Anomalous Polymer Particles of Narrow Size Distribution Prepared by Insertion and Evaporation of $Fe(CO)_5$ from Uniform Polystyrene Template Microspheres

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Uniform polystyrene template spherical particles of 2.5 ± 0.1 μm were prepared by dispersion polymerization of styrene in a mixture of ethanol and 2-methoxy ethanol. Uniform biphase hemispherical polystyrene/$Fe(CO)_5$ particles were formed by swelling the polystyrene template particles dispersed in water with emulsion droplets containing mixtures of methylene chloride and different volumes of $Fe(CO)_5$, followed by evaporation of the methylene chloride. Additional evaporation of the $Fe(CO)_5$ from the biphase polystyrene/$Fe(CO)_5$ particles leads to uniform anomalous shapes monodispersed polystyrene particles. The anomalous morphologies (dents, holes, and cupola) are dependent on the $Fe(CO)_5$volume entrapped within the polystyrene particles. Evaporation of relatively high volume of $Fe(CO)_5$ leads to uniquely shaped pierced uniform particles. The described method may open the door for developing a new methodology for preparing PS particles of controlled morphologies, by insertion and then evaporation of various precursors from PS template particles.

Introduction

Micrometer-sized particles of narrow size distribution have attracted much attention in many applications such as adsorbents for high-pressure liquid chromatography, calibration standards, spacers for liquid crystals, inks, catalysis, and so forth.[1–7] Dispersion polymerization is the common method for preparing uniform nonporous micrometer-sized particles in a single step.[8–11] However, the particles formed by this method possess a relatively small surface area and their properties, such as porosity, surface morphology, and functionality, can hardly be manipulated.[8,11] Furthermore, uniform particles of a diameter larger than approximately 5 μm usually cannot be prepared by dispersion polymerization. These limitations have been overcome by several swelling methods of micrometer-sized template particles (usually polystyrene, PS) with appropriate monomer(s) and initiator(s), e.g., multistep swelling,[12–18] dynamic swelling,[19,20] and a single-step swelling,[21] followed by polymerization of the monomer(s) within the swollen template particles.

Biphase hemispherical micrometer-sized composite particles are usually generated by swelling PS template particles with a monomer which after polymerization within the swollen particles produces polymer immiscible with the PS. Micrometer-sized polymer particles with anomalous morphologies were prepared by seeded dispersion polymerization under different conditions, where a secondary monomer is polymerized in the presence of seed latex particles, with or without the preswelling of the seed particles by the second monomer.[22–26] Anomalously shaped particles were also

