

Monomer Emulsification and Polymerization Kinetics in Styrene Miniemulsion

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ABSTRACT

Miniemulsions of styrene with sodium dodecyl sulphate (SDS) as the surfactant and hexadecane (HD) as the co-stabilizer were prepared and polymerized. The on-line conductivity measurements were employed to characterize the emulsification by ultrasonication. Both the dynamic light scattering (DLS) and the transmission electron microscopy (TEM) were employed to determine the droplet and the particle size. The effects of various reaction parameters on the droplet (or particle) size and the polymerization kinetics were investigated. These parameters include the sonication time and the concentrations of SDS ([SDS]), potassium persulphate ([KPS]), and HD ([HD], as weight percent with respect to monomer). Moreover, their influence on the droplet nucleation was also discussed. It is shown that a critically steady state can be obtained after ultrasonication of the emulsion system for at least 24 min and relatively stable miniemulsions were prepared. The polymerization rate of miniemulsions increases with the increase in [SDS], [HD], and [KPS] due to different mechanisms, and the rate is faster than that of the corresponding macroemulsions. In addition, the predominant droplet nucleation is achieved in current miniemulsion systems and the required condition is concluded. Finally, nanosize polystyrene latexes were synthesized.

Key Words:

miniemulsion polymerization;
styrene;
emulsification;
kinetics;
droplet nucleation.

INTRODUCTION

In conventional emulsion polymerization of styrene, particle nucleation taking place in the emulsified monomer droplets is generally considered insignificant as compared with micellar nucleation. This is because these monomer droplets are incapable of competing effectively with the monomer-swollen micelles for oligomeric radicals

generated in the aqueous phase due to the relatively small droplet-water interfacial area. Nevertheless, with the aid of an efficient homogenization device, the average size of the resultant monomer droplets may become small enough to allow the droplets to become the predominant particle nucleation loci. This process has been termed miniemul-

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sion polymerization. The monomer droplets can be stabilized by a surfactant to prevent them from coalescing and a co-stabilizer to retard the diffusion of monomers from small droplets to large ones (Ostwald ripening). The feature that each monomer droplet can be regarded as an individual batch reactor makes miniemulsion polymerization quite attractive as a polymerization technique.

Recently, considerable efforts have been devoted to the application of this new polymerization process, including the synthesis of organic-inorganic hybrids, [1,2] fluorinated latex, [3] high-solid-content latexes, [4] nitroxide-mediated living free-radical miniemulsion polymerization, [5,6] and polyurethane dispersions [7]. However, the successful use of this technology relies on producing a stable emulsion during the reaction and the fundamental knowledge about the techniques involved in the preparation and polymerization of monomer miniemulsion is still limited [8].

Therefore the fundamental research including the monomer emulsification and polymerization kinetics in styrene miniemulsion was further investigated in present work. Furthermore, the on-line conductivity measurement was employed during homogenizing and an optimum ultrasonication time required to prepare stable monomer miniemulsions was evaluated. In addition, the nucleation mechanism was discussed in a much more readable way, plotting the droplet and particle size in the same figure. The required condition for the predominant droplet nucleation was concluded.

EXPERIMENTAL

Materials

Potassium persulphate (KPS), anhydrous sodium sulphate (Na_2SO_4) and hydroquinone (HQ) (Tianjin Chemical Co., China) were analytical grade and used as received. Hexadecane (HD) (Tianjin Guang-Fu Fine Chemical Institute, China), sodium dodecyl sulphate (SDS) (Tianjin Reagent Chemical Ltd., China) were used as received. Styrene (Tianjin Guang-Fu Fine Chemical Institute, China) was repeatedly washed with aqueous NaOH 10 wt% followed by deionized water and then dried over anhydrous sodium sulphate. The monomer was kept refrigerated until use. Deionized

water was applied for polymerization and treatment processes.

