Thin Silica Film with a Network Structure as Prepared by Surface Sol-Gel Transcription on the Poly(styrene-*b*-4-vinylpyridine) Polymer Film

Norifumi Fujita, Hideyuki Otsuka,[†] Atsushi Takahara,[†] and Seiji Shinkai*
Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 6-10-1 Hakozaki,
Higashi-ku, Fukuoka 812-8581
[†]*Institute for Fundamental Research of Organic Chemistry, Kyushu University, 6-10-1 Hakozaki,*
Higashi-ku, Fukuoka 812-8581

(Received December 18, 2002; CL-021074)

Sol-gel polycondensation of tetraethyl orthosilicate (TEOS) was carried out on the cast film of poly(styrene-*b*-4-vinylpyridine) under basic (benzylamine), acidic (AcOH), and neutral (no catalyst) conditions. It was found that only under the acidic and neutral conditions, the phase-separated periodic structure of the copolymer is finely transcribed into the silica. This is a new, convenient method to create the thin, mosaic film from inorganic materials.

Inorganic materials, although diverse in composition, lack the structural variety that is one of the characteristics of supramolecular and other organic structures.[1] Since inorganic materials with well-defined shapes have many potential applications (catalysis, chromatography, adsorbents, controlled release materials, etc.), scientists working in materials as well as in other fields of chemistry have devoted a great deal of their research effort toward the development of efficient and innovative methods in order to obtain these challenging materials.[2] In one of the methods most commonly employed, formation of the inorganic material takes place under the influence of an organic template (transcription).[3] A variety of organic templates have been successfully used for this transcription process; e.g., surfactants,[4–6] latex particles,[7,8] organogel systems,[9–13] polymers or polymer aggregates,[14,15] and even organic crystals.[16] It is generally accepted that the actual transcription of the template takes place because of interactions between the precursor of the inorganic material (or prehydrolyzed oligomers) and the template surface.[3] When discussing these interactions, two types are generally distinguished. In the first, negatively charged prehydrolyzed inorganic precursor moieties in solution can interact with positively charged moieties X^+ on the template surface. The second type of interaction that can take place is hydrogen bonding between donating moieties in the template (RNH_2, $RR'NH$) and negatively charged precursor moieties in solution. In both cases, these interactions lead to a deposition of inorganic material on the template surface. These two pathways are considered to be the only mechanisms through which transcription can take place. Since both involve the use of a catalyst that is free in solution, they can be classified as solution mechanisms for transcription. Recently, it was suggested that there is a third possibility through which transcription of a template may be accomplished.[17,18] If the surface of the template contains moieties that can catalyze the formation of the inorganic material, this will lead to the formation of small amounts of inorganic material on the surface; silica growth will then proceed on the surface of these nuclei. This means that transcription may take place directly and exclusively on the template surface, without the need for catalyst in solution. We recently demonstrated this transcription through a surface *mechanism* in which the sol-gel transcription process takes place as a result of catalyzed formation of inorganic material on the surface of the amino-linked organogel template.[17,18] The finding implies that the sol-gel transcription under the influence of the organic supramolecular pattern is also possible on the two-dimensional surface. To realize this intriguing idea, we carried out sol-gel polycondensation of TEOS on a diblock copolymer film of poly(styrene-*b*-4-vinylpyridine). We have found that the pattern created by the block copolymer is finely transcribed into the thin silica film.[19]

The diblock copolymer [M_n = polystyrene (21400)-poly(4-vinylpyridine) (20700), $M_w/M_n = 1.13$] was purchased from Polymer Source Inc. (Québec, Canada). The copolymer was dissolved in 3-pentanone (1.0 mg mL^{-1}) and a carbon-coated grid was dipped into this solution for several seconds. The solvent was evaporated at room temperature and the resultant grid was annealed under nitrogen at 150 °C for 3 h. The TEM image shows the phase-separated periodic structure, indicating that each polymer segment is phase-separated (Figure 1).

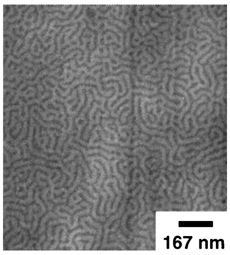

Figure 1. TEM image of the surface obtained from poly(styrene-*b*-4-vinylpyridine). The dark stripes correspond to 4-vinylpyridine domains as a result of staining by iodine.

