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Regular honeycomb porous polymer films based on amphiphilic block copolymer

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1. Introduction

The design of highly ordered microporous membranes has attracted considerable attentions in the past decade because of their great interests in basic research and industrial applications. Among many methods for fabricating microporous polymeric film, the “breath figure” method [1–3] has attracted much attention due to the simple process. It employs solvent evaporative cooling on the surface under humid conditions and water droplets are formed at the interface of the solution and water vapor. Then, water droplets interact with one another and are finally ordered in a hexagonal lattice. In this paper, we prepared a series of amphiphilic diblock copolymer poly(vinyl phenol-*b*-styrene) (PVPh-*b*-PS). These diblock copolymers are first dissolved in THF solution with various concentration (20–50 mg/mL), and then add the selective toluene solvent which exhibit complex self-assembling behavior of supramolecular structures for PVPh segment to induce the aggregation of the PVPh-*b*-PS diblock copolymer. Then the honeycomb-patterned structures were observed. Furthermore, we study the micellization

behavior, water repellency and honeycomb structure of the amphiphilic diblock copolymer of PVPh-*b*-PS.

2. Results and discussion

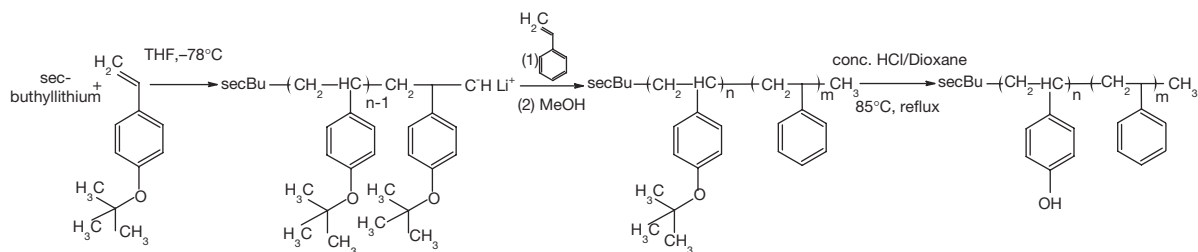
2.1. Synthesis of poly(vinyl phenol)-block-polystyrene (PVPh-*b*-PS) diblock copolymers

Scheme 1 illustrates our strategy for the preparation of the PVPh-*b*-PS diblock copolymers. The anionic polymerization of 4-*tert*-butoxystyrene was carried out in THF for a period of time at -78°C using *sec*-butyllithium as the initiator and adds styrene as sequential living anionic polymerization. The molecular weights and polydispersity indexes of the PtBOS homopolymer were determined using gel permeation chromatography (GPC); the block copolymer in the phenol form was hydrolyzed to PVPh-*b*-PS by refluxing overnight with concentrated HCl in dioxane. Finally, the PVPh-*b*-PS diblock copolymers were obtained.

2.2. Preparation of honeycomb-architected film

The *honeycomb-architected films* were obtained by “breath figures” method. The block

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Scheme 1. Synthesis of PVPh-*b*-PS copolymer by anionic polymerization.

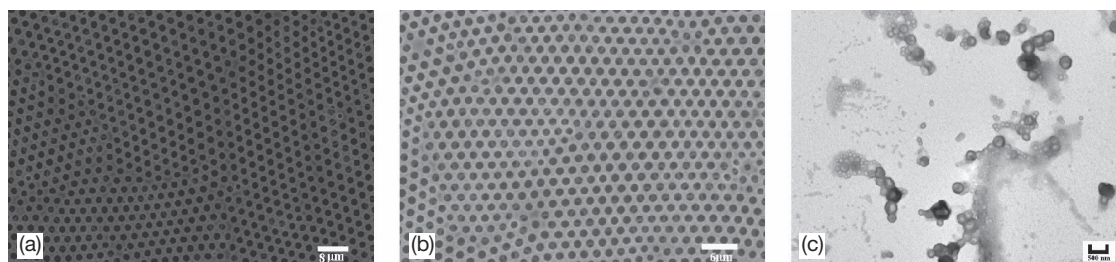


Fig. 1. (a) 20 mg/THF + 0.1 mL toluene, (b) 50 mg/THF + 0.1 mL toluene and (c) solution morphology of block copolymer by TEM.

copolymer was first dissolved in THF, which is a solvent suitable for both copolymer blocks. Subsequently, a given volume of toluene was added into the polymer THF solution with stirring, which is a precipitant for the PVPh blocks. The presence of micelles was indicated by the appearance in the solution. The formation of microporous structure essentially consists of four steps: (1) condensation of water droplets at the solution surface; (2) growth of the water droplets; (3) packing of the water droplets by capillary forces; (4) complete evaporation of the solvent. Fig. 1 shows the honeycomb structure which characterized by SEM and TEM analyses. Clearly, the honeycomb structure was observed from SEM with different initial concentration (Fig. 1a, b). Additionally, we found that the block copolymer solution morphology in THF/toluene = 1/0.1 (vol./vol.) content is the giant vesicles (Fig. 1c), which transfer into three-dimensional order honeycomb morphology with some intervesicle voids range from

micrometric sizes by the casting film, which were formed by the “breath figures” method.

3. Conclusions

We were first to investigate concentrated micellar solution casting onto solid matrixes based on amphiphilic diblock copolymers. When the concentrated vesicular solution was casting onto glass plate under humid airflow, it forms honeycomb-patterned structure. Furthermore, we attempted to control the honeycomb pattern of the resulting amphiphilic diblock copolymer film via adding the selective solvent content methods. The honeycomb-patterned films have surface roughness and they provide water repellency.

References

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