Highly ordered microporous films containing a polyolefin segment fabricated by the breath-figure method using well-defined polymethylene-*b*-polystyrene copolymers

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Highly ordered microporous films containing polyolefin segment were successfully fabricated *via* the breath-figure (BF) method using well-defined polymethylene-*b*-polystyrene (PM-*b*-PS) diblock copolymers in CS_2 under a static humid condition. The effects of molecular weight of diblock copolymers, relative humid, fabrication method and temperature on the morphology of film are investigated. The honeycomb porous films with different pore size (1.2–2.5 μm) were obtained by using PM-*b*-PS with different PM : PS ratio. The thick (7 μm) and thin (2 μm) films were fabricated *via* a different process. The film with a pothole-like structure was fabricated when using PM-*b*-PS with the shortest PS segment. Smaller satellite pores were found to surround the regular micropores of honeycomb films when the BF process was carried out at 28 °C.

Introduction

Porous materials based on polyolefins are widely used in various applications such as matrices for functional films,[1] films for in-package processing of food,[2] conical orbital implant,[3] superhydrophobic film[4] and so on. Until now, porous polyolefins have been fabricated by several strategies including a process based on melt extrusion with subsequent annealing and uniaxial extension,[5] gel-technology based on phase separation,[6] technology using a polyolefin melt/channeling agent system[3] and the controlled crystallization of polyolefins,[4,7] *etc.* However, to the best of our knowledge, there haven't yet been any reports on the fabrication of highly ordered porous polyolefins or their composites which are believed to have special surface properties themselves or after functionalization by physical or chemical methods.

Recently, highly ordered honeycomb-structured microporous films fabricated by the so-called breath-figure (BF) method first described by François and co-workers[8] have attracted a great deal of attention in the research area of functional materials.[9] The formation of highly ordered honeycomb films in the BF procedure were influenced by various parameters such as relative humidity (RH), temperature, solvent, the architecture and component of polymers, polymer concentration *etc.*[10] To fabricate such porous films targeting different application through the BF method, a variety of polymers with different architectures have been employed such as rod–coil block copolymers,[8,11] block copolymers,[10,12] conjugated polymers,[13] amphiphilic copolymers,[14] dendronized polymers,[15] star polymers,[16] core-crosslinked star polymers,[17] just to name a few. However, to the best of our knowledge, there has been no study on the fabrication of highly ordered honeycomb film using polymers with non-polar polyolefin segments. Here we report the fabrication of honeycomb polyolefin composite films *via* the BF method using well-defined polymethylene-*b*-polystyrene (PM-*b*-PS) diblock copolymers.

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Experimental

Synthesis of PM-*b*-PS

A series of narrow molecular weight distributed PM-*b*-PS diblock copolymers with different molecular weight ratios of PM and PS segments were synthesized according to the procedure described in our previous work.[18]

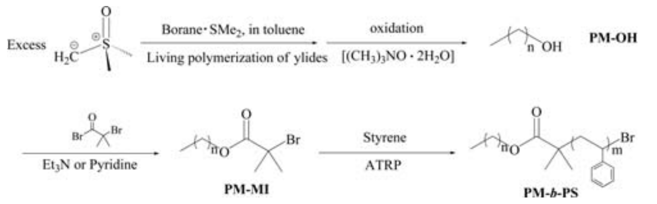
Preparation of honeycomb films

Two different methods were employed to fabricate the porous films. Method 1:[14e] one solution of PM-*b*-PS in CS_2 (3.0 wt%) was cast onto the surface of glass slide with a microsyringe in a glass vessel with a cap at 20 °C or 28 °C until the solvent evaporated totally. Saturated relative humidity in the glass vessel was achieved by adding several droplets of distilled water beforehand. After complete solvent evaporation, a honeycomb thin film was formed on a glass slide. Method 2: the glass slide was dipped into the solution of PM-*b*-PS in CS_2 (3.0 wt%), drawn out slowly and sustained by a bracket in the vessel describe above. When the solvent had evaporated completely, the white and opaque films on the both sides were formed.

The honeycomb 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.

Results and discussion

Among the various copolymers used in the BF method to fabricate the honeycomb films, diblock copolymers with non-polar polyolefin segments have not been employed yet. In our work, a series of PM-*b*-PS polymers (PM_{2k}-*b*-PS_{10k}, PM_{2k}-*b*-PS_{8k}, PM_{2k}-*b*-PS_{5k} and PM_{2k}-*b*-PS_{2k}. Note: the subscript numbers mean the number molecular weight (g mol^{-1}) of PM and PS segments; $k = 10^3$) with



Scheme 1 Synthesis of polymethylene-*b*-polystyrene (PM-*b*-PS) *via* a combination of living ylides polymerization and ATRP of styrene.[18]

narrow molecular weight distributions (M_w/M_n < 1.1) were firstly prepared *via* a combination of living ylides polymerization and atomic transfer radical polymerization according to our previous work[18] (Scheme 1) and then employed in the BF procedure to fabricate polymer films.

