Polystyrenes with Hydrophilic End Groups: Synthesis, Characterization, and Effects on the Self-Assembly of Breath Figure Arrays

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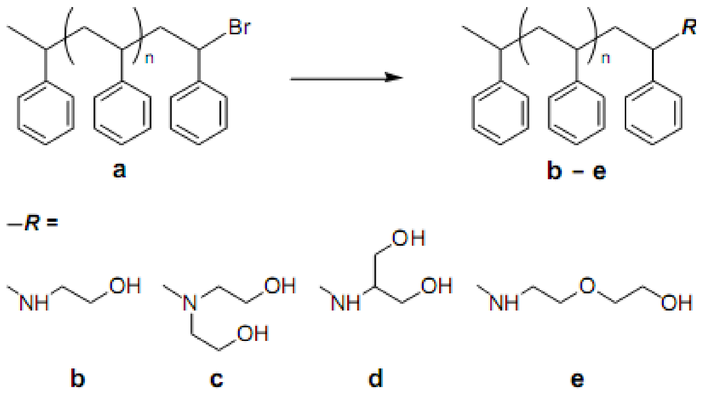
The breath figure method, which is inspired by the formation of fog on cold surface, has been widely used to prepare highly ordered honeycomb porous films. The structure of the honeycomb films is dependent on the topology and chemical composition of the film-forming materials. In this work, we report the synthesis and characterization of a series of hydroxyl-end-functionalized polystyrenes (PS−OH) and the formation of patterned porous films. Results reveal that the subtle chain-end modification leads to a dramatic change in the morphology of the films. Honeycomb films with large area ordered structure can be easily prepared from PS−OH. Effects of the end groups as well as blending PS−OH with PS−Br on the surface pore diameter, pore center distance, and the hierarchical structure were studied in detail. As supported by the results of polymer hydrophilicity, *in situ* observation of the film formation process, as well as the chain mobility, the film structure is supposed to be mainly determined by the precipitation of polystyrene at the solution/water droplet interface and the interfacial activity enhanced by the end groups.



Scheme 1. Hydroxyl-Functionalized PS.

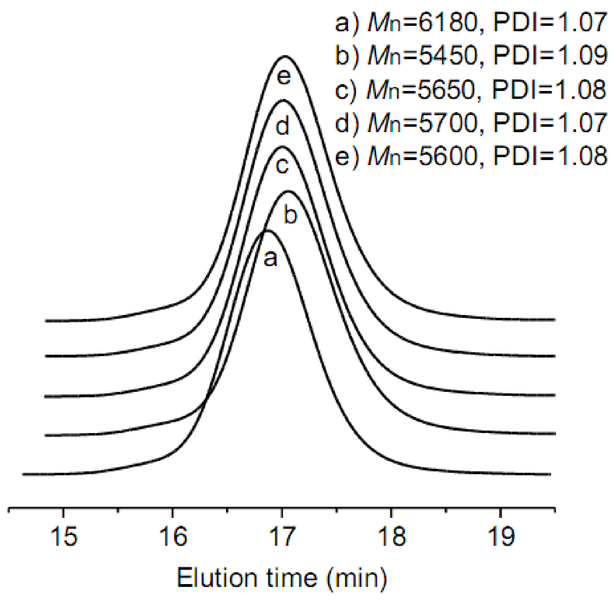


Figure 1. GPC curves of PS with different end groups.

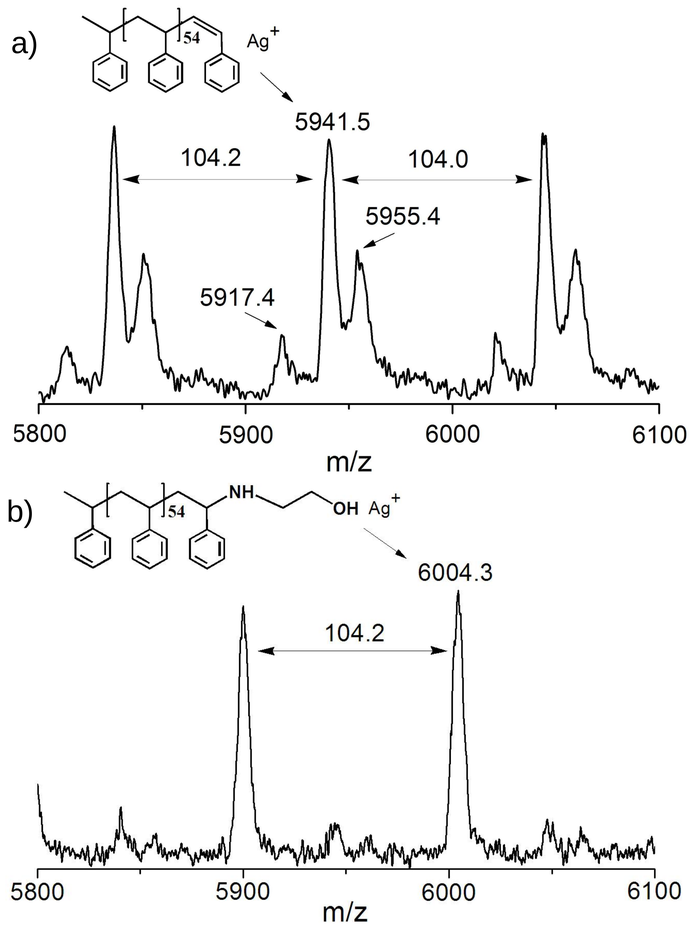


Figure 2. Typical MALDI-TOF MS spectra of PS with different end groups: a) PS-Br, b) PS-$NHCH_2CH_2OH$.

