Particle Size Measurements. The average particle diameter was measured using transmission electron microscopy (TEM, Phillips 400). Prior to TEM examination, the unreacted monomers (which swell the particles) 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 polymerization (<5% conversion) owing to some hindered access of the OsO_4 to the particles created by a high carboxylic acid group concentration at the particle surface. Typically 1000−1500 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 of water), as follows:

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

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

Serum Composition. As described in detail previously,[3] the aqueous phase was separated from the particle phase by ultracentrifugation at the optimal separation conditions: 37 000 rpm and 4 °C for 36 h. The clear serum was concentrated using a special technique,[3] and ^{1}H NMR spectra (500 MHz) were obtained by using a Bruker AM-500 NMR spectrometer. 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.

Partitioning of Monomers. Based on the model recipe shown in Table 1, the three monomers and DDI water were charged into a high-pressure glass bottle without surfactant and initiator and sealed with a rubber gasket and metal crown cap. Then, the bottle was placed in a 70 °C constant-temperature bath for 20 min to reach equilibrium. About 2 g of the aqueous solution was removed from the bottle by syringe. A Teflon valve was used between the needle and syringe in order to avoid solution loss due to the pressure. The aqueous solution was injected into an 8 mL vial, which was sealed with a Teflon gasket. After cooling to room temperature, the vial was weighed (W_1). After degassing by insertion of a syringe needle (to release the butadiene monomer), the vial was again weighed (W_2). Theoretically, the aqueous solubility of the butadiene should be obtained from the weight difference of the vials before and after degassing (i.e., $W_1 - W_2$). Unfortunately, the amount was too small to obtain a reasonable value for the water solubility of butadiene by this method.

The amounts of acrylic acid and styrene monomers dissolved in the aqueous phase were measured by gas chromatography (GC) as described previously in detail.[3] A Hewlett-Packard 5890 GC with an HP 3393A computing integrator was employed. Acrylic acid monomer must be preneutralized by using trimethylphenylammonium hydroxide (in 0.1 M methanol solution) before injection into the GC instrument in order to avoid AA adsorption on the GC column. Dioxane was used as an internal standard.

^{13}C Spectra of Water-Soluble Oligomers. The ^{13}C NMR spectra of the water-soluble oligomers in the serum (as shown in Figure 12) were obtained with a Bruker AM-500 spectrometer, operating at 125.8 MHz. D_2O was used as internal locking agent for all NMR spectra, and the chemical shift was referred to dioxane (67.3 ppm in D_2O). The measurement conditions were as follows: spectral width, 29411 Hz; acquisition time, 1.14 s; flip angle, 45°; pulse delay, 10 s. The number of scans was 13 200 (for [AA] = 8 mol %, [SLS] = 32 mM), 18 734 (for

Table 2. Monomer Feed and Composition of Bu/AA Bulk Copolymers at 70 °C

sample	conv (%)	Bu in feed (mol)	AA in feed (mol)	F_{Bu}	f_{Bu}
1	0.56	0.320	0.049	6.504	4.717
2	0.87	0.272	0.104	2.629	2.046
3	1.24	0.237	0.146	1.620	1.638
4	1.26	0.201	0.189	1.065	1.327
5	1.67	0.131	0.273	0.479	0.905
6	2.40	0.095	0.311	0.365	0.457

[AA] = 4 mol %, [SLS] = 32 mM), and 19 850 (for [AA] = 4 mol %, [SLS] = 6 mM). The line broadening for all spectra is 8 Hz.

Bu/AA Monomer Reactivity Ratios. The monomer reactivity ratios for the bulk copolymerization of styrene/butadiene and styrene/acrylic acid monomer pairs have been well studied by many workers and can be found in the literature.[5] The monomer reactivity ratios for the bulk copolymerization of the butadiene/acrylic acid monomer pair have not been reported and therefore needed to be determined in this work. Copolymerizations based on the recipe shown in Table 2 were carried out at 70 °C. 20 mg of 2,2′-azobis(isobutyronitrile) (AIBN) initiator was first placed into each of a series 42 mL glass pressure bottles. Monomer mixtures having different AA/Bu monomer ratios as shown in Table 2 were then added to fill 67% of the total volume of each bottle. About 0.5 g of excess butadiene was added to each reaction bottle initially to be removed later. After adding the mixtures, the bottles were capped with a rubber gasket and a metal crown cap containing two holes to insert syringe needles. The excess butadiene was vented by inserting a syringe needle until the exact weight was reached. The bottles were placed in a temperature-controlled water bath and were tumbled end-over-end at 16 rpm. The bottles were taken out of the water both at specified times (<50 min to keep the conversion below 5%) and were immediately chilled in ice water to stop the reaction. The unreacted butadiene monomer was vented through a needle before opening the caps and precipitating the samples. The copolymers were precipitated in 250 mL of hexane (Aldrich) two times. The final products were dried in air overnight and then at 60 °C in a vacuum oven for 48 h. The total conversion, determined gravimetrically, is shown in Table 2.

The copolymer compositions were measured using a 500 MHz ^{1}H NMR (Bruker). All copolymer samples were dissolved in DMSO-d_6 and placed in 5 mm sample tubes. The ^{1}H NMR spectra were recorded by the spectrometer operating at 500.17 MHz at 25 °C. The recording conditions were as follows: sample concentration around 1% (g/mL); spectral width, 6024 Hz with a 23° pulse angle; acquisition time, 2.72 s; pulse repetition, 10 s; number of data points (FID), 32K; and number of scans, 150−180, depending on the sample.

Figure 1 shows a typical 500 MHz ^{1}H NMR spectrum of a Bu/AA low-conversion bulk copolymer in DMSO-d_6 (2 Hz line broadening and 1 zero filling). The peaks representing the different protons are peak (1) for the methyl protons from the AIBN initiator, peak (2) for all methane ($-CH-$) and methylene ($-CH_2-$) protons of the AA and Bu units in the copolymer chains, peaks (3) and (4) for the protons in DMSO and H_2O, peak (5) for the two double-bond protons ($CH_2=$) in Bu-*1,2*, peak (6) for the double-bond protons ($-CH=CH-$ and $-CH=$) in Bu-*1,4* and Bu-*1,2* units, peak (7) for the one H_α proton and the two H_β protons from unreacted AA monomer, and peak (8) for the $-OH$ protons of the carboxylic groups from both AA and PAA and also from HOH. The molar ratios of Bu and AA in the copolymer (i.e., M_{Bu}/M_{AA}) were calculated from the peak areas of the ^{1}H NMR spectra (see Figure 1) using the relationship

$$M_{Bu}/M_{AA} = (6A_6 + 3A_5)/(4A_2 - 8A_6 - 2A_5) \tag{2}$$

where A_2, A_5, and A_6 indicate the areas of peaks (2), (5), and (6), respectively, in Figure 1.

Table 3. Monomer Feed and Composition of Bu/AA Bulk Copolymers at 60 °C

sample	conv (%)	Bu in feed (mol)	AA in feed (mol)	F_{Bu}	f_{Bu}
1	0.86	0.153	0.102	1.5	1.29
2	1.42	0.129	0.131	0.98	1.04
3	2.09	0.107	0.160	0.67	0.83
4	3.47	0.067	0.219	0.32	0.53
5	4.01	0.042	0.248	0.17	0.42

Although both Finemann−Ross[6] and Kelen−Tudos[7] methods can be used to determine the r_1 and r_2 values, the Finemann−Ross method was selected for this system because of the better linear fit compared to the Kelen−Tudos method. In addition, this treatment of the experimental data is similar to the Mayo−Lewis method, which has been used to obtain reactivity ratio data for the other two monomer pairs, St−Bu and St−AA. Figure 2 shows the plot of $(F/f)(f - 1)$ vs (F^2/f), where F (or F_{Bu}) is the molar ratio of Bu to AA in the feed and f (or f_{Bu}) is the molar ratio of Bu to AA in the copolymer. The r_1 (Bu) and r_2 (AA) values obtained from the slope and intercept of the curve are 0.59 and 0.33, respectively.

The reactivity ratios of Bu/AA were also measured at T = 60 °C for the purpose of comparison with the r_1 and r_2 values of Bu/St and St/AA obtained from the literature for the same temperature. r_{Bu} and r_{AA}, in this case, were 0.49 and 0.36 (obtained from the Finemann−Ross plot, based on the experimental results listed in Table 3 and shown in Figure 3), respectively. These are close to the results obtained at 70 °C. The variation of reactivity ratio with temperature will depend on the difference in propagation activation energies of the monomers.[8] Since differences in activation energies for radical propagation generally are relatively small for most pairs of monomers, the effect of temperature on the values of r_{ij} is not large.

Results and Discussion

As mentioned before, an interesting result observed with respect to the concentration of each monomer unit in the oligomers as a function of conversion is that the water-soluble oligomers were unexpectedly composed of significantly more butadiene monomeric units than acrylic acid during interval I and the beginning of interval II, even for the system in which the concentration of acrylic acid was increased to 8 mol %.[3] This phenomenon was found in all systems studied with the surfactant concentration initially added above the cmc.

