Electronic Supplementary Information for:

Monosaccharide-Functionalized Poly(phenylacetylenes): in situ Polymerization, Hybridization with Multiwalled Carbon Nanotubes, and Application in the Reinforcement of Chitosan Rods

Xiao Wang, Yuan Gao, Hui Zhao, Xiao-Qing Liu, Zhengke Wang, Anjun Qin, Qiaoling Hu, Jing Zhi Sun and Ben Zhong Tang

MoE Key Laboratory of Macromolecule Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China.

Guangdong Innovative Research Team, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China.

Department of Chemistry, Institute for Advanced Study, State Key Laboratory of Molecular NeuroScience, and Division of Biomedical Engineering, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China.

Correspondence to: Jing Zhi Sun (E-mail: sunjz@zju.edu.cn) and Ben Zhong Tang (E-mail: tangbenz@ust.hk)
**Synthetic details:**

**Protection of monosaccharide.** For pristine monosaccharides, there are five hydroxyl groups, which should be selectively protected to avoid the side reactions with 4-ethynylbenzoic acid and their poisoning effects on the successive polymerization catalyst. Here in, we use three monosaccharides, i.e., D-glucose, D-mannose and D-galactose. Acetone was chosen to selectively protect four out of the five hydroxyl groups. The synthetic routes are shown in Scheme 1.

Scheme S1. Protection the hydroxyl groups of the monosaccharides.

![Scheme S1](image)

**2,3:5,6-Di-O-isopropylidene-α-D-mannofuranose (10).** Into a 500 mL two-necked round-bottom flask was added 10 g (0.056 mol) α-D-glucose, 200 mL dried acetone and 22 g CuSO₄. With continuous stirring, 1 mL concentrated H₂SO₄ was added into the mixture dropwise. The reaction was ceased after 24 h and the resultant mixture was filtrated. 9.5 g Ca(OH)₂ powder was added into the filtrate to neutralize the acid, and a red solution was formed. Remove to the resulted CaSO₄ and unreacted Ca(OH)₂, the solid was washed with dried acetone. Combing the eluant with the filtrate and the solvent was largely removed by vacuum evaporation. The crude resultant was dissolved in 50 mL CHCl₃, and then washed with 50 mL deionized water. The water solution was extracted with 50 mL CHCl₃ for three times. Put all of the organic solution together and concentrated it. The residual was recrystallized in cyclohexane and white crystal formed. After drying, 9.03 g resultant (9) was obtained in a yield 60.2%. Characterization data: ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 5.4 (d, 1H, CH in 1-mannofuranose), 4.8 (m, 1H, CH in 4-mannofuranose), 4.6 (d, 1H, CH in 2-mannofuranose), 4.4 (m, 1H, CH₂ in 2,3:5,6-di-O-isopropylidene-α-D-mannofuranose).
in 5-mannofuranose), 4.2 (m, 1H, CH in 3-mannofuranose), 4.1 (m, 2H, CH$_2$ in 6-mannofuranose) 1.47, 1.46, 1.38, 1.33 (s, 12H, ((CH$_3$)$_2$CO$_2$)$_2$).

**1,2:5,6-Di-O-isopropylidene-D-glucofuranose (9).** Into a 500 mL two-necked round-bottom flask was added 10 g (0.056 mol) α-D-glucose and 200 mL dried acetone, the mixture was cooled with ice bath. After the temperature was below 5 °C, 8 mL concentrated H$_2$SO$_4$ was introduced into the mixture with stirring and keeping the temperature below 10 °C and then the ice bath was removed. The reaction was kept at room temperature for 8 h. 25 mL 50% NaOH aqueous solution was added into the resultant mixture to make the system neutral (pH = 7). A small amount of NaHCO$_3$ was dropped into for maintaining the mixture to be neutral. The salt precipitate was filtrated and the filtrate was concentrated by vacuum evaporation. The thick solution stood still over night and crude salt was formed. Dissolving the crude resultant in 50 mL CHCl$_3$ and washed with 50 mL deionized water twice. The water phase was collected and extracted with 50 mL CHCl$_3$ three times. Put all of the organic solution together and concentrated it. The residual was recrystallized in cyclohexane and white crystal formed. After drying, 4.37 g resultant (10) was obtained in a yield 30.0%. Characterization data: ¹H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 5.9 (d, 1H, CH in 1-glucofuranose), 4.5 (d, 1H, CH in 2-glucofuranose), 4.3 (m, 2H, CH$_2$ in 4,5-glucofuranose), 4.2, 4.0 (m, 2H, CH$_2$ in 6-glucofuranose), 4.1 (m, 1H, CH in 3-glucofuranose), 1.50, 1.45, 1.37, 1.32 (s, 12H, ((CH$_3$)$_2$CO$_2$)$_2$).

