*Macromolecules* **2002,** *35,* 574−576

# Notes

## 50 nm Polystyrene Particles via Miniemulsion Polymerization

**Christopher D. Anderson, E. David Sudol, and Mohamed S. El-Aasser***

*Emulsion Polymers Institute, Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015*

*Received February 9, 2001*
*Revised Manuscript Received October 16, 2001*

### Introduction

Miniemulsions are stable, submicron dispersions of monomer in a continuous, usually aqueous medium.[1−3] Formation of submicron monomer droplets is brought about by the application of energy through homogenization. The diameter of the miniemulsion droplets is controlled by, among other factors, the amount of surfactant relative to the monomer. The low surfactant concentration in the aqueous phase of a miniemulsion eliminates micellar nucleation and reduces the probability of homogeneous nucleation. The high number of droplets per unit volume of miniemulsion increases the probability of particle nucleation by direct oligoradical entry into monomer droplets relative to particle nucleation by homogeneous and/or micellar nucleation. As a result, the monomer droplets are the main locus of polymerization in miniemulsion (as well as in microemulsion) polymerization.

Microemulsions consist of spontaneously formed droplets that are less than 50 nm in diameter but generally require high concentrations of surfactant and costabilizer and relatively low solids contents. The resulting monomer/surfactant ratio is quite limited, even in optimized microemulsion systems.[4]

It may be possible to prepare miniemulsion latexes with similarly small particle diameters (<50 nm) and higher solids contents, using concentrations of surfactant and costabilizer significantly lower than used in microemulsions due to the relatively low surfactant surface coverage (about 20%) and reduced amount of costabilizer required for the stability of miniemulsion droplets.

### Experimental Section

To produce nanosize polystyrene particles by miniemulsion polymerization, higher levels of surfactant may be necessary to reduce the interfacial tension and enhance the colloidal stability of the extremely small monomer droplets. Accordingly, a series of miniemulsions were prepared in order to examine the effects of varying the surfactant concentration. The costabilizer (hexadecane, HD) level was maintained constant at 4 wt % based on monomer while the sodium lauryl sulfate (SLS) concentration was varied (10, 20, 40, 60, and 80 mM based on water).

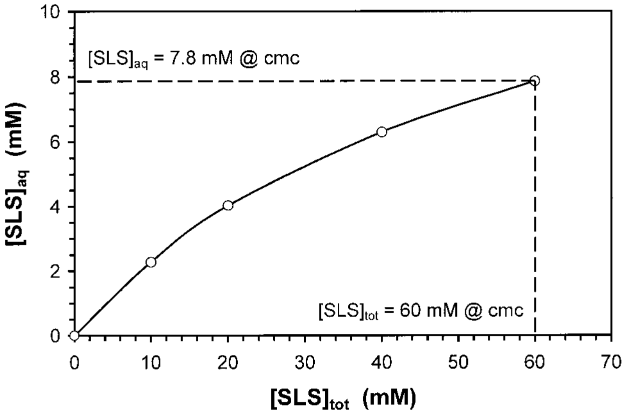

**Figure 1.** Surfactant concentration in the aqueous phase ([SLS]$_{aq}$) as a function of the total surfactant concentration ([SLS]$_{tot}$) for styrene miniemulsions (20 wt % monomer; 4 wt % HD based on monomer; 25 °C).

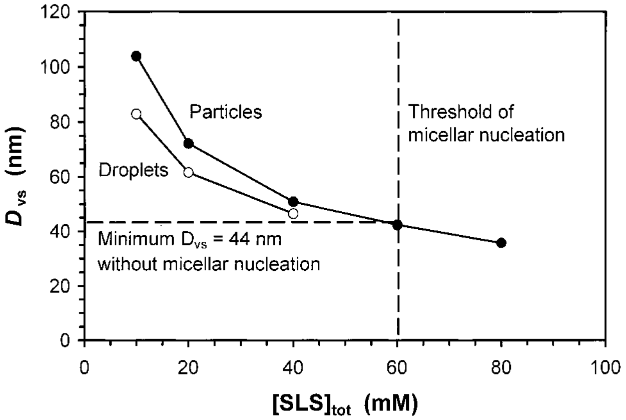

**Figure 2.** Volume-surface average diameter ($D_{vs}$) of styrene miniemulsion droplets and their corresponding particles as a function of the total surfactant concentration ([SLS]$_{tot}$) (20 wt % monomer; 4 wt % HD based on monomer; 25 °C).

