

## 블록 공중합체 주형 나노포러스 실리카 및 고분자 재료의 상 전이 연구

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## Phase Transition in Polymer-Templated Nanoporous Silica and Nanostructured Polymeric Resins

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서론

Mesoporous materials with uniform pore sizes in the range of 2 - 50 nm have received interest due to their excellent material characteristics such as large surface area, unique pore structure and adsorption capacity and tunable pore sizes.<sup>1</sup> Typical examples are the M41S family that may be efficient to process large molecules in a nanometer level in many practical applications.<sup>2</sup> It has reported that these types of materials are synthesized by hydrothermal reaction in the aqueous media through the combination of ionic surfactants as the structure directing agents and appropriate amount of a silica source with the addition of a catalyst.<sup>2</sup> Most procedures developed thus far use low molecular weight surfactants as structure-directing agents and auxiliary inorganic precursors for assembly into the mesophase precipitant. Recently, amphiphilic block copolymers, structurally analogous to low molecular weight nonionic surfactants, can be used as templating agents to produce the nanoporous materials with large pore size.<sup>3</sup> These mesoporous materials obtained by the use of amphiphilic block copolymers would expand the areas for their applications, e.g. shape selective catalysts for large molecules and cooperative complexes for enantioselective catalytic reactions.

Significant advances of the physicochemical properties of these materials can be expected when the crystalline zeolites are incorporated into the silica frameworks. Recent research effort has focused on developing nanoporous materials with various framework compositions in an attempt to expand the range of materials available for the applications in many practical uses.<sup>4</sup> Porous materials with organically modified or organic framework are potentially useful in the separation of isomers and enantiomers, protein purification, trace adsorption and drug assays, and stereoselective synthesis.<sup>5-7</sup> These compounds are prepared by polymerizing organic monomers with the addition of surfactant in organic solvent media. Structure-directing templating materials are ionic surfactants or non-ionic amphiphilic block copolymers. Since the interaction between the monomers and amphiphiles is known to be absent, a long-range nanoscopic ordering is unaffected during the polymerization of monomers in the framework phase.

In the present study, we synthesize nanoporous silica using an amphiphilic block copolymer as structure-directing template in sol-gel solution. The morphology change of nanoporous silica is monitored as a function of the molar ratio between inorganic species and block copolymer by X-ray diffraction (XRD), transmission (TEM)

and BET analysis. Small angle neutron scattering (SANS) technique is employed at various reaction stages during sol-gel processing and provides the detailed information on the self-organization process of the organic and inorganic species into a supramolecular organic-inorganic self-assembly. Nanoporous organic polymeric nanostructures were also synthesized using an amphiphilic block copolymer in a hydrophobic media. The effect of water on the phase structure of block copolymer micelles in the reaction mixtures was explored by SANS technique.

## 본론

### 실험

The inorganic precursor solution of tetraethoxyorthosilane (TEOS) in ethanol (EtOH) was prehydrolyzed in aqueous HCl solution. The molar ratio of TEOS : EtOH : H<sub>2</sub>O : HCl was 1 : 3 : 4 : 0.04. This solution was refluxed at 60 °C for 90 min and then stirred at 25 °C for 15 min. The final solution was aged at 55 °C for additional 15 min without stirring. The solution of organic phase was prepared by dissolving the 10 g of EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub> (20 and 70 are molar ratios of ethylene oxide (EO) and propylene oxide (PO) in a single polymer chain) in a mixture of 23.33 g of D<sub>2</sub>O/H<sub>2</sub>O (60/40 in vol. %) mixed solvent and aqueous hydrochloric acid solution (0.145 g HCl / 2.658 g of D<sub>2</sub>O/H<sub>2</sub>O (60/40 in vol. %) mixed solvent). The molar ratio of TEOS to EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub> varied from 20 to 120. For convenience, the mesostructures synthesized with molar ratios of TEOS to EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub> of 20, 40, 60 and 120 denote M20, M40, M60 and M120, respectively. The interaction between the poly(ethylene oxide) (PEO) part of EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub> and hydrolyzed TEOS through PEO-SiO<sub>2</sub> complexation was mediated by HCl in 2.8 g 0.5 M aqueous HCl solution. Then both organic and inorganic precursor solutions were mixed for further reactions at 55 °C for 5 hrs. The resultant mixture was then poured into a petri dish and dried in air at room temperature for several weeks.

Nanostructured polymeric resins were synthesized as follows. Triblock copolymers EO<sub>15</sub>PO<sub>53</sub>EO<sub>15</sub> ( $\bar{M}_n=2700$ ), EO<sub>25</sub>PO<sub>7</sub>EO<sub>25</sub> ( $\bar{M}_n=2000$ ), EO<sub>14</sub>PO<sub>24</sub>EO<sub>14</sub> ( $\bar{M}_n=8400$ ), EO<sub>8</sub>PO<sub>22</sub>EO<sub>8</sub> ( $\bar{M}_n=5800$ ), EO<sub>76</sub>PO<sub>29</sub>EO<sub>76</sub> ( $\bar{M}_n=4400$ ), EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub> ( $\bar{M}_n=3300$ ) were purchased from Aldrich and used as received. Styrene, divinylbenzene were purchased from Aldrich and washed with aqueous NaOH (25 wt %) and distilled water for several times for removal of inhibitor and any residual reagent. Then they were dried with anhydrous magnesium sulfate prior to use. 2,2'-azobisisobutyronitrile (AIBN) was purchased from Aldrich and recrystallized before use. Then the polymerization of St / DVB in the mixtures of polymer / St / DVB / water was carried out by UV in the time scale of 4 ~ 5 hours in the presence of 2 weight % of AIBN.