**1,2:3,4-Di-O-isopropylidene-D-galactopyranose (8).** The experiment procedure was similar to the synthesis of (7), except that D-mannose was used as starting material. The yield was 65.2% (9.5 g). Characterization data: ¹H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 5.5 (d, 1H, CH in 1-galactopyranose), 4.5 (m, 1H, CH in 2-galactopyranose), 4.3 (m, 1H, CH in 3-galactopyranose), 4.2 (d, 1H, CH$_2$ in 6-galactopyranose), 3.8 (m, CH$_2$OH), 3.7, 3.6 (m, 2H, CH$_2$OH), 1.47, 1.38, (s, 6H, (CH$_3$)$_2$CO$_2$), 1.27 (d, 6H, (CH$_3$)$_2$CO$_2$).

**Methyl 4-bromobenzoate (6).** 10 g 4-Bromobenzolic acid (7) and 200 mL dry methanol were added into a 500 mL flask. Then, 5 mL concentrated H$_2$SO$_4$ (98%) was introduced into the mixture under vigilant stirring. The reaction system was refluxing for 8 h. The solvent was removed on a rotary evaporator, and the residual was diluted with water, then using chloroform to extract the resultant three times. The chloroform solution was dried with 5 g MgSO$_4$ and the crude resultant was purified on a silicon gel chromatographic column using petroleum ether (PE)/ethyl acetate (EA) (10/1) as eluting agent. White powder resultant was obtained in a yield of 97.6% (10.4 g).
4-[(2-trimethylsilyl)ethynyl]benzoate (5). Into a 250 mL two-necked flask added compound 6 (7.2 g, 33.4 mmol) and a stirring bar and transferred into a glove box to remove the oxygen thoroughly. In the glove box, 232 mg (0.33 mmol) PdCl₂(PPh₃)₂, 125 mg (0.66 mmol) CuI and 86 mg (0.33 mmol) PPh₃ were added into the flask and then the flask was sealed and transferred out of the glove box. 100 mL Triethylamine was injected into the flask and 3.56 g (36.3 mmol) followed by the injection of trimethylsilylacetylene (TMSA) under stirring. The reaction system was heated to 60 °C and kept for 24 h. A black suspension was resulted and the solid was collected by filtration. The crude resultant was purified on a silicon gel chromatographic column using PE/EA (10/1) as eluting agent. Brown powder resultant was obtained in a yield of 67.3% (4.8 g).

4-Ethynylbenzoic acid (4). Into a 250 mL round-bottom flask, 4.5 g (20 mmol) compound 5, 4.4 g (60 mmol) KOH and 150 mL methanol were added. Refluxing the reaction system for 5 h and cooling to room temperature, then the resultant was poured into 500 mL dilute HCl aqueous solution (1M) with vigilant stirring. Brown precipitate formed and collected by filtration. The crude resultant was washed repeatedly with deionized water, and the solid was drying at 40 °C to constant weight. Brown powder was obtained in a yield of 89.0% (2.6 g).

1,2:5,6-Di-O-isopropylidene-3-O-(4-ethynylbenzonyl)-α-D-mannofuranose (1). Into a 250 mL round-bottom flask, compound 4 (0.46 g, 3.15 mmol), compound 10 (0.73 g, 2.8 mmol), DCC (1.03 g, 5 mmol). DMAP (0.073 g, 0.6 mmol) were added and then 150 mL dry dichloromethane was introduced. The mixture was stirring at room temperature for 8 h, white salt was generated, which was collected by filtration and washed with dry ether. After drying, the crude resultant was purified on a silicon gel chromatographic column using PE/EA (5/1) mixture as eluting agent. White salt was obtained in a yield of 48.3%.

Characterization data: IR (KBr), ν (cm⁻¹): 3271 (s, HC≡C), 2110 (m, C≡C), 1729 (s, C=O). ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 8.0 (m, 2H, aromatic protons o-C=O), 7.6 (m, 2H, aromatic protons m-C=O ), 6.4 (s,1H, CO₂CH₂), 4.8 (m, 2H, CH in 2,4-mannofuranose), 4.4 (m, 1H, CH₂ in 5-mannofuranose), 4.1 (m, 3H, CH in 3-mannofuranose, CH₂ in 6-mannofuranose), 3.3 (s, 1H, =CH), 1.53, 1.47, 1.39, 1.38 (s, 12H, ((C₃H₃)₂CO₂)₂). ¹³C NMR (75 MHz, CDCl₃), δ (TMS, ppm): 164.3 (CO₂), 132.31 (aromatic carbons m-C=O), 129.6 (aromatic carbons o-C=O), 129.4 (aromatic carbon attached to C=O), 127.3 (aromatic carbons p-C=O), 113.4, 109.3 (((C₃H₃)₂CO₂)₂), 101.7 (CO₂CH₂), 85.2 (CH in mannofuranose), 82.6 (PhC≡, CH in mannofuranose), 80.5 (HC≡), 79.3, 72.8, 66.8 (CH in mannofuranose), 26.9, 25.9, 25.1, 24.6 (((CH₃)₄).
2,3:5,6-Di-O-isopropylidene-1-O-(4-ethynylbenzonyl)-α-D-glucofruranose (2). The synthetic procedure is identical to monomer 1, except that compound 9 instead of 10 was used here. The product was white solid and the yield was 82.8% (0.9 g).

