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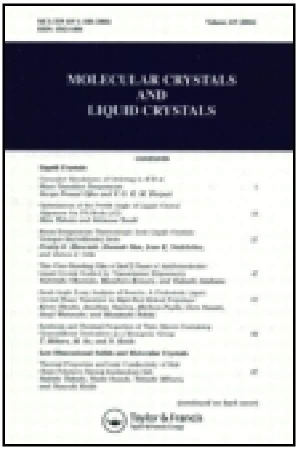

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Synthesis of Mesoporous Silica by Templating of Amphiphilic Diblock Copolymer Under Neutral Condition

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Synthesis of Mesoporous Silica by Templating of Amphiphilic Diblock Copolymer Under Neutral Condition

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Mesoporous silicas have been synthesized by templating of a linear diblock copolymer, poly(ethylene glycol-b-propylene glycol) in the neutral aqueous solution. The N_2 adsorption behavior with the Barrett-Joyner-Halenda(BJH) method showed monodisperse pore size distribution. The high-resolution scanning electron micrograph showed that the pore size ranges 20 to 80nm. The results were compared to those templates by a triblock copolymer, poly(ethylene glycol-b-propylene glycol-b-ethylene glycol).

Keywords poly(ethylene glycol-b-propylene glycol, poly(ethylene glycol-b-propylene glycol-b-ethylene glycol), templating, neutral aqueous solution, mesoporous silica, nanoporous materials

INTRODUCTION

Synthesis of nanoporous materials by using template of surfactant has attracted much interests due to their wide applications in catalytic reaction, separation, and purification. For templating, most studies focused on the low molecular weight surfactants such as cetyltrimethylammonium bromide (CTAB)[1], which easily form aggregates with globular, cylindrical, and hexagonal shape in solution. On the other hand, amphiphilic block copolymers in the aqueous or other solutions have ability to self-assemble and invoke well-ordered micelles or liquid crystal, around which the silicate source condense or

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chemicals attract. This process hints that some macromolecular architecture can be employed as template in the synthesis of nanoporous materials at different space and time scales.

Stucky and co-workers have synthesized successfully the ordered mesoporous silicas with pore size of 30nm by templating of poly (ethylene oxide)-b-poly (propylene oxide)-b-poly (ethylene oxide) *triblock copolymer (PEO-PPO-PEO)* at $pH<<1$[2]. Under neutral aqueous conditions, the disordered mesoporous material was prepared in the presence of polyethylene oxide (C_mEO_n) as the structure-directing agent [3]. Yaser, et al [4], using poly (ethylene oxide-b-butylene oxide-b-ethylene oxide), have reported the synthesis of silica products with spherical morphology in the acid aqueous solution.

It is evident that preparation of nanoporous materials at neutral route has important advantages compared with that at acidic or basic condition for further commercialization. The present work concerns the use of poly (ethylene glycol-b-propylene) diblock copolymer, $E_{205}P_{51}$, as a template in the synthesis of nanostructured precipitates in the neutral aqueous solution. The results were compared to those templated by poly (ethylene glycol-b-propylene glycol-b-ethylene glycol)(denoted as $E_{76}P_{29}E_{76}$) triblock copolymer.

RESULTS AND DISCUSSION

The phase behavior of amphiphilic block copolymer in solution strongly depends on not only temperature and concentration of copolymers, but also the relative length of hydrophobic block PPG and hydrophilic block PEG [5]. The characteristic pore sizes calculated by BET, Langmuir and BJH method are in Table 1. The results here indicate that mesoporous silicas have high surface area, pore volume and large pore-size, even under templating of a linear diblock copolymer. As in the case of $E_{76}P_{29}E_{76}$ with longer hydrophobic block PPG, the average pore size of nanoporous silica was larger when using $E_{76}P_{29}E_{76}$ than using $E_{205}P_{51}$.

