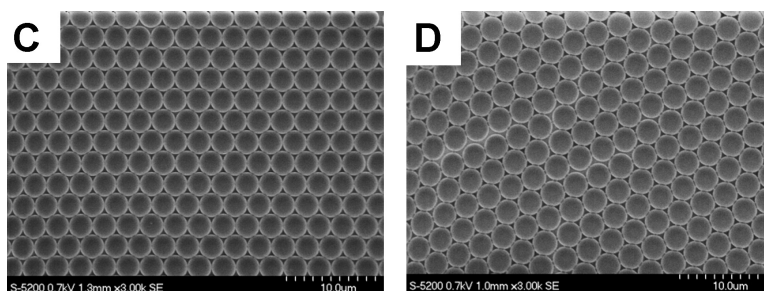


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## Two-Stage Dispersion Polymerization toward Monodisperse, Controlled Micrometer-Sized Copolymer Particles

Jing-She Song, Frédéric Tronc, and Mitchell A. Winnik\*

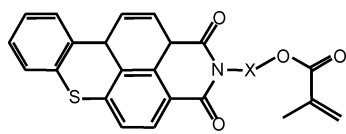
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In this communication we describe a modification of the dispersion polymerization protocol that allows us to overcome three serious limitations of this otherwise impressive polymer particle synthesis strategy.<sup>1</sup> By delaying the addition of functional monomers until after the end of the nucleation stage, we are able to (1) introduce polar and dye-containing comonomers, (2) achieve unprecedented control of the particle diameter ( $D$ ), and (3) synthesize cross-linked particles, all while maintaining a narrow particle size distribution.

Monodisperse polymeric beads of micrometer-sized diameters have many important applications as separation media, ion-exchange beads, toners, coatings, calibration standards, and in medical diagnostics.<sup>2</sup> For most of these applications, size control and narrow size distribution are of key importance. At present, most particles of this type are prepared by the successive seeded emulsion polymerization method developed by Vanderhoff<sup>3</sup> or by the Ugelstad<sup>4</sup> activated-swelling suspension polymerization method, although other approaches are also available.<sup>5,6</sup> These processes for making polymer particles have limitations. They are complex and also difficult to implement on a large scale.

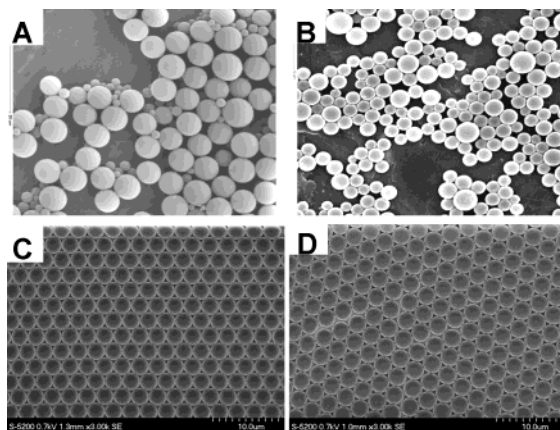
Dispersion polymerization was invented in the 1960s,<sup>7,8</sup> but it was the contributions of Lok and Ober<sup>9</sup> on dispersion polymerization of styrene in alcohol, using water-soluble polymers such as poly(vinylpyrrolidone) (PVP) as the stabilizer, that stimulated the current widespread interest in this methodology. The reaction is easy to carry out, lends itself to scale-up, and yields particles with a very narrow size distribution. It is most suited to the preparation of beads in the diameter range of 1–15  $\mu\text{m}$ .<sup>10–12</sup>



**1a** X =  $-(\text{CH}_2)_6-$

**1b** X =  $-(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_2\text{CH}_2-$

Despite the many attractive features of this reaction, problems remain that limit its applications. One problem is that particle size control is very difficult. Two reactions that are run under seemingly identical conditions both give monodisperse particles but with somewhat different diameters. Various research groups have found that when they added cross-linking agents, or even hydrophilic monomers to a dispersion polymerization recipe in which all the ingredients were added at the beginning, they obtained poor results.<sup>9–16</sup> The final particle size was affected significantly. The size distribution became much broader, and sometimes coalescence occurred. We obtained similar results when we added a small amount of a dye-comonomer to the reaction. For example, addition of less than 0.5 wt % **1b** to a traditional one-step dispersion polymerization of styrene in ethanol led to polystyrene (PS) particles

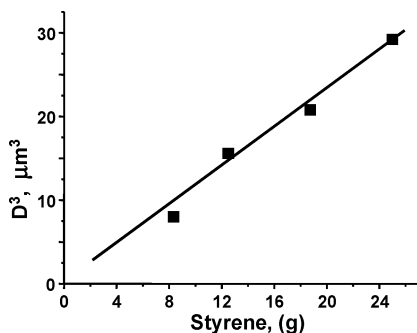


**Figure 1.** SEM images of copolymer particles prepared by the one-stage method (A and B) and the two-stage method (C, D). (A) 1 wt % dye-comonomer **1b**; (B) 0.35 mol % DVB; (C) 1 wt % **1a**; (D) 1 mol % EGDMA.

that were spherical and uniform in size, but addition of larger amounts of dye-comonomer ( $\geq 1$  wt %) led to polydisperse particles (Figure 1A).

