Patterning Thin-Layer Material of Oriented Meso- and Macroscopic Hollow Hemispheres and Its Facile Lithography

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Thin-layer materials of high-density ordered arrays of meso- and macropores were fabricated by self-assembly of organic-functionalized hollow hemispheres on a substrate, and low center of gravity and organic-functional groups of the hemispheres played an important role in forming these ordered arrangements. By the use of the thin-layer material as a mold, the fabrication of nanometer-sized structure extended to replica molding from studies of the self-assembly of the hemispheres. As a result, solvent-assisted cast micromolding of a thermoplastic resin afforded microlens arrays on the polymer fabricated by filling the surface of the master with a fluid polymer softened by a solvent which was subsequently evaporated. On the other hand, compression micromolding provided pore arrays in a polymer sheet, and the pores were packed together as closely as the geometry allowed in the sheet. The concave microstructures were obtained by stamping the master on a thermoplastic resin that had been thermally softened. The developed lithographic methodology offers a facile method for generating a number of nanostructures and, therefore, has potential for the manufacturing of nanostructures.

Introduction

In recent years, there has been increasing interest in the fabrication of patterned structures on micrometer-length scales because of their potential utilization in many electronic, optical, and mechanical devices.[1] Patterning technology is well-established for semiconductors and metals, but is relatively undeveloped for organic polymers except for the specialized polymers used in photolithography.[2,3] These techniques are flexible and capable of providing very small features, but their development into methods for generating large numbers of nanostructures at low cost will require great ingenuity.[4] Both chemistry and biology can help in the development of new methodologies for generation of small structures. Among the methodologies, self-assembly often provides routes to structures having greater order than can be reached in non-self-assembling structures. Therefore, various strategies of self-assembly have been developed to fabricate two- and three-dimensional structures with dimensions ranging from molecular and mesoscopic to macroscopic sizes.[5−8]

If thin layers of ordered mesoporous or macroporous inorganic/organic hybrid materials on metal, polyester film, or glass surfaces could be obtained by self-assembly of hollow particles,[9,10] this method would be a synthetic strategy for fabricating membrane interfaces formed by an array of microreactors with a well-controlled thickness and structure. Thus, the patterning self-assembled thin layers provide a wide range of new opportunities for micro- and nanofabrication.[11−16]

We report here a novel highly ordered mesoporous or macroporous thin layer formed by the particle with a uniform size, which contains organic fragments and inorganic oxide within the framework of a uniform hollow-hemispherical morphology. Furthermore, a facile lithograph method using the thin layer as a master is also described. The development of facile lithographic techniques to pattern materials with structural features on the nano- or micrometer scale is important for the

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

particle	MTS (mol)	TOES (mol)	DMDS (mol)	GTS (mol)	MCTS (mol)	median diameter (μm)	
						LA-700	CAPA-700
1	0.67	0.32				2.13	1. 72
2	0.60	0.29	0.087			2.18	2.04
3	0.54	0.26	0.17			2.01	1.86
4	0.57	0.43				2.25	1.44
5	0.52	0.38	0.087			2.11	1.47
6	0.46	0.34	0.17			1.97	1.55
7	0.47	0.22	0.26			1.97	1.86
8	0.52	0.29		0.034		2.18	1.68
9[a]	0.43	0.38		0.034		0.22	0.30
10	0.43	0.38			0.046	2.41	1.64

[a] Particle **9** was obtained by polymerization using sodium hydroxide (0.087 wt % per water) as a catalyst.[9]

manufacturing of nanostructures, that is, the making of multiple copies reproducibly, rapidly, and inexpensively.[17] The challenge for the future in considering this lithographic technique for use in microelectronics or optics is to control distortions in the dimensions of the master during molding and curing of the polymer. Therefore, the thermal and physical stability of the master is an important factor for a set of lithographic techniques of compression micromolding[18] and cast micromolding,[19] and we apply the thin-layer material to a mold of these facile lithographic methods because of it being thermostable.

Experimental Section

General Data. The scanning electron microscopy photographs were taken by a JEOL JSM-T300 microscope. The IR spectra were measured by a HORIBA FT-210 spectrometer and a HORIBA FT-520 spectrometer. Thermogravimetric analysis was performed in flowing N_2 with a RIGAKU thermo plus TG-8120 thermal analysis system. The median diameter was measured on a HORIBA CAPA-700 centrifuge sedimentation particle size distributor and a HORIBA LA-700 laser scattering particle size distributor.

