

Electronic Supplementary Information

**Control of 10 nm Scale Cylinder Orientation in Self-Organized Sugar-Based Block Copolymer Thin Films**

*Issei Otsuka,<sup>a</sup> Salomé Tallegas,<sup>a,b</sup> Yoko Sakai,<sup>a</sup> Cyrille Rochas,<sup>a</sup> Sami Halila,<sup>a</sup>  
Sébastien Fort,<sup>a</sup> Ahmad Bsiesy,<sup>b</sup> Thierry Baron,<sup>b</sup> and Redouane Borsali<sup>a\*</sup>*

<sup>a</sup> Centre de Recherches sur les Macromolécules Végétales (CERMAV, UPR-CNRS 5301), affiliated with the Université Joseph Fourier (UJF) and member of the Institut de Chimie Moléculaire de Grenoble (ICMG, FR-CNRS 2607), BP53, 38041 Grenoble, France

<sup>b</sup> Laboratoire des Technologies de la Microélectronique (LTM, UMR-CNRS 5129), CEA/Leti/D2NT, 17 Avenue des Martyrs, 38054 Grenoble, France

## Experimental

*Materials:* Hydroxy terminated polystyrene (4,500 g/mol, PDI = 1.09, functionality > 95%) was purchased from Polymer Source, Inc. (QC, Canada). Azide-terminated polystyrene (**PS<sub>4.5k</sub>-N<sub>3</sub>**)<sup>1</sup> and *N*-maltoheptaosyl-3-acetamido-1-propyne (**propargyl-MH**)<sup>2</sup> were synthesized according to previous reports. Tetrahydrofuran (THF, purity > 99.5%) was purchased from Acros Organics and used as received. *N,N*-Dimethylformamid (DMF, purity > 99.7%) was purchased from Carlo Erba Reagenti and used as received. Water was purified by a Milli-Q water purification system (Billerica, MA, U.S.A.). *N,N,N',N'',N''*-Pentamethyldiethylenetriamine (PMDETA, purity = 99%) and Copper(I) bromide (CuBr, purity > 99.999%) were purchased from Sigma-Aldrich and used as received.

*Instruments:* <sup>1</sup>H NMR spectrum was recorded using a 400 MHz Bruker Avance DRX400. Size exclusion chromatography (SEC) was performed at 40 °C using a Agilent 390-MDS system (290-LC pump injector, ProStar 510 column oven, 390-MDS refractive index detector) equipped with Knauer Smartline UV detector 2500 and two Agilent PolyPore PL1113–6500 columns (linear, 7.5 × 300 mm; particle size, 5 μm; exclusion limit, 200–2,000,000) in DMF containing lithium chloride (0.01 M) at the flow rate of 1.0 mL min<sup>-1</sup>. Infrared (IR) spectra were recorded using a Perkin-Elmer Spectrum RXI FTIR spectrometer. Dynamic light scattering (DLS) experiments were carried out using an ALV laser goniometer, which consists of a 22 mW HeNe linearly polarized laser operating at a wavelength of 632.8 nm, and an ALV-5000/EPP multiple τ digital correlator with 125 ns initial sampling time at room temperature. AFM phase images were realized using a PicoPlus atomic force microscope (Molecular Imaging, Corp., AZ, U.S.A.).

*Synthesis of MH<sub>1.2k</sub>-b-PS<sub>4.5k</sub>:* **Propargyl-MH** (0.85 g, 0.69 mmol) and PMDETA (0.14 g, 0.80 mmol) were added to a flask and dissolved in DMF (125 mL). **PS<sub>4.5k</sub>-N<sub>3</sub>** (2.5 g, 0.53 mmol) and

CuBr (0.11 g, 0.80 mmol) were added to another flask and dissolved in DMF (125 mL). Both mixtures were degassed with argon for 10 minutes. The mixture of **propargyl-MH** and PMDETA was added into the flask containing **PS<sub>4.5k</sub>-N<sub>3</sub>** and CuBr under argon atmosphere by cannula transfer. The mixture was stirred for 1 week at 60 °C and then passed through short alumina column to remove the copper. The filtrate was concentrated under vacuum and precipitated in methanol/acetone to remove excess **propargyl-MH** and unfunctionalized polystyrene. The precipitate was filtered and then dried in vacuo to afford **MH<sub>1.2k</sub>-b-PS<sub>4.5k</sub>** as a white solid (2.7 g). <sup>1</sup>H NMR (DMF-*d*7):  $\delta_{\text{ppm}}$  7.86 and 7.78 (2 × s, triazole), 7.50-6.30 (br, aromatic), 5.90-4.55 (br, H-1<sup>MH</sup>), 3.90-3.35 (br, H-2, 3, 4, 5, 6<sup>MH</sup> and NCH<sub>2</sub>), 2.35-1.15 (br, CH, CH<sub>2</sub>, CH<sub>3</sub>).

