Effect of drying rate on mesoporous silica morphology templated from PEO-PPO-PEO block copolymer assemblies

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Since the first synthesis of mesoporous MCM-41 by Mobil Corporation in 1992 [1], the use of surfactant as template or structure directing agent has opened new opportunities in the synthesis of porous materials. Nonionic triblock poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) copolymers have been successfully used as surfactant templates for the synthesis of a series of periodic mesoporous silicas including hexagonal, lamellar, and cubic structures [2, 3]. Considerable attention has been paid to controlling the pore size and enhancing the porosity by varying such synthetic parameters as the aging time and temperature. Obviously, these heat treatments during the preparation are important in determining the final mesoporous structure of silicas. The finally solidified silica structure is considered to be determined by a competitive process of two simultaneously occurring solidifications of the structure directing agent and silica, whose structural arrest is due to desiccation and condensation polymerization, respectively. This means that the finally replicated mesoporous structure of silica does not necessarily agree with the thermodynamically preferred phase structure of the structure directing agent. Therefore, exploring the possibility of giving a variety in the final silica structure by heat treatments can be an intriguing research subject from the viewpoint of materials nanostructure manipulation. Until now, most of the mesoporous silicas were prepared by templating of surfactant and block copolymer liquid crystalline mesophases which usually give rise to an open pore structure. However, little attention has been paid on the closed pore structure, although in some cases, closed pores are more desirable than open pores due to the mechanical strength or resistance to humidity. Therefore, clarifying important factors for the closed pores is an interesting research subject which is expected to be valuable for preparing low dielectric films with high closed porosity. The authors have shown that the rapid drying process of the nanocomplex of silicate and pluronics is favorable for the formation of closed nanopores, where the enclosure of the pores is promoted due to the solidification of silica prior to the formation of the liquid crystalline phase of pluronics molecular assemblies [4].

Here, we report the effect of drying rate on the morphology of mesoporous silicas templated from the pluronic triblock copolymer aggregates, and the formation of closed pores in the mesoscopic structure of the silica.

Mesoporous silicas were synthesized using triblock copolymer Pluronic P123 ($M_{\mathrm{av}} = 5800$), $\mathrm{EO}_{20}\mathrm{PO}_{70}\mathrm{EO}_{20}$, as surfactant template. Agents with the molar ratio of 0.04 (TEOS), 1 (water), 0.022 (Ethanol), and 0.001 (HCl) were mixed in a glass beaker and stirred at room temperature until a transparent solution was obtained. Then P123 was added and dissolved in this homogenous solution. The weight fraction of P123 to water was 10%. Samples were prepared by three different drying methods to carry out the preparation of the samples at three rates of drying. Sample A was obtained by keeping the beaker in a drying oven at 90 °C for a day with a cap for slower drying. Sample B was obtained by transferring the precursor solution into a glass dish and keeping it in a drying oven at 90 °C for a day without a cap on it. For drastically more rapid drying, sample C was obtained by spraying the resulting solution onto a TEFON-coated plate, thermostatted at 90 °C followed by complete desiccation in a drying oven for several hours. Finally, all the dried samples were calcined at 600 °C for 5 h in air to remove the pluronic P123 template.

The closed porosity (P_{c}) of the mesoporous silica was evaluated from the apparent mass density of the sample measured by helium pycnometer where the bulk density of silica matrix was assumed to be 2230 kg/m^3. The open porosity (P_{o}) was obtained from the adsorpted amount of nitrogen at the relative pressure of 0.9814 at 77 K. Fig. 1 shows the closed porosity and the ratio of the closed porosity to the open

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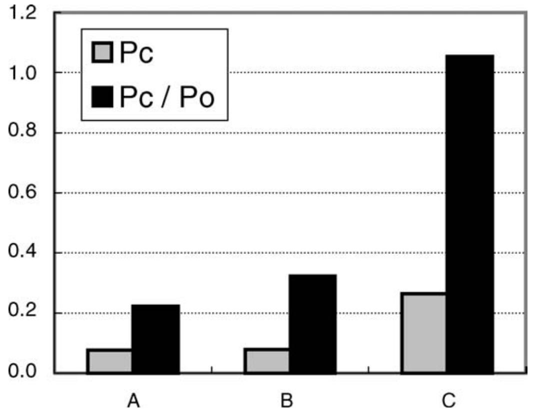

Figure 1 Comparison of the closed porosity and the ratio of the closed porosity to the open porosity of the samples obtained by the different drying methods.

porosity of the samples prepared by those three different drying methods. Both P_c and P_c/P_o increase as the drying is more rapid. This trend indicates that the pore geometry is changed from the open one to the closed one in the silica structure as the drying rate is increased.

