

Supporting Information.

Unexpected stereomutation dependence on the chemical structure of helical vinyl glycopolymers

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Experimental Section

Material. 2-Iodo-5-bromo-toluene (97%, Aldrich), N-bromosuccinimide (NBS, 99%, Aldrich), triphenylphosphine (PPh₃, 99%, Acros), tetrachloromethane (CCl₄, AR, Beijing Chemical Co.), 2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl bromide (95%, Sigma), silver oxide (AR, Beijing Chemical Co.), and aqueous formaldehyde (40%, AR, Beijing Chemical Co.) were used as purchased. Azobisisobutyronitrile (AIBN, Wuhan Chemical Co., AR) was recrystallized from ethanol and dried under vacuum at room temperature. Tetrahydrofuran (THF, Beijing Chemical Co. AR) was refluxed with sodium and distilled out just before use. Dimethyl sulfoxide (DMSO, Beijing Chemical Co. AR) and N,N-dimethylformamide (DMF, Beijing Chemical Co. AR) were distilled out from calcium hydride. Quinoline (Beijing Chemical Co. AR) and methanol were purified by distillation. Tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) was prepared according to the literature procedure and kept in a refrigerator under argon (Brandsma, L.; Vasilevsky, S. F.; Verkruijsse, H. D. *Application of transition metal catalysis in organic synthesis, New York* **1999**, P5). 4-(Butoxy)phenylboronic acid and 4-(tetrahydro-2*H*-pyran-2-yloxy)phenylboronic acid were prepared according to the literature procedure (Cui, J.; Liu, A.; Zhi, J.; Zhu, Z.; Guan, Y.; Wan, X.; Zhou, Q. *Macromolecules* **2008**, *41*, 5245. Cui, J.; Zheng, J.; Qiao, W.; Wan, X. *J. Colloids Interface. Sci.* **2008**, *326*, 267). All other reagents and solvents were used as obtained unless otherwise specified.

Measurements. ¹H NMR and ¹³C NMR spectra were obtained on Bruker ARX400 or Bruker ARX300 spectrometers. The chemical shifts were reported in ppm (δ) relative to tetramethylsilane. Elementary analysis was carried out on a GmbH Vario EL instrument. Mass spectrum was recorded on a Bruker Inc. BIFLEX III spectrometer. Infra-Red (IR) spectra were recorded on a Nicolet Magna-IR 750 fourier transform infrared spectrometer. The number-average molecular weight (*M_n*), weight-average molecular weight (*M_w*), and polydispersity (*M_w/M_n*) of polymers were determined by a gel permeation chromatography (GPC) apparatus equipped with a Waters 2410 refractive-index detector and a Water 515 pump. Three Waters Styragel columns with a 10-mm bead size were connected in series. Their effective molecular weight ranges were 100-10,000 for Styragel HT2, 500-30,000 for Styragel HT3, and 5000-600,000 for Styragel HT4, separately. The pore sizes were 50, 100, and 1000 nm for Styragel HT2, HT3, and HT4, respectively. THF was employed as the eluent at a flow rate of 1.0 mL/min at 35 °C. All GPC curves were calibrated against a series of monodispersed polystyrene standards. Optical rotations were estimated with a JASCO Model P-1030 digital polarimeter using a

water-jacketed 100 mm cell at 25 °C. The temperature of water bath was mediated with a PolyScience programmable temperature controller. UV-vis absorption measurements were run on a Varian Cary 1E UV-vis spectrometer. CD spectra were recorded on a JASCO J-810 spectrometer. The sample solution was thermostatted at 25 °C. The light pathlength of the quartz cell used was 10 mm. The concentration was 2×10^{-5} mol/L and the solvent was THF or DMSO.

Synthesis (Schemes 1 and 2)

2-(4'-Butoxyphenyl)-5-bromotoluene. To a degassed mixture of 2-iodo-5-bromo-toluene (12.0 g, 40 mmol), 4-(butoxy)phenylboronic acid (7.8 g, 40 mmol), and Pd(PPh₃)₄ (0.20 g, 0.18 mmol) were added into a solution containing benzene (80 mL), ethanol (40 mL) and aqueous Na₂CO₃ solution (2 M, 80 mL) under a continuous stream of argon. The solution was vigorously stirred at reflux for 4 h. Afterwards, the organic layer was separated and dried over anhydrous Na₂SO₄. The solvent was taken away under reduced pressure and the residue was purified by column chromatography on silica gel (dichloromethane/petroleum ether: 1/5 (v/v) as eluent) to give 9.4 g of product as a yellow liquid. Yield: 73%. ¹H NMR (300MHz, CDCl₃, δ ppm): 0.96-1.01 (t, 3H, CH₃), 1.47-1.54 (m, 2H, CH₂), 1.77-1.81 (m, 2H, CH₂), 2.23 (s, 3H, CH₃), 3.97-4.01 (t, 2H, CH₂), 6.91-6.94 (d, 2H, Ar), 7.05-7.08 (d, 1H, Ar), 7.17-7.20 (d, 2H, Ar), 7.32-7.35 (d, 1H, Ar), 7.40 (s, 1H, Ar). ¹³C NMR (75MHz, CDCl₃, δ ppm): 158.3, 140.5, 137.7, 132.9, 132.8, 131.4, 130.0, 128.7, 120.6, 114.1 (12C, Ar), 20.4 (1C, ArCH₃), 67.7, 31.3, 19.3, 13.9 (4C, butoxyl). Anal. Calcd. for C₁₇H₁₉BrO: C, 63.96; H, 6.00; Found: C, 63.92; H, 6.01. MS: *m/e* = 318 (100%) and 320 (97%) (calcd. 319).

2-(4'-Butoxyphenyl)-5-bromostyrene. A solution of 2-(4'-butoxyphenyl)-5-bromotoluene (9.41 g, 30 mmol), NBS (5.34 g, 30 mmol), and BPO (0.11 g, 0.45 mmol) in CCl₄ (100 mL) was refluxed for 3 h. After cooling to room temperature, the solids suspended on the surface of the reaction mixture were separated by filtration. After evaporation of solvent under vacuum, yellow solids were obtained and were directly mixed with PPh₃ (7.73 g, 30 mmol) and acetone (100 mL). The mixture was heated to reflux for 4 h. Afterwards, the solvent was evaporated out under reduced pressure and the residue was purified by column chromatography on silica gel using dichloromethane at first and then methanol as eluent. The methanol phase was collected. After the removal of methanol, the residue was dissolved in aqueous formaldehyde (40 wt%, 120 mL). With a rapid stirring, aqueous NaOH solution (2.5 M, 80 mL) was dropped slowly at room temperature. The mixture was stirred for 24 h. After the reaction was completed, 3 × 150 mL portions of CH₂Cl₂ were used to extract the mixture. The organic layers were combined and dried over anhydrous Na₂SO₄. The solvent was taken away under reduced pressure and the residue was purified by column chromatography on silica gel (dichloromethane/petroleum ether: 1/3 (v/v) as eluent) to give 5.21 g of yellow solids. Yield: 53%. ¹H NMR (300 MHz, CDCl₃, δ ppm): 0.97-1.02 (t, 3H, CH₃), 1.48-1.58 (m, 2H, CH₂), 1.75-1.85 (m, 2H, CH₂), 3.99-4.03 (t, 2H, CH₂), 5.21-5.25 (d, 1H, vinyl), 5.70-5.73 (d, 1H, vinyl); 6.61-6.70 (dd, 1H, vinyl); 6.93-6.97 (d, 2H, Ar), 7.13-7.16 (d, 1H, Ar), 7.20-7.25 (d, 2H, Ar), 7.41-7.44 (d, 1H, Ar), 7.74-7.75 (d, 1H, Ar). ¹³C NMR (75 MHz, CDCl₃, ppm): 158.6, 139.4, 137.7, 131.6, 130.7, 130.5, 128.6, 114.7 (12C, Ar), 135.0, 115.7 (2C, vinyl), 67.7, 31.4, 19.3, 13.9 (4C, butoxyl). Anal. Calcd. for C₁₈H₁₉BrO: C, 65.27; H, 5.78; Found: C, 65.17; H, 5.80. MS: *m/e* = 330 (100%) and 332 (97%) (calcd. 331).

