A Systematic Investigation on Formation of Honeycomb-Patterned Porous Films from Amphiphilic Block Copolymers

Bai-Heng Wu (11429020), Liang-Wei Zhu, Yang Ou, Wen Tang, Ling-Shu Wan*, Zhi-Kang Xu

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

The breath figure method is a very simple and high-efficient technique to prepare honeycomb-patterned porous structures. Amphiphilic block copolymers are the mostly used film-forming materials. In this work, we synthesized more than 30 amphiphilic block copolymers with different chemical compositions by atom transfer radical polymerization (ATRP). Honeycomb films from polystyrene-*block*-poly(N,N-dimethyl-aminoethly methacrylate) (PS-*b*-PDMAEMA) were prepared by breath figure method, and an empirical phase diagram has been obtained to show the relationship between the block copolymer composition and the film-forming ability. Moreover, interfacial tensions of these copolymers were measured by pendant drop method. A polymerization degree ratio of PDMAEMA to PS blocks between 0.01~0.02, which has an interfacial tension of 34.5~46.0 mN/m, is favorable for the preparation of highly ordered honeycomb films. For polystyrene-*block*-poly(2-hydroxyethyl methacrylate) (PS-*b*-PHEMA) that has a more hydrophilic block, it shows different interfacial tensions and self-assembling behaviors when the PHEMA block is long.

Table 1. Ratios of polymerization degrees of PDMAEMA to PS of PS-*b*-PDMAEMA.

Run	PS_{73}	PS_{145}	PS_{208}	PS_{345}	PS_{456}
b0	0	0	0	0	0
b1	0.04	0.02	0.02	0.02	0.01
b2	0.08	0.04	0.06	0.05	0.02
b3	0.14	0.10	0.11	0.07	0.05
b4	0.21	0.18	0.16	0.12	0.09

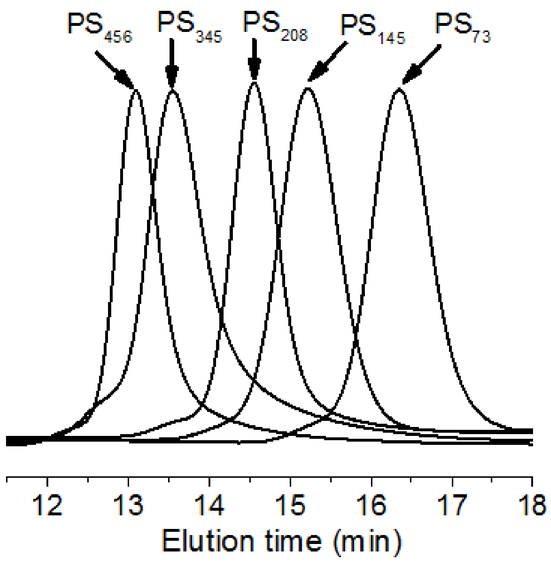

Figure 1. GPC curves of macroinitiators.

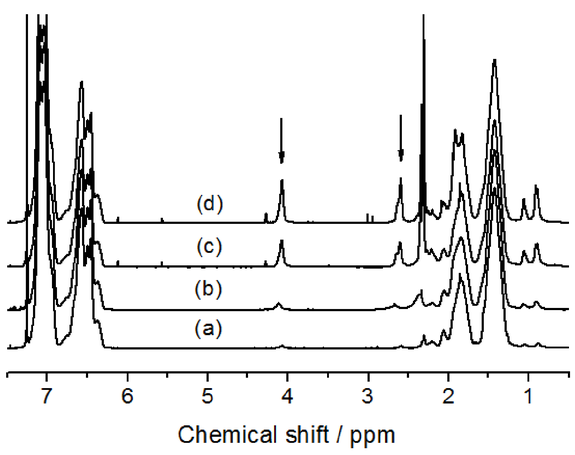

Figure 2. ^1H NMR spectra.

