Supporting Information for

Control over Molecular Architectures of Carbohydrate-Based Block Copolymers for Stretchable Electrical Memory Devices

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1. Experimental Section

Materials. N,N,N',N'',N''-Pentamethyldiethylenetriamine (PMDETA, 99%), *n*-butyl acrylate (BA, >99%), sodium azide (NaN₃, 99%), copper(I) bromide (CuBr, 98%), and ethyl 2-bromo-2-methylpropanoate (\geq 98%) were purchased from commercial resources and used as received. Ethylene bis(2-bromoisobutyrate),¹ pentaerythritol tetrakis(2-bromoisobutyrate),² and *N*-maltoheptaosyl-3-acetamido-1-propyne (MH-C=CH)³ were prepared according to the previous report. Other reagents and solvents were used without further purification.

Synthesis of AB-type Diblock Copolymers. Synthesis of PBA-N₃. CuBr (202.2 mg, 1.39 mmol) was added in a 100 ml Schlenk flask, which was then evacuated for 1 hour and backfilled with argon. A 50 ml Schlenk flask was added BA (20 ml, 139 mmol), PMDETA (291 *u*l, 1.39 mmol), ethyl 2-bromo-2-methylpropanoate (195 *u*l, 139 mmol), and anhydrous toluene (3 ml), and then degassed by three freeze-pump-thaw cycles. The mixture was backfilled with argon and transferred into the 100 ml Schlenk flask. The reaction was performed in preheated oil bath at 70 °C. The polymerization was terminated after 10 minutes by exposing to air, and the monomer conversions was determined to be 26.5% by ¹H NMR. The product was purified by alumina column chromatography followed by dialysis against acetone with a Spectra/Por 6 dialysis membrane (molecular weight cutoff of 1.0 kDa) to give ω -bromo end-functionalized poly(*n*-butyl acrylate) (PBA-Br: 3.6 g) as a light yellow oil. Yield: 68%. $M_{n,NMR} = 3,300$ g mol⁻¹, $M_w/M_n = 1.22$. Number-average degree of polymerization (DP) was estimated to be 26 from ¹H NMR.

The obtained PBA-Br (2.13g, 1.55 mmol) and sodium azide (503 mg, 7.75 mmol) were dissolved in DMF (15 mL) and stirred for 2 days at 40 °C. The residue was diluted

with DCM and purified by passing through a silica gel column to remove the excess of sodium azide to give ω -azido end-functionalized poly(*n*-butyl acrylate) (PBA_{3k}-N₃) as a yellow viscous liquid. Yield: 90%. $M_{n,NMR} = 3,400 \text{ g mol}^{-1}$, $M_{n,SEC} = 4,100 \text{ g mol}^{-1}$, $M_{w/M_n} = 1.21$, DP = 26.

PBA_{7k}-N₃ ($M_{n,NMR} = 6,900 \text{ g mol}^{-1}$, $M_{n,SEC} = 7,100 \text{ g mol}^{-1}$, $M_{w}/M_n = 1.16$, DP=54) was prepared in a same manner from PBA_{7k}-Br that had been obtained by ATRP of BA with the [BA]₀/[ethyl 2-bromo-2-methylpropanoate]₀/[CuBr]/[PMDETA] ratio of 100/1/1/1 for 20 min (monomer conversion of 53.2%).

