Electronic Supplementary Material (ESI) for Soft Matter.

Semi-crystalline polymethylene-*b*-poly(acrylic acid) diblock copolymers: aggregation behavior, confined crystallization and controlled growth of semicrystalline micelles from dilute DMF solution†

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1. Characterization

The morphology of the PM-*b*-PAA was characterized by atomic force microscope (AFM) in a tapping mode. ANTEGRA Prima system (NT-MDT, Zelenograd, Russia) and Si probes (NSG10, NT-MDT) were used. The sample was fabricated by spin-coating (2500 rpm, 60 s) the dilute BCPs solution at room temperature on the precleaned silicon wafers.

Transmission electron microscope (TEM) analysis was performed using a Tecnai TEM instrument (Tecnai G2 F20, FEI) with an accelerating voltage of 200 kV to characterize the high resolution transmission electron microscopy (HRTEM), selected-area electron diffraction (SAED) of BCPs. Besides, H-7650 (Hitachi) TEM was also employed to characterize the morphology of the samples. All the specimens were prepared by depositing ~7 uL of the BCP solution on a copper grid coated with carbon, which was placed onto a filter paper to blot away the excess solution. Subsequently, the sample was dried under ambient condition for several hours prior to

TEM observation.

Dynamic light scattering (DLS) was measured on the Malvern Zetasizer Nano ZS90 (Worcestershire, UK) at 25 °C with a He–Ne laser at 633 nm to obtain the hydrodynamic diameters and the zeta potentials of PM-*b*-PAA solution, which was allowed to equilibrate before measurement.

X-ray diffraction (XRD) measurements were performed to investigate the confined crystallization of the PM-*b*-PAA micelle, and the sample was obtained by vacuum freezing drying from the aqueous solution. The diffraction data was collected on an X-ray diffractometer (XD-3, Persee, China) with Cu Kα radiation (λ = 0.154 nm) at 40 kV and 40 mA in the angular range from 10 to 40 °.

Differential scanning calorimetry (DSC) measurements were conducted on Q2000 differential scanning calorimeter (TA Instruments, New Castle, DE) with a nitrogen purge of 50 mL min^{-1} to trace the melting and crystallization behavior of PM-*b*-PAA bulk samples. For the test, a sample (*ca.* 3 mg) loaded in aluminum pans was first heated to 180 °C and held for 3 min to erase previous thermal history, then was cooled to 30 °C at a rate of 10 °C min^{-1}, and finally was heated again to 180 °C at a rate of 10 °C min^{-1}. And the obtained cooling and reheating DSC curves were employed for analysis.

A polarized optical microscope (POM) (PM6000, Jiangnan Novel, China) was used to investigate the crystalline morphology of PM-*b*-PAA sample, which was prepared by dropping the freshly prepared BCPs/DMF solution onto the cleaned cover glass, and drying at room temperature before observation.

Grazing-incidence small-angle x-ray scattering (GISAXS) experiments were carried out at 1W2A beam line of Beijing Synchrotron Radiation Facility (BSRF) with a Cu Kα wavelength of 1.54 Å. GISAXS patterns were collected with a 2D detector (MAR165 CCD; 2048×2048 pixels) placed at a distance of 5.01 m from the sample. And the incidence angle α_i was chosen as 0.2°, which is an optimal angle between the critical angles of samples and substrates. [1]

Grazing-incidence x-ray diffraction (GIXRD) experiments were conducted at the

1W1A beam line (BSRF, Beijing) using a Huber five-circle diffractometer with a Cu Kα wavelength of 1.54 Å. Samples were scanned from 10° to 40° at a rate of 0.05 °/s. The incident-beam angel was 0.2° higher than the critical angle (0.18°) of Si substrates in order to remove the Si (100) peak.[2]