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(1) Arshady, R.; Margel, S.; Pichot, C.; Delair, T. *Microspheres, Microcapsules, and Liposomes*; Citus Ltd.: London, 1999, Vol. 1, p 165.
(2) Margel, S.; Nov, E.; Fisher, I. *J. Polym. Sci. A, Polym. Chem.* **1991**, *29*, 347.
(3) Margel, S.; Sturchak, S.; Ben-Bassat, E.; Reznikov, A.; Nitzan, B.; Krasniker, R.; Melamed, O.; Sadeh, M.; Gura, S.; Mandel, E.; Michael, E.; Burdygine, I. *Microspheres, Microcapsules, and Liposomes*' Citus Ltd., London, 1999, Vol. 2, p 11.
(4) Vanderhoff, J. W.; El-Aasser, M. S.; Micale, F. J.; Sudol, E. D.; Tseng, C. M.; Silwanowicz, A.; Sheu, H. R.; Kornfeld, D. M. *Polym. Mater. Sci. Eng.* **1986**, *54*, 587.
(5) Ugelstad, J.; Berge, A.; Ellingsen, T.; Schmid, R.; Nilsen, T. N.; Moerk, P. C.; Stenstad, P.; Hornes, E.; Olsvik, O. *Prog. Polym. Sci.* **1992**, *17*, 87.
(6) Asua, J. M. *Polymeric Dispersions: Principles and Applications*, Proceedings of the NATO Advanced Study Institute on Recent Advances in Polymeric Dispersions, Elizondo, Spain, June 23−July 5, 2006; Springer: New York,1997.
(7) Margel, S.; Burdygin, I.; Reznikov, V.; Nitzan, B.; Melamed, O.; Kedem, M.; Gura, S.; Mandel, G.; Zuberi, M.; Boguslavsky, L. *Recent Res. Dev. Polym. Sci.* **1997**, *1*, 51.
(8) Bamnolker, H.; Margel, S. *J. Polym. Sci., A: Polym. Chem.* **1996**, *34*, 1857.
(9) Almog, Y.; Reich, S.; Levy, M. *Br. Polym. J.* **1982**, *14*, 131.
(10) Paine, A. J. *Macromolecules* **1990**, *23*, 3109.
(11) Kim, J. W.; Suh, K. D. *Polymer* **2000**, *41*, 6181.
(12) Ugelstad, J. *Makromol. Chem.* **1978**, *179*, 815.
(13) Ugelstad, J.; Moerk, P. C.; Herder Kaggerud, K.; Ellingsen, T.; Berge, A. *Adv. Colloid Interface Sci.* **1980**, *13*, 101.
(14) Cheng, C. M.; Micale, F. J.; Vanderhoff, J. W.; El-Aasser, M. S. *J. Polym. Sci., A: Polym. Chem.* **1992**, *30*, 235.
(15) Hosoya, K.; Frechet, J. M. J. *J. Polym. Sci., A: Polym. Chem.* **1993**, *31*, 2129.
(16) Smigol, V.; Svec, F.; Hosoya, K.; Wang, Q.; Frechet, J. M. J. *Angew. Makromol. Chem.* **1992**, *195*, 151.
(17) Smigol, V.; Svec, F. *J. Appl. Polym. Sci.* **1992**, *46*, 1439.
(18) Liang, Y. C.; Svec, F.; Frechet, J. M. J. *J. Polym. Sci., A: Polym. Chem.* **1997**, *35*, 2631.
(19) Okubo, M.; Ise, E.; Yamashita, T. *J. Appl. Polym. Sci.* **1999**, *74*, 278.
(20) Okubo, M.; Shiozaki, M. *Polym. Int.* **1993**, *30*, 469.
(21) Shpaisman, N.; Margel, S. *J. Chem.Mater.* **2006**, *18* (2), 396.
(22) Du, Y. Z.; Ma, G. H.; Ni, H. M.; Nagai, M.; Omi, S. *J. Appl. Polym. Sci.* **2002**, *84*, 1737–1748.
(23) Cho, I.; Lee, K. W. *J. Appl. Polym. Sci.* **1985**, *30*, 1903–1926.
(24) Okubo, M.; Katsuta, Y.; Matsumoto, T. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 481–486.
(25) Sundberg, D. C.; Casassa, A. P.; Pantazopoulous, J.; Muscato, M. R. *J. Appl. Polym. Sci.* **1990**, *41*, 1425–1442.

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prepared by Okubo et al. using a solvent-absobing/releasing method,[27] by absorbing toluene in PS template particles using the dynamic swelling process, followed by releasing the toluene at different rates into ethanol/water continuous phase.

The present study describes a new way to obtain anomalously shaped micrometer-sized PS particles of narrow size distribution. This was accomplished by the following steps: (1) insertion of $Fe(CO)_5$ into uniform PS template particles, by swelling the template particles with emulsion droplets of methylene chloride and various volumes of $Fe(CO)_5$; (2) evaporation of the methylene chloride from the swollen template particles to form biphase hemispherical PS/$Fe(CO)_5$ particles; (3) evaporation of the $Fe(CO)_5$ from the PS/$Fe(CO)_5$ particles. The influence of different parameters, e.g., $Fe(CO)_5$concentration, on the formation of the biphase and anomalously shaped particles was elucidated.

Experimental Section

Materials. The following analytical-grade chemicals were purchased from Aldrich and used without further purification: $Fe(CO)_5$(>99%), benzoyl peroxide (BP, 98%), sodium dodecyl sulfate (SDS), polyvinylpyrrolidone (PVP, MW 360,000), ethanol (HPLC), 2-methoxy ethanol (HPLC), and methylene chloride (HPLC). Styrene (Aldrich 99%) was passed through activated alumina (ICN) to remove inhibitors before use. Water was purified by passing deionized water through Elgastat Spectrum reverse osmosis system (Elga Ltd., High Wycombe, U.K.).