Synthesis of MH-b-PBA. MH-C=CH (288 mg, 0.234 mmol), PBA_{3k}-N₃ ($M_{n,NMR}$ = 3,400 g mol⁻¹, 600 mg, 0.180 mmol), and CuBr (38 mg, 0.270 mmol) were placed in a Schlenk flask, which was then evacuated under high vacuum and flushed with argon. After repeating the evacuation–flush cycle three times, degassed PMDETA (112 *u*l, 0.540 mmol) and DMF (6 ml) were added using a syringe. After stirring at 60 °C for 2 days, the reacting mixture was passed through a pad of alumina and eluted with THF/DMF mixture to remove the catalyst and dialyzed against methanol with a Spectra/Por 6 dialysis membrane (molecular weight cutoff of 3.5 kDa). After removing the solvent, MH-*b*-PBA_{3k} (269 mg) was obtained as a light yellow sticky solid. Yield: 45%. $M_{n,NMR}$ = 4,430 g mol⁻¹, $M_{n,SEC}$ =10,100 g mol⁻¹, M_{w/M_n} = 1.18. MH-*b*-PBA_{7k} ($M_{n,NMR}$ = 7,830 g mol⁻¹, $M_{n,SEC}$ =12,500 g mol⁻¹, M_{w/M_n} = 1.18) was prepared from PBA_{7k}-N₃ by following the same procedure.

Synthesis of ABA-type Triblock Copolymers. Synthesis of N_3 -PBA- N_3 . The general procedure for ATRP is as follows: CuBr (200 mg, 1.39 mmol) was added in a 100 ml Schlenk flask and then evacuated and backfilled for 1 hour with argon. To a 50 ml Schlenk flask were added BA (20 ml, 139 mmol), PMDETA (291 *u*l, 1.39 mmol),

ethylene bis(2-bromoisobutyrate) (502 mg, 139 mmol) and anhydrous toluene (3 ml) and degassed by three freeze-pump-thaw cycles. The mixture was backfilled with argon and transferred into the 100 ml Schlenk flask. The reaction was performed in preheated oil bath at 70 °C. The polymerization was terminated after 4 minutes by exposing to air, and the monomer conversion was determined to be 43% by ¹H NMR. The product was purified by passing through an alumina column to remove the catalyst and dialyzing against acetone with a Spectra/Por 6 dialysis membrane (molecular weight cutoff of 1.0 kDa g mol⁻¹) for three times. The polymer was obtained by dried under vacuum to give bi- ω -bromo end-functionalized PBA (Br-PBA-Br) as a light yellow viscous liquid. Yield: 72%. $M_{n,NMR} = 5,500$ g mol⁻¹, $M_{n,SEC} = 6,300$ g mol⁻¹, $M_w/M_n = 1.17$. DP was estimated to be 45 from ¹H NMR.

The general procedure for bi- ω -end azidation is as follows: The obtained Br-PBA-Br (458 mg, 5.58 mmol) and sodium azide (3.5 g, 7.75 mmol) were dissolved in DMF (15 mL) and stirred for 2 days at 40 °C. The residue was diluted with DCM and purified by passing through a silica gel column to remove unreacted sodium azide. The polymer was obtained by dried under vacuum to give ω -azido end-functionalized PBA (N₃-PBA_{3k}-N₃) as a light yellow viscous liquid. Yield: 88%. $M_{n,NMR} = 5,880$ g mol⁻¹, $M_{n,SEC} = 5,700$ g mol⁻¹, $M_{w/M_n} = 1.18$, DP=46).

Synthesis of MH-b-PBA-b-MH. The general procedure for the click reaction is as follows: MH-C=CH (167 mg, 0.096 mmol), N₃-PBA_{6k}-N₃ ($M_{n,NMR} = 5,880$ g mol⁻¹, 380 mg, 0.064 mmol), and CuBr (13.9 mg, 0.097 mmol) were placed in a Schlenk flask, which was then evacuated under high vacuum and flushed with argon. After repeating the evacuation–flush cycle three times, degassed PMDETA (40.5 *u*l, 0.194 mmol) and DMF (6 ml) were added using a syringe. After stirring at 60 °C for 2 days, the reacting mixture

was passed through a pad of alumina and eluted with THF/DMF mixture to remove the catalyst and dialyzing against methanol with a Spectra/Por 6 dialysis membrane (molecular weight cutoff of 3.5 kDa) for three times. The copolymer was obtained by dried under vacuum to give MH-*b*-PBA_{6k}-*b*-MH (282 mg) as a light yellow solid. Yield: 52%. $M_{n,NMR} = 7,200$ g mol⁻¹, $M_{n,SEC} = 15,400$ g mol⁻¹, $M_{w/M_n} = 1.16$. MH-*b*-PBA_{10k}-*b*-MH ($M_{n,NMR} = 11,800$ g mol⁻¹, $M_{n,SEC} = 20,500$ g mol⁻¹, $M_{w/M_n} = 1.17$) was prepared from N₃-PBA_{10k}-N₃ by following the general click reaction procedure.

