Modified Structural Model for Predicting Particle Size in the Microemulsion and Emulsion Polymerization of Styrene under Microwave Irradiation[†]

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In this study, the microemulsion and emulsion polymerization of styrene at 70 °C in the presence of sodium dodecyl sulfate (SDS, surfactant) and potassium persulfate (KPS, initiator) was conducted under microwave radiation. Laser light scattering was used to characterize the resultant polystyrene latex particles formed at different polymerization stages. The influence of the initial emulsion composition, that is, the SDS, KPS, and styrene concentrations, on the final particle size led us to a simple modified structural model in which we considered the stabilization effects of both the surfactant and the ionic end groups generated from the initiator. This model extended the application of the previous Wu plot from microemulsion polymerization to emulsion polymerization. Using this model, we were not only able to control the particle size but were also able to predict the monomer concentration dependence of the number of the resultant latex particles and the effect of diluting the reaction mixture on the resultant particle size.

Introduction

Emulsion and microemulsion polymerization are widely used to prepare polymeric latex particles.[1−11] It was shown that, in the microemulsion polymerization of styrene, the resultant particle size could be quantitatively controlled by the initial fleet ratio, that is, the macroscopic monomer-to-surfactant weight ratio (W_m/W_s).[10−16] Antonietti et al.[12] proposed a simple geometric model in which all the oil microdroplets were assumed to have a similar size and surfactant molecules were located at the microdroplet/water interface to form a monolayer. Later, Wu[10] proposed a more realistic structural model on the basis of the assumption that the surface area occupied per surfactant molecule (stabilizer) was a constant if we let thermodynamics take over the process. It predicts that the particle radius (R) is a linear function of the monomer/surfactant weight ratio (W_m/W_s), that is,

$$\frac{W_m}{W_s} = s\frac{\rho N_A}{3M_s}R + C \tag{1}$$

where s is the average surface area occupied per stabilizer; ρ, M_s, and C are the average particle density, the molar mass of surfactant, and a constant, respectively. Equation 1 has been confirmed by a number of microemulsion systems.[12−15] However, it has been questioned whether eq 1 can also be used for a conventional emulsion or miniemulsion.[15]

It is generally recognized that it is difficult to predict and prepare a batch of latex in emulsion polymerization in terms of particle size distributions and stability because it is not completely clear how each experimental condition affects the emulsion polymerization. Recently, we found that using microwave radiation as a heating source for emulsion polymerization could result in reproducible and narrowly distributed surfactant-free latex particles.[16] It should be stated that microwave radiation has already been used in chemical reactions,[17,18] but its application in emulsion polymerization has only occured recently.[19,20]

Experimental Section

Sample Preparation. Styrene monomer was purified by a normal procedure.[16] Potassium persulfate (KPS, from Merck) was recrystallized from water. Sodium dodecyl sulfate (SDS, from

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(1) Roe, C. P. *Ind. Eng. Chem.* **1968**, *60*, 20.

(2) Smith, W. V.; Ewart, R. H. *J. Chem. Phys.* **1948**, *16*, 592.

(3) Maxwell, I. A.; Morrison, B. R.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1991**, *24*, 1629.

(4) Cochin, D.; Laschewsky, A.; Nallet, F. *Macromolecules* **1997**, *30*, 2278.

(5) Biggs, S.; Grieser, F. *Macromolecules* **1995**, *28*, 4877.

(6) Lovell, P. A., El-Aasser, M. S., Eds. *Emulsion Polymerization and Emulsion Polymers*; John Wiley and Sons: New York, 1997.

(7) Guo, J. S.; El-Aasser, M. S.; Vanderhoff, J. W. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 691.

(8) Gan, L. M.; Lee, K. C.; Chew, C. H.; Ng, S. C. *Langmuir* **1995**, *11*, 449.

(9) Gan, L. M.; Chew, C. H.; Lee, K. C.; Ng, S. C. *Polymer* **1994**, *35*, 2659.

(10) Ming, W. H.; Zhao, J.; Lu, X. L.; Wang, C. C.; Fu, S. K. *Macromolecules* **1996**, *29*, 7678.