Synthesis of PS Template Microspheres. PS template microspheres of 2.5 ± 0.1 μm were prepared according to a procedure similar to that described in the literature.[8–10] Briefly, a solution containing PVP, (3.75 g, 1.5% w/v of total solution) dissolved in a mixture of ethanol (150 mL) and 2-methoxy ethanol (62.5 mL) was introduced into a 1 L reaction flask. The temperature of the mechanically stirred solution (200 rpm) was then preset to 73 °C. Nitrogen was bubbled through the solution for ca. 15 min. to exclude air, and then a blanket of nitrogen was maintained over the solution during the polymerization period. A deairated solution containing the initiator BP (1.5 g, 0.6%w/v of total solution) and styrene (37.5 mL, 16% w/v of total solution) was then added to the reaction flask. The polymerization reaction continued for 24 h, and was then stopped by cooling to room temperature. The microspheres formed were washed by extensive centrifugation cycles with ethanol and then with water. The particles were then dried by lyophilization.

Swelling of PS Template Microspheres with Methylene Chloride Containing $Fe(CO)_5$. In a typical experiment, the PS template microspheres (245 mg) of 2.5 ± 0.1 μm were swollen up to 6.3 ± 0.2 μm, by adding to a 20 mL vial, 10 mL of SDS aqueous solution 1.5% (w/v), and a swelling solvent consisting of 1.5 mL of methylene chloride and 1.5 mL of $Fe(CO)_5$. Emulsion droplets of the swelling solvent were then formed by sonication (sonics and materials, model VCX-750, Ti-horn 20 KHz) of the former mixture at 4 °C for 30 s. 3.5 mL of an aqueous suspension of the PS template microspheres (7% w/v, 245 mg) were then added to the stirred aqueous emulsion. After the swelling was completed, and the mixture did not contain any small emulsion droplets of the swelling solvent, as verified by optical microscopy, the diameter of the swollen microspheres was measured. PS swollen microspheres of various diameters were prepared by retaining the methylene chloride volume (1.5 mL) while changing the volume of $Fe(CO)_5$.

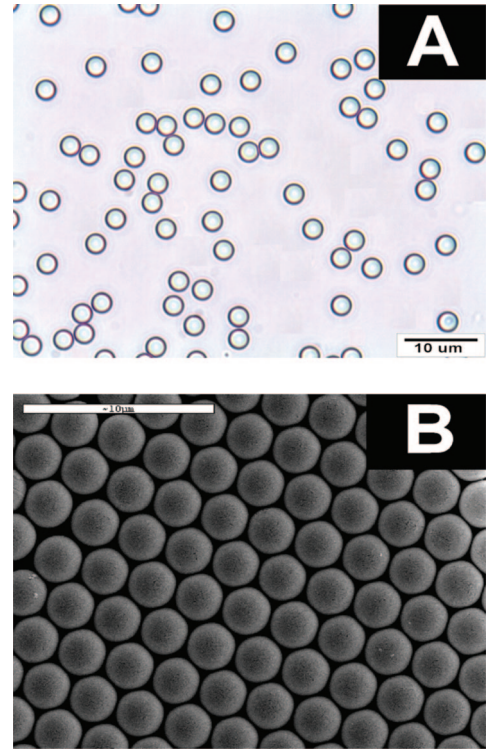

Figure 1. Light microscope (A) and SEM (B) pictures of the PS template particles.

Formation of Biphase Hemispherical PS/$Fe(CO)_5$ Particles. Biphase hemispherical PS/$Fe(CO)_5$ particles were formed by evaporating the methylene chloride from the former swollen particles. This was performed by purging nitrogen at room temperature for ca. 4 h through the shaken open vial containing the swollen particles aqueous mixture. Biphase hemispherical microspheres were observed only when the volume ratio of [methylene chloride]/ [$Fe(CO)_5$] ≤ 1.

Formation of Anomalous Shapes PS Particles. Anomalously shaped PS particles were formed by decantation of the PS/$(CO)_5$ particles from the aqueous continuous phase, followed by evaporation of $Fe(CO)_5$ (bp = 103 °C) from these particles for 1 h under a pressure of 1×10^{-3} mbar using a rotary vane vacuum pump (Vacuubrand, model RZ 5, Vaccubrand GMBH + Co KG).