2-(4'-Butoxyphenyl)-5-(4'-hydroxyphenyl)styrene. To a degassed mixture of 2-(4'-butoxyphenyl)-5-bromostyrene (5.2 g, 16 mmol), 4-(tetrahydro-2H-pyran-2-yloxy)phenylboronic acid (5.0 g, 23 mmol), hydroquinone (0.44 g, 4 mmol) and Pd(PPh₃)₄ (0.20 g, 0.18 mmol) were added benzene (80 mL), ethanol (40 mL) and aqueous Na₂CO₃ solution (2 mol/L, 80 mL) under a continuous stream of argon. The solution was vigorously stirred at reflux for 6 h under argon. Afterwards, the

organic layer was separated and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the residue was dissolved in the mixture solvent of THF (50 mL), methanol (20 mL), and HCl (37 wt%, 10 mL). The mixture was then stirred at room temperature for 4 hours. The solution was diluted with ethyl acetate (200 mL) and washed with aqueous NaHCO₃ and water. The organic layer was dried over anhydrous Na₂SO₄. The solvent was taken away under reduced pressure and the residue was purified by column chromatography on silica gel (dichloromethane as eluent) to give 4.8 g of yellow solids. Yield: 89%. ¹H NMR (300 MHz, CDCl₃, δ ppm): 0.97-1.02 (t, 3H, CH₃), 1.48-1.58 (m, 2H, CH₂), 1.75-1.85 (m, 2H, CH₂), 3.99-4.03 (t, 2H, CH₂), 5.21-5.25 (d, 1H, vinyl), 5.73-5.79 (d, 1H, vinyl); 6.75-6.85 (dd, 1H, vinyl); 6.92-76.98 (m, 4H, Ar), 7.29-7.32 (m, 3H, Ar), 7.47-7.51 (dd, 1H, Ar), 7.54-7.56 (d, 2H, Ar), 7.81-7.82 (d, 1H, Ar). ¹³C NMR (75 MHz, CDCl₃, ppm): 158.3, 155.1, 139.5, 139.0, 136.3, 133.7, 132.6, 130.9, 130.5, 128.4, 126.0, 124.1, 114.7, 114.0 (18C, Ar), 136.0, 115.7 (2C, vinyl), 67.7, 31.3, 19.3, 13.9 (4C, butoxyl). Anal. Calcd. for C₂₄H₂₄O₂: C, 83.69; H, 7.02; Found: C, 83.41; H, 7.12. MS: *m/e* = 344 (calcd. 344.5).

2-(4'-Butoxyphenyl)-5-[4'-(2,3,4,6-tetra-*O*-acetyl-β-D-galactosyloxy)phenyl]styrene (1). A mixture of 2-(4'-butoxyphenyl)-5-(4'-hydroxyphenyl)styrene (3.78 g, 11.0 mmol), 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl bromide (4.86 g, 11.9 mmol), Ag₂O (2.75 g, 11.9 mmol), and CaSO₄ (1.64 g, 11.9 mmol) in ethyl acetate (40 mL) containing anhydrous quinoline (20 mL) was stirred at room temperature for 48 hours in a flask protected from light. Afterwards, the solution was diluted with ethyl acetate (100 mL). After filtration, the solution was washed with 10 wt% HCl, aqueous NaHCO₃ and brine following by drying over anhydrous Na₂SO₄ and concentrated to dryness. The product was purified further by column chromatography on silica gel (dichloromethane/ethyl acetate: 20/1 (v/v) as eluent) to give 2.4 g of product as yellow solid. Yield: 31%. ¹H NMR (400 MHz, CDCl₃, ppm): 0.98-1.02 (t, 3H, CH₃), 1.48-1.57 (m, 2H, CH₂), 1.77-1.84 (m, 2H, CH₂), 2.202, 2.097, 2.042, 2.031 (s, 12H, COCH₃), 4.00-4.09 (t, 2H, OCH₂), 4.09-4.29 (m, 3H, sugar), 5.10-5.16 (m, 2H, sugar), 5.48-5.49 (m, 1H, sugar), 5.51-5.56 (m, 1H, sugar), 5.22-5.25 (d, 1H; vinyl), 5.73-5.78 (d, 1H; vinyl), 6.75-6.83 (dd, 1H, vinyl), 6.95-6.98 (d, 2H, Ar), 7.08-7.12 (d, 2H, Ar), 7.28-7.31 (d, 2H, Ar), 7.33-7.35 (d, 1H, Ar), 7.47-7.48 (dd, 1H, Ar), 7.57-7.60 (d, 2H, Ar), 7.72-7.78 (d, 1H, Ar). ¹³C NMR (100 MHz, CDCl₃, ppm): 170.3, 170.2, 170.1, 169.4 (4C, C=O), 158.4, 156.4, 139.4, 139.2, 136.2, 132.4, 130.8, 130.6, 128.2, 126.1, 124.3, 117.2, 114.0 (18C, Ar), 136.0, 114.7 (2C, vinyl), 99.7, 71.0, 77.0, 76.7, 71.0, 70.82, 66.9, 61.3, 60.3 (6C, sugar), 67.7, 31.3, 19.2, 13.8 (4C, butoxyl), 20.7, 20.6, 20.5 (4C, COCH₃). Anal. Calc. for C₃₈H₄₂O₁₁: C, 67.64; H, 6.27. Found: C, 67.58; H, 6.24. 20. MS: *m/e* = 697 (MNa⁺) (C₃₈H₄₂O₁₁ calcd. 674.7). Specific optical rotation [α]₃₆₅²⁵ = 90° (c: 2.0 mg/mL, THF)

2-(4'-Butoxyphenyl)-5-[4'-(β-D-galactosyloxy)phenyl]styrene (2). A mixture of 1 (1.35 g, 0.20 mmol) and freshly prepared CH₃ONa in methanol (0.1 mmol/L, 50 mL) was stirred at room temperature for 12 h. The precipitated product was filtered and washed with methanol. After drying under vacuum, white powder of 0.98 g 2 was obtained. Yield: 97%. ¹H NMR (400 MHz, DMSO-d₆, ppm): 0.93-0.97 (t, 3H, CH₃), 1.42-1.51 (m, 2H, CH₂), 1.69-1.76 (m, 2H, CH₂), 3.42-3.73 (m, 6H, sugar), 4.00-4.03 (t, 2H, OCH₂), 4.54-5.20 (4H, OH), 4.88-4.90 (d, 1H, sugar-C₁), 5.26-5.29 (d, 1H, vinyl), 5.91-5.95 (d, 1H, vinyl), 6.65-6.72 (dd, 1H, vinyl), 7.01-7.23 (d, 2H, Ar), 7.14-7.16 (d, 2H, Ar), 7.25-7.27 (d, 2H, Ar), 7.31-7.33 (d, 1H, Ar), 7.59-7.61 (d, 1H, Ar), 7.69-7.71 (d, 2H, Ar), 7.87(s, 1H, Ar). ¹³C NMR (100 MHz, CDCl₃, ppm): 158.0, 157.3, 138.6, 138.5, 135.4, 133.2, 131.8, 130.6, 130.5, 127.7, 125.8, 123.5, 116.7, 114.2 (18C, Ar), 135.3, 115.6 (2C, vinyl), 101.1, 75.6, 73.3, 70.3, 68.1, 60.4, (6C, sugar), 67.2, 30.8, 18.8, 13.7 (4C, butoxyl), Anal. Calc.: C, 71.13; H, 6.76. Found: C, 70.68; H, 6.80. Anal. Calc. for

C₃₀H₃₄O₇: C, 67.64; H, 6.27. Found: C, 67.58; H, 6.24. MS: 529 (MNa⁺) (calcd. 506.6) Specific optical rotation [α]₃₆₅²⁵ = -64° (c: 2.0 mg/mL, DMSO).