General Method. Average diameter and standard deviation of particle size were determined by the SEM technique following our previous reports.[10,20]

Materials. Methyltrimethoxysilane, tetraethoxysilane, dimethyldimethoxysilane, and sodium dodecylbenzenesulfonic acid (DBSNa) were of commercial grades and used without further purification. NP-5, NP-10, NP-14, and NP-40 of poly-(ethylene glycol) nonylphenyl ether were of commercial grades, and the number represents the repeat units of ethylene glycol. 4-Acryloylmorpholine and 1-hydroxy cyclohexyl phenyl ketone were of commercial grades. Polycarbonate resin (IUPILON S-3000S, Mitsubishi Gas Chemical Co.) was used without further purification. The synthesis of particles **1**−**10** followed the literature procedure.[9,10,20] The synthetic condition and physical properties are summarized in Table 1.

Preparation of Patterning Thin-Layer Material. The dispersion of hollow hemispheres followed the literature procedure,[9,10] where particle/water/methanol molar ratio was varied. The dispersions were coated on glass substrates to form thin films, which were dried for 5 h at room temperature. The

wet coat layer with a uniform thickness was obtained by using a rod coater. Then, the thin-layer material was fixed on the substrate by heating at 120 °C for 3 h.

Preparation of the Master. The thin-layer material using as the original master for Figure 3 was fabricated by further heating at 400 °C for 5 h. Then, the master was sprayed with a releasing agent (SEPA-COAT, Shinetsu Chemical Co.), and aged at 110 °C for 3 h.

Compression Micromolding. The thin-layer material using as a stamp was placed by hand onto a polycarbonate resin which was softened by heating at 320−350 °C for 20 min. After stamping at 320−350 °C for 10 min, a replica was obtained by releasing the master from the substrate.

Solvent-Assisted Cast Micromolding. Polycarbonate dissolved by THF was cast onto the master. The solvent was slowly evaporated at room temperature for 7 h and heated to 70 °C for 3 h. The replica automatically peeled off the master. The replica obtained in the first cycle was not good because dust particles and plastic impurity remained in the molded polymer. Each cycle of use cleans the mold, and the replica molded in the third cycle was almost clear.

Curable Cast Micromolding. Prepolymer or monomer containing a small amount of 1-hydroxy cyclohexyl phenyl ketone as a catalyst was cast onto the master. Another glass substrate treated by releasing agent was placed on the master, and these substrates interposing a thickness control were fixed by stoppers. The UV-curable polymer was cured with an ultraviolet light (mercury vapor lamp, HL-10201BF, USHIO UTEC) for 30 min, with a unicure system. After aging at 100 °C for 3 h, once the polymer had polymerized sufficiently, the mold and the support could be removed from the polymeric replica. These polymers did not adhere to the master and the support.

Curable Compression Micromolding. The master as a stamp was placed by hand onto UV-curable prepolymer containing a small amount of catalyst on the substrate, and the prepolymer was cured photochemically (the thin-layer materials are optically transparent). Once the polymer had cured sufficiently, the master could be removed from the substrate, and the patterned polymeric layer remained on the substrate.

Results and Discussion

Formation of Patterning Thin-Layer Materials. We have already reported that hollow hemispherical particles were prepared by polymerization of methyltrimethoxysilane (MTS) and tetraethoxysilane (TEOS) using sodium hydroxide as a catalyst.[9,10,20] SEM images exhibited the hollow hemispherical shapes of the particles. The images of hemispheres with the major axis of about 2.5 μm show no ordered arrangement. The SEM images of hemispheres with the major axis less than 0.6 μm, which indicated short-range ordering, occurred in the hemispheres. This ordered arrangement may be caused by sedimentation, which maintains a balance between buoyancy and gravitation. The relation between buoyancy and a low center of gravity also seems to play an important role. The following investigation focused on why the short-range order of large hemispheres was destroyed by the difference in particle size. We reported that the hemispheres gradually assumed the shape of a red corpuscle as the particle size decreased.[9] As a result, since the center of the convex side of the hollow hemisphere became depressed, the shape seemed to keep the particles from rolling. Thus, the ordered arrangement of small hemispheres still remained after drying. On the basis of these speculations, we arrived at a conclusion that the arrangement is broken by rolling of particles.

