

## Electronic Supplementary Information

### **Synthesis of bottlebrush cellulose-*graft*-diblock copolymer elastomers via atom transfer radical polymerization utilizing a halide exchange technique†**

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## Experimental Details

### Materials

Methyl methacrylate (MMA), *n*-butyl acrylate (*n*-BA), copper (I) bromide (CuBr), copper (I) chloride (CuCl), *N,N*-dimethylformamide (DMF), 2,2'-bipyridyl (bpy), diphenyl ether (DPE) and tetrahydrofuran (THF) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). MMA and *n*-BA were passed through an alumina column and stored under argon, respectively. CuBr and CuCl were purified prior to use. Cellulose-based macroinitiator (Cell-BiB) with the degree of substitution of 1.02 was synthesized according to our previous method using wood pulp cellulose with viscosity-averaged degree of polymerization (DP) of 650.<sup>1,2</sup> *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA, TCI) and other reagents were used without further purification.

**Fourier Transform Infrared Spectroscopy (FTIR).** FTIR spectra were collected by employing a Nicolet 6700 FT-IR spectrometer. FTIR spectra of cellulose and Cell-BiB were measured by using the KBr pallet holder method. Cell-*g*-PBA and Cell-*g*-PBA-*b*-PMMA were dissolved in THF, respectively. The THF solutions were then dropped onto KBr pallets, and the obtained film samples were tested after dried under an infrared lamp.

**Nuclear Magnetic Resonance (NMR).**  $^1\text{H}$  NMR spectra of Cell-BiB in  $\text{DMSO-}d_6$  and bottlebrush Cell-*g*-PBA-*b*-PMMA copolymers in  $\text{CDCl}_3$  were conducted by using a Bruker AVANCE 400 spectrometer. Tetramethylsilane (TMS) was used as the internal standard.

**Differential Scanning Calorimetry (DSC).** Glass transition temperatures were determined using a TA Q2000 DSC (TA Instruments) under a nitrogen atmosphere. Each sample (5-10 mg) was placed in an aluminum pan and then sealed. First, the sample was equilibrated at 20 °C for 5 min, and then heated to 150 °C at a heating rate of 10° C/min. The sample was further held at 150 °C for 5 min to erase the thermal history and then quenched to -90 °C at a cooling rate of 50 °C/min. The sample was heated again from -90 to 150 °C at a heating rate of 10 °C/min. Universal Analysis 2000 software (TA Instruments) was used to determine the glass transition temperature ( $T_g$ ) of bottlebrush Cell-*g*-PBA-*b*-PMMA copolymers.

**Atomic Force Microscopy (AFM).** The microphase morphology of the bottlebrush copolymers was observed by using the Dimension FastScan Atomic Force Microscope (Bruker). Ultrathin films of the copolymer samples were prepared by spin-coating of the copolymer THF solutions (10 mg/mL) on silicon wafer. The spin-coating rate was set at 3000 rpm. The silicon wafer was treated by sulfuric acid and hydrogen peroxide prior to use. After solvent evaporation at ambient temperature for 2 h, the ultrathin films

were dried under vacuum at 40 °C for 12 h, and then was further annealed at 150 °C for 24 h.

**Small-Angle X-ray Scattering (SAXS).** The SAXS measurements on the films were collected on a Xeuss system of Xenocs SA (Sassenage, France) with X-ray detector of Pilatus 100K (Dectris, Swiss) at room temperature. Collected SAXS patterns corrected for the background scattering were output as the plot of the scattering intensity,  $\log(I)$  versus the scattering wave vector,  $q=(4\pi/\lambda)\sin (2\theta/2)$ , where  $2\theta$  is the scattering angle and  $\lambda$  the X-ray wavelength of 0.154 nm.