Our hypothesis was that most of these problems were due to the high sensitivity of the nucleation stage. From a mechanistic perspective, the dispersion polymerization process can be separated into two stages, a “nucleation stage” (first stage) and a “particle growing stage” (second stage). The nucleation stage is short but very complex and sensitive, whereas the particle growth stage is relatively long, simple, and robust. To avoid the difficulties described above, we designed syntheses in which the problematic reagents were added to the reaction after the nucleation stage was complete. We were guided by recent results from two Asian laboratories that suggested that the nucleation stage was complete at less than 1% monomer conversion.<sup>13,14</sup> We found that comonomers added after this point became incorporated into the particles without disturbing the final particle size and size distribution.<sup>17</sup> In this way we prepared dye-labeled or functional group-containing micrometer-sized particles with a very narrow size distribution. By varying the amount of monomer added in the second stage, we could control the final particle diameter precisely without changing the narrow size distribution. Most important of all, we found that this synthetic strategy allowed us to prepare cross-linked particles containing up to 3 mol % cross-linking agent.

The two-stage dispersion polymerization was carried out as follows. All of the stabilizer (PVP), the co-stabilizer (Triton X-305), and initiator [2,2'-azobis(2-methylbutyronitrile), AMBN], and half of the monomer and ethanol were added to a 250-mL three-neck reaction flask equipped with a condenser and a gas inlet. Once the solution became homogeneous, it was deoxygenated by bubbling nitrogen gas at room temperature for ca. 30 min. Then the flask was placed in a 70 °C oil bath and stirred mechanically at 100



**Figure 2.** Effect of the amount of styrene added in successive stages on the final particle volume.

rpm. The solution turned cloudy and became milky over 10 min. The dye–comonomer or other comonomers were dissolved in the remaining styrene plus ethanol at 70 °C under nitrogen. After the polymerization reaction had run for 1 h, the hot dye solution was added to the reaction flask. The reaction was continued until the styrene conversion reached 90–95%. When 1 wt % of **1a**, based on total monomer, was added to the reaction in the second stage, the particles retained their narrow size distribution (Figure 1C) and had the same diameter as those obtained in the absence of dye–comonomer. Similar results were obtained for 3 wt % dye.

We next turned our attention to particle size control. We carried out experiments in which additional aliquots of styrene plus ethanol were added to the reaction at times corresponding to 20–50% conversion of the monomer already added. The final particle size increased, and without any additional initiator or PVP, the beads remained colloidally stable. In one experiment, we added a total of five aliquots of the same amount of styrene and ethanol. If no new particles were formed (no secondary nucleation), the particle volume (proportional to  $D^3$ ) should increase linearly with the amount of styrene added. We found that our reaction followed this prediction (Figure 2). In addition, we found that the particle size distribution remained very narrow. Thus, we could control the particle size precisely by adding different amounts of monomer in the second stage.

The most important application of the two-stage method is to prepare cross-linked particles. Many research groups have tried to prepare monodisperse cross-linked PS particles by dispersion polymerization. All of these groups encountered problems. The first experiments to prepare cross-linked micrometer-sized polymer particles by dispersion polymerization were reported by Tseng et al.<sup>15</sup> In their work, when 0.3 mol % divinylbenzene (DVB) or ethylene glycol dimethacrylate (EGDMA), was added to the reaction mixture, the particle size changed, and the size distribution broadened significantly. Further increase in DVB (or EGDMA) concentration resulted in coagulation of the dispersion. Figure 1B shows a SEM image of PS particles prepared in our group by the one-stage method with only 0.35 mol % DVB, similar to the results of Tseng et al. These particles had a very broad size distribution. With a higher DVB content (e.g., 1 mol %), flocculation occurred after only 5 min of polymerization, and the amount of aggregates increased during the polymerization. Rudin et al.<sup>16</sup> carried out the most extensive studies of the effects of DVB on dispersion polymerization. They found that they could obtain a narrow size

distribution with tiny amounts of DVB (up to 0.2 mol %). They were able to incorporate up to 1 mol % DVB by linear addition over the major particle growth period, but the resulting particles were heavily dented with a small fraction of coagulum.

We can avoid these problems if we add a cross-linker such as EGDMA after the end of the nucleation stage. Monodisperse particles were obtained (Figure 1D). Similar monodisperse particles were also obtained for DVB-cross-linked PS particles when DVB (1–3 mol %) was added after the end of the nucleation stage, but slowly over 12 h. This approach takes into account the different reaction rates for the two vinyl groups of DVB and avoids early consumption of the cross-linker.

For some applications, one needs cross-linked dye-labeled particles to increase the stability of the particles to heat or solvent treatment. We were able to prepare these particles by adding both the dye comonomer **1a** and EGDMA in the second stage of the two-stage method. These particles are monodisperse (for one reaction,  $D = 2.5 \mu\text{m}$ , coefficient of variation <1%).

In summary, we described a new synthesis strategy to allow unprecedented flexibility and control in dispersion polymerization. With this methodology, one can synthesize  $\mu\text{m}$  diameter polymer beads with an exceptionally narrow size distribution and with control over bead diameter. Dye-labeled beads, cross-linked beads, and functionalized beads were synthesized in this way. In future experiments, we plan to explore the scope of this reaction, including extension to other monomers and control of functional groups at the particle surface.

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