Styrene Miniemulsion Polymerizations

A styrene sample of 9 g and the respective amount of co-stabilizer were mixed and added to a solution of SDS in 36 g of deionized water. After stirring for 1 h, the miniemulsion was prepared by ultrasonating the emulsion for a distinct time, e.g., 30 min, with an ultrasonic cell crusher type JY92-II by Scient Biotechnology Co., Ltd. The conductivity measurement was monitored with a conductometer model DDA-11A by Shanghai Rex Instruments Co., Ltd. For polymerization, the temperature was increased to 72°C, and 180 mg of KPS was added. The time between miniemulsification and initiation was minimized to 5 min to reduce the droplet degradation (Ostwald ripening) period. The initial charge and monomer feeds were protected with nitrogen during the polymerization. The reaction is usually completed after 3 h. The theoretical solid content of the latex product is approximately 20%.

Determinations of Monomer Droplet Size (or Latex Particle Size)

The data of the average monomer droplet size (or latex particle size) were obtained from dynamic light scattering (DLS) measurements using a Brookhaven BI-200SM instrument. The sample was diluted with water saturated with SDS and styrene. Consequently, the diffusion of surfactant and monomer molecules from the monomer droplet (or monomer-swollen latex particles) into water could be prohibited.

The transmission electron microscopy (TEM) was performed with a JEOL JEM-100CXII electron microscope operating at 100 kV. In a typical experiment, one drop of the colloidal dispersion was put on a carbon film supported by a copper grid and allowed to air-dry before observation.

Characterization of Latex Products

The latex product was filtered to collect the filterable solids. Scraps adhering to the agitator, thermometer and reactor wall were also collected. In general, the latex stability was satisfactory because the amount of coagulum formed during polymerization was insignificant. Total solid content and conversion of styrene (X) as a

Table 1. Comparison of DLS measurement with TEM method for the determination of droplet and particle sizes.

Run No.	1		2		3	
	TEM	DLS	TEM	DLS	TEM	DLS
Droplet size (nm)	119.2	112.4	75.2	71.7	65.4	62.4
Particle size (nm)	63.2	64.8	98.0	99.1	64.0	64.6

function of time were determined by gravimetric method in which the reaction was quenched in a solution of 1% hydroquinone, immediately.

RESULTS AND DISCUSSION

Comparison of Characterization Methods on the Droplet (or Latex Particle) Size

Table 1 compares the DLS measurement and the TEM results for three samples. Several typical TEM micrographs and the corresponding DLS results being displayed in Figures 1 and 2, respectively. It can be seen that the DLS data are in good agreement with those of the TEM micrographs. This indicates that the dynamic light scattering (DLS) measurements are credible in determining the size of the monomer droplets and the latex particles in current systems. Furthermore, from the TEM micrographs, it also can be found that perfect polystyrene particles are synthesized in nanosize.