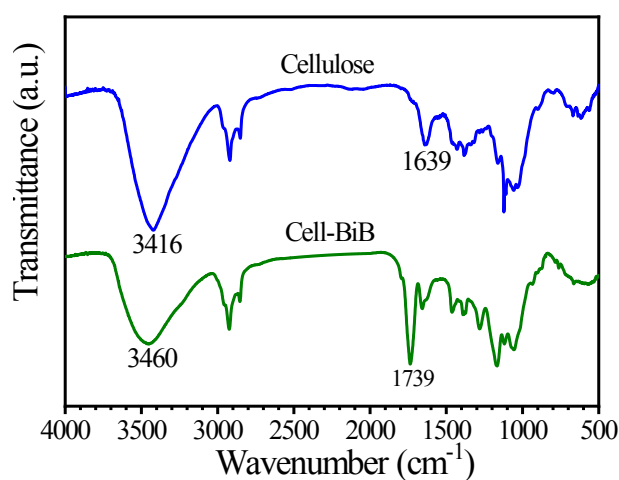
**Mechanical Tensile Tests.** The mechanical tensile tests with the crosshead speed of 5 mm/min on the dumbbell-shaped film samples (length of 35 mm, width of 2 mm, and thickness of 0.3 mm) were carried out on an electronic universal testing machine (Suns Model UTM2502) in a temperature-controlled environment ( $23\pm 1$  °C). The film samples were prepared by solution casting. The THF solutions of the copolymer samples had a concentration of 0.1 g/mL. The solvent was allowed to evaporate at ambient temperature for 12 h at first to obtain the film samples. The film samples were dried under vacuum at 60 °C for 24 h and then thermally annealed at 150 °C for 24 h. Step-cyclic tensile tests on the film samples were designed to extend up to 20% of the original length in the first cycle, and the subsequent cycle was increased by 20% at a constant crosshead speed of 5 mm/min in each step and was unloaded at the same speed

until zero stress before the subsequent cycle started. The elastic recovery (*ER*) values were obtained from the stress-strain curves of these step cycles.

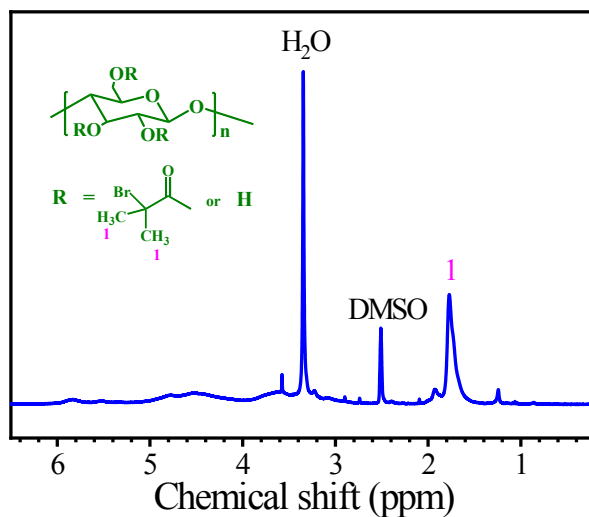
**Synthesis of Cell-g-PBA via ATRP.** Cell-BiB (30 mg, 0.1 mmol of Br), *n*-BA (10.24 g, 80.0 mmol), bpy (187.4 mg, 1.2 mmol) and DMF (12 mL) were added into a flask equipped with a magnetic stirring bar. After Cell-BiB was dissolved, CuBr (57.4 mg, 0.4 mmol) was introduced into the flask and the solution was degassed by three freeze-pump-thaw cycles in liquid nitrogen and then sealed. Subsequently, the flask was immersed into an oil bath set at 70 °C for 30 h. The reaction was stopped by quenching and dissolution with THF. The obtained mixture was precipitated into a large amount of cold methanol and the precipitate was washed with methanol thoroughly. The precipitate was dissolved in THF again to obtain the solution, which was precipitated in methanol. The dissolution-precipitation operation was repeated for 3 times to obtain the sample, Cell-g-PBA, which was further dried under vacuum at 40 °C for 24 h.

