

# Effects of Short Chain Alcohols on the Styrene Emulsion Polymerization

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**ABSTRACT:** The effects of a series of short chain alcohols, 1-butanol ( $C_4OH$ ), 1-pentanol ( $C_5OH$ ), and 1-hexanol ( $C_6OH$ ), on the styrene (ST) emulsion polymerization mechanisms and kinetics were investigated. The CMC of the ST emulsions stabilized by sodium dodecyl sulfate (SDS) first decreases rapidly and then levels off when the  $C_iOH$  ( $i = 4, 5, \text{ or } 6$ ) concentration ( $[C_iOH]$ ) increases from 0 to 72 mM. Furthermore, at constant  $[C_iOH]$ , the CMC data in decreasing order is  $CMC(C_4OH) > CMC(C_5OH) > CMC(C_6OH)$ . The effects of  $C_iOH$  ( $i = 4, 5, \text{ and } 6$ ) on the ST emulsion

polymerization stabilized by 6 mM SDS are significant. This is attributed to the reduction in CMC by  $C_iOH$ , the different oil-water interfacial properties, the different concentrations of monomer within latex particles, and the different effectiveness of SDS/ $C_iOH$  in stabilizing latex particles. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4406–4411, 2006

**Key words:** polystyrene; emulsion polymerization; kinetics (polym); micelles; particle nucleation

## INTRODUCTION

Monomer-swollen micelles are the primary nucleation loci for the conventional styrene (ST) emulsion polymerization, with the surfactant level greater than its critical micelle concentration (CMC), according to the Smith-Ewart theory.<sup>1–6</sup> Micelle nucleation begins by the capture of free radicals by micelles. This is followed by the conversion of these nucleated micelles into the growing particle nuclei. On the contrary, the polymerization is characterized by homogeneous nucleation when the level of surfactant is below the CMC.<sup>7–11</sup> Upon polymerization, radicals generated in the aqueous phase become insoluble when a critical chain length is achieved. They may thus coil up and form particle nuclei, followed by the formation of stable primary particles via the limited flocculation of the relatively unstable particle nuclei and adsorption of surfactant on their particle surfaces. Although the amount of surfactant required to prepare stable latex products is rather low (5% based on total monomer weight), surfactant plays an important role in the polymerization mechanisms and kinetics.

It was shown that the CMC of sodium dodecyl sulfate (SDS) decreased with increase in the short-chain alcohol concentration.<sup>12–15</sup> We then demonstrated that 1-pentanol ( $C_5OH$ ) had a significant influence on the ST emul-

sion polymerization.<sup>16</sup> The effect of  $C_5OH$  increased to a maximum occurring at the SDS concentration ( $[SDS]$ ) equal to 6 mM and then decreased when  $[SDS]$  increased from 2 to 18 mM. The maximal effect of  $C_5OH$  was attributed to the fact that the particle nucleation mechanisms spanned homogeneous nucleation (low  $[C_5OH]$ ), a mixed mode of particle nucleation (homogeneous nucleation and micellar nucleation; medium  $[C_5OH]$ ), and micelle nucleation (high  $[C_5OH]$ ). The values of the hydrophile-lipophile balance (HLB) for  $C_4OH$ ,  $C_5OH$ , and  $C_6OH$  are estimated to be 7, 6.53, and 6.05, respectively, which are in the range between the oil-in-water emulsifier ( $HLB = 8–18$ ) and water-in-oil emulsifier ( $HLB = 3.5–6$ ). Thus,  $C_iOH$  ( $i = 4, 5, \text{ or } 6$ ) tends to adsorb onto the micelle surface layer and this is the reason why the effect of  $C_5OH$  is so dramatic.<sup>16</sup> In this work, we focus on the effects of the alkyl chain length of 1-butanol ( $C_4OH$ ),  $C_5OH$ , or 1-hexanol ( $C_6OH$ ) on the ST emulsion polymerizations with  $[SDS] = 6$  mM and various levels of  $[C_iOH]$ . Short chain alcohols are widely used in the formulation of industrial surfactants. Thus, the results obtained from this study, especially the kinetics of emulsion polymerization in the presence of short chain alcohols and with the surfactant concentration greater than its CMC, should be useful for the scale-up and plant production of latex products.

