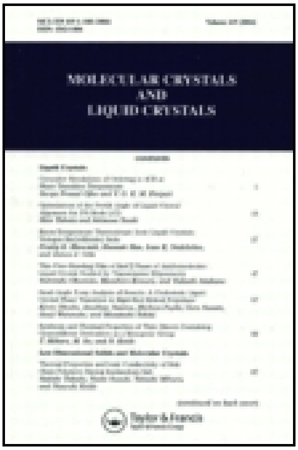

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Synthesis of Mesoporous Silica by Templating of Amphiphilic Poly (ethylene glycol)-Block-Poly (propylene glycol)-Block-Poly(ethylene glycol)

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Mesoporous silicas have been prepared using poly (ethylene glycol)-b-poly (propylene glycol)-b-poly (ethylene glycol) with average molecular weight of 8400 and 5800 as directed structure agent under neutral condition in the presence of methanol. X-ray diffraction experiment indicated that samples are mesoporous silicas with certain ordered structural pore. Thermogracimetric and differential thermal analyses (TGA/DTA) measurement showed two exothermic peaks in the DTA curve, the second peak proved that there is strong interaction between silica framework and organic template.

Keywords: poly (ethylene glycol)-b-poly (propylene glycol)-b- poly (ethylene glycol); templating; mesoporous silica; neutral condition

INTRODUCTION

Mesoporous materials are considered solid containing pore size in range of 2-50 nm. In the past several years, these materials have been developing because of their potential applications: shape-selective catalysis of large organic molecules, hosts for organic polymer during preparation of organic/inorganic nanocomposites, sorption and chromatographic separations and so on. Traditional techniques for synthesis of mesosilicas utilize low molecular weight surfactant as structure-directing agent [1-4]. Since amphiphilic block copolymers are various in molecular weight and properties, and the relative length of hydrophobic and hydrophilic segment, the preparation of porous materials with pore size in meso-, macro- scale and various pore shape became entirely possible. Pinnaavaia et al., by using nonionic polyethylene oxide surfactant [5], have been prepared mesoporous sieve with wormlike disordered channel structure and uniform pore diameter. After that, Stucky group successfully prepared mesoporous silicas with well-ordered hexagonal pores structure and uniform pore sizes up to 300 angstroms under strong acidic condition in the presence of triblock copolymer and cosolvent organic molecules as a swelling agent [6, 7]. Recently, researchers paid attention to the catalytic role of fluoride on organization of the periodic porous materials and tried to extend the pH range of template solution, but fluoride leads to regularity decreasing, when pH exceed 2.7, disorder materials would be obtained [8]. Obviously, synthesis of mesoporous materials with ordered porous structure under neutral condition is significant in the commercialization. However, there is not any report relate to synthesis of periodic well-ordered structure mesoporous silica that assembled by nonionic amphiphile and inorganic precursor in neutral or basic media so far.

Here we reported synthesis of mesoporous silicas with certain ordered pore structure in neutral aqueous solution by using poly(ethylene glycol)-b-poly(propylene glycol)-b-poly(ethylene glycol)(PEG-PPG-PEG, abbrevuated $E_n P_m E_n$) as templates.

EXPERIMENTAL

Preparation of sample #1: The template solution was prepared by dissolving 1.68g (2.0×10^{-3} mol.l^{-1}) poly(ethylene glycol)-b-poly (propylene glycol)-b-poly(ethylene glycol) (Aldrich, PEG_{76}-PPG_{29}-PEG_{76}) in 90ml de-ionized water under moderate stirring at 50℃ for 6h.. The mixture of 10ml methanol and 11.1ml Tetraethylene orthosilicate (TEOS, from TCI, Japan) was dropped slowly into the template solution, precipitation occurred after stirring 24h. The solid precipitate was filtered by membrane with pore size of 0.01 μm. During filtering, products were allowed to be washed in de-ionic water and ethanol. White fine powder can be obtained by drying in air for 7 days at room temperature. The solid products were kept at 100℃ for 2h in the oven, and were then calcined at 500℃ in air for 8h to simultaneously remove template and condense the framework formed. Sample #2-#4 have been synthesized under condition showed in TABLE 1.

N_2 adsorption /desorption experiments were carried out on a Micrometeritics Instrument corporation ASAP2010 with accelerated surface area and porosimetry system at 77K. The parameters related to pore were calculated by BJH or BET method with software of the apparatus. Thermogravimetric and differential thermal analyses (TG/DTA) were carried out in nitrogen on a Netzxch Thermoanalyzer STA409 with heating rate of 10K/min. Small angle X-ray diffraction (SAXRD) experiments were performed on a Siemens D500 X-ray diffractometer using Ni-filtered radiation (λ = 0.154178 nm, coming from accelerated equipment, PLA in POSTECH).

TABLE 1. Synthetic condition of mesoporous silicas

Sample Number	Block Copolymer	Concentration of Copolymer(mol.l^{-1})	Synthetic Temperature	Synthetic Time (h)
#1	$E_{76}\,P_{29}\,E_{76}$	2.0×10^{-3} mol.l^{-1}	50℃	24
#2	$E_{76}\,P_{29}\,E_{76}$	0.5×10^{-3} mol.l^{-1}	50℃	24
#3	$E_{20}\,P_{70}\,E_{20}$	2.0×10^{-3} mol.l^{-1}	45℃	144
#4	$E_{20}\,P_{70}\,E_{20}$	3.0×10^{-3} mol.l^{-1}	45℃	144

RESULTS AND DISCUSSION

Some parameters of mesoporous silicas obtained by N_2 adsorption experiments were shown in TABLE 2., and N_2 adsorption and desorption isotherm of four samples were illustrated in FIGURE 1.