Characterization of the Particles. Optical microscope pictures were obtained with an Olympus microscope, model BX51. Particles average size and size distribution were determined by measuring the diameters of more than 100 particles on optical micrographs with the image analysis software AnalySIS Auto (Soft Imaging System GmbH, Germany). Surface morphology was characterized with a JEOL scanning electron microscope (SEM) (model JSM-840).

Results and Discussion

Light microscopy and SEM pictures of the PS template particles are shown in images A and B in Figure 1, respectivly. These pictures illustrate that the PS template particles are perfectly spherical and monodispersed with average diameter of 2.5 ± 0.1 μm.

Figure 2 shows light microscope pictures of swollen PS particles prepared by swelling these template particles (245 mg) with emulsion droplets of 3 mL of each of the following

(26) Lovell P. A.; El-Aasser, M. S. *Emulsion Polymerization and Emulsion Polymer*; John Wiley & Sons: Chichester, U.K., 1997; p 294.
(27) Okubo, M.; Konishi, Y.; Takebe, M.; Minami, H. *Colloid Polym. Sci.* **2000**, *278*, 919.

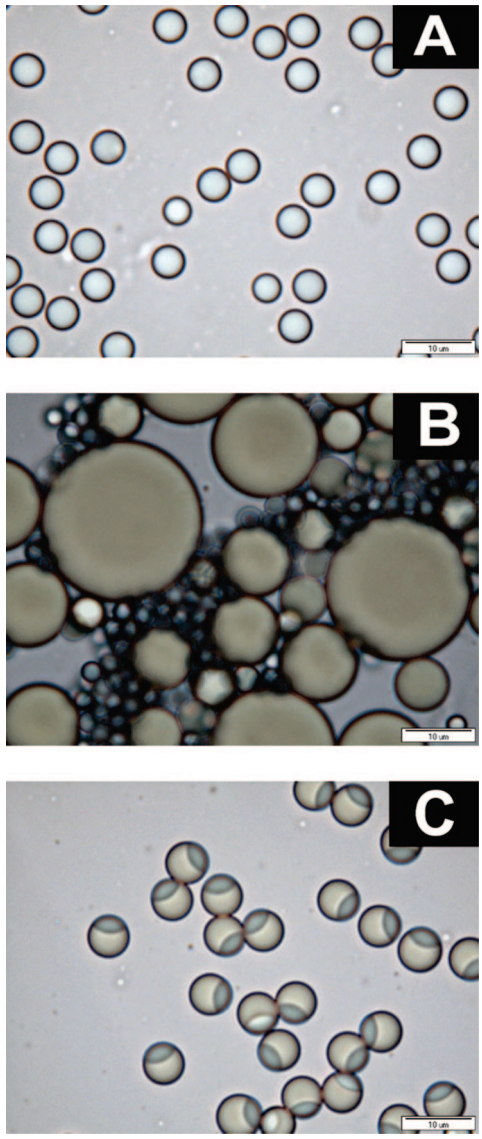

Figure 2. Light microscope pictures of the PS template particles (245 mg) swollen with 3 mL of: methylene chloride (A), $Fe(CO)_5$ (B) and a mixture of methylene chloride/$Fe(CO)_5$ 1:1 v/v (C).

swelling solvents: methylene chloride (Figure 2A), $Fe(CO)_5$ (Figure 2B) and a mixture of methylene chloride and $Fe(CO)_5$(1/1 v/v) (Figure 2C). Images A and B in Figure 2 clearly show the swelling ability of the PS template particles by methylene chloride and $Fe(CO)_5$, respectively. The size distibution was retained while the diameter of the PS template particles increased from 2.5 ± 0.1 to 5.5 ± 0.2 μm as a consequence of their swelling with 3 mL of methylene chloride. However, a similar swelling process, substituting the 3 mL methylene chloride for 3 mL $Fe(CO)_5$, resulted in nonuniform swelling of the template particles, i.e., the size and size distribution changed from 2.5 ± 0.1 to 7.6 ± 5.5 μm. Approximately 80% of the template particles were hardly swollen by $Fe(CO)_5$, whereas ca. 20% of these particles were swollen by $Fe(CO)_5$ to a large extent up to 25.3 μm. These results may indicate that methylene chloride is a good swelling solvent for the PS template particles, while $Fe(CO)_5$ is rather poor. Images A and B in Figure 2 also demonstrate that both swelling solvents, methylene chloride and $Fe(CO)_5$, retain the spherical shape of the particles after completion of the swelling process. On the other hand, Figure 2C demonstrates that when an equal volume mixture of methylene chloride and $Fe(CO)_5$ is used for the swelling process, biphase hemispherically shaped particles are produced. This result is in a good agreement with our previous studies demonstrating that biphase hemispherically shaped particles are formed only by swelling the PS template particles with a mixture of these solvents with a volume ratio: [methylene chloride]/[$Fe(CO)_5$] ≤ 1.0.[21]