**Synthesis of Bottlebrush Cell-g-PBA-*b*-PMMA Copolymers Using A Halogen Exchange Technique in ATRP.** The sequential ATRP for the further polymerization of the second monomer MMA from Cell-g-PBA followed a similar procedure for the synthesis of Cell-g-PBA. The synthesized Cell-g-PBA took the role as the macroinitiator. Cell-g-PBA (2 g, 0.1 mmol of Br) was completely dissolved in DMF (10 mL) under magnetic stirring, and then DPE (40 mL) as a co-solvent was added in the flask. MMA (1 g, 10 mmol), PMDETA (12 μL, 0.06 mmol), and CuCl (3 mg, 0.03

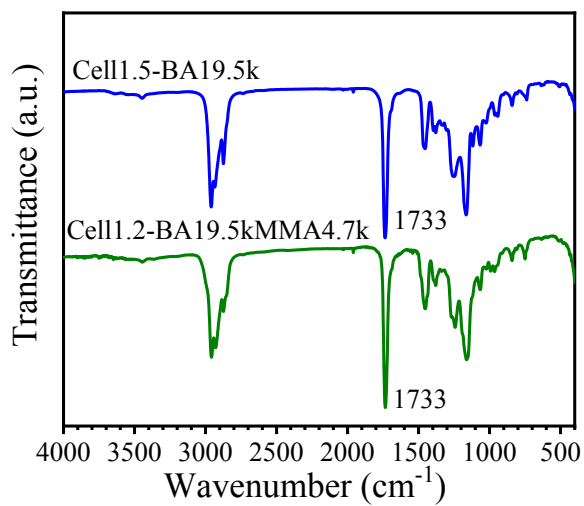
mmol) were added into the flask and then the solution was degassed by three freeze-pump-thaw cycles in liquid nitrogen and then sealed. Thereafter, the flask was placed in an oil bath set at 90 °C for 12 h. The reaction was stopped by exposing the reactive mixture to air and addition of THF. After that, the solution was poured into a large amount of cold methanol and stirred for half an hour to obtain the precipitate. The dissolution-precipitation operation for cleanup of the obtained sample was repeated for three times. Finally, the obtained Cell-*g*-PBA-*b*-PMMA sample was dried under vacuum at 60 °C for 24 h. For obtaining the bottlebrush Cell-*g*-PBA-*b*-PMMA samples with other two longer outer block lengths, the MMA amounts of 2.5 g (25 mmol) and 3.3 g (33 mmol) were used respectively.



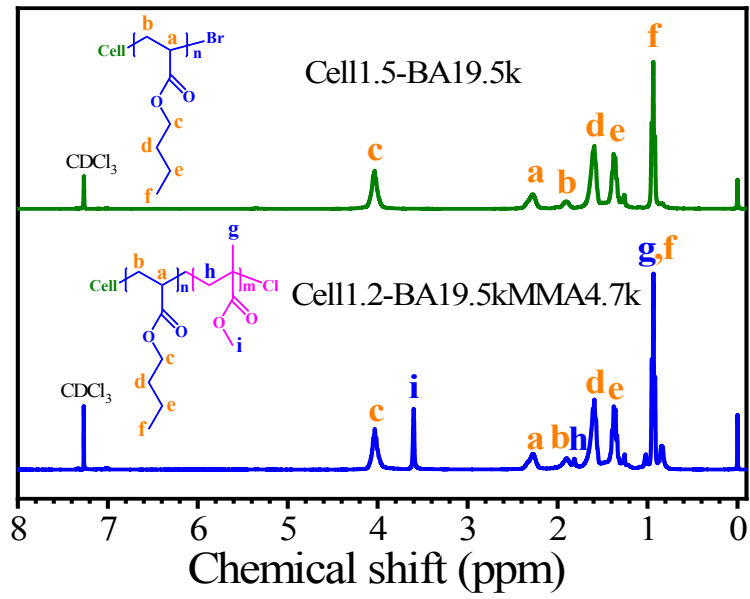
**Fig. S1** FTIR spectra of cellulose and macroinitiator Cell-BiB.