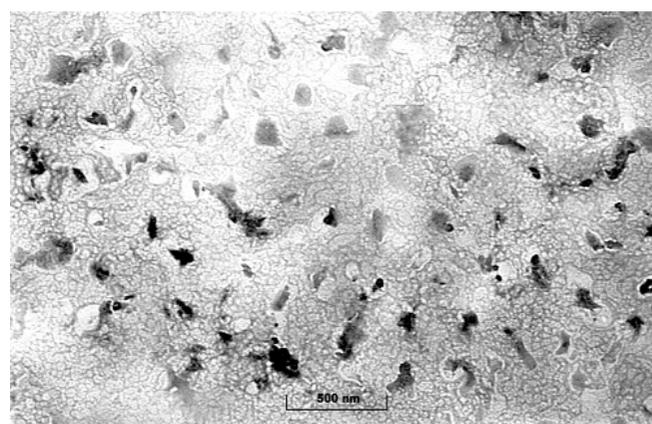
Effects of Process Variables

Effect of Ultrasonication Time

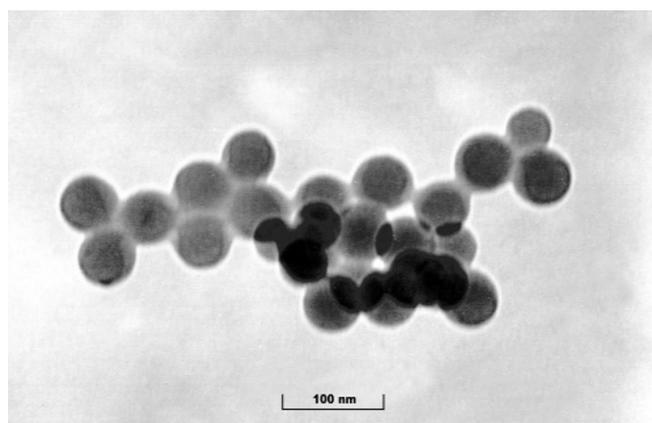
Figure 3 illustrates the effect of ultrasonication time on the monomer droplet size. From Figure 3, it can be seen that the size of droplets decreases with the ultrasonication time initially, and then approaches a steady value. This is reasonable. As we all know, cavitation is the mechanism generally regarded as crucial in ultrasound emulsification [9]. During the compression cycle, a great amount of interface will be formed. At the beginning, there are sufficient surfactant molecules available for stabilizing the newly created surface in the system. The droplet coalescence can be effectively retarded and thus the droplet size decreases dramatically during the early stage. As the process proceeds, a large amount of surfactant molecules dissolved in water is rapidly con-

sumed and the role of the droplet coalescence becomes important. Finally, when the equilibrium between the fission by ultrasound and fusion by collisions is established, the droplet size shows a little dependence on the ultrasonication time and the curve reaches a plateau when the sonic time is longer than 24 min.

On the other hand, further evidence is provided by the on-line conductivity measurement. When studying



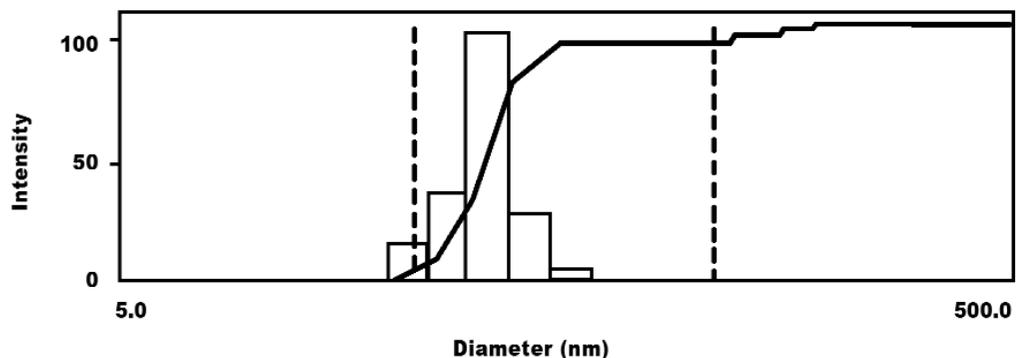
(a)



(b)

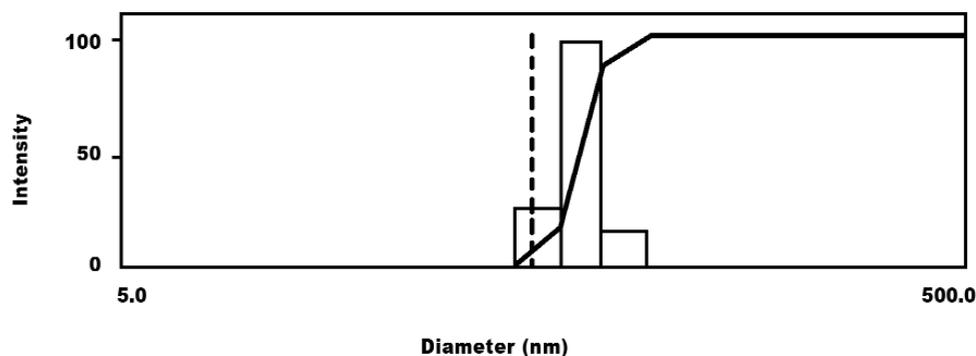
Figure 1. TEM Micrographs of (a) monomer droplets and (b) latex particles.

