PMMA Encapsulated Silica Particles by Dispersion Polymerization in Supercritical Carbon Dioxide

Eun Ju Park,[1] *Won Soo Kim,*[1] *Ha Soo Hwang,*[1] *Chan Park,*[2] *Kwon Taek Lim**[1]

Summary: PMMA encapsulated silica particles were synthesized by the dispersion polymerization of MMA in supercritical carbon dioxide ($scCO_2$). Nanosized silica particles pretreated with 3-(trimethoxysilyl) propyl methacrylate (γ-MPS) were used as seeds in the polymerization. Polymeric stabilizer, poly(dimethylsiloxane)-*b*-poly (methacrylic acid) (PDMS-*b*-PMA) copolymer provided sufficient stabilization to the silica/PMMA composite latexes in $scCO_2$ to produce spherical particles. SEM and TEM analysis revealed that the composite particles have core-shell type morphology.

Keywords: dispersion polymerization; encapsulation; PMMA; silica; supercritical carbon dioxide

Introduction

Recently, there has been a lot of work on the elaboration of nanocomposite systems by embedding of inorganic particles into polymeric matrices.[1–10] These materials represent a new class of polymeric materials which combine the unique physical properties of the inorganic particles with the processability and the flexibility of the organic polymer matrix. Among them, the preparation of core-shell composite particles has received particular attention due to their great potential applications.[11–13] While various techniques were used to synthesize the core-shell polymer particles, a traditional method has been the emulsion polymerization with inorganic seed particles. Recently, Zhang et al. used silica nanoparticles grafted by 3-(trimethoxysilyl) propylmethacrylate (MPS) as seeds in the emulsion polymerization and succeeded in preparing monodisperse silica–polystyrene core–shell particles.[14]

The dispersion polymerization in $scCO_2$ has been extensively studied since CO_2 was widely recognized as an interesting alternative to conventional organic solvent.[15,16] The advantages of $scCO_2$ solvent include liquid-like density, low viscosity, high diffusivity, zero surface tension, fast mass-transfer and tunable solvent power.[17] Moreover it is non-toxic, non-flammable, inexpensive, recyclable, and environmentally sound.[18] It also offers advantages of easy separation of products and resolves problems related to solvent removal. Very recently, macroporous monoliths consisting of silica nanoparticles embedded in poly(methyl methacrylate) (PMMA) were synthesized in $scCO_2$ by using well dispersed, surface modified silica particles.[19]

In this paper, we report the preparation of silica/PMMA nanocomposites in $scCO_2$. The method involves the dispersion polymerization of MMA using PDMS-*b*-PMA as the surfactant in the presence of well dispersed silica nanoparticles which were surface functionalized with the silane coupling agent bearing a polymerizable group.

Experimental Part

Materials

MMA (Aldrich) was purified by passing the liquids through a neutral alumina column to

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[1] Division of Image Science and Engineering, Pukyong National University, Pusan 608-739, Korea
Fax: (82) 51-625-2229
E-mail: ktlim@pknu.ac.kr
[2] Division of Materials Science & Engineering, Science and Engineering, Pukyong National University, Pukyong National University, Pusan 608-739, Korea

remove inhibitor. 2,2- Azobisisobutyronitrile (AIBN) was purified by recrystallization in methanol. Silica powder (Aldrich), 3-(trimethoxysilyl) propyl methacrylate (γ-MPS, Aldrich) as silane coupling agent, and research grade CO_2 (Daeyoung Co., 99.99%) were used as received. Tetrahydrofuran (THF) (Aldrich) was distilled from sodium naphthalide under reduced pressure prior to use.

The block copolymer, PDMS-*b*-PMA ($M_n = 5000$ g/mol for PDMS and $M_n = 1000$ g/mol for PMA) was prepared by the group transfer polymerization (GTP) as previously described.[20] The structure of the copolymer is depicted in Figure 1.

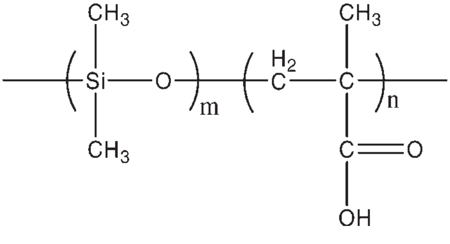

Figure 1.
The structure of PDMS-*b*-PMA stabilizer. The total molecular weight is approximately 6000 g/mol (PDMS block = 5000 g/mol, PMA block = 1000 g/mol).