2-(4'-Acetoxyphenyl)-5-bromotoluene. To a degass mixture of 2-(4'-butoxyphenyl)-5-bromotoluene (12.55 g, 40 mmol) and CH₂Cl₂ (40 mL) which was previously cooled to -78 °C, was added BBr₃ (26.5g, 106 mmol) slowly. The solution was then stirred for 12 h. After addition of water (50 mL), the mixture was stirred for 0.5 hours and then was extracted with ethyl acetate (3×150 mL). After evaporation of solvent under reduced pressure, the residue subsequent dried under vacuum to give a white powder. Acetic anhydride (30 mL) and H₂SO₄ (1 mL) were added and the mixture was vigorously stirred at reflux for 4 h. After added into water (200 mL), the mixture was extracted by 3×150 mL portions of CH₂Cl₂. The organic layers were combined and dried over anhydrous Na₂SO₄. The solvent was taken away under reduced pressure and the residue was purified by column chromatography on silica gel (dichloromethane/petroleum ether: 1/5 (v/v) as eluent) to give 10.35 g white solid. Yield: 84%. ¹H NMR (300MHz, CDCl₃, δ ppm): 2.22 (s, 3H, ArCH₃), 2.33 (s, 3H, OCH₃), 7.06-7.17 (m, 3H, Ar), 7.25-7.32 (m, 2H, Ar), 7.35-7.40 (m, 1H, Ar), 7.43 (s, 1H, Ar). ¹³C NMR (75 MHz, CDCl₃, ppm): 169.6, 21.2 (COCH₃), 150.0, 140.0, 137.7, 135.6, 133.1, 131.4, 130.1, 129.5, 128.9, 121.4 (12C, Ar), 20.4 (1C, ArCH₃). Anal. Calcd. for C₁₅H₁₃BrO₂: C, 59.04; H, 4.29; Found: C, 59.01; H, 4.33. MS: *m/e* = 304 (100%) and 306 (97%) (calcd. 305.17).

2-(4'-Acetoxyphenyl)-5-(4'-butoxyphenyl)toluene. This compound was synthesized via the method used for 2-(4'-butoxyphenyl)-5-bromotoluene. Yield: 69%. 0.97-1.02 (t, 3H, CH₃), 1.49-1.56 (m, 2H, CH₂), 1.78-1.83 (m, 2H, CH₂), 2.24 (s, 3H, ArCH₃), 2.34 (s, 3H, OCH₃), 4.00-4.04 (t, 2H, CH₂), 6.97-7.00 (m, 2H, Ar), 7.14-7.16 (d, 2H, Ar), 7.27-7.30 (d, 1H, Ar), 7.36-7.39 (d, 2H, Ar), 7.43-7.47 (m, 2H, Ar), 7.55-7.58 (d, 2H, Ar). ¹³C NMR (75 MHz, CDCl₃, ppm): 169.5, 21.2 (COCH₃), 158.6, 154.4, 139.8, 139.5, 135.7, 134.2, 133.3, 130.5, 130.3, 128.6, 128.0, 124.1, 115.0, 114.8 (18C, Ar), 20.7 (ArCH₃), 67.7, 31.4, 19.3, 13.9 (4C, butoxyl). Anal. Calcd. for C₂₅H₂₆O₃: C, 80.18; H, 7.02; Found: C, 80.21; H, 7.03. MS: *m/e* = 374 (calcd. 374.5).

2-(4'-Hydroxyphenyl)-5-(4'-butoxyphenyl)styrene. Yield: 55%. ¹H NMR (300 MHz, CDCl₃, δ ppm): 0.97-1.02 (t, 3H, CH₃), 1.46-1.58 (m, 2H, CH₂), 1.76-1.85 (m, 2H, CH₂), 3.99-4.04 (t, 2H, CH₂), 5.21-5.25 (d, 1H, vinyl), 5.73-5.79 (d, 1H, vinyl), 6.74-6.83 (dd, 1H, vinyl), 6.88-6.91 (d, 2H, Ar), 6.98-7.02 (d, 2H, Ar), 7.25-7.33 (m, 3H, Ar), 7.48-7.52 (dd, 1H, Ar), 7.56-7.61 (d, 2H, Ar), 7.79-7.80 (d, 1H, Ar). ¹³C NMR (75 MHz, CDCl₃, ppm): 158.7, 154.7, 139.7, 138.7, 136.2, 136.1, 133.1, 131.1, 130.5, 128.1, 126.0, 124.1, 114.9, 114.8 (18C, Ar), 133.2, 114.7 (2C, vinyl), 67.8, 31.3, 19.2, 13.9 (4C, butoxyl). Anal. Calcd. for C₂₄H₂₄O₂: C, 83.69; H, 7.02; Found: C, 83.33; H, 7.02. MS: *m/e* = 344 (calcd. 344.5).

2-[4'-(2,3,4,6-Tetra-O-acetyl- β -D-galactosyloxy)phenyl]-5-(4'-butoxyphenyl)styrene (3). Yield: 45%. ¹H NMR (400 MHz, CDCl₃, ppm): 0.98-1.02 (t, 3H, CH₃), 1.51-1.53 (m, 2H, CH₂), 1.78-1.82 (m, 2H, CH₂), 2.03-2.20 (s, 12H, COCH₃), 4.00-4.03 (t, 2H, OCH₂), 4.08-4.29 (m, 3H, sugar), 5.10-5.16 (m, 2H, sugar), 5.48-5.49 (d, 1H, sugar), 5.51-5.57 (m, 1H, sugar), 5.22-5.25 (d, 1H, vinyl), 5.73-5.78 (d, 1H, vinyl), 6.75-6.83 (dd, 1H, vinyl), 6.98-7.00 (d, 2H, Ar), 7.07-7.08 (d, 2H, Ar), 7.30-7.33 (m, 3H, Ar), 7.49-7.52 (dd, 1H, Ar), 7.56-7.58 (d, 2H, Ar), 7.79-7.80 (d, 1H, Ar). ¹³C NMR (100 MHz, CDCl₃, ppm): 170.3, 170.2, 170.1, 169.3 (4C, C=O), 158.8, 156.0, 140.1, 138.3, 136.0, 135.6, 133.0, 130.9, 130.4, 128.0, 126.1, 124.1, 116.4, 114.8 (18C, Ar), 136.1, 114.9 (2C, vinyl), 99.5, 71.0, 70.8, 68.6, 66.9, 61.3 (6C, sugar), 67.7, 31.3, 19.2, 13.8 (4C, butoxyl), 20.7, 20.6, 20.5 (4C, COCH₃). Anal. Calc. for C₃₈H₄₂O₁₁: C, 67.64; H, 6.27. Found: C, 67.58; H, 6.24. MS: *m/e* = 697 (MNa⁺) (C₃₈H₄₂O₁₁ calcd. 674.7). Specific optical rotation [α]₃₆₅²⁵ = 72° (c: 2.0 mg/mL, THF)

