Advantages of Supercritical Carbon Dioxide for Composite Particle Synthesis Using Water-Soluble or Water-Reactive Monomers

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Experimental

Materials

Styrene (STY, Aldrich) and vinyl pyrrolidone (VP, Aldrich) were deinhibited by passage through an alumina column (Aldrich). Azobis(isobutyronitrile (AIBN, Aldrich) was recrystallized from methanol. Glycidyl methacrylate (GMA, Aldrich), isocyanatoethyl methacrylate (IEM, Aldrich), tetrahydrofuran (THF, Mallinckrodt), HPLC grade THF (Allied Signal), cyclohexane (Aldrich), deuterated methylene chloride (Cambridge), perfluorosolv (Fomblin® PFS-1, Ausimont), and 0.5 % RuO₄ aqueous solution (Polysciences, Inc) were used as received. Carbon dioxide (SFC/SFE grade) was kindly provided by Air Products and was used as received. PS-b-PFOA [MₚPS = 6.6 kg/mol, MₚPFOA = 53 kg/mol (6.6 K/53 K)] was synthesized by Betts. PS-b-PFOA (4.2 K/19.7 K) and PS-b-PFOA (4.2 K/37.5 K) were prepared by Shiho. Poly(hydroxyethyl methacrylate) (PHEMA) (with an average particle diameter, dₚ, of 0.26 μm and particle size distribution of 1.02 ) was syntheiszed by dispersion polymerization in supercritical CO₂ using PS-b-PFOA (4.2 K/ 37.5 K) stabilizer by Shiho.

Synthetic Procedure

The reactor, with a maximum volume of 39 mL, is a HiP pressure generator (High Pressure Equipment, Inc) modified with three ports and a sapphire window on the end for visual observations. Following the addition of PS-b-PFOA and AIBN to the variable volume reactor through the sapphire window opening, the reactor was sealed and purged with Ar. The degassed first-stage monomer was injected into the reactor with a syringe through one of the reactor ports. The reactor was pressurized with CO₂ to approximately 70 bar using an ISCO model 260D automatic syringe pump. The reaction mixture was stirred with a magnetic stir bar and heated to 65 °C with electric heating rope. Once the temperature reached 63 °C, the reactor was pressurized with CO₂ to the final reaction pressure. Initially the reaction mixture appeared clear and colorless upon reaching the reaction temperature and pressure then progressed from cloudy white to milky white.

Near the end of the reaction time, CO₂ was added to maintain the reaction pressure while the reactor volume was increased to the desired volume. The HPLC pump (Acuflow Series III pump, SSI) was primed then pressurized to the reactor pressure with second-stage monomer/AIBN solution and run at 1 mL/min until the desired amount was injected. During the addition, the reactor pressure was maintained by manually increasing the reactor volume. The dispersion remained stable and milky white in appearance during the entire reaction period, with no polymer precipitation or settling even when the stirring was momentarily stopped. After the second-stage reaction time of 24 h, the reactor was rapidly cooled to 25
°C in an ice bath then the \( \text{CO}_2 \) was slowly vented into hexane. Dry polymer powder was recovered from the reactor and the remaining polymer was recovered with THF. Polymer was dried under vacuum overnight and yield was determined gravimetrically.

**PVP/PS Composite Particles**

For the synthesis of PVP/PS composite particles, the amounts of VP, PS-\( b \)-PFOA, reactor volumes, and styrene/AIBN solution are listed in Table 1. The reactant concentrations for the dispersion polymerization of VP were optimized by Carson.\(^{5,6} \) The AIBN concentration was 0.06 M AIBN in VP and 0.11 M AIBN in styrene. The reaction pressure typically increased during the reaction from an initial pressure of 350 bar to a final pressure of 365 – 385 bar during the first-stage polymerization and remained relatively constant at about 350 bar during the second-stage polymerization. The typical pressure increase during the PVP polymerization stage was comparable to pressure increases observed by Carson for polymerizations conducted at lower initial pressures.\(^{5,6} \) The first-stage reaction was allowed to proceed for at least 4 h.

**Table 1.** Reaction conditions for PVP/PS composite particle synthesis.

<table>
<thead>
<tr>
<th>target PVP/PS ratio (mol %)</th>
<th>VP (mL)</th>
<th>PS-( b )-PFOA (6.6 K/53 K) (g)</th>
<th>initial volume (mL)</th>
<th>volume during addition (mL)</th>
<th>STY/AIBN (g)</th>
<th>final volume (mL)</th>
</tr>
</thead>
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<tr>
<td>90/10</td>
<td>2</td>
<td>0.2</td>
<td>17</td>
<td>17</td>
<td>0.26</td>
<td>17</td>
</tr>
<tr>
<td>50/50</td>
<td>1</td>
<td>0.2</td>
<td>17</td>
<td>17</td>
<td>0.82</td>
<td>18</td>
</tr>
<tr>
<td>20/80</td>
<td>0.55</td>
<td>0.11</td>
<td>9</td>
<td>14.5</td>
<td>1.6</td>
<td>19</td>
</tr>
</tbody>
</table>