N_2 sorption isotherm plot of the prepared porous silica from TEOS and amphiphiles are shown in Fig. 1, which exhibits a hysteresis loop instead of nearly retracing the adsorption curve. This behavior is typical of mesoporous and macroporous materials. The corresponding insets are BHJ pore size distribution determined from the N_2 adsorption isotherm.

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TABLE 1. The characteristic pore size calculated from N_2 sorption isotherm.

Pore size Tem-Plate	BET Surface Area (m^2g^{-1})	Langmuir Surface Area (m^2g^{-1})	BET Average Pore Diameter	BJH Average Pore Diameter	Single Point Total Pore Volume (cm^3g^{-1})
$E_{76}P_{29}E_{76}$	630.3	877.6	138.0Å	102.6Å	2.17
$E_{205}P_{51}$	1173.7	1628.8	104.3Å	84.6Å	3.06

Although the range of pore-size is wider than that at strong acid condition [2], the distributions of pore-size are monodisperse for both $E_{205}P_{51}$ and $E_{76}P_{29}E_{76}$ templating. The high-resolution SEM micrographs clearly showed that calcined solid products have rod-like pore, and the morphology of nanoporous silica by templating of $E_{205}P_{51}$ is different from that by $E_{76}P_{29}E_{76}$. In the case of $E_{76}P_{29}E_{76}$, there are many nanoparticles covered in the surface.

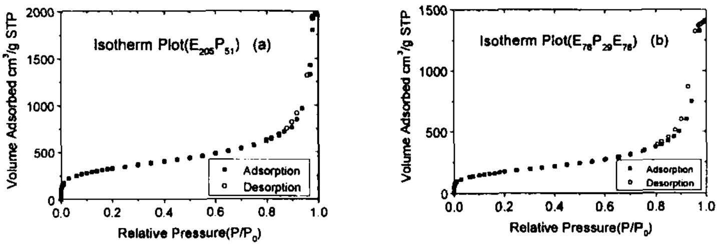

FIGURE 1. N_2 sorption isotherm and pore-size distributions. (a)$E_{205}P_{51}$, 1.0×10^{-3}mol.l^{-1}; (b)$E_{76}P_{29}E_{76}$,4.0×10^{-3}mol.l^{-1}.

The data obtained here for $E_{76}P_{29}E_{76}$ and $E_{205}P_{51}$ templated silica are insufficient to assign conclusively pore shape and characteristic pore size at moment. However, it is allowed to suggest that nanoporous silica with certain order pore can be synthesized under neutral condition by templating of linear diblock copolymer as well as triblock copolymer.

Finally, we noticed that the pore diameters observed from the high-resolution SEM micrograph (Fig 2a) are larger than 30nm, which Stucky group[2] reported. It was concluded that the templating by $E_{205}P_{51}$ favors to form products with large pore except that the order of pore structure was sacrificed, in comparison to that by $E_{76}P_{29}E_{76}$.

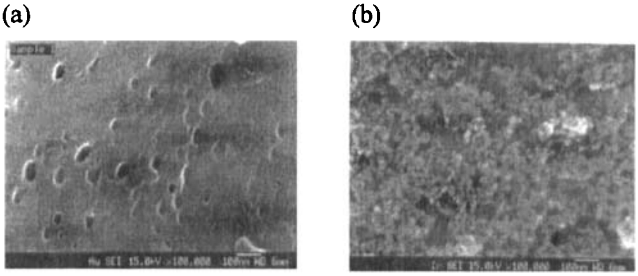

FIGURE 2. Scanning Electron Micrographs of mesoporous silicas.
(a) $E_{205}P_{51}$ (b) $E_{76}P_{29}E_{76}$

CONCLUSION

In neutral condition, nanoporous silicas with high surface area and pore volume have been synthesized by templating of a linear diblock copolymer $E_{205}P_{51}$ as well as of a triblock copolymer $E_{76}P_{29}E_{76}$. The distribution of pore size measured by BJH method in N_2 adsorption was monodisperse. The range of pore size is 20-80nm from high-resolution scanning electron microscope.

Acknowledgment
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