# Enthalpy Relaxation and Morphology Evolution in Polystyrene-*b*-poly(methyl methacrylate) Block Copolymer

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### Supporting Information:

#### Materials:

The atactic Polystyrene-*b*-poly(methyl methacrylate) block copolymer was purchased from Polymer Source Inc and prepared by living anionic polymerization. The ratio for Syndio, hetero and iso contents is 42:51:6. The 1H-NMR spectroscopy is shown in Fig.S1.<sup>S1</sup>

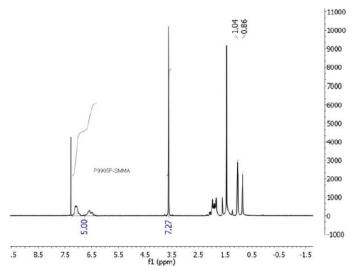
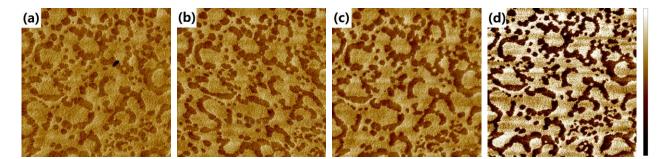


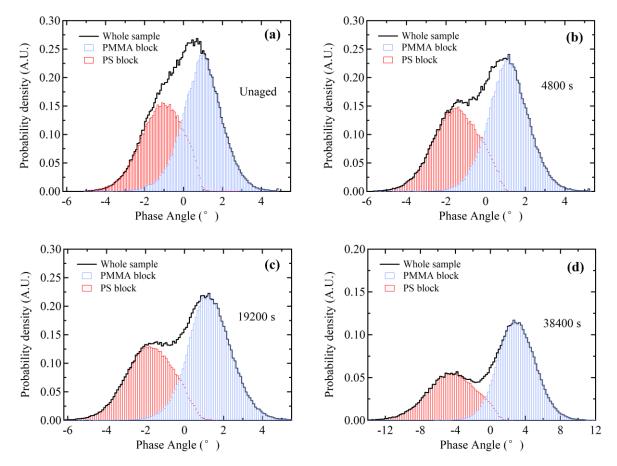
Figure S1. 1H-NMR spectroscopy of PS-b-PMMA copolymer

#### Morphology Evolution:

The *in-situ* phase figures of PS-*b*-PMMA copolymer for  $T_a = 114$  °C are depicted in Fig. S2 and the corresponding phase angle data are summarized in Fig. S3.



**Figure S2**. Phase figure of PS-PMMA diblock copolymer under very high aging temperature ( $T_{g,PMMA block}$  - 13 °C). (a) - (d) The sample was heated to 180 °C and hold for 10 min first which likes aging test. The color scales -6 ° ~ 10 ° were set the same for all the panels. The diagrams are from same position whose size is 2x2 µm with different aging time: (a) Unaged, (b) 4800 s, (c) 19200 s, (d) 38400 s.



**Figure S3.** Phase angle histograms of PS-PMMA diblock copolymer under very high aging temperature ( $T_{g,PMMA block}$  - 13 °C). (a) - (d) The black cityscapes are the phase angle statistics of whole sample. The red and blue bars are the statistics of PS block and PMMA block from AFM results respectively. The sum of two blocks contribution is equal to the whole sample distribution histograms. (a) Unaged. (b)  $t_a$ =4800 s. (c)  $t_a$ = 19200 s. (d)  $t_a$ = 38400 s.

## **REFERENCES**:

S1. Sample Introduction of P9905P-SMMA from Polymer Source Inc.