Sol-gel polycondensation of TEOS was carried out by three different methods. In Method A, benzylamine ($BzlNH_2$, 0.50 mL), which is known to act as capable base catalyst for sol-gel transcription of molecular assemblies,[9,15,18] was used in CH_3CN (20 mL), water (0.50 mL), and TEOS (1.0 mL). In Method B, sol-gel polycondensation was carried out in the absence of catalyst, expecting that the 4-pyridyl nitrogens in the polymer would act, although weakly, as catalyst. In Method C, acetic acid (20 mL) was used, with water (1.0 mL) and TEOS (2.0 mL), which serves as solvent and acid catalyst as well as an acid to protonate the 4-pyridyl nitrogens. One may thus expect for Method C that the cationic pyridinium units act as adsorption sites for anionic silica microparticles. In all cases, a diblock-copolymer-coated grid was submerged in the solution spread on a Petri dish (75 mm in diameter).

In Method A, some network structure of silica was observed on the copolymer film, but the size was much larger than the stripe size in the cast copolymer and the shape did not reflect the pattern. Presumably, sol-gel polycondensation catalyzed by $BzlNH_2$ mainly proceeds in the bulk solution and the produced silica particles are adsorbed or precipitated onto the copolymer film.

In Method B, sol-gel polycondensation proceeded very slowly (judging from a change in the turbidity). In Figure 2, the TEM images at several different reaction periods are shown. After 18 h, a characteristic periodic structure was recognized in the TEM picture even without staining (Figure 2a), which was very similar to that of the cast polymer film of **1**. The periodic structure of the cast polymer film in Figure 1 was observed only after staining treatment with iodine, whereas nothing was observed without staining. Thus, one can attribute this pattern structure in Figure 2a to the silica grown up according to the surface mechanism. After 3 days, one can observe many dots on the stripes (Figure 2b). Presumably, the silica microparticles grown up in the bulk solution are adsorbed on the striped silica on the surface. After 7 days, the surface is covered by many dots and the identification of the original periodic structure becomes very difficult (Figure 2c).

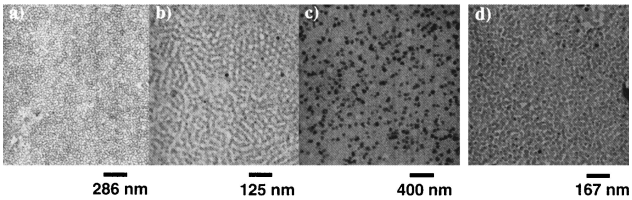

Figure 2. TEM images of silica on the copolymer film without staining: a) 18 h, b) 3 days, and c) 7 days. (d) TEM image of the networked silica structure obtained after calcination of 18 h immersion sample.

The sample obtained after 18 h sol-gel polycondensation (Figure 2a) was subjected to calcination. To avoid the crumbling or the asymmetrical distortion of the silica film, the temperature was raised very slowly: i.e., 1 h at 100 °C, 1 h at 200 °C, 1 h at 300 °C, and then 2 h at 500 °C in a nitrogen atmosphere. Finally, it was heated at 500 °C for 4 h in air. By this treatment the polymer film can be entirely decomposed. The TEM picture of the residual silica is shown in Figure 2d. It is clearly seen from Figure 2d that the silica layer has a mosaic structure with 15–25 nm string width. The width of the silica strings is comparable with that of black stripes in the polymer film (Figure 1). Thus, one can easily obtain a porous, thin silica layer.

In Method C, AcOH as catalyst mediates the sol-gel polycondensation in the bulk solution and the cationic pyridinium groups as the adsorption sites exist on the film surface. Being different from the surface mechanism in Method B, therefore, sol-gel polycondensation should proceed rapidly, followed by efficient adsorption of the resultant silica microparticles onto the film surface. In fact, the sol-gel polycondensation occurs very rapidly. Only after 30 min, a clear periodic pattern can be recognized by TEM observation (Figure 3a). After 1 h, the pattern has become rather vague because of adsorption of too much amount of silica microparticles (Figure 3b). TEM pictures taken after 3 h and 6 h show that the white open space is no longer continuous and becomes isolated dots. The results establish that Method C is most efficient in order to transcribe the stripe pattern of the polymer film of **1** into the silica.[20]

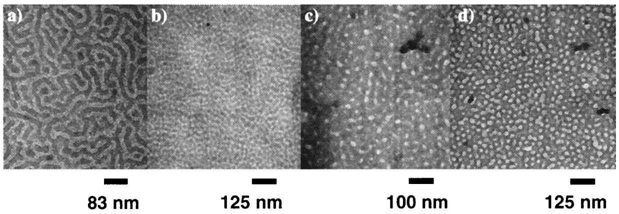

Figure 3. TEM images of the silica formed on the poly(styrene-*b*-4-vinylpyridine) film without staining: a) 30 min, b) 1 h, c) 3 h, d) 6 h of immersion into acetic acid/water (20 mL/1.0 mL) solution of TEOS (2.0 mL).

