Differential Microemulsion Polymerization of Styrene: A Mathematical Kinetic Model

Guangwei He, Qinmin Pan, Garry L. Rempel

Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Received 23 March 2006; accepted 6 September 2006
DOI 10.1002/app.25622

ABSTRACT: A mathematical model has been developed for the differential microemulsion polymerization of styrene. In the model, both homogeneous and heterogeneous nucleation mechanisms are considered. It is confirmed that the predictions of the particle size and the fractional conversion by the model are in good agreement with the experimental data. It is indicated that the particle size of polystyrene decreases with an increase in the amount of the initiator or surfactant. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 2129–2137, 2007

Key words: emulsion polymerization; kinetics (polym.); modeling; particle nucleation; polystyrene

INTRODUCTION

Microemulsion polymerization is a commonly used method for making polymer particles with sizes of less than 100 nm.[1–5] Styrene, among the many monomers with much less water solubility than methyl methacrylate (MMA), is most often involved in studying microemulsion polymerization. However, in the traditional and modified microemulsion polymerization processes, a large amount of a surfactant is usually used to make a stable and clear microemulsion. Sometimes, the amount of the surfactant employed is even more than the amount of the monomer used. A few studies have been published on the modeling of microemulsion polymerization.[6–11] The focus of these papers is on the polymerization kinetics, the fractional conversion, and the number of polymer particles generated. There is only one publication on a model dealing with the size of polystyrene nanoparticles synthesized by the microemulsion polymerization method.[7] It was found through simulation that no matter what the conditions were for the microemulsion polymerization of styrene, the size of the polystyrene nanoparticle was always around 40 nm.[7]

We previously developed a differential microemulsion polymerization method by which particle sizes of poly(methyl methacrylate) of less than 20 nm and particle sizes of polystyrene of less than 30 nm were achieved with a rather low amount of a surfactant.[12,13] This article is the continuation of our previous approach and is aimed at developing a mathematical model for the differential microemulsion polymerization of styrene, which can help us to understand the mechanism of the phenomenon observed in the experimental investigation and provide the fundamentals of a potential process design.

EXPERIMENTAL

The chemicals used in the experiments, the procedure for the differential microemulsion polymerization, and the techniques for the characterization of the resultant polymer latexes were the same as those reported previously.[13] Ammonium persulfate (APS) was used as the initiator, and sodium dodecyl sulfate (SDS) was used as the surfactant. APS, SDS, and deionized water were added to a three-necked, round-bottom flask (250 mL) equipped with a magnetic stirrer, a reflux condenser, and a thermometer. After the temperature was raised to 80°C, the monomer was added dropwise over 1–1.5 h. After the completion of the monomer addition, the reaction temperature was kept at 80–85°C for about 1 h. The *z*-average particle size was measured with a dynamic light scattering method with a 90 Plus particle size analyzer (Brookhaven Instrument Corp., Holtsville, NY). The number-average particle sizes were measured with a Natrac 250 instrument (Microtrac, Inc., North Largo, FL).

The representative experimental conditions are listed in Table I.

MODEL DEVELOPMENT

As the reaction system for differential microemulsion polymerization is extremely complex, the following

---

Correspondence to: Q. Pan (qpan@cape.waterloo.ca) or G. L. Rempel (grempel@cape.waterloo.ca).

Contract grant sponsor: Natural Sciences and Engineering Research Council of Canada.
Contract grant sponsor: Canada Foundation for Innovation.

Journal of Applied Polymer Science, Vol. 105, 2129–2137 (2007)

TABLE I
Experimental Conditions for the Differential Microemulsion Polymerization of Styrene

Styrene (mL)	Deionized water (mL)	SDS (g)	APS (g)	Temperature (°C)	Addition time (s)	Aging time (s)
14	84	0.7–4.2	0.08	80	2400–5880	3600

assumptions are proposed to reasonably simplify the mathematical treatment: (1) the polymer particles are spherical; (2) the polymer nanoparticles contain at most one free radical; (3) the monomer in the polymer particles is in equilibrium with that in the water phase; (4) a quasi-steady state of free radicals is adopted in this process; (5) the particle volume is equal to the monomer volume plus the polymer volume; (6) the reactivity of the radicals is independent of their degree of polymerization; and (7) the effect of collisions is not considered in this work.

On the basis of these assumptions and conventional radical polymerization theory, the following mathematical expressions of the process can be formulated.

Initiation

On the basis of the conventional radical theory,[14] the initiation kinetics can be described by the following equation:

$$R_I = \frac{d[\mathrm{R}^{\cdot}]}{dt} = 2fk_d[\mathrm{I}] \tag{1}$$

where R_I is the initiator decomposition rate (mol L^{-1} s^{-1}); f is the initiator efficiency; [R$^{\cdot}$] is the concentration of radicals (mol/L); [I] is the initiator concentration (mol/L); and k_d, the initiator decomposition rate constant (s^{-1}), is temperature-dependent. This is usually represented by the Arrhenius equation:

$$k_d = Ae^{-E_a/RT} \tag{2}$$

where A is the frequency factor, R is the gas constant, T is the reaction temperature, and E_a is the activation energy.

For a persulfate-type initiator, A is 8×10^{15}, and E_a is 135 kJ/mol.[14]

Fractional conversion

On the basis of a material balance, the fractional conversion of styrene can be expressed as follows:[15]

$$x = \frac{\frac{1}{V_w}\int_0^t M_{\mathrm{charge}}dt - [\mathrm{M}]_s}{\frac{1}{V_w}\int_0^t M_{\mathrm{charge}}dt} \tag{3}$$

where x is the fractional conversion of the monomer to the polymer, M_{charge} is the monomer charge rate (mol/s), and V_w is the volume of water (L). $[\mathrm{M}]_s$ is the monomer concentration in the system based on water (in water and the particles; mol/L):

$$\frac{d[\mathrm{M}]_s}{dt} = -R_p + M_{\mathrm{charge}}/V_w \tag{4}$$

$$R_p = k_p[\mathrm{M}]_p N_1 + k_{pw}[\mathrm{M}]_w[\mathrm{R}^{\cdot}]_w \tag{5}$$

where R_p is the polymerization rate (mol L^{-1} s^{-1}), k_p is the propagation rate constant (L mol^{-1} s^{-1}), $[\mathrm{M}]_p$ is the monomer concentration in the polymer particles (mol/L), $[\mathrm{M}]_w$ is the monomer concentration in the aqueous phase (mol/L), N_1 is the concentration of free radicals in the polymer particles per unit of volume of water (mol/L), and $[\mathrm{R}^{\cdot}]_w$ is the concentration of total free radicals in the aqueous phase (mol/L).