Dispersion Polymerization of MMA in the Presence of Silica in $scCO_2$

Silica particles with average diameters of 107 nm were used in this study. These particles are hydrophilic with hydroxyl groups on the surface. For the surface functionalization, γ-MPS was added to 20 g of particles dispersed in 250 mL toluene and stirred for 24 h under argon atmosphere. Modified SiO_2 was isolated by ultracentrifuge and washed with toluene several times to remove unreacted γ-MPS. The γ-MPS functionalization changes the silica surface into hydrophobic and provides methacrylate terminal groups for polymer grafting. It also prevents the condensation between silica particles during the drying process.

The dispersion polymerizations of MMA in $scCO_2$ were performed in a 4 mL stainless steel high-pressure view cell reactor. A typical synthetic procedure of composite particles was given as follows: 0.75 g of MMA, 0.015 g of AIBN, 0.375 g of γ-MPS-functionalized SiO_2, a given amount of $PDMS_{5k}$-*b*-PMA_{1k} and a Teflon-coated stir bar were placed in a stainless-steel high-pressure reactor. The reactor was pressurized to approximately 345 bar by ISCO syringe pump (Model 260D) containing compressed CO_2, and then the reactor was heated to 65 °C. The remaining CO_2 was added into the reactor at 65 °C and 345 bar and the polymerization continued for 12 h. After polymerization, the reactor was cooled to room temperature, and unreacted MMA was extracted with liquid CO_2 at the flow rate of 20 $mL \cdot min^{-1}$. The remaining CO_2 was slowly vented at the end of extraction, and the product was collected and weighed.

Characterization

FTIR characterizations of pristine and functionalized powders were performed using a BOMEM Hartman & Braun FTIR spectrometer. Transmission Electron Microscopy (TEM) analysis was performed with a JEOL JEM-2010 (accelerating voltage of 200 kV) and a HITACHI H-7500 microscope (accelerating voltage of 80kV) for silica and composites, respectively. Scanning Electron Microscopy (SEM) observation was performed with a HITACHI S2700 scanning electron microscope operating at 20 kV.

Results and Discussion

The reaction scheme for core-shell nanocomposites is illustrated in Figure 2. In this work, we used commercially available silica as inorganic particles. As shown in Figure 3, silica particles have average diameter of 107 nm with slightly broad particle size distribution. After treatment with γ-MPS, the surface functionalized SiO_2 were characterized by FTIR measurement. The FTIR spectroscopy of γ-MPS-functionalized SiO_2 showed the absorption bands at 2953, 1718, and 1633 cm^{-1} result from the stretching vibration of CH_3, C=O, and C=C groups of γ-MPS, respectively (see Figure 4).

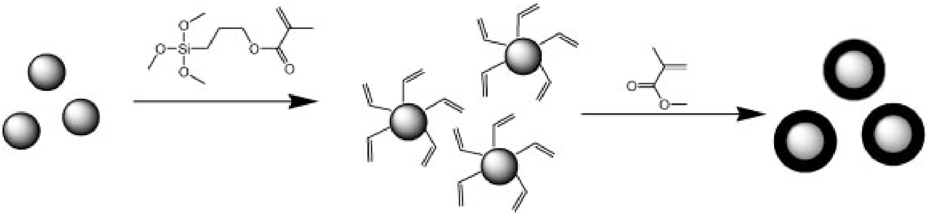

Figure 2.
Schematic representation of the process for the synthesis of silica/PMMA composite particles.

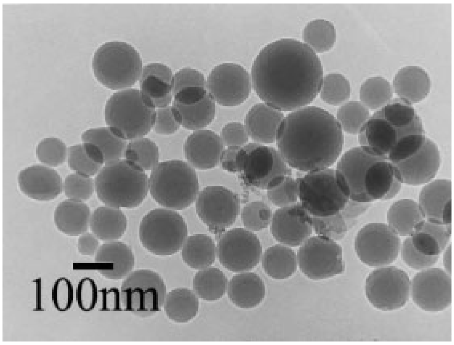

Figure 3.
TEM image of the silica nanoparticles.

