Supporting information

1. **Figure 1** shows the time-course of the fabrication of mercapto-functionalized hemisphere.

2. **Figure 2** indicates that aggregation of hemispheres was not observed by measuring the particle size distribution.

3. **Figure 3** indicates how the morphology would be varied by the pyrolysis at 900℃.

4. **Figure 4** shows that the second weight loss of hemispheres increases as the amount of $RSiO_{3/2}$ and $RSi(OH)O_{2/2}$ units formed by GTS increases.

5. **Figure 5** indicates SEM images of microstructures patterned by compression micromolding using a rigid structure on the mold rather than an elastometric one.

6. **Figure 6** shows SEM images of microstructure fabricated by curable compression micromolding and curable cast micromolding using the thin-layer materials as a master.

7. **Table 1** indicates the recipes for polymerization of particles **1**—**10** described in **Figures 1, 2, 4, 5** and **6**.

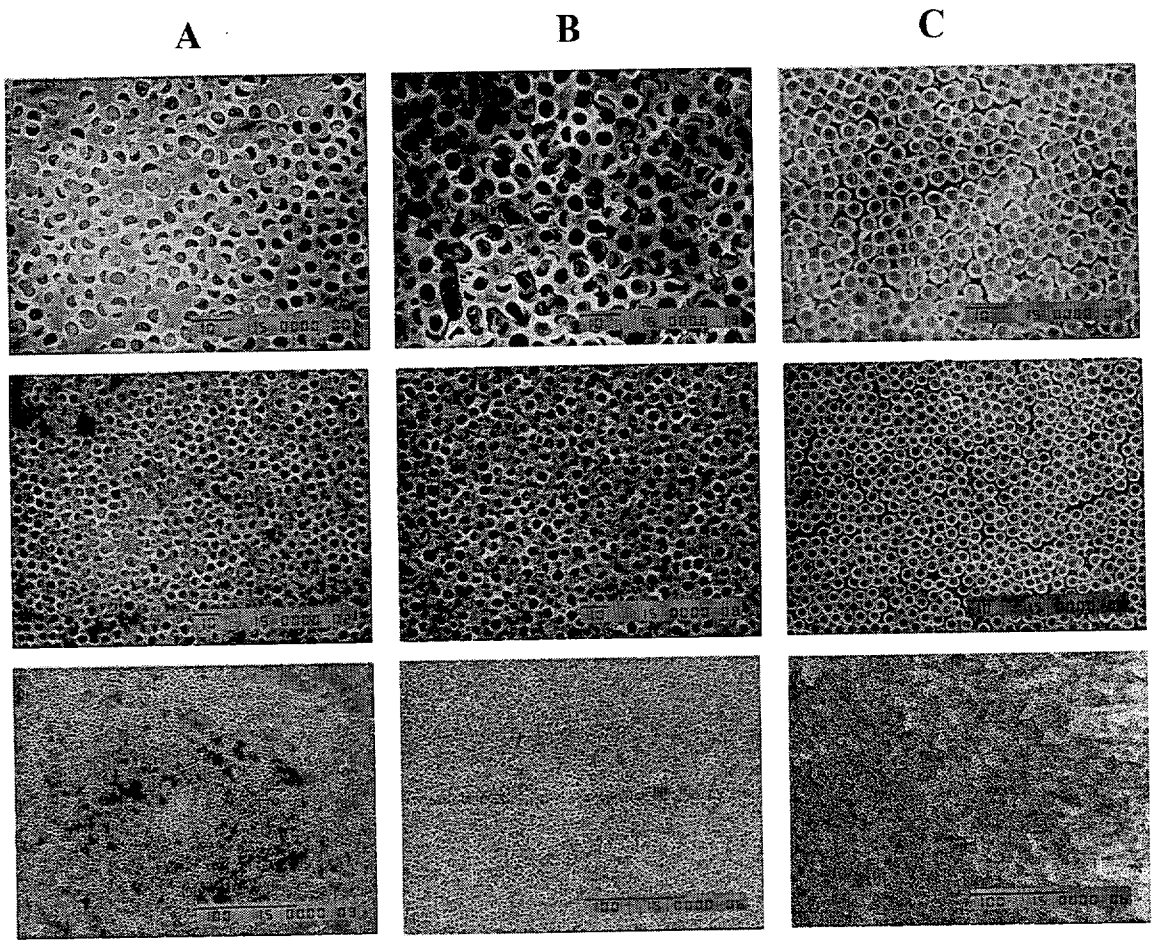


Figure 1. The time-course of the fabrication of mercapto-functionalized hemisphere **10** with an average major axis of 5.0 μm. The thin-layer materials were obtained by casting a colloid solution of the particles on the metal at regular time intervals. (A) SEM images after a period of approximately 10 hr. (B) after approximately 24 hr. (C) after about 36 hr.