To determine $[\mathrm{M}]_p$, the following empirical equation is used:[14]

$$\frac{[\mathrm{M}]_w}{[\mathrm{M}]_w^*} = \left(\frac{[\mathrm{M}]_p}{[\mathrm{M}]_p^*}\right)^a \tag{6}$$

For styrene, a is 0.6.[14]

Generation rate of polymer particles

Polymer particles will be generated if the free radicals diffuse out of the polymer particles containing free radicals or if free radials in water enter the particles containing free radicals. The polymer particles will disappear if free radicals from the water phase enter them:

$$\frac{dN_0}{dt} = -k_{cp}[\mathrm{R}^{\cdot}]_w N_0 + (k_{\mathrm{des}} + k_{cp}[\mathrm{R}^{\cdot}]_w)N_1 \tag{7}$$

$$\frac{dN}{dt} = k_{pw}[\mathrm{R}^{\cdot}_{c-1}]_w[\mathrm{M}]_w + k_{cm}[\mathrm{R}^{\cdot}]_w N_d \tag{8}$$

$$[\mathrm{R}^{\cdot}]_w = \frac{-A + \sqrt{A^2 + 4k_{tw}(R_I + k_{\mathrm{des}}N_1)}}{2k_{tw}} \tag{9}$$

$$A = k_{cp}N + k_{cm}N_d \tag{10}$$

where k_{des} is the radical desorption rate coefficient of the monomer radical from the polymer particle (L mol^{-1} s^{-1}), k_{pw} is the propagation rate constant in water (L mol^{-1} s^{-1}), and $[\mathrm{R}^{\cdot}_{c-1}]_w$ is the concentration of radicals with a critical length in the water phase (mol/

L). Equation (9) is obtained from the quasi-steady state of the free radicals in the aqueous phase:

$$k_{\mathrm{des}} = k_{tr,\mathrm{M}}[\mathrm{M}]_p \frac{K_0}{\beta K_0 + k_p[\mathrm{M}]_p} \tag{11}$$

$$K_0 = \frac{12D_w/m_d d_v^2}{1 + 2D_w/m_d D_p} \tag{12}$$

$$\beta = \frac{k_{pw}[\mathrm{M}]_w + k_{tw}[\mathrm{R}^\cdot]_w}{k_{pw}[\mathrm{M}]_w + k_{tw}[\mathrm{R}^\cdot]_w + k_{cp}N + k_{cm}N_d + \varphi} \tag{13}$$

where k_{trM} is the chain-transfer rate constant to the monomers (L mol^{-1} s^{-1}); k_{cm} is the apparent rate constant for radical capture by microemulsion droplets (L mol^{-1} s^{-1}); k_{cp} is the apparent rate constant for radical capture by polymer particles (L mol^{-1} s^{-1}); k_{tw} is the water-phase termination rate constant (L mol^{-1} s^{-1}); N_0 is the concentration of inactive polymer particles (mol/L), N is the total concentration of polymer particles (mol/L); N_d is the concentration of monomer droplets (mol/L); D_p is the diffusion coefficient for the monomer radicals in the polymer particles (dm^2/s); d_v is the volume-average diameter (dm); D_w is the diffusion coefficient for the monomer radicals in the water phase (dm^2/s); m_d is the partition coefficient for the monomer radicals between the polymer particles and water phase; and φ is the contribution of radicals terminated by reacting with chain-transfer agents, surfactants, or other impurities. Because there are some unknown factors in the calculation of β, it is used as an empirical parameter, which is over a range of 0–1, to be determined experimentally.

Volume growth of polymer particles

The total volume growth of all polymer particles is determined by the conversion of the monomer into the polymer by homogeneous nucleation (polymer particles generated in the water phase) and micellar nucleation:

$$\frac{dV_p}{dt} = \frac{(k_p[\mathrm{M}]_p N_1 + k_{pw}[\mathrm{R}^\cdot_{c-1}]_w[\mathrm{M}]_w)V_w M_m}{\rho_p \Phi_p} \tag{14}$$

where V_p is the particle volume (L), ρ_p is the polymer density (g/cm), M_m is the molecular weight of the monomer (mol/L), and Φ_p is the volume fraction of the polymer in the particle.

Rate of micelle depletion

The micellar concentration is calculated as follows:

$$N_d = \frac{[\mathrm{S}]_{\mathrm{total}} - [\mathrm{S}]_{\mathrm{CMC}}}{N_{\mathrm{agr}}} - \frac{A_p}{S_a N_A V_w N_{\mathrm{agr}}}, \ (\mathrm{If}\ M_{\mathrm{mic}} > 0) \tag{15}$$

$$A_p = (36\pi V_w N_A)^{1/3} N^{1/3} V_p^{2/3} \tag{16}$$

where S_a is the area covered by a monolayer of surfactant molecules (dm^2), N_A is Avogadro's number, N_{agr} is the average aggregation number of SDS in a micelle, A_p is the surface area of the polymer particles, $[\mathrm{S}]_{\mathrm{CMC}}$ is the concentration of the surfactant (mol/L), M_{mic} is the monomer amount in the micelles (mol), and $[\mathrm{S}]_{\mathrm{total}}$ is the total concentration of surfactant (mol/L).

