PREPARATION OF POLYMERIC NANOCAPSULES WITH PERFLUOROALKYL WHISKERS IN SUPERCRITICAL CARBON DIOXIDE

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Introduction

Being an inexpensive, non-toxic, non-flammable[1] and environmentally friendlier[2] alternative to other organic solvents, CO_2 became increasingly attractive especially for synthetic procedures of polymers. Moreover, $scCO_2$ has unique properties[3] and formation of ordered polymer microstructures may be achieved by free radical heterogeneous polymerizations with the utilization of specific CO_2-soluble stabilizers.[4] Particularly, regular microsphere structured cross-linked polymers (microgels) are practical for wide range of applications of numerous fields including drug delivery[5], catalysis[6], pollution control[7], and sensors.[8] In this work we present a new method for the synthesis of core-shell microgels by a single step reaction procedure. The proposed method involves the polymerization and cross-linking of styrene monomer by heterogeneous free radical mechanism in $scCO_2$. Stabilization of the reactants is achieved by utilization of initially synthesized reactive surfactant (RS) and a surfactant-like azo polymerization initiator (SLAPI), both containing fluorinated tails compatible with CO_2. The obtained structures consist of a cross-linked polystyrene shell covered with hydrophobic, fluorinated chains (perfluoroalkyl whiskers) on the upper surface and polyethylene glycol (PEG-1500) based hydrophilic chains within the shell. The nanocapsules fall in the size range 200 – 300 nm and show regular distribution. The different chemical functionalities form the basic potential for applications based on chemical and physical phenomena occurring between diverse response giving systems.

Experimental

Materials. Hexane and tetrahydrofuran (THF) were dried over $CaCl_2$. All other reagents were used without further purification. Polyethylene glycol (PEG-1500) was purchased from Merck and dried by vacuum for 24h before use. Maleic anhydride (95%) obtained from J.T. Backer was recrystallized from toluene. 2-(Perfluorohexyl) ethanol (EA600) was kindly received from Clariant and divinylbenzene was obtained from Fluka. Styrene monomer was passed through neutral alumina column, then purged with N_2 and stored in refrigerator till use. All water used throughout the experiments was deionized initially.

Instrumentation. Characterizations of RS and SLAPI were performed by Fourier transform infrared spectroscopy (FT-IR) recorded on Equinox 55/S Fourier transform (Bruker). Polymerizations held in $scCO_2$ were performed by P-50 High Pressure Pump Contrivance (Thar) in a 100mL high-pressure stainless-steel vessel. Heating was achieved with a heating band and temperature was controlled by a thermocouple adapted to the vessel. Thermo gravimetric analysis (TG) was used to determine salt content incorporated into microgels swollen in salt solutions with STA 449C Jupiter (Netzsch). Scanning electron microscope analyses were performed with Supra 35VP Field Emission SEM (Leo) to photograph the nanocapsules. Samples were gold coated with K950X Turbo Evaporator (Emitech) before SEM analyses. Contact angle measurements were performed with DSA10 Drop Shape Analysis System (Kruss) in order to account for fluorinated chain presence on the surfaces of materials.

Synthesis of Surfactant-Like Azo Polymerization Initiator (SLAPI). EA600 (28.4×10^{-3} mol, 10.34g) was dissolved in 80mL 1,1,2-trichlorotrifluoroethane (Freon-113) in a 2-neck round-bottom flask equipped with a magnetic stirring bar. A separate solution of 4,4-Azobis (4-cyanovaleryl chloride) (ABCVCl) (28.4×10^{-3} mol, 6g) synthesized previously[9] and 150mL THF was prepared and added drop wise to the first solution. The flask was sealed with rubber septa and was purged with N_2. The reaction proceeded in dark, at room temperature (25 °C) for 12h under N_2 atmosphere. 5g (7.76×10^{-3} mol) of the isolated intermediate product (SLAPI-1) and PEG-1500 (7.76×10^{-3} mol, 11.64g) were dissolved in 150mL $SOCl_2$ in a 3-neck round-bottom flask equipped with a condenser, thermometer and a stirring bar, and were refluxed at 80 °C for 1h. The final product (SLAPI) was precipitated in 150mL cold hexane. SLAPI-1 and SLAPI were characterized by FT-IR spectroscopy. SLAPI was tested for $scCO_2$-solubility and stored under vacuum in dark.