This behavior may be explained by the significantly different solubility at room temperature of the PS template particles by methylene chloride and $Fe(CO)_5$: 0.3 and 0.02 g/mL, respectively. Indeed, mixing at room temperature of 1.5 mL of methylene chloride with an equal volume of $Fe(CO)_5$ results in the formation of a homogeneous solution. The addition of 245 mg of the PS template particles to this homogeneous solution results in the dissolution of the PS, followed by phase separation of the two solvents. A careful examination of the two phases indicates that the PS content in the methylene chloride phase is at least 10 times higher than in the $Fe(CO)_5$ phase. The dissolution of the PS particles in the homogeneous mixture of methylene chloride and $Fe(CO)_5$ probably leads to the decrease in the solubility of these two solvents, thereby resulting in phase separation. Similar behavior may explain the swelling process of the PS template particles by a mixture of methylene chloride and $Fe(CO)_5$ where the volume ratio [methylene chloride]/[$Fe(CO)_5$] is ≤1.0. The $Fe(CO)_5$ separates from the methylene chloride phase thereby forming the biphase hemispherically shaped particles. It should be noted that the composition of these biphase hemispherical particles is different than most of the previous reported ones, since the present particles are composed of a solid polymeric phase (PS) and a liquid phase ($Fe(CO)_5$), whereas most previous biphase shape particles are composed of two solid polymers: PS and a second solid polymer produced by polymerization of the respective liquid monomer within the swollen particles.[28]

In order to form PS/$Fe(CO)_5$ biphase hemispherical particles it is essential to remove the methylene chloride from the previous PS template particles swollen by methylene chloride and $Fe(CO)_5$. This was accomplished by purging nitrogen at room temperature for ca. 4 h through the shaken open vials containing the swollen particles aqueous mixtures. As a consequence of this process, the PS swollen particles shrank until all the methylene chloride evaporated. Figure 3 shows light microscopy pictures of the PS/$Fe(CO)_5$ biphase hemispherical particles containing different volumes of $Fe(CO)_5$: 0.3 (A), 0.6 (B), 0.9 (C), and 1.2 (D) mL.

Figure 3 clearly demonstrates, as expected, an increase in the diameter of the PS/$Fe(CO)_5$ swollen particles with increasing volume of the encapsulated $Fe(CO)_5$. For example, PS/$Fe(CO)_5$ particles containing 0.3, 0.6, 0.9, and 1.2 mL of $Fe(CO)_5$ have a diameter of 3.4 ± 0.1, 4.1 ± 0.1, 5.9 ± 0.2, and 7.3 ± 0.1 μm, respectively. Figure 3 also demonstrates the relative increase in the $Fe(CO)_5$ yellowish phase with increasing volume of the encapsu-

(28) Akiva, U.; Margel, S. *J. Colloids Interface Sci.* **2005**, *288*, 61.

