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

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Polymer composite particles, or spherical, micron- or submicron-sized polymer particles containing two or more distinctly separate polymer phases in the same particle, offer unique combinations of physical properties from their component polymers, as described in several reviews.[1−4] The applications for composite particles vary widely depending on the properties of the particle polymer phases and the morphology or distribution of polymer phases within the particle.

Composite particles are typically formed through sequential particle-forming heterogeneous polymerizations, usually free-radically initiated, emulsion or dispersion polymerizations, in which the resulting polymers are insoluble in the polymerization medium but are stabilized by a polymeric dispersant or surfactant. Some possible morphologies include core−shell, inverted core−shell, half-moon, microdomains, raspberry, and sandwich, illustrated in Figure 1.[5−7] For a given set of reaction conditions, only one of the morphologies (either core−shell, inverted core−shell, or half-moon) is the most thermodynamically stable, as determined by the polymer/medium and polymer/polymer interfacial tensions. Other conditions, such as polymer viscosity, glass transition temperature (T_g), molecular weight, and rate of second monomer addition, can prevent polymer migration to the most thermodynamically stable morphology and cause a kinetically trapped morphology to result. Thus, the accepted notation for naming composite particles, “first-stage polymer/second-stage polymer”, is based on the order of monomer addition to the reaction system and does not designate a core−shell morphology.

Most composite particle syntheses have been conducted primarily in aqueous-based systems and to a more limited extent in organic solvents.[1−4] Supercritical CO_2 is a newly emerging solvent for conducting dispersion polymerizations and generating polymer particles. To date, dispersion polymerizations in CO_2 have primarily been single-stage polymerizations,[8−10] though there have been a few reports on composite particle synthesis in CO_2.[11,12] In this study, CO_2 was explored as a solvent for two-stage, sequential dispersion polymerizations for the formation of unique composite polymer particles. The specific Lewis acid−Lewis base interactions and cooperative interactions between CO_2 and carbonyl groups, reported by others,[13−15] were expected to have an influence on the morphology of methacrylate-containing composite particles. Examples of two types of composite particles that would be difficult to synthesis in aqueous-based systems are described in this Note, one system incorporating both hydrophilic and hydrophobic polymers and another incorporating reactive epoxy or isocyanate functionalities.

The polymers chosen for the hydrophilic/hydrophobic composite particles were poly(1-vinyl-2-pyrrolidone) (PVP) and polystyrene (PS), of which the dispersion polymerization of both systems in CO_2 has been previously studied.[16,17] CO_2 provides advantageous solubility properties for composite particle synthesis by dispersion polymerization as most hydrophilic and hydrophobic vinyl monomers are soluble in CO_2 while their respective polymers are not. A series of three different PVP/PS compositions were synthesized by a two-stage dispersion polymerization in supercritical CO_2.[18−20] It is evident by comparison of the representative single particle transmission electron microscopy (TEM) images (Figure 2) that PVP/PS 89/11 mol % and 58/42 mol % formed kinetically trapped nanoscale domains of PS (stained by RuO_4) in PVP and 26/74 mol % formed the more thermodynamically favorable inverted core−shell morphology with a PVP shell and PS core. Scanning electron microscopy (SEM) images of particles from which the PS was selectively extracted further supports these morphology assignments.[18,19] The preference of the PVP for the outer-shell regions over PS is attributed to specific interactions between the carbonyl groups with CO_2,[13−15] a behavior which has been previously observed with the poly(methyl methacrylate) (PMMA)/PS system.[20]

The propensity for carbonyl containing polymers to form shells around PS when introduced in the first stage, as just described for PVP/PS and PMMA/PS, can be exploited for the generation of surface-functional and reactive composite particles in CO_2 and is attempted with the following four reactive composite particle systems.[18] Reactive epoxy or isocyanate functionalities, both of which are sensitive to nucleophilic solvents (i.e., water and protic organic solvents), are ideally suited for synthesis in CO_2 due to its inertness. Composites incorporating either poly(glycidyl methacrylate) (PGMA) homopolymers or copolymers provide useful surface epoxy functionalities to act as particle supports for enzymes or catalysts or as cross-linking agents for toughened epoxy resins.[21] Composites incorporating highly reactive isocyanate-containing groups, such as 2-isocyanatoethyl methacrylate (IEM) copolymers or homopolymers (PIEM), can also be utilized.

Particle compositions for the first two reactive systems, PGMA/PS (29/71 mol %) and PIEM/PS (14/86 mol %), were chosen with a high fraction of styrene in the second stage to favor formation of the inverted core−shell morphology, since similar polymerization conditions for PVP/PS and PMMA/PS resulted in the inverted core−shell morphology. In the third reactive composite particle composition, P(GMA-*co*-MMA)/PS (7/18/75 mol %), the concentration of reactive functionalities was tailored through copolymerization of the reactive monomer. In the fourth reactive system, P(IEM-*co*-MMA)/P(HEMA-*co*-STY) (4/16/4/76 mol %) depicted in Figure 3, mutually reactive functionalities were expected to be compartmentalized in the separate phases of the com-

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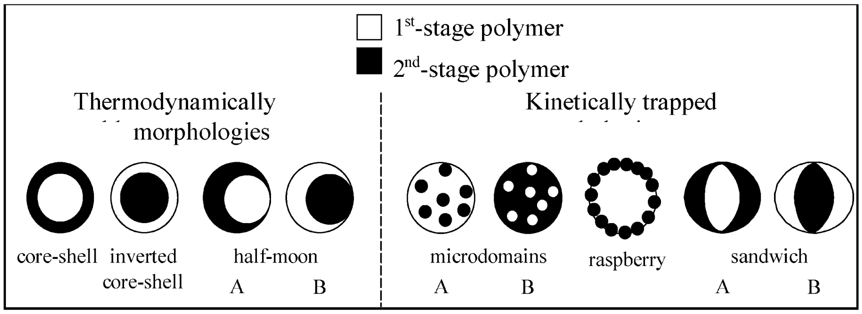

Figure 1. Common morphologies for composite particles containing two polymer phases.

