

Preparation of Monodisperse Polystyrene Particles from Emulsifier-free Miniemulsion Polymerization

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This work reports a new way to prepare monodisperse polystyrene (PS) particles by emulsifier-free miniemulsion polymerization. Only a small concentration (1.9×10^{-3} g/mL) of potassium persulfate (KPS) is needed to initiate the polymerization of styrene (St) to produce a certain amount of PS oligomer, which can be utilized to form a stable miniemulsion. Subsequently, the St monomers polymerize by a droplet nucleation mechanism. The particle number keeps constant before and after polymerization.

In recent years, emulsifier-free emulsion polymerization has received considerable attention as a method for producing monodisperse and “clean” latexes.¹ This technique has been extraordinarily useful for the preparation of model polymers with well-characterized surface properties, such as adhesion and water resistance.² One of the most popular nucleation mechanisms on emulsifier-free emulsion polymerization is the micellar nucleation model.³ The water-soluble initiator first reacts with monomer to form surface active oligomer, which subsequently aggregates to form micelles where the emulsion polymerization proceeds. The diameter of polymer particles prepared in emulsifier-free emulsions usually have the same order as that prepared by emulsion polymerizations with emulsifier, generally bigger than 300 nm.⁴ Much smaller polymer particles could be prepared from miniemulsion polymerization.⁵ Miniemulsions are aqueous dispersions of oil droplets stabilized by surfactants and hydrophobic costabilizers, such as hexadecane (HD).⁶ In miniemulsions, the diffusion of monomer (Ostwald ripening) is suppressed and the polymerization takes place in each individual monomer droplet.⁷ The one-to-one correlation of monomer droplets versus latex particles in miniemulsion polymerization can be utilized for particle size control.⁸ Although extensive work has been reported for the emulsifier-free emulsion polymerization, there is little information about emulsifier-free miniemulsion polymerization to the best of our knowledge. Compared with emulsion polymerization in which a relatively higher amount of emulsifier is needed, stable miniemulsions can be prepared at a lower concentration of surfactant even below its critical micelle concentration (CMC).⁹ This means that less initiator which acts as emulsifier may be needed for an emulsifier-free miniemulsion system. Moreover, whether the advantages of miniemulsion polymerization can be transferred to the emulsifier-free system and be applied to fabricate monodisperse small particles is obviously an interesting subject.

In this work, PS particles were synthesized via emulsifier-free miniemulsion polymerization. The procedure was carried out in a two-stage procedure: (1) preparation of miniemulsion: in a typical recipe, the solution containing 8 g of St and 0.32 g

of HD was added to 72 g of distilled water, followed by agitating for 20 min. Then, the reaction flask was moved to a 70 °C water bath. After bubbling nitrogen gas into the reaction mixture to remove oxygen, 0.32 g of KPS (4×10^{-3} g/mL) was added to initiate the polymerization of St. One and a half hours later, the reaction flask was moved to 0 °C ice water bath and ultrasonicated for 5 min to achieve a stable miniemulsion. (2) Miniemulsion polymerization: the miniemulsion was put back to the 70 °C water bath and the polymerization continued for another 4 h, white milky latex was obtained. The whole experiment was conducted under nitrogen atmosphere.

The mechanism of emulsifier-free miniemulsion polymerization is schemed in Figure 1. First, KPS decomposes to produce free radicals and then a certain amount of PS oligomer is generated. The decomposed KPS fragments contribute to particle stabilization through the incorporation of charged groups ($\text{SO}_4^{\cdot-}$) to the PS oligomer chain ends. The hydrophilic $\text{SO}_4^{\cdot-}$ portions stay at the monomer droplet surfaces also provide steric interactions to prevent the coalescence of St droplets. The conversion of St to PS oligomer is controlled to 15%, which can be determined by gravimetric analysis. Subsequently, the above system is ultrasonically homogenized and becomes a stable miniemulsion with the help of PS oligomer capped with $\text{SO}_4^{\cdot-}$. In addition, PS oligomer inside St droplets can also help HD to suppress the Ostwald ripening effect, as pointed out by Miller and Sudol.¹⁰ Clearly seen from Figure 2, the hydrodynamic radius of St droplets ($R_{h,St}$) is 101 nm (PDI = 0.14), measured by dynamic light scattering (DLS). The miniemulsion polymerization continues by the initiation of KPS and monodisperse PS particles with a diameter of about 200 nm have been prepared finally as shown in Figure 3.