2. Results

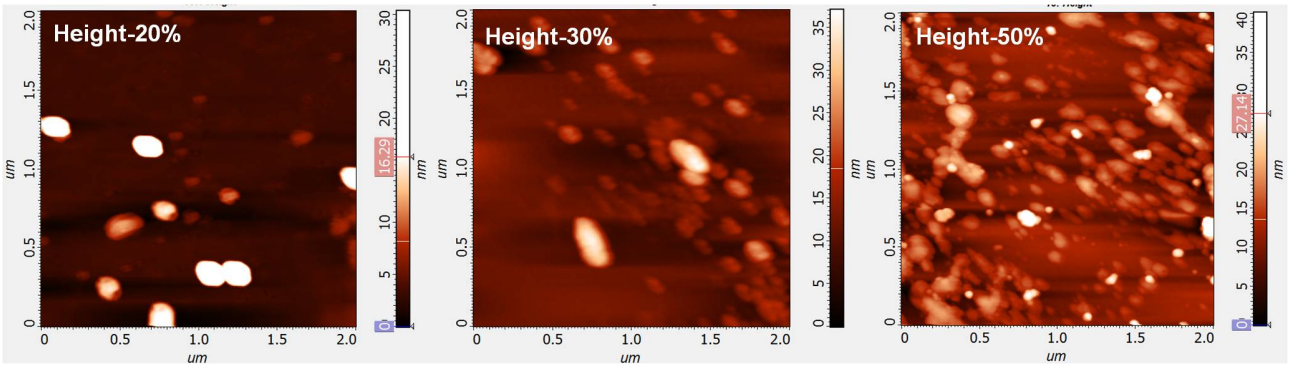

Fig. S1 AFM height images of $\mathbf{M_{107}A_5}$ in solution (0.2 mg mL^{-1}) prepared from 0.2 mg mL^{-1} solution with different DMF-water mixture solvents (x %, volume content of water).

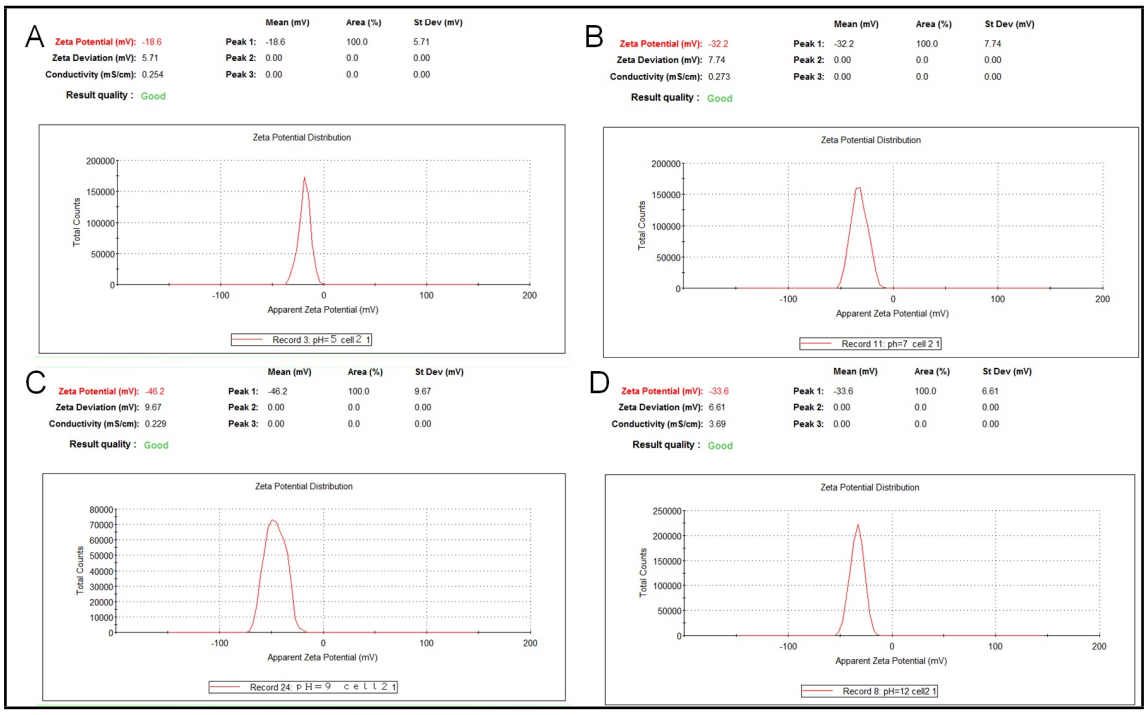

Fig. S2 Zeta potential pictures of $\mathbf{M_{107}A_5}$ micelles prepared from 0.2 mg mL^{-1} solution with different pH value of 5 (A), 7 (B), 9 (C) and 12 (D), respectively.