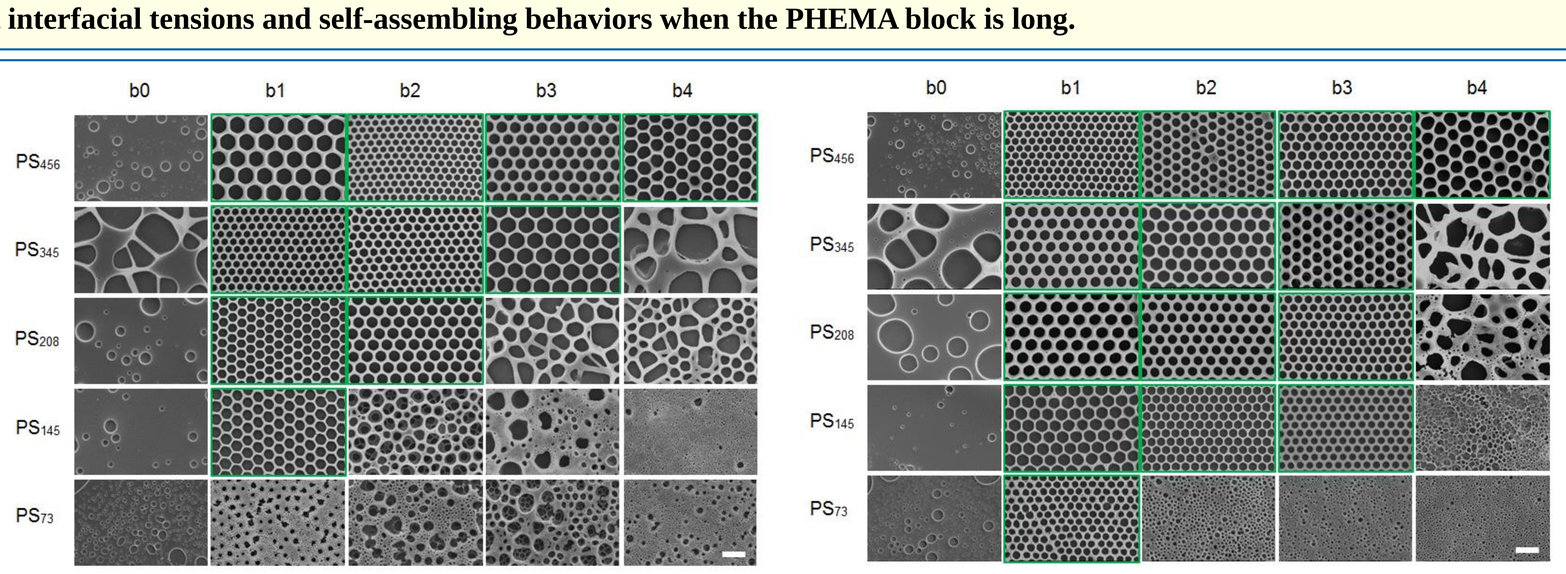

Figure 3. SEM images of films prepared from PS-*b*-PDMAEMA in CS_2. Concentration: 1 mg/mL (left) and 2 mg/mL (right).

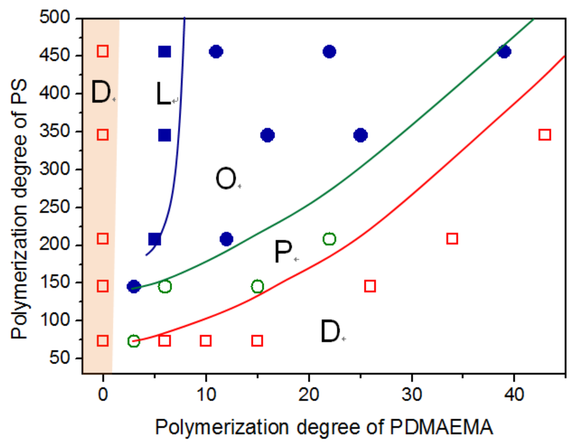

Figure 4. Dependence of the regularity on the composition of PS-*b*-PDMAEMA.

As the length of PS block increases, longer hydrophilic PDMAEMA block is endurable, i.e., the fabrication window for ordered honeycomb films becomes wider for copolymers having longer PS block. Regularity is represented using different symbols. There are four main zones, **L**, **O**, **P**, and **D**, which means large-area ordered, ordered, partially ordered, and disordered films, respectively. In the **L** zone, the length of hydrophilic block is short with a block length ratio between 0.01~0.02. These polymers are able to form narrow pore size distribution, large-area, almost defects-free, and highly reproducible honeycomb-patterned porous films. The main difference between **L** and **O** zones is that copolymers in the latter zone are more sensitive to experimental conditions such as humidity and defects may appear. The **P** zone is highly dependent on solution concentration and defects further develop. This zone can be considered as a transitional region between ordering and disordering (**D**).