The SLS used was from Fisher Scientific, and the HD was from Aldrich. Styrene monomer (Aldrich) was cleaned using an inhibitor removal column (Aldrich). The monomer content was 20 wt % in all miniemulsions. Deionized (DI) water was used as the continuous phase. Miniemulsification was carried out by first making a crude emulsion using sonification (Branson, model 450) for 60 s, at 60% duty cycle, and at a power level of 7. Miniemulsification was completed by 10 passes through a Microfluidizer (Microfluidics Corp., model 110T) at an air inlet pressure of 80 psi.

The time between miniemulsification and initiation was minimized to 5 min to reduce the droplet degradation (Ostwald ripening) period. Rapid nucleation was produced using a redox initiator system consisting of ascorbic acid (0.26 wt % based on monomer) and hydrogen peroxide (0.46 wt % based on monomer). The polymerization temperature was 50 °C.

Surface tensiometry by the maximum bubble pressure method (Sensadyne, model 6000) was used to monitor the aqueous phase surfactant concentration ([SLS]$_{aq}$) via a calibration curve. The volume-surface average droplet and particle

---

* To whom correspondence should be addressed.

10.1021/ma010242z CCC: $22.00

**Table 1. Miniemulsion and Latex Properties; 4 wt % HD Based on Monomer; Redox-Initiated Polymerizations at 50 °C**

| | | | | | |
|---|---|---|---|---|---|
| $[\mathrm{SLS}]_{\mathrm{tot}}$[a] [mM] | 10 | 20 | 40 | 60 | 80 |
| g of SLS/g of styrene | 0.012 | 0.024 | 0.048 | 0.072 | 0.096 |
| miniemulsion $[\mathrm{SLS}]_{\mathrm{aq}}$ [mM] | 2.3 | 4.0 | 6.3 | 7.9 | |
| miniemulsion $D_{\mathrm{vs}}$ [nm] | 83.0 | 61.6 | 46.5 | | |
| latex $D_{\mathrm{vs}}$ [nm] | 103.9 | 72.2 | 50.9 | 42.4 | 35.7 |
| latex $N_{\mathrm{p}}$ (no./dm$^3$ $H_2O$) | $3.83 \times 10^{17}$ | $1.14 \times 10^{18}$ | $3.27 \times 10^{18}$ | $5.64 \times 10^{18}$ | $9.47 \times 10^{18}$ |
| latex $D_{\mathrm{vs}}$ (TEM) [nm] | 92.9 | 76.1 | 54.3 | 46.9 | 35.9 |
| latex PDI (TEM) | 1.03 | 1.06 | 1.08 | 1.34 | 1.38 |

[a] [HD] was constant at 4 wt % based on monomer.