The fabrication of honeycomb structured polyolefin composite films was carried out at 20 °C in a static humid conditions of 50% relative humid (RH) *via* casting[14e] or dip coating polymer solution onto a clean glass substrate. In our cases, considering the solubility of PM-*b*-PS in CS_2, the PM_{2k}-*b*-PS_{10k} with the highest molecular weight of PS which can be well-dissolved in CS_2, was firstly used in the BF method. As observed by scanning electron microscopy (SEM) in Fig. 1(a), a highly ordered honeycomb structure film with average pore diameters of 2.5 μm was successfully fabricated *via* the BF method. Furthermore, the M_n of the PS segment was decreased gradually to 8000, 5000 and 2000 g mol^{-1}, respectively, in order to know how the content of PS in PM-*b*-PS influences the morphology of the films. The results indicated that both PM_{2k}-*b*-PS_{8k} and PM_{2k}-*b*-PS_{5k} in CS_2 solution can still generate the honeycomb films under the same casting condition (Fig. 1(b) and 1(c)). The average pore diameter of such films decreased to 1.50 μm and 1.40 μm, respectively. Although various mechanisms for the BF method have been proposed, the water templating mechanism[8] is generally used to explain the formation of this ordered morphology, *i.e.*, in our cases, firstly, water in the humid environment condensed onto the surface of the polymer solution because of its significantly decreased temperature resulting from rapid evaporation of solvent. Secondly, the water droplets arranged into a hexagonal array, sank into the polymer solution and were stabilized from coalescence by the precipitated PM-*b*-PS at the water–solvent interface. Finally, the highly ordered honeycomb film was generated after the evaporation of water droplets and solvent. According to the mechanism mentioned above , the faster evaporation of CS_2, which results from the decreased viscosity of the solution when using polymers with lower molecular weight, probably leads to smaller pores.[10b]

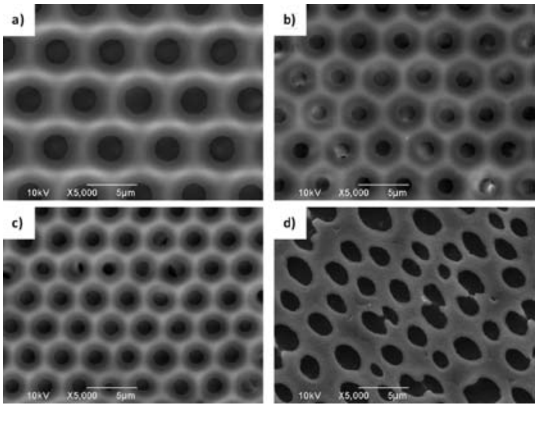


Fig. 1 SEM images of porous PM-*b*-PS films fabricated *via* the casting/BF method at 20 °C in 50% RH. (a) PM_{2k}-*b*-PS_{10k}; (b) PM_{2k}-*b*-PS_{8k}; (c) PM_{2k}-*b*-PS_{5k}; (d) PM_{2k}-*b*-PS_{2k}.

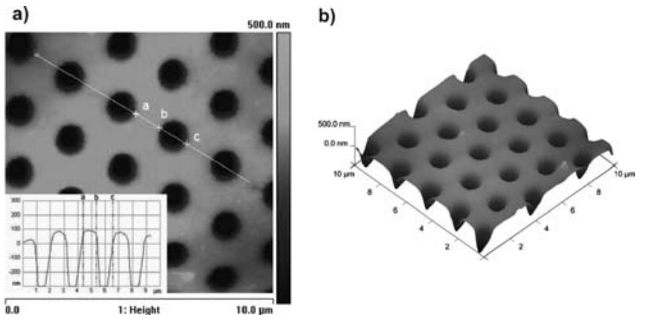


Fig. 2 AFM images of PM_{2k}-*b*-PS $_{5k}$ honeycomb film. (a) height image (inset: section analysis of the white straight line); (b) 3D image of film.

Interestingly, an irregular oval pothole-like structure was formed on the surface of film when using PM_{2k}-*b*-PS_{2k} with a shorter PS segment (Fig. 1(d)). This phenomenon will be discussed later.

The AFM images display the regular structure of the film (Fig. 2) with pore diameter of 1.2 μm (from point b and point c in the section line, Fig. 2(a)) and spacing between pores (from point a to point b in the section line, Fig. 2(a)) of 1 μm. The three-dimensional (3D) image of the honeycomb film is shown in Fig. 2(b). The inversion-cone indicates that the tip of AFM cantilever can't touch the bottom of the pore in the film.