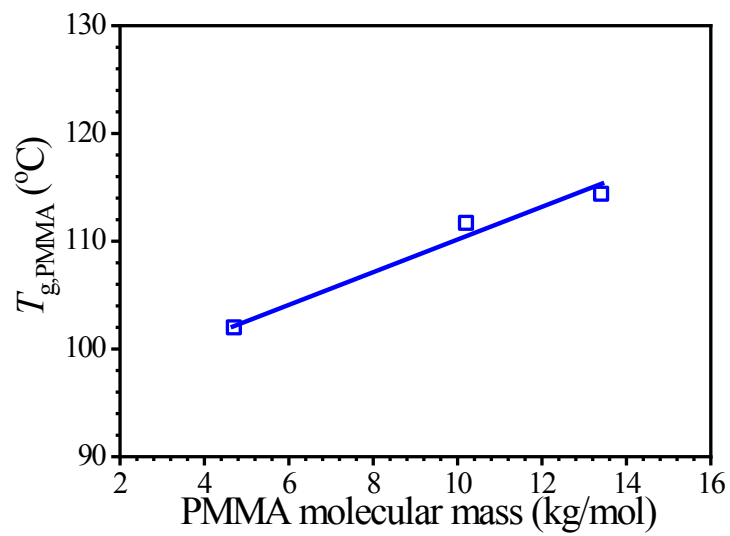
**Fig. S2**  $^1\text{H}$  NMR spectrum of macroinitiator Cell-BiB in  $\text{DMSO-}d_6$ .



