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Highly ordered microporous polystyrene-*b*-poly(acrylic acid) films: Study on the influencing factors in their fabrication via a static breath-figure method

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ABSTRACT

A series of well-defined amphiphilic polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) diblock copolymers with different molar ratios of PS and PAA segment were were synthesized via subsequential atomic radical polymerizations of styrene and *tert*-butyl acrylate (*t*BuA) followed by hydrolyzation of *tert*-butyl groups. Highly ordered microporous films of such copolymers were fabricated by a static breath-figure (BF) method using carbon dioxide (CS_2) or chloroform ($CHCl_3$) as solvent under a saturated relative humidity of water. The porous films of PS-*b*-PAA copolymers with average pore size of 0.64–1.79 μm and good regularity were fabricated. Some critical influencing factors, such as concentration of the diblock polymer solution, solvent, temperature, particularly molar ratio of PAA and PS segment were investigated to control the morphology of PS-*b*-PAA microporous films.

1. Introduction

Amphiphilic diblock polymers are of increasing interest in many areas of modern science and technology due to their unique polymeric structure with both hydrophilic and hydrophobic segment and its fascinating solution properties, with applications including polymer science [1–5], electrochemistry [6–8], pharmaceutical [9–12], biochemistry [13–16], medicine and engineering [17], microprinting [18], templating agent [19]. Amongst many kinds of amphiphilic diblock copolymer, the polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) with polystyrene as hydrophobic segment and poly(arcylic acid) as hydrophilic segment has always received considerable attention all the time. In selective solvents, PS-*b*-PAA can self-assemble into micelles with various morphologies such as spheres, rod, vesicles and large compound micelles. Eisenberg et al. first reported that PS-*b*-PAA aggregate to micelle-like morphologies in both aqueous solutions [20] and organic media [21]. He et al. have done much investigation on self-assembly of PS-*b*-PAA and its applied research [22,23]. Amphiphilic PS-*b*-PAA self-assembles into spherical core–shell micelles in the selective solvent water with the PS segment as the core and the PAA segment as the shell. When adding suitable organic solvent to the micellar solution and then casting the micellar solution at suitable temperature, the spherical core–shell micelles are assembled into flower-like or spindlelike aggregates on substrates. Zhang et al. employed PS-*b*-PAA to obtain nanometer-scaled hollow spherical micelles with hydrophilic channels which can used in controlling release of ibuprofen [24]. As stimuli-sensitive microstructure exhibit a distinct and elastic property in response to subtle variations of the vesicle size in external stimuli, thereby PS-*b*-PAA vesicle membranes can serve as sensors, microanalyses and microreactors, Vancso et al. studied the impact of the spatial

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confinement of PS-*b*-PAA diblock copolymer vesicles on the reactivity of encapsulated bovine pancreas trypsin and α-chymotrypsin-catalyzed reaction [25,26], which make its application extend to the field of biochemistry. Core–shell structured dual-mesoporous silica spheres and titanium dioxide nanospheres have been successfully synthesized by utilizing an amphiphilic diblock copolymer PS-*b*-PAA as templates [27,28].

In addition to the applications mentioned above, the amphiphilic PS-*b*-PAA, in particular, is extensively studied in the aspect of fabricating porous films. Mi et al. obtained crack patterns of square, rectangular, stripe-like and mesh-like structures in micron scale with high regularity using PS-*b*-PAA diblock copolymer micelles as the nanobuilding blocks through a one-step evaporation-induced cracking process [29]. Cohen et al. reported the amphiphilic PS-*b*-PAA micelles formed in toluene that can be cast onto a planar substrate to create quasi-hexagonal arrays of spherical PAA domains in a PS matrix [30]. Hu et al. [31] presented a facile approach to fabricate three-dimensional ordered microporous thin films by casting a commercial PS-*b*-PAA diblock copolymer(molecular weight is 12,500 g mol^{-1}; molar ratio of PS to PAA is 2:1) onto a glass slide under high humidity conditions. Robust honeycomb polymer films are also prepared by a static breath-figure method using PS-*b*-PAA (molecular weight is 11,500 g mol^{-1}; molar ratio of PS to PAA is 2.5:1) diblock copolymer [32]. However, to the best of our knowledge, there are a few systematic studies on the important factors in the fabrication of highly ordered microporous PS-*b*-PAA films via breath-figure method.

Herein, a series of PS-*b*-PAA diblock copolymer with different molar ratio of PS and PAA segment were firstly synthesized and then fabricated into microporous films via a static breath-figure method. The effects of some important factors in the fabrication of PS-*b*-PAA microporous films such as solvent, concentration of PS-*b*-PAA solution, temperature and molar ratio of PAA and PS segment on their morphologies were investigated systematically.