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## EXPERIMENTAL

### Materials

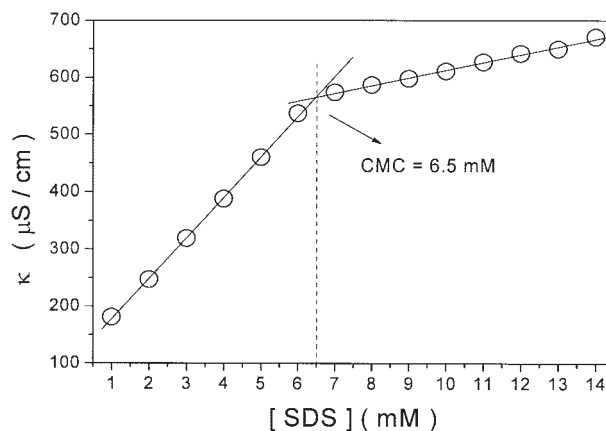
ST (Taiwan Styrene Co.), SDS (J. T. Baker), methanol (Acros),  $C_4OH$  (Acros),  $C_5OH$  (Janssen Chimica),

C<sub>6</sub>OH (Riedel-de Haen), sodium persulfate (Riedel-de Haen), sodium bicarbonate (Janssen Chimica), hydroquinone (Nacalia Tesque), sodium chloride (J. T. Baker), a series of polystyrene standards for GPC calibration (Shodex), tetrahydrofuran (THF; Merk), nitrogen (Ching-Feng-Harng Co.), and deionized water (Barnsted Nanopure Ultrapure Water System, specific conductance  $<0.057 \mu\text{S cm}^{-1}$ ) were used in this work. ST was distilled at 40°C under reduced pressure. All other chemicals were used as received.

### Experimental methods

The CMC values of SDS in the emulsions comprising 1.7M ST, 2.66 mM NaHCO<sub>3</sub>, and various concentrations of C<sub>5</sub>OH were determined by the electric conductance technique (Orion, Model 115).<sup>16–18</sup> The emulsion was stirred using a 45°-pitched 4-bladed agitator at 250 rpm for 1 h. Note that the emulsion at the time of the conductivity measurement was kinetically stable. Furthermore, the mechanical agitation resulted in some fluctuation in the conductivity reading. Thus, 1 min before the start of measurement, the agitation was stopped and the average of three measurements at 0.5, 1, and 1.5 min was reported as the conductivity ( $\kappa$ ). The above procedure was repeated for different [SDS]. The CMC was then determined from the break of the slope on the  $\kappa$  versus [SDS] curve. This method gave satisfactory reproducibility of the CMC data.<sup>16</sup>

Batch emulsion polymerization initiated by 2.58 mM sodium persulfate was carried out in a 750 mL reactor equipped with a 45°-pitched 4-bladed agitator, a thermometer, and a reflux condenser. The reaction mixture was purged with N<sub>2</sub> to remove the dissolved O<sub>2</sub> for 45 min before the start of polymerization. The temperature was controlled within the range of (70 ± 0.5)°C and the agitation speed was kept constant at 250 rpm throughout the reaction. The total solid content of the latex product is about 15% for complete monomer conversion. The product was filtered through 40-mesh (0.42 mm) and 200-mesh (0.074 mm) screens in series to collect filterable solids. Scraps adhering to the agitator, thermometer, and reactor wall were also collected. The levels of filterable solids and scraps are relatively low for all the polymerizations investigated. The total solid content and conversion of ST (X) were determined gravimetrically. Hydroquinone in combination with an ice water bath was used to stop the polymerization of samples during the reaction. The weight-average particle diameter ( $d_w$ ), volume-average particle diameter ( $d_v$ ), and polydispersity index of the particle size distribution [PDI (PSD) =  $d_w/d_n$ ] were measured by transmission electron microscopy (TEM, JEOL TEM-1200 EXII). The parameter  $d_n$  is the number-average particle diameter. At least 300 particles per sample were counted. Based on



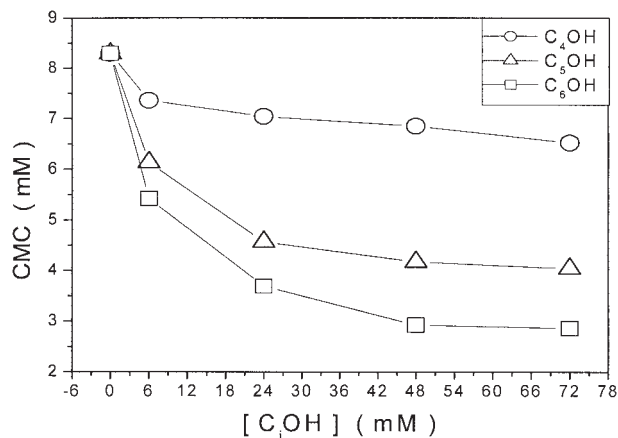
**Figure 1** Specific conductivity of SDS as a function of the bulk SDS concentration for the emulsions containing 2.66 mM NaHCO<sub>3</sub>, 1.7M ST, and 72 mM C<sub>4</sub>OH.

the  $d_v$  data, the number of particles per liter of water produced at the end of polymerization ( $N_p$ ) was calculated.

