One-pot Preparation of Mesoporous Silica Particles Having Mesopore Surface Functionalized with Poly(propylene oxide) Chains

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Mesoporous silica particles having mesopore surface functionalized with poly(propylene oxide) (PPO) chains were prepared in one pot by using newly designed triethoxysilyl-terminated poly(ethylene oxide) (PEO)–PPO–PEO triblock copolymers with structure-directing and surface-modifying dual functions.

PEO–PPO–PEO triblock copolymers, such as P123, F127, etc., are composed of hydrophilic PEO chains and hydrophobic PPO chains. Such triblock copolymers are self-assembled to form core–corona-like spherical micelles in aqueous solutions.[1] The core consisting of hydrophobic PPO chains is surrounded by hydrophilic PEO chains. Therefore, water-insoluble molecules, such as nonsteroidal anti-inflammatory drugs, antitumor drugs, and genes, can easily be incorporated into the core of the micelles.[1] Such micelles have been studied as careers for drug and gene delivery systems. However, such applications have been limited under mild conditions because of their low mechanical and chemical stabilities.[1]

By using such triblock copolymers as structure-directing agents,[2] mesoporous silica with larger mesopores can be synthesized. As-prepared mesostructured silica as a precursor has hydrophilic PEO chains incorporated partly within the silica wall, while hydrophobic PPO chains are present at the core.[3] The material can be regarded to take a core–corona-like structure surrounded with a rigid matrix of silica. Therefore, the as-synthesized mesostructured silica should have excellent mechanical and chemical stabilities and be applicable under various conditions (e.g., changes of temperature and solution concentration). However, assembled triblock copolymers within mesopores are easily removed/extracted in solutions,[2a,4] because they are not covalently bonded to the pore walls. Therefore, it is highly desirable that PEO–PPO–PEO copolymers are covalently bonded to the silica wall.

In this study, we prepared mesoporous silica particles (MS) having pore surface functionalized with PPO chains, by using a newly designed triethoxysilyl-terminated P123 (TES-P123, shown schematically in Figure 1)[5] as templates. TES-P123 dissolved in ethanol was added into dil HCl, followed by the addition of tetraethoxysilane (TEOS). The mixed solution was stirred at 45 °C for 20 h and aged at 80 °C for 24 h. After centrifugation the resultant powders were refluxed with a THF/HCl solution to remove unreacted TES-P123-derived species that were not bonded to the walls. TES-P123 was almost retained within the mesochannels (Only 10% of TES-P123 was extracted.), as confirmed by CHN data. The experimental details are described in the Supporting Information.[12]

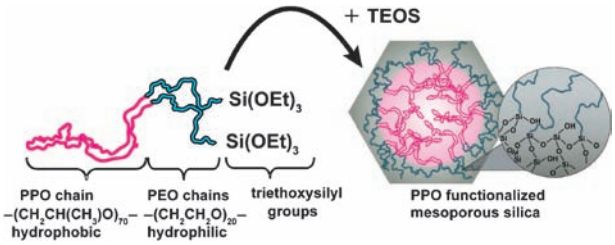

Figure 1. Schematic structure of newly designed TES-P123.

The low-angle XRD pattern of MS shows two peaks at the d values of 11 and 5.8 nm (Supporting Information, Figure S1).[12] The FE-SEM image shows the aggregation of particles of 100 nm in size (Figure S2).[12] Such morphology provides high accessibility of guest molecules. The TEM images (Figures 2 and S3)[12] show a wormhole-like mesostructure over the entire area. After the complete removal of the templates by calcination at 540 °C for 6 h in an air flow, the two peaks were retained and shifted toward the higher 2θ angles ($d = 9.1$ and 4.9 nm), meaning the formation of a 3D network porous structure. The reason for the formation of wormhole-like mesostructure rather than 2D hexagonal can be explained as the hindrance of smooth transformation from spherical micelles into 1D cylinderical ones of TES-P123 because of its high reactivity. The transformation is essential to form SBA-15 type 2D hexagonal mesostructure.[4]

The ^{29}Si CP/MAS NMR spectrum of MS shows three sharp signals at 108, 100, and 89.4 ppm assignable to Q^4, Q^3, and Q^2 units, respectively, indicating that the siloxane network is well developed (Figure S4).[12] Importantly, a weak signal at 63.0 ppm assigned to T^3 and/or T^2 unit can be observed. Therefore, TES-P123 is covalently anchored to the silica wall. As mentioned above, almost all TES-P123-derived species remained even after refluxing with a THF/HCl solution, being in contrast to conventional as-synthesized SBA-15 in which most of P123

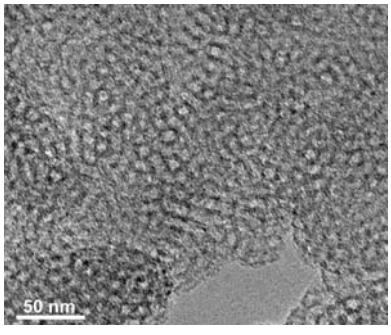

Figure 2. TEM image of MS.

