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Mesoporous silica with block copolymer templates: Modulation of porosity *via* block copolymer reaction with silica

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ABSTRACT

A polystyrene-*block*-poly(2-hydroxyethylacrylate) diblock copolymer (PS-*b*-PHEA) was synthesized *via* a reversible addition-fragmentation chain transfer (RAFT) polymerization approach. This novel amphiphilic diblock copolymer was successfully used as the template to obtain the mesoporous silica materials. In order to modulate the porosity of mesoporous silica materials, this diblock copolymer was further functionalized *via* its reaction with 3-isocyanatopropyltriethoxysilane (IPTES) to afford a new diblock copolymer bearing an alkyloxysilane subchain. This derivate diblock copolymer was also employed to prepare the mesoporous silica materials through the inter-component reaction between the block copolymer and silica matrix. The results of small angle X-ray scattering (SAXS), transmission electron microscopy (TEM) and Brunauer–Emmett–Teller (BET) measurements showed that the inter-component reaction can be utilized to modulate the morphologies and porosity of the mesoporous silica materials.

1. Introduction

Porous silica materials have been applied in a variety of fields such as catalysis, sorption, separation, sensors and biotechnologies [1–7]. Generally, porous silica can be prepared *via* sol–gel process of organic silanes (*e.g.*, tetraethoxysilane, TEOS) with various pore-forming strategies [8–19]. According to pore sizes, this class of materials can be divided into micro-, meso- and macroporous silica. Of them, mesoporous silica materials have been attached considerable importance owing to their large surface areas and accessible pores. Mesoporous silicas are generally prepared from the nanostructured silica gels containing organic microdomains *via* the self-assembly of surfactants in silicon source [20–22]. The mesopores are created with the removal of the labile organic microdomains with different approaches. In practice, ionic and nonionic surfactants are utilized to form the self-assembled microdomains in the silica gels. Amphiphilic block copolymers are a class of important nonionic surfactants; they can self-assemble into the microdomains in the precursors of silica gels *via* evaporation-induced self-assembly mechanism [19,23–27]. The microdomains are trapped in silica gels with the occurrence of sol–gel reactions. To avoid macroscopic phase separation in the sol–gel process, amphiphilic block copolymers are generally designed to have both silica-philic and silica-phobic blocks. In previous reports, the affinity of copolymer blocks with silica is mainly achieved through physical interactions (*e.g.*, hydrogen bonding). It is realized that in the sol–gel process a great number of silanol hydroxyl groups are generated owing to the incomplete condensation of alkoxysilanes [28]. These silanol hydroxyl groups can form the intermolecular hydrogen bonding interactions with some proton-accepting polymers such as poly(ethylene oxide) (PEO). The hydrogen bonding interactions are critical to suppress the macroscopic phase separation of the organic block copolymers in the sol–gel process. In ample literature, there have been many reports on the utilization of the block copolymer containing PEO subchains to prepare mesoporous silica materials. For instance, polyisoprene-*block*-poly(ethylene oxide) [29], polystyrene-*block*-poly(ethylene oxide) [30–34], polystyrene-*block*-poly(ethylene oxide)-*block*-polystyrene [35], poly(methyl methacrylate)-*block*-poly(ethylene oxide) [36] diblock copolymer and poly(ethylene oxide)-*block*-poly(methyl methacrylate)-*block*-polystyrene [37] and polyethylene-*block*-poly(ethylene oxide)-*block*-poly(ε-caprolactone) [11,38] triblock copolymers have been used as the templates to direct the

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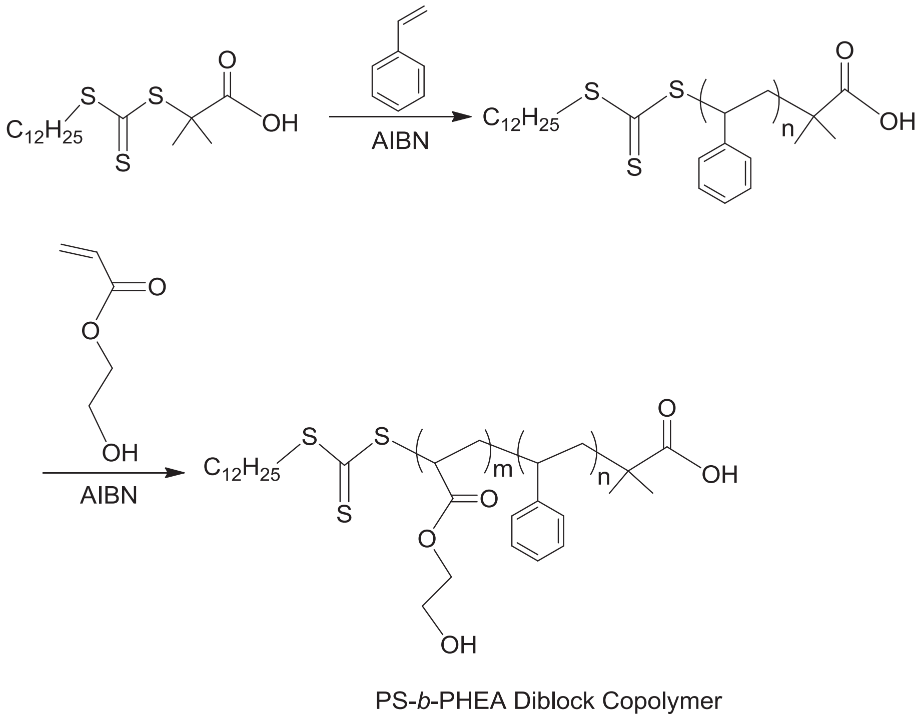