Monomer balance

In microemulsion polymerization, the monomer is distributed among three possible positions: the water phase, the monomer droplets (monomer-swollen micelles), and the polymer particles:

$$M_{\mathrm{unreacted}} = [\mathrm{M}]_p V_p + [\mathrm{M}]_w V_w + M_{\mathrm{mic}} \tag{17}$$

$$M_{\mathrm{unreacted}} = (1 - x) \int_0^t M_{\mathrm{charge}} dt \tag{18}$$

$$M_{\mathrm{mic}} = N_d V_w K_{eq} [\mathrm{M}]_w \tag{19}$$

where $M_{\mathrm{unreacted}}$ is the amount of the unreacted monomer in the reaction system (mol) and K_{eq} is the equilibrium constant of the monomer between the aqueous phase and micelles.

RESULTS AND DISCUSSION

Nucleation mechanism

The monomer styrene used in this differential microemulsion polymerization process is only slightly soluble in water; its solubility in water is about 6.2 × 10^{-3} mol/L from the extrapolation of eq. (20) to 80°C:[14]

$$\ln[\mathrm{M}]_w^* = -1.514 - \frac{1259}{T(\mathrm{K})} \tag{20}$$

Because of the low water solubility, the particle nucleation in the water phase is not as significant as that in an MMA monomer system,[18] which has a water solubility of 0.15 mol/L at 50°C. Thus, for the styrene system, the nucleation both in the aqueous phase and in the micelles should be taken into consideration, whereas the contribution from the homogeneous nucleation in the water phase is not as important as the heterogeneous nucleation in the micelles (heterogeneous nucleation refers to the mechanism via which the particles are generated from the micelles.).

Determination of the model parameters

There is no specific value for k_{cm} in the literature. Guo et al.[6] used 5.5 ×10^2 L mol^{-1} s^{-1} for k_{cm} in the microe-

TABLE II
Parameters Used for the Simulation of Styrene Differential Microemulsion Polymerization at 80°C

Parameter	Value	Reference
k_p (L mol^{-1} s^{-1})	664	14
k_{pw} (L mol^{-1}s^{-1})	$4 \times k_p$	14
M_m (g mol^{-1})	104	
ρ_m (g cm^{-3})	0.878	15
ρ_p (g cm^{-3})	1.044	15
D_w (dm^2 s^{-1})	1.7×10^{-7}	14
D_p (dm^2 s^{-1})	1.7×10^{-7}	14
N_A	6.02×10^{23}	
k_{trM} (L mol^{-1} s^{-1})	$1 \times 10^{-4} \times k_p$	17
k_{tw} (L mol^{-1} s^{-1})	3.7×10^9	11, 14
k_d (L mol^{-1} s^{-1})	8.6×10^{-5}	14
f	0.6	
j_{cr}	5	14
k_{cp} (L mol^{-1} s^{-1})	3×10^6	6
$[\mathrm{M}]_p^*$ (mol/L)	5.8	14
$[\mathrm{M}]_w^*$ (mol/L)	6.1×10^{-3}	14
m_d	1300	10
$[\mathrm{S}]_{\mathrm{CMC}}$ (mol/L)	0.008	16
S_a (dm^2)	4.3×10^{-17}	15
K_{eq}	1.68×10^4	15
β	0.4	
k_{cm} (L mol^{-1} s^{-1})	5.5×10^3	

TABLE III
Results of the Simulations and Experiments

SDS (g)	Predicted result (nm)	Experimental result (nm)
0.7	55.0	36.3
1.4	36.2	30.5
2.1	28.7	26.7
2.8	25.5	27.1
3.5	23.2	23.3
4.2	21.6	23.1
4.9	19.2	—

mulsion polymerization of styrene and 8×10^4 L mol^{-1} s^{-1} for k_{cm} in the miniemulsion polymerization of styrene with SDS as the surfactant and cetyl alcohol as the cosurfactant. The higher value of k_{cm} used in the miniemulsion polymerization of styrene was possibly due to its much thinner surfactant layer covering the particles. In the differential microemulsion polymerization of styrene, the surfactant amount is much larger than that used for miniemulsion polymerization, and the surfactant layer is much thicker; therefore, k_{cm} in the differential microemulsion polymerization system should be less than 8×10^4 L mol^{-1} s^{-1}. In this work, k_{cm} is used as an adjustable parameter, with the value chosen within the range of 5.5×10^2 to 8×10^4 L mol^{-1} s^{-1}, as determined by experimental data. The values of the parameters used in this model, obtained from the literature or estimation, are listed in Table II.

Particle size

The particle size of polystyrene obtained from the differential microemulsion polymerization method is 20–40 nm. The evolution of the particle size with respect to time, calculated on the basis of the model (all the simulations in this article were made via Matlab ODE23), is shown in Figure 1. The experimental results are provided in Table III. The simulation results are in good agreement with the experiments, except when the SDS amount is quite low. The particle size decreases significantly when the SDS amount increases. However, the decreasing rate of the particle size becomes lower when the amount of SDS used is higher. For 1.4–2.1 g of SDS, the reducing rate of the particle size is 10.7 nm/g of SDS from the simulation and 5.4 nm/g of SDS from experimentation. When the

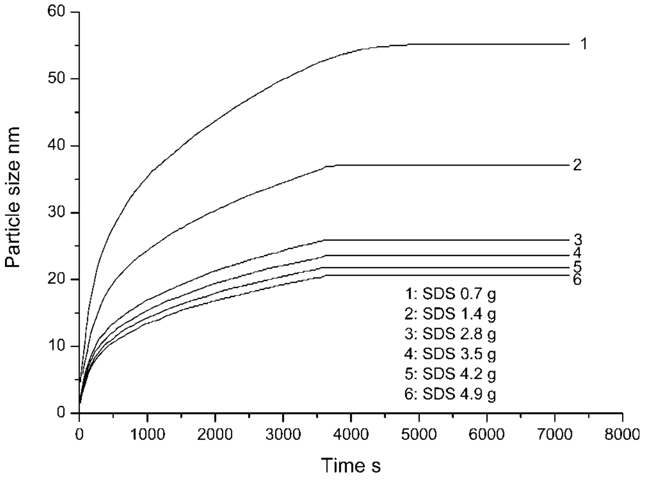

Figure 1 Time evolution of the particle size of polystyrene with different amounts of SDS (14 mL of styrene, 0.08 g of APS, 84 mL of deionized water, addition time of 3600 s, and aging time of 3600 s).

