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Multi-length scale porous polymer films from hypercrosslinked breath figure arrays

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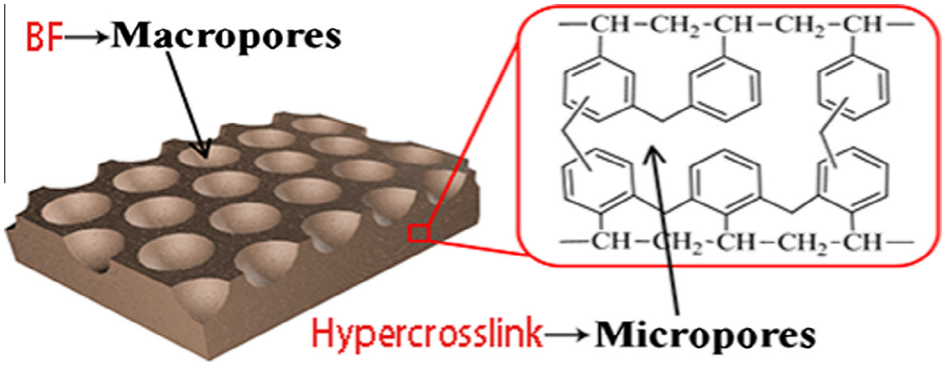
HIGHLIGHTS

- Breath figure is combined with hypercrosslinking to create pores in polystyrene film.
- The produced films have multi-length scale porous structure.
- The resulted films possess large specific surface areas.
- The resulted films show excellent chemical and thermal stabilities.

GRAPHICAL ABSTRACT



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ABSTRACT

Multi-length scale porous polymer (MLSPP) films were fabricated using commercially available polystyrene (PS) *via* static breath figure (BF) process and sequent hypercrosslinking reaction. One level of ordered pores in microscale were introduced using static BF process, and the other level in nanoscale were produced by the sequent Friedel–Crafts hypercrosslinking reaction. The chemical structure of the PS MLSPP film was investigated by Fourier transformation infrared spectrometry and solid state nuclear magnetic resonance, and the morphology of the film was observed with electron microscopes. The MLSPP films showed large specific surface areas and excellent chemical and thermal stabilities, owing to the micropores and the crosslinked chemical structure produced by the Friedel–Crafts reaction. The methodology reported in this paper is a template-free, low cost and general strategy for the preparation of MLSPP films, which has potential applications in the areas of environment and energy.

1. Introduction

Porous polymeric materials with multi-level pores are of increasing importance owing to their potential applications in catalysis, separation technology, and bio-engineering [1–4]. Particular interest has been focused on porous polymers integrating micropores (<2 nm) with continuous macropores (>50 nm), because they combine high specific surface area with high flux and pore accessibility. However, although a large number of hierarchically porous inorganic materials have been prepared so far, very few multi-length scale porous polymers (MLSPPs) are reported, and it is still challenging to fabricate such polymeric materials [5–10]. Block copolymes (BCPs) are the commonly used materials to prepare MLSPPs because of their predictable self-assembly behavior [11–17]. Usually, one level of ordered porosity originates from the micro-phase separation of the BCPs,

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and the other level is introduced by the preset template or chemical/physical post-treatments. For example, Seo et al. constructed nanoscopic bicontinuous structure in a diblock copolymer PLA-*b*-P(VBzCl-*co*-DVB). Hypercrosslinking of the polymer sample by $FeCl_3$ generated micropores in the P(VBzCl-*co*-DVB) microdomain *via* Friedel–Crafts alkylation, and simultaneously degraded PLA blocks, producing mesopores in the sample. Therefore, MLSPPs containing micropores in the mesoporous framework was obtained [18]. Sai et al. developed a strategy using spinodal decomposition of mixtures of BCP/small molecule additive to prepare hierarchical macro- and mesoporous polymer scaffolds. The spinodal decomposition of BCP/additive mixture produced an additive-rich phase and a BCP-rich phase, in which one block of the BCP was selectively swollen by the additive. After both the additive-rich phase and the additive in swollen BCP block were removed by selective solvent, hierarchical pore formed in the polymer matrix [5]. Evidently, the combination of specific chemical reactions, narrow synthesis parameter windows and multiple tedious steps is required, to facilitate the escape of the decomposed fragments. These disadvantages strongly limit the development of MLSPPs. Therefore, a simple, versatile and etching-free technique for the preparation of MLSPPs is desirable in both scientific and practical viewpoints.