Plots of the mole concentrations of the individual monomer units (mol/g of serum) present in the oligomer chains vs conversion for the three systems with different AA concentrations (AA = 0, 4, and 8 mol % as discussed previously[3]) are presented in Figure 4. The results show that the St, Bu, and AA monomeric units in the oligomers increase with increasing conversion in the early stages of the reactions; after reaching maximum values, they all rapidly decrease to low values. The maximum amount of each monomeric unit (St, Bu, AA) in the oligomers increases with increasing AA concentration (comparing the maximum in each curve), which means that more water-soluble oligomers were formed as more AA monomer was added to the system. However, as noted under other conditions, the oligomers contain more Bu than AA, even for the system with 8 mol % AA. Figure 5 shows the relative amounts (mole percentage) of styrene, butadiene, and acrylic acid units in the oligomers as a function of conversion for these three systems. For the 4 mol % AA system, the percentage of AA monomeric units was low from the very beginning of the polymerization (about 20% at ∼1% conversion). By increasing the AA monomer concentra-

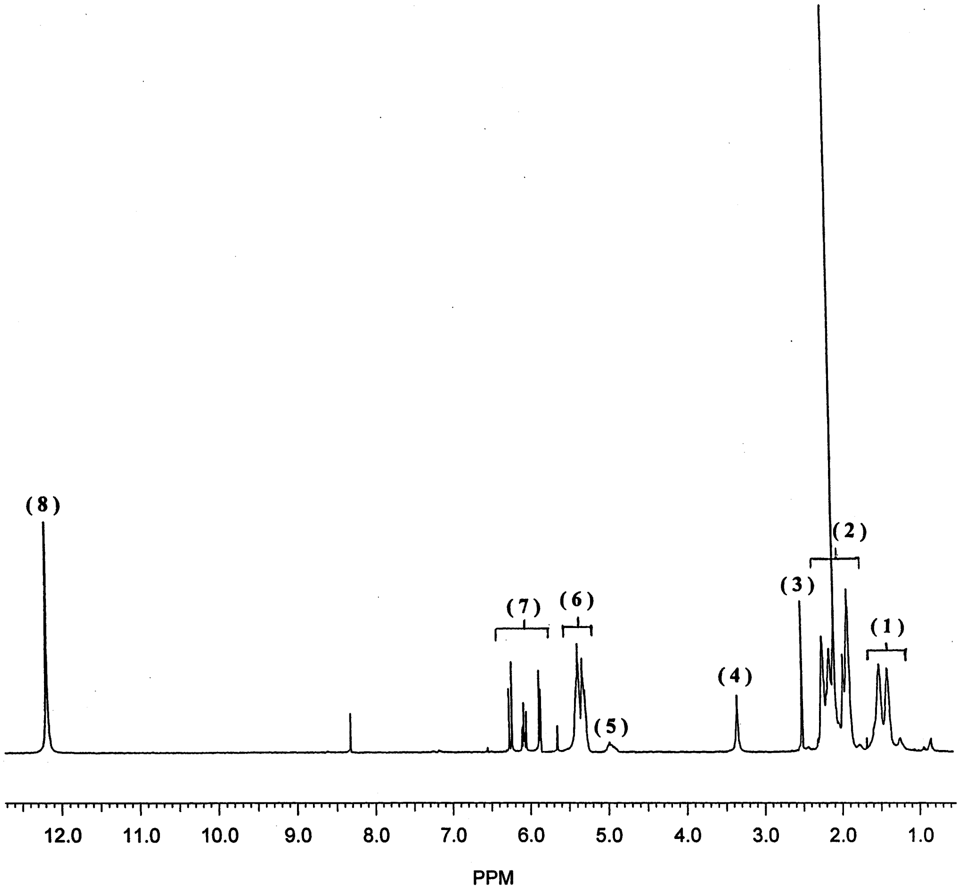

Figure 1. ^{1}H NMR spectrum of acrylic acid and butadiene copolymer obtained at 3.5% conversion and T_r = 70 °C: (1) CH_3- protons in AIBN initiator; (2) $-CH_2-$ and $-CH-$ protons in 1,4-Bu and poly-AA; (3) H_2O protons; (4) DMSO protons; (5) $CH_2=$ double-bond protons in 1,2-Bu; (6) $-CH=$ and $-CH=CH-$ double-bond protons in 1,4-Bu and 1,2-Bu units; (7) H_α and H_β protons of AA monomer; (8) $-OH$ protons of AA, PAA, and H_2O.

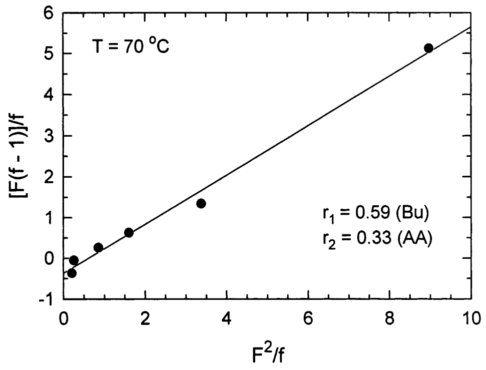

Figure 2. Finemann−Ross plot for the determination of the reactivity ratios of AA/Bu at 70 °C. Slope = r_{Bu} = 0.59; intercept = r_{AA} = 0.33.

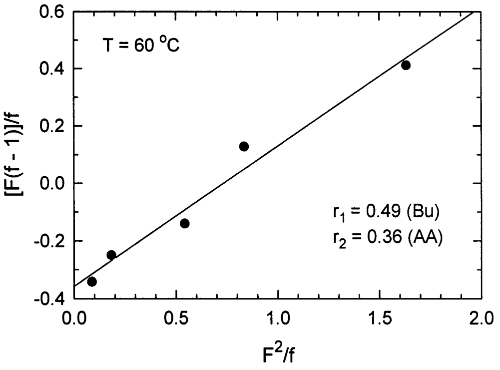

Figure 3. Finemann−Ross plot for the determination of the reactivity ratios of AA/Bu at 60 °C. Slope = r_{Bu} = 0.49; intercept = r_{AA} = 0.36.

tion to 8 mol %, the composition of the oligomers appears richer in AA at the beginning of the reaction (55 mol % AA, 35 mol % Bu, 10 mol % St at ∼1% conversion). After that, the AA composition decreased rapidly to ∼35 mol %, as the Bu composition increased to ∼50 mol % and the St composition increased to ∼20 mol % at around 50% conversion. The question here is why the Bu in the water-soluble oligomers is present in such high amounts early in the reaction.

According to the homogeneous-coagulative and micellar-entry nucleation mechanisms in emulsion polymerization, for a hydrophilic−hydrophobic monomer system like that used in this study, one would expect that, in the early stages of the polymerization, the oligomer radicals formed in the aqueous phase would be comprised primarily of the more water-soluble monomer (i.e., AA). This should particularly be the case for 8 mol % AA system, since oligomeric radicals are first generated in the aqueous phase and the acrylic acid concentration is the highest there.

In general, the composition of copolymers depends on the reactivity ratios of each polymer pair and the monomer concentrations at the reaction site. Consequently, for reactions carried out in a heterogeneous system (i.e., both aqueous and organic phases in an emulsion polymerization), the locus of polymerization will also affect the composition of the polymer formed. These parameters will be considered one by one in detail in the following discussions.

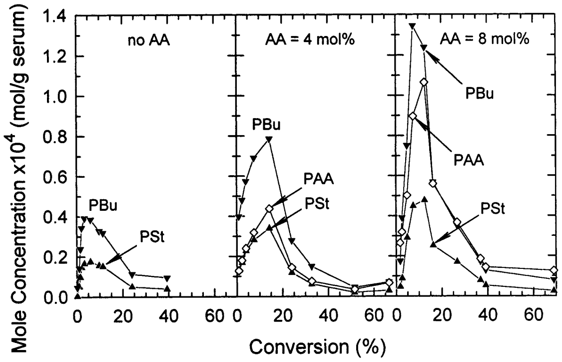

Figure 4. Mole concentrations of Bu, St, and AA monomeric units present in the water-soluble oligomers in the aqueous phase vs conversion for [AA] = 4 mol % (St/Bu/AA = 39/57/4 mol %), 8 mol % (St/Bu/AA = 37.5/54.5/8 mol %), and St/Bu + acetic acid (AcA) with [AA] = 0 mol % (St/Bu/AA = 49/51/0 mol %) emulsion polymerizations carried out with [SLS] = 32 mM, [I] = 3.17 mM, and T_r = 70 °C.

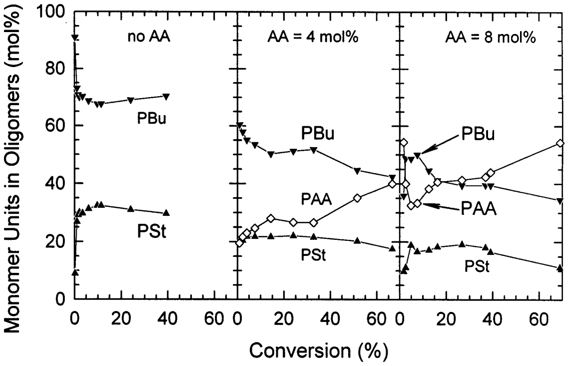

Figure 5. Mole percent of Bu, St, and AA monomeric units present in the water-soluble oligomers in the aqueous phase vs conversion for [AA] = 4 mol % (St/Bu/AA = 39/57/4 mol %), 8 mol % (St/Bu/AA = 37.5/54.5/8 mol %), and St/Bu + acetic acid (AcA) with [AA] = 0 mol % (St/Bu/AA = 49/51/0 mol %) emulsion polymerizations carried out with [SLS] = 32 mM, [I] = 3.17 mM, and T_r = 70 °C.

Table 4. Reactivity Ratios by Bulk Polymerization at 60 °C

1−2	r_1	r_2	r_1r_2
St−Bu	0.78	1.39	1.08
St−AA	0.25	0.15	0.04
Bu−AA	0.49[a]	0.36[a]	0.18

[a] Measured values; all others are from *Polymer Handbook*[5] as determined by bulk free radical copolymerizations at 60 °C (Mayo−Lewis method).

Monomer Reactivity Ratios. The reactivity ratio of each monomer in a pair is one of the most important parameters in determining the composition of the resulting copolymers. Since the reactivity ratios of these three copolymer pairs in the aqueous phase cannot be measured easily owing to the low water solubility of Bu and St monomers, bulk polymerization results have to be used as reference. The monomer reactivity ratios of St/Bu and St/AA comonomer pairs in bulk polymerizations are well-determined and can be found in the literature.[5] However, the reactivity ratios for Bu/AA have not been reported and thus were determined as part of this study. The results, listed in Table 4, show that for the St/Bu copolymerization system $r_1 < 1$ (0.78) and $r_2 > 1$ (1.39); this results in r_1r_2 being slightly greater than unity (1.08). This means that Bu monomer is more reactive than St monomer toward both propagating oligomeric free radical species. Therefore, the copolymer should contain a large proportion of the more reactive Bu monomer in random placement.[8] Considering that the water solubility of Bu monomer (15 mM at 25 °C) is higher than St (3 mM at 25 °C),[9] it is not difficult to understand the higher PBu content relative to PSt obtained for the water-soluble oligomers (Figure 4). For the copolymerizations of St/AA and Bu/AA, the reactivity ratios are all smaller than unity and both r_1r_2 products are close to zero, which implies that the copolymers in both cases are more likely to form alternating copolymers. Therefore, from the reactivity ratio point of view, the copolymers should contain almost equal proportions of AA and Bu monomeric units if the monomer concentrations at the reaction locus are the same.