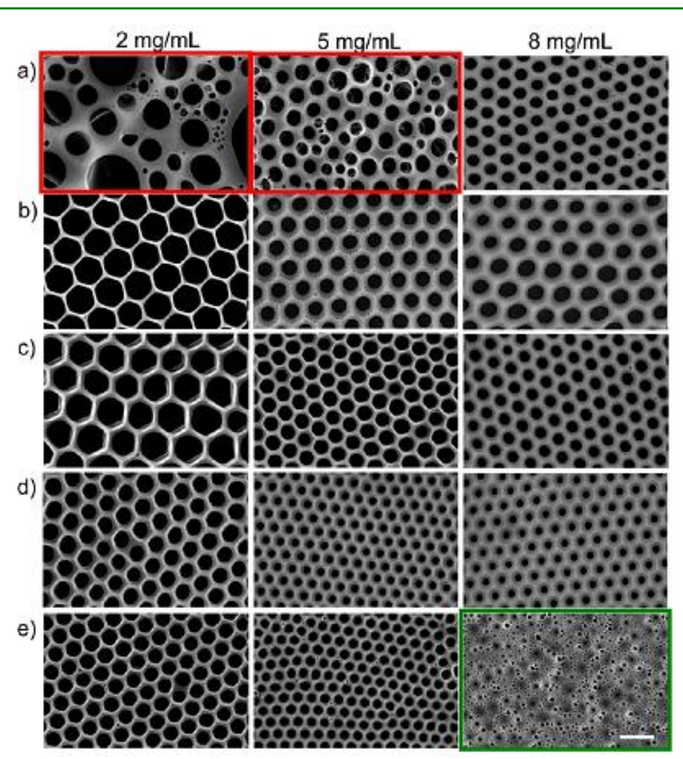


Figure 3. Top-down SEM images of honeycomb porous. Scale bar is 5 μm.

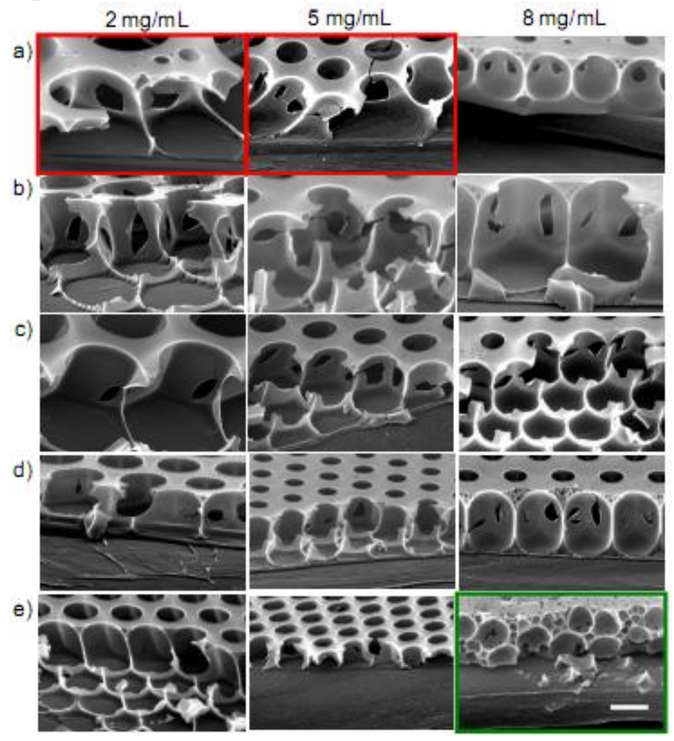


Figure 4. Cross-sectional SEM images of honeycomb porous films. Scale bar is 2 μm.

Figure 5. Water contact angle on the dense films.