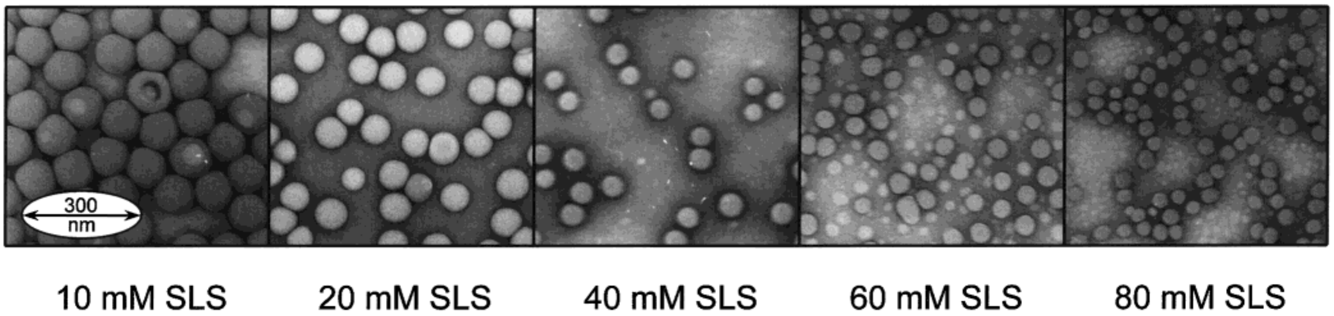

**Figure 3.** TEM micrographs of polystyrene miniemulsion latexes prepared with varying $[\mathrm{SLS}]_{\mathrm{tot}}$ and constant 4 wt % HD based on monomer; polymerization at 50 °C with redox initiator system.

diameters ($D_{\mathrm{vs}}$) were measured by surfactant titration.[5,6] Known surface area coverage per molecule of surfactant values (44.0 Å$^2$/molecule on polystyrene and 71.2 Å$^2$/molecule on styrene/HD) were used in the surfactant titration calculations.[6] Transmission electron microscopy (TEM, Phillips, model 400) was used to confirm the particle diameters and measure the particle size distributions.

## Results and Discussion

Two related but distinct quantities describing the surfactant concentration are used here. The total surfactant concentration ($[\mathrm{SLS}]_{\mathrm{tot}}$) is simply the total moles of surfactant in the miniemulsion (regardless of where it is located) divided by the volume of water. Alternatively, the surfactant concentration in the aqueous phase ($[\mathrm{SLS}]_{\mathrm{aq}}$) is the moles of free surfactant divided by the volume of water. The relationship between these terms (particularly in the case of miniemulsion systems) will be discussed.

$[\mathrm{SLS}]_{\mathrm{aq}}$ was estimated for each of the four miniemulsions prepared with increasing $[\mathrm{SLS}]_{\mathrm{tot}}$. For reasons noted below, the total droplet surface area was not constant in these miniemulsions. $[\mathrm{SLS}]_{\mathrm{aq}}$ increased as $[\mathrm{SLS}]_{\mathrm{tot}}$ increased (Figure 1). Surfactant molecules were partitioned between the aqueous phase and the surface of the miniemulsion droplets according to an adsorption isotherm. As the surface became saturated with surfactant, $[\mathrm{SLS}]_{\mathrm{aq}}$ reached the critical micelle concentration (cmc). $[\mathrm{SLS}]_{\mathrm{tot}}$ at this point was 60 mM. For comparison, Chang et al.[7] reported that $[\mathrm{SLS}]_{\mathrm{tot}}$ was 34 mM at the cmc in styrene miniemulsions. The latter system obviously had a smaller droplet surface area (larger droplets) with a lower capacity to adsorb additional surfactant.

Droplet diameters were estimated by surfactant titration for miniemulsions containing free surfactant concentrations below the cmc (i.e., $[\mathrm{SLS}]_{\mathrm{tot}} < 60$ mM). The droplet diameter decreased as the total SLS concentration was increased (Figure 2). The smallest measurable average droplet diameter was 46.5 nm at $[\mathrm{SLS}]_{\mathrm{tot}} = 40$ mM. The droplet/water interfacial tension may be the limiting factor determining the minimum droplet diameter in miniemulsions. Smaller droplets require lower interfacial tensions (i.e., greater amounts of surfactant in the miniemulsion) to form during emulsification. In any case, the surface charge density must be sufficient to maintain colloidal stability.

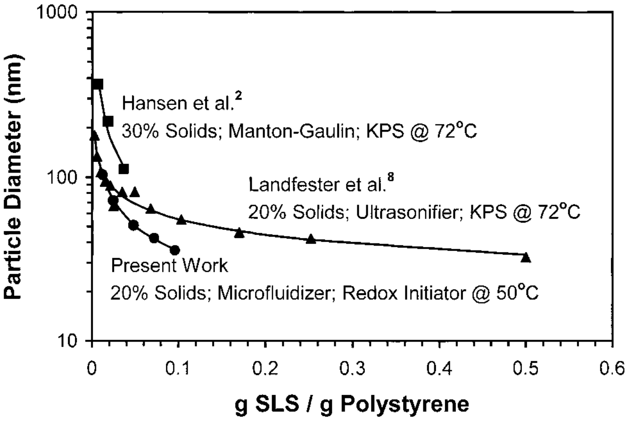

**Figure 4.** Final particle diameter for polystyrene miniemulsion latexes prepared with hexadecane and varying $[\mathrm{SLS}]_{\mathrm{tot}}$ as a function of the ratio of grams SLS to grams polystyrene.