The combined results for the reactivity ratios obtained by bulk polymerization seem to indicate that Bu is more reactive than St but only slightly more reactive than AA and that St is comparable to AA. It should be pointed out that, in general, monomer reactivity ratios are independent of the reaction medium in radical copolymerization. However, this will not be the case if one of the comonomers bears a functional group that can form a hydrogen bond with the solvent (e.g., carboxylic acids and acrylamide).[10,11] Copolymerizations involving the combination of polar (M_1) and nonpolar (M_2) monomers often show different behaviors depending on the polarity of the reaction medium. It was noted that the copolymer composition is richer in the less polar monomer for reactions in a polar solvent (either aprotic or protic) compared to a nonpolar solvent. According to this trend, for the St/Bu/AA emulsion terpolymerization, the reactivity of Bu and St monomers (nonpolar) may be increased and that of AA monomer (polar) may be decreased when the polymerization site is in the aqueous phase (e.g., during the particle nucleation period). This may result in an increase in the Bu concentration in the oligomers. This effect can be considered negligible by simply comparing the results obtained in the two systems using 4 and 8 mol % AA. Since the only difference between these two systems is the concentration of AA monomer, the reactivities should be the same. The fact is that, at 8 mol % AA, the oligomers are richer in AA monomeric units (~55 mol %) at the very beginning of polymerization (~1%). After that, the AA content decreased sharply to ~33% at ~5% conversion. This decrease cannot be explained by the effect of solvent on the monomer reactivity ratios. It must be caused by something else.

Monomer Concentration. The monomer concentration at the reaction loci is another important parameter controlling the rate of polymerization and also the composition of the oligomers. The Bu and St monomer concentrations in the aqueous phase can be basically compared to their water solubilities at the reaction conditions. The AA monomer can completely dissolve in water with a certain amount partitioning into the organic phase. Shoaf and Poehlein[12] have studied the partitioning of AA in the emulsion polymerization of St/AA. They reported that the partitioning of AA between the styrene monomer and the aqueous phases depends on several parameters such as the acid level, the monomer-to-water ratio, the ionic strength, and the neutralization of the AA monomer. Therefore, the determination of the partitioning of AA under the specific reaction conditions in this study is required. The partitioning of AA and St monomers in the aqueous and

Table 5. Partitioning of Monomers into the Phases

system	T (°C)	AA_{aq} (wt %)	AA_{aq} (mM)	AA_{oil} (mM)	Bu_{aq} (mM)	St_{aq} (mM)
4 mol % AA	70	77	188	55.6	50[a]	6.2
8 mol % AA	70	68.5	329	150.3	60[a]	12.9

[a] Estimated.

organic phases was measured by the GC method for the systems containing 4 and 8 mol % AA (without the addition of initiator) at 70 °C. Table 5 lists the results of the monomer partitioning in the aqueous phase for both the 4 and 8 mol % AA systems. The water solubility of Bu monomer unfortunately could not be obtained by this method; therefore, an estimation had to be made. Water solubilities of 15 mM at 25 °C and 37 mM at 50 °C have been reported for Bu in the literature.[9] Therefore, by referring to the trend of the variation of the water solubility of styrene in this system in the presence of AA from 6.2 to 12.9 mM for 4 and 8 mol % AA, respectively, as shown in Table 5, the water solubility of Bu at 70 °C could be approximated as 50 mM for 4 mol % AA and 60 mM for 8 mol % AA (an increase in the same order of magnitude). These values would indicate that the AA concentrations (taking into account the partitioning into the organic phase) are initially 3 and 6 times higher than the Bu concentrations for the two systems, respectively. Therefore, from the monomer concentration point of view, AA should have the highest content in the oligomers if the reaction only takes place in the aqueous phase.

Loci of Oligomer Formation. From the preceding results, it seems that both the reactivity ratios of the three monomer pairs and the monomer concentrations in the aqueous phase indicate that, under the given experimental conditions, oligomers should have a higher content of AA if the oligomers are generated only in the aqueous phase. It is also believed that the high Bu content cannot be obtained by aqueous phase growth only. Therefore, the only possible place that allows oligomers to add sufficient Bu units is the organic phase, that is, micelles, particles, and monomer droplets. Polymerization in the monomer droplets is often neglected in conventional emulsion polymerization because of the small total surface area. In addition, the mobility of oligomers between particles in the aqueous phase is also considered to be limited.[4] Then the most likely place for oligomers to add more Bu units should be in the micelles. It was also noted that the highest concentration of water-soluble oligomers was observed when micelles were present.

A possible mechanism for the formation of the Bu-rich oligomers is as follows. Free radicals are first formed in the aqueous phase by the decomposition of the initiator. After adding monomer units in the aqueous phase, these oligomers become surface active. Then they can be absorbed into micelles or become surrounded by surfactant molecules. They might propagate in the micelles adding St or Bu monomer units and remain there if they lose their water solubility, or they might desorb from the micelles and return to the aqueous phase as long as they are still sufficiently water-soluble. This chain growth in the organic phase (micelles) is probably the main reason for the high concentration of Bu monomer units in the oligomers. To prove this hypothesis, a St/Bu/AA emulsion polymerization was carried out in the absence of micelles (i.e., at a surfactant concentration below the cmc).

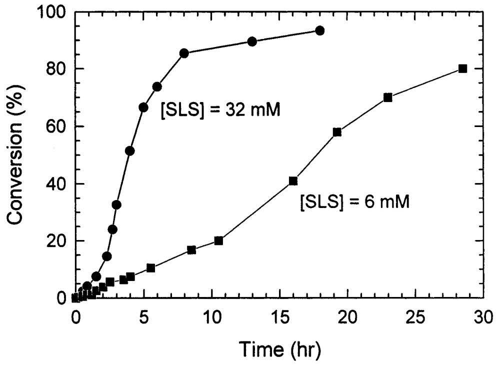

Figure 6. Conversion (measured gravimetrically) vs time for St/Bu/AA (39/57/4 mol %) emulsion polymerizations carried out with [SLS] = 6 and 32 mM; [AA] = 4 mol %, [I] = 3.17 mM, and T_r = 70 °C.

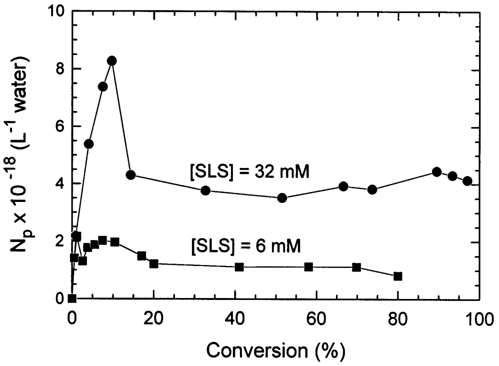

Figure 7. Number of particles per liter of water (N_p) vs conversion for St/Bu/AA (39/57/4 mol %) emulsion polymerizations carried out with [SLS] = 6 and 32 mM; [AA] = 4 mol %, [I] = 3.17 mM, and T_r = 70 °C.

Influence of Surfactant Concentration. If micelles represent an essential locus of oligomer growth producing water-soluble oligomers with high Bu content, then the oligomer composition should change dramatically for reactions carried out below the cmc of the surfactant.

a. Effect of SLS Concentration on Kinetics Behavior. Based on the model recipe shown in Table 1, a St/Bu/AA emulsion polymerization was carried out with an SLS concentration of 6 mM (< cmc), keeping everything else the same (i.e., [AA] = 4 mol %, [I] = 3.17 mM, 70 °C). The conversion vs time and the number of particles (N_p) vs conversion curves for the St/Bu/AA emulsion polymerization carried out at 32 mM SLS (> cmc) and 6 mM SLS (< cmc) are presented in Figures 6 and 7, respectively. As expected, the polymerization was more rapid at the higher emulsifier concentration. It is reasonable to believe that when the SLS concentration exceeded its cmc, particle formation took place by both micellar-entry and homogeneous-coagulative mechanisms, while only homogeneous-coagulative nucleation could occur when the emulsifier concentration was below the cmc.

The rapid increase in the rate of polymerization above the cmc is caused by the large number of small particles generated in the early stages of the polymerization. This can be clearly seen in the N_p vs conversion curve in Figure 7. In this case, at the very beginning of the reaction (<10% conversion), a large number of precursor particles are formed by both micellar and homogeneous nucleation mechanisms, and their concentration increases with conversion. This results in a rapid increase

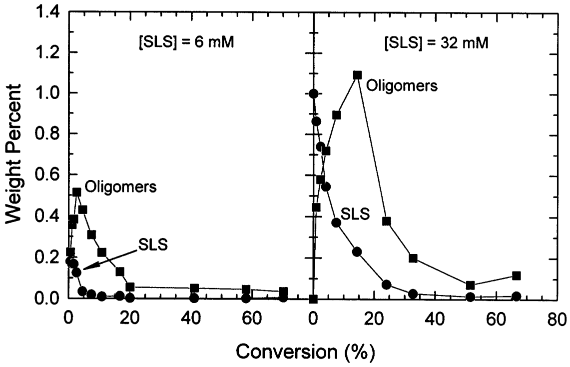

Figure 8. Weight percent of water-soluble oligomers and emulsifier (SLS) vs conversion for St/Bu/AA (39/57/4 mol %) emulsion polymerizations carried out with (a) [SLS] = 6 mM (left) and (b) [SLS] = 32 mM (right), with [AA] = 4 mol %, [I] = 3.17 mM, and T_r = 70 °C.

in the number of particles. Meanwhile, surfactant is required to stabilize the newly formed particles. After the surfactant concentration in the aqueous phase drops to below the cmc, limited flocculation occurs (due to insufficient surfactant available to stabilize the growing particles, which leads to the observed decrease in N_p) until a new "stabilization" condition is reached. For the polymerization begun below the cmc, homogeneous–coagulative nucleation results in a lower nucleation rate and larger particles.

b. Effect of Surfactant Concentration on Oligomer Characteristics. Figure 8 presents the evolution of the water-soluble oligomer and surfactant concentrations with conversion for the two SLS concentrations. The maximum oligomer concentration decreased by approximately one-half when the SLS concentration was decreased from 32 mM (> cmc) to 6 mM (< cmc). Actually, the initial increase in the concentration of oligomers was almost the same in both systems (below ~3% conversion). This is attributed to the initial formation of the oligomers in the aqueous phase. After reaching a maximum at about 3% conversion, the oligomer concentration in the 6 mM SLS system decreased, whereas the oligomer concentration continued to increase up to about 12% conversion in the 32 mM SLS system. This indicates that some fraction of the water-soluble oligomers was formed when micelles were present. In both systems, the maximum in the oligomer concentration is followed by a rapid decrease and correlates with the reduction in the aqueous SLS concentration. This behavior may be explained by an insufficient amount of surfactant to stabilize the newly formed particles, which results in the formation of larger size particles (fewer numbers) by aggregation (see Figure 7). The capture of oligomers by the particle surfaces increases at the same time and thus results in the observed decrease in the oligomer concentration in the aqueous phase.