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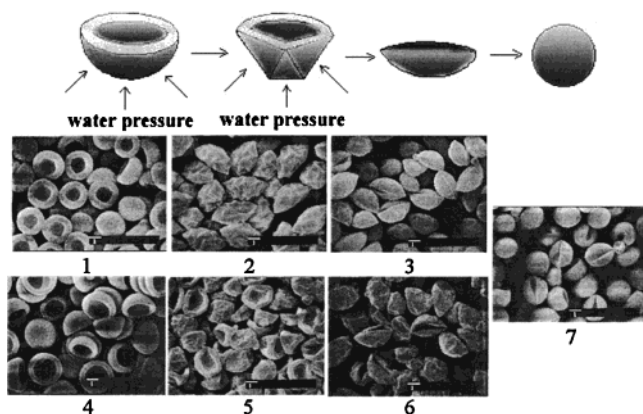
Figure 1. SEM images of particles **1**−**7** obtained by polymerization of TEOS, MTS, and dimethyldimethoxysilane (DMS). The bars are 1.0 μm.

To prevent the hemispheres from rolling, we investigated whether (1) hollow particles such as a red corpuscle can be obtained by self-assembly of siloxane segments and (2) organic-functionalized hemispheres, which would have greater affinity toward the substrate than the original hemispheres, can be fabricated. If our hypothesis is correct, the ordered arrangement of the hollow particles in a layered composite should be observed.

First of all, we investigated how particle shape is changed by raising the structural freedom in the framework. The hemispherical shape is wrapped by external water pressure since the $(CH_3)_2SiO_{2/2}$ unit acts as a soft unit, and the internal stress in the particle decreases with an increase in the unit.[10] As a result, a wrapped hemisphere, a clam shell, a hollow ellipse, a dimple ellipse, and a hollow sphere as the intermediate topologies between hemisphere and sphere are observed, as shown in Figure 1. It is assumed that these intermediate shapes are caused by the difference of the hardness and the thickness of the wall of each particle. However, hollow particles such as a red corpuscle were not obtained.

Second, possible routes for obtaining organic-functionalized hemispheres with a uniform hollow were investigated. In a typical synthesis, in a manner similar to the preparation of hemispheres, epoxy-functionalized hemispheres with an average major axis of 0.2−5.0 μm were obtained by polymerization of TEOS, MTS, and (3-glycidoxypropyl)trimethoxysilane (GTS) as an epoxy-functionalized monomer.[9,10] The above approaches were applied to the synthesis of hemispheres containing methacryl groups or thiol groups using {3-(methacryloyloxy)propyl}trimethoxysilane (MATS) or (3-mercaptopropyl)trimethoxysilane (MCTS) as organic-functionalized silicone monomers. These particles were analyzed by thermogravimetry, infrared spectroscopy, and particle distributors. The iodine value (Wijs method) of hemispheres increased with an increase in the amount of MATS in the silicone monomers.

Pyrolysis of these particles can be divided into two stages.[21] The first stage involved the evolution of water and volatile materials from 100 to 400 °C, and the second one occurs between ca. 400 and 900 °C. The second weight loss of hemispheres increases as the

amount of $RSiO_{3/2}$ and $RSi(OH)O_{2/2}$ units (R represents (3-glycidoxy)propyl group), formed by GTS, increases, and this result almost quantitatively indicates that the particle contains these units. The particle size distributions and median diameters of these particles were determined by a laser-scattering size distributor and a centrifuge sedimentation particle size distributor. From the results, aggregation of particles was not observed.

The SEM images indicated that the ordered arrangement of these particles with a wide distribution occurred due to the orientation of their pores in contact with the boundary between air and the solution, as shown in Figure 2. The results of particle characterization suggested that the ordered arrangement of particles with a wide distribution differs from the aggregation of particle colloids. Furthermore, Figure 2 indicates that the probability of observing this orientation increases as the pore size increases. The thin layer cracked as the layer coating the metal dried.[22] The deformation of these particles did not prevent the cracks caused by shrinkage of the coating layer on the metal. This problem could be solved by selecting a suitable binder. Furthermore, the binder is a joining material that can settle particles on PET film, which has a flat and inactive surface.