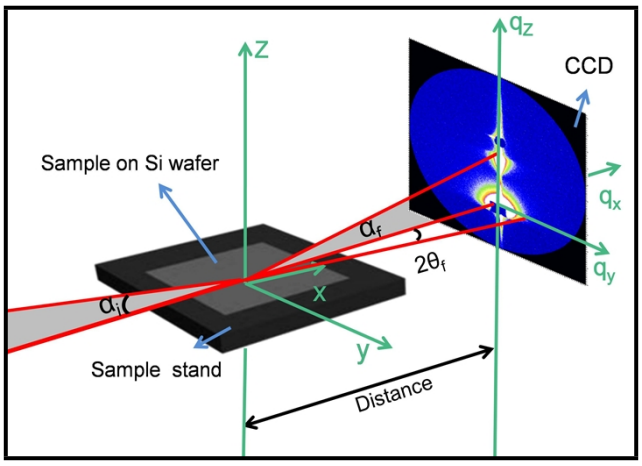

Fig. S3 Schematic drawing of the GISAXS set up.

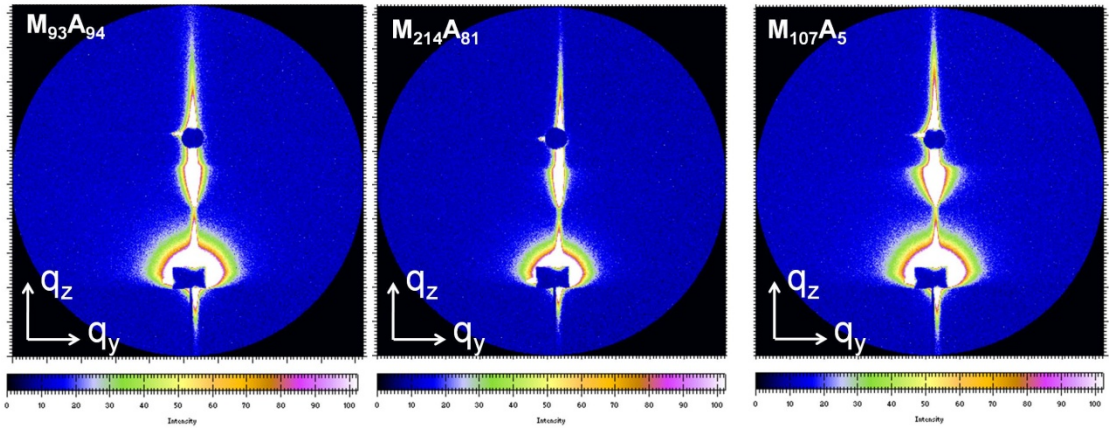

Fig. S4 2D GISAXS patterns of PM-*b*-PAA films spin-coated from 2 mg mL^{-1} DMF solution.

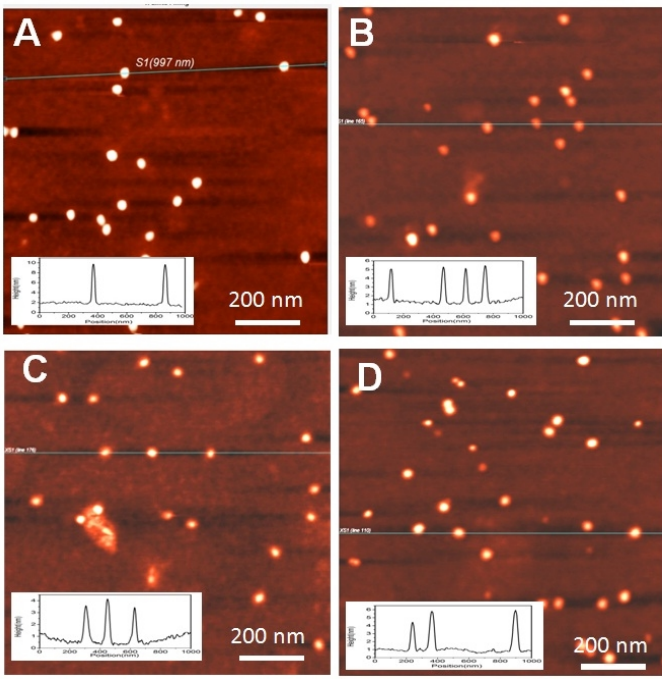

Fig. S5 AFM Height images of $\mathbf{M_{93}A_{94}}$ spin-coated from 0.2 mg mL^{-1}: (A) controlled samples without any treatment, (B) samples after annealing at 80 °C for 12 h, (C) samples after annealing under DMF atomosphere at 80 °C for 12 h, (D) samples after annealing under water vapor atmosphere at 80 °C for 12 h. The insets are the cross-section profiles of the marked positions in corresponding height images.