(11) Dreja, M.; Tieke, B. *Langmuir* **1998**, *14*, 800.

(12) Antonietti, M.; Bremser, W.; Muschenborn, D.; Rosenauer, C.; Schupp, B. *Macromolecules* **1991**, *24*, 6636.

(13) Wu, C. *Macromolecules* **1994**, *27*, 298; **1994**, *27*, 7099.

(14) Antonietti, M.; Basten, R.; Lohnmann, S. *Macromol. Chem. Phys.* **1995**, *196*, 441.

(15) Baumann, F.; Schmidt, M.; Deubzer, B.; Geck, M.; Dauth, J. *Macromolecules* **1994**, *27*, 6102.

(16) Zhang, W. M.; Gao, J.; Wu, C. *Macromolecules* **1997**, *30*, 6388.

(17) Galema, S. A. *Chem. Soc. Rev.* **1997**, *26*, 233.

(18) Michael, D.; Mangos, P.; Baghurst, D. R. *Chem. Soc. Rev.* **1991**, *20*, 1.

(19) Murray, M.; Charjesworth, D.; Snowden, M. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1999.

(20) Correa, R.; Gonzalez, G.; Dougar, V. *Polymer* **1998**, *39*, 1471.

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BDH) was used as received. Deionized water with a resistivity of 18 MΩ·cm was used in all the experiments. A conventional microwave oven (Whirlpoor-VIP20) with a double emission system, operating at 2450 MHz with a maximum output power of 900 W, was used as the irradiation source. A flask equipped with a glass stirrer, a reflux condenser, a feeding head, and a thermometer was assembled inside the oven. The mixture of styrene, water, and SDS was dispersed in the flask with a stirring speed of ~300 rpm for 15 min under N_2 flux before a certain amount of KPS was added to initiate the polymerization. The total volume of the reaction mixture was 250 mL. Typically, under microwave radiation, the reaction mixture could reach ~70 °C within only 2 min. The polymerization was carried at 70 ± 2 °C under N_2 with a reduced microwave radiation power of ~80 W. More than 97% of the monomers (measured by weighing and also by laser light scattering) were polymerized within ~40 min, and the polymerization was completed in 1 h. Note that the reaction rate was much faster than a conventional emulsion polymerization heated by a normal water bath.

Laser Light Scattering (LLS). A modified commercial LLS spectrometer (ALV/SP-125) equipped with a multi-τ digital time correlator (ALV-5000) and a solid-state laser (ADLAS DPY 425 II, output power ~400 mW at $\lambda_0 = 532$ nm) was used. The details of the LLS theory and instrumentation can be found elsewhere.[21,22] In static LLS, the angular dependence of the absolute excess time-averaged scattered intensity, known as the Rayleigh ratio ($R_{vv}(\theta)$), of a set of dilute solutions could lead to the weight-average molar mass (M_w), the second virial coefficient (A_2), and the z-average root-mean-square radius of gyration ($\langle R_g^2\rangle_z^{1/2}$ or $\langle R_g\rangle$). In this study, the dispersion was so dilute that the extrapolation to infinite dilution was not necessary. At a small scattering angle, $R_{vv}(\theta) \cong KCM_w$, where K is a constant for a given polymer/solvent system and C is the polymer concentration. In dynamic LLS, the measured intensity–intensity time correlation function was analyzed by both the Laplace inversion (CONTIN) and cumulant programs in the correlator, which led to the hydrodynamic radius distribution ($f(R_h)$) and the average hydrodynamic radius ($\langle R_h\rangle$) of the latex particles. All the LLS measurements were done at 25.0 ± 0.1 °C. The specific refractive index increment (dn/dC) of the polystyrene nanoparticles in water is 0.256 ± 0.002 mL/g.[23]

Results and Discussion

The resultant dispersions with particles larger than 60 nm are milky and opaque, while those with smaller particles (10 nm < R_h < 30 nm) appeared to be blue or yellowish. There was no detectable change for the particles after they stood at room temperature for more than 1 year. A combination of static and dynamic LLS results showed that the ratios of the radius of gyration to the hydrodynamic radius ($\langle R_g\rangle/\langle R_h\rangle$) were ~0.8, very close to the value $(3/5)^{1/2}$ predicted for a uniform nondraining sphere. All the resultant particles were nearly monodispersed with a polydispersity index of ~1.05. Figure 1 shows that $\langle R_h\rangle$ decreases as the surfactant concentration increases. However, the inset shows that $\langle R_h\rangle$ is not a linear function of the reciprocal of $C_{\text{surfactant}}$, contradicting eq 1. Therefore, the model developed on the basis of microemulsion should be modified for our present emulsion polymerization.