The ability of hemisphere **8** in the layers to capture methylsilsesquioxane spheres with a narrow size distribution was investigated. The hollow of the hemisphere captured spheres with an average diameter of 0.6 μm under ultrasonic wave, as shown in Figure 2. Thus, it is possible to produce thin multilayer materials coated with colloids of nano- or microparticles. The encapsulation of, for example, magnetic or catalytic particles in the ordered pores on the surface of the thin layer can give a magnetic or catalytic composite.[23] The interfacial effects, like guest−host effects, may find some application in a two-phase or membrane reactor in the field of catalysis or in high-density recording media in the field of magnetics.[24]

Properties of a Mold for Lithography. To use the patterning thin-layer materials as a mold, the thermal stability of hemispheres above molding temperature is required. Therefore, we have investigated how the morphology and the chemical properties of the particles would be varied by pyrolysis.[21] Despite the large weight loss between 400 and 900 °C, the SEM images of these particles showed no transformation of particle shape upon heating. However, after curing from room temperature to 900 °C, each particle became smaller than those before curing, as estimated from SEM images. An increase in cross-linking density upon further condensation of the silicate network was assumed to cause the decrease in particle size. The conversion from polymeric particle to ceramic materials[25] was monitored by changes in the transmission IR spectra at 900 °C.[21,26] These results show that the thin-layer materials are stable on

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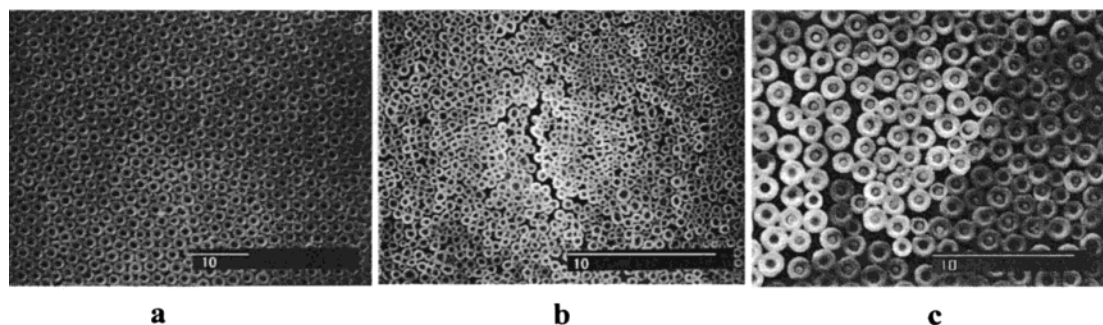
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Figure 2. (a) SEM images of hollow hemisphere **8** containing GTS units. These bars are 10 μm. A thin-layer composite was obtained by casting a colloid solution of hemisphere **8** on a metal surface. The colloid solution containing hemisphere **8** (0.5 wt % in total solution) was prepared by diluting the emulsion containing hemisphere **8** (5 wt % in water) with methanol. (b) SEM images of hollow hemisphere **9** containing GTS units. In a manner similar to preparation of a thin-layer composite of hemisphere **8**, a thin-layer composite on metal was prepared from a colloid solution of hemisphere **9**. (c) A thin-layer composite was obtained by coating glass with a colloid of hollow hemisphere **8** and dried at 200 °C for 4 h. The composite was coated with a colloid solution containing spherical particles (0.01 wt % in total solution) with an average diameter of 0.6 μm under ultrasonic vibration and dried at 200 °C.

heating at the molding temperature of thermoplastic resins.

The next challenge for using the thin-layer materials as a mold is to prevent the particles from transferring from the master to the polymer replica. The Si–OH groups on the particle surface should be allowed to react with the Si–OH groups on the glass substrate by heating the thin-layer material above 200 °C.[26] Consequently, the particles were not transferred from the master to the replica.

In addition to the foregoing properties, it is important to manipulate the mechanical deformation of the mold by the size and shape of structure on the mold since procedures of a set of lithographic techniques reported here have the capability of generating multiple copies of nanostructures starting from a single master. The softness of the framework of the hollow hemispheres on the mold can be controlled by changing the thickness of the wall covering the hollow,[10] and the elasticity of the structure on the master is proportional to their softness of the wall of hollow hemispheres. From this result, the elasticity should also be controlled by changing the thickness of the wall. Furthermore, we have reported a synthetic method to control the size of the hollow hemispheres on a nano- or microscale,[9] and the size of the hollow is simultaneously controlled by changing the particle size and the thickness of the wall.

Solvent-Assisted Cast Micromolding and Curable Cast Micromolding. First, we attempted to fabricate negative replicas of the patterns on the surface of the master, as shown in Scheme 1.