*DLS measurements:* DLS measurements were performed using an ALV laser goniometer, which consists of a 22 mW HeNe linearly polarized laser operating at a wavelength of 632.8 nm, an ALV-5000/EPP multiple  $\tau$  digital correlator with 125 ns initial sampling time, and a temperature controller. The accessible scattering angles ( $\theta$ s) range from 30 to 140°. The solutions of **MH<sub>1.2k</sub>-b-PS<sub>4.5k</sub>** (2 g L<sup>-1</sup>) in H<sub>2</sub>O/THF = 1/4 and 1/1 (w/w) were filtered directly into the glass cells through a 0.2  $\mu$ m Whatman hydrophilic PTFE filter. Data were collected using digital ALV correlator control software and the counting time for measuring the dynamic light scattering was 120 s. The relaxation-time ( $\tau$ ) distributions were obtained using the CONTIN analysis applied to the dynamic light scattering autocorrelation functions ( $g^{(2)}-1$ s). From the linear dependence of the relaxation frequency ( $1/\tau$ ) on the square of the wave vector ( $q^2$ ), the diffusion coefficient ( $D_{\text{diff}}$ ) was calculated. The  $R_h$  value was then obtained from  $D_{\text{diff}}$  with the Stokes–Einstein relation. The detailed analysis of data was reported in the previous publications.<sup>5</sup> The viscosity of the water/THF mixtures at 25° C was computed from the viscosities of the pure water and THF.

*Film preparation:* BCP thin films were prepared for AFM by spin coating 0.5-4.0 % (w/w) polymer solutions in THF at 2000 rpm for 30 sec onto a silicon (100) wafer which was treated with a mixture of  $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4 = 1/2$  (v/v) at 80 °C for 1 hour. Solvent annealing of the bulk and thin film samples were performed in tightly sealed 100 mL glass beaker, in which the samples and an uncapped 20 mL vial filled with a mixture of THF and  $\text{H}_2\text{O}$  (total 5 g) were placed, at room temperature for 24 h under atmospheric pressure. The annealed samples were dried in the atmosphere over night before AFM or SAXS experiments.

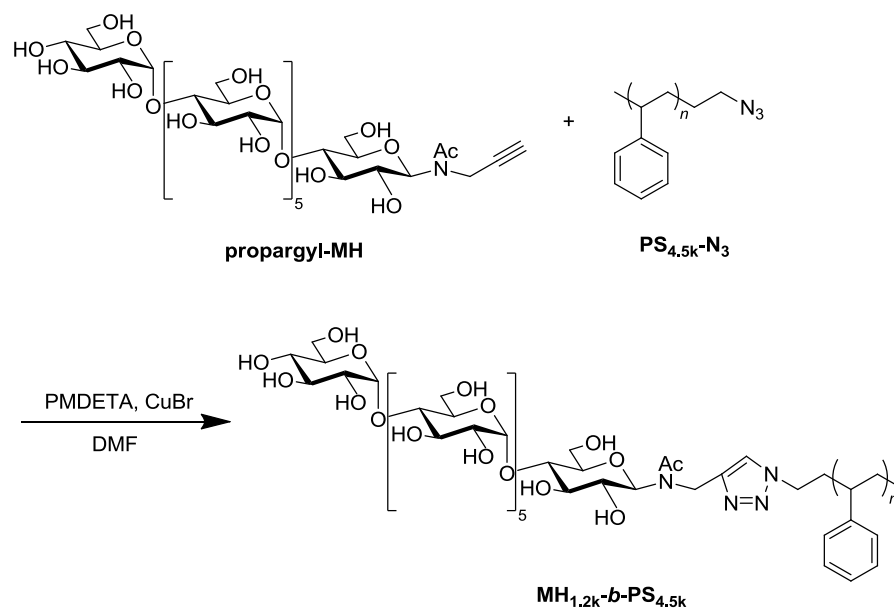
*Small angle x-ray scattering (SAXS) measurements:* SAXS experiments were performed on the BM02 beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). Bulk samples were put into glass capillaries of 1.5 mm diameter and then flame-sealed. These samples were disposed in sample holders equipped with an integrated heating system. The experiments were performed using 15 keV ( $\lambda = 0.083$  nm) X-rays at room temperature. Scattered intensities were recorded during 2-5 sec exposures on a CCD detector (Ropper Scientific) placed about 80 cm behind the sample. The scattering intensities were corrected for grid distortion, the detector response, dark current, empty cell scattering and sample transmission. A silver behenate sample was used for calibrating the  $q$  scale of the detector.