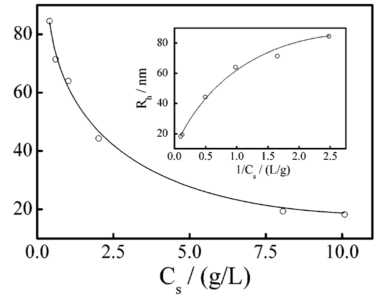

Figure 1. SDS concentration dependence of the average hydrodynamic radius ($\langle R_h\rangle$) of the resultant latex particles, where the styrene monomer and initiator concentrations were kept at 22.6 and 0.305 g/L, respectively.

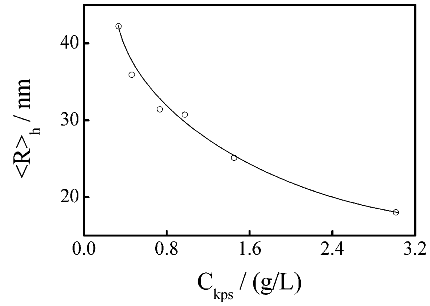

Figure 2. Initiator (KPS) concentration dependence of the average hydrodynamic radius ($\langle R_h\rangle$) of the resultant latex particles, where the monomer and surfactant concentrations were kept at 22.6 and 2.02 g/L, respectively.

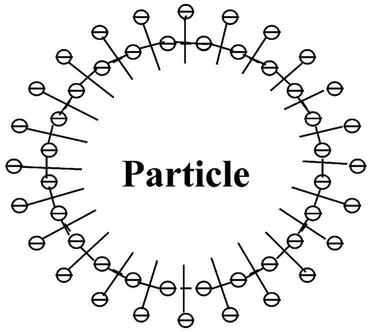

Figure 3. Schematic of the structure of a polystyrene latex particle, where both the surfactant molecules and the $-SO_4^-$ ionic ends generated from KPS are considered as "stabilizers" located at the interface.

On the other hand, Figure 2 shows that $\langle R_h\rangle$ also decreases with an increasing initiator KPS concentration (C_{KPS}), indicating that the ionic end groups generated from the water-soluble initiator KPS played a similar role to that of surfactant molecules in the stabilization. In the polymerization process, each persulfate ion could decompose into two ionic radicals, that is, $S_2O_8^{2-} \rightarrow 2SO_4^-$, and each ionic radical could initiate a chain reaction to form a polystyrene chain with an ionic end acting as a "surfactant molecule". It is reasonable to expect that both the surfactant molecules and the ionic ends of the polystyrene chains were on the particle surface, as schematically shown in Figure 3.

Considering both the ionic ends and surfactant as "stabilizers" and assuming each of the stabilizers occupies a similar surface area denoted as "s", we are ready to extend eq 1 by assuming all the ionic groups are on the particle surface. For a monodispersed latex, s should be the ratio of the total surface area (S_T) to the total number (N_s) of "stabilizing groups" adsorbed on the particle surface, that is,

$$s = \frac{S_T}{N_s} = \frac{4\pi R^2\{(W_m + W_s + W_i)/[\rho(4\pi R^3/3)]\}}{[N_A(W_s/M_s + 2W_i/M_i)]} \quad \text{or}$$

$$R = \frac{3}{N_A \rho s} w \quad (2)$$

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[21] Berne, B.; Pecora, R. *Dynamic Light Scattering*; Plenum Press: New York, 1976.

[22] Chu, B. *Laser Light Scattering: basic principles and practice*, 2nd ed.; Academic Press: New York, 1974.