Following polymerization, the corresponding miniemulsion latex particle diameters, as measured by surfactant titration, also decreased as increasing amounts of SLS were used in preparing the miniemulsions (Figure 2). Particle diameters measured by TEM were close to those values obtained by surfactant titration (Table 1).

Approximately 80% of the total surfactant was adsorbed on the surface of the droplets. This value is in agreement with the literature.[7] About 95% was adsorbed on the surface of the corresponding latex particles. The packing density of SLS was higher on the polystyrene latex particles than on the styrene monomer droplets as a result of a higher energy of interaction.

Under the present experimental conditions, the smallest particles that may be produced by miniemulsion polymerization just below the cmc ($[\mathrm{SLS}]_{\mathrm{tot}}$ = about 55 mM) would be 44 nm, as extrapolated from the data in Figure 2. It may be possible to produce even smaller particles at the same total surfactant concentration by providing more energy during emulsification to overcome the high interfacial tension of the droplets. The surface coverage will be reduced as new surface area is created, so it is still necessary to have a sufficient surface coverage to maintain colloidal stability.

Above the cmc, micellar nucleation was a significant nucleation mechanism, in addition to droplet nucleation. The polydispersity indexes (PDI's) of the latex particles were greatly increased in the miniemulsions that were prepared with a free surfactant concentration exceeding the cmc (i.e., $[\text{SLS}]_{\text{tot}} = 60$ and 80 mM SLS) due to secondary (micellar) nucleation. Transmission electron micrographs of all the miniemulsion latexes are shown in Figure 3. The secondary population of particles is evident in the micrographs of the miniemulsions prepared with 60 and 80 mM total surfactant.

Final latex particle diameters are compared with literature values in Figure 4. Particle size data from Landfester et al.[8] are from their Table 3, and the particle size data of Hansen et al.[2] were estimated from their Figure 1 and other data within the article. The latex particles of the present system were smaller than those reported in the literature at the same surfactant concentration. Surfactant was used more efficiently (i.e., the surface coverage of the particles was lower). This is attributed to the enhanced creation, preservation, and/or nucleation of droplets through the combined use of Microfluidization, lower reaction temperature (50 °C), and redox initiator.

The present results narrow the particle size gap between miniemulsion and microemulsion polymerizations while requiring significantly lower amounts of surfactant. Care must be taken to avoid micellar nucleation when reducing droplet diameter by using higher levels of surfactant.

**Acknowledgment.** Financial support from the Emulsion Polymers Liaison Program and TEM microscopy by Olga Shaffer are highly appreciated.

## References and Notes

(1) Ugelstad, J.; El-Aasser, M. S.; Vanderhoff, J. W. *J. Polym. Sci., Polym. Lett. Ed.* **1973**, *11*, 503.
(2) Hansen, F. K.; Ugelstad, J. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 3069.
(3) Chamberlain, B. J.; Napper, D. H.; Gilbert, R. G. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 591.
(4) Xu, X. J.; Chew, C. H.; Siow, K. S.; Wong, M. K.; Gan, L. M. *Langmuir* **1999**, *15*, 8067.
(5) Maron, S. H.; Elder, M. E.; Moore, C. *J. Colloid Sci.* **1954**, *9*, 104.
(6) Erdem, B.; Sully, Y.; Sudol, E. D.; Dimonie, V. L.; El-Aasser, M. S. *Langmuir* **2000**, *16*, 4890.
(7) Chang, H. C.; Lin, Y. Y.; Chern, C. S.; Lin, S. Y. *Langmuir* **1998**, *14*, 6632.
(8) Landfester, K.; Bechthold, N.; Tiarks, F.; Antonietti, M. *Macromolecules* **1999**, *32*, 5222.

MA010242Z