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Supporting Information

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Chemically Controlled Bending of Compositionally Anisotropic Microcylinders**

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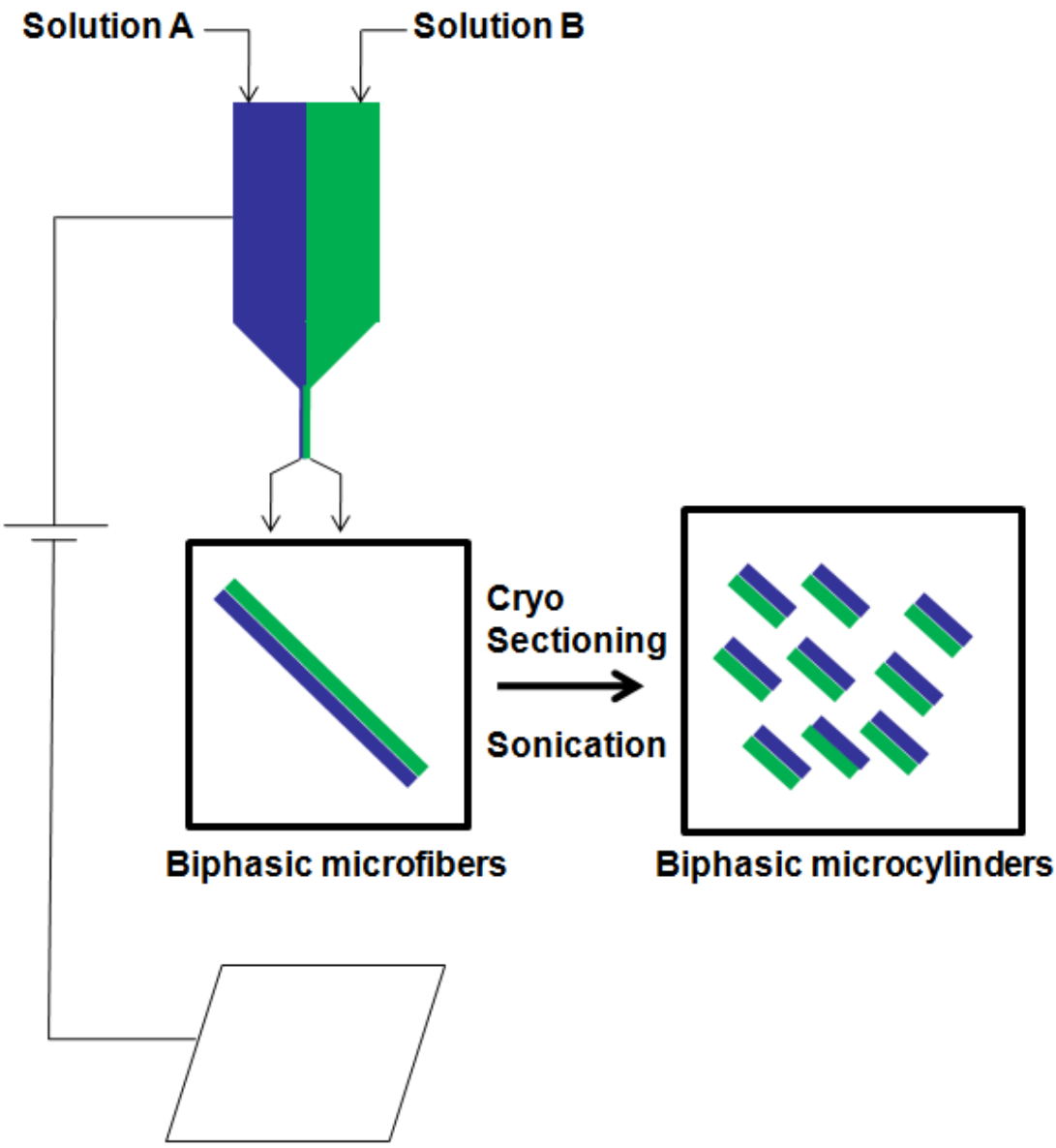
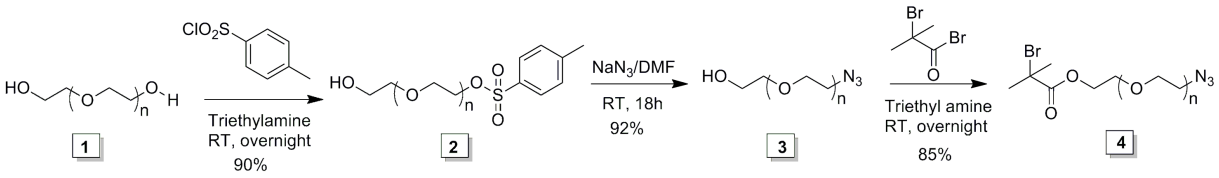


Figure S1: Scheme depicting the electrohydrodynamic co-jetting process to produce biphasic microcylinders from microfibers.