Figure 9 presents the mole concentration of the individual monomer units in the oligomers as a function of conversion. These results further confirm the existence of an organic phase growth mechanism. When the SLS concentration was below the cmc, the concentrations of the three monomer units decreased significantly, especially the Bu units, which no longer was the dominant component of the oligomers.

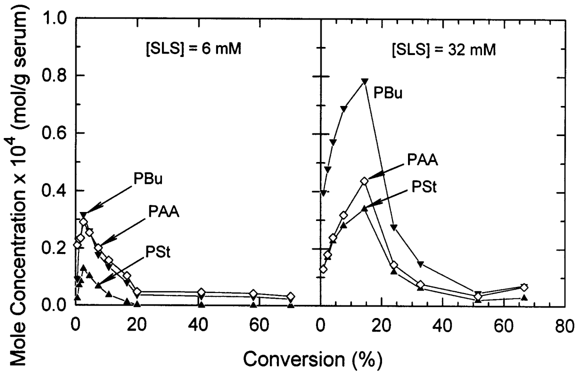

Figure 9. Mole concentration of Bu, St, and AA monomeric units present in the water-soluble oligomers in the aqueous phase vs conversion for the St/Bu/AA (39/57/4 mol %) emulsion polymerizations carried out with (a) [SLS] = 6 mM (left) and (b) [SLS] = 32 mM (right), with [AA] = 4 mol %, [I] = 3.17 mM, and T_r = 70 °C.

Table 6. Maximum Mole Concentrations and Mole Ratios of Monomeric Units in the Oligomers

system	[St], [Bu], [AA] ($\times 10^{-4}$ mol/g of serum)	St/Bu/AA (mole ratios)
$[C_{6\text{ mM}}]_{max}$	0.13, 0.32, 0.31	1/2.5/2.4
$[C_{32\text{ mM}}]_{max}$	0.34, 0.79, 0.43	1/2.2/1.5
$[C_{32\text{ mM}}]_{max} - [C_{6\text{ mM}}]_{max}$	0.21, 0.47, 0.12	1/2.3/0.6
organic phase	5.2,[a] 3.8,[a] 0.13[a]	1/1.9/0.2

[a] Expressed in units of grams.

On the basis of these data, it is possible to make a rough estimation of the growth that takes place in the organic phase. Using the monomer mole concentrations at the maximum in the oligomer concentration for each system (i.e., $[St]_{max} = 0.13 \times 10^{-4}$ mol/g of serum, $[Bu]_{max} = 0.32 \times 10^{-4}$ mol/g of serum, and $[AA]_{max} = 0.31 \times 10^{-4}$ mol/g of serum for the 6 mM SLS system and $[St]_{max} = 0.34 \times 10^{-4}$ mol/g of serum, $[Bu]_{max} = 0.79 \times 10^{-4}$ mol/g of serum, and $[AA]_{max} = 0.43 \times 10^{-4}$ mol/g of serum for the 32 mM SLS system), the mole ratios of monomer units can be obtained as listed in Table 6. If it is assumed that the oligomers obtained at 6 mM SLS are formed mainly by aqueous phase growth, and the oligomers obtained at 32 mM SLS are formed by both aqueous phase and organic phase growth, by subtracting the concentration of each monomeric unit at the maximum (i.e., $[C_{32\text{ mM}}]_{max} - [C_{6\text{ mM}}]_{max}$) as shown in Table 6, the mole ratio of the difference in these oligomers is obtained (i.e., St/Bu/AA = 1/2.3/0.6). This is assumed to roughly represent the composition of the oligomers grown in the micelle phase. This result shows that the AA component primarily attributed to organic phase growth is much lower than that attributed to aqueous phase growth. Table 6 also reports the theoretical composition of the terpolymer composition (i.e., St/Bu/AA = 1/1.9/0.2) calculated by using the termonomer composition equations,[13] based on the bulk reactivity ratios listed in Table 4 and the recipe monomer concentrations. This calculation accounts for the extent of AA partitioning into the organic phase ($[AA]_{aq}$ = 188 mM and $[AA]_{oil}$ = 55.6 mM for the 4 mol % AA system, as listed in Table 5). The calculated composition is not far from the rough estimation based on the above subtraction.

Proposed Mechanisms of Water-Soluble Oligomer Formation: Aqueous and Organic Phase Growth. The water-soluble oligomer compositions and concentrations found for increasing AA and decreasing SLS concentrations provide information supporting an oligomer formation mechanism that considers both aqueous phase and organic phase growth when the

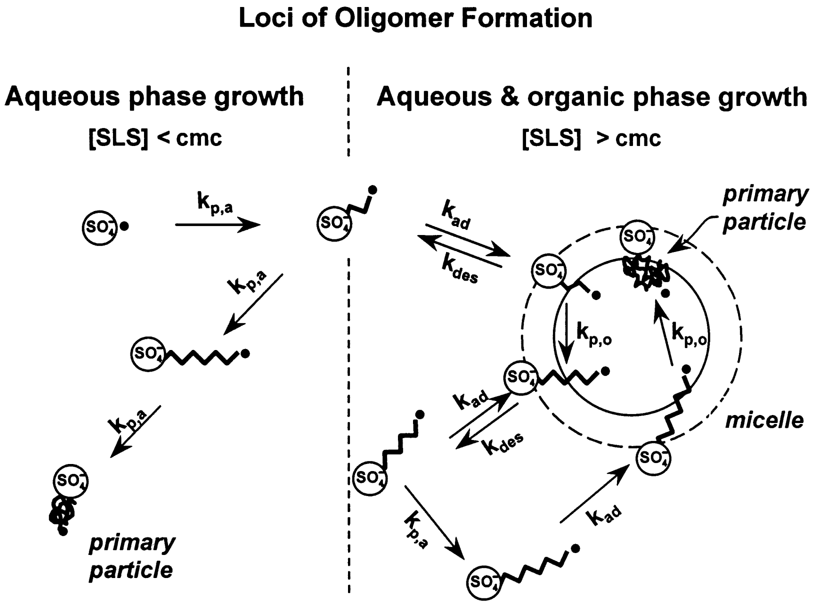

Figure 10. Schematic representation of the mechanisms of water-soluble oligomer formation through both aqueous and organic phase growths.

surfactant concentration is above the cmc. This mechanism is reiterated here as a schematic in Figure 10. Surface active oligomeric radical species will be absorbed into the micelles. They should also be able to desorb back into the aqueous phase before and after propagating in the micelles as long as they remain water-soluble. Obviously, this kind of activity may be repeated many times before their limit of water solubility is reached. In the micelles (organic phase), the propagation of oligomeric radicals will be faster than in the aqueous phase due to the higher Bu and St monomer concentrations there, so that significant amounts of Bu units will be added to the oligomer chains. On the other hand, when the reaction is in the aqueous phase, more AA monomer units would be added to the oligomer chains owing to the higher AA concentration there. According to this mechanism, differences should be seen in the molecular weights, composition, and monomer sequence distributions of the water-soluble oligomers formed by aqueous phase growth alone and by both aqueous and organic phase growths in micelles. Some further experimental evidence in this regard was obtained and will be discussed below.

Experimental Evidence. a. Oligomer Molecular Weight. Among the experimental evidence for organic phase growth of the water-soluble oligomers are the results obtained from molecular weight measurements for the polymerizations using different initiator concentrations. It is well-known that one of the most interesting characteristics of emulsion polymerization is the production of high molecular weight polymer with a simultaneous rapid rate of reaction.[14,15] In bulk, suspension, and solution (with chain transfer resistant solvents) polymerizations, increasing the initiation rate can increase the rate of polymerization. But this leads to a shorter radical growth time because of more rapid termination and a decrease in molecular weight.[15] However, this can be countered in emulsion polymerization by using more emulsifier to stabilize a larger number of particles, which increases the average growth time for individual molecules. Then, high rates can result in high molecular weights.

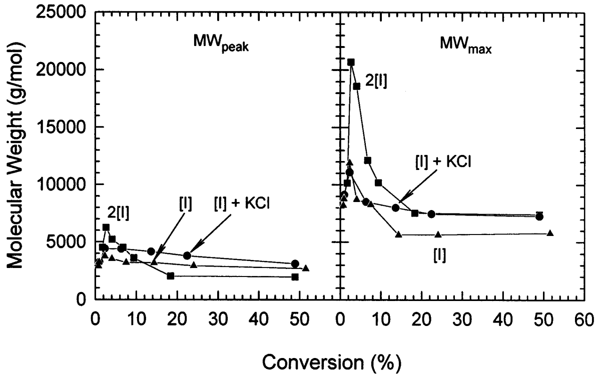

Figure 11. Water-soluble oligomer molecular weights: (a) MW_{peak} (left) and (b) MW_{max} (right) vs conversion for the St/Bu/AA (39/57/4 mol %) emulsion polymerization systems carried out with [I] = 3.17 mM, 2[I] = 6.34 mM, and [I] = 3.17 mM + 3.17 mM KCl = 6.34 mM, with [AA] = 4 mol %, [SLS] = 32 mM, and T_r = 70 °C.