Nitrogen adsorption–desorption isotherms were used to characterize the open pores of the mesoporous silica. As shown in Fig. 2, the three samples were all featured by the type IV isotherms attributed to typical mesoporous structures [5]. Sample A shows a small type-H_2 hysterisis loop characteristic of cage-like pore structure, while sample B shows a clear type-H_1 hysteresis loop with parallel adsorption and desorption branches indicating a uniform pore size distribution characteristic of cylindrical pore geometry [6, 7]. The isotherm of sample C features a two-step hysteresis loop at the relative pressure range of 0.4–0.72 and 0.72–0.9, indicating that the sample has two types of pores with different sizes as observed in the TEM image. It should be noted that the size of the open pores captured by nitrogen adsorption gradually increases as the drying rate is higher (from sample A to sample C).

Typical TEM images of samples A, B, and C were shown in Fig. 3. Significant influence of the drying method on the resultant mesoporous structure can clearly be seen. Sample A shows random worm-like pore structure with the pore size of about 3 nm. In contrast, sample B exhibits entirely arrayed cylindrical pores with pore diameter of approximately 5 nm. However, in sample C, liquid crystalline structure abates where both the spherical and the rod-like pores are clearly seen with slightly larger pore diameter of about 7 nm.

As the drying rate is increased, the pore geometry is changed from the open one constituting the liquid crystalline array typically seen in Fig. 1B to the mutually isolated one in the amorphous micellar phase. Therefore, the more rapid drying can be considered to be more advantageous to replicate the mutually isolated micelles of pluronic P123. On the other hand, the moderate drying leads to the formation of open pores. More detailed discussion of the mechanism of formation of closed pore structure will be given in our following work.

The difference of the structure among these three samples is also indicated by TGA. The three samples exhibited different weight loss profiles and different peak positions of weight loss derivative curves. The copolymers in samples A and B were decomposed in a similar temperature range, centering at 228 and 229 °C, respectively, while sample C decomposed at a higher temperature of 316 °C. This peak temperature shift is considered to be related to the structure affecting the interaction between silica matrix and the block copolymer [8]. When the block copolymers arrange into ordered arrays and form interconnected pore structure,

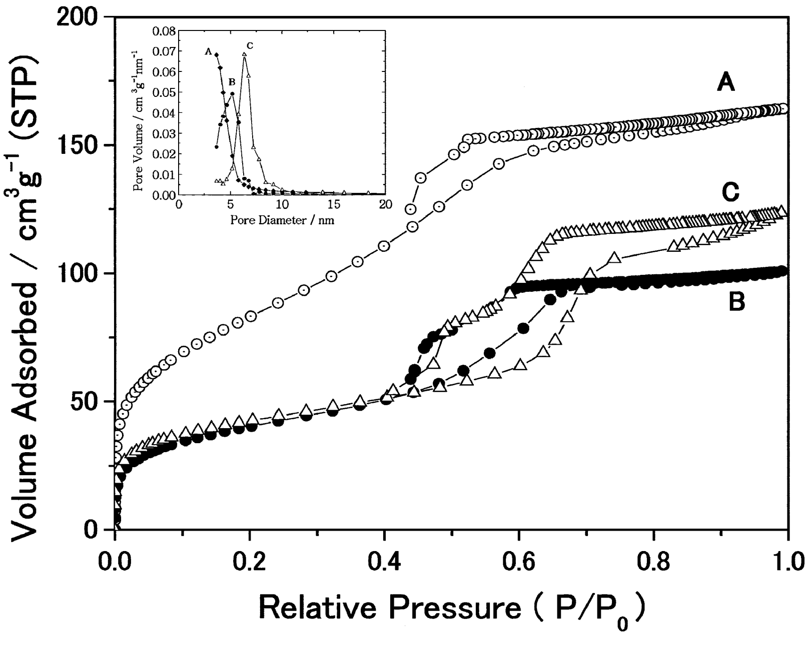

Figure 2 Nitrogen adsorption–desorption isotherms for the mesoporous silica prepared by three different drying methods at the same temperature of 90 °C. The inset shows the corresponding pore size distributions obtained from the isotherm.