Scheme S1. Synthesis of the water-soluble clickable ATRP initiator **4**.

Experimental section.

Materials: Poly(lactide-co-glycolide) PLGA 85:15 (Mw 50-75,000 g/mol), Poly[(m-phenylenevinylene)-alt-(2,5-dibutoxy-p-phenylenevinylene)] (MEHPPV), Poly[tris(2,5-bis(hexyloxy)-1,4-phenylenevinylene)-alt-(1,3-phenylenevinylene)] (PTDPV) chloroform, N, N- dimethylformamide (DMF), dichloromethane, ethanol, Copper sulfate pentahydrate ($CuSO_4.5H_2O$), Sodium Ascorbate, Polyethylene glycol (average Mw~600 g/mol), *p*-toluene sulfonyl chloride, triethyl amine, sodium azide, 2-bromo isobutyryl bromide, OEGMA (average M_w~475 g/mol), CuBr, $CuBr_2$, 2,2' bipyridine, phosphate buffered saline and tween-20 were purchased from Sigma-Aldrich, USA and used as received. All solvents were ACS reagent grade and used as received from commercial suppliers. Acetylene-modified PLGA, Poly (lactide-co-propargyl glycolide) (PPGL) was synthesized via a previously reported protocol.[1]

Polymer Characterizations: The chemical structures of the polymers corresponding to each synthetic procedure were analyzed by ^{1}H and ^{13}C NMR (Cobalt 400 MHz, Varian Co., USA). CLSM micrographs were obtained with a FluoView 500 confocal laser scanning microscope (Olympus, Japan). MEHPPV and PTDPV were excited by 405 nm UV and 488 nm Argon lasers respectively. Optical filters of emission wavelength 430-460 nm and 505-525 nm respectively were used to visualize the fluorescence of

MEHPPV and PTDPV. For SEM imaging, cylinders were subjected to lyophilization (Labconco Inc, USA) 10h, sputtered with gold, and visualized through an Amray SEM. **Electrohydrodynamic co-spinning:** Bi- and tetracompartmental fibers and cylinders were fabricated following a procedure described elsewhere.[2,3] In case of bicompartmental fibers, the following two jetting solutions were used: (i) 18:100 w/w PLGA8515 in 97:3 chloroform: DMF (by vol.), labeled with trace amounts of MEHPPV (ii) 18:100 w/w solution of 1:3 w/w PLPG: PLGA (85:15) in 97:3 chloroform: DMF (by vol.), labeled with trace amounts of PTDPV. These two solutions were pumped through a modified dual capillary needle system (Micromedics Inc, USA) at a flow rate of 0.03 ml/h through a syringe pump (kD Scientific, USA). The flow rate reported is the reading on the pump, and the actual flow rate equals the product of flow rate and number of capillary needles employed. A DC voltage source (Gamma voltage source, USA) connected to the capillaries was employed to apply an electric potential to the jetting solutions. Fibers were deposited onto a grounded, aluminum foil covered spinning wheel (Synthecon, Inc., USA, modified to experimental requirements) rotating at 20 rpm, placed at a distance of 5-8 cm from the capillary tip. Tetracompartmental fibers were prepared by employing four capillaries in a square configuration. Fiber bundles were converted into cylinders via cryosectioning (Microme, USA) followed by ultrasonication of the sections in an ice bath.[3]

Synthesis of hetero-bi functional PEG initiator (4): The compound 4 has been synthesized via the following steps (Scheme S1).

(a) Synthesis of Monotosyl-PEG (2): Polyethylene glycol 600 (**1**) (8.4 mL, 7.0 equiv), Et_3N (0.29 mL, 1.1 equiv) and CH_2Cl_2 (2 mL) were stirred vigorously at RT. A solution of *p*-toluene sulfonylchloride (0.375 g, 1.0 equiv) in CH_2Cl_2 (2.5 mL) was added slowly using a dropping funnel. Then, the reaction mixture was stirred for 24 h at RT before a 1.0 M solution of HCl (2.5 mL), H_2O (2.5 mL) and a saturated solution of brine (3.0 mL) were added. The resultant aqueous layer was further extracted with dichloromethane (3×20 mL). The combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed under rotary evaporation. The crude product was then purified by flash column chromatography (EtOAc/MeOH: 99:1) to afford the title compound 2 as viscous colorless oil. Yield: ~90%. ^{1}H NMR (400 MHz, $CDCl_3$, *d* in ppm): 7.76 (d, Ar), 7.29 (d, Ar), 4.12 (t, C*H*$_2$OTs), 3.56-3.68 (m, O-(C*H*$_2$)$_2$-O), 3.54 (s, C*H*$_2$-OH), 2.41 (s, Ar-C*H*$_3$) and 2.04 (s, O*H*).