Sample D
 Elapsed Time 00:02:00
 Mean Diam. 112.4 (nm)
 Rel. Var. 1.645
 Skew 5.169
 Rms Error 2.2300×10^{-3}



(a)

Sample D
 Elapsed Time 00:02:00
 Mean Diam. 64.8 (nm)
 Rel. Var. 0.020
 Skew 0.439
 Rms Error 1.6659×10^{-3}



(b)

Figure 2. The DLS data of (a) monomer droplets and (b) latex particles.

mini-emulsion polymerization of MMA, Fontenot et al. [10] have found that conductivity measurement could be a powerful tool to study the mini-emulsion systems. The conductivity of the present styrene system as a function of the ultrasonication time was thus determined which the results are displayed in Figure 3. Due to the rapid depletion of surfactant molecules in the water, the conductivity of the system dramatically decreases after about 24 min. And then the curve reaches to a plateau when the steady state is formed. Additionally, the sudden decline may mark the disappearance of the micelles in present system on the basis of the relationship between the conductivity and the surfactant concentration. Furthermore, according to the research of Anderson et al. [11] the total concentration of SDS was 60 mmol/L at the critical micelle concentration (CMC) in styrene mini-emulsion with a monomer droplet size ranging from 40 nm to 85 nm, which was due to the adsorption of SDS molecules on the huge monomer droplet-water interfacial areas. Based on the droplet size data presented in Figure 3, this result again ensures the absence of micelles in the studied styrene mini-emul-

sions. Therefore, when the homogenization steady state is obtained, the micellar nucleation that is the main mechanism of macroemulsion polymerization can be ruled out during the subsequent polymerizations.

The influence of ultrasonication time on the kinetics of mini-emulsion polymerization was studied as well, and is presented in Figure 4. It is shown that the poly-

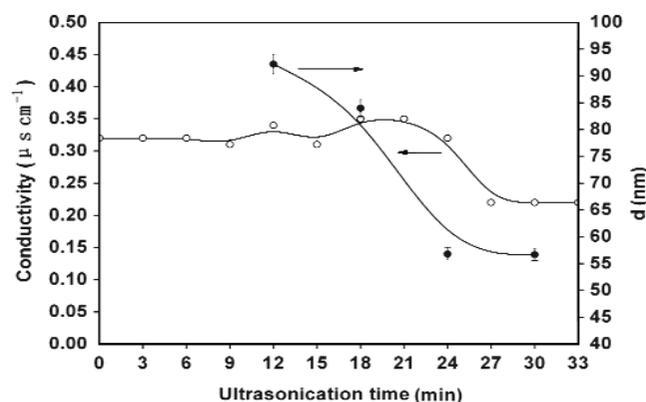


Figure 3. The influence of ultrasonication time on the monomer droplet size ([SDS]: 58.76 mmol/L, based on total water; [HD]: 4.26 wt% based on monomer).

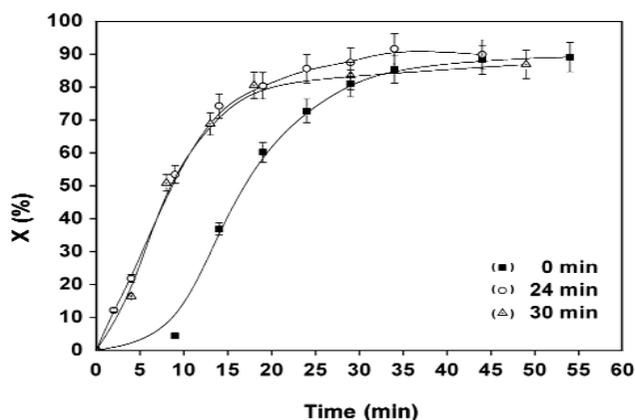


Figure 4. Conversion of styrene as a function of time for the miniemulsion polymerizations homogenized by varied ultrasonication time ([SDS]: 58.76 mmol/L, based on total water; [KPS]: 18.50 mmol/L, based on total water; [HD]: 4.26 wt% based on monomer).

merization rate of miniemulsions is faster than that of corresponding macroemulsions. This can be attributed to the different nucleation mechanisms. The miniemulsions polymerize predominantly in monomer droplets.

