

Effect of Homopolymer Chain Length on Phase Behavior of Polystyrene-Block-Poly(methyl Methacrylate) Films

The morphology and phase interactions of polystyrene-block-poly(methyl methacrylate) blended with homopolystyrenes of three molecular weights were investigated.

Self-assembling block copolymers (BCPs) offer an extremely versatile method for forming various types of nanodomains with diverse morphologies and orientations. The complexity of BCP thin films can be increased by blending a homopolymer with them. A team led by Ya-Sen Sun (National Central University) systematically studied the effects of chain length on the phase behavior of polystyrene-block-poly(methyl methacrylate) (PS-*b*-PMMA): homopolystyrene (hPS) ($B_{wt\%}H_{wt\%}$) blend films.

Figure 1 shows the scheme for the phase behavior of $B_{75}H_{25}^x$ ($x = 2.8, 6, \text{ and } 17$) blend films. This scheme is based on the morphological observations and grazing-incidence small-angle X-ray scattering (GISAXS) characterizations at **TLS 23A1**. The perforated layers (PLs) in the PS-*b*-PMMA-rich region of the $B_{75}H_{25}^{2.8}$ films form with a parallel orientation only, regardless of film thickness. Because of their short length, hPS^{2.8} chains tend to be distributed uniformly in polystyrene (PS) perforations and layers. Furthermore, the uniform distribution of hPS^{2.8} chains in PS perforations causes a swell in the chemical junctions at the interface between PS and poly(methyl methacrylate) (PMMA) (case i). A uniform distribution may not exist for hPS⁶ and hPS¹⁷. hPS⁶ and hPS¹⁷ exhibit different local segregation behaviors (cases ii and iii). Almost all hPS¹⁷ chains locally segregate at the middle of the perforation, whereas hPS⁶ chains tend to be distributed in an intermediate state in which uniform distribution and local segregation coexist. The local segregation behavior affects the phase behavior of $B_{75}H_{25}^6$ and $B_{75}H_{25}^{17}$ films.

To further investigate the morphology, the team of Sun used neutron reflectometry (NR) instrument (**PLATYPUS**) at the Australia's Nuclear Science and Technology Organisation (ANSTO) to trace the vertical distribution of hPS^x chains within self-assembled nanodomains. Two deuterated homopolymers (dPS) were used to enhance the contrast in scattering length density (SLD) between PS-*b*-PMMA and dPS. The fitting model contained (1) a top layer of mixed PS and dPS near the free surface of a film, (2) alternating layers with a certain periodicity as the middle region of the film, and (3) a bottom layer of PMMA chains richly anchored onto the substrate interface.

Comparisons of the SLD profiles displayed in **Figs. 2(c) and 2(d)** indicate one similarity and two discrepancies between the prepared $B_{75}D_{25}^4$ and $B_{75}D_{25}^{17}$ films. The similarity is that the top layer always consists of mixed PS and dPS chains. Therefore, the SLDs of the top half-layer were 3.57×10^{-6} and $4.80 \times 10^{-6} \text{ \AA}^{-2}$ for $B_{75}D_{25}^4$ and $B_{75}D_{25}^{17}$, respectively. The top layer containing mixed PS and dPS was formed because of their lower surface energies. The first discrepancy is that the bottom half-layer near the substrate interface may consist of either neat PMMA chains or a mixture of dPS and PMMA chains. The SLDs of the bottom

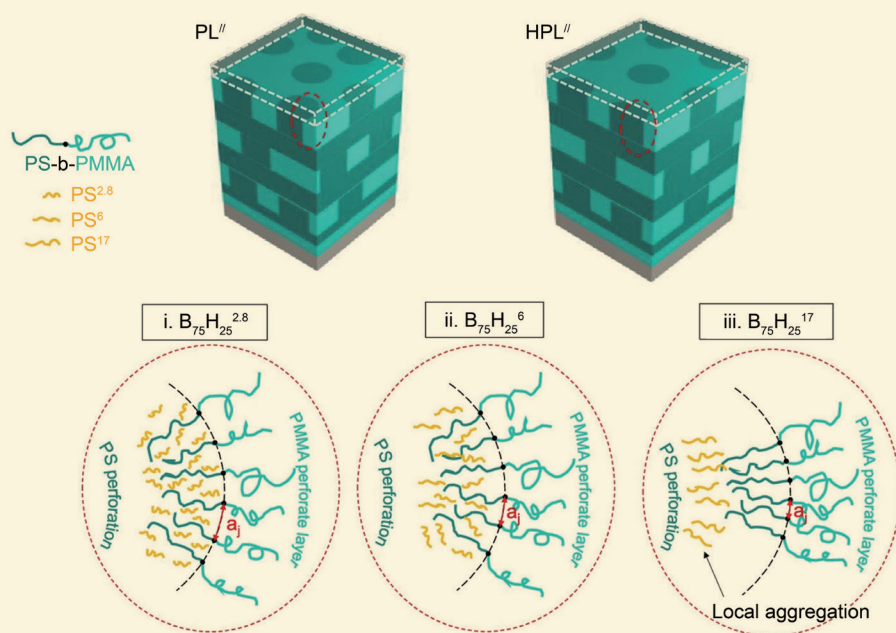


Fig. 1: Scheme for the spatial distributions of hPS^x chains in the PS-*b*-PMMA-rich region of $B_{75}H_{25}^x$ thin films (thickness = 80 nm) annealed at 270 °C: $x = 2.8$ (i), 6 (ii), and 17 (iii). [Reproduced from Ref. 1]

layer were 2.05×10^{-6} and $1.18 \times 10^{-6} \text{ \AA}^{-2}$ for $B_{75}D_{25}^4$ and $B_{75}D_{25}^{17}$, respectively. The bottom layer of $B_{75}D_{25}^{17}$, which contained neat PMMA, was formed because of the strong affinity toward the Si substrate. The second discrepancy existed in the middle region. For the $B_{75}D_{25}^x$ ($x = 4$ and 17) films, each middle region consisted of a periodic structure of alternating PS and PMMA layers. For the $B_{75}D_{25}^{17}$ film, the overall interlayer spacing of the hexagonal PLs (HPLs) was 27.2 nm, as shown in Fig. 2(d). The PS-dominated layers had a high SLD value ($> 3.44 \times 10^{-6} \text{ \AA}^{-2}$), whereas the PMMA-dominated layers had a low SLD value ($1.38 \times 10^{-6} \text{ \AA}^{-2}$).

