Disorder-to-Order Transitions Induced by Alkyne/Azide Click Chemistry in Diblock Copolymer Thin Films

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Electronic Supplementary Information

Determining the composition of the di-BCPs from 1H NMR Fig. S1 shows a typical 1H NMR spectra of the PEO-b-P(nBMA-r-PgMA) di-BCP. The peaks at chemical shift of 3.5 ppm (a), 4.0 ppm (d) and 4.6 ppm (h) correspond to the proton resonances of the -CHR2 group in the PEO block, nBMA comonomer and PgMA comonomer, respectively. Since the molecular weight of the PEO block is already known, the total number of repeating unit of the nBMA and PgMA comonomers can be calculated as follows:

\[
DP(nBMA) = \frac{I_a/2}{I_d/4} \times \frac{M_o(PEO)}{44}
\]

\[
DP(PgMA) = DP(nBMA) \times \frac{I_h}{I_d}
\]

Here \( I_a, I_d \) and \( I_h \) correspond to the integration area of peak a, d and h, respectively.
Fig. S1 $^1$H NMR spectra of PEO-$b$-P(nBMA-$r$-PgMA) di-BCP 19-10-33
**Fig. S2** SFM height images (a, b) and GISAXS patterns (c, d) of thin films of binary blend of di-BCP 19-10-33 and Rhodamine B azide, annealed at 110 °C for 3 h (a, c) and 6 h (b, d), respectively. For both samples, the mole ratio between the alkyne and azide groups is 1:1, and the film thickness is around 45 nm. GISAXS incident angle is 0.20°.

**Fig. S3** SFM height image (a) and GISAXS pattern (b) of a thin film of binary blend of di-BCP 19-10-33 and Rhodamine B azide, annealed at 90 °C for 12 h. The mole ratio between the alkyne and azide groups is 1:1, and the film thickness is around 45 nm. GISAXS incident angle is 0.20°.
Fig. S4 SFM height image (a, b) and GISAXS pattern (c, d) of thin films of binary blend of Rhodamine B azide and di-BCP 19-10-33 (a, c) and 10.5-20.5-67 (b, d), annealed at 110 °C for 12 h. For both samples, the mole ratio between the alkyne and azide groups is 4:1, and the film thickness is around 45 nm. GISAXS incident angle is 0.20°.
Fig. S5 X-ray reflectivity profile of a thin film of binary blend of di-BCP 19-10-33 and Rhodamine B azide, annealed at 110 °C for 12 h. The mole ratio between the alkyne and azide groups is 1:1, and the film thickness is around 150 nm.

Fig. S6 PSD profiles of SFM images of thin films of binary blend of PEO-b-P(nBMA-r-PgMA) di-BCP 10.5-20.5-67 and Rhodamine B azide, annealed at 110 °C for 12 h. The mole ratio between the alkyne and azide groups is 4:3 for both samples. The film thickness is around 45 nm (a) and 20 nm (b), respectively. Profile curves are offset for clarity.
Fig. S7 SFM height images (a) and GISAXS patterns (b) of a thin film of binary blend of di-BCP 10.5-20.5-67 and Rhodamine B azide, annealed at 110 °C for 12 h. The mole ratio of between the alkyne and azide groups is 2:1, and the film thickness is around 120 nm. GISAXS incident angle is 0.20°.