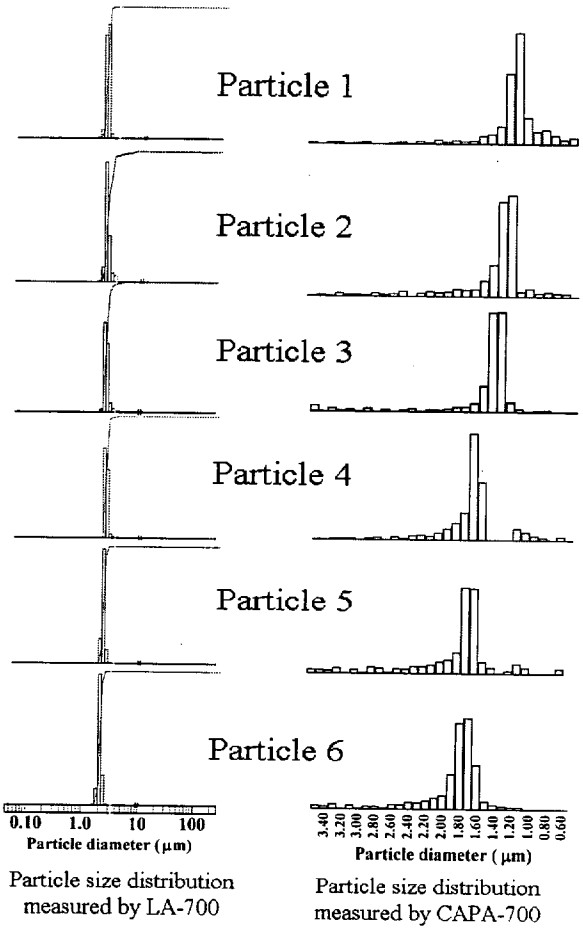


Figure 2. Particle size distribution of organic-functionalized hollow hemispheres **1** – **6** of methylsilsesquioxane derivatives obtained by suspension polymerization were measured by LA-700 and CAPA-700, respectively.