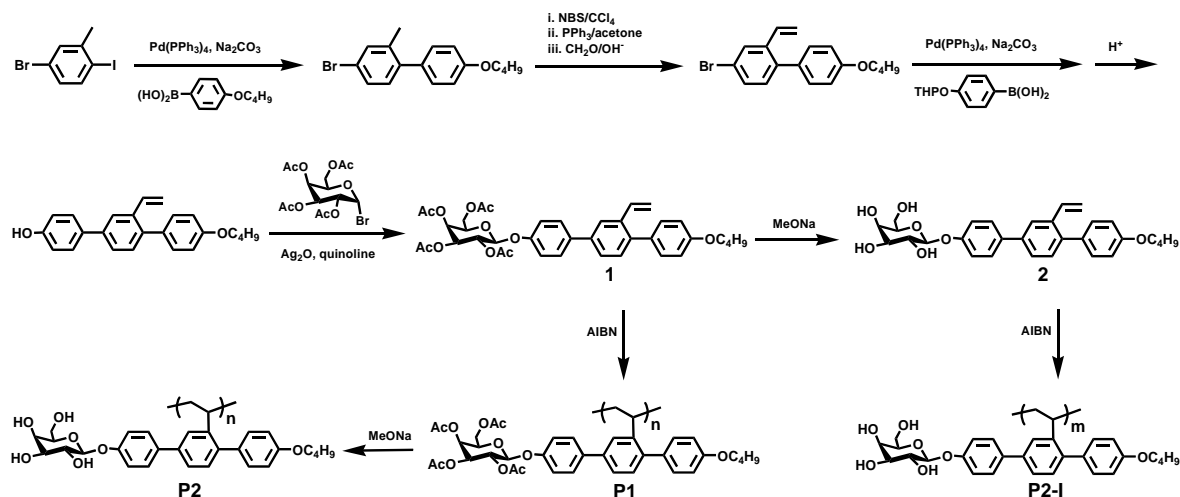
2-[4'-(β-D-Galactosyloxy)phenyl]-5-(4'-butoxyphenyl)styrene (4). Yield: 95%. ¹H NMR (400 MHz, DMSO-d₆, ppm): 0.93-0.97 (t, 3H, CH₃), 1.43-1.49 (m, 2H, CH₂), 1.69-1.74 (m, 2H, CH₂), 3.42-3.73 (m, 6H, sugar), 4.00-4.03 (t, 2H, OCH₂), 4.54-4.90 (4H, OH), 4.88-4.90 (d, 1H, sugar-C₁), 5.27-5.30 (d, 1H, vinyl), 5.90-5.94 (d, 1H, vinyl), 6.66-6.73 (dd, 1H, vinyl), 7.02-7.04 (d, 2H, Ar), 7.12-7.14 (d, 2H, Ar), 7.28-7.33 (d, 2H, Ar), 7.31-7.33 (d, 1H, Ar), 7.58-7.60 (d, 1H, Ar), 7.67-7.69 (d, 2H, Ar), 7.86 (s, 1H, Ar). ¹³C NMR (100 MHz, CDCl₃, ppm): 158.5, 156.9, 138.9, 138.3, 135.4, 133.2, 131.9, 130.5, 130.4, 127.8, 125.7, 123.3, 116.0, 114.9 (18C, Ar), 135.4, 115.7 (2C, vinyl), 101.1, 75.6, 73.3, 70.3, 68.2, 60.4, (6C, sugar), 67.2, 30.8, 18.8, 13.7 (4C, butoxyl), Anal. Calc.: C, 71.13; H, 6.76. Found: C, 70.68; H, 6.80. Anal. Calc. for C₃₀H₃₄O₇: C, 71.13; H, 6.76. Found: C, 70.91; H, 6.84. MS: 529 (MNa⁺) (calcd. 506.6) Specific optical rotation [α]₃₆₅²⁵ = -51 ° (c: 2.0 mg/mL, DMSO).

Radical Polymerization. Take **1** for example. Into a reaction tube, **1** (0.203 g, 0.30 mmol), AIBN (0.16 mg, 0.001 mmol) and DMF (1.0 mL) were added. After three freeze-pump-thaw cycles, the tube was sealed under vacuum and put into an oil-bath thermostated at 90 °C for 20 h. After being cooled to room temperature, the tube was opened and the solution was diluted with THF (10 mL). The mixture was dropped into cold methanol (200 mL). The precipitates were collected by filtration and washed by methanol. After drying under vacuum at room temperature for 24 h, 0.176 g white solids were obtained. Yield: 87%.

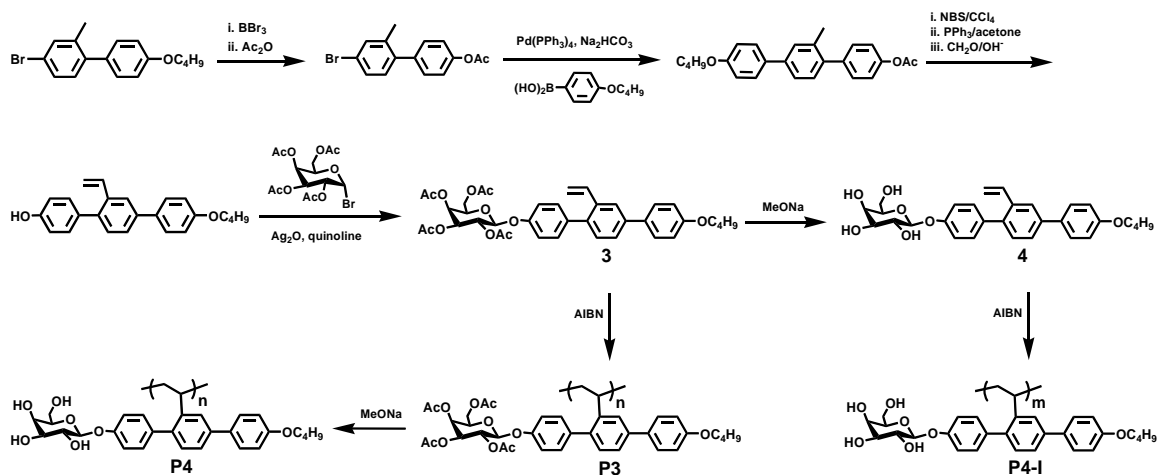
Deacetylation. Take **P1** for example. A mixture of **P1** (0.067g) and freshly prepared CH₃ONa in methanol (0.1 mol/L, 50mL) was stirred at room temperature for two days. The precipitated product was filtered and washed with methanol for three times and then dried under vacuum. 0.046g white powder was obtained. Yield: 92%.

Molecular simulation. The molecular modeling and molecular mechanics calculations were performed using the Compass Force Field as implemented in the Materials Studio software (version 5.0; Accelrys Software Inc.). First, the structures of repeated units were optimized using the Geometry Optimization of the Forcite module until the root-mean-square value became less than 0.1 kcal mol⁻¹ Å⁻¹. The backbone dihedral angles of the repeat unit, hereafter named θ_1 and θ_2 , were varied systematically in steps of 30°. The isotactic polymers with 20-mer were then built up using Polymer Builder in the Material Studio, in which the dihedral angles were constrained to specific degrees. The structures without apparent steric contacts were subjected to energy minimization with the Smart Minimizer of the Discover module at first. Atomistic MD simulations were performed with the Dynamics of Discover module. A NVT ensemble at 298 K was selected. The total simulation time is 0.1 ns and time step is 1 fs. Energy deviation is 5000 kcal/mol.