The zeta potential of particles ( $\zeta$ ) was measured with the Malvern Zetamaster. The dilution solution for the sample (total solid content = 0.01%) was 0.01M NaCl. The reported  $\zeta$  data represent an average of at least five measurements. Latex particles were precipitated by excess of methanol, followed by thorough washes with methanol and water to remove residual SDS, C<sub>5</sub>OH, and other impurities. The weight-average polymer molecular weight ( $M_w$ ) and polydispersity index of the molecular weight distribution [PDI (MWD) =  $M_w/M_n$ ] were then determined by gel permeation chromatography (GPC; Waters 515/2410/Styragel HR2, HR4, and HR6) calibrated by a series of polystyrene standards (Shodex).  $M_n$  is the number-average molecular weight.

### RESULTS AND DISCUSSION

Representative  $\kappa$  versus [SDS] data for the emulsions containing 2.66 mM NaHCO<sub>3</sub>, 1.7M ST, and 72 mM C<sub>4</sub>OH are shown in Figure 1. The corresponding CMC is 6.52 mM, which is lower than that of the SDS solution in the absence of C<sub>4</sub>OH (8.0–8.3 mM<sup>16–18</sup>). Figure 2 shows the influence of [C<sub>i</sub>OH] ( $i = 4, 5, \text{ or } 6$ ) on the CMC. The CMC first decreases rapidly and then levels off when [C<sub>i</sub>OH] increases from 0 to 72 mM. Furthermore, at constant [C<sub>i</sub>OH], the CMC data in decreasing order is CMC (C<sub>4</sub>OH) > CMC (C<sub>5</sub>OH) > CMC (C<sub>6</sub>OH). The greatly reduced CMC can be explained by the concept of solubility parameter ( $\delta$ ). The closer the two  $\delta$  values, the stronger the interaction between the pair of molecules is. The values of  $\delta$  for H<sub>2</sub>O, SDS, C<sub>4</sub>OH, C<sub>5</sub>OH, and C<sub>6</sub>OH are 47.9, 28.8, 23.5, 22.3, and 21.9 J<sup>1/2</sup> cm<sup>-3/2</sup>, respectively.<sup>19,20</sup> Taking C<sub>4</sub>OH as an example, C<sub>4</sub>OH tends to be associated

