나노기공 함유 고분자 물질과 응용

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Nanoporous Polymeric Materials and Their Applicaions

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Surfactant-templated mesoporous silica materials have attracted great interest since the discovery of hexagonally ordered mesoporous silica material (M41S) by Mobil Corporation.[1] Structures and pore sizes of the mesoporous silica materials have been varied by several surfactants and polymeric templates. Particularly, nonionic poly(ethylene oxide) surfactants or triblock poly-(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) copolymers as structure directing templates have been widely used for preparing mesoporous silicas such as SBA-15,[2-4] SBA-16,[3] and MSU-X.[5,6] The synthetic route of employing nonionic block copolymers has advantages for forming thicker walls, nontoxicity, and easy removal of the polymer during calcination. The block copolymer templates obviously yield larger structural features compared with the structural size obtained with low molecular weight surfactants. Recently, a new class of mesoporous materials have been reported such as the periodic mesoporous organosilicas (PMOs).[7-11] These materials are unique in containing organic functional groups inside the channel wall. The organic modification of the silica framework provides diverse variation of optical, electrical, and mechanical properties. However, the organosilicas prepared by block copolymer templates have not yet been reported extensively in the literature.

In the present study, we describe the synthesis of mesoporous organosilicas from the co-condensation of TEOS and 1,2-bis(trimethoxysilyl)ethane (BTMSE) by using PEO-containing triblock copolymer templates such as F127 ($EO_{106}PO_{70}EO_{106}$; BASF) and poly-(ethylene oxide)-poly(DL-lactic acid-*co*-glycolic acid)-poly(ethylene oxide) (LGE76, $EO_{43}(L_{23}G_6)EO_{43}$, PEO-PLGA-PEO). More hydrophobic PLGA block, compared with the PPO block in the PEO-PPO-PEO block templates, is chosen to provide more contrast between hydrophilicity and hydrophobicity of a block template such that the organosilicate is confined in the aqueous matrix phase.[12] We also report the hydrothermal stability of cylindrical mesoporous organosilicas (MOL-1) from 1,2-bis(triethoxysilyl)ethane (BTESE) using a LGE54 ($EO_{16}(L_{23}G_6)EO_{16}$, PEO-PLGA-PEO) template.

Figure 1 shows the SAXS data for mesoporous organosilicas containing different amounts of BTMSE in TEOS templated with two different types of block copolymers. In the case of employing the F127 triblock template, we found that the cubic morphology is maintained until 10 wt % of BTMSE is incorporated into the silica source, as shown in Figure 1a (traces A to C). The analysis of higher order peaks in traces A-C of Figure 1a confirms the formation of cubic (*Im*3h*m*) morphology as previously verified by Zhao and co-workers.[3] The high periodicity, surface area, and pore volume of the mesoporous organosilicas containing BTMSE of <10 wt %

are also verified with N_2 adsorption data (Table 1). Figure 1b illustrates the powder small-angle X-ray scattering patterns of calcined ethanesilicas obtained with the LGE76 triblock template as a function of BTMSE content in the total silica. Scattering patterns show a single intense reflection with *d* spacing values from 91 ($2\theta = 0.97$) to 98 Å ($2\theta = 0.91$). N_2 adsorption data (Table 1) also verify that a large amount of mesopore is still maintained, even after the addition of 60 wt % BTMSE in the silica, although the samples are found to be less ordered in the long range. These results imply that the LGE76 triblock template is quite effective for forming mesoporous organosilica materials containing a large amount of BTMSE. We, however, noticed that the LGE76 triblock copolymer in dilute aqueous solution is not homogeneously dissolved, as evidenced in the dynamic light scattering data (i.e., a small amount of micelle cluster is observed) and thus does not form monodisperse micelles, which is necessary for forming the ordered cubic morphology.

