Small Angle X-ray Diffraction on Mesostructures Formed by Diblock Copolymer/Silicates Composite

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Studies of amphiphilic block copolymers have received a great deal of attention in recent years, particularly for those consisting of both hydrophilic and hydrophobic block in the molecules. As for the chemical nature, the hydrophilic portion of copolymers is generally consisted of polar functionality, which directs the incoming silicate molecules during the sol-gel process. In this context, polyethyleneglycol (PEO), a neutral ether linkage, ought to be a common use under acidic condensation of silicates, presumably due to the hydrogen bonding interaction (figure 1), as illustrated in SBA-15. In a recent work, we found that with a careful tuning the composition (f) and combination parameter (χN) of copolymer, the *Ia3d* cubic mesoporous silica could be synthesized by using a proper process and composition. poly(ethylene oxide)-*b*-poly(methyl acrylate) diblock copolymer ($EO_{23}MA_{17}$). Continuing on this trend, we have developed a method of polymerization based on atom transfer radical polymerization (ATRP), which can make precisely controlled amphiphilic block copolymers. The ATRP synthetic method provides a convenient way to control the composition and combination of the neutral diblock or triblock copolymers.

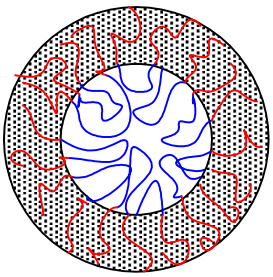
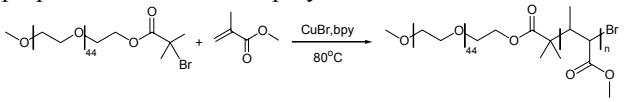


Figure 1. Self-assembly of PEO-PMA under acidic solution containing TEOS.

With a well tuning in the surfactant micellar properties and liquid-crystal phases, one can design the porosity, pore size, morphologies and mesostructures for extending the applications of mesoporous materials. Thus preparation of diblock copolymers is shown below



The EO_mMA_n-silica mesostructural composites were synthesized in acidic media as that for SBA-15 silicas. The as-synthesized mesoporous silica products were obtained after 1 day agitation at 25-50 °C. The final gel composition (in gram) is: (0.5)g PEO-PMA : (25.0)g H_2O : (6.0)g 37%HCl : (1~2.5)g TEOS. In order to increasing the mesostructural orderness and stability, 1.0 g dried acid-made mesoporous silicas was combined with 50.0 g water (pH ≈7.0) and then hydrothermally treated at 100 °C for 24 hr. In addition, the additon of organosilane as another silicon source was also investigated.

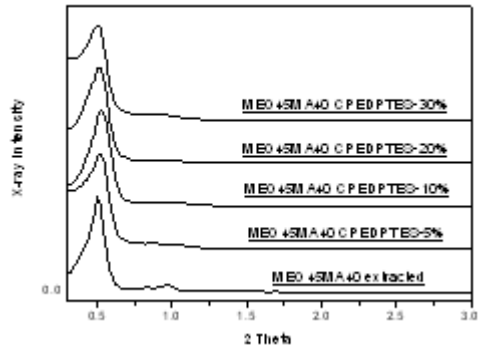


Figure 2. $PEO_{40}PMA_{44}$ with CPEDPTES

The powder x-ray diffraction patterns (XRD) were taken on Wiggler-A beamline (λ = 0.1326 nm) of Taiwan Synchrotron Radiation Research Center, Hsin-Chu, Taiwan. The TEM mesostructural images of mesoporous silicas were recorded on Hitachi S-7100 transmission electron microscope (TEM) with an operating voltage of 75 keV. The N_2 adsorption-desorption isotherms were obtained at 77 K on a Micromeritics ASAP 2010 apparatus, and the pore size distribution was calculated from the adsorption isotherms using the Barrett-Joyner-Halenda (BJH) method. Figure 2 shows the diffraction pattern of the synthesized materials.

From the BET dtermination, the pore size of the prepared samples is in the range of 9.5 – 10.9 nm for these mesoporous silicas, which are consistent with the XRD masurement. TEM image of the sample is shown below.