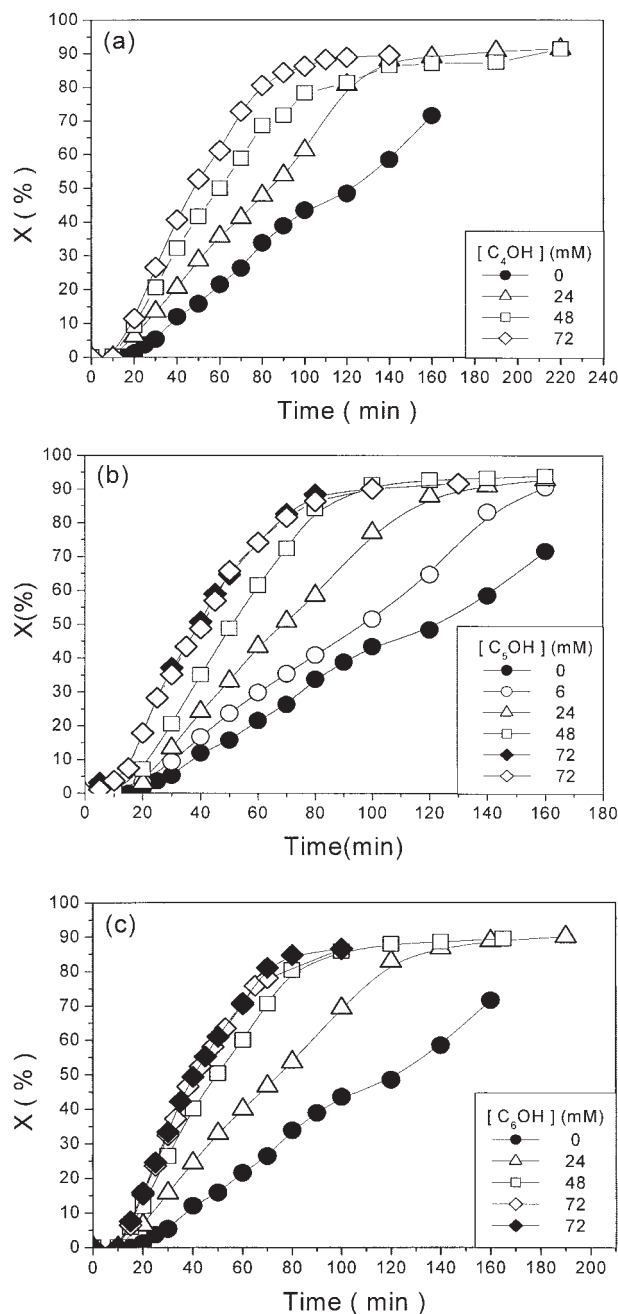


**Figure 2** Critical micelle concentration of SDS as a function of the bulk  $C_iOH$  ( $i = 4, 5$  or  $6$ ) concentration for the emulsions containing  $2.66$  mM  $NaHCO_3$  and  $1.7M$  ST. (○)  $C_4OH$ , (△)  $C_5OH$ , and (□)  $C_6OH$ .

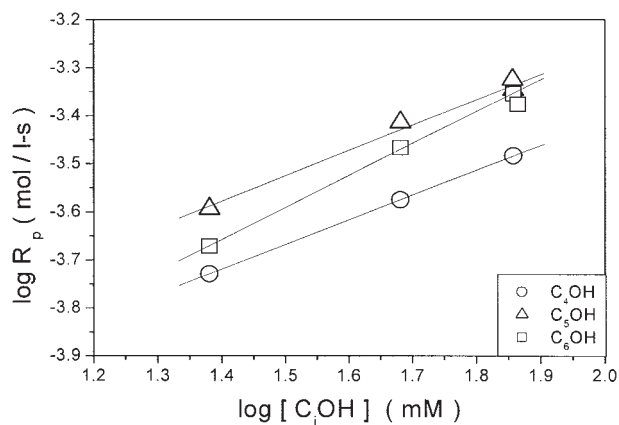
with SDS via the hydrophobic interaction in the three-component mixture. This will then result in the decrease of the water solubility of SDS (i.e., CMC). It should be noted that the presence of  $1.7M$  ST does not exhibit a significant effect on the CMC because the total monomer droplet surface area is not large enough to adsorb SDS to an appreciable extent.<sup>21</sup>

The conversion ( $X$ ) versus time ( $t$ ) curves for the ST emulsion polymerizations with  $[SDS] = 6$  mM and different  $[C_iOH]$  are shown in Figure 3. All the kinetic data show similar characteristic; the rate of polymerization ( $R_p = [M]_0 dX/dt$ ) increases rapidly with increasing  $[C_iOH]$ .  $[M]_0$  is the initial monomer concentration based on total water ( $1.7M$ ). The value of  $dX/dt$  was obtained from the least-squares-best-fitted slope of the linear portion of the  $X$  versus  $t$  curve. The correlations between  $R_p$  and  $[C_iOH]$  are as follows:  $R_p \sim [C_4OH]^{0.51}$  [coefficient of determination ( $r^2$ ) = 1.000],  $R_p \sim [C_5OH]^{0.53}$  ( $r^2 = 0.989$ ), and  $R_p \sim [C_6OH]^{0.66}$  ( $r^2 = 0.990$ ) (Fig. 4). According to the micelle nucleation mechanism,  $R_p$  is proportional to the surfactant concentration to the 0.6 power.<sup>4-6</sup> It is amazing that at constant  $[SDS]$  ( $6$  mM),  $C_iOH$  plays such an important role as the key component, surfactant, in the ST emulsion polymerization. This was attributed to the transition from homogeneous nucleation ( $[SDS] < CMC(C_iOH)$ ) to a mixed mode of particle nucleation (homogeneous nucleation and micelle nucleation) ( $[SDS] \sim CMC(C_iOH)$ ) and then to micelle nucleation ( $[SDS] > CMC(C_iOH)$ ) when  $[C_iOH]$  increases from  $0$  to  $72$  mM.<sup>16</sup> Furthermore, at constant  $[C_iOH]$ ,  $R_p$  in decreasing order is  $R_p(C_5OH) > R_p(C_6OH) > R_p(C_4OH)$ . Recall that at constant  $[C_iOH]$ , CMC ( $C_iOH$ ) in decreasing order is CMC ( $C_4OH$ )  $>$  CMC ( $C_5OH$ )  $>$  CMC ( $C_6OH$ ). Figure 5 shows the  $(R_p - R_{p0})/R_{p0}$  data as a function of  $([SDS] - CMC(C_iOH))/CMC(C_iOH)$ , where  $R_{p0}$  is the rate of

polymerization in the absence of  $C_iOH$ . If the degree of reduction in CMC is the sole parameter that controls the polymerization kinetics, then all the experimental data should fall on a single curve, regardless of the alkyl chain length of  $C_iOH$ . However, this is only true for the series of polymerizations using a particular short chain alcohol (Fig. 5). The corresponding  $d_v$  and  $N_p$  versus  $[C_iOH]$  data are shown in Figures 6 and 7, respectively. All the PDI (PSD) data are centered

