Decorating Conjugated Polymer Chains with Naturally Occurring Molecules: Synthesis, Solvatochromism, Chain Helicity, and Biological Activity of Sugar-Containing Poly(phenylacetylene)s

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Experimental Section

Materials. Dioxane, toluene and THF were purchased from Aldrich, dried over 4 Å molecular sieves, and distilled in an atmosphere of dry nitrogen from sodium benzophenone ketyl immediately prior to use. Dichloromethane (DCM, from Lab-Scan) and acetone (from RdH) were distilled under nitrogen over calcium hydride. Triethylamine and pyridine (both from RdH) were distilled under normal pressure and dried over KOH. 2,3:4,6-Di-*O*-isopropylidene-2-keto-L-gulonic acid monohydrate (**14**), D-glucose, D-galactose, D-mannose, bis(triphenylphosphine)palladium(II) chloride, copper(I) chloride, 4-iodoaniline, 4-bromobenzyl alcohol, (trimethylsilyl)acetylene, 1,3-dicyclohexylcarbodiimde (DCC), 4-dimethylaminopyridine (DMAP), trifluoroacetic acid, tungsten(VI) chloride, tetraphenyltin (all from Aldrich), molybdenum(V) chloride (Acros), copper sulfate, potassium hydroxide, dimethylforamide (DMF), dimethylsulfoxide (DMSO) and methanol (all from RdH) were used as received without further

purification. 4-Ethynylbenzoyl chloride (**9**) was prepared by the reaction of 4-ethynylbenzoic acid with thionyl chloride.[1] The organorhodium complexes of $[Rh(nbd)Cl]_2$, $Rh(nbd)(tos)(H_2O)$, $[Rh(cod)Cl]_2$, $Rh(cod)(NH_3)Cl$, and $Rh(cod)(tos)(H_2O)$ were prepared according to previously published procedures.[2]

Instrumentation. IR spectra were recorded on a Perkin Elmer 16 PC FT-IR spectrometer. ^1H and ^{13}C NMR spectra were measured on a Bruker ARX 300 NMR spectrometer or a JEOL 400 NMR spectrometer using chloroform-*d* or alkalified deuterium oxide (KOH) as solvents. Tetramethylsilane (TMS), chloroform-*d*, or D_2O was used as internal references for NMR analysis. UV-vis spectra were recorded on a Milton Roy Spectronic 3000 Array spectrophotometer and molar absorptivities (ε) of the polymers were calculated on the basis of their repeating units. MALDI-TOF spectra were recorded on a GCT Premier CAB048 mass spectrometer operating in a chemical ionization (CI) mode with methane as carrier gas. Elemental analysis was performed on an Eager 300 microelemental analyzer.

Molecular weights (M_w and M_n) and polydispersities (M_w/M_n) of the polymers were estimated by gel permeation chromatography (GPC) using a Waters Associates liquid chromatograph equipped with a Waters 510 HPLC pump, a Rheodyne 7725i injector with a stand kit, a set of Styragel columns (HT3, HT4, and HT6; molecular weight range: 10^2–10^7), a column temperature controller, a Waters 486 wavelength-tunable UV detector, a Waters 410 differential refractometer, and a system DMM/scanner with an 8-channel scanner option. All the polymer solutions were prepared in THF (~2 mg/mL) and filtered through 0.45 μm PTFE syringe-type filters before being injected into the GPC system. THF was used as eluent at a flow rate of 1.0 mL/min. The column temperature was maintained at 40 °C, and the working wavelength of the UV detector was set at 254 nm. A set of monodisperse polystyrene standards (Waters) was used for calibration purposes.

Thermogravimetric analysis (TGA) was performed on a Perkin Elmer TGA 7 under nitrogen at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) thermograms were recorded on a Setaram DSC 92 under nitrogen at a scanning rate of 10 °C/min. Specific optical rotations ($[\alpha]^{23}_D$) were measured on a Perkin Elmer 241 polarimeter at room temperature (~23 °C) using a beam of plane-polarized light of the D line of a sodium lamp (589.3 nm) as the monochromatic light source. Circular

dichroism (CD) measurements were done with a Jasco J-720 spectropolarimeter using 1 mm quartz curette at room temperature. The spectra were recorded with a step resolution of 0.2 nm, a scan speed of 50 nm/min, a sensitivity of 100 millidegrees and a response time of 0.5 s. Each spectrum was the average of 5−10 scans. Concentrations of the solutions of the polymers were calculated based on their monomer repeating units.