*AFM observations:* AFM phase images were realized by tapping mode using a silicon cantilever (FORTG-50, Applied Nano Structures, Inc., CA, U.S.A.) with a tip radius of < 10 nm, a resonant frequency of 47-76 kHz and a force constant of 1.2-6.4 N/m. Film thicknesses were determined with HORIBA Jobin Yvon ellipsometer using 500 nm wavelength with a 70° angle of incidence.

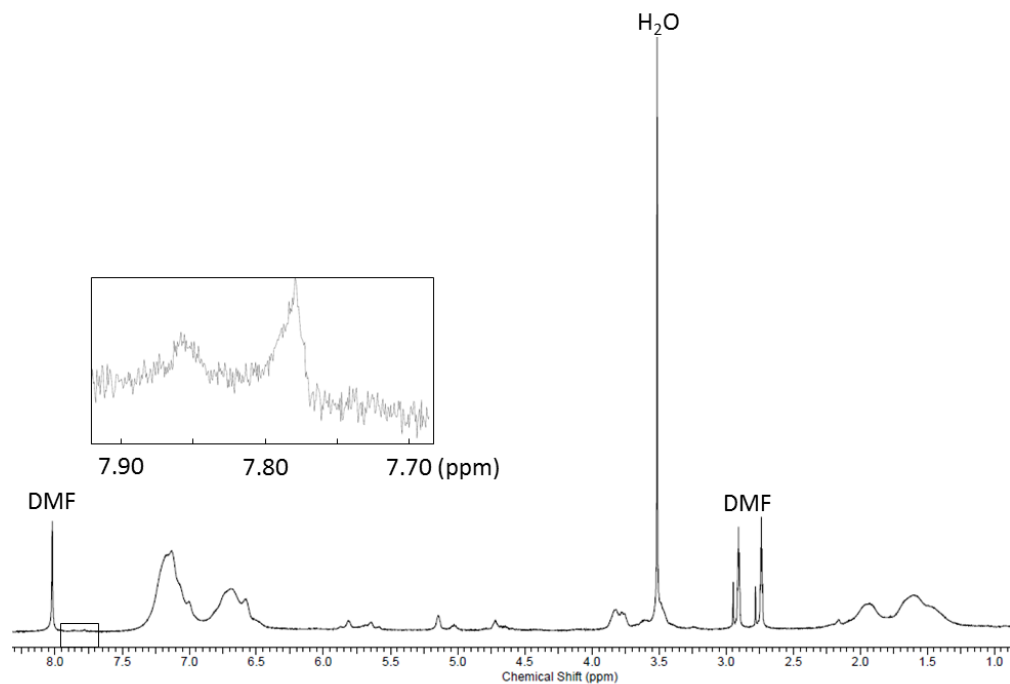
## References

1. I. Fallais, J. Devaux, R. Jérôme *J. Polym. Sci.; Part A: Polym. Chem.* 2000, **38**, 1618-1629.

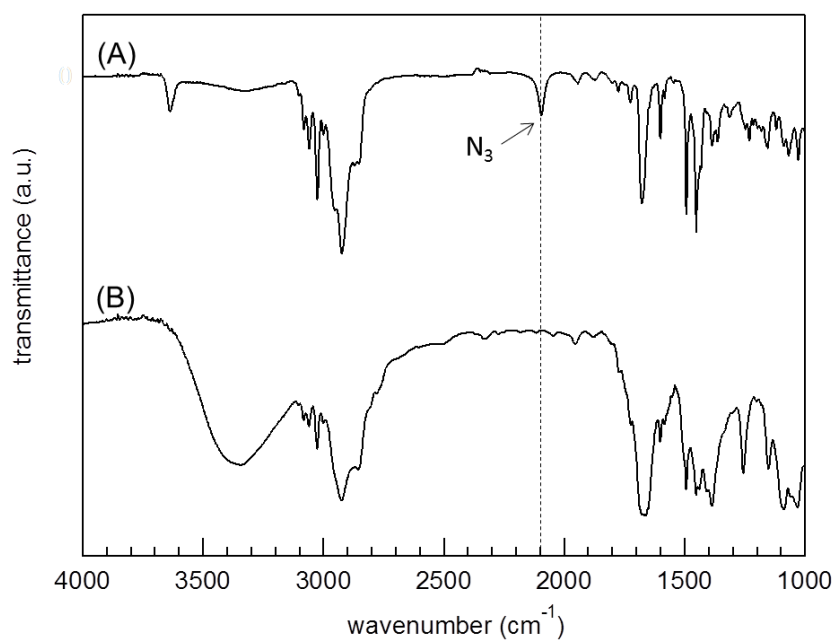
2. I. Otsuka, K. Fuchise, S. Halila, S. Fort, K. Aissou, I. P.-Paintrand, Y. Chen, A. Narumi, T. Kakuchi, R. Borsali *Langmuir* 2010, **26**, 2325-2332.