The dispersion polymerization of MMA with γ-MPS-functionalized SiO_2 particles dispersed in $scCO_2$ was attempted in the presence of siloxane based block copolymeric stabilizer, PDMA-*b*-PMA. In order to obtain core-shell type composites, it is necessary to make a stable suspension of the silica nanoparticles in the reaction medium. The γ-MPS-functionalized silica dispersed very well in $scCO_2$, which is due to the favorable interactions between γ-MPS molecules and CO_2.[19] The polymerization was examined with three different stabilizer concentrations, from 5 to 15% w/w with respect

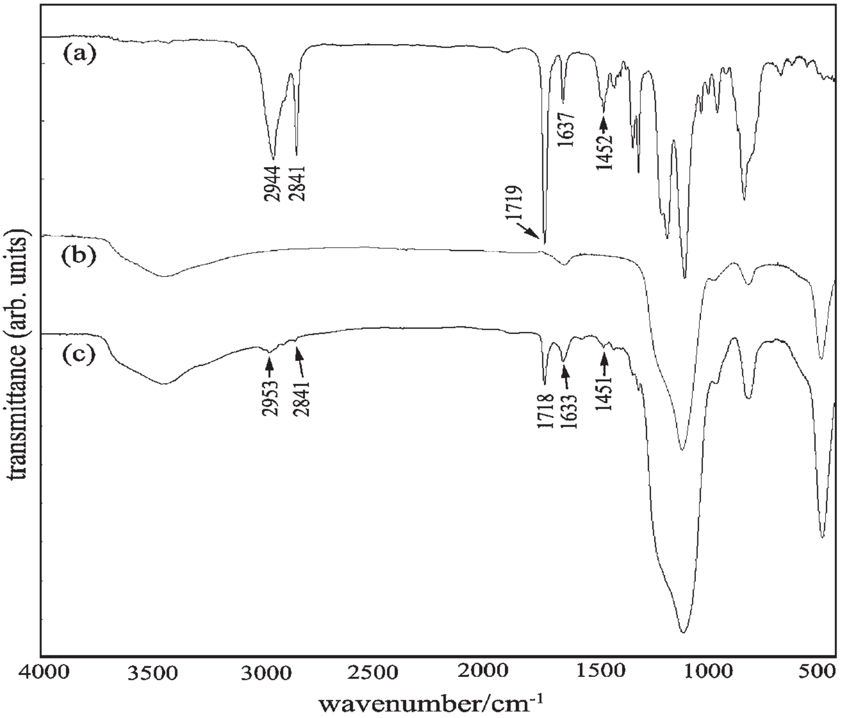

Figure 4.
FTIR spectra of: (a) γ-MPS, (b) pristine SiO_2, (c) γ-MPS-functionalized SiO_2.

Table 1.
Characterization of Silica/PMMA composites prepared with $PDMS_{5k}$-*b*-PMA_{1k} stabilizers. Reaction condition: 20% MMA (v/v to CO_2), 2% AIBN (w/w to MMA), 5wt% γ-MPS-functionalized SiO_2 (w/w to MMA), temp; 65 °C, initial pressure; 345 bar, polymerization time; 12 h.

Sample	Concentration of surfactant w/w% to MMA	Conversion (%)	Diameter (μm)	Product morphology
SiPM-1	–	78.4	–	aggregation
SiPM-2	5	96.3	1.87	powder
SiPM-3	10	99	0.51	powder
SiPM-4	15	99.5	0.36	powder
SiPM-5[a)]	15	96.7	0.3	powder

[a)] Reaction time; 6 h.

to the monomer. For comparison, the dispersion polymerization without the stabilizer was also performed under the same condition. The result of the polymerization was summarized in Table 1. The polymerization without stabilizer resulted in hard clumpy product with low monomer conversion. However, interestingly, dry powder was obtained with PDMS-*b*-PMA copolymeric stabilizer in high yield. The conversion reached above 95 % after the polymerization for 6 h. (see Table 1) As shown in Table 1, the particle diameter was affected by the concentration of the PDMS-*b*-PMA. The particle size decreases from 1.87 to 0.3 μm when the concentration of PDMS-*b*-PMA increased from 5 to 15 w/w % (to the monomer). The inverse proportion of particle size to stabilizer concentration is common in dispersion polymerization.[21] Figure 5 shows the SEM images of composite particles. At