On the basis of these concepts, if the water-soluble oligomers are formed only by aqueous phase growth, that is, solution polymerization, lower molecular weights should be expected with increasing initiator concentration. On the other hand, if they grow primarily in the organic phase, higher molecular weights would be expected due to growth under isolated conditions.

The molecular weight of the water-soluble oligomers was determined by aqueous phase GPC using 0.01 M $NaNO_3$ solution as the mobile phase. The columns were calibrated using water-soluble poly(ethylene oxide) standards with molecular weights in the range 660−37 000.[3] The maximum molecular weight, MW_{max}, which is obtained at the beginning of the oligomer peak in the GPC chromatogram and represents the highest MW measured, and the peak molecular weight, MW_{peak}, which is obtained at the peak maximum and represents the MW of the majority of the oligomers present in the system, are used here as measures of the molecular weight of the oligomers. These are shown in Figure 11 as a function of conversion for St/Bu/AA emulsion polymerizations carried out at different initiator concentrations (i.e., [I], 2[I], and [I] + KCl). [Note: KCl was

Table 7. Composition of Water-Soluble Oligomers for St/Bu Emulsion Polymerization at 70 °C

composition	St/Bu molar ratio	r_{St}	r_{Bu}
organic phase	1/1.9	0.78	1.36
aqueous phase	1/6.7	0.78[a]	1.36[a]
real oligomers	1/2.3		

[a] Assumed.

added to the [I] system to adjust the ionic strength to the same level as the 2[I] system. Thereby, the effect of the initiator concentration on the molecular weight of the oligomers could be better compared.] The MW_{max} vs conversion profiles show that increasing the initiator concentration substantially increased the maximum in MW_{max}. The ionic strength had no effect at low conversions (<10%). The more interesting result observed here is that the MW_{peak} vs conversion profiles show an increase in MW_{peak} with the increasing initiator concentration only in the early stages of the reactions (i.e., <12% conversion). This is the period when micelles are present in the system. After this, a decrease in MW_{peak} occurred with increasing initiator concentration. These results clearly indicate that, when micelles exist in the system, the oligomeric radicals grow in both the aqueous and organic phases; an increasing molecular weight was obtained owing to slower termination (relative to propagation) within the micelle phase. When the micelles disappeared, the primary growth of oligomeric radicals occurred in the aqueous phase, and then lower molecular weights were observed due to the relatively high rate of termination under solution polymerization conditions. Thus, high molecular weight oligomers can only be obtained in isolated micelles or particles, not by aqueous phase growth. Therefore, this supports the existence of an organic phase growth mechanism when micelles are present.

b. Oligomer Composition. As mentioned previously, the oligomer composition would be different with growth in the organic phase vs in the aqueous phase. This is caused by the difference in monomer concentrations in both phases and also by the differences in the monomer reactivity ratios when a polar monomer (i.e., AA) is involved. Compositional changes were also noted in the St/Bu (without AA) emulsion copolymerization.

Solvent-dependent phenomena are not considered to be significant for systems using low water solubility monomers such as styrene and butadiene.[16] Therefore, the theoretical composition of water-soluble oligomers formed by only aqueous phase growth or organic phase growth can be calculated substituting the known reactivity ratios of St/Bu and the concentrations of these two monomers in each phase into a copolymer composition equation.[17] The monomer concentration for St/Bu in bulk is based on the recipe and in the aqueous phase is assumed to be proportional to their respective water solubilities. The molar composition of P(St/Bu) oligomers by aqueous phase growth alone should be 1/6.1 and 1/1.9 by organic phase growth, as reported in Table 7. However, the composition of the water-soluble oligomers found in the actual polymerization system was 1/2.3, as shown in Figure 5. This composition is close to the composition calculated for organic phase growth and, therefore, may also be evidence that, even for low water solubility monomers like styrene and butadiene, the water-soluble oligomers may also be formed by both aqueous and organic phase growth when the surfactant concentration is above the cmc.

c. Monomer Sequence Distribution in Oligomers. The measurement of the oligomer monomer sequence distribution should not only help us to understand the reason for the water solubility of the oligomers with a high Bu content but should also help to reveal the mechanism of oligomer formation. Theoretically, if the water-soluble oligomers were formed only by aqueous phase growth, these would contain more acrylic acid blocks in the sequence distribution than for growth in the organic phase, because of the high acrylic acid concentration in the aqueous phase. On the other hand, the oligomeric radicals formed by organic phase growth should contain more random acrylic acid dyads (such as AB_{trans}, AB_{cis}, AB_{vinyl}, and AS), because of the low concentration of AA in the organic phase. Therefore, the oligomers formed in the 6 mM SLS (< cmc) system should have a high fraction of −AA− block dyad sequences (only by aqueous phase growth), and those formed in the 32 mM SLS (> cmc) system should have a high fraction of random AA dyad sequences (both aqueous and organic phase growth).

Completely resolving all the resonances for a St/Bu/AA terpolymer in a ^{13}C NMR spectrum is very complex and extremely difficult, especially when butadiene monomer is involved. Since there are five monomer units involved in the polymer chains, even considering the simplest way to study the sequence distribution (i.e., by dyad distribution), a total of around 25 dyad peaks should be resolved in the spectra. A higher resolution NMR instrument and more powerful program may be required to achieve this. Fortunately, it is not necessary to resolve all the resonances in this work. The fraction of the block dyad sequence and the random dyad sequence of acrylic acid in the oligomer chains can be obtained as long as the peak for the −AA− homo block dyad can be resolved and the peak area related to the peak area of the carbonyl carbon peak (in −COOH) of acrylic acid (which includes the whole acrylic acid sequence information).

Three serum samples were used to study the sequence distribution. They were taken from the St/Bu/AA emulsion polymerizations carried out at 70 °C, differing in surfactant concentration (6 mM SLS and 32 mM SLS) and acrylic acid concentration (4 mol % AA and 8 mol % AA) and all having the highest oligomer concentration in each system. Their ^{13}C NMR spectra are shown in Figure 12. These spectra were obtained with a Bruker AM-500 spectrometer, operating at 125.8 MHz. D_2O was used as internal locking agent, and the chemical shift was referred to dioxane (67.3 ppm in D_2O). The sequence distribution at the dyad level was characterized by the resonance of the methylene carbon ($-CH_2-$) of acrylic acid.

The ^{13}C NMR spectra of the methylene ($-CH_2-$) and methane ($-CH-$) carbon regions of the poly(acrylic acid) (PAA), the neutralized poly(acrylic acid) (PAANa) in D_2O, the Bu-*co*-AA copolymer, and the St/Bu/AA terpolymer samples dissolved in dioxane-d_6 are shown in Figure 13. The measurement conditions are listed in Table 8. The methylene carbon peak in PAA is ~35.2 ppm, and the methane carbon is in the region of 42.3 ppm. Both peaks were shifted downfield as they were in the copolymers and terpolymers, and the carboxyl groups were neutralized (i.e., PAANa). Also, the same shifts in the methylene and methane carbon peaks were noted when AA was in the Bu-*co*-AA copolymer and the Bu-St-AA terpolymers. A larger shift in the methane

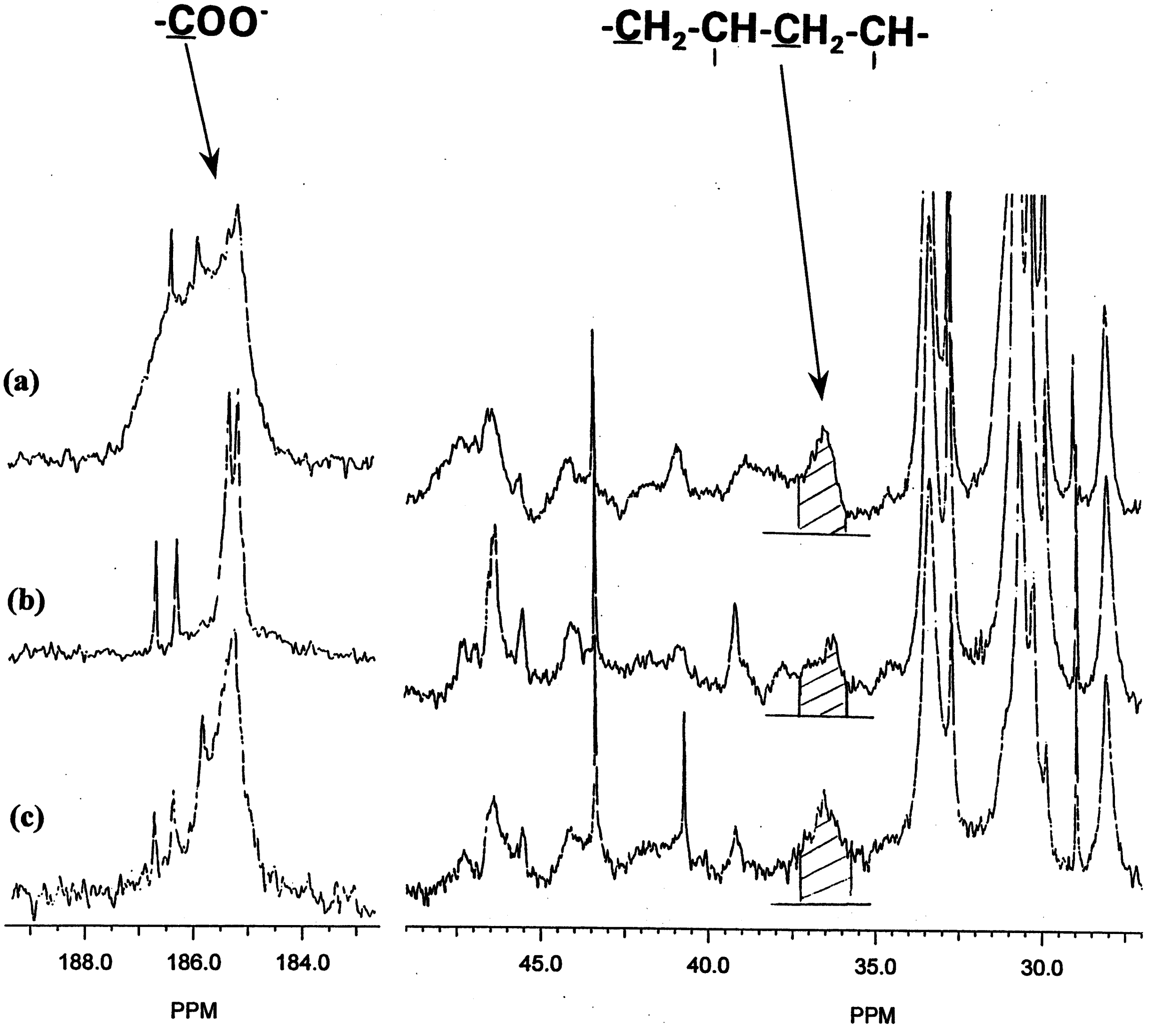

Figure 12. ^{13}C NMR spectra of sera obtained from emulsion polymerizations of St/Bu/AA carried out with (a) [SLS] = 32 mM, [AA] = 8 mol %; (b) [SLS] = 32 mM, [AA] = 4 mol %; and (c) [SLS] = 6 mM, [AA] = 4 mol %; T_r = 70 °C.

