## **Electronic Supplementary Information**

Perpendicularly aligned nanodomains on versatile substrates *via* rapid thermal annealing assisted by liquid crystalline ordering in block copolymer films

Ting Qu,<sup>a</sup> Song Guan,<sup>a</sup> Xiaoxiong Zheng,<sup>a</sup> and Aihua Chen\*<sup>a</sup>

<sup>a</sup>School of Materials Science and Engineering, Beihang University, Beijing 100191,

P. R. China

\*E-mail: chenaihua@buaa.edu.cn



Fig. S1 <sup>1</sup>H NMR spectra of PS macroinitiators and PS-*b*-PMA(Az) BCPs.



**Fig. S2** GPC curves of the PS macroinitiators and PS-*b*-PMA(Az) BCPs with THF as eluent.



Fig. S3 DSC curves of polymers on the first cooling (a) and second heating (b) processes with a heating/cooling rate of  $\pm 10$  °C min<sup>-1</sup>.



Fig. S4 POM image (a) and WAXD profile (b) of the  $PS_{100}$ -*b*-PMA(Az)<sub>44</sub> samples.



Fig. S5 SEM top (a, c, e, g) and cross-sectional (b, d, f, h) images of  $PS_{100}$ -*b*- $PMA(Az)_{44}$  thin films after thermal annealing at 140 °C for different times before RIE: (a, b) 0 min, (c, d) 1 min, (e, f) 3 min and (g, h) 5 min.



**Fig. S6** TEM images (inset: FFT images) of cylindrical  $PS_{100}$ -*b*-PMA(Az)<sub>44</sub> (a) and lamellar  $PS_{100}$ -*b*-PMA(Az)<sub>22</sub> (b) thin films after thermal annealing at 140 °C for 5 min.



Fig. S7 The etching rate of PS, PMMA and PMA(Az) polymer films at the same RIE conditions:  $O_2/Ar$  (40/10) sccm/50 W/75 mTorr.



Fig. S8 SEM images of  $PS_{100}$ -*b*-PMA(Az)<sub>44</sub> self-assembled cylindrical films after different RIE conditions: (a, b) O<sub>2</sub>/50 sccm/50 W/75 mTorr/30 s, (c, d) O<sub>2</sub>/Ar (15/3) sccm/50 W/75 mTorr/30 s, (e, f) O<sub>2</sub>/Ar (40/10) sccm/100 W/75 mTorr/30 s, (g, h) O<sub>2</sub>/Ar (40/10) sccm/50 W/75 mTorr/60 s, (i, j) O<sub>2</sub>/Ar (40/10) sccm/50 W/75 mTorr/30



Fig. S9 SEM top (a, c, e, g) and cross-sectional (b, d, f, h) images of  $PS_m$ -*b*-PMA(Az)<sub>n</sub> self-assembled cylindrical films with different diameters after RIE: O<sub>2</sub>/Ar (40/10) sccm/50 W/75 mTorr/30 s. (a, b)  $PS_{100}$ -*b*-PMA(Az)<sub>59</sub>, (c, d)  $PS_{100}$ -*b*-PMA(Az)<sub>35</sub>, (e, f)  $PS_{100}$ -*b*-PMA(Az)<sub>32</sub>, (g, h)  $PS_{100}$ -*b*-PMA(Az)<sub>27</sub>, respectively.



Fig. S10 TEM (a) and AFM (b) images of  $PS_{100}$ -*b*-PMA(Az)<sub>24</sub> self-assembled thin films. SEM top (c) and cross-sectional (d) images of above films after RIE: O<sub>2</sub>/Ar (40/10) sccm/50 W/75 mTorr/30 s.



Fig. S11 SEM top (a) and cross-sectional (b) images of  $PS_{100}$ -*b*-PMA(Az)<sub>18</sub> selfassembled lamellar films after RIE: O<sub>2</sub>/Ar (40/10) sccm/50 W/75 mTorr/30 s.



Fig. S12 SEM top (a) and cross-sectional (b) images of  $PS_{42}$ -*b*-PMA(Az)<sub>16</sub> films after RIE: O<sub>2</sub>/Ar (40/10) sccm/50 W/75 mTorr/30 s.



**Fig. S13** (a) TEM image of cylindrical  $PS_{28}$ -*b*-PMA(Az)<sub>68</sub> thin film. (b) The magnification of the boxed area inserts in (a).



Fig. S14 Cross-sectional TEM (a) and top-view AFM height (b) images of the annealed  $PS_{100}$ -*b*-PMA(Az)<sub>44</sub> film on PET sheet.