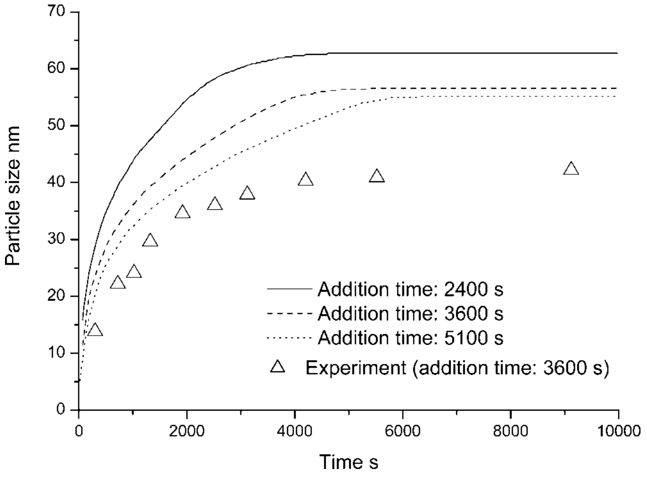

Figure 2 Micelle concentration as a function of time with various amounts of SDS (14 mL of styrene, 0.08 g of APS, 84 mL of deionized water, addition time of 3600 s, and aging time of 3600 s).

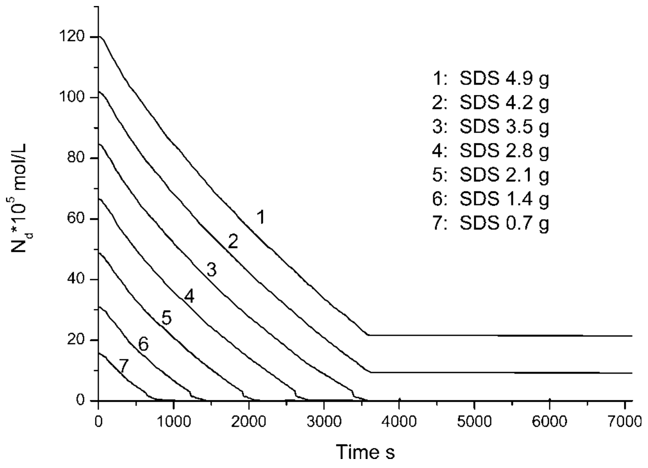

Figure 3 Change in the particle size of polystyrene with different addition rates of styrene (14 mL of styrene, 0.08 g of APS, 0.7 g of SDS, 84 mL of deionized water, and total reaction time of 10,000 s).

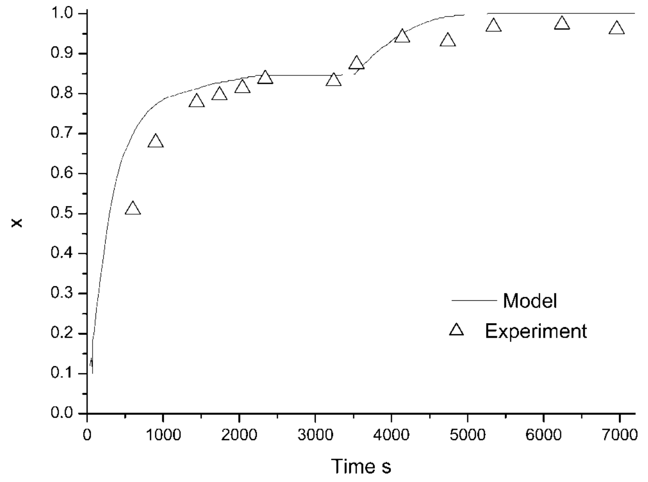

Figure 5 Prediction of the change in the particle size versus time with different amounts of APS (14 mL of styrene, 3.5 g of SDS, 84 mL of deionized water, and addition time of 3600 s).

SDS amount is increased from 3.5 to 4.2 g, the reducing rate is lowered to 2.3 nm/g of SDS in the simulation and 0.3 nm/g of SDS in the experiment. From Figure 2, it is very clear that when the SDS amount is larger than 3.5 g, the micelles will exist during the whole polymerization period, and this is why the particle size does not decrease very much when the SDS amount is sufficiently high.

In this differential polymerization process, styrene is added dropwise to the reaction mixture. The monomer addition rate will have some effect on the particle size. When the addition rate is fast, the amount of styrene added could be more than the amount consumed by polymerization, and some of the monomer could form large monomer droplets in the reaction system; then, the traditional emulsion polymerization will occur, and the particle size will be larger (see Figs. 3 and 4). In Figure 4, the plateau of the monomer concentration in a polymer particle occurs because of the existence of monomer droplets in the reaction system. To obtain a smaller particle size, the monomer addition rate should be sufficiently low, and the $[M]_p$ plateau should be prevented.

The amount of the initiator APS can also affect the particle size. The model shows that a larger amount of APS will result in a smaller particle size (see Fig. 5).