In comparison with macroemulsion polymerization, the droplet nucleation mechanism may result in a higher monomer concentration or radical number in the reaction loci in miniemulsion polymerization, and thus exhibits a faster polymerization rate. Furthermore, the little difference in polymerization rate at ultrasonication time of 24 min and 30 min may again confirm the generation of the steady state during ultrasonication.

According to the above discussions, it can be con-

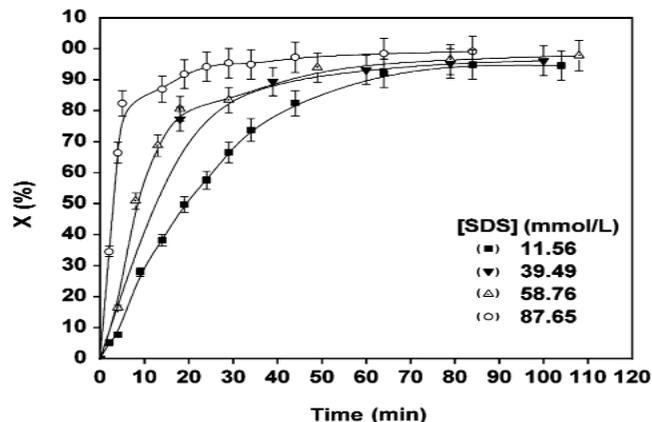


Figure 6. Conversion of styrene as a function of time for the miniemulsion polymerizations stabilized by varied [SDS] ([KPS]: 18.50 mmol/L, based on total water; [HD]: 4.26 wt% based on monomer; ultrasonication time: 30 min).

cluded that 30 min may be the optimum ultrasonication time for preparing relatively stable monomer miniemulsions under present conditions. For the following experiments, the level of ultrasonication time was set to 30 min.

Effect of Surfactant Concentration

Figure 5 illustrates the influence of SDS concentration on the monomer droplet and latex particle size. It is shown that the monomer droplet size decreases significantly with increasing [SDS]. This is because more SDS molecules are available for stabilizing the oil-water interface area generated during homogenization at higher concentration and the coalescence among the monomer droplets is reduced. At the meantime, a same trend can be observed for latex particle size as a function of SDS concentration. This is due to the reduction of the coalescence among monomer droplets and polymer particles with increase in surfactant concentration. In addition, the gap breadth between the two curves in Figure 5 may reflect the proportion of the droplet nucleation. That is, the narrower the gap, the higher the droplet nucleation proportion.

As can be seen in Figure 5, the final latex particle size is slightly larger than the initial monomer droplet size. This may indicate that droplet nucleation is the predominant nucleation mechanism in the studied range. As can be further appreciated from Figure 5, the droplet nucleation is enhanced with the increase in SDS concentration, which is reflected by the narrowing gap between

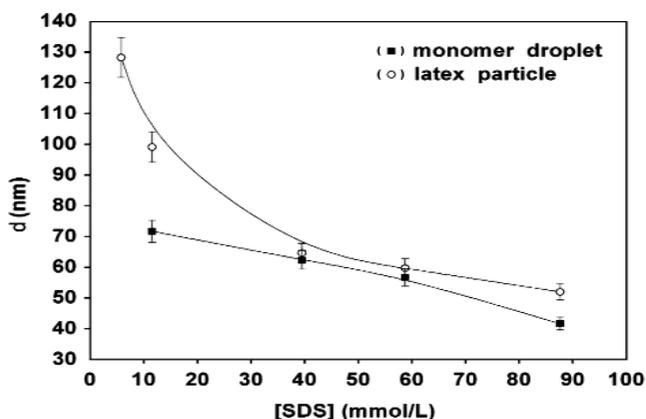


Figure 5. The effect of SDS concentration on the monomer droplet and latex particle size ([KPS]: 18.50 mmol/L, based on total water; [HD]: 4.26 wt% based on monomer; ultrasonication time: 30 min).