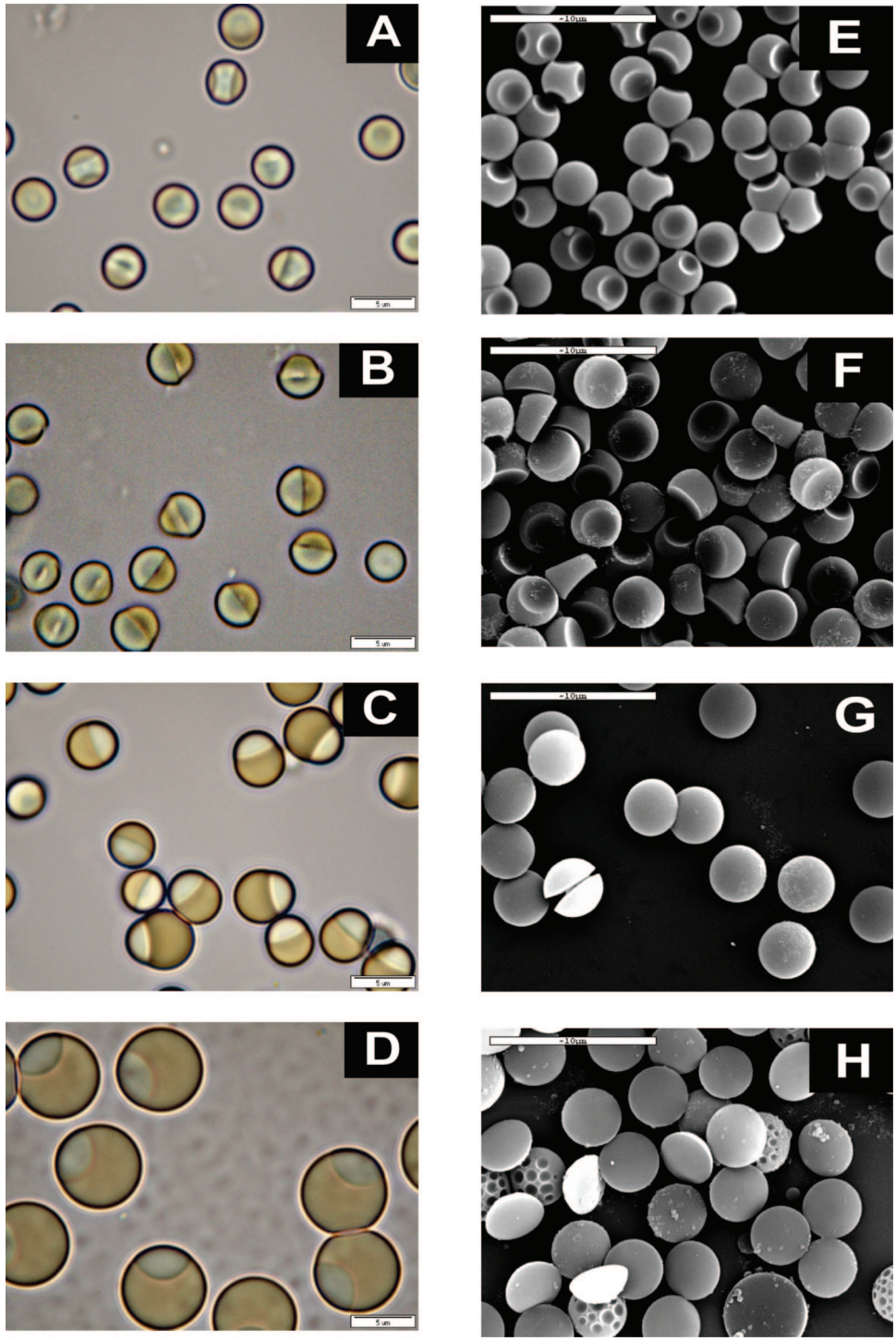

Figure 3. Light microscope (A−D) and SEM (E−H) pictures of the PS/$Fe(CO)_5$ hemispherical particles containing 0.3 (A), 0.6 (B), 0.9 (C), and 1.2 (D) mL $Fe(CO)_5$; and of the PS particles remained after evaporation of the $Fe(CO)_5$ from the PS/$Fe(CO)_5$ particles of A (E), B (F), C (G), and D (H). Biphase PS/$Fe(CO)_5$ hemispherical particles were produced by swelling the PS template particles (245 mg) with 1.5 mL of methylene chloride containing various volumes (0.3, 0.6, 0.9, and 1.2 mL) of $Fe(CO)_5$, followed by evaporation of the methylene chloride from the particles according to the experimental part.

lated $Fe(CO)_5$. The storing morphology stability of the PS/$Fe(CO)_5$ particles was investigated by gentle shaking at room temperature of the produced PS/$Fe(CO)_5$ particles containing 0.9 mL $Fe(CO)_5$ (Figure 3C) for 10 days. Figure 4 demonstrates by light microscope images the change in the morphology of these particles after 3, 6, and 10 days. These morphology changes enable the particles to reach a more thermodynamically favorable morphology. This Figure clearly shows that the PS/$Fe(CO)_5$ particles lose stepwise their biphase hemispherical morphology, and, after 10 days, PS, $Fe(CO)_5$ and PS containing $Fe(CO)_5$ microspheres are formed (Figure 4C).