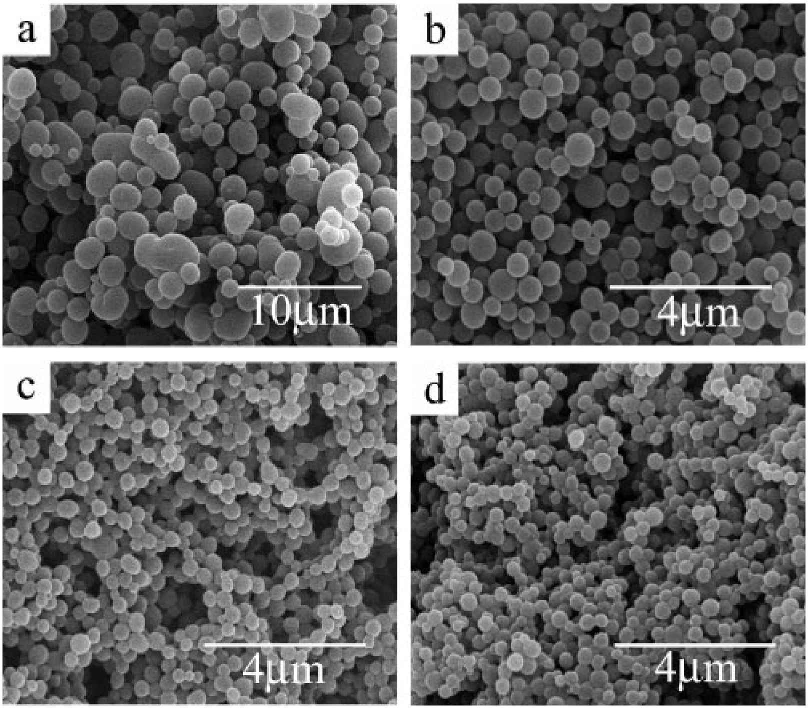

Figure 5.
SEM images of silica/PMMA composite particles produced with PDMS-*b*-PMA. Stabilizer concentrations are (a) 5, (b) 10, (c) 15, and (d) 15 % w/w with respect to MMA and reaction time is 12 h except (d) (6 h).

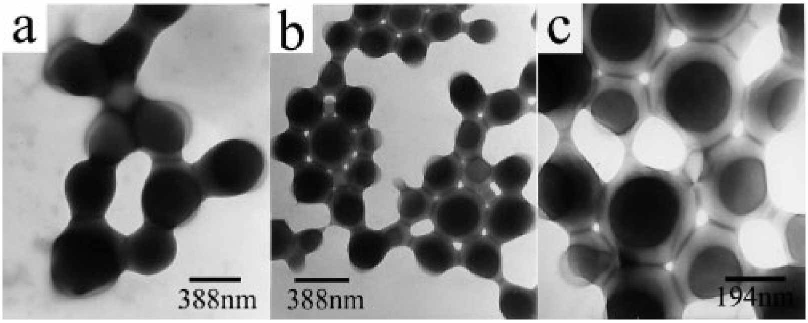

Figure 6.
TEM images of silica/PMMA composite particles (a) SiPM-2, (b) SiPM-3, and (c) SiPM-4.

lower concentration of stabilizer (5 %), the polymer particles have irregular shape as evident from the representative SEM picture shown in Figure 4(a). This is attributed to the fact that the stabilizer could not provide enough stabilization to the growing polymer composite particles and the particles tend to aggregate each other.

Figure 6 shows the TEM image of the silica/PMMA composite particles synthesized with PDMS-*b*-PMA stabilizer. It is clearly evident that the core-shell type morphology was produced successfully. Light PMMA shell coats the dark silica cores. Slight aggregation between particles also observed in the images, which is, however, often seen from the dispersion polymerization with silicone based stabilizer in $scCO_2$.[22] This can be explained by the fact that the polymer particles usually agglomerate at the later stage of polymerization due to the low solubility of silicone based polymers in pure CO_2.[23] From the above results, it is demonstrated that PDMS-*b*-PMA stabilizer provided an efficient stabilization for the composite latex to ensure the formation of spherical particles.

Conclusions

The spherical SiO_2/PMMA core-shell nanocomposite particles were successfully produced from the dispersion polymerization in $scCO_2$. The γ-MPS-functionalized SiO_2 were first dispersed in the reaction medium, followed by the polymerization with MMA. The $PDMS_{5k}$-*b*-PMA_{1k} stabilizer could sterically stabilize the composite latex particles in $scCO_2$ to prevent a flocculation during the polymerization. The size of composite particles could be adjusted with varying the stabilizer concentration.

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