Both the calculated and experimental results show that the particle size of polystyrene increased steadily during the addition period. However, in the polymerization system for poly(methyl methacrylate), both the calculated particle size and the experimental results confirmed that the particle size did not change during

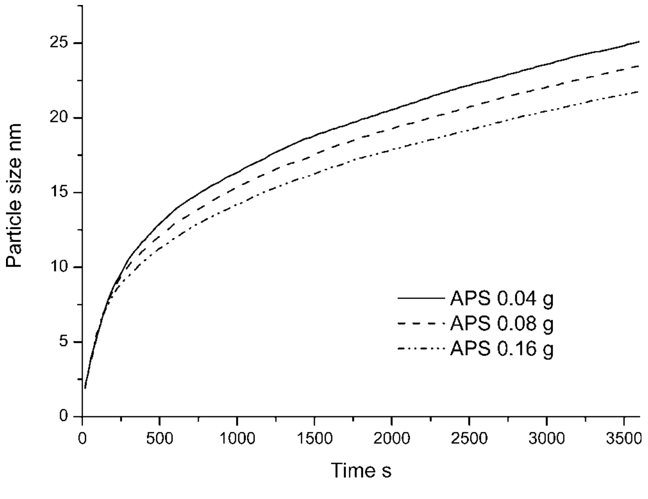

Figure 4 $[M]_p$ profile during styrene differential microemulsion polymerization (14 mL of styrene, 0.08 g of APS, 0.7 g of SDS, 84 mL of deionized water, and total reaction time of 7200 s).

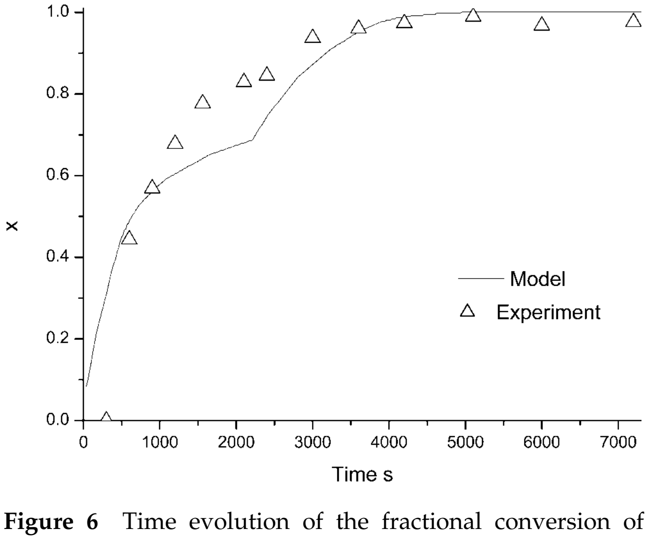

Figure 6 Time evolution of the fractional conversion of styrene (14 mL of styrene, 0.08 g of APS, 0.7 g of SDS, 84 mL of deionized water, addition time of 3600 s, and aging time of 3600 s).

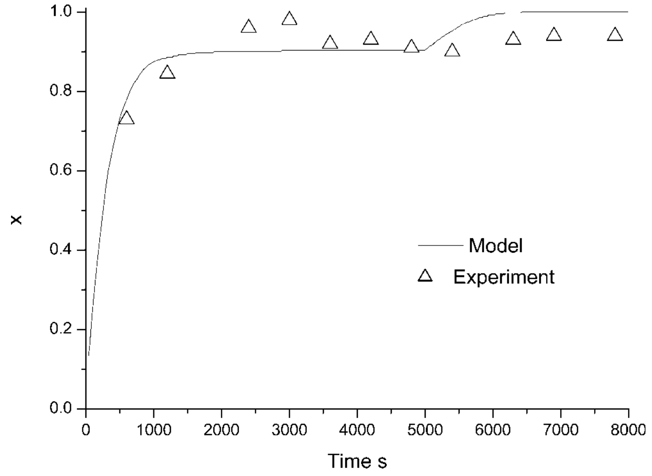

Figure 7 Time evolution of the fractional conversion of styrene (14 mL of styrene, 0.08 g of APS, 0.7 g of SDS, 84 mL of deionized water, addition time of 2400 s, and aging time of 4800 s).

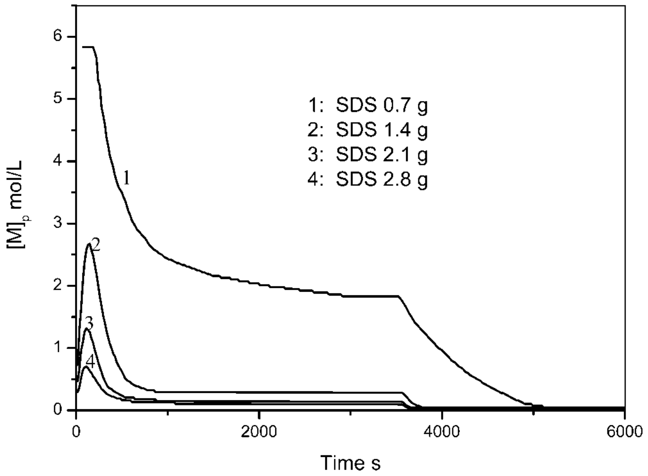

Figure 9 $[M]_p$ profile during styrene differential microemulsion polymerization with various amount of SDS (14 mL of styrene, 0.08 g of APS, 84 mL of deionized water, and addition time of 3600 s).

the addition period of the monomer.[18] The difference between the styrene and MMA systems can be attributed to the difference in the water solubility and then their nucleation mechanisms. It is suggested here that if the particle nucleation of polystyrene, which is highly dependent on heterogeneous nucleation, can be changed to that of MMA differential microemulsion polymerization, the particle size might be reduced.

Fractional conversion

F6-F8

The fractional conversions, defined as the amount of the monomer polymerized at a certain time t with respect to the total monomer added to the reaction system until time t, obtained from the model and from the experiments for styrene polymerization are shown in Figures 6–8. If the addition rates are slow, the conversion can reach a plateau zone, in which the reaction rate is controlled by the addition rate. After the reaction enters the aging zone, the conversion increases again to nearly 100%. For the fast addition rate (the addition of styrene in 40 min), the model predicts a lower conversion than that obtained from the experimental results. At the slow addition rate (the addition of styrene over 85 min), the calculated conversion is predicted to reach nearly 100%; however, the experimental conversion could reach only 92%. The reason may be that over this long addition period, the reaction time is comparable to $t_{1/2}$ of APS ($t_{1/2}$ = 140 min for APS). The lower amount of APS and the lower level of $[M]_p$ during the aging period may cause the smaller conversion for the slow addition rate.