Anomalously shaped PS particles were created by evaporating all the $Fe(CO)_5$ from the PS/$Fe(CO)_5$ particles, using a high vacuum pump as described in the experimental part. Figures 3 E-H show SEM pictures of the PS template particles after evaporation of the $Fe(CO)_5$ from the PS/$Fe(CO)_5$ particles containing different volumes of $Fe(CO)_5$:

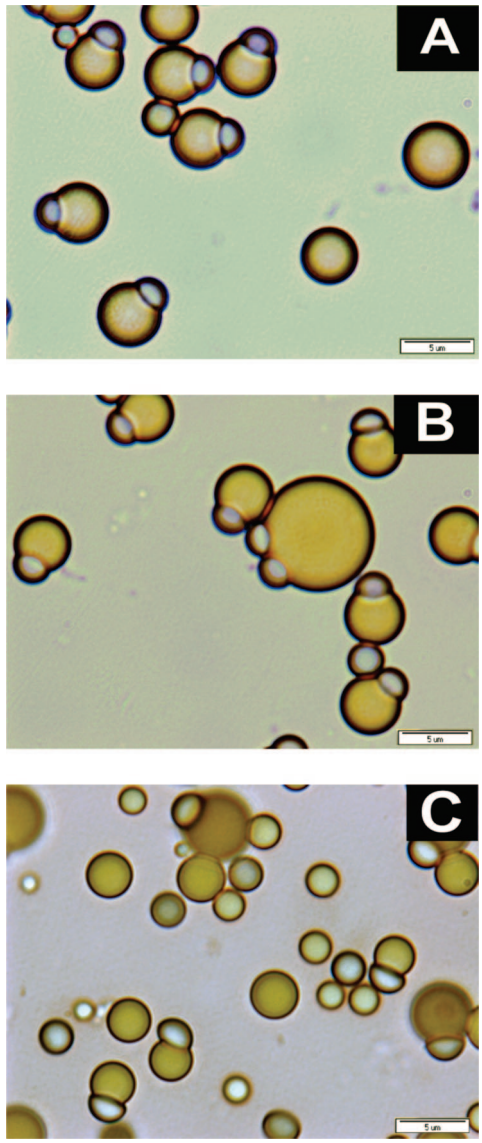

Figure 4. Light microscope pictures of the PS/$Fe(CO)_5$ hemispherical particles containing 0.9 mL $Fe(CO)_5$ dispersed in 1.5% SDS aqueous solution after shaking at room temperature for 3 (A), 6 (B), and 10 (C) days . PS/$Fe(CO)_5$ particles were produced by swelling the PS template particles (245 mg) with 1.5 mL of methylene chloride containing 0.9 mL of $Fe(CO)_5$, followed by evaporation of the methylene chloride from the particles according to the experimental part.

0.3 (E), 0.6 (F), 0.9 (G), and 1.2 (H) mL. Figure 3 exhibits, as expected, that the particles shrank as a consequence of the evaporation of the $Fe(CO)_5$. For example, the size of PS/$Fe(CO)_5$ particles containing 0.3, 0.6, 0.9, and 1.2 mL of $Fe(CO)_5$ decreased after the evaporation process from 3.4 $\pm$ 0.1, 4.1 $\pm$ 0.1, 5.9 $\pm$ 0.2, and 7.3 $\pm$ 0.1 μm to 2.6 $\pm$ 0.1, 3.1 $\pm$ 0.1, 3.4 $\pm$ 0.1, and 4.0 $\pm$ 0.1 μm, respectively. It is interesting to note that the diameter of the PS particles after evaporation of the encapsulated $Fe(CO)_5$ does not return to its original diameter (2.5 $\pm$ 0.1 μm). This behavior may due to a change in the packing of the PS chains within the particles as a consequence of the entrapment and then removal of the $Fe(CO)_5$ from the PS particles. Figures 3 E−H clearly emphasize the correlation between the volume of the evaporated $Fe(CO)_5$ and the formed anomalous shapes of the PS particles. It can be seen that the size of the dents increases with the increase in the volume of the evaporated