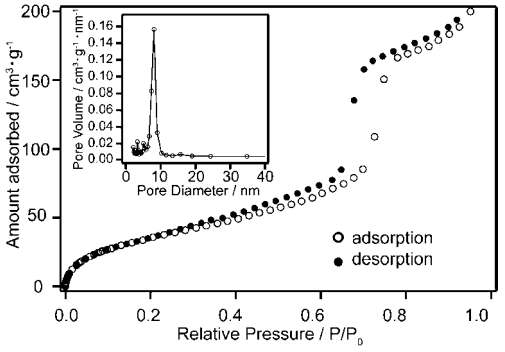

Figure 3. N_2 adsorption–desorption isotherm of MS. Inset: pore-size distribution calculated by the BJH method.

molecules can be removed by solvent extraction.[2a,4] More than 70% of P123 was extracted by the same reflux process (THF) for conventional as-synthesized SBA-15. The TG-DTA curves of the product show that the exothermic peak due to oxidative decomposition of the P123 fraction appears at around 140 °C, and the temperature is almost the same as that of P123 alone.

The N_2 adsorption–desorption isotherm of MS (Figure 3) shows type IV with clear H_1-type hysteresis. The surface area and pore volume were calculated to be $140\,m^2/g$ (BET) and $0.31\,cm^3/g$ (*t*-plot), respectively. The top of pore-size distribution is located at ca. 8 nm (Figure 3, inset).[6] Microporosity was not confirmed at all by *t*-plot, while calcined SBA-15 prepared with conventional P123 possesses microporosity.[7] This is one of the evidences that PEO chains are incorporated within the wall.

It is worth noting that the MS has uniform mesopores even though a large amount of TES-P123 is present within the mesopores. The micelle core consists of PPO chains containing a significant quantity of water.[8] The presence of water within the core can provide the mesoporosity of as-synthesized mesostructured silica even before the removal of templates (See Figure 3 in Ref. 9).[9] Therefore, MS obtained in this study possess uniform mesopores and provide the surface area higher than $100\,m^2/g$.

The surface property of MS was compared with that of calcined MS (BET surface area: $620\,m^2/g$) by water vapor adsorption–desorption isotherms (Figure S5).[12] The isotherm of MS shows a type III behavior without capillary condensation, indicating that the inner pore surface has a hydrophobic nature.[10] On the other hand, the isotherm of calcined MS shows a type V with capillary condensation. The difference is attributed to the nature of the pore surfaces, because the organically modified surfaces show more hydrophobic property than that of SiO_2 surface. In addition, the desorption branch of the MS was closed at $P/P_0 = 0$, whereas that of the calcined MS was not closed. This means that the cleavage of siloxane bridges does not occur owing to the fully covered PPO chains on the silica surface.[11] Though the surface is hydrophobic, the total amount of adsorbed water molecules ($0.43\,g/g$) in MS in spite of low pore volume ($0.31\,cm^3/g$) means that the surface is less hydrophobic than the surfaces modified with alkysilyl groups.[10]

In conclusion, mesoporous silica particles having wormhole-like mesopores were successfully prepared by using newly designed triethoxysilyl-terminated P123. The surface within the mesopores was functionalized with PPO chains. This material has potential applications in diverse fields, such as carriers for biomolecules under mild conditions (e.g., human body) and adsorbents for toxic molecules from contaminated water. Moreover, this new material should be usable under various conditions because the PEO–PPO–PEO copolymers are covalently bonded to the silica wall.

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References and Notes

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5 Although Sosnik et al. reported the formation of triethoxysilyl-terminated PEO_{99}–PPO_{67}–PEO_{99} triblock copolymer containing urethane bond (A. Sosnik, D. Cohn, *Biomaterials* **2004**, *25*, 2851.), the urethane bond is cleavable in strongly acidic media like the present conditions. Therefore, in order to prevent the cleavage of terminal triethoxysilyl groups, we chose Williamson reaction followed by hydrosilylation for the preparation of TES-P123 (Supporting Information, Experimental Section).

6 Recently, the NLDFT method has been adopted to calculate the porosity of mesoporous materials. However, the PPO functionalized surface of MS is too complicated to simply adopt NLDFT. Therefore, we applied the BJH method for comparison with published data.

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12 Supporting Information is available electronically on the CSJ-Journal web site, http://www.csj.jp/journals/chem-lett/.

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