Scheme S1. Syntheses of 2-(4'-butoxyphenyl)-5-[4'-(2,3,4,6-tetra-O-acetyl-β-D-galactosyloxy)phenyl]styrene (**1**), 2-(4'-butoxyphenyl)-5-[4'-(β-D-galactosyloxy)phenyl]styrene (**2**), and the corresponding polymers **P1** and **P2**



Scheme S2. Syntheses of 2-[4'-(2,3,4,6-tetra-O-acetyl-β-D-galactosyloxy)phenyl]-5-(4'-butoxyphenyl)styrene (**3**), 2-[4'-(β-D-galactosyloxy)phenyl]-5-(4'-butoxyphenyl)styrene (**4**), and the corresponding polymers **P3** and **P4**



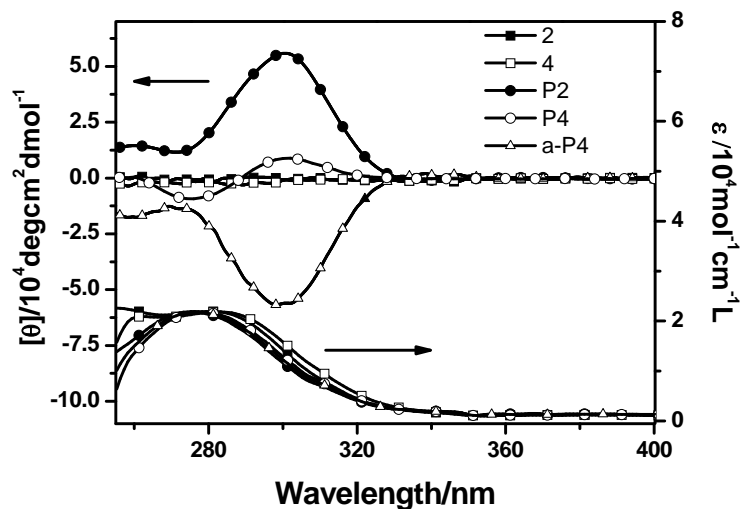


Figure S1. CD and UV-vis absorption spectra of **2**, **4**, **P2**, **P4**, and annealed **P4** (**a-P4**) in DMSO at a concentration of 2×10^{-5} mol/L

Figure S1 shows the CD and UV-vis absorption spectra of the deacetylated monomers and their polymers. Both monomers **2** and **4** exhibit negligible CD effects in the absorption region of *p*-terphenyl side groups. The polymer **P2** displays a similar CD image to its precursor, suggesting the stereostructure of **P1** was retained in **P2**. However, the CD spectrum of **P4** is much different from that of **P3**, probably due to the rapid stereomutation. The CD spectrum of **P4** after annealing in DMSO also shows a negative Cotton effect, opposite to the positive one before annealing, an indicative of a reversed helical sense. We speculate that the position of glycosyl does affect the stability of TCC of the helical polymers, that is, the glycosyl groups closer to the polymer backbone have stronger induction power at a high temperature.

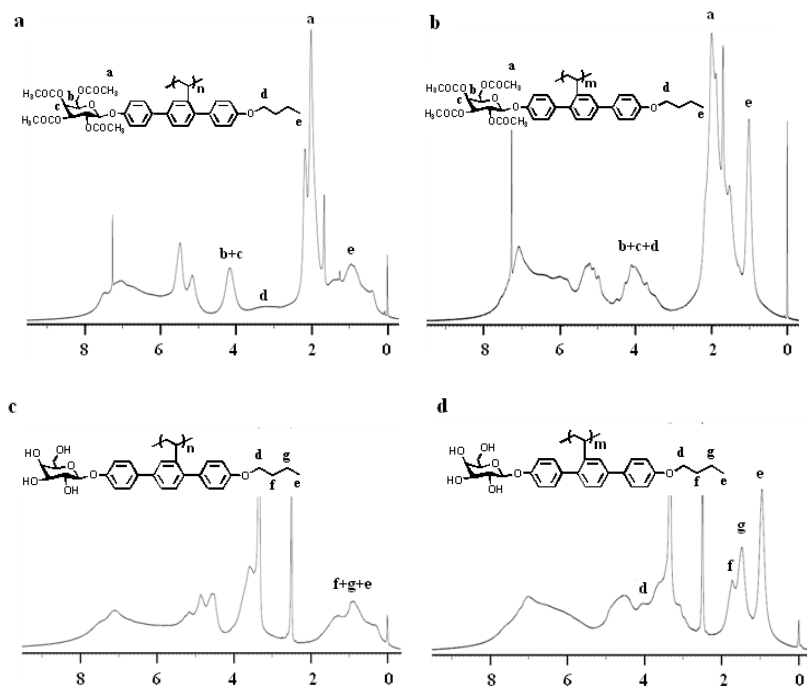


Figure S2. ^1H NMR spectra of **P1** (a), **P3** (b), **P2** (c), and **P4** (d). The solvent is CDCl_3 for **P1** and **P3** but DMSO-d_6 for **P2** and **P4**

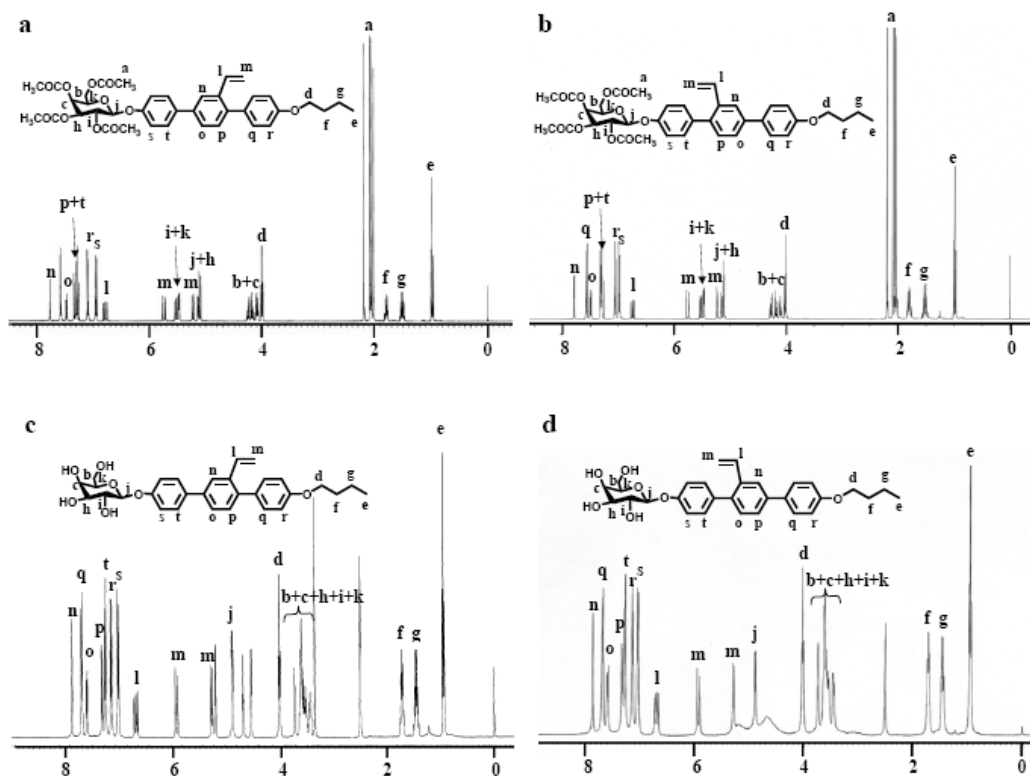


Figure S3. The ^1H NMR spectra of **1** (a), **3** (b), deacetylated product of **1** (c), and deacetylated product of **3** (d). The solvent is CDCl_3 for **1** and **3** but DMSO-d_6 for the other two compounds.