In conclusion, the present study has demonstrated that either the solution mechanism or the surface mechanism in sol-gel polycondensation[17] operates efficiently, depending on the reaction conditions, on the surface of the phase-separated diblock copolymer film to transcribe the characteristic periodic structure into the thin silica film. Undoubtedly, this is a new concept to achieve transcription in a two-dimensional expanse. We thus believe that the resultant silica film with a mosaic structure is useful, for example, as filters, molds for metal patterning, nanowiring of circuits, etc.

References and Notes

1 For recent reviews see: a) J. H. van Esch and B. L. Feringa, *Angew. Chem.*, **39**, 2263 (2000). b) D. J. Abdallah and R. G. Weiss, *Adv. Mater.*, **12**, 1237 (2000). c) G. F. Swiegers and T. J. Malefetse, *Chem. Rev.*, **100**, 3483 (2000). d) D. T. Bong, T. D. Clark, J. R. Granja, and M. R. Ghadiri, *Angew. Chem., Int. Ed.*, **40**, 988 (2001). e) L. J. Prins, D. N. Reinhoudt, and P. Timmerman, *Angew. Chem., Int. Ed.*, **40**, 2382 (2001). f) B. J. Hollida and C. A. Mirkin, *Angew. Chem., Int. Ed.*, **40**, 2022 (2001).

2 For recent reviews see: a) S. Weiner and L. Addadi, *J. Mater. Chem.*, **7**, 689 (1997). b) S. Mann, *Angew. Chem., Int. Ed.*, **39**, 3392 (2000). c) L. A. Estroff and A. D. Hamilton, *Chem. Mater.*, **13**, 3227 (2001).

3 For a recent review see: R. A. Caruso and M. Antonietti, *Chem. Mater.*, **13**, 3272 (2001).

4 D. H. W. Hubert, M. Jung, P. M. Frederik, P. H. H. Bomans, J. Meuldijk, and A. L. German, *Adv. Mater.*, **12**, 1286 (2000).

5 M. Adachi, T. Harada, and M. Harada, *Langmuir*, **15**, 7097 (1999).

6 H. Imai, N. Takahashi, R. Tamura, and H. Hirashima, *Langmuir*, **17**, 17 (2001).

7 X. D. Wang, W. L. Yang, Y. Tang, Y. J. Wang, S. K. Fu, and Z. Gao, *Chem. Commun.*, **2000**, 2161.

8 R. A. Caruso, A. Susha, and F. Caruso, *Chem. Mater.*, **13**, 400 (2001).

9 J. H. Jung, Y. Ono, and S. Shinkai, *Angew. Chem., Int. Ed.*, **39**, 1862 (2000).

10 J. H. Jung, Y. Ono, K. Hanabusa, and S. Shinkai, *J. Am. Chem. Soc.*, **122**, 5008 (2000).

11 J. H. Jung, Y. Ono, K. Sakurai, M. Sano, and S. Shinkai, *J. Am. Chem. Soc.*, **122**, 8648 (2000).

12 J. H. Jung, Y. Ono, and S. Shinkai, *Chem.—Eur. J.*, **6**, 4552 (2000).

13 K. Sugiyasu, S.-i. Tamaru, M. Takeuchi, D. Berthier, I. Huc, R. Oda, and S. Shinkai, *Chem. Commun.*, **2002**, 1212.

14 Y. Ono, Y. Kanekiyo, K. Inoue, J. Hojo, M. Nango, and S. Shinkai, *Chem. Lett.*, **1999**, 475.

15 K. J. C. Van Bommel, J. H. Jung, and S. Shinkai, *Adv. Mater.*, **13**, 1472 (2001).

16 H. Nakamura and Y. Matsui, *J. Am. Chem. Soc.*, **117**, 2651 (1995).

17 K. J. C. van Bommel and S. Shinkai, *Langmuir*, **18**, 4544 (2002).

18 A. Friggeri, O. Gronwald, K. J. C. van Bommel, and S. Shinkai, *Chem. Comuun.*, **2001**, 2432.

19 Very recently, a Korean group reported the similar idea: G. Cho, J. Jang, S. Jung, I.-S. Moon, J.-S. Lee, Y.-S. Cho, B. M. Fung, W.-L. Yuan, and E. A. O'Rear, *Langmuir*, **18**, 3430 (2002). However, our system has presented several new findings which were not attained by them: that is, (1) sol-gel polycondensation proceeds, without catalyst, utilizing the polymeric pyridine nitrogens as catalytic sites, (2) the mild condition in (1) results in the finer silica network structure, (3) the acidic, basic, and neutral conditions are all examined, and (4) the thin silica film with a network structure is directly observed by TEM.

20 The resultant silica material on the polymer film also gave the same porous silica layer as that of shown in Figure 2d after the calcination treatment. The same calcination process was adopted as that for the sample prepared by Method B.