(b) Synthesis of monoazide-PEG (3): To a solution of compound **2** (2.0 g, 1.0 equiv) in DMF (8 mL) was added a solution of NaN_3 (0.52, 3.0 equiv) in DMF (2 mL). The resulting mixture was stirred at RT for 18 h. Upon completion (judged by NMR), the solvent was distilled out under reduced pressure. The titled crude product 3 (yellow oil) has been used for the next step without further purification. Yield: ~92%. ^{1}H NMR (400 MHz, $CDCl_3$, *d* in ppm): 3.54-3.68 (m, O-(C*H*$_2$)$_2$-O), 3.33 (t, C*H*$_2$-N$_3$), and 2.36 (s, C*H*$_2$-OH).

(c) Synthesis of 2-bromoisobutyrate terminated-PEG-azide (4): As a final step of synthesis, the conjugation of 2-bromo isobutyryl bromide to monoazide-PEG (**3**) was

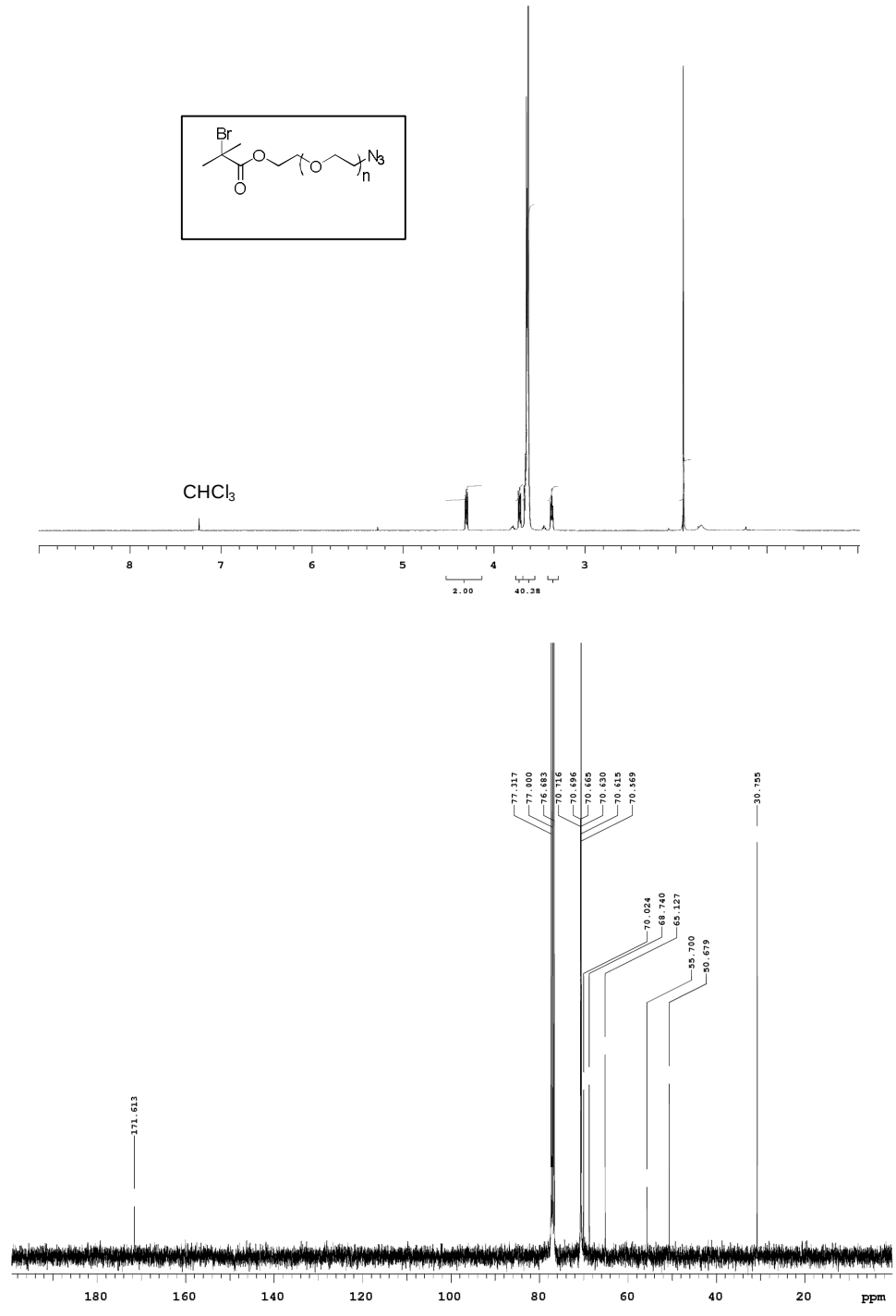
carried out using the following procedure. A solution of 2-bromoisobutyryl bromide (0.48 g, 1.3 equiv) and triethylamine (0.29 g, 1.3 equiv) in CH_2Cl_2 (5 mL) was cooled to 0°C in a shlenk flask. A solution of monoazide PEG (1 g, 1 equiv) in CH_2Cl_2 (5 mL) was added dropwise with stirring. The reaction mixture was then stirred under N_2 at RT for 16 h, filtered, and the solvent was removed by rotatory evaporator. The crude product was then purified by flash column chromatography (EtOAc/MeOH: 95:5) to provide compound **4** as pale-yellow oil. Yield: ~85 %. ^{1}H NMR (400 MHz, $CDCl_3$): d (ppm) 1.92 (s, -OCOC-(C*H*$_3$)$_2$Br), 3.37 (t, C*H*$_2$-N$_3$), 3.62-3.67 (m, O-(C*H*$_2$)$_2$-O), 3.72 (t, C*H*$_2$-CH$_2$-OCOCMe$_2$Br), 4.31 (t, -C*H*$_2$-OCOCMe$_2$Br). ^{13}C NMR (100 MHz, $CDCl_3$): d (ppm) 30.7, 50.7, 55.7, 65.1, 68.7, 70.0, 70.5, 70.61, 70.62, 70.66, 70.69, 70.71, 171.6.