[23] Brandrup, I., Immergut, E. H., Eds. *Polymer Handbook*, 3rd ed.; Wiley: New York, 1989.

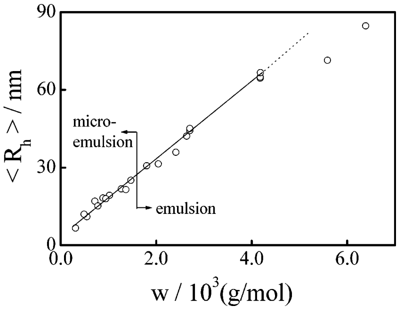

Figure 4. Replot of all the data points in Figures 1 and 2 on the basis of eq 2, where w is the particle mass stabilized by per mole of stabilizers (see the text for details).

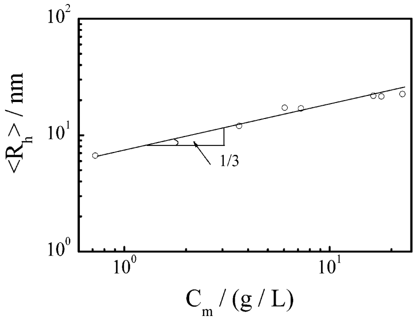

Figure 5. Monomer concentration (C_m) dependence of the average hydrodynamic radius ($\langle R_h \rangle$), where the surfactant and initiator concentrations were kept at 4.03 and 0.305 g/mL, respectively.

where W_m, W_s, and W_i are the macroscopic weights of monomer, surfactant, and initiator, respectively, ρ is the average density of the particles, M_s and M_i are the molar masses of the surfactant and initiator, respectively, and $w = (W_m + W_s + W_i)/(W_s/M_s + 2W_i/M_i)$, representing the particle mass stabilized per mole of stabilizers. The factor "2" is due to the fact that each initiator molecule can generate two ionic groups.

Figure 4 shows that $\langle R_h \rangle$ is indeed proportional to w in the range $(0.3-4.0) \times 10^3$ g/mol, well beyond the range of microemulsion. The least-squares fitting had a regression coefficient of 0.992, and the slope of the line led to a reasonable value of $s \sim 0.27$ nm^2, where we took $\rho \sim 1$ g/cm^3. In practice, as long as the monomer/surfactant ratio is not too high, we are able to use eq 2 to control and predict the particle size in emulsion polymerization just as what we did in microemulsion polymerization. It should be noted that, in microemulsion polymerization, R is simply proportional to the monomer weight (W_m) according to eq 1.

Further, Figure 5 shows that the particle volume ($\langle R_h \rangle^3$) is proportional to the initial monomer concentration (C_m), that is, $\langle R_h \rangle \propto C_m^{1/3}$, for given surfactant (SDS) and initiator (KPS) concentrations (4.03 and 0.305 g/mL, respectively). This is similar to what we have found in a previous study of the preparation of surfactant-free polystyrene latex dispersions.[13] The monomer concentration (C_m) is related to the number of latex particles in a unit volume (n_p); namely, $C_m = (^4/_3)\pi \langle R_h \rangle^3 \rho n_p$. The fact that $\langle R_h \rangle \propto C_m^{1/3}$ indicates that n_p must be a constant, independent of the initial monomer concentration. It suggests that, due to high initiation rate in a very short time under the microwave radiation, there was nearly no continuous nucleation and n_p was mainly determined by the KPS and SDS concentrations if other experimental conditions, such as the microwave power and the reaction temperature, were fixed. Recently, Winnik and co-workers used this idea to prepare uniform copolymer particles by using dispersion polymerization.[24] We also found that using higher reaction temperatures led to smaller latex particles, reflecting one of the characteristics of emulsion polymerization.[1]

After considering the above results, we were able to discuss the main difference between microemulsion polymerization and emulsion polymerization. In a microemulsion reaction, the monomers (oil) are thoroughly dispersed in the form of monomer-swollen micelles, resulting in a thermodynamically stable dispersion. The initial surfactant/monomer weight ratio (W_m/W_s, the fleet ratio) determines the size of the final latex particles.[9,10] In an emulsion, much more monomers are added so that they can not be completely dispersed into the swollen micelles and part of the monomers exist in the form of large monomer (oil) droplets which are thermodynamically unstable. This is why the resultant particle size is not simply controlled by the fleet ratio. It is reasonable to view an emulsion as a mixture of monomer saturated swollen micelles and large monomer droplets.