TABLE 2 showed that all characteristic pore sizes of samples are range of mesoscale (2.0-50nm) and the average pore diameters of sample #3 and sample #4 prepared by using $E_{20}\,P_{70}\,E_{20}$ are more long than of sample #1 and sample #2 synthesized by $E_{76}\,P_{29}\,E_{76}$. Generally, PEG-PPG-PEG block copolymer formed micelles with regular shape that consisted of PEG hydrophilic block in shell and PPG hydrophobic block in core. Longer hydrophobic block may result in mesophase with larger pore size and longer hydrophilic block may lead to mesophase with larger surface area and make reaction between aggregates of amphiphile and inorganic precursor rapidly complete. In our present, mesophase precipitation occurred after 24h adding silica precursor when using amphiphile E_{76} P_{29} E_{76} with long EG segment, whereas this process need 144h in E_{20} P_{70} E_{20} with short hydrophilic block case.

TABLE 2. Characteristic pore size calculated by N_2 sorption experiments

Sample number	BET surface area (m^2g^{-1})	BET average pore diameter (nm)	BJH average pore diameter (nm)	Single point total pore volume ($cm^3.g^{-1}$)
#1	553	2.25	2.10	0.311
#2	345	5.50	4.42	0.469
#3	529	14.6	10.34	1.93
#4	538	17.2	13.38	2.31

FIGURE 1 is the N_2 sorption isotherm of mesoporous material (sample #1), exhibiting a VI type isotherm [9]. A condensation step can be observed at relative pressure (P/P_0) of 0.3-0.5, a hysteretic loop appeared in desorption curve. The other samples have similar shape curves with FIGURE 1. So we suggested that mesoporous silicas were formed.

Although methanol initially destroys the liquid crystalline order formed by surfactant [7], in our work the methanol added was evaporated in short time due to high synthetic temperature contrast with boiling point of methanol. Methanol makes TEOS molecules fully disperse, and thereby enhance assemble ability of TEOS molecules. Moreover, the addition of methanol has brought several advantages: (1) high yields with respect to silica and surfactant can be achieved; (2) the degree of order in pore can be made greater than in a pure aqueous solution, etc [10].

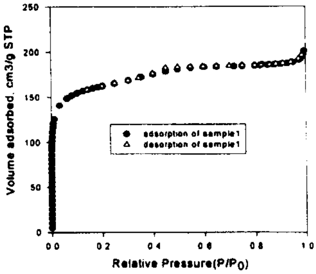

FIGURE 1 The N_2 sorption isotherm of sample#1.

FIGURE 1 is the N_2 sorption isotherm of mesoporous material (sample #1), exhibiting a type IV isotherm [9]. A condensation step can be observed at relative pressure (P/P_0) of 0.3-0.5, a hysteretic loop appeared in desorption curve. The other samples have similar shape curves with FIGURE 1. So we suggested that mesoporous silicas were formed.

SAXD pattern of mesoporous silicas prepared in the presence of methanol by templating of amphiphilic block copolymer E_{76} P_{29} E_{76} under neutral condition. This pattern contained a sharp diffraction peak at 9.53nm and two peaks with high intensity at 10.3nm and 8.76nm. These peaks are obvious narrower than peak of disordered mesoporous material such as MSU-1 silica [5] and very similar to SBA-11 calcined with well ordered hexagonal pore [7]. Although we can not determine the pore shape from this pattern, but it is clear that mesoporous silicas in this work have certain ordered pore.

There are two exothermic peaks in DTA curve that were measured by Thermogravimetic (TG) and differential thermal (DTA) analyses of sample #1 (shown in FIGURE 3) An exothermic peak at 194.2℃ (18wt%) is assigned to desorption and decomposition of E_{76} P_{29} E_{76} on the surface of silicas powder, another peak at 313.5℃ (35wt%) can be assigned to pyrolytic degradation of E_{76} P_{29} E_{76} combined at inner surface of silica channel.

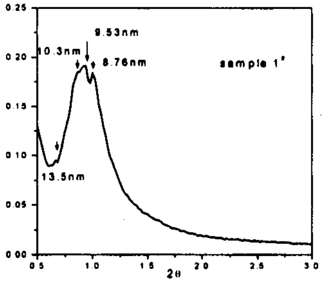

FIGURE 2 Small angle X-ray diffraction pattern of mesosilicas sample *1.

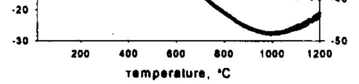

FIGURE 3 TG-DTA curve of mesoporous silica by templating of E_{76} P_{29} E_{76}

CONCLUSION

By using triblock copolymers PEG_{76}-PPG_{29}-PEG_{76} and PEG_{20}-PPG_{70}-PEG_{20} as template, mesoporous silicas with certain ordered porous structure have been prepared in the presence of methanol under neutral condition. Though low yield of mesoporous silica with well-ordered pore, some of characteristic parameters have been not measured perfectly. But there is not doubt that certain ordered pore indeed exits in mesoporous silicas.

Acknowledgments

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