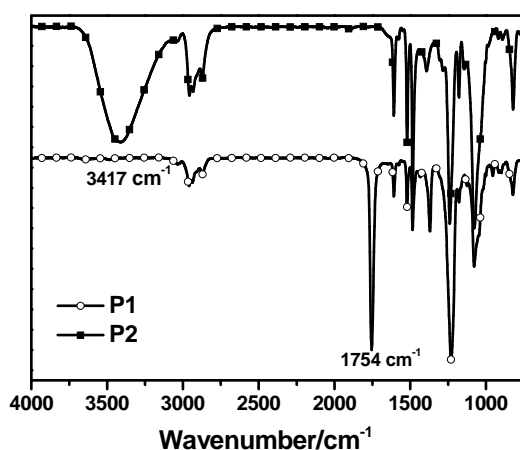


Figure S4 FT-IR spectra of **P1** and **P2**

Figure S4 displays the FT-IR spectra of **P2** and **P4**. It is evident that the C=O absorption peak of the acetyl group of **P1** at 1754 cm^{-1} disappears after deacetylation and a broad absorption peak at 3417 cm^{-1} corresponding to hydroxyl groups. Thus it can be concluded that the *O*-protective acetyl groups were removed completely via this method. The formation of polymers was confirmed by ^1H NMR and FTIR spectra.

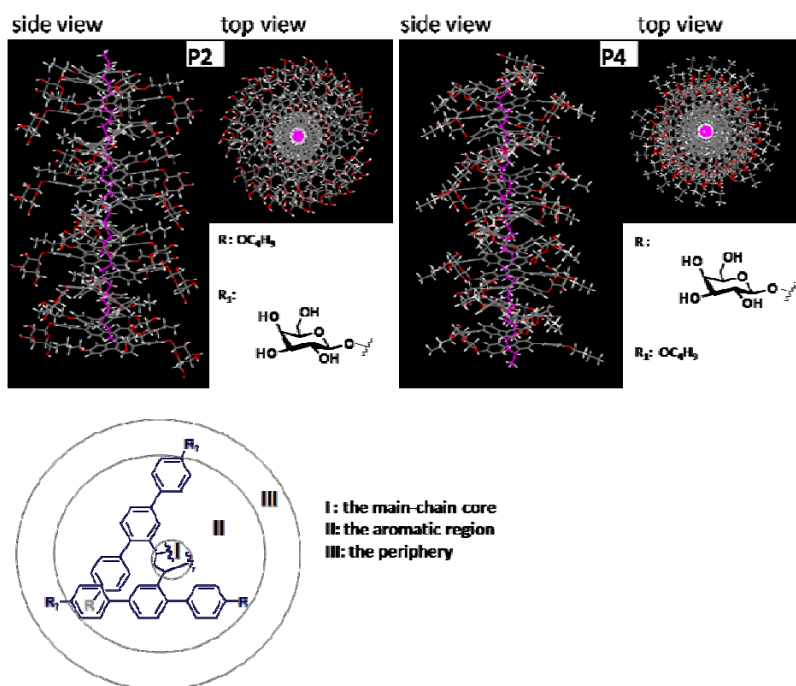


Figure S5. Computer simulated conformations of isotactic **P2** and **P4**. The exterior groups have more freedom to rotate than the interior ones, which are restricted by each other within the chiral environments.

Figure S5 exhibits the most stable conformation of isotactic P2 and P4. Initially, the conformation of 2-[4'-(β -D-galactosyloxy)phenyl]-5-(4'-butoxyphenyl)ethylbenzene, a model of the repeating unit of **P4**, was examined by the geometry optimization. It was assumed that the repeating unit adopts the most stable conformation. In order to build sterically accessible helical model, the backbone dihedral angles of the repeating unit, hereafter named θ_1 and θ_2 , were varied systematically in steps of 30° within an isotactic model system of **P4** consisting of 20 repeating units, which were kept with identical conformation. 35 helical structures without apparent steric contacts in total were obtained. After energy minimization with the Compass forcefield followed by MD at 298 K in the absence of environment, the stable conformations were obtained (Table S1). The similar method was also used to search the stable conformation of **P2**. It was found that both polymers adopt pine-like helix in which side chains connected at given tilt angles occupy equably the space around the backbone. The column of the rigid chains can be divided into three parts: the twisting main-chain core, the aromatic region with high electron density, and the periphery. The glycosyl groups of **P2** sit in the periphery of the polymer chain while those of **P4** in the aromatic region. The exterior groups have more freedom to rotate, but those interior ones are restricted by each other to form chiral environment.

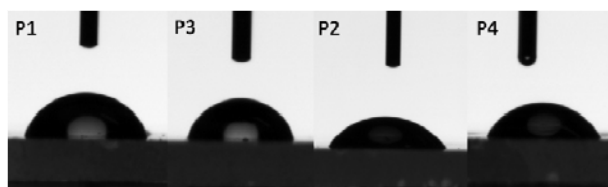


Fig. S6 The images of bead on the films of **P1**, **P3**, **P2**, and **P4**. The films on quartz glass were prepared via spin coating from DMSO solution of 1×10^{-2} mol/L.

Table S1. Energies of isotactic **P4** after MD simulation

| run | θ_1^a | θ_2^a | Total ^b | Pot ^c | Helix ^d |
|-----------|--------------|--------------|--------------------|------------------|--------------------|
| 1 | -180 | 120 | 5712 | 4471 | L |
| 2 | -150 | 180 | 6210 | 4948 | R |
| 3 | -150 | -60 | 6177 | 4924 | R |
| 4 | -150 | -90 | 5878 | 4609 | R |
| 5 | -120 | 180 | 5859 | 4581 | R |
| 6 | -120 | -150 | 5970 | 4751 | R |
| 7 | -90 | 180 | 5754 | 4440 | R |
| 8 | -90 | 150 | 5497 | 4236 | R |
| 9 | -90 | -60 | 5930 | 4647 | R |
| 10 | -90 | -90 | 5478 | 4217 | R |
| 11 | -60 | 150 | 5376 | 4136 | R |
| 12 | -60 | -90 | 5746 | 4503 | R |
| 13 | -60 | -120 | 5399 | 4145 | R |
| 14 | -60 | -150 | 6136 | 4909 | R |
| 15 | -30 | 180 | 5723 | 4462 | R |
| 16 | -30 | 120 | 6420 | 5158 | R |
| 17 | -30 | -120 | 5524 | 4244 | L |
| 18 | -30 | -150 | 5862 | 4616 | R |
| 19 | 0 | 150 | 5978 | 4712 | R |
| 20 | 0 | -120 | 5911 | 4664 | R |
| 21 | 0 | -150 | 5679 | 4394 | L |
| 22 | 30 | 180 | 5897 | 4632 | R |
| 23 | 30 | 90 | 5889 | 4622 | R |
| 24 | 30 | -150 | 5710 | 4415 | L |
| 25 | 60 | 180 | 6468 | 5193 | L |
| 26 | 60 | 150 | 5881 | 4601 | L |
| 27 | 60 | 120 | 5727 | 4466 | R |
| 28 | 60 | 90 | 5643 | 4346 | R |
| 39 | 90 | 90 | 5805 | 4525 | R |
| 30 | 90 | 60 | 5703 | 4439 | L |
| 31 | 120 | 120 | 5595 | 4316 | L |
| 32 | 120 | 90 | 6405 | 5139 | R |
| 33 | 120 | 60 | 5765 | 4465 | L |
| 34 | 120 | 30 | 5760 | 4463 | R |
| 35 | 150 | 150 | 5923 | 4656 | L |

- a. The backbone dihedral angles of the repeat unit (below);
 b. Total energy of polymer after MD;
 c. potential energy;
 d. The helical sense of mainbone.