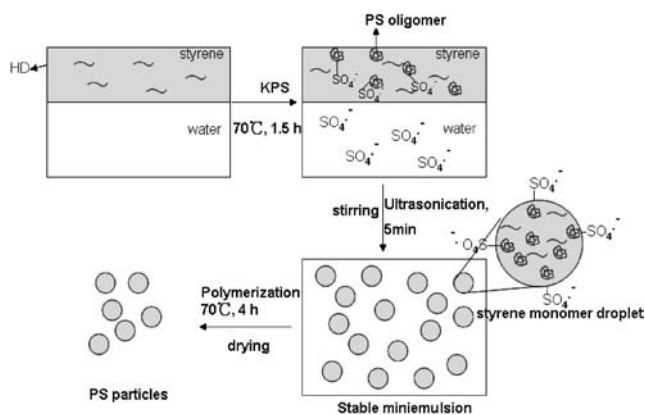


Figure 1. Schematic representation of the formation of monodisperse PS particles by emulsifier-free miniemulsion polymerization.

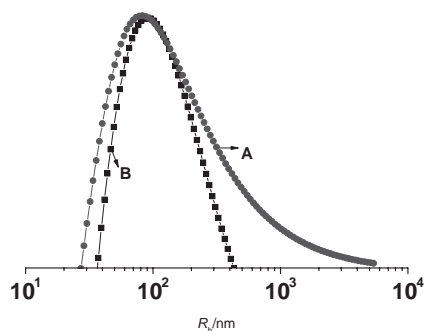


Figure 2. DLS measurements of St miniemulsion before (A) and after (B) polymerization.

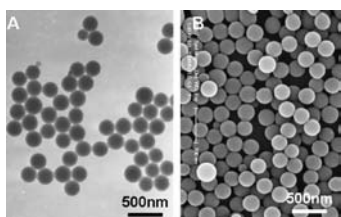


Figure 3. TEM (A) and SEM (B) images of the PS particles synthesized.

In order to check the nucleation mechanism of the emulsifier-free miniemulsion polymerization process, the hydrodynamic radius of the final PS latex particles ($R_{h,PS}$) was also detected, as seen from Figure 2. $R_{h,PS}$ is 106 nm (PDI = 0.04), which is very close to that of St droplets mentioned before. Moreover, the initial number of St droplets ($N_{St} = 2.23 \times 10^{16}/g$) calculated is almost equivalent to the final number of PS particles ($N_{PS} = 2.21 \times 10^{16}/g$). The nucleation efficiency (N_{PS}/N_{St}) reaches 99%, which shows the typical characteristic of miniemulsion polymerization that the particle number remains constant before and after polymerization. These results demonstrate that the monomer droplet nucleation mechanism also predominates in the emulsifier-free miniemulsion polymerization.¹²

Figure 4 shows the change of particle radius R_{PS} with an increasing [KPS] in the range of $1.9\text{--}4.0 \times 10^{-3}$ g/mL when other conditions remain unchanged. Apparently, for a fixed monomer concentration, more KPS molecules can generate more ionic groups and stabilize a larger total surface area, which results in the decrease of R_{PS} . This agrees well with the stabilization mechanism of Hearn et al.³ that the decomposed KPS fragments

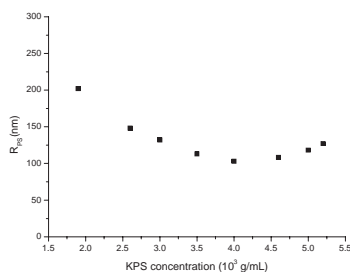


Figure 4. Influence of [KPS] on R_{PS} , measure by TEM.

act as emulsifier. However, a further increase of [KPS] beyond 4.0×10^{-3} g/mL results in an increase of R_{PS} . Since the decomposition of more KPS also increases the ionic strength of the dispersion, it will lead to a compression of the electrostatic double layer on the particle surface and a decrease of the particle stability. As a result, the PS particles tend to coagulate so that the particle size increases, which coincides with the studies of Ngai and Wu¹¹ on the emulsifier-free emulsion polymerization.

As a comparison, a common emulsifier-free emulsion polymerization process was also studied. The procedure is the same as the typical sample listed above except that it has no costabilizer HD. And ultrasonication is unnecessary. The as-prepared PS latex have a bigger particle size and broader particle size distribution ($R_{PS} = 167$ nm, PDI = 0.19). When [KPS] is reduced to 3.6×10^{-3} g/mL, a translucent mixture instead of white milky latex as the case of the miniemulsion counterpart has been prepared. While observed under SEM microscope, almost no regular spherical PS particles can be found, which suggests that the emulsion is unstable at this lower initiator concentration. It means that the emulsifier-free miniemulsion system could be stabilized by lower [KPS] in comparison with the emulsifier-free emulsion system.

In conclusion, miniemulsion polymerization can also be successfully carried out without emulsifier. Compared with emulsifier-free emulsion polymerization, emulsifier-free miniemulsion polymerization proves to be a more efficient and economical route to the fabrication of monodisperse nanosized polymer latex.

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- 12 Supporting Information is also available electronically on the CSJ-Journal web site, <http://www.csj.jp/journals/chemlett/index.html>.