Initiator immobilization on microcylinders via click reaction: Around 40,000 cylinders have been added to 1 mL aqueous solution of 1.33 mg of $CuSO_4$, 5.33 mg of Sodium Ascorbate and 28 mg of ATRP initiator 4 (see Scheme 2) and stirred at RT for overnight. Cylinders were extensively washed with DI water containing 2 wt-percent tween 20 and analyzed via Confocal Laser Scanning Microscopy.

Polymerization of OEGMA from initiator immobilized micro cylinders: 5.6 mg of bipyridine and 1 g of OEGMA in 1 ml DI water containing 0.01 wt-percent tween 20 was taken in a N_2-filled Schlenk flask. Around 40,000 clicked cylinders were added to the solution and sonicated for 10 second. Then the mixture has been degassed by passing through 3 times of freeze pump thaw cycles. Finally, 1.5 mg of CuBr and 0.7 mg of $CuBr_2$ was added to the degassed solution. The polymerization was run at RT under N_2 for about 1 hr. After polymerization, cylinders were thoroughly washed with DI water

containing 0.1 M EDTA and 2 wt-percent Tween 20. Cylinders were analyzed via Confocal Laser Scanning Microscopy.

^{1}H NMR and ^{13}C spectrum of the initiator 4



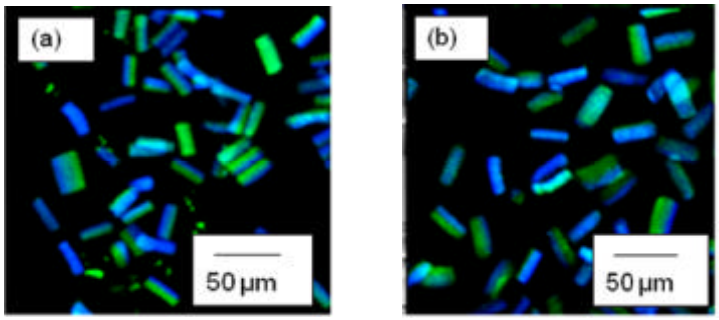


Figure S2: Representative images of 30 µm cylinders (a) before clicking (b) after clicking with initiator 4.

Finite Element Analysis: Microcylinder bending was simulated using large deflection finite element analysis using ANSYS. We took advantage of the symmetry of the pillar geometry and modeled only one quarter of the volume of the cylinder. Material properties as described in the manuscript were applied to the geometry. Three dimensional structural elements with twenty nodes were used to mesh the cylinder volume. The free end of the cylinder was capped by a stiff area to reduce locally excessive element deformation, and this increased the range of convergence. Isotropic thermal expansion was used to model the swelling of the PEGMA compartment. Last, a displacement based convergence criteria were used for the non-liner analysis with auto time stepping enabled, but the maximum step size was restricted to 1% of the maximum deflection.

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[1] X. Jiang, E. B. Vogel, M. R. Smith III, G. L. Baker, *Macromolecules* **2008**, *41*, 1937.
[2] S. Bhaskar, J. Lahann, *J. Am. Chem. Soc.* **2009**, *131*, 6650.
[3] S. Bhaskar, J. Hitt, S. L. Chang, J. Lahann, *Angew. Chem. Int. Ed.* **2009**, *48*, 4589.