A variety of new strategies for preparing porous structures in different scales offer opportunities of overcoming these disadvantages. Breath figure (BF) process is a simple, template-free and high throughput method of preparing ordered polymer films in large area [19–21]. Upon casting a polymer solution in a water-immiscible solvent under high humidity, the rapid evaporation of solvent leads to a sharp decrease in the temperature of the solution, thereby initiating the formation of water droplets on the solution surface. These water droplets are stabilized by a polymer layer around them, and self-assemble into a hexagonal array driven by the Marangoni convection. After total evaporation of the solvent and water, ordered pores are left on the polymer film surface, and these pores are termed breath figure arrays (BFAs). BF method has been widely employed to prepare porous film with the pore size ranging from several hundred of nanometers to tens of micrometers [22]. Takekoh and Russell prepared thin BFA films with micrometer-sized pores and nanoscopic pores generated by selectively removing the PMMA cylinders with a deep UV-irradiation inherent to a BCP of polystyrene-*b*-polymethyl methacrylate (PS-*b*-PMMA) [23]. However, a cylindrical equilibrium phase is necessary to facilitate the escape of the decomposed fragments from the BCP template. Another template-free porogenic method, hypercrosslinking reaction, which is most frequently performed by Friedel–Crafts alkylation, attracts more and more interesting. Hypercrosslinked (HCl) polymers contain a very high density of crosslinking bonds together with molecular-sized pores, and exhibit attractive properties such as ultra-high surface area and the excellent adsorbing ability [24–30]. Thus hypercrosslinking reactions were used to produce functional polymeric adsorbents and molecular sieve films.

In this article, we report a new strategy to prepare MLSPP film with commercial available polystyrene (PS), combining BF process with hypercrosslinking post-treatment. One level of ordered pores in microscale are introduced using BF process, and the other level in nanoscale are then produced by the sequent Friedel–Crafts hypercrosslinking reaction. The beauty of this method is that delicate chemical etching and the use of template are avoided. Thus it provides a low cost, template-free and general way to prepare MSLPP films that may be valuable for the nanoscale engineering.

2. Experimental section

2.1. Materials

A commercially available PS sample with a molecular weight (*Mw*) of 214.8 k and a polydispersity index (PDI) of 1.67, was purchased from Asahi Chemical Company and used as received. Analytical grade carbon disulfide (CS_2) was purchased from Shanghai Chemical Reagent Plant. A commercially available dimethoxymethane (FDA) was purchased from Tokyo Chemical Industry Co., Ltd. Iron (III) chloride ($FeCl_3$) (98%) was purchased from Alfa Aesar Company and used without further purification. A commercially available 1,2-dichloroethane (DCE) was purchased from Sinopharm Chemical Reagent Co., Ltd and washed with concentrated sulfuric acid, sodium carbonate solution and water for several times, then refluxed with CaH_2 and fractionally redistilled. All the chemical reagents were used as received without further purification unless specifically noted.

2.2. Preparation of BF array films

The static breath figure (BF) process was operated in a 25 mL straight-mouth glass bottle with a cap. A saturated relative humidity in the vessel was achieved by adding 2 mL of distilled water into the bottle beforehand. A piece of glass substrate was adhered onto the top of a plastic stand with a double-sided tape and placed into the glass vessel. The substrate was 1 cm higher than the liquid level. A piece of glass slide was placed onto the center of the glass substrate. Polymer solutions with concentration of 1–4 wt% were prepared by dissolving PS in CS_2. The micro-patterned film was prepared by casting a 5 μL polymer solution onto the piece of glass slide. With the quick evaporation of CS_2, the temperature of the solution quickly decreased and water droplets were condensed onto the surface of the solution. After complete solvent evaporation, PS breath figure array (BFA) film with microporous was formed on the substrate. All the experiments were carried out at room temperature unless stated otherwise.

2.3. MLSPP films via hypercrosslinking reaction

In a 2-necked flask, $FeCl_3$ (4.875 g, 0.030 mol), FDA (1.140 g, 0.015 mol) and 5 mL DCE were mixed and stirred until well dispersed. Several pieces of PS BFA films pre-dried in a vacuum oven overnight were added to the mixture at room temperature, and then the mixture was heated to 80 °C for 8 h in the flask equipped with a condenser without stirring. The resulting films were washed with methanol for at least three times, then Soxhlet extracted in methanol and tetrahydrofuran for 12 h, respectively, and at last dried in a vacuum oven for 24 h.

2.4. Characterization

The morphology of honeycomb films were observed by scanning electron microscopy (SEM) (TM3000, Hitachi) under an electron beam with an accelerating voltage of 15 kV and a working distance of 2 mm. The multi-length scale porous structures of the films were characterized by high-resolution transmission electron microscopy (TEM) (JEM-2100) with an acceleration voltage of 200 kV. The TEM specimens were prepared by dispersing the films ground *via* agate mortar in ethanol. A drop of the suspension was deposited on a carbon-film coated copper grid. Thermal Gravity Analysis (TGA) of HCl films was performed on a thermal analyzer (Q500 V6.7 Build 203) under an air atmosphere with a heating rate of 10 °C min^{-1} from 50 °C to 550 °C. Specific surface areas were measured on a BET (TRISTAR II3020). Fourier transform infrared spectra (FT-IR) were obtained with a NICOLET iS10 instrument. Solid-state nuclear magnetic resonance (NMR) was carried out on a BRUKER AV 400.

3. Results and discussion

The new strategy to prepare MLSPP films is shown schematically in Scheme 1. A static BF process was employed to create por-