Table 2. The data of particle size and number obtained with varied SDS concentration^a.

Run No.	1	2	3	4
[SDS] (mmol/L)	11.56	39.49	58.76	87.65
D _p (nm)	99.1	64.6	59.7	52
N _p × 10 ⁻¹⁷ (L ⁻¹ -H ₂ O)	4.76	17.27	21.51	33.14

(a) [KPS]: 18.50 mmol/L, based on total water; [HD]: 4.26 wt % based on monomer; ultrasonication time: 30 min.

the two curves. Furthermore, the remaining gaps may be attributed to the slight Ostwald ripening.

The data of conversion (*X*) as a function of time are displayed in Figure 6. With the knowledge of the latex particle size, *D_p*, the particle number, *N_p*, can be calculated according to the following equations:

$$N_p = \frac{W_m [\rho_m X_f + \rho_p (1 - X_f)]}{\frac{\pi}{6} D_p^3 W_w \rho_m \rho_p} \quad (1)$$

where *W_m* and *W_w* are the initial monomer weight and total water weight, in the reaction system, respectively. The parameters ρ_m and ρ_p are the monomer density (0.90 g/cm³) and polymer density (1.05 g/cm³), respectively. In addition, the parameter *X_f* is the final conversion of styrene. The results are listed in Table 2.

It is illustrated that the polymerization rate increases with increasing [SDS]. This is reasonable since the stability of the monomer droplets is enhanced with the increase in SDS concentration, leading to the more

nucleated monomer droplets. Consequently, the larger the number of reaction loci (latex particles) available for consuming the imbibed monomer, the faster the polymerization rate. This is confirmed by the data of the particle number, *N_p*, in Table 2. That is, with the increasing [SDS], the number of particles increases. When the surfactant concentration exceeds CMC (i.e., [SDS] = 87.65 mmol/L), the micellar nucleation may also contribute to the increasing polymerization rate.

Effect of Co-stabilizer Level

Figure 7 illustrates the effect of HD level ([HD], which is the weight percent of HD with respect to monomer) on the monomer droplet and latex particle size. It can be seen that the droplet size decreases with increasing HD concentration. This is due to the fact that the Ostwald ripening rate is inversely proportional to the volume fraction of co-stabilizer in the droplet according to the modified LSW theory [12]. Thus, under the same homogenization condition, the higher the [HD] value, the smaller the resultant monomer droplets. When the level of HD reaches a critical value, Ostwald ripening is counterbalanced by osmotic pressure built up in the monomer droplets. As a consequence, further increasing in the co-stabilizer level cannot significantly reduce the droplet size. Interestingly enough, an opposite trend is observed for the latex particle size, that is, the latex particle size shows a slight increase with increasing HD concentration. This result may be caused by the mixed modes of particle nucleation (i.e., monomer droplet nucleation in combination with the homogeneous nucleation), which is also responsible for the broad gaps between the two curves in the case of low HD level. As can be further appreciated from Figure 7, droplet nucleation is enhanced with the increasing HD level. When the value is larger than 4 wt%, the predominant droplet nucleation is achieved.

