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:

**Table S1:** Common methods for the preparation of polystyrene

| Method                        | Description                                                                 | Advantages                                                                                                      | Disadvantages                                                                                     |
|-------------------------------|----------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|
| Emulsion polymerization       | - Radical polymerization                                                   | - Uniform heat transfer and easily controlled reaction temperature  
- Poorly water-soluble monomer  
- Water-soluble initiator  
- Final polymer is poorly soluble in the reaction medium  
PS size between 40 nm to 5 μm | - 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      | - Radical polymerization                                                   | - Almost the same as emulsion 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 | - No surfactant molecules adsorbed on the surface of the particles meaning less processing 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                                                   | - Can produce micron size monodisperse polymer  
- 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 | - 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. |