carbon compared to the methylene carbon was also noted. Neutralization of the carboxylic acid caused the methylene carbon peak to shift from ~35.2 to ~37.0 ppm and the methane carbon from ~42.3 to ~45.5 ppm. Split peaks for both the methylene and methane carbons, which provide information on the tacticity of the AA monomeric units in the poly(AA), appeared in the homo-PAA spectrum but were not seen in the spectra of the Bu-AA copolymer and the Bu-St-AA terpolymer. This indicated that the tacticity of AA is not measurable for the latter polymers.

Using this information, the methylene carbon peak at a chemical shift of 36−37 ppm can be assigned to the −AA− homo dyad sequence in the oligomer. To determine the integration region and limit the overlapping of peaks from other randomly linked acrylic acid units, a theoretical calculation can be used to check how far the methylene carbon chemical shift can be and in which direction as AA is linked with other monomeric units. The extent of randomly linked acrylic acid can be calculated theoretically[18] by using parameters from the literature.[19] These results are listed in Table 9. The purpose of performing this calculation is to determine the trend in the chemical shift of the methylene carbon in acrylic acid as the other monomer units are directly linked to the AA monomer, but not the absolute chemical shift values, which change depending on the sample. The results show that the chemical shifts of the methylene carbon in AA will all be downfield (i.e., higher ppm) more than 1 ppm when the acrylic acid monomer is directly connected to St or Bu monomer. Therefore, the integration area taken between 36 and 37 ppm can be taken as the −AA− homodyad. Although this peak is partially overlapped with other random dyad peaks, the comparative results listed in Table 10 are still good evidence for the proposed mechanism. The results show that, for the experiment carried out with an SLS concentration below the cmc, the homodyad sequence in the oligomers was ~80%, and therefore the random sequence was ~20%. Above the cmc, the −AA− dyad sequence decreased to ~30%; even increasing the acrylic acid to 8 mol % only increased this value to ~35%. These results further prove that, when the surfactant concentration is above the cmc, the water-soluble oligomers are formed by both aqueous and organic phase growth. In addition, it also seems to explain why oligomers containing large amounts of Bu units can still remain water-soluble as they contain more random AA linkages.

Discussion

Possible explanations for the formation of water-soluble oligomers through organic phase growth are described in the following.

Desorption (k_{des}) of Oligomeric Radicals from a Micelle. According to the homogeneous-coagulative and

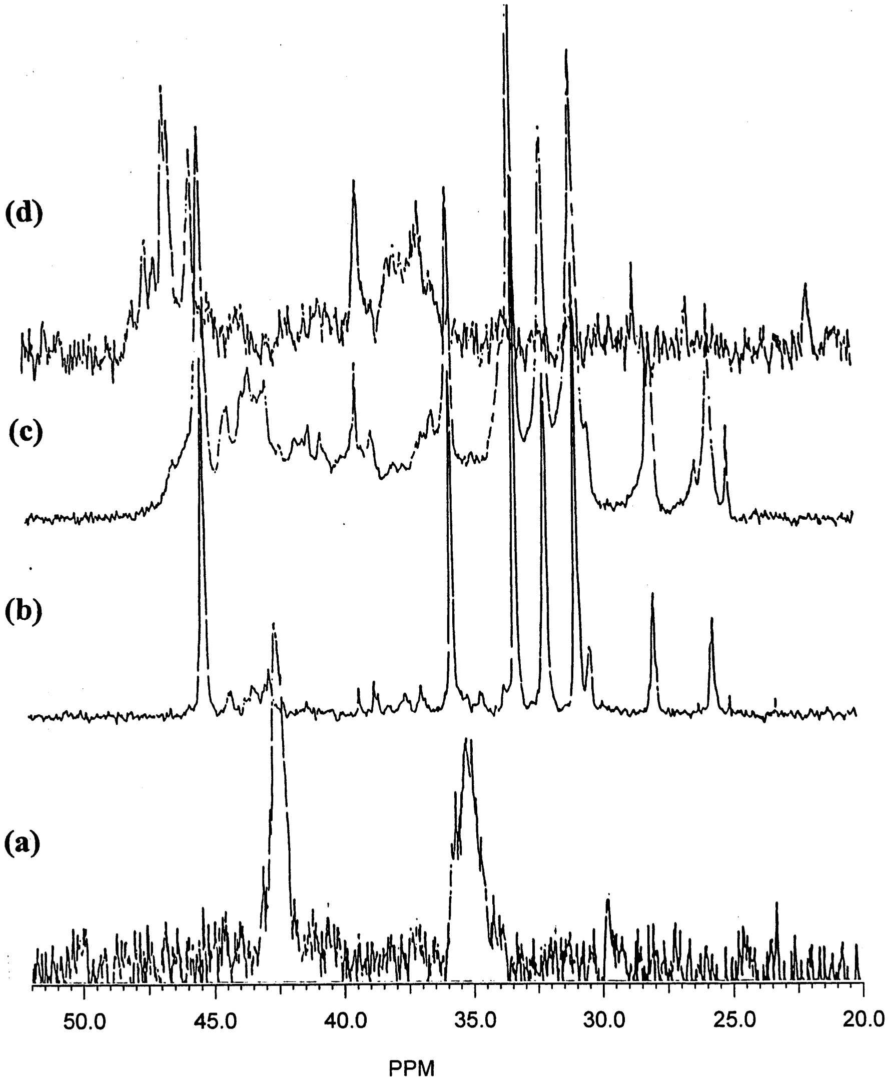

Figure 13. ^{13}C NMR spectrum of (a) PAA and (d) PAANa polymers in D_2O, (b) Bu-*co*-AA copolymer, and (c) St-Bu-AA terpolymer in dioxane-d_6.

Table 8. Measurement Conditions for Some ^{13}C NMR Spectra of Polymers[a]

condition	NaPAA	PAA	St/Bu/AA	Bu/AA
acquisition time (s)	1.114	1.114	1.114	1.114
flip angle (deg)	45	45	45	45
pulse delay (s)	0.002	0.10	0.4	15
no. of scans	570	800	9109	2669

[a] The spectra of the polymers were obtained using a Bruker AM-500 spectrometer operating at 125.8 MHz.

micellar-entry nucleation mechanisms,[20] during emulsion polymerization, the free radicals are generated by decomposition of initiator, which then propagate to form oligomeric radicals in the aqueous phase. When the surfactant concentration is below the cmc, primary particles are formed by precipitation of these oligomeric radicals after reaching their critical chain length (j_{crit}) by the addition of monomer units to become water-insoluble. Above the cmc, nucleation is dominated by micellar-entry. Oligomeric radicals will become surface active when they grow to a certain chain length (i.e., *z*-mer, $M_zSO_4^-$, which is termed "the formation of in-situ surfactant" by Casey et al.[20]) and will adsorb onto a micelle surface. Therefore, at the micelle surface, these oligomeric radicals will act like the surfactant molecules themselves by orienting their hydrophobic chains and the radical end into the micelle and leave the hydrophilic end group ($-SO_4^-$) facing the water phase. In this way, they can propagate by adding monomer units in the micelle−monomer "interphase" and can also desorb back into the aqueous phase before they become water-insoluble (i.e., become a *j*-mer).

Maxwell et al.[21] have presented compelling evidence, both theoretical and experimental, that two styrene units need to be added to a sulfate ion free radical before it will enter a monomer-swollen polymer particle. One would expect similar requirements for radicals that enter micelles. According to Maxwell et al., an anionic (sulfate) surfactant with eight CH_2 groups is considered to have sufficient chain−chain lateral interactions to be "surface active". The free energy of adsorption of one styrene monomeric unit in an oligomer chain is equivalent to that of about three and one-half methylene groups.[21,22] Therefore, the *z*-mer would contain at least two styrene monomeric units. This value may not vary much for low water solubility monomers, such as styrene; however, it will be very different when a monomer with higher water solubility (e.g., AA) is part of the oligomer chain. In this case, the existence of highly water-soluble carboxylic acid groups results in an increase in the water solubility of the oligomers and an increase in the chain length of the *z*-mers.