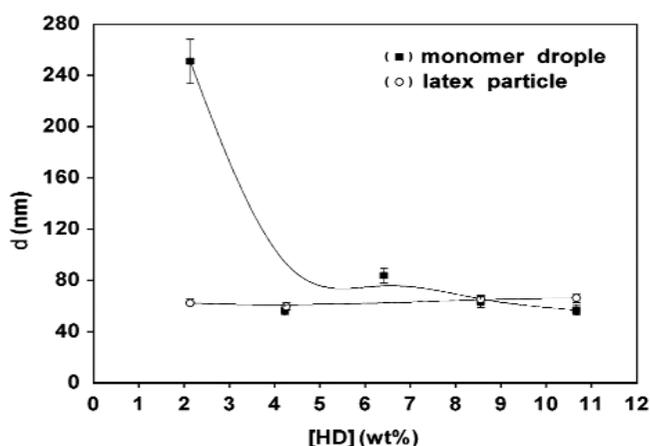


Figure 7. The influence of HD level (based on the styrene) on the droplet and latex particle size ([SDS]: 58.76 mmol/L, based on total water; [KPS]: 18.50 mmol/L based on total water; ultrasonication time: 30 min).

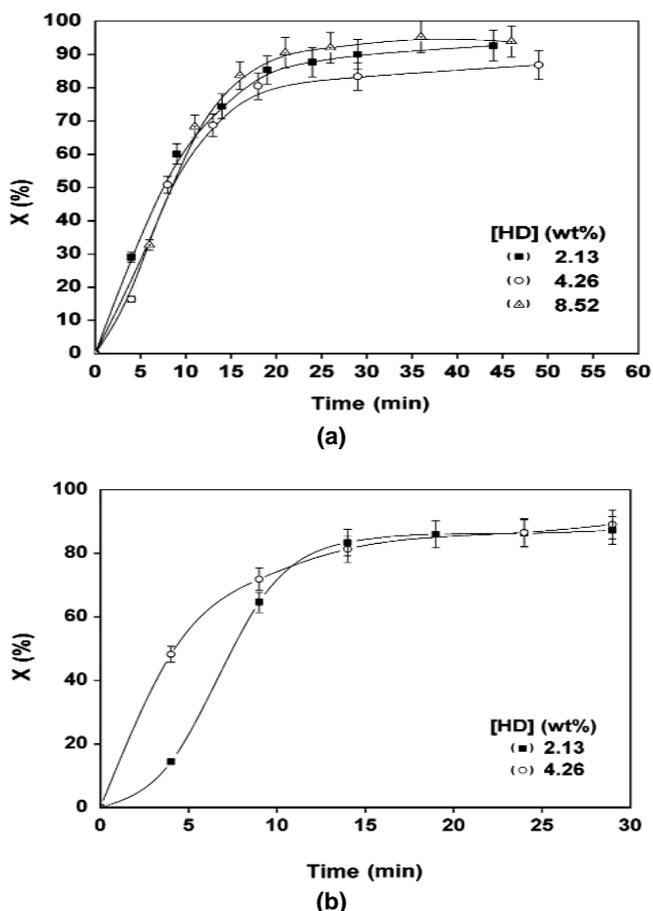


Figure 8. Conversion of styrene as a function of time for the miniemulsion polymerizations stabilized by varied HD level: (a) [SDS]=58.76 mmol/L, (b)[SDS]=87.65 mmol/L ([KPS]: 18.50 mmol/L based on total water; ultrasonication time: 30 min).

The effects of HD level on the polymerization rate were also determined and the results are presented in Figure 8. It is shown that the polymerization rate is insensitive to the HD level at a relatively low SDS concentration (Figure 8a). A possible explanation is that the system is not stable enough and the coalescence of the monomer droplets occurred. Under this condition, the

Ostwald ripening effect is masked. Consequently, the polymerizations seem to show little dependence on the co-stabilizer concentration. Based on this discussion, enhancing the stability of the present system may be helpful to make the influence of HD level observable.