Synthesis of Star-shaped Block Copolymers. Synthesis of (PBA-N₃)₄. The general procedure for ATRP is as follows: CuBr (50 mg, 0.348 mmol) was added in a 100 ml Schlenk flask and then evacuated and backfilled for 1 hour with argon. To a 50 ml Schlenk flask were added BA (20 ml, 139 mmol), PMDETA (72.8 *u*l, 0.348 mmol), pentaerythritol tetrakis(2-bromoisobutyrate) (251 mg, 0.348 mmol) and anhydrous toluene (3 ml) and degassed by three freeze-pump-thaw cycles. The mixture was backfilled with argon and transferred into the 100 ml Schlenk flask. The reaction was performed in preheated oil bath at 70 °C. The polymerization was terminated after 20 minutes by exposing to air, and the monomer conversion was determined to be 22.3% by ¹H NMR. The product was purified by passing through an alumina column to remove the catalyst and dialyzing against acetone with a Spectra/Por 6 dialysis membrane (molecular weight cutoff of 1.0 kDa) for three times. The polymer was obtained by dried under vacuum to give tetra- ω -bromo end-functionalized PBA (PBA-N₃)₄ as a light yellow viscous liquid. Yield: 75%. $M_{n,NMR} = 11,800$ g mol⁻¹, $M_{n,SEC} = 10,200$ g mol⁻¹, $M_w/M_n = 1.23$. DP was estimated to be 91 from ¹H NMR.

The general procedure for tetra- ω -end azidation is as follows: The obtained (PBA-Br)₄ (1.37g mg, 0.12 mmol) and sodium azide (145.5 mg, 2.239 mmol) were

dissolved in DMF (10 mL) and stirred for 2 days at 40 °C. The residue was diluted with DCM and purified by passing through a silica gel column to remove unreacted sodium azide. The polymer was obtained by dried under vacuum to give tetra- ω -azido end-functionalized PBA (PBA_{12k}-N₃)₄ as a light yellow viscous liquid. Yield: 86%. $M_{n,NMR} = 11,800 \text{ g mol}^{-1}, M_{n,SEC} = 10,200 \text{ g mol}^{-1}, M_w/M_n = 1.23, DP=91.$ (PBA_{20k}-N₃₎₄ ($M_{n,NMR} = 20,100 \text{ g mol}^{-1}, M_{n,SEC} = 12,600 \text{ g mol}^{-1}, M_w/M_n = 1.22, DP=157$) was prepared from corresponding (PBA_{20k}-Br)₄ that had been obtained by ATRP of BA with the [BA]₀/[Pentaerythritol tetrakis(2-bromoisobutyrate)]₀/[CuBr]/[PMDETA] ratio of 400/1/1/1 for 35 minutes polymerization with monomer conversion of 38.6 %.