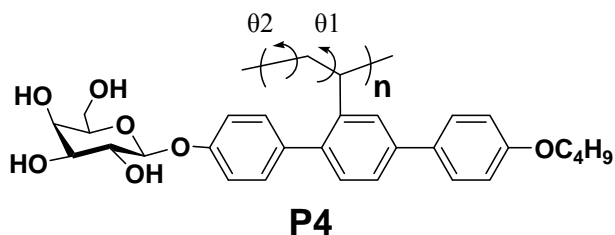


Table S2-1. Energies of syndiotactic **P4** after MD simulation

| run | $\theta 1^a$ | $\theta 2^a$ | Total ^b | Pot ^c | Helix ^d |
|-----|--------------|--------------|--------------------|------------------|--------------------|
| 1 | -30 | -60 | 5508.791 | 4258.804 | L |
| 2 | -30 | -150 | 5536.048 | 4247.372 | L |
| 3 | -60 | -30 | 5550.880 | 4280.304 | L |
| 4 | -150 | -30 | 5612.796 | 5092.909 | L |
| 5 | -90 | -90 | 5697.180 | 4454.837 | L |
| 6 | -120 | -120 | 5704.231 | 4418.150 | R |
| 7 | -60 | -120 | 5706.347 | 4433.469 | L |
| 8 | -120 | -60 | 5709.714 | 4446.631 | L |
| 9 | -120 | 30 | 5714.283 | 4434.679 | L |
| 10 | 30 | -120 | 5718.745 | 4460.241 | L |
| 11 | 0 | -120 | 5737.784 | 4487.928 | L |
| 12 | -150 | -60 | 5772.712 | 4638.187 | R |
| 13 | 120 | 120 | 5779.377 | 4540.921 | L |
| 14 | -150 | 90 | 5784.442 | 4531.671 | R |
| 15 | -150 | 30 | 5794.790 | 4542.701 | R |
| 16 | -90 | 0 | 5795.959 | 4537.936 | L |
| 17 | -60 | -150 | 5806.121 | 4557.032 | L |
| 18 | -120 | -150 | 5834.015 | 4597.402 | L |
| 19 | -120 | 0 | 5857.032 | 4622.689 | R |
| 20 | -120 | 60 | 5881.739 | 4644.552 | L |
| 21 | -150 | -120 | 5905.918 | 4616.469 | L |
| 22 | -150 | 60 | 5932.189 | 4696.529 | L |
| 23 | 60 | -150 | 5955.777 | 4698.916 | L |
| 24 | -30 | -120 | 5956.947 | 4701.954 | L |
| 25 | 90 | -150 | 5958.917 | 4720.170 | L |
| 26 | -120 | -30 | 5965.764 | 4692.570 | L |
| 27 | 60 | 180 | 5999.020 | 4733.938 | Zigzag |
| 28 | -60 | -90 | 6016.021 | 4752.473 | L |
| 29 | -150 | -90 | 6018.226 | 4750.482 | R |
| 30 | 180 | 30 | 6019.760 | 4788.994 | L |
| 31 | 120 | 0 | 6031.406 | 4781.555 | L |
| 32 | -90 | -60 | 6058.663 | 4789.074 | L |
| 33 | -90 | -150 | 6099.461 | 4838.271 | R |
| 34 | 30 | 180 | 6112.957 | 4821.527 | L |
| 35 | 120 | 150 | 6135.607 | 4877.527 | R |

- a. The backbone dihedral angles of the repeat unit;
b. Total energy of polymer after MD;
c. potential energy;
d. The helical sense of mainbone.

Table S2-2. Energies of syndiotactic **P2** after MD simulation

| run | θ_1^a | θ_2^a | Total ^b | Pot ^c | Helix ^d |
|-----|--------------|--------------|--------------------|------------------|--------------------|
| 1 | 30 | 60 | 5416.726 | 4184.187 | L |
| 2 | 60 | 30 | 5494.510 | 4219.047 | R |
| 3 | 150 | 0 | 5518.702 | 4234.141 | L |
| 4 | 120 | 120 | 5568.595 | 4331.939 | ZIGZAG |
| 5 | 60 | 60 | 5591.528 | 4327.853 | ZIGZAG |
| 6 | -120 | -120 | 5604.787 | 4367.676 | R |
| 7 | 120 | 150 | 5619.651 | 4391.923 | L |
| 8 | 150 | 120 | 5638.912 | 4355.708 | L |
| 9 | 30 | 120 | 5645.031 | 4370.554 | R |
| 10 | 180 | 0 | 5669.633 | 4409.082 | L |
| 11 | -30 | 120 | 5683.119 | 4410.359 | L |
| 12 | 60 | 90 | 5712.761 | 4466.673 | R |
| 13 | 90 | 30 | 5715.511 | 4411.062 | L |
| 14 | 90 | 150 | 5718.425 | 4493.451 | L |
| 15 | 90 | 60 | 5718.703 | 4447.738 | R |
| 16 | 150 | 30 | 5747.095 | 4482.674 | R |
| 17 | 120 | 30 | 5757.945 | 4459.487 | R |
| 18 | 30 | 150 | 5773.011 | 4445.754 | R |
| 19 | 120 | -30 | 5773.592 | 4516.564 | R |
| 20 | 30 | 90 | 5806.244 | 4537.096 | L |
| 21 | -90 | -60 | 5836.991 | 4555.769 | L |
| 22 | -60 | 120 | 5892.420 | 4611.291 | R |
| 23 | 150 | -60 | 5897.569 | 4676.674 | L |
| 24 | 120 | -60 | 5900.939 | 4662.081 | L |
| 25 | -60 | -90 | 5918.061 | 4696.107 | L |
| 26 | -60 | -120 | 5969.594 | 4718.360 | L |
| 27 | -60 | 150 | 5978.965 | 4685.844 | L |
| 28 | 150 | 90 | 5998.607 | 4741.981 | L |
| 29 | -120 | -60 | 6029.714 | 4792.891 | L |
| 30 | -120 | 180 | 6036.804 | 4760.190 | R |
| 31 | 90 | 0 | 6050.485 | 4751.142 | L |
| 32 | 180 | -120 | 6061.991 | 4805.903 | L |
| 33 | 90 | 90 | 6070.649 | 4797.285 | R |
| 34 | 180 | -30 | 6111.791 | 4862.230 | L |
| 35 | -90 | -90 | 6112.145 | 4826.030 | ZIGZAG |

a. The backbone dihedral angles of the repeat unit (below);

b. Total energy of polymer after MD;

c. potential energy;

d. The helical sense of mainbone.