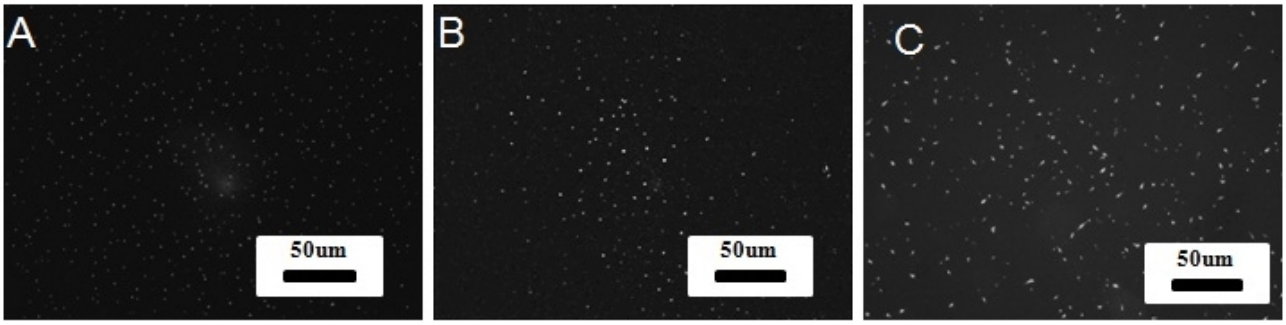

Fig. S6 POM photographs of $\mathbf{M_{93}A_{94}}$ (A), $\mathbf{M_{214}A_{81}}$ (B) and $\mathbf{M_{107}A_5}$ (C) films drop-coated from freshly prepared 0.2 mg mL^{-1} BCPs/DMF solution.

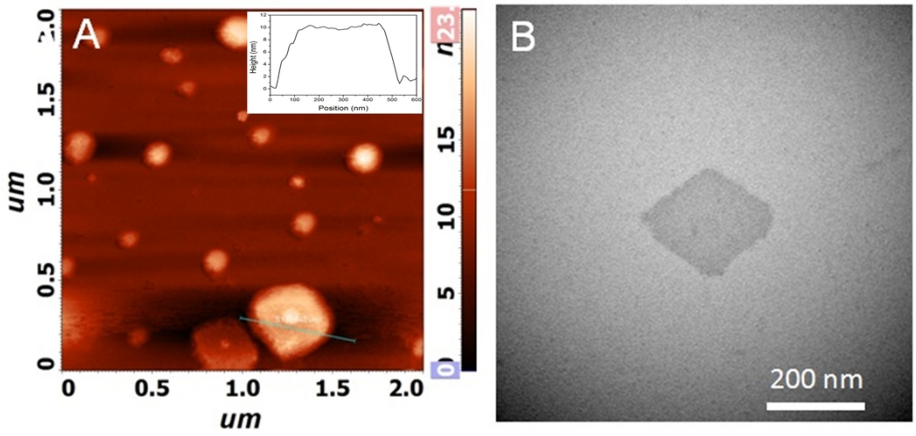

Fig. S7 AFM height image (A) and TEM photographs (B) of $\mathbf{M_{93}A_{94}}$ during the controlled growth in 0.2 mg mL^{-1} dilute DMF solution for 6h and 24 h, respectively. The inset is the cross-section profile of the marked position in corresponding height image.

References

1. Z. Guo, M. Lin, Y. Chang, Y. Sun, Y. Chiang, C. Chou, W. Woon and M. Chuang, *Polymer*, 2012, **53**, 4827-4833.
2. H. C. Yang, T. J. Shin, L. Yang, K. Cho, C. Y. Ryu and Z. N. Bao, *Adv. Funct. Mater.* 2005, **15**, 671-676.