**PGMA/PS and P(GMA-co-MMA)/PS Composite Particles**

The reaction conditions for PGMA/PS and P(GMA-co-MMA)/PS composite particle synthesis are included in Table 2. The PS-\( b \)-PFOA (4.2 K/19.7 K) concentrations for the first-stage polymerizations were based on similar conditions used by Shiho producing particles less than 300 nm in diameter with the same surfactant.\(^3 \) The reaction pressure was 390 bar during the first-stage reaction and 370 bar during the second stage. For the synthesis of P(GMA-co-MMA) in the first stage, the GMA/MMA ratio was 20/80 mol\%. The AIBN concentration was 0.06 M AIBN in GMA, 0.03 M in GMA/MMA, and 0.11 M in styrene. In all experiments, the GMA-containing polymerization was allowed to proceed for at least 20 h.
Table 2. Reaction conditions for PGMA/PS and P(GMA-co-MMA) composite particle synthesis.

<table>
<thead>
<tr>
<th>Target Ratio</th>
<th>First Stage (mL)</th>
<th>PS-b-PFOA (4.2 K/19.7 K) (g)</th>
<th>Initial Volume (mL)</th>
<th>Volume During Addition (mL)</th>
<th>STY/AIBN (g)</th>
<th>Final Volume (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20/80 PGMA/PS</td>
<td>0.7</td>
<td>0.22</td>
<td>12</td>
<td>17</td>
<td>1.6</td>
<td>19</td>
</tr>
<tr>
<td>4/16/80 PGMA/PMMA/PS</td>
<td>0.58</td>
<td>0.12</td>
<td>11</td>
<td>17</td>
<td>1.6</td>
<td>19</td>
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</table>

PIEM/PS and P(IEM-co-MMA)/P(HEMA-co-STY) Composite Particles

Table 3 details the reaction conditions for particles containing PIEM. In polymerizations involving IEM, extra care was taken to prevent the exposure of IEM to ambient moisture due to the reactivity of isocyanates with water. The reactor was purged constantly with Ar while heated to 100 °C for an hour then cooled prior to the addition of reactants in order to dry the reactor. The AIBN concentration was 0.07 M in IEM, 0.11 M in styrene, 0.03 M in IEM/MMA, and 0.11 M in HEMA/STY, and the comonomer ratios were 20/80 mol% for IEM/MMA and 5/95 mol% HEMA/STY. The reaction pressure was 365 bar during first stage and 360 bar during the second stage. The IEM-containing polymerization was allowed to proceed for at least 20 h. The isocyanate-functionalized polymers were stored with desiccant and exposure to air was minimized.

Table 3. Reaction conditions for PIEM/PS and P(IEM-co-MMA)/P(HEMA-co-STY) composite particle synthesis.

<table>
<thead>
<tr>
<th>Target Ratio</th>
<th>First Stage (mL)</th>
<th>PS-b-PFOA (4.2 K/37.5 K) (g)</th>
<th>Initial Volume (mL)</th>
<th>Volume During Addition (mL)</th>
<th>Second Stage (g)</th>
<th>Final Volume (mL)</th>
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<tr>
<td>20/80 PIEM/PS</td>
<td>0.73</td>
<td>0.1</td>
<td>11</td>
<td>17</td>
<td>1.6</td>
<td>19</td>
</tr>
<tr>
<td>4/16/4/76 PIEM/PMMA/ PHEMA/PS</td>
<td>0.6</td>
<td>0.1</td>
<td>9</td>
<td>17</td>
<td>2</td>
<td>19</td>
</tr>
</tbody>
</table>
Characterization

Polymerization yields were determined gravimetrically. The polymer composition was determined in deuterated methylene chloride by \(^1H\) NMR obtained from a Varian 300 MHz NMR spectrometer. Thermal analysis was conducted on a Seiko-Haake DSC 220C calibrated with indium and tin.

The scanning and transmission electron microscopy (SEM and TEM, respectively) characterization of composite particle morphology was conducted on the composite particles. SEM analysis was conducted on the gold-coated polymer powders, before and after PS was extracted from the composite particles, using a JOEL 6400 FE SEM. The particle size and size distribution was determined by measuring the diameters of at least 100 particles. For the PS extraction, polymer was stirred in cyclohexane at 40-43 °C for 4-7 h. The remaining polymer that did not dissolve was collected in a Buchner funnel, rinsed with warm cyclohexane, dried, and examined by SEM (see Figure 1).

For TEM analysis, the polymer was dropped onto the grid from a dispersion in perfluorosolv. The whole particles were examined using a Philips CM12 TEM before and after exposure to RuO\(_4\) vapors. The TEM images were taken at dilute conditions to prevent overlap of particles. Therefore, a representative image of a single particle is shown.