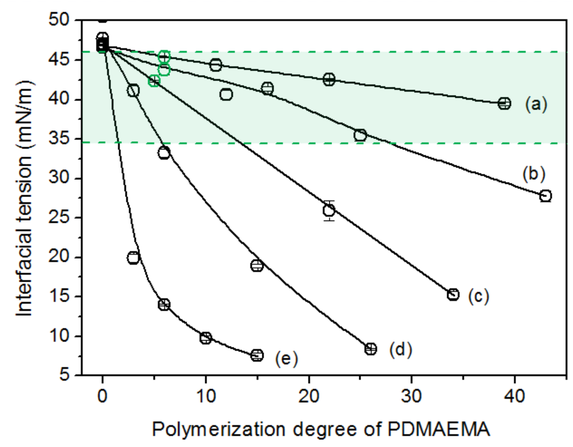

Figure 5. Interfacial tension between water and PS-*b*-PDMAEMA solutions in CS_2

Interfacial tension decreases with the polymerization degree of PDMAEMA block. It is reasonable because these amphiphilic block copolymers may be considered as surfactants which could decrease interfacial tension between water and polymer solutions. As for macroinitiator PS-Br with different molecular weights, the interfacial tensions change little. For PS_{456} series with the longest PS block, the chain extension by PDMAEMA makes the interfacial tension decrease gradually. When the hydrophobic PS block is shortened, the polymerization degree of PDMAEMA block would impact the interfacial tensions more effectively. Hence, PS_{73} series have the most dramatic decrease of interfacial tensions. Combined with film formation, it can be concluded that an interfacial tension between 34.5 and 46.0 mN/m is beneficial to the formation of ordered honeycomb films via the dynamic breath figure method for the PS-*b*-PDMAEMA system.

Table 2. Results of PS-*b*-PHEMA.

Run	Polymer	PHEMA/PS
b5	PS_{197}-*b*-$PHEMA_4$	0.02
b6	PS_{197}-*b*-$PHEMA_8$	0.04
b7	PS_{197}-*b*-$PHEMA_{12}$	0.06
b8	PS_{197}-*b*-$PHEMA_{18}$	0.09
b9	PS_{197}-*b*-$PHEMA_{35}$	0.18
b10	PS_{197}-*b*-$PHEMA_{49}$	0.25

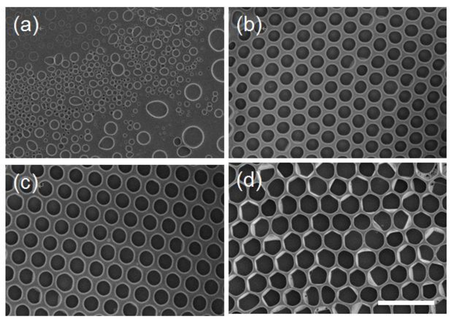

Figure 6. SEM images of honeycomb films prepared from (a) PS_{197}, (b) b5, (c) b6, (d) b7.

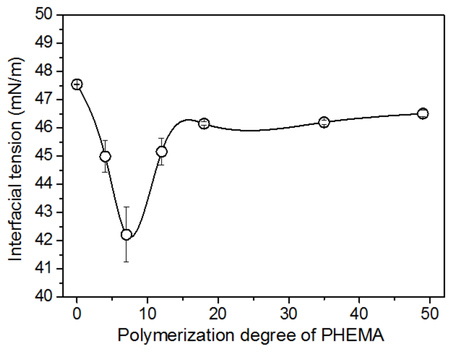

Figure 7. Interfacial tensions between PS_{197}-*b*-PHEMA solutions and water.

Because of the large number of hydroxyl groups, polymers b8, b9 and b10 cannot fully dissolve in apolar solvent CS_2.

As the PHEMA block length increases, the interfacial tension decreases first and then increases slightly, and finally it levels off. This could be explained by the aggregation state transition from unimers to reverse micelles.

Conclusions:

In summary, an empirical phase diagram of different zones showing large-area ordered (L), ordered (O), partially ordered (P), and disordered (D) films, which highly depend on the chemical compositions of the block copolymers, was obtained. For PS-*b*-PDMAEMA, a polymerization degree ratio of PDMAEMA to PS blocks between 0.01~0.02, which has an interfacial tension between 34.5 and 46.0 mN/m, is the best for the preparation of highly ordered honeycomb films in a reproducible way under a wide experimental window. For PS-*b*-PHEMA in which the PHEMA is more hydrophilic than PDMAEMA, the results are consistent with those of PS-b-PDMAEMA when the polymerization degree of PHEMA is smaller than 8; however, it forms reverse micelles and shows different self-assembling behaviors when the polymerization degree of PHEMA is larger than 12.

References:

[1] Wong, KH; Davis, TP; Stenzel, MH. *Polymer* 2007(48), 4950-4965.

[2] Fukuhira, Y; Yabu, H; Ijiro, K; Shimomura, M. *Soft Matter* 2009(5), 2037-2041.

[3] Wan, LS; Zhu, LW; Ou, Y; Xu, ZK. *Chem. Commun.* 2014(50), 4024-4039.

Acknowledgements:

This work is supported by the National Natural Science Foundation of China (21374100 and 51173161).