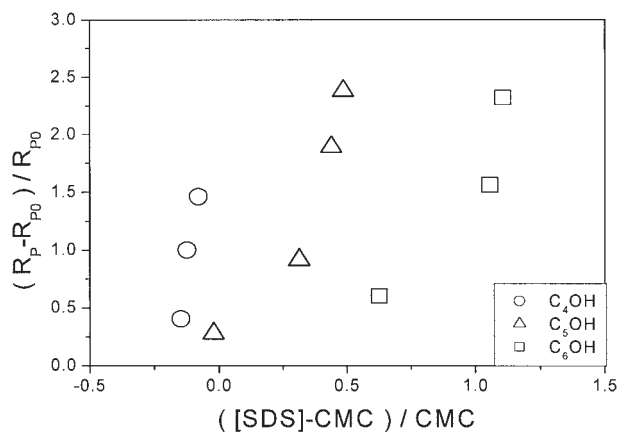


**Figure 3** Conversion as a function of time for the ST emulsion polymerizations with  $[SDS] = 6$  mM and various bulk  $C_iOH$  concentrations: (a)  $C_4OH$ , (b)  $C_5OH$ , (c)  $C_6OH$ .  $[C_iOH]$  ( $i = 4, 5$  or  $6$ ; mM) = (●)  $0$ , (○)  $6$ , (△)  $24$ , (□)  $48$ , (◇), and (◆)  $72$ .

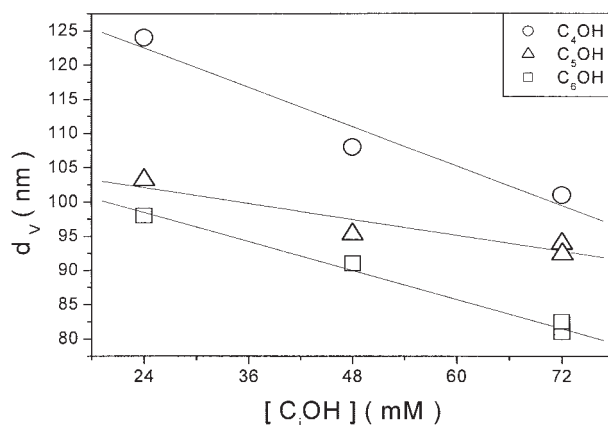


**Figure 4** Logarithm plot of the polymerization rate as a function of the bulk  $C_iOH$  ( $i = 4, 5$  or  $6$ ) concentration. (○)  $C_4OH$ , (△)  $C_5OH$ , and (□)  $C_6OH$ .

around 1.01. This indicates that relatively monodisperse latex products are achieved in this work (data not shown here). Furthermore, all the polymerization recipes and conditions investigated in this work exhibit the characteristics of a quite short particle nucleation period and a very long particle growth period. All these results indicate that other parameters than the enhanced formation of micelles by  $C_iOH$  must come into play during the polymerization. For example, the aggregation number of micelles generally increases with increase in the hydrophobic character of the composition of micelles.<sup>22</sup> As mentioned earlier, the HLB of  $C_iOH$  in decreasing order is  $C_4OH > C_5OH > C_6OH$ . Thus, the aggregation number of micelles in the presence of  $C_iOH$  in decreasing order is  $C_6OH > C_5OH > C_4OH$ . Changes in the aggregation number of micelles in the presence of  $C_iOH$  are then expected to have an influence on the number of micelles formed initially in the polymerization system and, consequently, on the subsequent particle nucle-



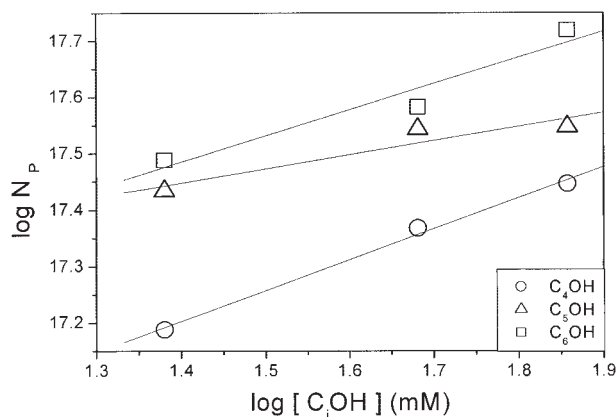
**Figure 5**  $(R_p - R_{p0})/R_{p0}$  data as a function of  $([SDS] - CMC(C_iOH))/CMC$  ( $C_iOH$ ). (○)  $C_4OH$ , (△)  $C_5OH$ , and (□)  $C_6OH$ .