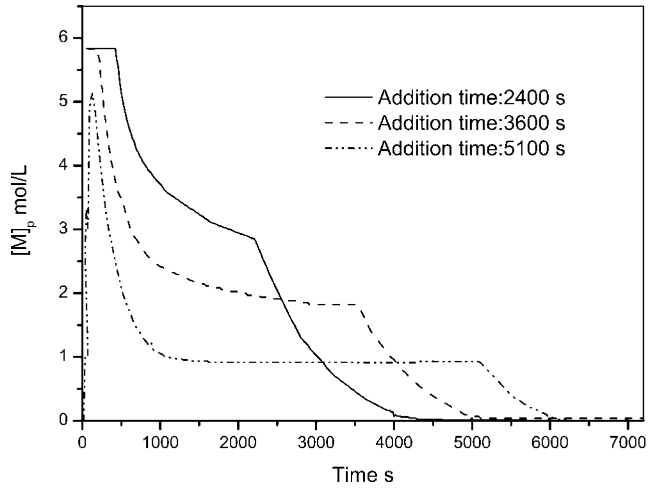

Figure 8 Time evolution of the fractional conversion of styrene (14 mL of styrene, 0.08 g of APS, 0.7 g of SDS, 84 mL of deionized water, addition time of 5100 s, and aging time of 2700 s).

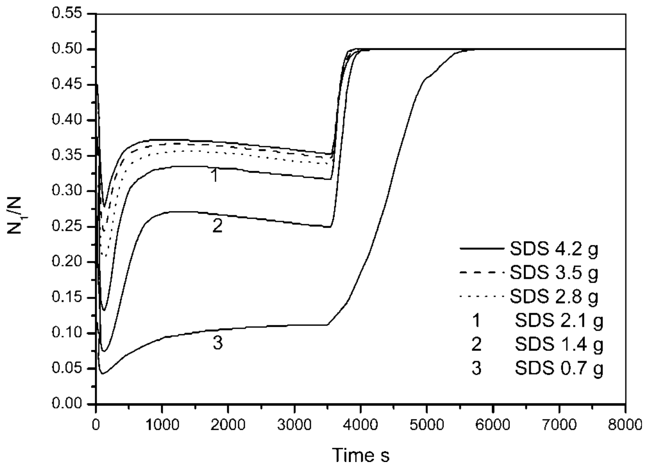

Figure 10 Change in N_1/N at different SDS values during the differential microemulsion polymerization of styrene (14 mL of styrene, 0.08 g of APS, 84 mL of deionized water, addition time of 3600 s, and aging time of 3600 s).

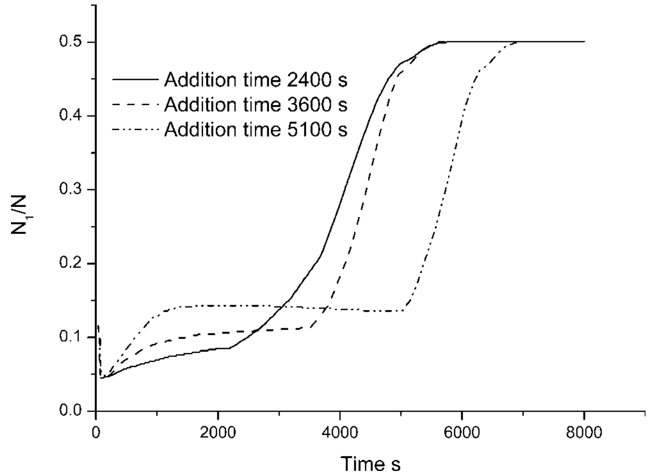

Figure 11 Change in N_1/N at different addition rates during the differential microemulsion polymerization of styrene (14 mL of styrene, 0.7 g of SDS, 0.08 g of APS, 84 mL of deionized water, and total reaction time of 7200 s).

Monomer concentration

The monomer concentrations in the polymer particles vary during the polymerization (see Figs. 4 and 9). After the addition of styrene, $[M]_p$ increases sharply to the saturation concentration in the polymer particles for the faster addition rates: less than a 60-min addition time in Figure 8 for 0.7 g of SDS. The plateau regions imply that there are monomer droplets in the reaction mixture. The behavior of the reaction is changed to that of the traditional emulsion polymerization in these plateau regions when the addition time is less than 1 h. When monomer droplets are present, the values of $[M]_p$ and $[M]_w$ become $[M]_p^*$ and $[M]_w^*$, respectively. When the amount of SDS is increased, more micelles will be formed in the system, and they will retain more styrene in them. In this way, $[M]_p$ can be kept under the saturation level, which can function as if the addition rate is slower (see Fig. 9).

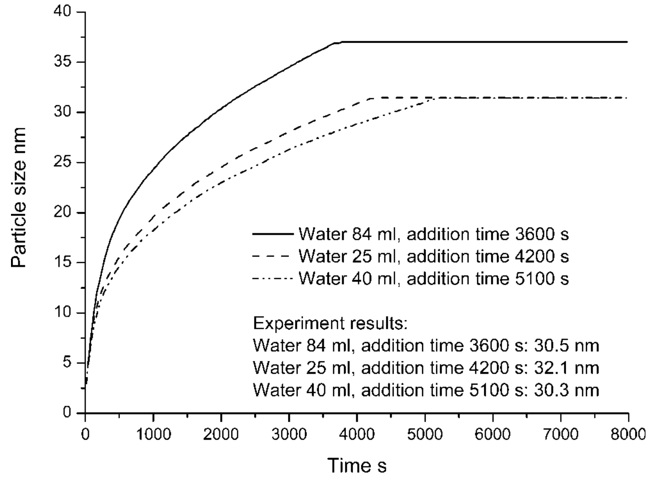

Figure 12 Change in the particle size of polystyrene with time with different amounts of deionized water (14 mL of styrene, 0.08 g of APS, 1.4 g of SDS, 84 mL of deionized water, and total reaction time of 7200 s).