As reported the literature (ref. 10b and references therein), the relative humidity in the BF process has an important influence on the pore diameter and the regularity of films. The SEM images in Fig. 3 show the different morphology of the films (PM_{2k}-*b*-PS_{8k}) fabricated in two different relative humidities. Irregular pores were formed when the relative humidity increased to 70% (Fig. 3(a)) and 80% (Fig. 3(b)). Meanwhile, the average diameter of pores increased to 1.6 μm to 2.1 μm, respectively.

The presence of the PS segment could benefit the solubility of PM-*b*-PS in CS_2 by forming micelles similar to those in THF.[18] So, the molar ratio of PS : PM might have profound influence on the formation of honeycomb or oval pothole-like structures. Moreover, the chain end bromine of the block copolymer, being a hydrophilic group, is also presumed to play an important role in the BF procedure. Further investigations on the mechanism of BF procedure in our case are currently underway.

Thick honeycomb films with one layer pores (∼2 μm depth) and dense polymer layer (∼5 μm thickness) (Fig. 4(b)) were generally

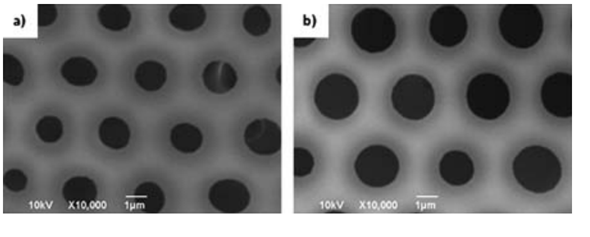


Fig. 3 SEM images of PM_{2k}-*b*-PS_{8k} honeycomb films fabricated in different relative humidities. (a) 70% RH; (b) 80% RH.

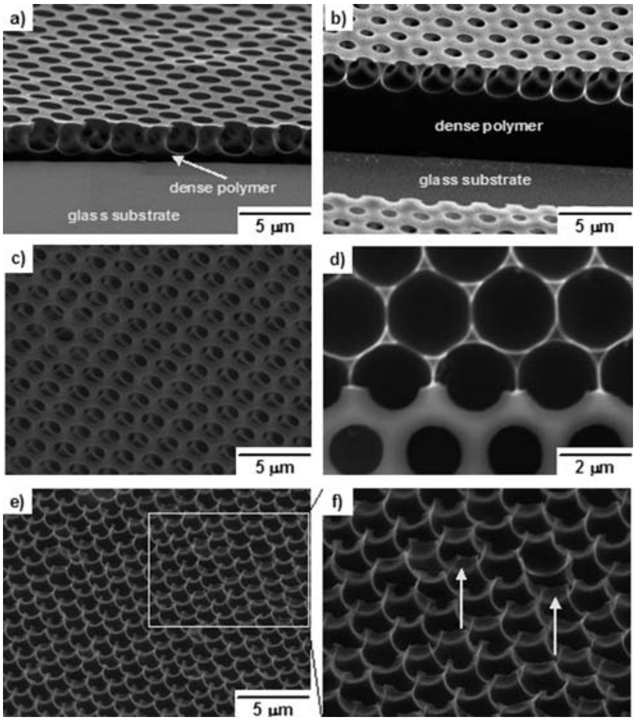


Fig. 4 SEM images of honeycomb films of PM_{2k}-*b*-PS_{10k}. (a) and (c)–(f) PM_{2k}-*b*-PS_{10k} film fabricated by the dipping/BF method at 20 °C in 50% RH; (b) PM_{2k}-*b*-PS_{10k} film fabricated by the casting/BF method at 20 °C in 50% RH; (c) side view at tilt angle 40°; (d) top view; (e) pincushion structure (side view at tilt angle 40°); (f) magnified local view of (e).

fabricated by the casting method following a static BF procedure. In order to obtain thin films, the dipping procedure of polymer solution (Method 2) was employed and then the BF method was performed under a static humid environment. As shown in Fig. 4(a), we were delighted to find that the thickness of film fabricated by the dipping mode is sharply decreased and there is only a very thin layer of dense polymer. The SEM image in tilt angle of 40° (Fig. 4(c)) reveals that there are regular 'pillars' underneath the surface of the film and inter-connected holes. When the upper porous layer was peeled off, the