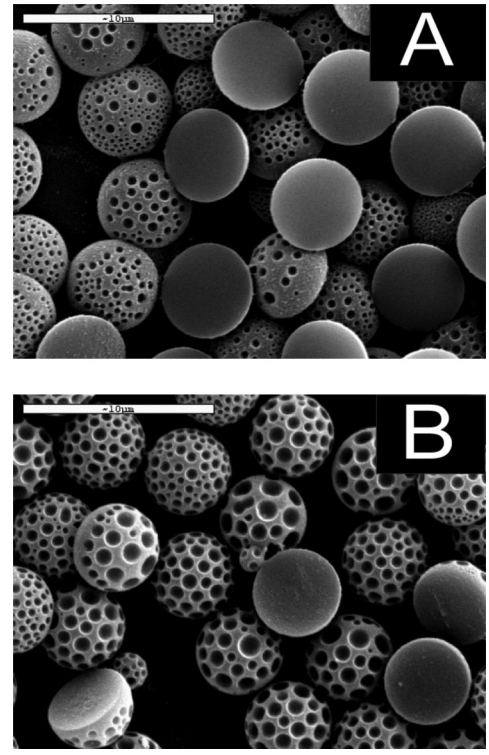

Figure 5. SEM pictures of the PS particles after evaporation of the entire $Fe(CO)_5$from the PS/$Fe(CO)_5$ particles containing different volumes of $Fe(CO)_5$: 1.5 (A) and 1.8 (B) mL. PS/$Fe(CO)_5$ particles were obtained by swelling the PS template particles (245 mg) with 1.5 mL of methylene chloride containing 1.5 and 1.8 mL of $Fe(CO)_5$ followed by evaporation of the methylene chloride from the particles according to the experimental part.

$Fe(CO)_5$ until the PS particles turn into a cupola shape, as shown by the evaporation of 0.9 and 1.2 mL of $Fe(CO)_5$). Furthermore, a unique morphology of pierced particles was observed upon evaporation of 1.2 mL of $Fe(CO)_5$, as shown in Figure 3H. These pierced shapes can be explained by the thin PS shell through which the $Fe(CO)_5$ evaporates and leaves holes. The thickness of the PS shell that wraps the $Fe(CO)_5$ decreases as the volume of the encapsulated $Fe(CO)_5$ increases, so that at relatively high volume of the Fe complex the evaporation through the PS shell leaves the holes as shown in Figure 3H. On the other hand, PS chains belonging to thicker PS shells can reorganize and close the tiny holes produced by the $Fe(CO)_5$ evaporation process. Similarly pierced PS particles were also obtained by evaporation of all the $Fe(CO)_5$ from PS particles containing 1.5 and 1.8 mL $Fe(CO)_5$ as shown in images A and B in Figure 5, respectively. Figure 5 also illustrates, as expected, that the hole size increases as the evaporation volume of the encapsulated $Fe(CO)_5$ increases. Another explanation for the pore formation in the PS particles may be due to the development of residual stresses during the swelling process. The coupling between the poor and rich Fe complex hemispheres yields an important constraint for the formation of tensile stress in the Fe complex rich hemisphere. The spatial distribution of the pore size and missing of pores at the basic plane of the PS hemispheres agree the assumption of stress controlled pore formation.

Conclusions and Future Work

In this study, biphase hemispherical shape particles were created by swelling PS template particles with a mixture of two swelling solvents: methylene chloride and $Fe(CO)_5$. Evaporation of the methylene chloride from the swollen particles leads to the formation of biphase PS/$Fe(CO)_5$ hemispherical particles. This biphase hemispherical morphology is completely lost after approximately 10 days of storing at room temperature, thereby enabling more thermodynamically favorable particle morphology to be obtained. Evaporation of $Fe(CO)_5$ from the PS/$Fe(CO)_5$ particles leads to the formation of PS particles with anomalous shapes having dents and holes on the particle surface. The morphology of the PS particles is dependent on the volume of the inserted and then evaporated $Fe(CO)_5$. This method may open the door for developing a new methodology for preparing PS particles of controlled morphologies, by insertion and then evaporation of various precursors from PS template particles. Current studies in this direction are ongoing in our laboratory.

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