2. Experimental

2.1. Synthesis of PS-b-PAA diblock copolymer

A series of well-defined amphiphilic PS-*b*-PAA diblock copolymers having various molar ratio of PS and PAA segment were synthesized in a similar procedure described in our previous work [32]. PS-*b*-P*t*BuA diblock copolymers were firstly prepared via a sequential atom transfer radical polymerizations (ATRP) of styrene and *tert*-butyl acrylate. Subsequently, the hydrolysis of *tert*-butyl groups of poly(-*tert*-butyl acrylate) segments in PS-*b*-P*t*BuA were preformed to obtain the amphiphilic PS-*b*-PAA diblock copolymers abbreviated as $\mathbf{PS}_x$**-*b*-**$\mathbf{PAA}_y$ (x and y are the unit number of monomer in diblock copolymer determined by M_n (GPC) of PS and PS-*b*-P*t*BuA). All the molecular weight distributions of PS-*b*-P*t*BuA diblock copolymers are narrow (1.07–1.09). Four $\mathbf{PS}_x$**-*b*-**$\mathbf{PAA}_y$ ($\mathbf{PS}_{84}$**-*b*-**$\mathbf{PAA}_8$, $\mathbf{PS}_{84}$**-*b*-**$\mathbf{PAA}_{16}$, $\mathbf{PS}_{84}$**-*b*-**$\mathbf{PAA}_{22}$ and $\mathbf{PS}_{104}$**-*b*-**$\mathbf{PAA}_{16}$) and $\mathbf{PS}_{84}$**-*b*-P*t*BuA**$_{16}$ were employed in this work.

2.2. Preparation of microporous polymer films

The method named as static breath-figure to fabricate the microporous polymer films is described as follows. The solution of PS-*b*-PAA or PS-*b*-P*t*BuA in CS_2 or $CHCl_3$ (polymer concentration of 2.0 wt%, 3.0 wt% and 5.0 wt%, respectively) was cast via microsyringe onto the surface of glass slide in a glass vessel with a cap. Saturated relative humidity in such glass vessel was achieved by adding several droplets of distilled water beforehand. After complete solvent and water evaporation, a microporous polymer film was formed on such glass slide and dried in vacuo at room temperature for characterization.

2.3. Characterization

The number molecular weight (M_n) and molecular weight distribution of PS-*b*-P*t*BuA were measured by a Waters gel permeation chromatography (GPC) system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector (RI), a Waters 2487 dual λ absorbance detector (UV) and a set of Waters Styragel columns (HR3, HR4 and HR5, 7.8 × 300 mm). GPC measurements were carried out at 35 °C using tetrahydrofuran (THF) as eluent with a flow rate of 1.0 mL min^{-1}. The system was calibrated with polystyrene standards. The unit of monomer in diblock copolymer was determined by M_n (GPC) of PS and PS-*b*-P*t*BuA, e.g. $\mathbf{PS}_{84}$: M_n (GPC) = 8750 g mol^{-1} (M_w/M_n = 1.08); $\mathbf{PS}_{84}$**-*b*-P*t*BA**$_{16}$: M_n (GPC) = 10,800 g mol^{-1} (M_w/M_n = 1.08).

The microporous polymer films were observed on a scanning electron microscope (JEOL 6390LV, Japan) operated at 10 kV. Atom force microscopic (AFM) images were obtained using a Veeco Nanoscope IVa Multimode system in tapping mode. A silicon cantilever with a bending spring constant of 20–60 N/m and a resonance frequency of about 300 kHz was used for imaging at a scan rate of 0.5–1.0 Hz.

3. Results and discussion

As has been reported, amphiphilic diblock copolymers are believed to be good candidates to self-assembly form aggregate in selective solvents because of their high segment density which could effectively stabilize water droplets in breath-figure method [33–38]. In this paper, amphiphilic PS-*b*-PAA diblock copolymers with PS as hydrophobic segment and PAA as hydrophilic segment were fabricated to microporous films via a static breath-figure method. The solution of such diblock copolymer in CS_2 or $CHCl_3$ was cast on the surface of glass slides by a microsyringe. During the evaporation of solvent, the temperature of the solvent–air interface decreases and water vapor in the vessel starts to condense into water droplets which arranged regularly and sank into polymer solution. The structure of ordered microporous was formed on the surface of film after the complete evaporation of solvent and water. There are some factors influencing the morphology of microporous film such as polymer architecture and component, molecular weight of polymer, solvent, polymer concentration, temperature, relative humidity,