Table 9. ^{13}C Chemical Shift of the Methylene Carbon in Neutralized Poly(acrylic acid) Obtained by Calculation

type of linkage	structure	chemical shift of methylene carbon (CH_2) in poly(acrylic acid) (ppm)
−A−A−A−A−	$-[CH_2-CH(COO^-)]_n-$	31.9
−S−A−S−A−	$-[CH_2-CH\ (Ph)-CH_2-CH(COO^-)]_n-$	35.9
−T−A−T−A−	$-[CH_2-CH{=}CH-CH_2-CH_2-CH(COO^-)]_n-$	33.0
−C−A−C−A−	$-[CH_2-CH{=}CH-CH_2-CH_2-CH(COO^-)]_n-$	33.0
−V−A−V−A−	$-[CH_2-CH(CH{=}CH_2)\text{-}CH_2-CH(COO^-)]_n-$	33.9

Table 10. Homo and Random Dyad Sequence of Acrylic Acid of Water-Soluble Oligomers in St/Bu/AA Terpolymer Obtained by ^{13}C NMR

system	peak area ($-CH_2-$)	peak area ($-COO^-$)	block AA (%)	random AA (%)
[AA] = 4 mol %, [SLS] = 6 mM	16	20	80	20
[AA] = 4 mol %, [SLS] = 32 mM	6	20	30	70
[AA] = 8 mol %, [SLS] = 32 mM	7	20	35	65

Table 11. Oligomer Molecular Weight and the Critical Chain Length vs Conversion[a]

system	conv (%)	MW_{max}	MW_{crit}	j_{crit}
St/Bu, 0 mol % AA, [I], 70 °C	1.0	4200	2100	28
	1.5	4600	2300	31
	5.9	4900	2500	35
	38.0	5000	2500	35
St/Bu/AA, 4 mol % AA, [I], 70 °C	0.8	9000	4500	68
	2.3	11900	5100	87
	7.5	8300	4200	62
St/Bu/AA, 4 mol % AA, 2[I], 70 °C	1.7	10200	5000	76
	4.0	18600	9300	130
	48.9	7400	3700	52
St/Bu/AA, 4 mol % AA, [I] + KCl, 70 °C	1.0	8500	4300	64
	2.3	10100	5000	75
	6.3	8500	4300	66
	22.3	7500	3800	54
	48.9	7300	3700	52
St/Bu/AA, 4 mol % AA, [I], 80 °C	1.8	12000	6000	76
	3.1	17900	8800	132
	6.8	9700	4800	76
	46.1	7400	3700	52

[a] [I] = 3.17 mM, and 2[I] = 6.34 mM initiator concentration.

The most important point here concerns the critical chain length. According to Maxwell et al.[21] and Gilbert,[23] for the styrene homopolymer system, j_{crit} equals 4 styrene units. This means that a sulfate free radical first becomes a *z*-mer by adding two styrene monomeric units; then, another two styrene monomeric units need to be added before it becomes water-insoluble. In this case, the *z*-mer rapidly becomes a *j*-mer, reducing the probability for it to return to the aqueous phase and grow there. Therefore, any water-soluble oligomers found in the aqueous phase will be formed mainly by aqueous phase growth. On the other hand, if many monomer units are required for the *z*-mer to become a *j*-mer, the formation of oligomeric radicals by organic phase growth cannot be excluded.

Table 11 lists the oligomer molecular weight results for several systems investigated, as measured by gel permeation chromatography. Again, MW_{max} represents the maximum molecular weight of the oligomers obtained as determined by the beginning of the oligomer peak. If we assume that the oligomers with MW_{max} are most likely formed by termination (by combination) of two oligomers having the maximum chain length of water-soluble oligomers, then the critical chain length (j_{crit} listed in Table 11) can be estimated from the critical molecular weight ($MW_{crit} = {}^1/_2 MW_{max}$) and the mole fraction of each monomer unit in the oligomers (measured by ^{1}H NMR), plus the sulfate end group. The results show that the j_{crit} values for the St/Bu copolymer system are in the range of 28−35 monomer units and in the range of 52−87 for the St/Bu/AA terpolymer. Fitch et al. reported values of j_{crit} for MMA of ∼50 and ∼65, as measured by 90° light scattering[24] and GPC,[25] respectively. It seems that the latter results for MMA homopolymer and those reported here for St/Bu copolymer (which should also apply to St polymer) are considerably higher than Maxwell et al.'s estimate.

By considering the HLB values and the rate constant of micelle dissociation of the surfactant molecules, a theoretical prediction of j_{crit} can be made for low water solubility monomers (i.e., styrene or butadiene).

Prediction of j_{crit} Using k_{dis}. It should be understood that the location of a water-soluble oligomeric radical having a chain length smaller than j_{crit} should not be static at the micelle surface. It should exist in a dynamic equilibrium with those in the aqueous phase, as are the surfactant molecules in the micelles. These oligomers actually have the same hydrophilic end group ($-SO_4Na$) as SLS but differ in the tail structure. Although the rate of adsorption (R_{ad}) and desorption (R_{des}) of the oligomeric radicals to and from the micelles cannot be directly determined in the system studied, this kind of information can be found in the study of surfactant micelle formation in the literature. In surfactant−aqueous systems, many studies have revealed that there is a dynamic equilibrium that exists between the monomeric and micellar surfactant species. Micelles are continuously being formed and re-formed at rates on the order of milliseconds. Several methods have been developed (e.g., ultrasonic relaxation (UR), temperature-and-pressure jump techniques, and stop-flow (SF) techniques) to determine the rate constants of micelle formation and dissociation due to the linear relationship between the reciprocal relaxation time ($1/\tau$) and the stoichiometric surfactant concentration:[26]

$$1/\tau = k_f C_D - k_{dis} \tag{3}$$

where τ represents the relaxation time, k_f is the rate constant for micellization, C_D is the concentration of surfactant, and k_{dis} is the rate of dissociation of micelles.

Fendler and Fendler[26] collected some k_f and k_{dis} values of surfactants determined using different methods. They clearly pointed out that the breakdown of micelles is rapid compared with the time scale of most micellar catalyzed reactions, although the dependence of k_f and k_{dis} on the technique used was noted. Table 12 lists the rate constants for micelle dissociation (k_{dis}) in aqueous solutions for some alkyl sulfate surfactants determined by UR at two temperatures, 25 and 40 °C. These data are graphed in Figure 14, showing the linear variation of the log(k_{dis}) with the chain length of the surfactant at both temperatures.

Table 12. Rate Constant (k_{dis}) of Micelle Dissociation[a]

surfactant	T (°C)	method	k_{dis} (s^{-1})
sodium hexyl sulfate	25	UR	5.9×10^7
	40	UR	8.5×10^7
sodium heptyl sulfate	25	UR	2.8×10^7
sodium octyl sulfate	25	UR	5.0×10^6
	40	UR	2.4×10^7
sodium nonyl sulfate	25	UR	4.2×10^6
	40	UR	7.0×10^6
sodium decyl sulfate	25	UR	1.6×10^6
	40	UR	4.6×10^6

[a] Data from ref 26.

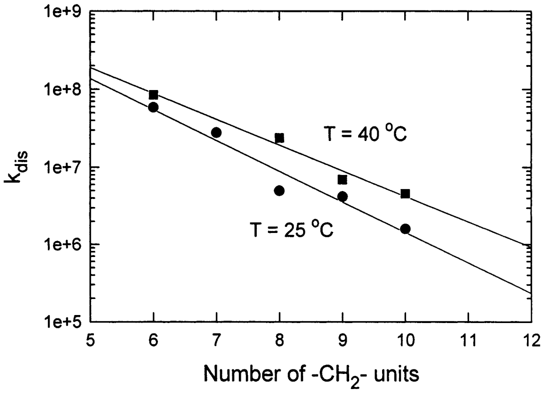

Figure 14. Logarithm of the rate constant of surfactant micelle dissociation, k_{dis} (measured by the ultrasonic relaxation technique), vs the number of methylene units in the molecular chain for 25 and 40 °C; based on data listed in Table 12.

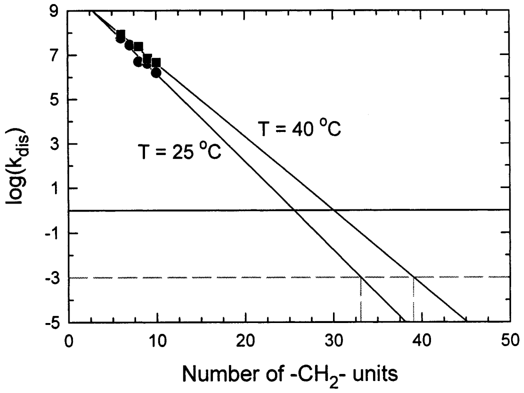

Figure 15. Extrapolation of log(k_{dis}) vs the number of CH_2 units shown in Figure 14 for the purpose of determining j_{crit}, i.e., when $k_{dis} \approx 10^{-3}$ $s^{-1} \approx 0$.

Now consider the limit of saturation. If it is assumed that the desorption of the surfactant molecules from the micelles can be neglected when k_{dis} reaches about 10^{-3} s^{-1} (i.e., almost zero) or when the molecule becomes insoluble in water (i.e., at j_{crit}), the number of $-CH_2-$ units in the chain required to reach this condition can be estimated by the extrapolation of the linear fit of the data in Figure 14 to a value of k_{dis} equal to 10^{-3}, as shown in Figure 15. Then, the number of methylene units should be approximately 33 for 25 °C and 39 for 40 °C, which are equivalent to about 8 and 10 styrene units (if 4 CH_2 groups, according to Maxwell et al., are equivalent to one styrene monomer unit) at 25 and 40 °C, respectively. It is clear that increasing temperature increases the water solubility of the hydrophobic chain, and the number of CH_2 units must be further increased when the reaction is carried out at 70 °C. Therefore, even at 40 °C, j_{crit} for styrene monomer is much longer than the four units predicted by Maxwell et al. This result also reveals that, even for the relatively low water solubility monomer styrene, after becoming surface active, it still requires the addition of more than eight monomer units to reach the critical degree of polymerization. On the other hand, the propagation rate constant (k_p) for styrene at 70 °C is in the range of $\sim 10^{2-3}$ s^{-1}, which is much smaller than the k_{dis} of surfactant molecules in the micelles (in the range of 10^7 s^{-1}). Therefore, these results support the notion that the oligomer radicals (surface active species) will adsorb–desorb or adsorb–propagate–desorb many times between the micelles and the aqueous phase before they become water-insoluble.