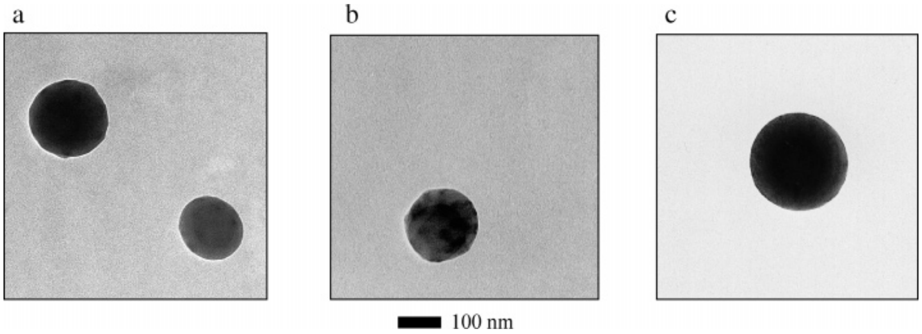

Figure 2. TEM images of RuO_4-stained PVP/PS whole particles (mol %) (a) 89/11, (b) 58/42 and (c) 26/74.

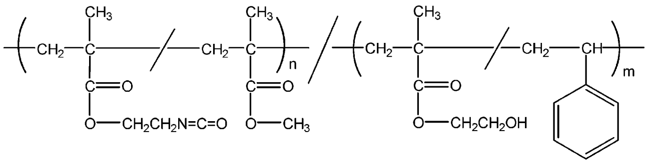

Figure 3. Chemical structure of P(IEM-*co*-MMA)/P(HEMA-*co*-STY) composite particles.

posite particle. With the P(IEM-*co*-MMA)/P(HEMA-*co*-STY) (4/16/4/76 mol %), the hydroxyl functionalities of the 2-hydroxyethyl methacrylate (HEMA) localized in the predominantly PS phase can react with the IEM isocyanate functionalities in the PMMA phase under appropriate reaction conditions. Since PGMA, PIEM, and PS are all stained by RuO_4, we were not able to find conditions to selectively stain the PS phases for morphology analysis by TEM. Instead, selective extraction of the PS in combination with scanning electron microscopy (SEM), as utilized for the PVP/PS system,[18] was used for morphology determination. By SEM, the morphology of all four composite particle compositions described above appear to have the first stage (co)-polymer predominantly in the shell regions rather than in the core, but further analysis is necessary for definitive morphology assignment.[18]

To demonstrate the utility of the isocyanate-containing composite particles, the P(IEM-*co*-MMA)/P(HEMA-*co*-STY) composite particles (Figure 3) were heated to 225 °C, significantly above the measured glass transition temperatures for both polymers to enhance polymer mobility but below their measured degradation temperatures.[18] The reaction between the isocyanate and alcohol functionalities was monitored by the decay of the isocyanate absorbance at 2273 cm^{-1} by IR spectroscopy. The urethane forming cross-linking reaction was not observed to occur at room temperature, but at 225 °C, the isocyanate group was almost completely gone after 1 h, as shown in Figure 4. In comparison, a physical blend of PHEMA homopolymer particles and PIEM/PS composite particles reacted slower at 225 °C. In this case, interparticle mixing would need to occur before urethane formation could begin. Localizing the functionalities within separate phases of the same particle, as in the previous example, provides for faster reactive group mixing and hence faster cross-linking.[22] It is expected that the addition of a catalyst, such as a common tin catalyst, would lower the reaction temperature to a more commercially applicable temperature.

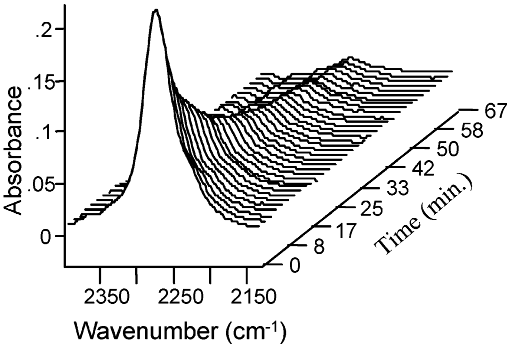

Figure 4. Reaction of isocyanate in P(IEM-*co*-MMA)/P(HEMA-*co*-STY) composite particles followed by FTIR spectroscopy.

These experiments demonstrate the feasibility of generating hard to synthesize, highly reactive polymer composites containing functionalities such as epoxy or isocyanate functional groups. Since the polymers in these examples are based upon high glass transition temperature polymers, they would be more suited for reactive polymer support applications rather than film-forming applications, but more suitable monomers can be incorporated to tailor the properties of the particles (i.e., flexibility or adhesion) for those applications. Last, the composite particles described in this Note further expand the utility of CO_2 as a heterogeneous polymerization medium for generating unique polymeric materials that would be incompatible with traditional polymerization solvents or water.

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Supporting Information Available: Experimental details of polymer composite particle synthesis, characterization (TEM and SEM), and FTIR spectroscopy. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) See the Supporting Information for plots of absorbance vs time.

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