With use of a solvent to soften the thermoplastic resin, the master was filled with the resin fluid, and the trapped air in the holes on the master seemed to escape by diffusing through the resin fluid. The solvent was selected to dissolve the substrate without affecting the mold forming by the methylsilsesquioxane derivatives. After the solvent evaporated, the mold was removed and a patterned relief structure complementary to that on the surface of the mold remained. The low surface energy of methylsilsesquioxane derivatives allows the replica to be separated from the mold easily. Especially, if the particles are fixed on the glass substrate by heating the thin-layer material above 200 °C, the surface energy of the thin-layer material estimated by

**Scheme 1. Typical Lithographical Techniques**
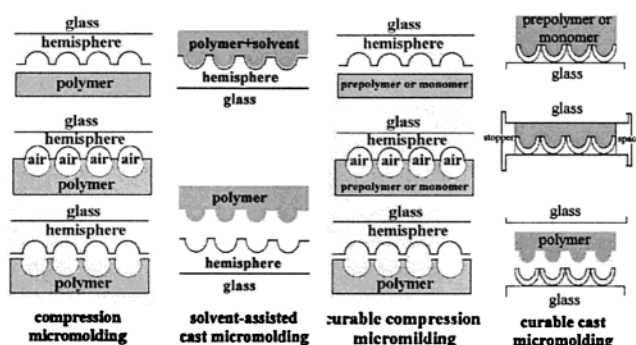
contact angle with liquids will decrease with the decrease in Si–OH groups on the particle surface.

Figure 3 illustrates the use of solvent-assisted cast micromolding (SAC-μM) to generate patterned nanostructure. Furthermore, an important characteristic of SAC-μM is that it is self-cleaning. Dust particles on the surface of the master tend to remain in the molded polymer.[17] Therefore, after several cycles of use clean the mold, the mold provided clear replicas. Figure 3A,B shows SEM images of nanostructures on a master that was fabricated by a self-assembly of hemisphere **10**. Figure 3C,D shows SEM images of polycarbonate (PC) negative replica that was prepared from this master. Figure 4B indicates features viewed at 45° compared with the features viewed at 0° (Figure 4A). From these images of the replica, a nanodot array of axial microlenses was patterned on the substrate. These axial microlenses have a potential for electro-optical devices and optical transmission.[27] Recently, the technique to relive the aberration had been examined as a method for producing a radial graded-index lens as a rod lens for office automation (OA) machines.[28] Perhaps, the most useful and versatile method of pattern formation is curable cast micromolding, as shown in Scheme 1. However, the spherical aberration of the axial lenses with a uniformed refractive index decreases as the diameter decreases.[28] In curable cast micromolding, the polymer replica is produced by casting prepolymers or

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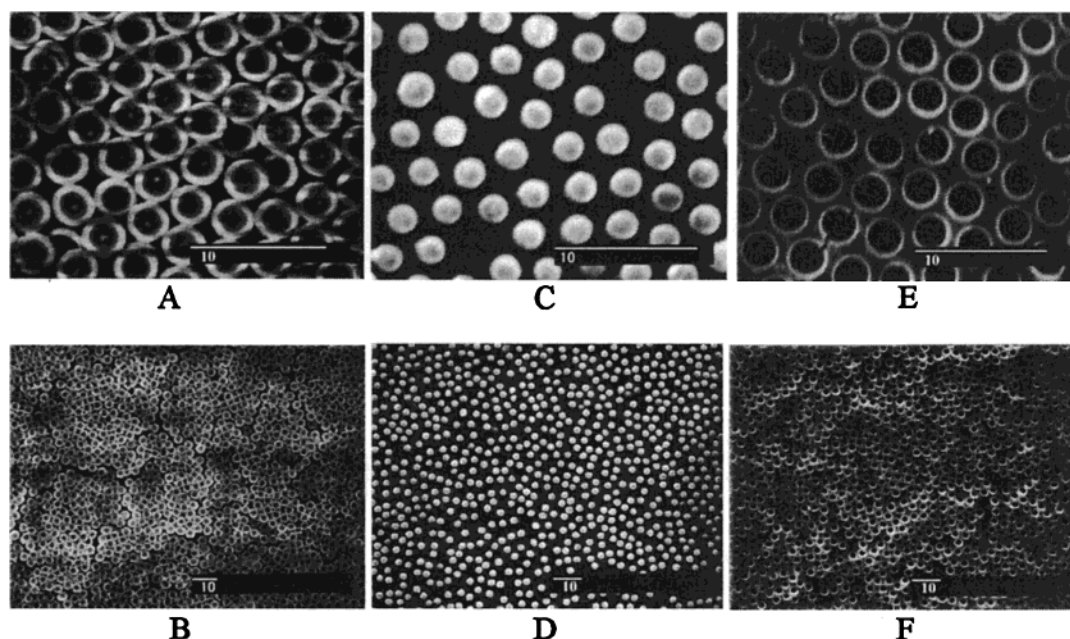
Figure 3. SEM images of nanostructures of hemisphere **10** on a master, polycarbonate replica prepared by compression micromolding using this master, and polycarbonate replica obtained by solvent-assisted cast micromolding using this master. (A, B) The thin-layer materials on a glass obtained by self-assembly of hemisphere **10**. (C, D) An array of microlenses of polycarbonate replica patterned by solvent-assisted cast micromolding. (E, F) Polycarbonate replica like a closest pore membrane filter patterned by compression micromolding.
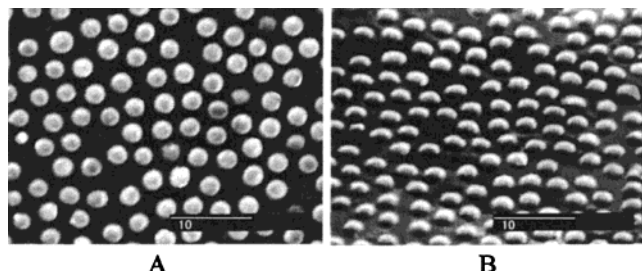
Figure 4. SEM images of polycarbonate replica prepared from the master by solvent-assisted cast micromolding. (A) SEM images of polycarbonate replica viewed at a 0° angle. (B) Featured viewed at a 45° angle.

