Morphological Transitions of Hierarchical Porous Nanostructures of Self-Assembled Block Copolymer/Dopamine Complexes

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Abstract

Hierarchical porous structures offer various remarkable properties, enabling the development of new materials and methods to expand their vast applications, which include catalyst, energy conversion, separation technology, and bioengineering. Hierarchical porous structures can be prepared using mixtures of self-assembly block copolymers (BCPs) and small molecules such as dopamine as a carbon source. Dopamine is capable of self-polymerization in the presence of alkaline compounds to form polydopamine which has high carbon yields when pyrolyzed at an elevated temperature. BCPs act as the template of developing porous structures during pyrolysis. The dimension of the hierarchical porous structure could be tailored by adjusting chemical architectures and micro-phase separation behavior of BCPs. However, the polymerization of BCP/Dopamine complexes usually yield microsphere structures and are unable to be synthesized under acid condition as the result of the hazardous acid-base reaction. In this research, we aim to study hierarchical porous structures of mixtures of polystyrene-block-poly(ethylene oxide) (PS-b-PEO) complexed with dopamine in the presence of hydrochloric acid in solution and bulk. These materials formed cylindrical micelles in solution due to the use of co-solvent H_2O/THF. Cylindrical micelles can be kinetically trapped in dried bulk due to the quick removal of the solution. Our preliminary experimental results show that the PS-b-PEO acts as a building block to form a mixture of spherical and cylindrical micelles through the microphase separation as dried from a mixed solution of H_2O/THF co-solvents. PS-b-PEO formed a complex with dopamine molecules through hydrogen bonding interaction between the catechol as well as N-H groups in dopamine and -OH group in the PEO block. Addition of HCl to the solution facilitates a morphological evolution through the interaction change of BCPs due to the added ions. Dopamine polymerization was induced by solvent annealing (264 h) in NH_4OH vapor. Slow dopamine polymerization could maintain the cylindrical nanodomains and form macropores. Carbonization at 700 ^oC (1h) resulted in the formation of interconnected pores with macro- and meso-size due to the removal of PS-b-PEO template. As a result, the carbonization can further increase the specific surface area and provide pore accessibility for potential applications. Morphological transition, surface topography, nanoparticles distribution and characteristic of partially ordered material were evaluated using scanning electron microscope (SEM), transmission electron microscopy (TEM), and small-angle X-ray scattering (SAXS). The results provide deeper insight and understanding of the structural transition and slow dopamine polymerization behavior of the BCPs/Dopamine complex in acid condition for broadening potential applications.

Keywords – Hierarchical porous structures, Self-assembly Block Copolymers, Polydopamine, Solvent annealing, Self-Polymerization