SANS measurement was carried out on the facility at the HANARO center in KAERI with two-dimensional position sensitive 65×65 cm<sup>2</sup> area detector. The neutron scattering intensity was measured using a neutron wavelength of 5.08 Å and the sample-to-detector distance of 3 m. The equipment employs circular pinhole collimation with Bi/Be filter.

## 결과 및 토론

The TEM image of M20 (a) shown in Fig. 1 displays a flake-like morphology, whereas that of M40 (b) shows a hexagonal array of pore structure in large area. By visual inspection on the image, we measured the average diameter of the pore to be approximately 60 Å. Increasing the amount of TEOS in the mixed solution of TEOS and polymer leads to the change in the morphology of the mesostructure. Fig. 1 (c) shows the TEM image of M60 where the ordered pore structure was barely observed. Since it is wormlike, it may be disorderd.

Fig. 2 shows typical XRD data of the calcined mesostructures: (a) M40 and (b) M60. In Fig. 2 (a), we found an intense peak at  $2\theta = 1.24 \pm 0.01^\circ$  and a broad peak in the  $2\theta$  region between  $1.8$  and  $2.6^\circ$  which corresponded to 100 peak and the overlap of two 110 and 200 peak intensities. Based on the position of the 100 main peak intensity, the unit cell parameters were determined as  $a = b = 82.3 \text{ \AA}$  ( $\gamma = 120^\circ$ ). The pore diameter,  $D [=2d_{100}(\sqrt{3}\phi_{\text{pore}}/2\pi)^{1/2}]$ , where  $\phi_{\text{pore}}$  was 0.87, determined by the  $\text{N}_2$  adsorption-desorption measurement] was  $69.8 \text{ \AA}$ , quite similar to one measured by the TEM image.

The absence of the mesoscopic ordering for M20 and M120 was caused by the fact that organic-inorganic micellar self-assembling structure was not formed for these compositions. On increasing the relative amount of TEOS, the following sequence of phases is observed: a flake-like disordered phase, hexagonally packed cylindrical phase, disordered co-continuous phase and again flake-like disordered phase.

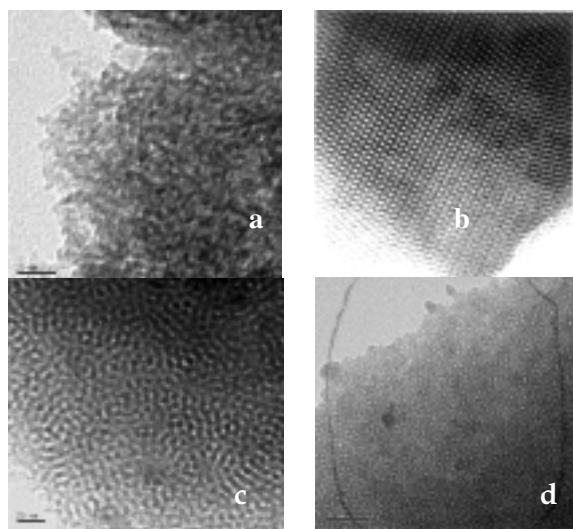


Figure 1. TEM images of the calcined mesostructures: (a) M20, (b) M40, (c) M60 and (d) M120.

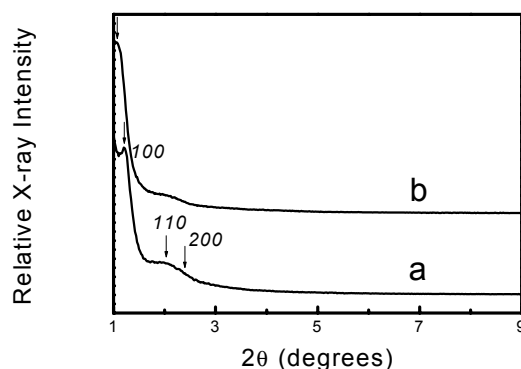


Figure 2. XRD data of the calcined mesostructures: (a) M40 and (b) M60.

The SANS intensity profiles were measured from the mixtures of  $\text{EO}_{76}\text{PO}_{29}\text{EO}_{76}$ /styrene/divinylbenzene/water at different  $\text{H}_2\text{O}/\text{EO}$  ratios. The characteristic features shown in the SANS patterns for  $w = 1.30$  are similar except the change especially in high order peak intensity. The major peaks for  $0.30 \leq w \leq 1.30$  were found at  $Q \sim 0.036 \pm 0.002 \text{ \AA}^{-1}$  and additional higher order peaks were

observed at  $Q_s$  which were in the ratio of  $\sqrt{3}$ , 2,  $\sqrt{7}$ , indicating a hexagonal packing of columnar micelles. Based on the position of the major peak, the lattice parameter was estimated as  $a = b = 202 \pm 9 \text{ \AA}$ . The similarity between the data for  $0.30 \leq w \leq 1.30$  revealed that the geometry of the lattice was not much changed by the increase of water content. It increased the population of columnar micelles, mostly arranged in a two dimensional hexagonal lattice, which caused the increase of the peak intensity. At higher  $w$  values, the major peak became broader than those at smaller  $w$  values and the scan profiles were changed, indicating the existence of the disordered, spherical mesocellular phase.

### 결론

Decreasing the relative amount of the structure-directing organic  $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$  during the TEOS sol-gel synthesis reaction led to the change in the morphology of the final pore structure from a disordered flake-like phase to a highly ordered columnar hexagonal phase, a disordered co-continuous phase morphology. During synthesis of nanostructured polymeric resins, the change of water in the reaction mixture leads to a change in morphology from a hexagonal columnar phase to a disordered, spherical mesocellular phase.

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