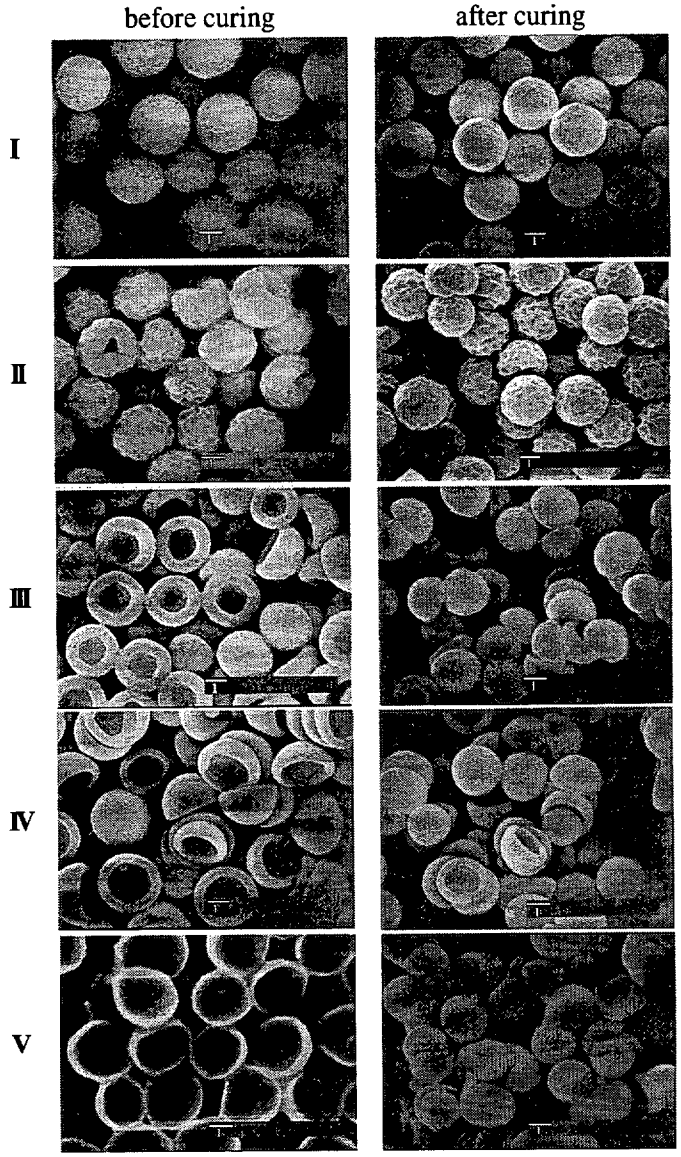


Figure 3. SEM images of methylsilsesquioxane derivatives upon curing at 900℃ under nitrogen atmosphere. All photographs enlarged ×10000 times. The marker bars are 1.0 μm. Empirical formulas of particles **I - V** were, $R_{0.9}SiO_{1.55}$, $R_{0.8}SiO_{1.60}$, $R_{0.7}SiO_{1.65}$, $R_{0.6}SiO_{1.70}$, and $R_{0.5}SiO_{1.75}$, respectively.

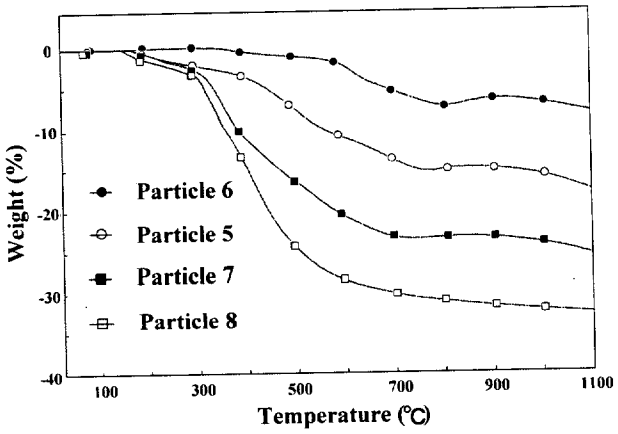
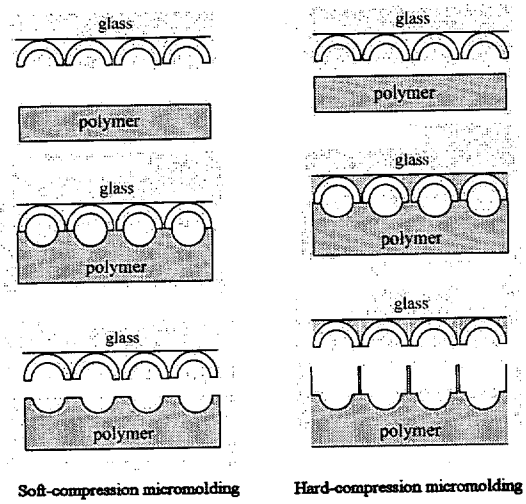


Figure 4. TGA curves of particles **5**, **7**, and **8** compared with hemisphere **6**.