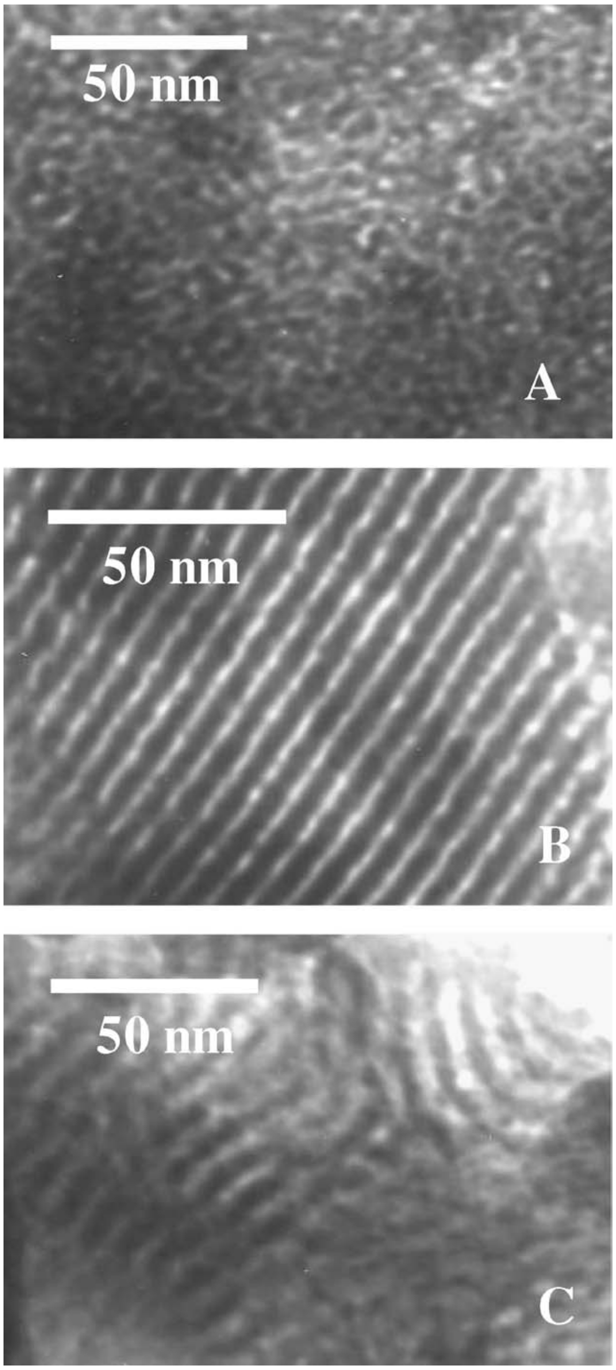

Figure 3 TEM images of calcined mesoporous silica using P123 triblock copolymer as template prepared by three different drying methods at 90 °C.

they can be easily removed because of the presence of the open channels along the arrays in the porous silica (samples A and B). As the pore structure gradually becomes more enclosed, a higher temperature will be required to remove the block copolymers because they are more highly embedded in the silica matrix (sample C).

In conclusion, closed pores can be formed in mesoporous silica templated by triblock copolymers. The rate of drying is quite influential for the finally templated mesoporous structure of the silica. The more rapid drying is more preferable for replicating the mutually isolated pluronic P123 micelles which results in the closed pores in the mesoporous silica. The rapid drying can be expected to be a pathway to nanoporous silica templated from pluronic molecular aggregates with superior mechanical or electrical properties in practical aspects.

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