Characterization data: IR (KBr), ν (cm⁻¹): 3262 (s, HC≡C), 2111 (m, C≡C), 1720 (s, C=O). ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 8.0 (m, 2H, aromatic protons o-C=O), 7.5 (m, 2H, aromatic protons m-C=O), 5.9 (d, 1H, CH in 1-glucofuranose), 5.5, (d, 1H, CO₂CH₂), 4.6 (d, 1H, CH in 2-glucofuranose), 4.3 (m, 2H, CH in 4,5-glucofuranose), 4.1 (m, 2H,CH₂ in 6-glucofuranose), 3.2 (s, 1H, =CH), 1.56, 1.41, 1.32, 1.27 [s, 12H,(CH₃)₂CO₂]. ¹³C NMR (75MHz, CDCl₃), δ (TMS, ppm): 164.5 (CO₂), 132.3 (aromatic carbons m-C=O), 129.6 (aromatic carbons o-C=O), 127.4 (aromatic carbons p-C=O), 112.4, 109.5 (((CH₃)₂CO₂)₂), 105.1 (CH in 1-glucofuranose), 83.4 (CH in glucofuranose), 82.6 (PhC≡), 80.6 (HC≡), 80.0, 76.9, 72.5, 67.3 (CH in glucofuranose), 26.8, 26.7, 26.2, 25.2 (((CH₃)₄).

1,2:3,4-Di-O-isopropylidene-6-O-(4-ethynylbenzonyl)-D-galactopyranose (3). The synthetic procedure is identical to monomer 1, except that compound 8 instead of 10 was used here. The product was white solid and the yield was 49.2%.

Characterization data: IR (KBr), ν (cm⁻¹): 3271 (s, HC≡C), 2110 (m, C≡C), 1721 (s, C=O). ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.9 (m, 2H, aromatic protons o-C=O), 7.5 (m, 2H, aromatic protons m-C=O), 5.5 (d, 1H, CH in 1-galactopyranose), 4.6 (m, 1H, CH in 3-galactopyranose), 4.4 (m, 2H, CO₂CH₂), 4.3 (m, 2H, CH in 2,4-galactopyranose), 4.1 (m, CH in 5-galactopyranose), 3.2 (s, 1H, =CH), 1.43,1.39, 1.27, 1.17 [s, 12H,((CH₃)₂CO₂)]. ¹³C NMR (75 MHz, CDCl₃), δ (TMS, ppm): 164.5 (CO₂), 131.0 (aromatic carbons m-C=O), 129.0 (aromatic carbon attached to C=O), 128.5 (aromatic carbons o-C=O), 125.8 (aromatic carbons p-C=O), 108.6, 107.7 (((CH₃)₂CO₂)₂), 95.2 (CH in 1-galactopyranose), 81.8 (PhC≡), 79.5 (HC≡), 70.1 (CH in 2-galactopyranose), 69.7 (CH in 3-galactopyranose), 65.1 (CO₂CH₂), 63.1 (CH in 5-galactopyranose), 24.9, 23.9, 23.4 (((CH₃)₄).
Fig. S1. FTIR spectra of (A) M1 and (B) P1 (sample from Table 1, no. 2).

Fig. S2. $^1$H NMR spectra of D-mannose-containing phenylacetylene 1 (A) and P1 (B) in chloroform-$d$. At elevated temperature, on one hand, the polymer chains are thermodynamically activated and the exchange between left-hand and right-hand stereo-isomers is speed up. Thus the CD signals decline. On the other hand, at elevated temperature, the *cis-trans* isomerization of the polyene backbone takes place.
Fig. S3. $^{13}$C NMR spectra of monomer 1 (A) and polymer P1 (B, sample from Table 1, no. 2) in chloroform-$d$.

Fig. S4. The circular dichromic spectra of P1 at temperature of 0, 20, 40, 60, 80 °C. Polymer concentration: 0.1 mM; Solvent: DMF.
Fig. S5. TGA thermograms of P1 (A) and P1/MWCNTs hybrid (B) measured under N$_2$ atmosphere at a heating rate of 10°C/min.