Prediction of j_{crit} from the HLB. It is believed that the critical chain length (j_{crit}) of an oligomer basically depends on the water solubility of the molecule and that it also depends on the balance of the hydrophilic–hydrophobic groups in the whole chain. This is known as the hydrophile–lipophile balance (HLB). The HLB values for anionic surfactants with straight hydrocarbon chains are found to be a linear function of the number of hydrophilic groups in the chain and can be calculated using the group numbers, as described by Davies[27] in the following relationship:

$$\text{HLB} = 7 + 3\ (\text{hydrophilic group numbers}) - 3\ (\text{lipophilic group numbers}) \quad (4)$$

where the last term on the right is usually $0.475n$, n being the number of $-CH_2-$ groups in the lipophile. According to Davies, the hydrophilic group number for $-SO_4Na$ is 38.7. Griffin[28] has studied the relationship between the water solubility of the surfactant and the HLB value. He reported that surfactants with HLB values above 13 will be water-soluble (i.e., a clear solution can be obtained). Therefore, eq 4 can be solved by setting HLB > 13 to obtain the maximum number (n) of hydrophobic groups (CH_2) in the molecule with a sulfate ion end group ($-SO_4Na$) below which the molecule will remain water-soluble, i.e.,

$$\text{HLB} = 7 + 38.7 - 0.475n > 13 \quad (5)$$

The solution of eq 5 gives $n < 69$. This results in a j_{crit} of 17 St or Bu monomer units (again, assuming that four CH_2 groups are equivalent to one styrene[21] or one butadiene monomer unit). On the basis of this result, taking the mole ratio of St to Bu to be 1/2.3 (i.e., 30/70 as shown in Figure 5, [AA] = 0 mol %), oligomers with length j_{crit} should contain 6 styrene and 11 butadiene monomer units with a total molecular weight of 1341 (including one $-SO_4Na$ end group). The j_{crit} values for this St/Bu system obtained by GPC were around 2100–2500 as listed in Table 11. The agreement with the theoretical prediction is satisfactory considering both the assumptions made and the experimental error.

The theoretical prediction of j_{crit} for the St/Bu/AA system will be much more complicated than the St/Bu system. This is because oligomers in this case will have a structure similar to a mixture of nonionic and anionic surfactants. As reported by Rosen,[29] the location of the hydrophilic carboxyl group in the oligomer chain will highly affect the hydrophilic–hydrophobic balance. Therefore, the prediction of an HLB value for this terpolymer should consider equations for both nonionic and anionic surfactant structures and, unfortunately, can only be performed after the exact structure of the oligomer is known. The differences arising in the St/

Bu/AA system (in this case, the values of z and j_{crit}) are dependent not only on the water solubility of the monomeric units in the oligomers but also on the terpolymer composition and the monomer sequence distribution of the oligomers. This results in a greater change in the chain length of the oligomers in the St/Bu/AA system than in the St/Bu system, as shown in Table 11.

Therefore, the above discussions indicate that the oligomeric radicals, after becoming surface active (z-mer), should adsorb−propagate−desorb many times from the micelles before they reach their critical chain length (j_{crit}). This process applies not only to oligomers formed in the St/Bu/AA system but also in the St/Bu copolymer system. The considerable difference between these experimental results and Maxwell et al.'s estimates may be caused by their choice of the standard compound, $CH_3(CH_2)_{16}$−sulfate, to perform the estimation. According to the definition of Rosen,[29] the Krafft point, or Krafft temperature (T_k), of a given ionic surfactant is the temperature at which the water solubility of this surfactant is equal to its cmc. It was suggested that a surfactant should be used above its Krafft point, since below T_k, the maximum reduction in surface tension will be determined by the concentration of the surfactant at solution saturation. These materials will show a lower effectiveness in reducing the surface tension compared to the case of similar materials that are used above their Krafft points. For $CH_3(CH_2)_{16}$−sulfate, the Krafft temperature is ~50 °C, the cmc is 3.5×10^{-4} mol/L, and the HLB is 37.6. Therefore, this seems to be a poor choice for choosing the maximum chain length of an alkyl sulfate compound that can remain water-soluble at 50 °C.

As shown in Figure 5, the composition of the water-soluble oligomers in the St/Bu system was almost constant (St/Bu $\approx$ 1/2.3) from ~1% to ~40% conversion. This may have occurred because, in this case, the monomer concentrations in both aqueous and organic phases exhibit the same trend (i.e., [Bu] > [St]) and the influence of the reaction medium on the reactivity ratios in the copolymerization is small. However, for the system involving AA (Figure 4), the composition of the monomeric units in the oligomers varies significantly, especially in the region below 20% conversion and for the system containing a high concentration of AA (8 mol % AA). This phenomenon is attributed to the tendency of the monomer concentration in the aqueous phase to be $[AA] \gg [Bu] > [St]$, whereas it is $[AA] \ll [St] < [Bu]$ in the organic phase. Therefore, during the propagation in the micelles, more Bu units will be added to the oligomer chains, owing to their higher concentration and higher reactivity. Meanwhile, the oligomers might maintain some degree of water solubility by adding AA units which have partitioned into the micelle. Also, the influence of the reaction medium on the reactivity ratios in the terpolymerization is not small being owing to the hydrogen bond interaction of the carboxyl groups of AA with the water molecules.[12]

It should also be mentioned here that the desorption of oligomeric radicals may also occur from the surface of droplets, especially when the surfactant concentration is far above the cmc (i.e., [SLS] $\gg$ cmc (many droplets)). Furthermore, the desorption of oligomeric radicals from the surface of polymer particles should be much more difficult than from micelles. This is because the chain−chain interactions between the oligomers and long chain polymer molecules at the particle surface are stronger than those between the oligomers and shorter chain surfactant molecules in the micelles. This was proven by the significant decrease in the water-soluble oligomer concentration after the micelles disappeared.

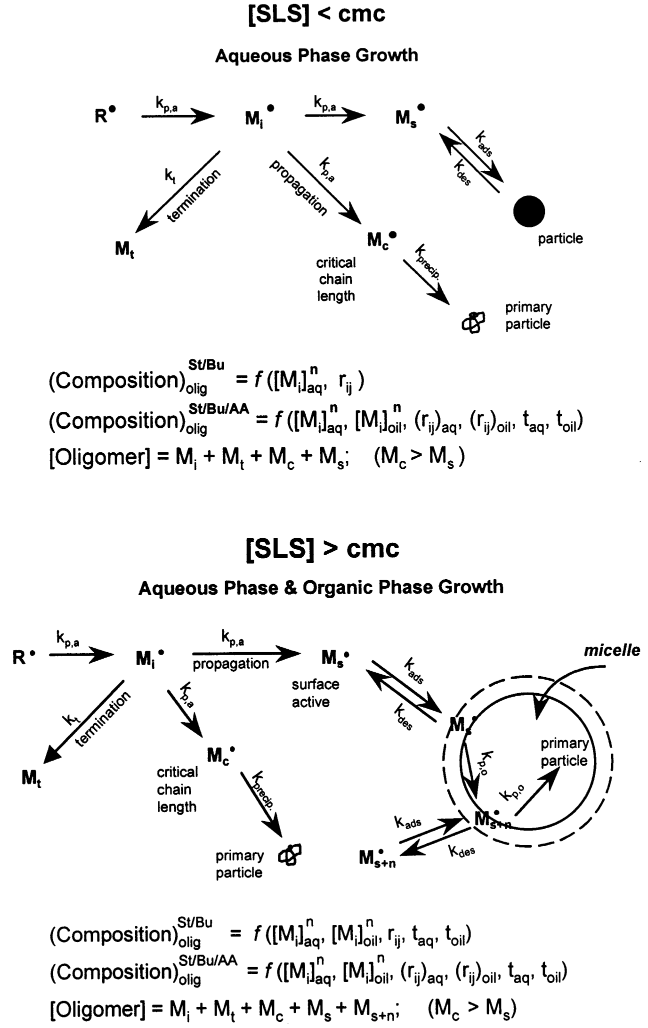

Figure 16. Schematic representation of the proposed mechanisms of water-soluble oligomer formation in systems where the SLS concentration is below (top) and above (bottom) the cmc.

Conclusions

Based on the experimental results and discussions above, a mechanism to describe the formation of water-soluble oligomers is proposed, as shown in Figure 16. Both aqueous and organic phase growth mechanisms are shown to affect the formation of water-soluble oligomers in the system.

When the surfactant concentration is below the cmc, the oligomeric radicals form by adding monomer units to the sulfate free radicals in the aqueous phase. After reaching their critical degree of polymerization ($M_c = j_{\mathrm{crit}}$), they precipitate out of the water to form primary particles. In this case, the composition of the water-soluble oligomers in a St/Bu copolymerization will be a function of the monomer concentration in the aqueous phase and the reactivity ratios of St and Bu in the bulk (since the solvent effect on reactivity ratio can be neglected). The concentration of water-soluble oligomers in the aqueous phase will increase at the beginning of the reaction and then start to decrease after reaching a maximum; this may be caused by an increase in the rate of capture of the oligomers by the particles and a decrease in the rate of desorption of water-soluble oligomers from the particles. The major mechanism determining the formation of these water-soluble oligomers is aqueous phase growth.

As the surfactant concentration is increased above the cmc, a large amount of micelles will exist at the beginning of the reaction. Similar to the preceding behavior, the sulfate free radicals will first add monomer units in the aqueous phase. After they become surface active (i.e., M_sSO_4Na), they can interact with the micelles. The oligomeric radicals will adsorb–desorb rapidly at the micelle surface just as a surfactant molecule, and they will also propagate in both the aqueous and organic phases until they reach their critical chain length, becoming a *j*-mer (M_cSO_4Na). Then, the desorption of oligomeric radicals from the micelles will not occur, resulting in the formation of primary particles. In this case, the composition of the oligomers for the St/Bu/AA system should be a function of the monomer concentration ($[M_i]_{aq}$ and $[M_j]_{oil}$), and the reactivity of each monomer pair $[(r_{ij})_{aq}$ and $(r_{ij})_{oil}]$ in both aqueous and organic phases, and also the time that the oligomeric radicals spend in each phase (t_{aq} and t_{oil}). Almost the same effect should be found for the St/Bu system, except that their reactivity ratios are not solvent dependent.

Obviously, the chain length of the surface active species (M_sSO_4Na) and the critical chain length of the oligomers (M_cSO_4Na) will be much different for a system with and without a water-soluble monomer, such as AA. This is because, in the latter case, the chain lengths of the oligomers are a function of not only the water solubility of each monomeric unit in the oligomer but also the terpolymer composition and monomer sequence distribution. Therefore, the organic phase growth process will result in the formation of water-soluble oligomers with higher molecular weights, higher fractions of random AA in the sequence distribution, and also compositions close to the polymer formed in the organic phase.

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