Supporting Information

Liquid Crystalline Moiety-Assisted Perpendicular Orientation of Cylindrical Domains within P4VP-b-PMA(Az) Films with High Aspect Ratio

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Figure S1. $^1$H NMR spectrum of MA(Az).
Figure S2. $^1$H NMR spectra of different P4VP macroinitiator and P4VP$_{m-b}$-PMA(Az)$_n$ BCPs.

Figure S3. GPC curves of the P4VP macroinitiators with DMF as eluent, and P4VP$_{m-b}$-PMA(Az)$_n$ BCPs with THF as eluent.

Table S1. Properties of the P4VP macroinitiators and P4VP-$b$-PMA(Az) BCPs synthesized by the ATRP method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^aM_n$ (NMR)</th>
<th>$^bM_n$ (GPC)</th>
<th>$^cM_w/M_n$</th>
<th>$^d$DP$_{P4VP}$</th>
<th>$^e$DP$_{PMA(Az)}$</th>
<th>$^f$f$_{P4VP}$</th>
<th>$^g$Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>P4VP$_{50}$</td>
<td>5,500</td>
<td>7,500</td>
<td>1.05</td>
<td>50</td>
<td>—</td>
<td>1</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>P4VP&lt;sub&gt;100&lt;/sub&gt;</td>
<td>10,500</td>
<td>12,500</td>
<td>1.12</td>
<td>100</td>
<td>—</td>
<td>1</td>
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<tr>
<td>P4VP&lt;sub&gt;100-b-MA(Az)&lt;sub&gt;15&lt;/sub&gt;</td>
<td>17,880</td>
<td>20,660</td>
<td>1.28</td>
<td>100</td>
<td>15</td>
<td>0.58</td>
<td>sphere</td>
</tr>
<tr>
<td>P4VP&lt;sub&gt;50-b-MA(Az)&lt;sub&gt;10&lt;/sub&gt;</td>
<td>10,180</td>
<td>13,800</td>
<td>1.28</td>
<td>50</td>
<td>10</td>
<td>0.50</td>
<td>lamellae</td>
</tr>
<tr>
<td>P4VP&lt;sub&gt;100-b-MA(Az)&lt;sub&gt;60&lt;/sub&gt;</td>
<td>40,020</td>
<td>53,400</td>
<td>1.30</td>
<td>100</td>
<td>60</td>
<td>0.25</td>
<td>cylinder</td>
</tr>
<tr>
<td>P4VP&lt;sub&gt;100-b-MA(Az)&lt;sub&gt;75&lt;/sub&gt;</td>
<td>47,400</td>
<td>60,300</td>
<td>1.33</td>
<td>100</td>
<td>75</td>
<td>0.21</td>
<td>sphere</td>
</tr>
</tbody>
</table>

*a* Number-average molecular weight determined by NMR.

*b* Number-average molecular weight determined by GPC.

*c* Polydispersity determined by GPC calibrated with polystyrene standards.

*d* Polymerization degree of P4VP.

*e* Polymerization degree of PMA(Az).

*f* The volume fraction of P4VP calculated by using molecular weight and density (P4VP: 1.15 g/cm<sup>3</sup> and PMA(Az): 1.10 g/cm<sup>3</sup>) of each block.

*g* The morphology of block copolymer film is determined by SEM observations.

![Figure S4](image_url). DSC curves of BCPs on first cooling (a) and second heating processes (b) with heating/cooling rate of ± 10 °C min<sup>-1</sup>.
Figure S5. SEM images of P4VP$_{100}$-b-PMA(Az)$_{60}$ self-assembled films with 2 µm by thermal annealing (160 °C/1 h and 105 °C/24 h) (a), solvent-annealed in THF vapor (b), IPA vapor (c) and chloroform vapor (d, e) at room temperature for 24 h. d with (10) planes of hexagonal alignment, e with (11) planes of hexagonal alignment, respectively.
Figure S6. SEM (a, b, d-h) and AFM (c) images of P4VPₘ⁻b-PMA(Az)ₙ self-assembled films with different $f_{P4VP}$, respectively. (a, b) P4VP₁₀₀⁻b-PMA(Az)₇₅ ($f_{P4VP} = 0.21$), (c, d) P4VP₁₀₀⁻b-PMA(Az)₆₀ ($f_{P4VP} = 0.25$), (e, f) P4VP₅₀⁻b-PMA(Az)₁₀ ($f_{P4VP} = 0.50$), (g, h) P4VP₁₀₀⁻b-PMA(Az)₁₅ ($f_{P4VP} = 0.58$). Right images are the schemes of these morphologies, respectively. Blue part and green part represent P4VP and PMA(Az) blocks, respectively.
Figure S7. SEM images of the TiO$_2$ nanomaterials from corresponding templates: (a) top-view of TiO$_2$ nanosphericals from the annealed P4VP$_{100}$-$b$-PMA(Az)$_{75}$ film with 50 nm thickness; (b) top-view of TiO$_2$ porous films from the annealed P4VP$_{100}$-$b$-PMA(Az)$_{15}$ film with 50 nm thickness.

Figure S8. (a) Geometrical relationship and center-to-center distances of perpendicular cylinders, wide stripes P and narrow stripes P1. (b) SEM image of (11) planes of hexagonal alignment.
Figure S9. Cross-section SEM images of the solvent-annealed P4VP$_{100-b}$-PMA(Az)$_{60}$ films with different thicknesses: 3 μm (a, b); 4 μm (c, d); 6 μm (e, f); a, c, e with (11) planes of hexagonal alignment; b, d, f with (10) planes of hexagonal alignment, respectively.