Table S3-1. Energies of atactic P4 after MD simulation

| run | θ_1^a | θ_2^a | Total ^b | Pot ^c | Helix ^d |
|-----|--------------|--------------|--------------------|------------------|--------------------|
| 1 | 0 | 150 | 5665.918 | 4409.456 | R |
| 2 | 60 | 0 | 5790.218 | 4530.647 | R |
| 3 | 120 | 120 | 5832.541 | 4527.021 | L |
| 4 | 90 | 150 | 5921.565 | 4665.811 | R |
| 5 | 330 | -90 | 5927.695 | 4672.713 | L |
| 6 | 240 | -120 | 5937.87 | 4679.878 | R |
| 7 | 330 | 180 | 5949.361 | 4691.025 | R |
| 8 | 90 | 90 | 5970.817 | 5970.817 | L |
| 9 | 180 | -30 | 6039.405 | 4780.924 | R |
| 10 | 150 | 60 | 6040.714 | 4781.823 | L |
| 11 | 210 | -120 | 6056.528 | 4799.091 | R |
| 12 | 240 | -60 | 6070.694 | 4811.827 | L |
| 13 | 60 | 150 | 6086.453 | 6086.453 | R |
| 14 | 300 | 180 | 6137.42 | 4916.858 | L |
| 15 | 180 | 60 | 6438.245 | 5180.067 | R |
| 16 | 90 | 60 | 7233.043 | 5977.108 | R |
| 17 | 330 | 120 | 7625.14 | 6366.341 | R |
| 18 | 60 | 30 | 7678.1 | 6420.793 | R |
| 19 | 30 | 120 | 7737.563 | 6481.533 | R |
| 20 | 330 | 90 | 7900.367 | 6643.2 | R |
| 21 | 0 | 90 | 8179.171 | 6922.476 | R |
| 22 | 330 | -150 | 8190.858 | 6930.488 | R |
| 23 | 120 | 150 | 8334.736 | 7075.441 | L |
| 24 | 60 | 120 | 8383.651 | 7126.006 | R |
| 25 | 60 | 90 | 8687.813 | 7431.592 | R |
| 26 | 120 | 90 | 8741.075 | 7482.787 | R |
| 27 | 300 | 120 | 8760.037 | 7502.926 | R |
| 28 | 120 | -60 | 8935.176 | 7676.008 | R |
| 39 | 150 | 90 | 8990.697 | 7732.654 | R |
| 30 | 330 | 150 | 9327.399 | 8069.921 | R |
| 31 | 90 | 30 | 9328.763 | 8069.559 | R |
| 32 | 120 | 0 | 9405.766 | 8148.792 | R |
| 33 | 30 | 60 | 9478.282 | 8220.023 | R |
| 34 | 120 | 30 | 9604.621 | 8345.312 | R |
| 35 | 300 | -150 | 9695.96 | 8433.897 | R |

- The backbone dihedral angles of the repeat unit (below);
- Total energy of polymer after MD;
- potential energy;
- The helical sense of mainbone.

Table S3-2 Energies of atactic **P2** after MD simulation

| run | θ_1^a | θ_2^a | Total ^b | Pot ^c | Helix ^d |
|-----------|--------------|--------------|--------------------|------------------|--------------------|
| 1 | -150 | 180 | 5909 | 4649 | R |
| 2 | -90 | -150 | 5948 | 4690 | R |
| 3 | 30 | -150 | 5974 | 4714 | R |
| 4 | 150 | 120 | 5995 | 4738 | L |
| 5 | 90 | 30 | 6020 | 4761 | R |
| 6 | 180 | 90 | 6058 | 4799 | L |
| 7 | 60 | 60 | 6087 | 4829 | R |
| 8 | 120 | 120 | 6088 | 4831 | R |
| 9 | -30 | -150 | 6103 | 4845 | R |
| 10 | 150 | 90 | 6106 | 4849 | L |
| 11 | 150 | 150 | 6113 | 4856 | L |
| 12 | -60 | 150 | 6148 | 4888 | R |
| 13 | -150 | -90 | 6158 | 4892 | R |
| 14 | 150 | -60 | 6176 | 4918 | R |
| 15 | 150 | -90 | 6179 | 4920 | R |
| 16 | 90 | 150 | 6211 | 4954 | R |
| 17 | 180 | 180 | 6266 | 5005 | R |
| 18 | -150 | -150 | 6269 | 5010 | R |
| 19 | -120 | -150 | 6279 | 5022 | R |
| 20 | -150 | 30 | 6285 | 5026 | R |
| 21 | 60 | 90 | 6309 | 5049 | R |
| 22 | -60 | -90 | 6324 | 5067 | R |
| 23 | -150 | -30 | 6404 | 5144 | L |
| 24 | -120 | -60 | 6680 | 5418 | R |
| 25 | 90 | 60 | 6707 | 5448 | R |
| 26 | -90 | -60 | 6770 | 5508 | R |
| 27 | 30 | 120 | 6910 | 5651 | R |
| 28 | -90 | -90 | 6948 | 5719 | R |
| 39 | -90 | 180 | 7126 | 5866 | R |
| 30 | -90 | 150 | 7156 | 5890 | R |
| 31 | -120 | 150 | 7183 | 5922 | R |
| 32 | 180 | -90 | 7207 | 5948 | R |
| 33 | 120 | 30 | 7216 | 5961 | L |
| 34 | -120 | -90 | 7246 | 5988 | R |
| 35 | 180 | -30 | 7767 | 6509 | L |

- a. The backbone dihedral angles of the repeat unit (below);
b. Total energy of polymer after MD;
c. potential energy;
d. The helical sense of mainbone.

Table S4 Polymerization results and optical properties of deacetylated glycopolymers^a

| Entry | Monomer | Polymer | Solvent | Yield (%) | $[\alpha]_{365}^{20}$ (°) ^b |
|-------|----------|----------------------------|---------|-----------|--|
| 1 | 2 | P2-I_{DMSO} | DMSO | 67 | 1240 |
| 2 | 2 | P2-I_{DMF} | DMF | 87 | 1329 |
| 3 | 4 | P4-I_{DMSO} | DMSO | 72 | -1566 |
| 4 | 4 | P4-I_{DMF} | DMF | 91 | -33 |
| 5 | | P2^c | | | 1344 |
| 6 | | P4^c | | | 23 |

^a Polymerization temperature, 60 °C; Initiator, AIBN; $[M]/[I] = 200$. ^b Specific optical rotation in unit of degree was measured in a 1 dm cell at a concentration of ca. 2.0 mg/mL in DMSO at 25 °C. A mixture of 5 mg of sample and 10 mL DMSO in volumetric flask was exposed to ultrasonic sound for 30 seconds at 20 °C to make the sample to dissolve completely. And the solution was transferred to a 1 dm cell and was measured instantly. ^c Obtained from **P1** and **P3** (Table 1) via deacetylation.

The monomers **2** and **4** reveal specific optical rotations of -64° and -51°, respectively. The chiroptical properties of their polymers are collected in Table S2. Because all the glycopolymers except for **P4-I_{DMSO}** are ready to undergo stereomutation, it was difficult to estimate their original values of $[\alpha]_{365}^{25}$. To get a $[\alpha]_{365}^{25}$ value close to the original one, the optical rotations of **P2** and **P4** in solution were measured as soon as they were dissolved. It was found that **P2-I_{DMSO}**, **P2-I_{DMF}**, and **P2** showed positive optical rotation of 1240°, 1329°, and 1344°, respectively. In contrast, **P4-I_{DMSO}**, **P4-I_{DMF}**, and **P4** exhibit values of -1566°, -33°, and 23°, separately. As indicated previously, DMF and methanol are not good solvents for the deacetylated polymers, i.e. **P2** and **P4**. This nature has led to the trapped KCCs of PGPS obtained in DMF and the reservation of PTAGPS structure after deacetylation in methanol (*Macromolecules*, 2008, **41**, 5245). The KCC of PGPS (specific optical rotation) is consistent with that of PTAGPS (specific optical rotation), both KCC and TCC of which are same, and evolves into low energy TCC in DMSO at elevated temperatures. The approximately same optical rotation values of **P2s** suggested that all these polymers adopted almost same stereostructures although they were obtained with different methods and the stereomutation rate of **P2-I_{DMSO}** in DMSO would be very slow if it happened. Given the insolubility of **P4** in DMF and methanol and similarity to **P2**, it is reasonable to consider that **P4-I_{DMF}** keeps its KCC, while **P4-II** keeps that of **P3**. The less remarkable differences in optical rotations between **P4-I_{DMSO}** with **P4-I_{DMF}** and **P4-II**, compared to **PGPS**, are attributed the drastically increased mutability. This will be discussed in more detail below.