Supporting Information

Anionic/Nonionic Surfactants for Controlled Synthesis of Highly Concentrated Sub-50 nm Polystyrene Spheres

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Figure S1: A histogram for randomly selected 40 particles (M9 recipe, Figure 4d) whose diameter was measured manually using ImageJ software. According to the histogram, the particle size is 50.2 ± 1.7 nm which is very similar to the DLS results.



Figure S2: Bar graph illustrating the standard errors of the size means calculated for three experiments for each recipe.

Tables:

Method	Description	Advantages	Disadvantages
Emulsion polymerization	 Radical polymerization Poorly water-soluble monomer Water-soluble initiator Final polymer is poorly soluble in the reaction medium PS size between 40 nm to 5 μm 	 Uniform heat transfer and easily controlled reaction temperature Low viscosity (almost like water), polymer molecules are inside the particles, and viscosity is not dependent on molecular weight. The resulting polymer may be used directly if wanted. It produces high molecular weight colloidal polymers at short times. Water is the medium. 	 A Surfactant is needed Need extra process to remove the surfactant and other contaminates and in drying. Works only for addition polymerization using a hydrophilic initiator. Water removal consumes a lot of energy. Cannot be used for condensation, ionic, or Ziegler-Natta polymerization
Surfactant free emulsion polymerization	 Radical polymerization Poorly water-soluble monomer Water-soluble initiator Initiator work as a stabilizing agent. Final polymer is poorly soluble in the reaction medium. PS size down to 100 nm 	 Almost the same as emulsion polymerization No surfactant molecules adsorbed on the surface of the particles meaning less proceing time to remove them. Environmentally friendly. 	 Almost the same as emulsion polymerization Usually results in wide size distribution. Particle size smaller than 100 are hard to obtain.
Dispersion polymerization	 Radical polymerization Monomer and Initiator dissolve in the reaction medium Final polymer is poorly soluble in the reaction medium PS size between 200 nm to 15 μm 	 Can produce micron size monodisperse polymer Particles in a single batch process polymer is easily separated Obtain polymer in a directly useful form. 	 Stabilizers or surfactants needs to be used. Organic solvent must be used.

Table S1: Common methods for the preparation of polystyrene