It has been known that emulsion polymerization normally has three stages.[1] In the first stage, radicals generated from the water-soluble initiator diffuse into the monomer-swollen micelles to start the polymerization. The resultant monomer-swollen polymeric particles further attract the surfactant molecules from the nonreacted micelles. The ending of this stage could be marked by the disappearance of the monomer-swollen micelles, and most of the surfactant molecules are used for the stabilization of the polymer particles generated.[1] Our previous study on emulsion polymerization under microwave radiation indicates a reaction rate ~10 times faster than that when conventional heating is used. We expect the emulsion polymerization to proceed in two stages. The first stage of emulsion polymerization resembles microemulsion polymerization; namely, the surface area (s) occupied per stabilizer should remain as a constant and the initial stabilizer concentration plays a dominant role in controlling the particle size. In the second stage, large monomer droplets serve as a reservoir to feed monomers into the growing particles, resulting in an increase of the particle size as well as the surface area (s) occupied per stabilizer, just imagining that stabilizers were on the surface of a blowing-up balloon. The final particle size is determined by the amount of the excess monomer. On the basis of eq 2, the increase of s should lead to a decrease of the slope of "R versus w". This can explain why the last two data points in Figure 4 deviate from the straight line when w is too high.

On the other hand, Figure 6 shows that $\langle R_h \rangle \propto C_{total}^{-2/3}$, where $C_{total} = C_m + C_s + C_i$. A qualitative explanation is as follows. According to the above discussion, in the first stage, the dilution of monomer has no effect on the particle size because monomers are abundant in emulsion polymerization. However, the dilution of stabilizers leads to an increase of $\langle R_h \rangle$; that is, $\langle R_h \rangle$ is proportional to C_{total}^{-1} on the basis of eq 1. In the second stage, the dilution of stabilizers should have no effect on $\langle R_h \rangle$ because the stabilizers were already on the particles, but the dilution of monomers reduces the amount of monomers in the reservoir so that the dilution should lead to a decrease of $\langle R_h \rangle$ because $\langle R_h \rangle \propto C_{total}^{1/3}$. Therefore, a combination of the results in these two stages leads to $\langle R_h \rangle \propto C_{total}^{-2/3}$.

In summary, the structural model developed for mi-

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(24) Winnik, M. Private communication, 2004.

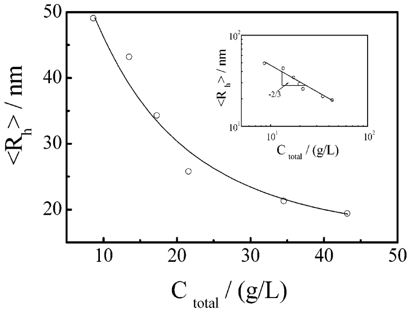

Figure 6. Effect of diluting the emulsion on the average hydrodynamic radius ($\langle R_h \rangle$), where C_{total}, the total concentration, was defined as $C_m + C_s + C_i$. The ratio of $C_m/C_s/C_i$ was kept at 79.1:14.1:1. The inset shows that $\langle R_h \rangle \propto C_{total}^{-2/3}$, and the line represents a least-squares fitting of $\langle R_h \rangle = 173C^{-2/3} + 4.4$.

croemulsion polymerization can be extended and applied to the emulsion polymerization of hydrophobic monomers, such as, styrene, in a certain monomer/surfactant range in a batch reaction process if we consider the initiator as a kind of stabilizer. Using this model, we will be able to control and predict the resultant particle size even in emulsion polymerization. The fact that $R_h \propto C_m^{1/3}$ revealed that, under microwave radiation, the number of the resultant particles remained constant after the nucleation stage. On the basis of the two-stage polymerization, we are able to qualitatively explain the fact that $\langle R_h \rangle \propto C_{total}^{-2/3}$.

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