**Figure 6** Logarithm plot of the volume-average particle diameter as a function of the bulk  $C_iOH$  concentration. (○)  $C_4OH$ , (△)  $C_5OH$ , and (□)  $C_6OH$ .

ation and polymerization kinetics. However, this subject is beyond the scope of this work.

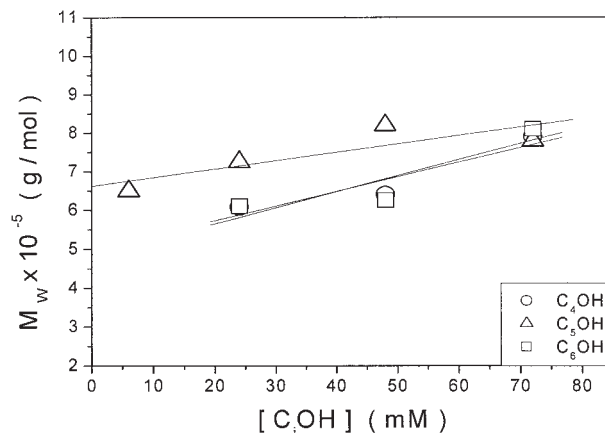
Both the HLB and  $\delta$  values suggest that the partitioning of  $C_iOH$  into the aqueous phase, the oil-water interface, and the oil phase should not be the same for these three  $C_iOH$  species with different alkyl chain lengths. For the ST microemulsion polymerization stabilized by SDS and  $C_5OH$ , the partitioning of  $C_5OH$  into the aqueous phase, the oil-water interface, and the oil phase is about 20.7, 66.8, and 12.5%, respectively.<sup>23</sup> It was also shown that the majority of ST resides in the core of microemulsion droplets ( $\sim 92.6\%$ ), and only a small fraction of ST is solubilized in the oil-water interface ( $\sim 6.8\%$ ). Berthod<sup>24</sup> reported that the partition coefficient between the micelle phase and the continuous aqueous phase is 25, 85, and 400 for  $C_4OH$ ,  $C_5OH$ , and  $C_6OH$ , respectively. It is, therefore, postulated that the fraction of  $C_iOH$  that can be partitioned into the interior of latex particles in decreasing order is  $C_6OH > C_5OH > C_4OH$  because of



**Figure 7** Logarithm plot of the number of latex particles per unit volume of water as a function of the bulk  $C_iOH$  concentration. (○)  $C_4OH$ , (△)  $C_5OH$ , and (□)  $C_6OH$ .

the increased hydrophobicity of  $C_i\text{OH}$  with the alkyl chain length. On the other hand, the fraction of  $C_i\text{OH}$  that can be partitioned into the continuous aqueous phase in decreasing order is  $C_4\text{OH} > C_5\text{OH} > C_6\text{OH}$ . As for the oil-water interface, we are uncertain about the order of the concentrations of  $C_i\text{OH}$  within the interfacial region of micelles (if present) at the very beginning of polymerization or growing particle nuclei during polymerization. This is because varying the alkyl chain length of  $C_i\text{OH}$  to shift the partitioning of  $C_i\text{OH}$  toward the aqueous phase (e.g.,  $C_5\text{OH} \rightarrow C_4\text{OH}$ ) or toward the oil phase (e.g.,  $C_5\text{OH} \rightarrow C_6\text{OH}$ ) does not disclose the relationship between the concentration of  $C_i\text{OH}$  in the oil-water interface and the alkyl chain length of  $C_i\text{OH}$ . Incorporation of amphipathic  $C_i\text{OH}$  into the adsorbed layer of SDS around a micelle or a particle nucleus greatly reduces the electrostatic repulsion force between two anionic SDS molecules and then minimizes the oil-water interfacial tension. Thus, more particle nuclei can be stabilized by SDS in combination with  $C_i\text{OH}$  to exhibit adequate colloidal stability in comparison with the emulsion polymerization in the absence of  $C_i\text{OH}$ .