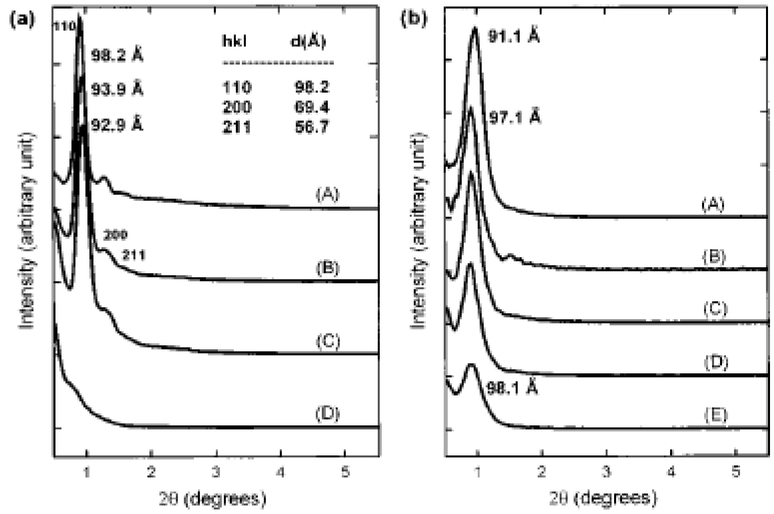

Figure 1. Powder small-angle X-ray scattering patterns of mesoporous ethanesilicas containing different weight proportions of TEOS and BTMSE. (a) Calcined samples of SBA-16 (trace A), S16-B5 (B), S16-B10 (C), and S16-B15 (D). (b) Calcined ethanesilicas prepared with LGE76 (EO43(L23G6)-EO43) template of LGE-B0 (trace A), LGE-B10 (B), LGE-B30 (C), LGE-B50 (D), and LGE-B60 (E). Numbers represent *d*-spacing values.

Table 1. Physicochemical Properties of Mesoporous Ethanesilicas[a]

sample code	block copolymer	BET surface area ($m^2 g^{-1}$)	pore volume[b] ($cm^3 g^{-1}$)	pore diameter[b,c] (nm)
S16-B5	$EO_{106}PO_{70}EO_{106}$	933	0.54	4.9
S16-B10	$EO_{106}PO_{70}EO_{106}$	640	0.38	4.2
S16-B15	$EO_{106}PO_{70}EO_{106}$	432	0.45	58.5
LGE-B10	$EO_{43}(L_{23}G_6)EO_{43}$	666	0.39	6.4
LGE-B30	$EO_{43}(L_{23}G_6)EO_{43}$	595	0.33	5.8
LGE-B50	$EO_{43}(L_{23}G_6)EO_{43}$	572	0.37	5.8
LGE-B60	$EO_{43}(L_{23}G_6)EO_{43}$	470	0.34	5.7

[a] N_2 adsorption-desorption isotherm data were measured on a Micromeritics ASAP 2010 analyzer. Samples were pre-degassed at 200 °C and 30 μm Hg for 6 h. [b] Pore volumes and sizes reported here were calculated from the adsorption branches of the isotherms by the BJH method. [c] Pore diameter represents the one at the maximum of pore volume in a pore size distribution.

In the case of employing the BTESE as an organosilica precursor source, we found that the MOL-1 organosilica material shows the cylindrical mesostructure, but is not highly ordered hexagonal structure, as shown in the scattering pattern of Figure 2(a) and the TEM images of Figure 2(b, c). It is thought that the hydrophobic contrast of the PLGA block is so large in comparison with the hydrophilic PEO block that most of BTESE organosilica precursors is easily confined in the aqueous continuous phase. Small angle X-ray scattering pattern in Figure 2(a) shows an intense reflection with a *d*-spacing value of 94 Å and rather weak reflections corresponding to (110) and (200) peaks. Figure 2(c) is the TEM image parallel to the channel axis of a solvent-extracted MOL-1 sample indicating the cylindrical pattern.