Monomer Synthesis. The sugar-containing phenylacetylene derivatives were prepared according to synthetic routes given in Schemes 1 and 2. The hydroxyl groups of the sugars were protected following the literature procedures with some modifications.[3] Detailed synthetic procedures are given below.

*Preparation of 1,2:5,6-Di-O-isopropylidene-D-glucofuranose (**6**).* Into a 2 L, round bottom flask was added 50 g (0.28 mol) of anhydrous α-D-glucose in 1 L of acetone. The mixture was stirred vigorously in an ice-water bath. Concentrated sulfuric acid (40 mL) was then added at 5 mL portions in 10−15 min at 5−10 °C. After all the acid was added, the temperature was risen gradually to room temperature. After further stirring for 8 h, the solution was cooled again and neutralized by 50% aqueous sodium hydroxide solution. A small amount of sodium hydrogen carbonate was added to maintain the pH of the solution at near 7. After standing overnight, the solution was filtered, and the solvent was removed under reduced pressure. The solid was redissolved in 100 mL of chloroform and the solution was washed with 100 mL of deionized water. The aqueous phase was then extracted three times with 100 mL of chloroform. The organic layers were combined and concentrated under reduced pressure. Recrystallization from cyclohexane gave 37 g of white crystals (50.8% yield). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 5.9 [d, 1H, Glucofuranose (Glu)–H at 1 position], 4.5 (d, 1H, Glu–H at 2 position), 4.3 (m, 2H, Glu–H at 4 and 5 positions), 4.2, 4.0 (m, 2H, Glu–H at 6 position), 4.1 (m, 1H, Glu–H at 3 position), 1.50, 1.45, 1.37, 1.32 {s, 12H, $[(CH_3)_2CO_2]_2$}.

*Preparation of 2,3:5,6-Di-O-isopropylidene-α-D-mannofuranose (**7**).* In a 2 L, round-bottom flask were placed 45 g (0.25 mol) of finely powdered anhydrous D-mannose, 100 g (0.63 mol) of anhydrous copper sulfate, and 5 mL of concentrated sulfuric acid in 1 L of anhydrous acetone. The mixture was vigorously stirred for 24 h. The copper sulfate was removed by filtration and washed with anhydrous

acetone. The filtrate was neutralized by calcium hydroxide. The unreacted calcium hydroxide and calcium sulfate were filtered and washed with dry acetone. The filtrate was concentrated by solvent distillation at normal pressure. The syrup was dissolved in 100 mL of chloroform, and the resultant solution was washed with 100 mL of deionized water. The aqueous phase was then extracted three times with 100 mL of chloroform. The organic layers were combined and concentrated under reduced pressure. Recrystallization from cyclohexane gave 53 g of white crystals (81.5% yield). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 5.4 [d, 1H, Mannofuranose (Man)–H at 1 position), 4.8 (m, 1H, Man–H at 4 position), 4.6 (d, 1H, Man–H at 2 position), 4.4 (m, 1H, Man–H at 5 position), 4.2 (m, 1H, Man–H at 3 position), 4.1 (m, 2H, Man–H at 6 position) 1.47, 1.46, 1.38, 1.33 {s, 12H, $[(CH_3)_2CO_2]_2$}.

*Preparation of 1,2:3,4-Di-O-isopropylidene-D-galactopyranose (**8**).* It was synthesized by protection of D-galactose, using experimental procedures similar to those for the preparation of **7** described above with some modifications. In the latter part of the procedures, the chloroform solution of the syrup was washed three times with 100 mL of deionized water. The combined aqueous phases were then extracted with 100 mL of chloroform. The organic layers were concentrated under reduced pressure to give colorless syrup product in 77.0% yield. ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 5.5 [d, 1H, Galactopyranose (Gal)–H at 1 position], 4.5 (m, 1H, Gal–H at 3 position), 4.3 (m, 1H, Gal–H at 4 position), 4.2 (d, 1H, Gal–H at 2 position), 3.8 (m, 1H, Gal–H at 5 position), 3.7, 3.6 (m, 2H, CH_2OH), 1.47, 1.38, [s, 6H, $(CH_3)_2CO_2$], 1.27 [d, 6H, $(CH_3)_2CO_2$].