Based on the above discussion, the different polymerization kinetics are attributed to (1) the different concentrations of micelles available for particle nucleation because of the different effectiveness of  $C_i\text{OH}$  in lowering their CMC values [ $\text{CMC}(C_4\text{OH}) > \text{CMC}(C_5\text{OH}) > \text{CMC}(C_6\text{OH})$ ], (2) the different oil-water interfacial properties that have a significant influence on the colloidal stability due to the different partitioning behavior of  $C_i\text{OH}$  among the three phases ( $C_5\text{OH}$  might be the best in stabilizing the latex particles), (3) the different concentrations of monomer within latex particles because of the different dilution effect of  $C_i\text{OH}$  therein ( $[M]_p$  in decreasing order is  $[M]_p(C_4\text{OH}) > [M]_p(C_5\text{OH}) > [M]_p(C_6\text{OH})$ ) ( $R_p \sim [M]_p$ ), and (4) the different effectiveness of SDS/ $C_i\text{OH}$  in stabilizing latex particles because of the different concentrations of  $C_i\text{OH}$  in water ( $[C_i\text{OH}]_w$ ) ( $[C_i\text{OH}]_w$  in decreasing order is  $[C_4\text{OH}]_w > [C_5\text{OH}]_w > [C_6\text{OH}]_w$ ). The higher the  $[C_i\text{OH}]_w$  is, the smaller the dielectric constant of the continuous aqueous phase is and, consequently, the less effective of SDS/ $C_i\text{OH}$  in stabilizing latex particles via the electrostatic stabilization mechanism. This is supported by the experimental data shown in Figures 6 and 7. At constant  $[C_i\text{OH}]$ , the polymerization with  $C_4\text{OH}$  results in the largest  $d_o$  (i.e., the smallest  $N_p$ ) ( $R_p \sim N_p$ ). In addition, the solubility (i.e., residence time) of oligomeric radicals in the continuous aqueous phase with high  $[C_i\text{OH}]$  might increase. This will then slow down the absorption of radicals by latex particles and, eventually, reduce the  $R_p$ . This phenomenon should be the most pronounced in the  $C_4\text{OH}$ -containing polymerization. As a result of this very complicated scenario,  $C_5\text{OH}$  with balanced prop-

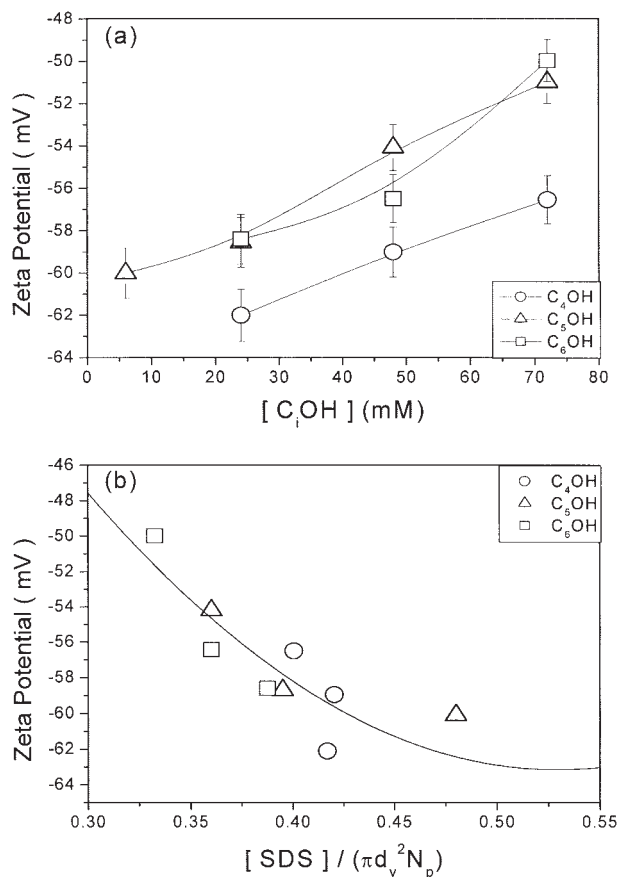


**Figure 8** Weight-average polymer molecular weight as a function of the bulk  $C_i\text{OH}$  concentration. (○)  $C_4\text{OH}$ , (△)  $C_5\text{OH}$ , and (□)  $C_6\text{OH}$ .

erties is the alcohol of choice in terms of polymerization kinetics.