Scheme 1. Synthesis of PS-*b*-PHEA diblock copolymer.

formation of nanostructures in the silica gels. Different polymerization techniques such as anionic, radical and ring-opening polymerizations must be combined to synthesize these PEO-containing block copolymers with a sequential polymerization methodology. Poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide)s (PEO-*b*-PPO-*b*-PEO) are a class of commercially available triblock copolymers, which have been frequently used to access ordered or disordered nanopores in silica [18,39–43]. Nonetheless, it is not easy to modulate the sizes of pores in mesoporous silica materials to use the commercial available PEO-*b*-PPO-*b*-PEO triblock copolymers owing to lower molecular weights [44,45]. Therefore, it is still of interest to utilize new block copolymers to synthesize mesoporous silica materials with adjustable porosity [46–48].

By the use of amphiphilic block copolymer templates, the size of pores and specific surface area of the mesoporous silica are controlled with the morphologies of the microdomains formed in the silica matrices, which are quite dependent on the compositions, molecular weights and architectures of the block copolymers [49,50]. In addition, the sizes of pores can be further adjusted by external adding so-called pore-expanding agents such as aromatic hydrocarbons [51–53], long chain alkanes [54–56] and/or auxiliary alkyl surfactants [57], which are some the microdomain-soluable compounds and thus can swell the microdomains in the silica matrix. For instance, Schmidt-Winkel et al. [51] first reported the control over the pore sizes of the mesoporous silica with Pluronic 123 template by adding 1,3,5-trimethylbenzene (TMB) as a cosolvent. It is found that with incorporation of TMB a phase transformation occurred from Pluronic 123 into Pluronic 123/TMB microdomains. More recently, Zhang et al. [54] synthesized the mesoporous silicas (*viz.* SBA-15) with the submicrometer-sized parallel channells by adding a large amount of decane as the cosolvent. In all these previous reports, the porosity of mesoporous silica was modulated by changing the volume of the hydrophobic microdomains whereas the affinity (or interactions) of silica matrix with silica-philic subchains of block copolymers remained almost invariant. Nonetheless, the porosity of the mesoporous silica can be further modulated by introducing the moderate chemical linkage between the block copolymer and silica matrix. On the one hand, the sizes of the microdomains could be changed with the occurrence of the reaction since the silica-philic/–phobic balance is changed. On the other hand, the silica-philic subchains of the block copolymers would participate in the formation of silica networks with the inter-component reaction. The removal of the organic subchains from the matrix would leave the micropores in the resulting silica. As a consequence, the porosity of the mesoporous silica was changed. However, such an investigation remains largely unexplored.

In this work, we reported the preparation of the mesoporous silica by the use of a novel amphiphilic diblock copolymer, *i.e.*, polystyrene-*block*-poly(hydroxyethyl acrylate) (PS-*b*-PHEA). In marked contrast to those copolymers used for the preparation of the mesoporous silica, this diblock copolymer does not contain PEO component. The affinity of the diblock copolymer with silica matrix could be also achieved through the hydrogen bonding interactions of PHEA block with silica matrix. More importantly, this diblock copolymer can be conveniently synthesized only *via* sequential living radical polymerization approach. To the best of our knowledge, this diblock copolymer has not been synthesized and used for the preparation of mesoporous silica. In this work, this diblock copolymer would be directly used as a template to nanostructure the silica gels. Alternatively, the PHEA block of this block copolymer can be derived into a silica-reactive subchain *via* its reaction with 3-isocyanatopropyltriethoxysilane (IPTES). The PS-*b*-PHEA diblock copolymer could be taken as the model to investigate the effect of the inter-component reaction on the porosity of the mesoporous silica. In this work, a comparative investigation was carried out. The purpose of this work is to elucidate the role of the intercomponent reaction between the block copolymer and silica matrix. In this work, the mesoporous silica materials would be characterized by