Electronic Supplementary Information for:

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

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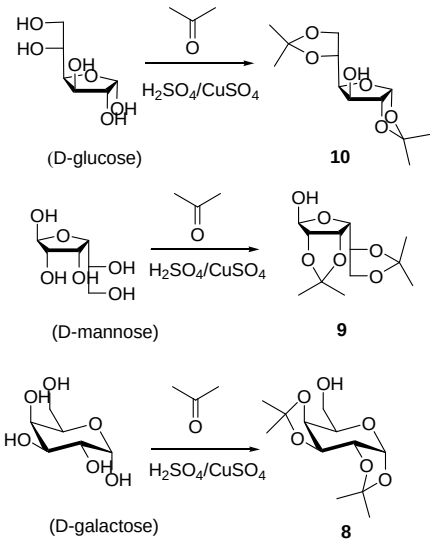
Synthetic details:

Protection of monosaccharide. For pristine monosaccharides, there are five hydroxyl groups, which should be selectively protected to avoid the side reactions with 4-ethynylbenzonic 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.



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 $CuSO_4$. With continuous stirring, 1 mL concentrated H_2SO_4 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 $CaSO_4$ 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 $CHCl_3$, and then washed with 50 mL deionized water. The water solution was extracted with 50 mL $CHCl_3$ 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: ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 5.4 (d, 1H, C*H* in 1-mannofuranose), 4.8 (m, 1H, C*H* in 4-mannofuranose), 4.6 (d, 1H, CH in 2-mannofuranose), 4.4 (m, 1H, CH_2

in 5-mannofuranose), 4.2 (m, 1H, C*H* 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 ^{o}C, 8 mL concentrated H_2SO_4 was introduced into the mixture with stirring and keeping the temperature below 10 ^{o}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: ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 5.9 (d, 1H, C*H* in 1-glucofuranose), 4.5 (d, 1H, C*H* in 2-glucofuranose), 4.3 (m, 2H, C*H* in 4,5-glucofuranose), 4.2, 4.0 (m, 2H, CH_2 in 6-glucofuranose), 4.1 (m, 1H, C*H* 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: ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 5.5 (d, 1H, C*H* in 1-galactopyranose), 4.5 (m, 1H, C*H* in 3-galactopyranose), 4.3 (m, 1H, C*H* in 4-galactopyranose), 4.2 (d, 1H, C*H* in 2-galactopyranose), 3.8 (m, C*H* in 5-galactopyranose), 3.7, 3.6 (m, 2H, CH_2OH), 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_2SO_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) $PdCl_2(PPh_3)_2$, 125 mg (0.66 mmol) CuI and 86 mg (0.33 mmol) PPh_3 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 ^oC 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 ^oC 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, $CDCl_3$), 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, CO_2CH), 4.8 (m, 2H, C*H* in 2,4-mannofuranose), 4.4 (m, 1H, CH_2 in 5-mannofuranose), 4.1 (m, 3H, C*H* in 3-mannofuranose, CH_2 in 6-mannofuranose), 3.3 (s, 1H, ≡CH), 1.53, 1.47, 1.39, 1.38 (s, 12H, $((CH_3)_2CO_2)_2$). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 164.3 (CO_2), 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 ($(((CH_3)_2CO_2)_2$), 101.7 (CO_2CH), 85.2 (*C*H in mannofuranose), 82.6 (Ph*C*≡, *C*H in mannofuranose), 80.5 (H*C*≡), 79.3, 72.8, 66.8 (*C*H in mannofuranose), 26.9, 25.9, 25.1, 24.6 ($(CH_3)_4$).

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). ^{1}H NMR (300 MHz, $CDCl_3$), 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, C*H* in 1-glucofuranose), 5.5, (d, 1H, CO_2CH), 4.6 (d, 1H, C*H* in 2-glucofuranose), 4.3 (m, 2H, C*H* in 4,5-glucofuranose), 4.1 (m, 2H,CH_2 in 6-glucofuranose), 3.2 (s, 1H, ≡CH), 1.56, 1.41, 1.32, 1.27 [s, 12H,$((CH_3)_2CO_2)_2$]. ^{13}C NMR (75MHz, $CDCl_3$), δ (TMS, ppm): 164.5 (CO_2), 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 ($((CH_3)_2CO_2)_2$), 105.1 (*C*H in 1-glucofuranose), 83.4 (*C*H in glucofuranose), 82.6 (Ph*C*≡), 80.6 (H*C*≡), 80.0, 76.9, 72.5, 67.3 (*C*H in glucofuranose), 26.8, 26.7, 26.2, 25.2 ($(CH_3)_4$).