Synthesis of $(PBA_n-b-MH)_4$. The general procedure for the click reaction is as follows: MH-C=CH (384mg, 0.312 mmol), (PBA_{3k}-N₃)₄($M_{n,NMR} = 11,800$ g mol⁻¹, 800 mg, 0.066 mmol), and CuBr (13.9 mg, 0.098 mmol) were placed in a Schlenk flask, which was then evacuated under high vacuum and flushed with argon. After repeating the evacuation–flush cycle three times, degassed PMDETA (40.7 *u*l, 0.19 mmol) and DMF (6 ml) were added using a syringe. After stirring at 60 °C for 2 days, the reacting mixture was passed through a pad of alumina and eluted with THF/DMF mixture to remove the catalyst and dialyzing against methanol with a Spectra/Por 6 dialysis membrane (molecular weight cutoff of 3.5 kDa) for three times. The copolymer was obtained by dried under vacuum to give (PBA_{3k}-*b*-MH)₄ (465 mg) as a light yellow solid. Yield: 52%. $M_{n,NMR} = 13,100$ g mol⁻¹, $M_{n,SEC} = 31,600$ g mol⁻¹, $M_w/M_n = 1.18$). (PBA_{5k}-*b*-MH)₄ ($M_{n,NMR} = 21,300$ g mol⁻¹, $M_{n,SEC} = 35,600$ g mol⁻¹, $M_w/M_n = 1.16$) was prepared from (PBA_{5k}-N₃)₄ by following the general click reaction procedure.

2. Characterization

Polymer Characterization. The ¹H NMR (400 MHz) spectra were recorded using a JEOL JNM-ECS400. Size exclusion chromatography (SEC) measurements of the obtained polymers were performed at 40 °C using a Jasco high performance liquid chromatography system (PU-980 Intelligent HPLC pump, CO-965 Colum oven, RI-930 RI detector, and Shodex DEGAS KT-16 degasser) equipped with a Shodex Asahipak GF310 HQ (linear, 7.6 mm × 300 mm) column and a Shodex Asahipak GF-7M HQ column (linear, , 7.6 mm × 300 mm) using DMF containing LiCl (0.01 M) at a flow rate of 0.60 mL min⁻¹. The number-average molar mass ($M_{n,SEC}$) and dispersity (M_w/M_n) of the polymers were calculated on the basis of a polystyrene calibration. The Fourier transform infrared spectroscopy (FTIR) analysis was carried out using a PerkinElmer Frontier MIR spectrometer equipped with a single reflection diamond universal attenuated total reflection (ATR) accessory.

Morphology Characterization. For solvent-annealing treatment, thin films and bulk samples were placed in a tightly capped 2-liter glass bottle containing an uncapped 20-mL beaker filled with a mixture of 2.5 g of tetrahydrofuran (THF) and 2.5 g of water. The nanostructures of polymer films were visualized with a Nanoscope 3D controller atomic force micrograph (AFM, Digital Instruments) operated in the tapping mode at room temperature. The spring constant of the silicon cantilevers (Nanosensor PPP-SEIHR) was 15 N/m and the resonant frequency was 330 kHz. The thicknesses of polymer films were measured with a Microfigure Measuring Instrument (Surfcorder ET3000, Kosaka Laboratory Ltd.). Small-angle X-ray scattering (SAXS) data for the bulk samples were collected on beamline BL23A1 in the National Synchrotron Radiation Research Center (NSRRC), Taiwan. A monochromatic beam of $\lambda = 0.827$ Å (15 keV) was

used. The grazing incidence small angle X-ray scattering (GISAXS) measurements were also performed on beamline BL23A1 in NSRRC. The incident angle was 0.1° . SAXS and GISAXS data were collected on a Pilatus 1 M detector with an area of 169 mm × 179 mm (981 pixels × 1043 pixels).

Mechanical Properties. Surface mechanical properties were obtained using an AFM apparatus (Dimension Icon, Bruker) operated in the PeakForceTM tapping mode. The spring constant of the cantilevers with standard silicon tips (OTESPA) is 5 - 42_N/m and the force was applied in the range between 5 and 300 nN. The force set point was adjusted for each measurement to obtain enough deformation for a reliable fit in the unload region (2 to 10 nm). During measurements, the tip oscillates at a frequency of 2 kHz, far below the cantilever resonant frequency (300 kHz). To determine the elastic moduli of samples, the data were fit with the Derjaguin-Muller-Toporov (DMT) model, applicable for systems with low adhesion and small tip radii. The reduced modulus E_r is given by