**Fig. S3** FTIR spectra of Cell1.5-BA19.5k and Cell1.2-BA19.5kMMA4.7k.

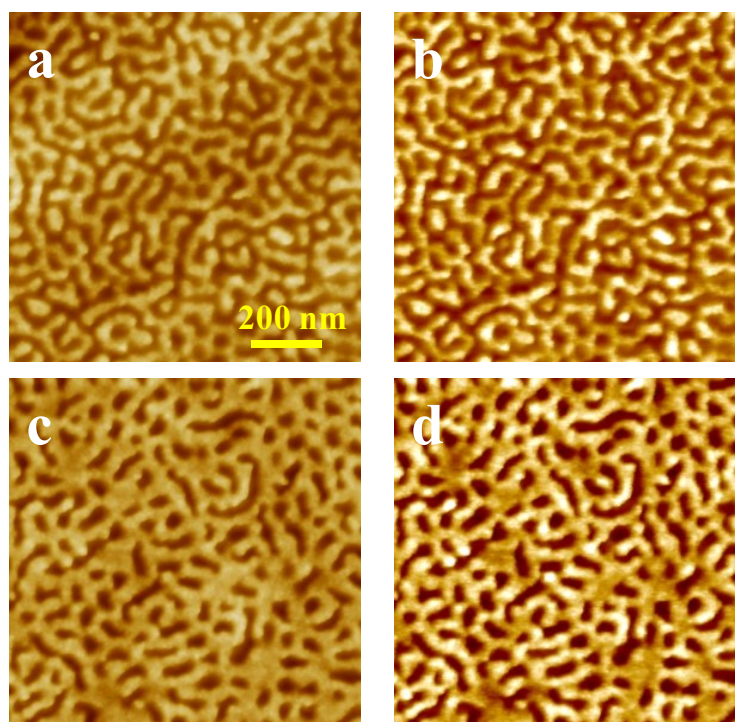


**Fig. S4** <sup>1</sup>H NMR spectra of Cell1.5-BA19.5k and Cell1.2-BA19.5kMMA4.7k in CDCl<sub>3</sub>.

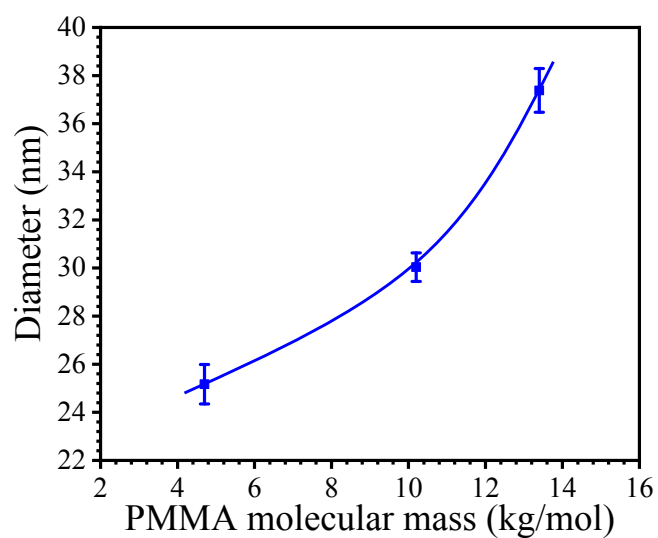


**Fig. S5** Change of  $T_{g,PMMA}$  with PMMA molecular mass for bottlebrush Cell-g-PBA-b-PMMA copolymers.

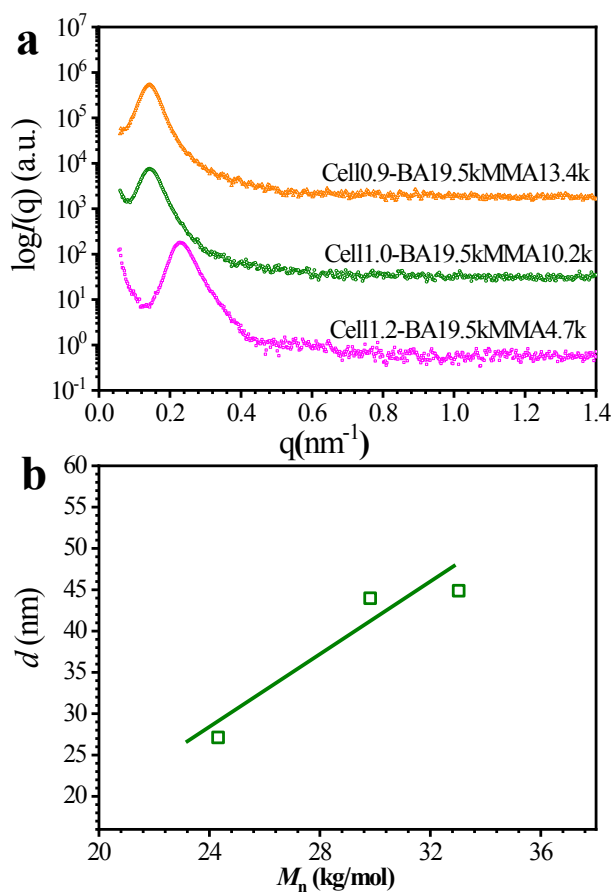




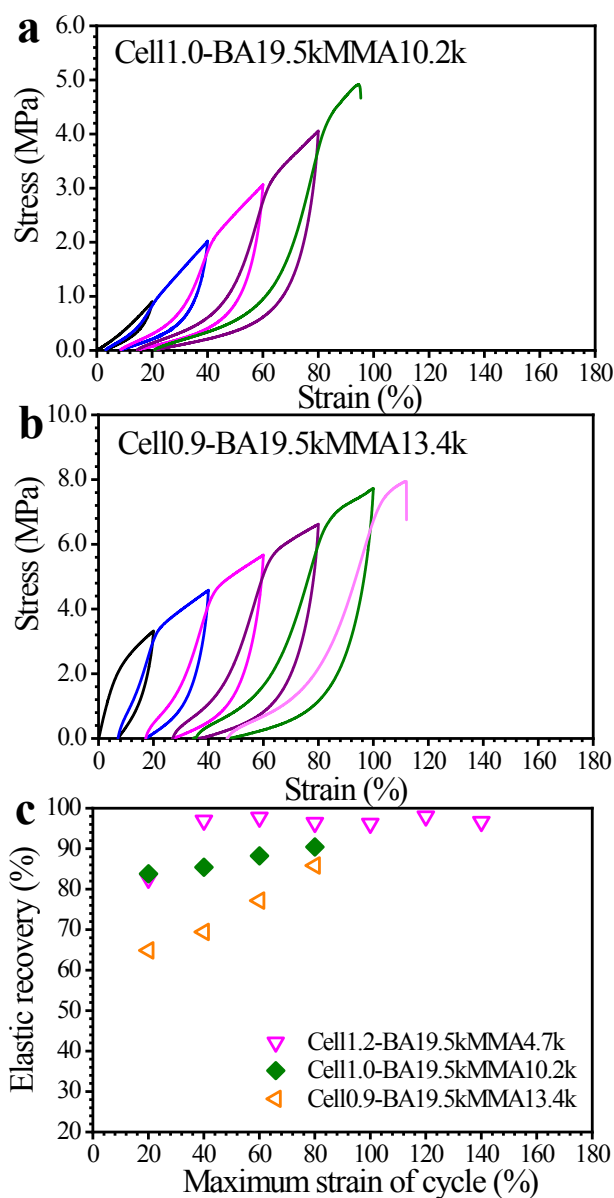
**Fig. S6** AFM height (left panel, a,c) and modulus (right panel, b,d) micrographs observed for bottlebrush Cell-*g*-PBA-*b*-PMMA copolymers adsorbed on silicon wafer surface: (a,b) Cell1.0-BA19.5kMMA10.2k, and (c,d) Cell0.9-BA19.5kMMA13.4k.