*Synthesis of 1,2:5,6-Di-O-isopropylidene-3-O-(4-ethynylbenzoyl)-α-D-glucofuranose (**1**).* Into a 100 mL, round-bottom flask were added 1.6 g (6.2 mmol) of **6** and 2 mL of pyridine in 10 mL of DCM under nitrogen. The flask was cooled and a solution of **9** (1.00 g, 6.1 mmol) in 10 mL of DCM was then injected. The resultant mixture was warmed to room temperature and stirred overnight. The solution was diluted with 100 mL of DCM and washed two times with dilute hydrochloric acid and one time with water. The organic layer was dried over 5 g of magnesium sulfate. After filtration and solvent evaporation, the crude product was purified by silica-gel column chromatography using a chloroform/ acetone mixture (20:1 by volume) as eluent. A white solid was isolated in 67.5% yield (1.6 g). IR

(KBr), ν (cm^{-1}): 3273 (≡C–H stretching), 2111 (C≡C stretching), 1712 (C=O stretching). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.0 [m, 2H, aromatic protons ortho (*o*) to C=O], 7.5 [m, 2H, aromatic protons meta (*m*) to C=O], 5.9 (d, 1H, Glu–H at 1 position), 5.5 (d, 1H, CO_2CH), 4.6 (d, 1H, Glu–H at 2 position), 4.3 (m, 2H, Glu–H at 4 and 5 positions), 4.1 (m, 2H, Glu–H at 6 position), 3.2 (s, 1H, ≡CH), 1.56, 1.41, 1.32, 1.27 {s, 12H, $[(CH_3)_2CO_2]_2$}. ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 164.5 (CO_2), 132.3 (aromatic carbons *m* to C=O), 129.6 (aromatic carbons *o* to C=O), 129.5 (aromatic carbon attached to C=O), 127.4 [aromatic carbon para (*p*) to C=O], 112.4, 109.5 {$[(CH_3)_2CO_2]_2$}, 105.1 (Glu–C at 1 posiiton), 83.4, 82.6 (Ph*C*≡), 80.6 (HC≡), 80.0, 76.9. 72.5, 67.3, 26.8, 26.7, 26.2, 25.2 [$(CH_3)_4$]. HRMS (MALDI-TOF): *m*/*z* 389.1602 [$(M + H)^+$, calcd 389.1556].

Monomers **2** and **3** were prepared by similar experimental procedures. Their characterization data are given below.

*2,3:5,6-Di-O-isopropylidene-1-O-(4-ethynylbenzoyl)-α-D-mannofuranose (**2**).* White solid; yield 72.3%. IR (KBr), ν (cm^{-1}): 3265 (≡C–H strectching), 2107 (C≡C strectching), 1729 (C=O stretching). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.0 (m, 2H, aromatic protons *o* to C=O), 7.6 (m, 2H, aromatic protons *m* to C=O), 6.4 (s, 1H, CO_2CH), 4.9 (m, 2H, Man–H at 2 and 4 positions), 4.4 (m, 1H, Man–H at 5 position), 4.1 (m, 3H, Man–H at 3 and 6 positions), 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 ($CDCl_3$, ppm): 164.3 (CO_2), 132.1 (aromatic carbons *m* to C=O), 129.6 (aromatic carbons *o* to C=O), 129.4 (aromatic carbon attached to C=O), 127.3 (aromatic carbon *p* to C=O), 113.4, 109.3 {$[(CH_3)_2CO_2]_2$}, 101.7 (CO_2CH), 85.2, 82.6 (Ph*C*≡ and Man–C), 80.5 (HC≡), 79.3, 72.8, 66.8, 26.9, 25.9, 25.1, 24.6 [$(CH_3)_4$]. HRMS (MALDI-TOF): *m*/*z* 373.1288 [$(M - CH_3)^+$, calcd 373.1288]. Anal. Calcd for $C_{21}H_{24}O_7$: C, 64.94; H, 6.23; O, 28.83. Found: C, 64.54; H, 6.21.

*1,2:3,4-Di-O-isopropylidene-6-O-(4-ethynylbenzoyl)-D-galactopyranose (**3**).* Pale yellow syrup; yield 78.3%. IR (KBr), ν (cm^{-1}): 3273 (≡C–H stretching), 2111 (C≡C stretching), 1712 (C=O stretching). ^{1}H

NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.9 (m, 2H, aromatic protons *o* to C=O), 7.5 (m, 2H, aromatic protons *m* to C=O), 5.5 (d, 1H, Gal–H at 1 position), 4.6 (m, 1H, Gal–H at 3 position), 4.4 (m, 2H, CO_2CH_2), 4.3 (m, 2H, Gal–H at 2 and 4 posiitons), 4.1 (m, 1H, Gal–H at 5 position), 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 ($CDCl_3$, ppm): 164.5 (CO_2), 131.0 (aromatic carbons *m* to C=O), 129.0 (aromatic carbon attached to C=O), 128.5 (aromatic carbons *o* to C=O), 125.8 (aromatic carbon *p* to C=O), 108.6, 107.7 {$[(CH_3)_2\mathit{C}O_2]_2$}, 95.2 (Gal–C at 1 position), 81.8 (Ph*C*≡), 79.5 (HC≡), 70.1 (Gal–C at 2 position), 69.7 (Gal–C at 4 position), 69.4 (Gal–C at 3 position), 65.1 ($CO_2\mathit{C}H_2$), 63.1 (Gal–C at 5 position), 24.9, 23.9, 23.4 [$(CH_3)_4$]. HRMS (MALDI-TOF): *m*/*z* 389.1609 [$(M + H)^+$, calcd 389.1556]. Anal. Calcd for $C_{21}H_{24}O_7$: C, 64.94; H, 6.23; O, 28.83. Found: C, 62.81; H, 6.27.

*Preparation of 4-(Trimethylsilylethynyl)benzyl alcohol (**10**).* To a 100 mL, round-bottom flask were added 140 mg (0.2 mmol) of $PdCl_2(PPh_3)_2$, 10 mg (0.05 mmol) of CuI, and 40 mL of a triethylamine solution of 4-bromobenzyl alcohol (1.87 g, 10 mmol) under nitrogen. After all the catalysts were dissolved, 1.7 mL (12 mmol) of (trimethylsilyl)acetylene was injected into the flask and the mixture was stirred at 40 °C for 24 h. The solids were removed by filtration and washed with triethylamine. The filtrate was evaporated to dryness by a rotary evaporator. The residue in the flask was redissolved in 100 mL of chloroform, washed with 50 mL of 1 M HCl, and then 50 mL of deionized water. The crude product was purified on a silica-gel column using a chloroform/acetone mixture (20:1 by volume) as eluent. Yield 88.1%. IR (KBr), ν (cm^{-1}): 2156 (C≡C stretching). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.5 (m, 2H, aromatic protons *m* to CH_2), 7.3 (m, 2H, aromatic protons *o* to CH_2), 4.7 (d, 2H, CH_2OH), 0.2 [s, 9H, $(CH_3)_3$Si].

*Preparation of 4-(Trimethylsilylethynyl)aniline (**11**).* It was synthesized by coupling reaction of 4-iodoaniline with (trimethysilyl)acetylene, using similar experimental procedures as described above. The reaction mixture was stirred at room temperature for 8 h instead of at 40 °C for 24 h. A pale yellow solid was obtained in 93.5% yield. ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.3 (m, 2H, aromatic

protons *m* to NH_2), 6.6 (m, 2H, aromatic protons *o* to NH_2), 3.8 (s, 2H, NH_2), 0.2 [s, 9H, $(CH_3)_3Si$]. ^{13}C NMR (75 MHz, $CDCl_3$), δ ($CDCl_3$, ppm): 146.8 (aromatic carbon attached to NH_2), 133.3 (aromatic carbons *m* to NH_2), 114.5 (aromatic carbons *o* to NH_2), 112.4 (aromatic carbon *p* to NH_2), 106.0 (Ph*C*≡), 91.3 [$Si(CH_3)_3C$≡], 0.1 [$(CH_3)_3Si$].

*Preparation of 4-Ethynylbenzyl Alcohol (**12**).* Into a 100 mL, round-bottom flask was placed 1.02 g (5.0 mmol) of **10** in 10 mL of 5% (w/v) methanol solution of KOH. After stirring at room temperature for 30 min, the mixture was poured into 100 mL of 1 M HCl. The aqueous phase was extracted two times with 100 mL of chloroform. The organic layer was dried over 5 g of magnesium sulfate. After solvent evaporation, the crude product was purified on a silica-gel column using a chloroform/acetone mixture (15:1 by volume) as eluent. A pale yellow liquid was obtained in 83.2% yield. ^1H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.5 (m, 2H, aromatic protons *m* to CH_2), 7.3 (m, 2H, aromatic protons *o* to CH_2), 4.7 (d, 2H, CH_2OH), 3.1 (s, 1H, ≡CH).

*Preparation of 4-Ethynylaniline (**13**).* It was synthesized by desilylation of **11** in a methanol solution of KOH. The procedures were similar to those described above. A pale yellow solid was obtained in 85.0% yield. IR (KBr), ν (cm^{-1}): 2120 (C≡C stretching). ^1H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.3 (m, 2H, aromatic protons *m* to NH_2), 6.6 (m, 2H, aromatic protons *o* to NH_2), 3.8 (s, 2H, NH_2), 3.0 (s, 1H, ≡CH).