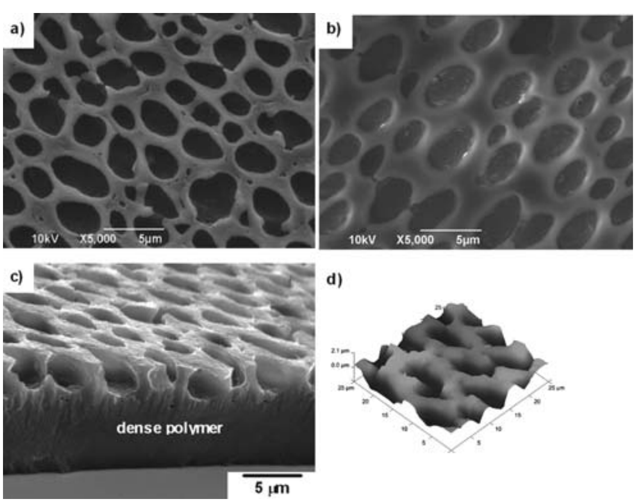


Fig. 5 SEM and AFM images of PM_{2k}-*b*-PS_{2k} film. (a) and (b) top view; (c) side view; (d) 3D AFM image.

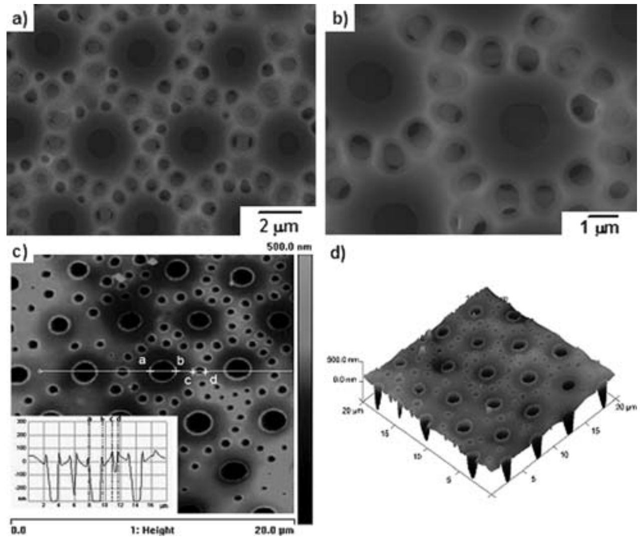


Fig. 6 SEM and AFM images of PM_{2k}-*b*-PS_{10k} film fabricated at 28 °C in 50% RH (a) SEM top view of film; (b) magnified image of (a); (c) AFM height image (inset: section analysis of the white straight line); (d) 3D AFM image of film.

pincushion structure could be observed (Fig. 4(d) and 4(f)). The diameter of the water droplet sunk in polymer solution is speculated to be about 2 µm from the SEM image in Fig. 4(d). The residual thin film walls connecting 'pillars' (the parts directed by arrows, Fig. 4(e) and 4(f)) are thought to be one evidence for the formation of precipitated polymer layers which surround the water droplets and prohibit their coalescence.

As mentioned earlier, the film with irregular morphology was obtained *via* the casting/BF method using PM_{2k}-*b*-PS_{2k}. Different from the morphology shown in Fig. 4(b), SEM image of the cross-sectioned film in Fig. 5(a) and the three-dimensional (3D) AFM image in Fig. 5(b) show irregular potholes separated by walls with thickness of 1–3 µm instead of partially penetrated holes. The factors which have influence on the stability and shape of water droplets, *i.e.*, the aggregation state of PM_{2k}-*b*-PS_{2k} with lower PS : PM ratio in CS_2, the decreased solubility, the concentration of Br, *etc.*, might be possible explanations for the formation of this structure. Further research will be carried out to investigate the formation mechanism of such a morphology.

A variety of parameters in the BF method such as temperature, relative humidity, polymer structure and polymer concentration, *etc.*, should be well controlled to fabricate the porous film with regular pattern. In an experiment using PM_{2k}-*b*-PS_{10k}, when the system temperature was accidentally raised to 28 °C, some satellite pores were formed surrounding the regular micropores (Fig. 6). This structure was mentioned by Stenzel and co-workers[12b] and explained as formation of water-swollen inverse aggregates. While, the mechanism in our case seems to be very different because the PM-*b*-PS is mainly hydrophobic except for the bromine end group. So, a possible explanation will be given after further investigation.

Conclusions

In summary, we have successfully fabricated honeycomb polyolefin composite films *via* the BF method using well-defined PM-*b*-PS diblock copolymers. The length of PS segment plays important role in the morphology of polymer film. The honeycomb films were obtained by using the solutions of PM_{2k}-*b*-PS_{10k}, PM_{2k}-*b*-PS_{8k} and PM_{2k}-*b*-PS_{5k} in CS_2. Interestingly, the PM_{2k}-*b*-PS_{2k} with shorter PS segments can fabricate films with pothole-like structure. The structure of regular micropores surrounded by some satellites was formed when the system temperature increased to 28 °C. The possible formation mechanisms of different morphologies, as well as the relationship between film structure and various parameters in the BF procedure, are under investigation.

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