These results are consistent with the dPS¹⁷ chains segregating within the PS layers and a few chains localizing within the PS perforations of the $B_{75}D_{25}^{17}$ film. By contrast, the $B_{75}D_{25}^4$ film (Fig. 2(c)) had an interlayer spacing of 23.9 nm in the middle region, in which the PS-rich layers had an SLD of $3.08 \times 10^{-6} \text{ \AA}^{-2}$ and the PMMA-rich layers had an SLD of $1.72 \times 10^{-6} \text{ \AA}^{-2}$.

The reduced contrast in SLD between the PS-rich and PMMA-rich layers for $B_{75}D_{25}^4$ indicated that the dPS⁴ chains were uniformly distributed within the PS layers and perforations. The uniform distribution of dPS⁴ resulted in a repeat distance of 23.9 nm within the $B_{75}D_{25}^4$ film (smaller than that for $B_{75}D_{25}^{17}$), with the thickness of the PS layers being comparable to that of the perforated PMMA layers. The NR results were consistent with the hypothesis proposed in the scheme displayed in Fig. 1.

In summary, the team of Sun demonstrated morphological diversity by varying the molecular weight ratios of PS-b-PMMA and hPS. When PS-b-PMMA was the major component and hPS^x was the minor component, the surface morphologies on the Si substrate were dominated by HPLs or double gyroids. In the PS-b-PMMA-rich region, the PLs were the only discernible phase, regardless of film thickness, if the PS-b-PMMA film contained short (PS^{2,8}) chains. By contrast, if the PS-b-PMMA film contained medium-length (PS⁶) chains, thin films prefer the HPL phase, and thick films prefer the double-gyroid phase. When the PS-b-PMMA film contained hPS¹⁷ chains whose length was comparable to that of the PS block, the HPL phase became the only discernible structure. (Reported by Tzu-Yen Huang)

This report features the work of Ya-Sen Sun and his collaborators published in Macromolecules 55, 2130 (2022).

TLS 23A1 Small/Wide Angle X-ray Scattering ANSTO PLATYPUS – Neutron Reflectometer

- GISAXS, NR
- Polymers, Morphology, Interfaces, Layers and Blend Films

Reference

1. J. W. Hong, J. H. Chang, H. H. Hung, Y. P. Liao, Y. Q. Jian, I. C. Y. Chang, T. Y. Huang, A. Nelson, I. M. Lin, Y. W. Chiang, Y. S. Sun, *Macromolecules* **55**, 2130 (2022).

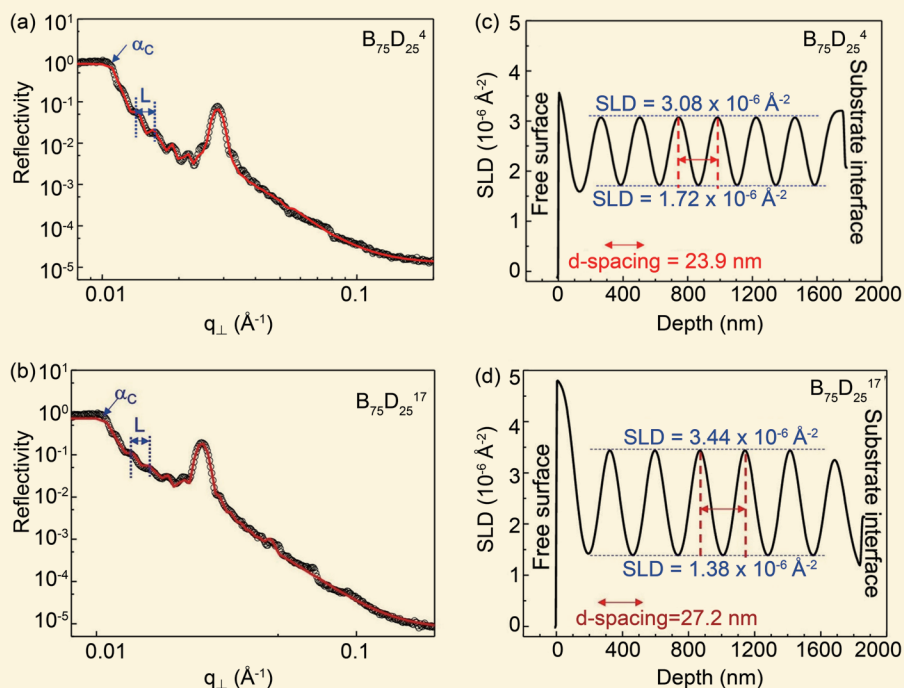


Fig. 2: (a,b) NR experimental curves (open circles) and fitted curves (red lines) and (c,d) corresponding SLD profiles of $B_{75}D_{25}^x$ ($x = 4$ and 17) films with a thickness of 162 nm that were annealed at 270 °C. The SLD values of the dPS layers and PMMA PLs are also shown in (c) and (d). Moreover, the d-spacing values are depicted in (c) and (d) for visual guidance. [Reproduced from Ref. 1]