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). ^{1}H NMR (300 MHz, $CDCl_3$), 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, C*H* in 1-galactopyranose), 4.6 (m, 1H, C*H* in 3-galactopyranose), 4.4 (m, 2H, CO_2CH_2), 4.3 (m, 2H, C*H* in 2,4-galactopyranose), 4.1 (m, C*H* in 5-galactopyranose), 3.2 (s, 1H, ≡CH), 1.43,1.39, 1.27, 1.17 (s, 12H, $((CH_3)_2CO_2)_2$). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 164.5 (CO_2), 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 ($((CH_3)_2CO_2)_2$), 95.2 (*C*H in 1-galactopyranose), 81.8 (Ph*C*≡), 79.5 (H*C*≡), 70.1 (*C*H in 2-galactopyranose), 69.7 (*C*H in 3-galactopyranose), 65.1 (CO_2CH_2), 63.1 (*C*H in 5-galactopyranose), 24.9, 23.9, 23.4 ($(CH_3)_4$).

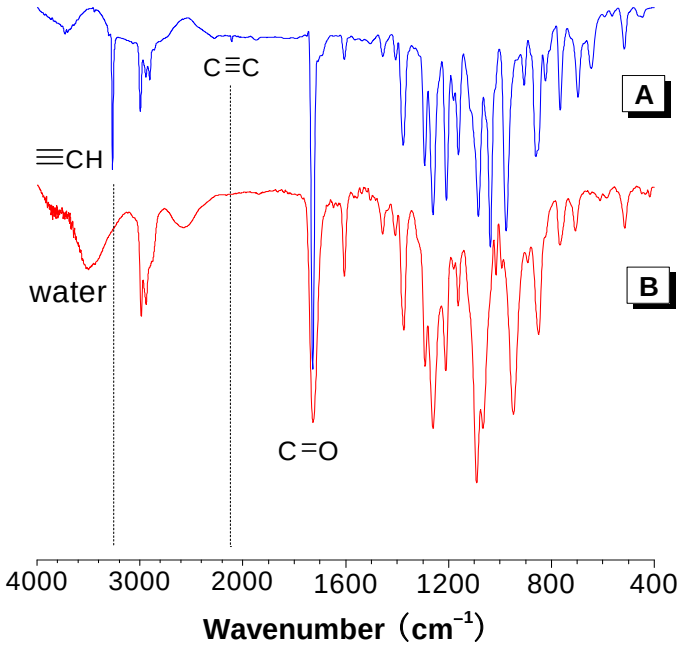


Fig. S1. FTIR spectra of (A) M**1** and (B) P**1** (sample from Table 1, no. 2).

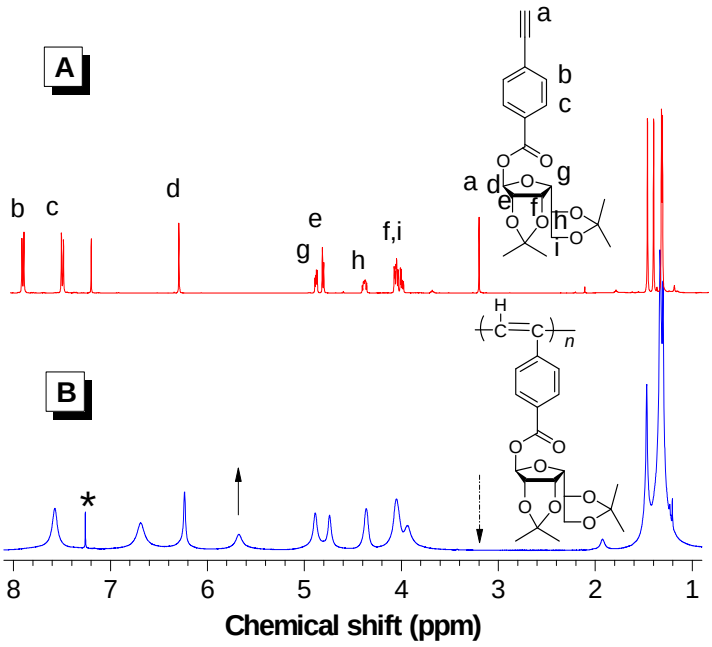


Fig. S2. [1]H NMR spectra of D-mannose-containing phenylacetylene **1** (A) and P**1** (B) in chloroform-*d*. At elevated temperature, on one hand, the polymer chains are thermodynamically activated and the exchange between left-hand and right-hand stereo-isomers is speed up. Thus the CD signals decline. On the other hand, at elevated temperature, the *cis-trans* isomerization of the polyene backbone takes place.