To verify the above postulation, the case of higher SDS concentration was measured. The results are displayed in Figure 8b. It can be seen that the influence of HD level becomes much more appreciable and the reaction rate increases with the increase of HD level. With the increasing surfactant concentration, the stability of the monomer droplets is improved. The coalescence of the monomer droplets is insignificant while the Ostwald ripening effect becomes the dominant factor. In this case, as the HD level increases, the diffusion degradation is effectively retarded. A large amount of small monomer droplets can be available for the reaction and thus the number of reaction loci increases significantly. As a consequence, the polymerization rate is increased. Furthermore, based on the observations, it can be also concluded that the droplet nucleation is still predominant in the polymerization even at this high SDS value. If it is not, then the rate should be decreased with the increasing HD level, due to the dependence on the monomer diffusion [13].

Effect of Initiator Concentration

In these series of experiments, the results including latex particle size (D_p) and particle number (N_p) are summarized in Table 3. The value of D_p ranging from 59.7 to 62.1 nm (Table 3) indicates that D_p and corresponding N_p are rather insensitive to changes in initiator concentration, [KPS]. This may be the most compelling evidence for the dominant droplet nucleation. [14]

The data of conversion (X) as a function of time are illustrated in Figure 9. As expected, the polymerization

Table 3. The data of particle size and number obtained with varied KPS concentration^a.

Run No.	1	2	3
[KPS] (mmol/L)	12.33	18.50	24.66
D_p (nm)	62.1	59.7	61.0
$N_p \times 10^{-18}$ ($L^{-1} \cdot H_2O$)	1.94	2.15	2.03
[KPS]/ $N_p \times 10^{-18}$	6.36	8.60	12.15

(a) [SDS]: 58.76 mmol/L, based on total water; [HD]: 4.26 wt %, based on monomer; ultrasonication time: 30min.

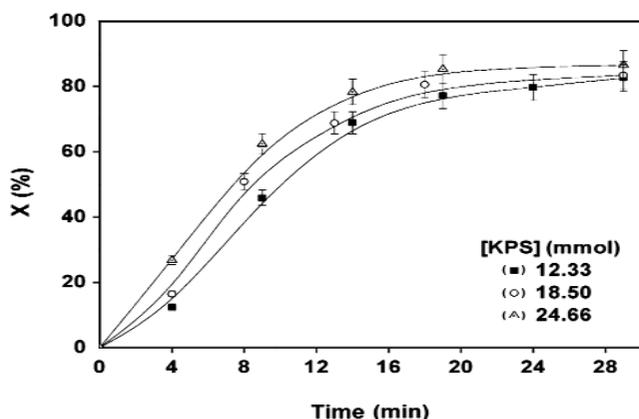


Figure 9. Conversion of styrene as a function of time for the miniemulsion polymerizations initiated by varied [KPS] ([SDS]: 58.76 mmol/L, based on total water; [HD]: 4.26 wt% based on monomer; ultrasonication time: 30 min).

rate, R_p , increases rapidly with increasing [KPS]. Interestingly enough, no apparent correlation exists between R_p and N_p in this series of polymerizations (Table 3). The increased R_p may be attributed to the increased average concentration of initiator per particle with increasing [KPS] (Table 3).

CONCLUSION

For the styrene miniemulsion polymerization stabilized by sodium dodecyl sulphate (SDS) and hexadecane (HD) at 72°C, the monomer droplet size decreases with the ultrasonication time initially and then reaches a constant value. By on-line conductivity measurements and off-line determination of droplet size in the un-polymerized miniemulsions, it is found 30 min may be the optimum ultrasonication time for preparing relatively stable monomer miniemulsions under present experimental conditions.

The polymerization rate increases with the increase in [SDS], [HD] and [KPS] values. However, the influencing mechanisms of these parameters are distinguished from each other. The effects of SDS and HD are attributed to the number of reaction loci while the influence of KPS is related to the initiator concentration in the reaction loci. Due to the high monomer or radical number, the polymerization rate of miniemulsions is faster than that of the corresponding macroemulsions.

The predominant droplet nucleation is achieved via analyzing the droplet and the particle size in the same

figure. To obtain the dominant droplet nucleation, the HD level should be above 4 wt% with respect to the monomer. Additionally, nanosize polystyrene latexes were synthesized.

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