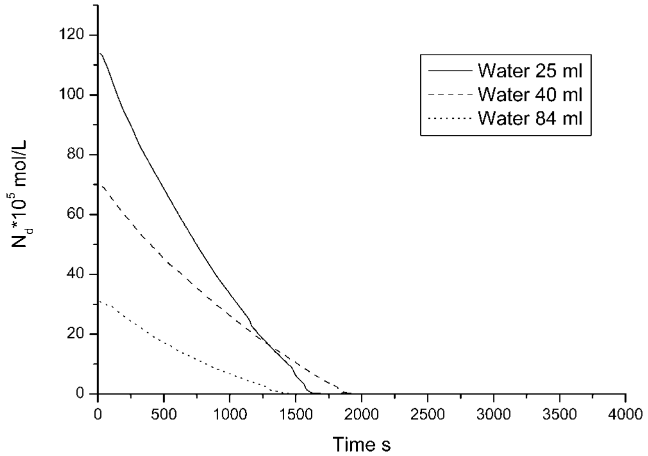

Figure 13 Change in N_d with time with different amounts of deionized water (14 mL of styrene, 0.08 g of APS, 1.4 g of SDS, 84 mL of deionized water, and total reaction time of 7200 s).

Average number of radicals per particle (N_1/N)

N_1/N during the differential polymerization of styrene increases when the amount of SDS is raised (see Fig. 10). The predicted N_1/N value in our work is much higher in most cases than the value calculated by Mendizabal et al.,[11] which is less than 0.1 in the traditional microemulsion polymerization of styrene. At a fixed amount of SDS, N_1/N increases when the addition rate decreases (see Fig. 11).

Effect of the solid content

An increase in the solid content of polystyrene in our experimental study was obtained by a reduction of

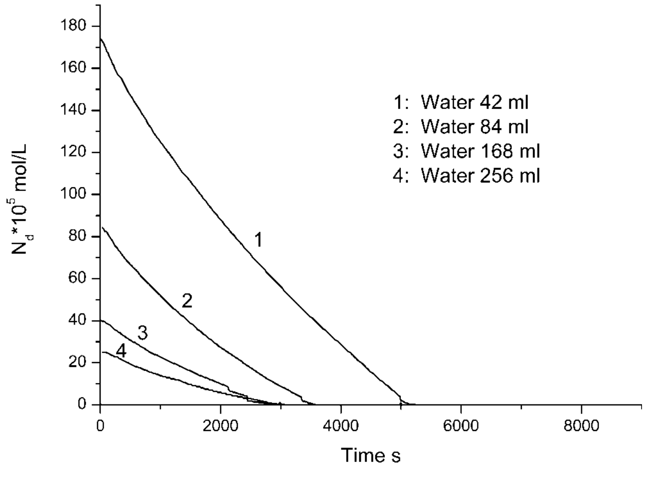

Figure 14 Change in N_d with time with different amounts of deionized water (14 mL of styrene, 0.08 g of APS, 1.4 g of SDS, 84 mL of deionized water, and 8000 s total reaction time).

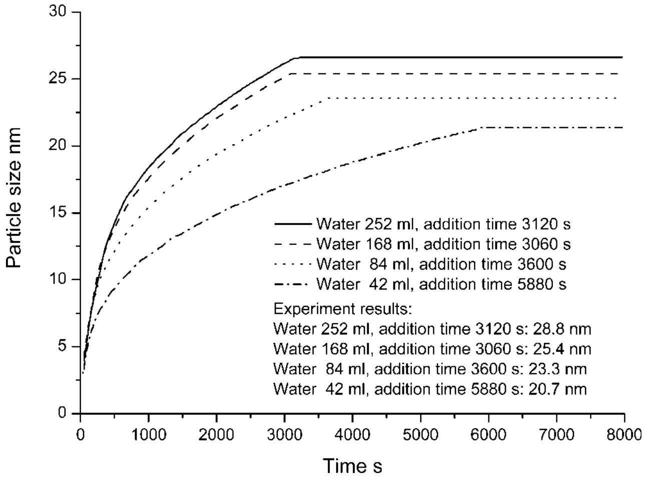

Figure 15 Change in the particle size of polystyrene with time with different amounts of deionized water (14 mL of styrene, 0.08 g of APS, 3.5 g of SDS, 84 mL of deionized water, and total reaction time of 7200 s).

the amount of water used in the polymerization. A decrease in the amount of water used causes the particle sizes to be smaller, as predicted by theoretical calculations and verified by experiments (see Fig. 12). When less water is used to increase the solid content, a number of the operational parameters are also changed in the polymerization system: (1) the initiator concentration will increase, the monomer amount in the aqueous phase will decrease, and monomer will be forced into the particles or the micelles or even be caused to form monomer droplets; (2) the micelle concentration will rise (see Figs. 13 and 14); and (3) the number of micelles will rise because of the smaller value of $V_w \times S_{\mathrm{CMC}}$. Items 1 and 2 do not affect the number of polymer particles. Item 3 will cause the number of polymer particles to become larger. The micellar nucleation loci will increase and the particle size will be smaller for a latex with a higher solid content (see Figs. 12 and 15).

CONCLUSIONS

A theoretical approach has been developed in this article to simulate the differential microemulsion polymerization of styrene. Both the homogeneous and heterogeneous nucleation mechanisms are taken into account. The predicted fractional conversion and particle size are in good agreement with the experimental data. The model shows that increasing the addition rate of styrene, increasing the APS amount, or using more SDS contributes to the reduction in the final particle sizes. However, when the amount of SDS is increased to a level such that the micelles exist during the whole polymerization process, further increasing the SDS amount will have little effect on the particle size. The average number of free radicals per polymer particle and the micelle concentration can also be calculated, and the information is very useful for explaining the phenomena of the practical polymerization process. In addition, this model can also predict the point at which the polymerization will enter the traditional emulsion polymerization domain. Faster monomer addition or a lower amount of surfactant SDS will cause the system to have larger monomer droplets, which will result in a larger particle size.