$$F = \frac{4}{3}E_{\rm r}\sqrt{Rd^3} + F_{\rm adh} = kz$$

where *F* is the force, *R* is the tip radius, *d* is the deformation, F_{adh} is the maximum adhesion force, and *z* is the vertical displacement. The relationship between E_r and the sample elastic modulus E_s is

$$E_{\rm r} = \left[\frac{1 - v_{\rm t}^2}{E_{\rm t}} + \frac{1 - v_{\rm s}^2}{E_{\rm s}}\right]^{-1}$$

where v_t and E_t are the Poisson's ratio and elastic modulus of the tip, and v_s is the Poisson's ratio of the sample.

Fabrication and Characterization of Field-Effect Transistor Memory. The BCP thin films were used as the charge-trapping layers in the field-effect transistor (FET) memory with a top-contact configuration. A 300 nm SiO₂ layer (capacitance per unit area = 10 nF cm⁻²) as a gate dielectric was thermally grown onto the highly n-type doped Si (100) substrates. The polymer solutions were prepared in THF at 10 mg mL⁻¹ and were then spin-coated onto SiO₂/Si substrates at a spin rate of 3000 rpm for 60 s. The polymer thin films were solvent-annealed with the mixture of THF: $H_2O = 1:1$ for 12 h. The 50 nm-thick semiconducting layers of pentacene were deposited onto the BCP layers with a deposition rate of 0.4-0.5 Å s⁻¹ at room temperature under a vacuum level of approximate 3×10^{-7} Torr. Finally, the top-contact source and drain electrodes were made by 70 nm-thick gold through a regular shadow mask. The channel length (L) and width (W) were 50 and 1000 µm, respectively. To prepare the FET memory devices with stretched BCP electret films, first, the BCPs thin films were transferred onto PDMS substrate and controlled the nanostructures by solvent-annealing. Second, the BCP thin film/PDMS were stretched or under stretch-release tests and then transferred onto SiO₂/Si substrates. The transferred stretched films could fully adhere to the SiO₂ layer and maintain the stretched state without recovery. The pentacene layer and gold layer were then deposited onto the stretched BCP thin films. The electrical characteristics of FET memory devices were recorded in a N₂-filled glovebox using a Keithley 4200 semiconductor parametric analyzer (Keithley Instruments Inc., Cleveland, OH).

3. Supplementary Tables

| Sample | $f_{\rm PBA}{}^a$ | $M_{n,SEC}^{b}$ | $N_{\rm PBA}{}^c$ | M _{n,NMR} (g/mol) | $M_{\rm w}/M_{\rm n}^{\ b}$ |
|--|-------------------|-----------------|-------------------|----------------------------|-----------------------------|
| N ₃ -PBA _{3k} | 1 | 4,000 | 26 | 3,330 | 1.21 |
| N ₃ -PBA _{7k} | 1 | 7,100 | 54 | 6,900 | 1.16 |
| N ₃ -PBA _{6k} -N ₃ | 1 | 5,700 | 46 | 5,880 | 1.18 |
| N ₃ -PBA _{10k} -N ₃ | 1 | 9,200 | 78 | 9,860 | 1.21 |
| (PBA _{3k} -N ₃) ₄ | 1 | 10,200 | 91 | 11,800 | 1.23 |
| $(PBA_{5k}-N_3)_4$ | 1 | 12,600 | 157 | 20,100 | 1.22 |

 Table S1. Molecular parameters of PBA homopolymers

^{*a*}Volume fraction of PBA block (f_{PBA}) was calculated using $d_{MH} = 1.36 \text{ g/cm}^3$ and $d_{PBA} = 0.90 \text{ g/cm}^3$. ^{*b*}Estimated by SEC in DMF containing 0.01 mol L⁻¹ LiCl using polystyrene standard. ^{*c*}Degree of polymerization of PBA block.

| No. | f_{PBA} | Modulus (MPa) |
|-----|-----------|---------------|
| A1 | 0.80 | 15.6 |
| A2 | 0.88 | 7.1 |
| B1 | 0.78 | 56.1 |
| B2 | 0.86 | 21.8 |
| C1 | 0.79 | 93.3 |
| C2 | 0.86 | 90.1 |

 Table S2. Elastic modulus of the block copolymers

4. Supplementary Figures



Figure S1. ¹H NMR spectrum (400 MHz) of PBA_{3k}-N₃.