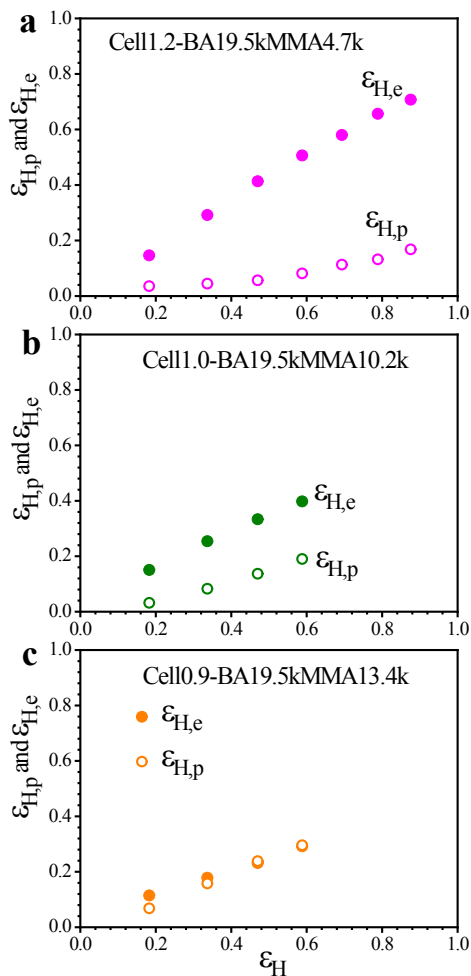
**Fig. S7** Change of diameter of cylinders for microphase-separated morphology with PMMA molecular mass for bottlebrush Cell-*g*-PBA-*b*-PMMA copolymers.



**Fig. S8** (a) SAXS intensity profiles ( $\log I(q)$  vs  $q$  curves) for Cell1.2-BA19.5kMMA4.7k, Cell1.0-BA19.5kMMA10.2k and Cell0.9-BA19.5kMMA13.4k. (b) Change of interdomain distance,  $d$  with number-average graft molecular mass for bottlebrush Cell- $g$ -PBA- $b$ -PMMA copolymers.



**Fig. S9** Step-cyclic stress-strain curves for (a) Cell1.0-BA19.5kMMA10.2k and (b) Cell0.9-BA19.5kMMA13.4k during step-cyclic tensile deformation. (c) Changes of *ER* value with maximum strain during cyclic tensile deformation for Cell1.2-BA19.5kMMA4.7k, Cell1.0-BA19.5kMMA10.2k and Cell0.9-BA19.5kMMA13.4k.



**Fig. S10** Changes of true plastic strain,  $\epsilon_{H,p}$  and true elastic strain,  $\epsilon_{H,e}$  with maximum strain,  $\epsilon_H$  in each cyclic step during step-cyclic tensile deformation for (a) Cell1.2-BA19.5kMMA4.7k, (b) Cell1.0-BA19.5kMMA10.2k and (c) Cell0.9-BA19.5kMMA13.4k.

## References

- 1 F. Jiang, Z. K. Wang, Y. L. Qiao, Z. G. Wang and C. B. Tang, *Macromolecules*, 2013, **46**, 4772-4780.
- 2 Z. K. Wang, Y. Q. Zhang, F. Jiang, H. G. Fang and Z. G. Wang, *Polym. Chem.*, 2014, **5**, 3379-3388.