NOMENCLATURE

A	frequency factor
A_p	surface area of the polymer particles (dm^2)
APS	ammonium persulfate
D_p	diffusion coefficient for the monomer radicals in the polymer particles (dm^2/s)
d_v	volume-average diameter (dm)
D_w	diffusion coefficient for the monomer radicals in the water phase (dm^2/s)
E_a	activation energy (kJ/mol)
f	initiator efficiency
[I]	initiator concentration (mol/L)
j_{cr}	critical length of the monomeric radicals in the aqueous phase
k_{cm}	apparent rate constant of radical capture by the monomer-swollen micelles (L mol^{-1} s^{-1})
k_{cp}	apparent rate constant of radical capture by the polymer particles (L mol^{-1} s^{-1})
k_d	initiator decomposition rate constant (L mol^{-1} s^{-1})
k_{des}	radical desorption rate coefficient of the monomer radical from the polymer particle (L mol^{-1} s^{-1})
K_{eq}	equilibrium constant of the monomer between the aqueous phase and micelles
k_p	propagation rate constant (L mol^{-1} s^{-1})
k_{pw}	propagation rate constant in water (L mol^{-1} s^{-1})
k_{trM}	chain-transfer rate constant to the monomers (L mol^{-1} s^{-1})
k_{tw}	water-phase termination rate constant (L mol^{-1} s^{-1})
M_{charge}	monomer charge rate (mol s^{-1})
m_d	partition coefficient for the monomer radicals between the polymer particles and water phase
M_m	molecular weight of the monomer (mol/L)
MMA	methyl methacrylate
M_{mic}	amount of the monomer in the micelles (mol)
$[\mathrm{M}]_p$	monomer concentration in the polymer particles (mol/L)

$[M]_p^*$	monomer concentration in the polymer particles at saturation (mol/L)
$[M]_s$	monomer concentration in the system based on water (mol/L)
$M_{\text{unreacted}}$	amount of the unreacted monomer in the reaction system (mol)
$[M]_w$	monomer concentration in the water phase (mol/L)
$[M]_w^*$	monomer concentration in water at saturation (mol/L)
N	total concentration of the polymer particles (mol/L)
N_0	concentration of the inactive polymer particles (mol/L)
N_1	concentration of the active polymer particles (mol/L)
N_A	Avogadro's number
N_{agr}	average aggregation number of SDS in a micelle
N_d	concentration of the monomer droplets (mol/L)
φ	contribution of the radicals terminated by reacting with chain-transfer agents, surfactants, or other impurities
Φ_p	volume fraction of the polymer in the particle
ρ_m	monomer density (g/cm)
ρ_p	polymer density (g/cm)
R	gas constant
$[R^{\cdot}]$	concentration of the radicals (mol/L)
$[R\cdot]_w$	concentration of the radicals in the water phase (mol/L)
$[R_{c-1}]_w$	concentration of the radicals with a critical length in the water phase (mol/L)
R_I	initiator decomposition rate (mol L^{-1} s^{-1})
R_p	polymerization rate (mol L^{-1} s^{-1})
S_a	area covered by a monolayer of surfactant molecules (dm^2)
$[S]_{CMC}$	concentration of the surfactant (mol/L)
SDS	sodium dodecyl sulfate
$[S]_{\text{total}}$	total concentration of the surfactant (mol/L)
T	reaction temperature (K)
V_p	particle volume (L)
V_w	volume of water (L)
x	monomer fractional conversion

References

1. Antonietti, M.; Bremser, W.; Miischenborn, D.; Rosenauer, C.; Schupp, B. Macromolecules 1991, 24, 6636.
2. Ming, W.; Zhao, J.; Lu, X.; Wang, C.; Fu, S. Macromolecules 1996, 29, 7678.
3. Ming, W.; Zhao, J.; Cui, J.; Fu, S.; Jones, F. N. Macromolecules 1999, 32, 528.
4. Xu, X. J.; Chew, C. H.; Siow, K. S.; Wong, M. K.; Gan, L. M. Langmuir 1999, 15, 8067.
5. Zhang, C.; Wang, Q.; Xia, H.; Qiu, G. Eur Polym J 2002, 38, 1769.
6. Guo, J. S.; Sudol, E. D.; Vanderhoff, J. W.; El-Aasser, M. S. J Polym Sci 1993, 48, 775.
7. Suzuki, K.; Nomuro, M. Macromol Symp 2002, 179, 1.
8. Mendizabal, E.; Flores, J.; Puig, J. E.; Lopez-Serrano, F.; Alvarez, J. Eur Polym J 1998, 34, 411.
9. Morgan, J. D.; Kaler, E. W. Macromolecules 1998, 31, 3197.
10. Suzuki, K.; Nomura, M.; Harada, M. Colloid Surf A 1999, 153, 23.
11. Mendizabal, E.; Flores, J.; Puig, J. E.; Katime, I.; Lopez-Serrano, F.; Alvarez, J. Macromol Chem Phys 2000, 201, 1259.
12. He, G.; Pan, Q.; Rempel, G. L. Macromol Rapid Commun 2003, 24, 586.
13. He, G.; Pan, Q. Macromol Rapid Commun 2004, 25, 1545.
14. Gilbert, R. G. Emulsion Polymerization: A Mechanistic Approach; Academic: San Diego, 1995.
15. Sajjadi, S. Polymer 2003, 44, 223.
16. Gao, J.; Penlidis, A. Prog Polym Sci 2002, 27, 403.
17. Brandrup, J.; Immergut, E. H.; Grulke, E. A. Polymer Handbook, 4th ed.; Wiley: New York, 1999.
18. He, G.; Pan, Q.; Rempel, G. L. Ind Eng Chem Res, to appear.