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Electronic Supplementary Information (ESI)

Determining order-to-disorder transitions in block copolymer

thin films using a self-referencing fluorescent probe

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Figure S1. (A) NMR spectra of C-PSMMA; (B) GPC trace of C-PSMMA (PS-*b*-PMMA: $M_n = 31,400 \text{ g/mol}; \phi_{ps} = 0.30; D = 1.23$) and (C) GPC trace of L-PSMMA ($M_n = 26,800 \text{ g/mol}; \phi_{PS} = 0.54; D = 1.24$). The peak area of –CH₃ (labeled as a) from PMMA and Ar-H from PS was used to determine the copolymer composition.



Figure S2. Intensity ratio (I_1/I_3) value of pyrene molecules as a function of temperature for C-PSMMA with different film thicknesses.



Figure S3. Intensity ratio (I_1/I_3) value of pyrene molecules as a function of temperature for L-PSMMA with different film thicknesses.



Figure S4. Water contact angle measurements for five different Si substrates. (A) After 12 h piranha treatment; (B) after 15 min Piranha treatment, (C) after 2 min Piranha treatment, (D) bare Silicon substrate and (E) Fluorinated Si surface.

Notes: Experimental procedure for functionalizing Si substrates with fluorinated groups (**Figure S4E**): The substrates were first treated with Piranha solution for 1 2 h, and then immersed in 3-(perfluoror-7-methyloctyl)-1,2-propeneoxide. After immersion for 3 min, the substrates were rinsed with toluene and hexane several times and dried with air.



Figure S5. Intensity ratio (I_1/I_3) value of pyrene molecules as a function of temperature for monolayer C-PSMMA films (approximately 20 nm) on five different Si substrates. The water contact angle of each substrate surface is indicated in the figure.