Synthesis of Reactive Surfactant (RS). Maleic anhydride (5.10×10^{-2} mol, 5g) and EA600 (5.10×10^{-2} mol, 18.57g) were dissolved in 150mL toluene in a 3-neck round-bottom flask and 2 drops of sulphuric acid was added as catalyst. The flask was equipped with a condenser, thermometer and a stirring bar and reactants were refluxed at 95 °C for 1.5h. 5g (1.08×10^{-2} mol) of the intermediate product (RS-1) and PEG-1500 (1.08×10^{-2} mol, 16.23g) were reacted in 500mL toluene by azeotropic distillation set-up. RS-1 and RS were characterized by FT-IR spectroscopy. RS was tested for $scCO_2$-solubility and stored under vacuum in dark as SLAPI.

Preparation of Polymer Nanocapsules. 9g of styrene monomer (80% of total weigh of monomer, initiator, surfactant, and water), 0.6g RS (~5%), 0.3g SLAPI (~3%), 1g water (~9%), and 3 drops of THF added as a co-solvent were mixed and stirred regularly in a beaker for 10min. The mixture was transferred to the high-pressure reactor vessel. 0.35g of divinyl benzene (~0.6%) was added as a cross-linker, the vessel was closed, and CO_2 was slowly pumped within. The pressure was gradually increased to 250bar while the temperature was increased to 75 °C. The formation of fine dispersions in a milky suspension form was observed. The reaction was run for 24h. The polymer was isolated as a clean powdery product. Swelling tests with various solvents and water-salt solutions were performed. Materials were characterized with SEM, TGA and contact angle measurements.

Results and Discussion

Surfactant-Like Azo Polymerization Initiator (SLAPI). The synthesis of SLAPI described in **Figure 1**, consisted of two-steps of reactions of ABCVCl with EA600, and SLAPI-1 with PEG-1500, respectively. Functional groups described on the FT-IR spectra of ABCVCl, SLAPI-1, and SLAPI present in **Figure 2**, clearly show the conversions to products. SLAPI is completely CO_2-soluble at mild conditions (150bar, 40 °C).

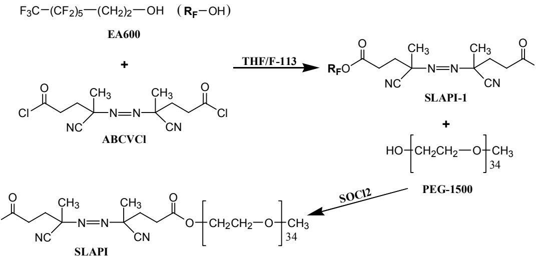

Figure 1. Synthesis of surfactant-like azo polymerization initiator (SLAPI).

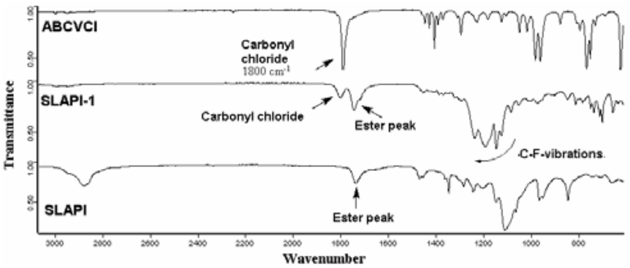

Figure 2. Stacked FT-IR spectra of ABCVCl, SLAPI-1, and SLAPI.

Reactive Surfactant (RS). The two-step synthetic procedure for RS is described in **Figure 3**. Similarly, **Figure 4** presents the detected functional groups in the FT-IR spectra of reactants and products, throughout the reactions. Conversions to RS-1 and RS can be clearly observed. RS is completely CO_2-soluble even at milder conditions (100bar, 30 °C).

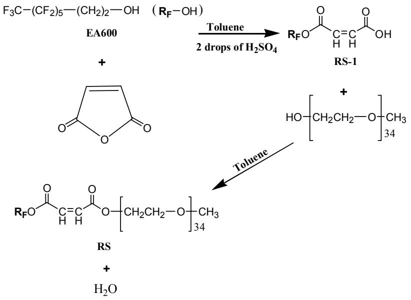

Figure 3. Synthesis of reactive surfactant (RS).

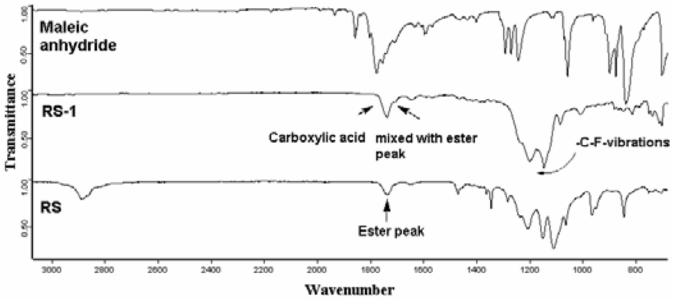

Figure 4. Stacked FT-IR spectra of maleic anhydride, RS-1, and RS.