Figure S2. ¹H NMR spectrum (400 MHz) of PBA_{7k}-N₃.



Figure S3. ¹H NMR spectrum (400 MHz) of N_3 -PBA_{6k}- N_3 .



Figure S4. ¹H NMR spectrum (400 MHz) of N₃-PBA_{10k}-N₃.



Figure S5. IR spectra of PBA_n-Br and PBA_n-N₃.



Figure S6. IR spectra of Br-PBA_n-Br and N₃-PBA_n-N₃.



Figure S7. IR spectra of (PBA_n-Br)₄ and (PBA_n-N₃)₄.



Figure S8. ¹H NMR spectrum (400 MHz) of MH-*b*-PBA_{3k}.



Figure S9. ¹H NMR spectrum (400 MHz) of MH-*b*-PBA_{7k}.



Figure S10. ¹H NMR spectrum (400 MHz) of MH-*b*-PBA_{10k}-*b*-MH.



Figure S11. ¹H NMR spectrum (400 MHz) of (PBA_{3k}-*b*-MH)₄.



Figure S12. ¹H NMR spectrum (400 MHz) of (PBA_{5k}-*b*-MH)₄.



Figure S13. (a-b) IR spectra and (c-d) SEC traces of PBA_{3k}-N₃, MH-*b*-PBA_{3k}, PBA_{7k}-N₃ and MH-*b*-PBA_{7k}, respectively.



Figure S14. (a) SEC traces of N₃-PBA_{6k}-N₃ and MH-*b*-PBA_{6k}-*b*-MH. (b) IR spectra and (c) SEC traces of N₃-PBA_{10k}-N₃ and MH-*b*-PBA_{10k}-*b*-MH.



Figure S15. (a-b) IR spectra and (c-d) SEC traces of $(PBA_{3k}-N_3)_4$, $(PBA_{3k}-b-MH)_4$, $(PBA_{5k}-N_3)_4$ and $(PBA_{5k}-b-MH)_4$, respectively.



Figure S16. 1-D SAXS profiles of as-cast and annealed (a) A1, (b) A2, (c) B1, (d) B2, (e) C1, and (f) C2 bulk samples.



Figure S17. AFM topographies of annealed (a) A2, (b) B2, and (c) C2 thin films. The *z* scale is 15 nm. 2-D GISAXS patterns of (d) A2, (e) B2, and (f) C2 thin films.



Figure S18. 2-D GISAXS patterns of as-cast (a) A1, (b) A2, (c) B1, (d) B2, (e) C1, and (f) C2 thin films.



Figure S19. OM images of A1, A2, B1, B2, C1 and C2 thin films under stretching at

100% strain.



Figure S20. Elastic moduli of the studied BCPs and various materials.



Figure S21. Schematic processes to prepare the FET memory devices with stretched BCP electret films.



Figure S22. (a) BCPs-based FET memory devices under 100% stretching. Transfer characteristics of the FET memory devices using charge trapping layers of (b) A1, (c) B1, and (d) C1 thin films.



Figure S23. OM images of A1, B1, and C1 thin films under cyclic stretching for 50 and 200 times at 50% strain.



Figure S24. 1-D GISAXS profiles of (a) A1 and (b) B1 thin film after stretch-release tests at 50 % strain for 0, 100, 400, and 1000 cycles.





5. Reference

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