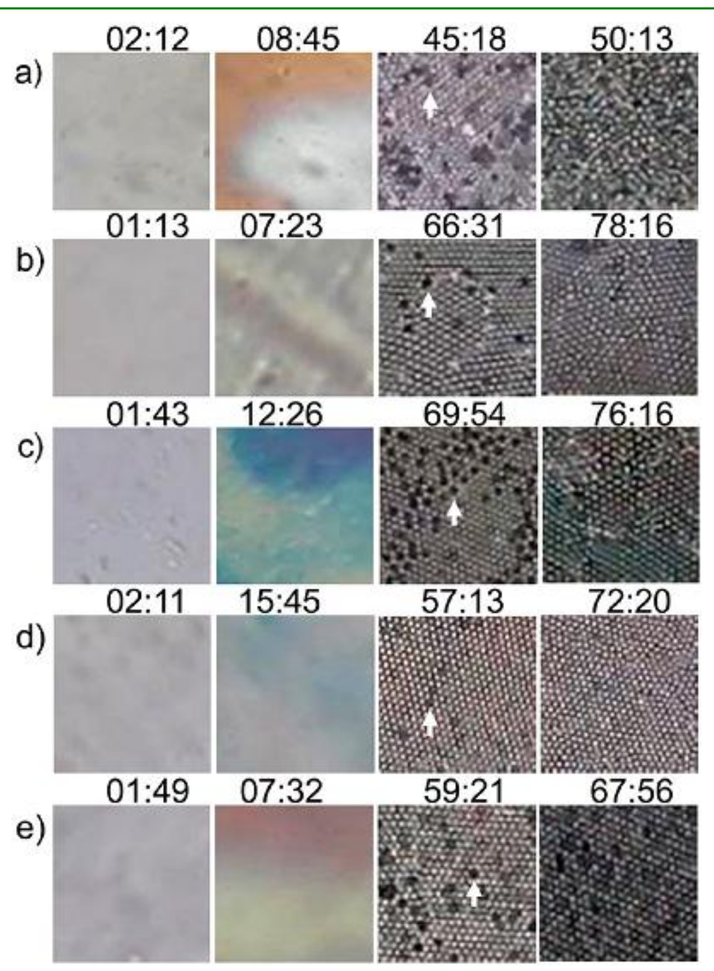


Figure 6. In situ optical micrographs of the breath figure process at different time (second). The process was observed by using polymer solutions with a concentration of 5 mg/mL.

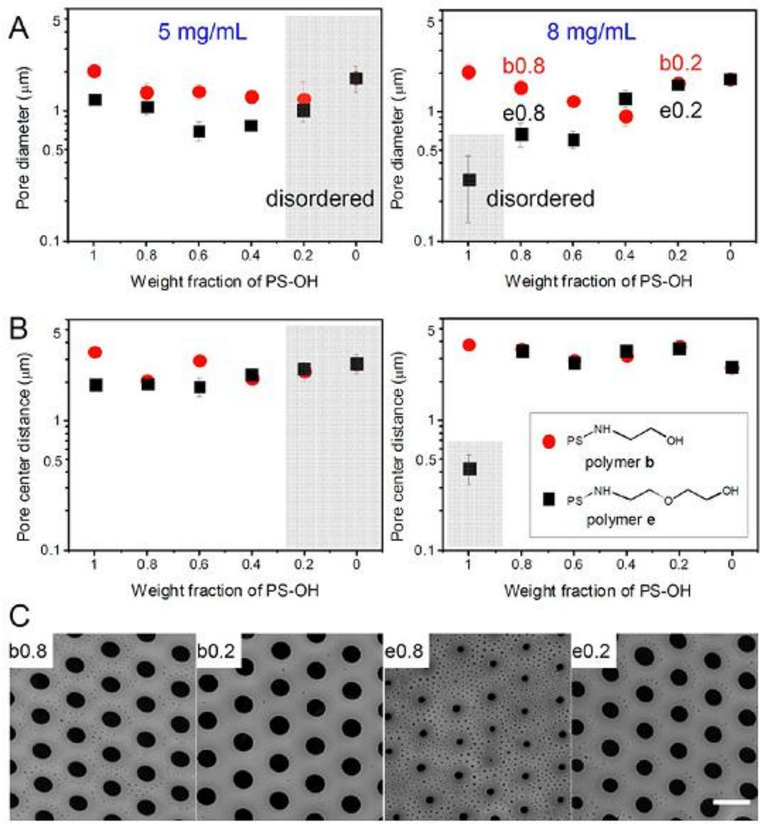


Figure 7. Pore diameter (A) and pore center distance (B) of honeycomb films prepared from the mixture of PS-OH and PS-Br at 5 mg/mL (left panel) and 8 mg/mL (right panel). (C) Typical SEM images of samples prepared from the blends with a total polymer concentration of 8 mg/mL. Scale bar is 5 μm.

Conclusions:

In summary, the hydrophilic end groups can dramatically improve the film-forming property of PS. The regularity of the film is mainly influenced by the interaction of film-forming polymers with condensed water droplets. Polymers with highly similar hydrophilic end groups resulted in greatly different films. Specifically, if the polymer can package the water droplets in a short period, honeycomb film with multilayer structure and nanometer sized surface pore can be formed. Otherwise, only monolayer structure can be formed. For 8 mg/mL polymer *e* that is the most hydrophilic, the addition of PS-Br can gradually increase the pore diameter. This work provides a further insight into the intrinsic mechanism of relationship between the functional end groups and the structure of the honeycomb film.

References:

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[3] Zhu LW, Ou Yang, Wan LS, Xu ZK. *J. Phys. Chem. B* 2014 (118), 845-854.

Acknowledgements:

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