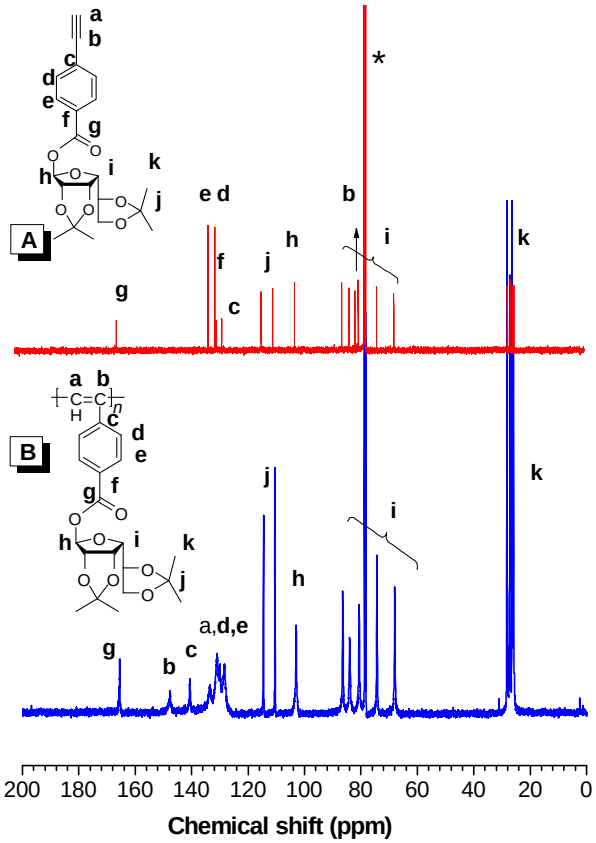


Fig. S3. ^{13}C NMR spectra of monomer **1** (A) and polymer P**1** (B, sample from Table 1, no. 2) in chloroform-*d*.

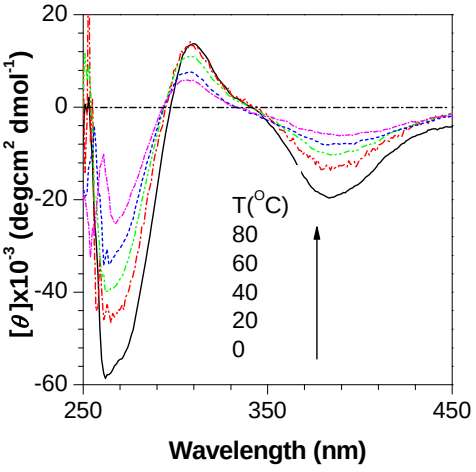


Fig. S4. The circular dichromic spectra of P**1** at temperature of 0, 20, 40, 60, 80 °C. Polymer concentration: 0.1 mM; Solvent: DMF.

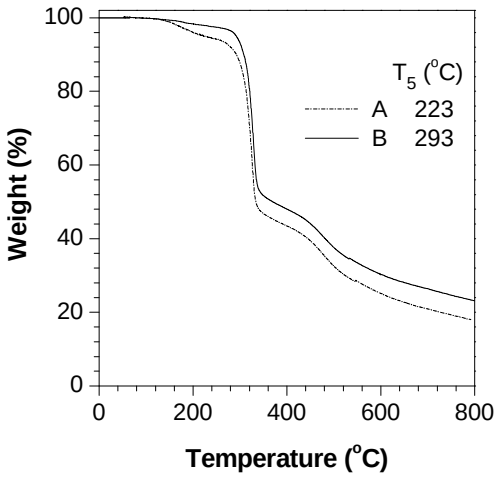


Fig. S5. TGA thermograms of P**1** (A) and P**1**/MWCNTs hybrid (B) measured under N_2 atmosphere at a heating rate of 10°C/min.