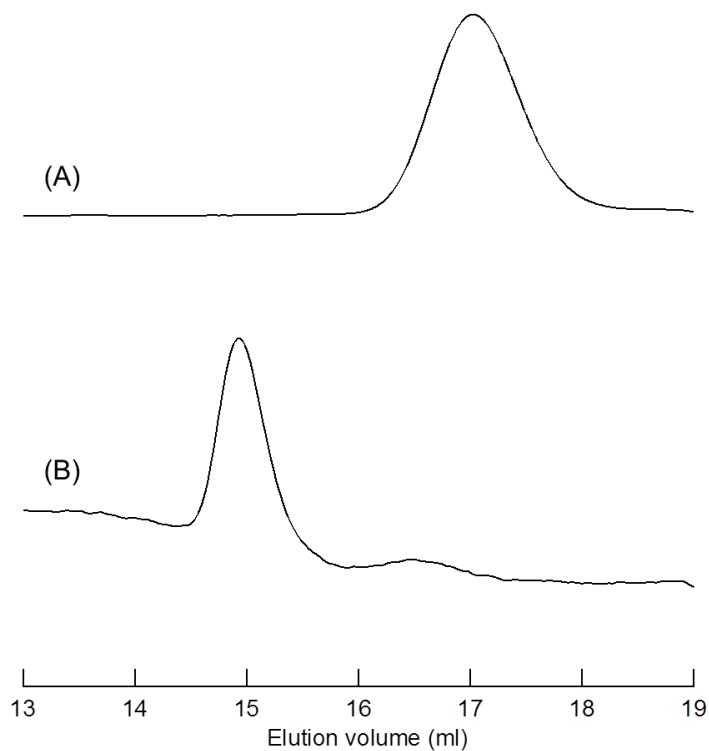
**Scheme S1.** Synthesis of MH<sub>1.2k</sub>-*b*-PS<sub>4.5k</sub>.



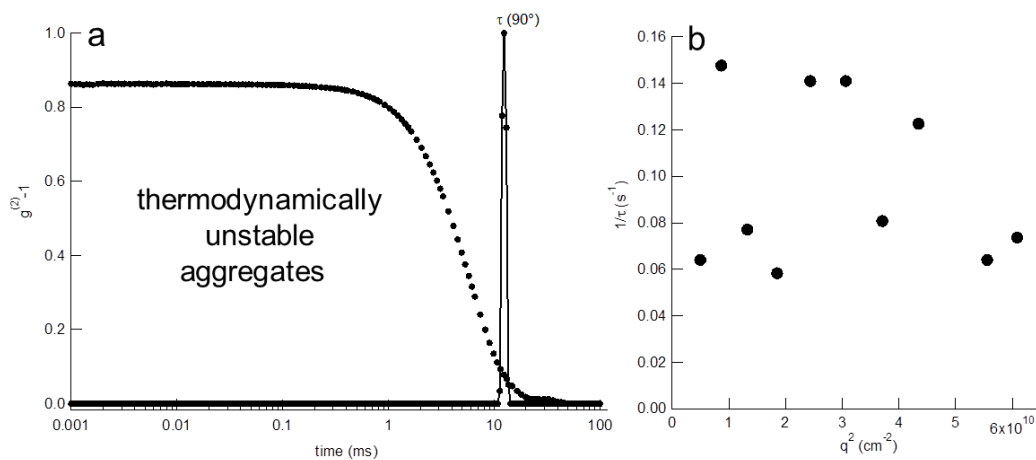
**Figure S1.**  $^1\text{H}$  NMR spectrum of  $\text{MH}_{1.2\text{k}}\text{-}b\text{-PS}_{4.5\text{k}}$  in  $\text{DMF-}d_7$ .



**Figure S2.** IR spectra of (A)  $\text{PS}_{4.5\text{k}}\text{-N}_3$  and (B)  $\text{MH}_{1.2\text{k}}\text{-}b\text{-PS}_{4.5\text{k}}$ .



**Figure S3.** SEC traces of (A) PS<sub>4.5k</sub>-N<sub>3</sub> and (B) MH<sub>1.2k</sub>-b-PS<sub>4.5k</sub>.



**Figure S4.** Dynamic light scattering (a) autocorrelation function ( $g^{(2)}-1$ ) and relaxation-time distribution measured at scattering angle of 90 ° and (b) dependence of the relaxation frequency ( $1/\tau$ ) on the square of the wave vector ( $q^2$ ) of MH<sub>1.2k</sub>-b-PS<sub>4.5k</sub> in H<sub>2</sub>O/THF = 1/1 (conditions: [MH<sub>1.2k</sub>-b-PS<sub>4.5k</sub>] = 2 g L<sup>-1</sup>; temperature, 25 °C).