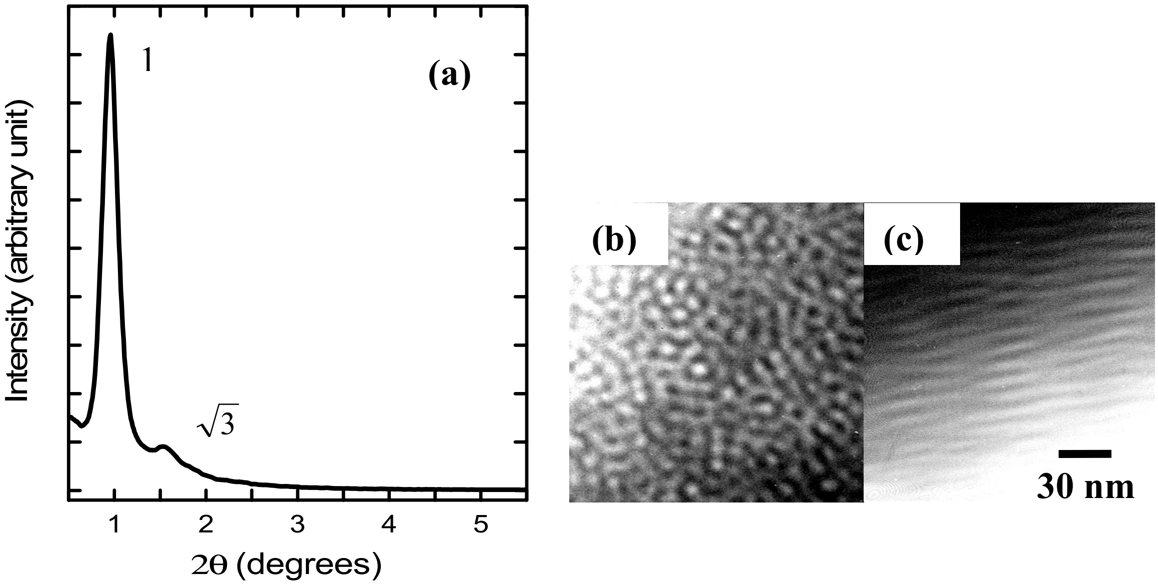

Figure 2. (a) SAXS pattern and (b) and (c) TEM images for a solvent-extracted MOL-1 (mesoporous ethanesilica prepared with a LGE54 ($EO_{16}(L_{23}G_6)EO_{16}$) triblock copolymer template).

To examine the hydrothermal property, a solvent-extracted MOL-1 was heated in boiling water at 100°C for several days without additional treatments. As shown in Figure 3, all the scattering patterns are retained after being treated in boiling water for approximately 600 h. This extraordinary hydrothermal stability of the MOL-1 compared to the general mesoporous materials is believed to originate from its thick pore wall, the high degree of condensation, and the hydrophobicity of the organosilica framework based on the ethane moieties of the BTESE organosilica precursor.

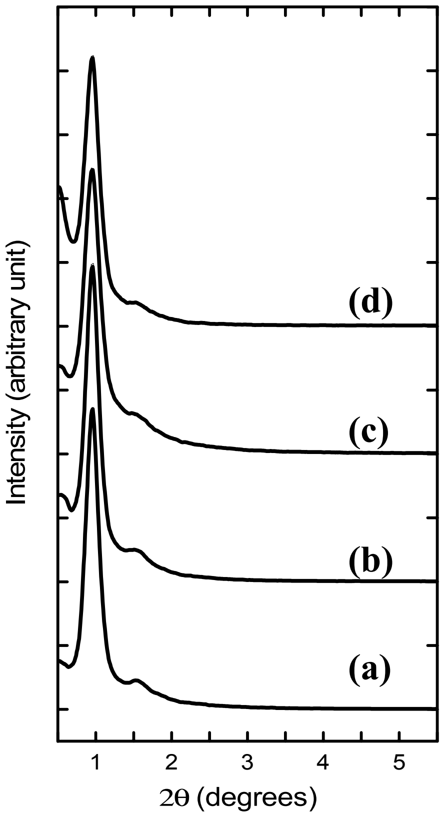

Figure 3. SAXS patterns of a solvent-extracted MOL-1 after different hydrothermal treatment: (A) is solvent-extracted and (B), (C) and (D) samples are obtained after treatment in boiling water for 240 h, 480 h, and 600 h, respectively.

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