Scheme 1. Soft- and hard-compression micromolding



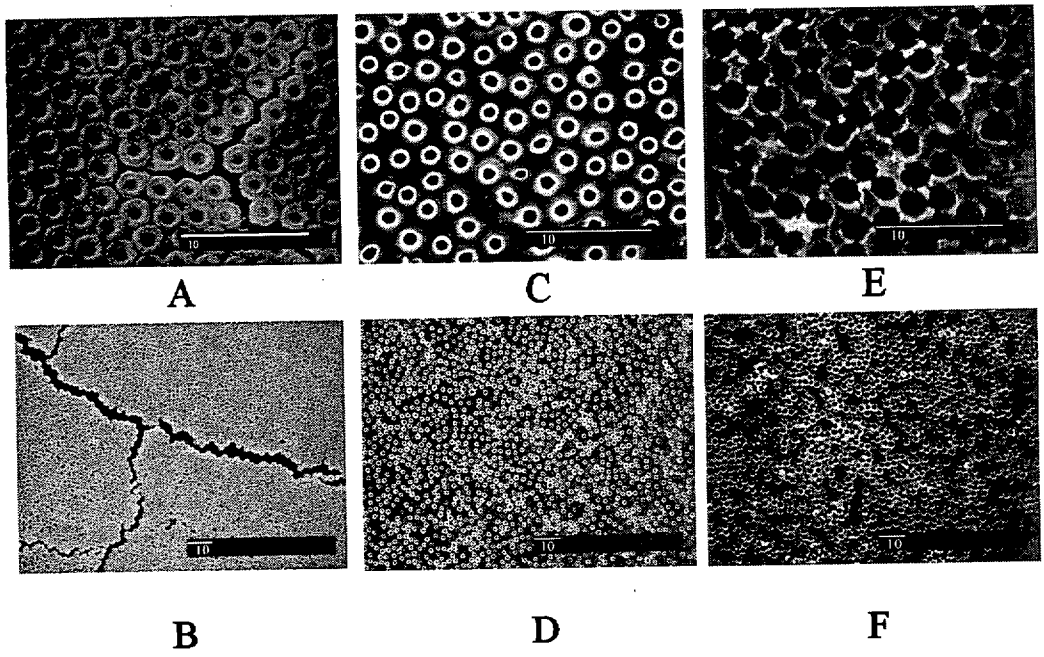


Figure 5. SEM images of nanostructure of hemisphere **1** on a master, polycarbonate replicas prepared by soft-compress and hard-compress micromolding, as shown in Scheme 1. (A, B) The thin-layer material as a rigid structure on the master rather than an elastometric one. (C, D) polycarbonate replica patterned by soft-compress micromolding. (E, F) polycarbonate replica embossed by hard-compress micromolding.

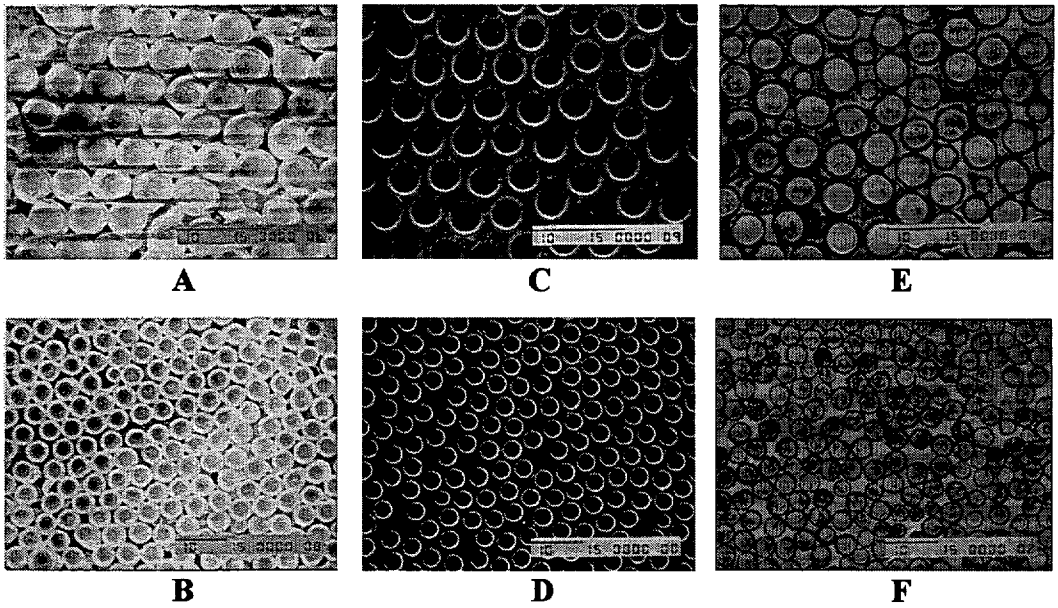


Figure 6. SEM images of microstructures of hemisphere **10** with an average major axis of 5.0 μm on a master, polymer replica fabricated by curable compression micromolding, and polymer replica obtained by curable cast micromolding. (A, B) The thin-layer material on a glass. (C, D) The replica of poly(4-acryloylmorpholine) obtained by curable compression micromolding. (E, F) The replica of poly(4-acryloylmorpholine) pattered by curable cast micromolding.

Table 1. Particles 1—10 Prepared by Polymerization under Constant Concentration of NaOH (0.020wt% per water)

particle	MTS (mol)	TOES (mol)	GTS (mol)	MATS (mol)	MCTS (mol)	median diameter (μm) LA-700	CAPA-700
1	0.43	0.38		0.032		2.14	1.18
2	0.43	0.38	0.034			2.25	1.34
3	0.57	0.38				2.25	1.44
4	0.52	0.29		0.032		2.11	1.64
5[a]	0.52	0.29	0.034			2.18	1.68
6	0.67	0.29				2.13	1.72
7	0.43	0.29	0.069			2.43	1.99
8	0.35	0.29	0.104			2.21	1.71
9[a]	0.43	0.38			0.046	2.41	1.64
10	0.43	0.38			0.046	5.02	3.76

[a] Particle **5** and **9** correspond to particles **8** and **10** in this report, respectively. [b] Particle **10** was obtained by polymerization using sodium hydroxide (0.0069 wt% per water).