monomers onto the master. Especially, it is important that the prepolymer has low viscosity to allow flow into the hollows and that it polymerizes under curable conditions. Therefore, a negative image of the master was obtained on the cured polymer.

Replication against Masters by Methods Based on Physical Contact. The following investigation addresses an application of stamping with a mold because of it being simple. In compression micromolding based on stamping, use of the master formed by self-assembly of hemispheres on the substrate as the mold against which new replicas are produced in organic polymers was also attempted (Scheme 1). Replica molding will make it easier to make multiple copies of small, fragile structures on the original master. Furthermore, it will be easier to separate the replica from the mold if a releasing agent is sprayed on the mold before molding. However, the micro- and macroholes on the surface of the master are not open so that some air remains in these holes.[29] Therefore, Figure 3C,D illustrates the use of compression micromolding to generate patterned

nanostructure like micro- and nanoporous filtration membranes. The holes of the replica were placed close to each other compared with the cylindrical pores of the membrane formed by projection neutron lithography via the "track-etch" method[30] since those in the membrane were orderly distributed on the membrane surface.[31] It was assumed that the holes patterned in the polymer were caused by the remaining air in the holes on the master since the air could not run away from the holes. Therefore, a similar patterned nanostructure was also obtained by curable compression micromolding since the trapped air in the hollows could not escape by diffusing through the master.

Conclusions

Two approaches to prevent hollow hemispheres from rolling were investigated. One of the approaches enabled the fabrication of thin layers by the self-assembly of hollow hemispheres (1) with a precontrolled major axis and size distribution, (2) with a controllable wall thickness (ranging from hundreds of nanometers to micrometers), and (3) by containing tethered organic functional groups inside the wall. Furthermore, a facile lithograph method using the thin layers as a mold permitted the formation of polymer microstructures on a substrate. The patterned structure on a substrate embossed by solvent-assisted or curable cast micromolding afforded a high-density ordered array of a convex hemisphere, while those obtained by lithographic techniques based on physical compression gave high-density ordered arrays of pores. Their patterning replicas might find applications in axial microlens for micro-optical devices[32] and pore membrane filters for separation tech-

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nology.[33] In case the holes of the patterning replica did not go through the substrate, an anisotropic etching with aqueous alkali[30] or solvent is used to remove the residue resin in the compressed area to expose the substrate underneath. If the thin film was used as a microporous template, magnetic nanorods would be grown in the holes by electrodeposition. Therefore, ordered arrays of nanorods will be formed in a polymer matrix.[34] The obtained film will be taken as a model of dot magnetic recording systems[35] at closest area densities, which incorporated magnetic rods into the hole of the microstructure formed by facile lithography followed by anisotropic etching.

Supporting Information Available: Figures and table of hemispherical data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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