Polymer Nanocapsules. Experiments conducted with various organic solvents such as THF, chloroform, dimethyl sulfoxide, isopropyl alcohol, and acetone showed swelling of material, which verified cross-linking. Water transfer to the core containing hydrophilic chains, was performed by initially swelling the particles in THF and then including the water. Further swelling was observed and characterizations are continuing. Tests in water with material not swollen initially in THF were also performed. Material did not wet, which is the evidence of fluorination on the surface that reduces the polymer surface energy and material affinity to interact with the water phase.[10] The contact angle of cast film obtained from THF dispersion was measured to be 145 °, which is another evidence for the fluorinated nature of the surface. **Figure 5** shows the general appearance and the cross-section of the nanocapsule structure by illustrations present in **a.** and **b.** on the left, and a photograph obtained from the contact angle measurement for the THF dispersion is present on the right of the image. The surface is covered with CO_2–philic, hydrophobic fluorinated chains, the shell consists of cross-linked styrene, and the hydrophilic chains form the inner core of the capsule.

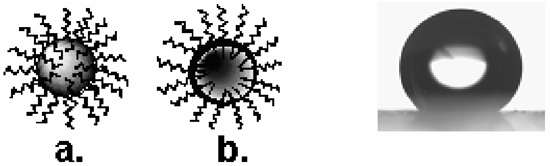

Figure 5. Proposed structures for the synthesized polymer nanocapsules at **a.** and cross-section at **b.** present on the left; and contact angle image obtained from the from THF dispersion present on the right.

Aqueous salt solution addition to the THF dispersions resulted even in higher degree of swelling. Samples were taken from swollen material, then were incorporated on glass thin plates and dried to remove solvent away. Electron micrographs of cast films from THF, THF + water, THF + water + salt dispersions were obtained. Most informative images were obtained from the THF + water + salt dispersion because of the highest degree of swelling of particles. Images taken from non-swollen polymer did not show the regular microstructure formation. **Figure 6** displays photographs of materials deposited on glass slide from THF + water + salt dispersion. The fine ordered smaller structures are in the size range 200 – 300 nm. Collapse of particles in some photographs may present evidence for the hollow nature of the core.

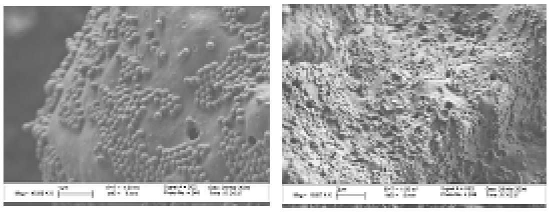

Figure 6. Electron micrographs of polymer nanocapsules from THF + water + salt dispersion.

TG analyses of samples taken from THF + water + salt dispersions with different salt concentration, were run in order to detect residual salt in the swollen sample by comparing the thermal behavior of the samples. Two samples were prepared, one from particles swollen for three days (A) and other from particles swollen for one week (B). The samples taken from the dispersion were finely washed with water and dried. Sample B showed final residual mass about 10% attributed to salt content, while sample A showed almost no residual mass. The results account for the time dependency of salt incorporation. **Figure 7** displays typical TG curves for sample A and sample B. Work is continuing to generate reasonable data and relations between thermal behaviors and varying salt concentration incorporated into the polymer particles.

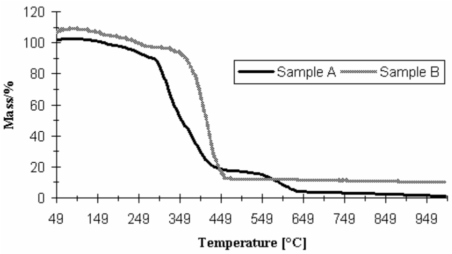

Figure 7. TG analysis for polymer samples A and B, swollen in salt, water, THF mixture.

Conclusions

We implemented a new method for the synthesis of core-shell microgels. The design of hydrophobic surface and a core of hydrophilic nature achieve selective permeability of particles. The obtained regular structured polymeric particles with diverse surface and core properties can find wide range of useful applications. Utilization of environmentally friendlier $scCO_2$ as a reaction medium constitutes another important dimension of this work.

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