Characterization of PVP/PS particle morphologies

Comparison of the TEM images in the paper and the SEM images of PS-extracted particles shown below in Figure 1 support the conclusions that the PVP/PS 89/11 mol% and 58/42 mol% formed microdomains of PS within PVP, and the PVP/PS 26/74 mol% formed a PVP shell around a PS core. The light-shell/dark-core appearance in the TEM images of PVP/PS 26/74 mol% particles are not due to the differences in particle density that is seen in un-stained particles, such as PS particles in Figure 2a below, because the presence of PS in the particle will be dramatically changed in appearance due to the staining by RuO\(_4\), as shown in Figure 2b.
Figure 1. SEM images of composite particles after PS extraction with cyclohexane of PVP/PS (mol%) (a) 58/42; (b) 26/74.

Figure 2. TEM images of (a) PS homopolymer particles without stain; (b) PS homopolymer particles with RuO₄ stain.

Characterization of PGMA/PS, P(GMA-co-MMA)/PS, PIEM/PS, and P(IEM-co-MMA)/P(HEMA-co-STY) by SEM

A comparison of the SEM images of particles before and after extraction of PS, in Figures 3-5 below, leads to the conclusion that the first-stage polymers are predominantly in the shell regions rather than in the core regions of the composite particles. These morphology assignments; however, are not definitive and some other analytical method will be required for absolute morphology determination.
Figure 3. SEM images of PGMA/PS (29/71 mol%) (a) before extraction; (b) after extraction with cyclohexane, with illustration.

Figure 4. SEM images of P(GMA-co-MMA)/PS (7/18/75 mol%) (a) before extraction; (b) after extraction with cyclohexane; and illustrations of 2 possible morphologies after PS extraction (c) half-moon B morphology; (d) inverted core-shell morphology.
Figure 5. SEM images of (a) PIEM/PS (14/86 mol%); (b) PIEM/PS after PS-extraction by cyclohexane; (c) illustration of PIEM/PS after extraction; (d) P(IEM-co-MMA)/P(HEMA-co-STY) (4/16/4/76 mol% targeted); (e) P(IEM-co-MMA)/P(HEMA-co-STY) after PS-extraction by cyclohexane; (f) illustration of P(IEM-co-MMA)/P(HEMA-co-STY) after extraction.

Reaction of PIEM with PHEMA Studied by FTIR Spectroscopy

The reaction of the isocyanate functionality in PIEM was studied by FTIR. A concentrated dispersion of either 1) equal weights of PIEM/PS and PHEMA [PHEMA $d_n = 260$ nm, PSD = 1.02 that were also synthesized by dispersion polymerization in supercritical CO$_2$ using PS-$b$-PFOA (4.2 K/ 37.5 K) stabilizer,$^4$] or 2) P(IEM-co-MMA)/P(HEMA-co-STY) was made in perfluorosolv and sonicated for one minute. The dispersion was placed dropwise on a CaF$_2$ window. The dropwise application was continued until the concentration of powder coating on the window gave a strong isocyanate IR absorbance at 2273 cm$^{-1}$. Once the SpectraTech variable-temperature IR cell reached 225 $^\circ$C, scans were collected with the Bio-rad FTS-7 FT IR spectrometer. The reaction temperature of 225 $^\circ$C was chosen as above above the glass transition temperatures for both polymers to enable polymer mobility but below the degradation temperature. Thermal analysis data for PIEM, PIEM/PS, and PHEMA, in Table 4, includes measured $T_g$s and temperatures for 5% weight loss. The temperatures measured for 5% weight loss are higher than 225 $^\circ$C.

Table 4. Thermal analysis data for PIEM, PIEM/PS, and PHEMA.
<table>
<thead>
<tr>
<th>polymer</th>
<th>$T_g$ (°C)</th>
<th>$T$ (°C) for 5% weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIEM</td>
<td>74.4</td>
<td>288</td>
</tr>
<tr>
<td>PIEM/PS (14/86 mol%)</td>
<td>93.7</td>
<td>250</td>
</tr>
<tr>
<td>PHEMA</td>
<td>108.7</td>
<td>287</td>
</tr>
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</table>

The reaction between the isocyanate and alcohol functionalities was monitored by the decay of the isocyanate absorbance at 2273 cm$^{-1}$ by IR spectroscopy. A typical IR spectrum of PIEM/PS and PHEMA powder mixture is shown in Figure 6. Similar IR spectra of PIEM and a PIEM-PHEMA copolymer have previously been reported. After 8 h at 225 °C, a significant portion of the isocyanate has reacted (Figure 7). The isocyanate and alcohol groups compartmentalized within the same composite particles in P(IEM-co-MMA)/P(HEMA-co-STY) reacted faster, shown in Figure 8.

![Figure 6. IR spectrum of PIEM/PS with PHEMA before heating.](image)
Figure 7. Reaction of PIEM/PS with PHEMA monitored by decay of isocyanate IR absorbance at 2273 cm$^{-1}$ with time at 225 °C.

Figure 8. Reaction between isocyanate and alcohol groups of P(IEM-co-MMA)/P(HEMA-co-STY) monitored by decay of isocyanate IR absorbance at 2273 cm$^{-1}$ with time at 225 °C.

References