Figure 8 shows the  $M_w$  data as a function of  $[C_i\text{OH}]$ . At constant  $[C_i\text{OH}]$ ,  $M_w(C_5\text{OH})$  is greater than  $M_w(C_4\text{OH})$  or  $M_w(C_6\text{OH})$  and the difference in  $M_w$  diminishes as  $[C_i\text{OH}]$  is increased. This is due to the fact that the polymerization with  $C_5\text{OH}$  has the largest  $N_p$  (i.e., the strongest radical segregation effect), thereby leading to the lowest probability of bimolecular termination of radicals within latex particles. This will then result in the largest  $M_w$ . Both the polymerizations with  $C_4\text{OH}$  and  $C_6\text{OH}$  show comparable  $M_w$  data in the range of  $[C_i\text{OH}]$  investigated. This can be explained by the following interactive factors. First, the polymerization with  $C_6\text{OH}$  has a larger  $N_p$  than the  $C_4\text{OH}$  counterpart (Fig. 7). Consequently, the former is expected to give a larger  $M_w$  due to the stronger radical segregation effect. On the contrary, the lower  $[M]_p$  associated with the  $C_6\text{OH}$ -containing polymerization would result in smaller  $M_w$  compared to the  $C_4\text{OH}$  counterpart. Furthermore, the chain transfer of radicals to  $C_i\text{OH}$  makes the polymerization with  $C_6\text{OH}$  produce polymer with lower  $M_w$  because the concentration of  $C_6\text{OH}$  in latex particles is larger compared to the  $C_4\text{OH}$  counterpart. Thus, comparable  $M_w$  data are observed for the polymerizations with  $C_4\text{OH}$  and  $C_6\text{OH}$  as a result of the coincidentally counterbalanced effects mentioned earlier. In addition, incorporating  $C_i\text{OH}$  into the ST emulsion polymerizations reduces the PDI (MWD) from 1.9 to 1.4–1.9, depending on the type and  $[C_i\text{OH}]$  (data not shown here). The reason for this observation is not clear at this point of time.

Figure 9(a) shows the zeta potential ( $\zeta$ ) data as a function of  $[C_i\text{OH}]$ . For any series of polymerizations,  $|\zeta|$  decreases with increasing  $[C_i\text{OH}]$ . Furthermore, at constant  $[C_i\text{OH}]$ ,  $|\zeta|$  in decreasing order is  $\zeta(C_4\text{OH}) > \zeta(C_6\text{OH}) \sim \zeta(C_5\text{OH})$ . This is most likely related to the particle surface charge density, as shown by the  $\zeta$



**Figure 9** Zeta potential of latex particles as a function of (a) the bulk  $C_i\text{OH}$  concentration and (b) the surface charge density. (○)  $C_4\text{OH}$ , (△)  $C_5\text{OH}$ , and (□)  $C_6\text{OH}$ .

versus  $[\text{SDS}]/(\pi d_v^2 N_p)$  data in Figure 9(b). The abscissa is linearly proportional to the particle surface charge density. Although the experimental data are somewhat scattered, all the data points fall in a single curve. This implies that at constant  $[\text{SDS}]$  (6 mM used in this work) but at different  $[C_i\text{OH}]$ ,  $\zeta$  is primarily controlled by the total particle surface area created during the nucleation stage regulated by SDS and  $C_i\text{OH}$ .

## CONCLUSIONS

The effects of  $C_i\text{OH}$  ( $i = 4, 5, \text{ or } 6$ ) on the ST emulsion polymerizations stabilized by 6 mM SDS at 70 °C are significant because of the reduction in the CMC values by  $C_i\text{OH}$ . The CMC first decreases rapidly and then levels off when the  $C_i\text{OH}$  concentration ( $[C_i\text{OH}]$ ) in-

creases from 0 to 72 mM. Furthermore, at constant  $[C_i\text{OH}]$ , the CMC data in decreasing order is CMC ( $C_4\text{OH}$ ) > CMC ( $C_5\text{OH}$ ) > CMC ( $C_6\text{OH}$ ), which was explained by the concept of solubility parameter. The following correlations were established:  $R_p \sim [C_4\text{OH}]^{0.51}$ ,  $R_p \sim [C_5\text{OH}]^{0.53}$  and  $R_p \sim [C_6\text{OH}]^{0.66}$ . It was also observed that, at constant  $[C_i\text{OH}]$ ,  $R_p$  in decreasing order is  $R_p$  ( $C_5\text{OH}$ ) >  $R_p$  ( $C_6\text{OH}$ ) >  $R_p$  ( $C_4\text{OH}$ ). The influence of  $C_i\text{OH}$  on CMC is one of the most important parameters that control the polymerization kinetics. Other factors such as (1) the different oil-water interfacial properties that have a significant influence on the colloidal stability because of the different partitioning behavior of  $C_i\text{OH}$  among the three phases, (2) the different concentrations of monomer within latex particles due to the different dilution effect of  $C_i\text{OH}$  therein, and (3) the different effectiveness of SDS/ $C_i\text{OH}$  also contribute to the complicated polymerization mechanisms and kinetics.

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