*Synthesis of 4-(2,3:4,6-Di-O-isopropylidene-2-keto-L-gulonoyloxymethyl)phenylacetylene or 4-(2,3:4,6-Di-O-isopropylidene-α-L-xylo-2-hexulofuranosonoyloxymethyl)phenylacetylene (**4**).* Into a 250mL, round bottom flask were dissolved 0.87 g (6.6 mmol) of **12**, 2.00 g (6.8 mmol) of 2,3:4,6-di-*O*-isopropylidene-2-keto-L-gulonic acid monohydrate (**14**), and 36 mg (0.27 mmol) of DMAP in 100 mL of dry DCM. The solution was cooled to ca. 0 °C, into which 1.65 g (8.0 mmol) of DCC in 50 mL of DCM was added with stirring via a dropping funnel with a pressure-equalization arm. The reaction mixture was stirred overnight. After filtering out the formed urea solid, the solution was concentrated by a rotary evaporator. The crude product was purified by silica-gel column chromatography using a

chloroform/acetone mixture (10/1 by volume) as eluent. A pale yellow syrup was obtained in 68.3 % yield (1.75 g). IR (KBr), ν (cm^{-1}): 3270 (≡C–H stretching), 2110 (C≡C stretching), 1710 (C=O stretching). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.5 (m, 2H, aromatic protons *m* to CH_2), 7.3 (m, 2H, aromatic protons *o* to CH_2), 5.3 (s, 2H, CO_2CH_2), 4.8 (s, 1H, sugar–H at 3 position), 4.3 (m, 1H, sugar–H at 4 position), 4.2 (d, 1H, sugar–H at 4 position), 4.1 (d, 2H, sugar–H at 6 position), 3.1 (s, 1H, ≡CH), 1.52, 1.41, 1.38, 1.26 {s, 12H, $[(CH_3)_2CO_2]_2$}. ^{13}C NMR (75 MHz, $CDCl_3$), δ ($CDCl_3$, ppm): 166.3 (CO_2), 136.0 (aromatic carbon attached to CH_2), 132.0 (aromatic carbons *m* to CH_2), 127.4 (aromatic carbons *o* to CH_2), 121.7 (aromatic carbon *p* to CH_2), 113.8 (sugar carbon at 2 position), 110.1, 97.3 {$[(CH_3)_2CO_2]_2$}, 87.3 (sugar carbon at 3 position), 83.1 (Ph*C*≡), 77.5 (≡CH), 73.8, 72.5, 66.4 (Ph*C*H_2), 59.6, 28.5, 26.7, 25.2, 18.6 [$(CH_3)_4$]. HRMS (MALDI-TOF): *m*/*z* 389.1605 [$(M + H)^+$, calcd 389.1556]. Anal. Calcd for $C_{21}H_{24}O_7$: C, 64.94; H, 6.23; O, 28.83. Found: C, 61.74; H, 7.44.

*Preparation of [4-(2,3:4,6-Di-O-isopropylidene-2-keto-L-gulonoylamino)phenylethynyl]trimethylsilane or [4-(2,3:4,6-Di-O-isopropylidene-α-L-xylo-2-hexulofuranosonoylamino)phenylethynyl]trimethylsilane (**15**).* It was synthesized from **11**, using experimental procedures similar to those for the preparation of **4**. The product was purified on a silica gel column using a chloroform/acetone mixture (20:1 by volume) as eluent. A white solid was obtained in 82.3% yield. ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 9.0 (s, 1H, NH), 7.6 (m, 2H, aromatic protons *o* to NH), 7.4 (m, 2H, aromatic protons *m* to NH), 4.6 (s, 1H, sugar–H at 3 position), 4.3 (m, 1H, sugar–H at 5 position), 4.2 (d, 1H, sugar–H at 4 position), 4.1 (d, 2H, sugar–H at 6 position), 1.55, 1.53, 1.38, 1.17 {s, 12H, $[(CH_3)_2CO_2]_2$}, 0.2 [s, 9H, $(CH_3)_3Si$].

*Synthesis of 4-(2,3:4,6-Di-O-isopropylidene-2-keto-L-gulonoylamino)phenylacetylene or 4-(2,3:4,6-Di-O-isopropylidene-α-L-xylo-2-hexulofuranosonoylamino)phenylacetylene (**5**).* It was synthesized by base-catalyzed hydrolysis of **15**. The procedures were similar to those for the preparation of **12**. A pale yellow solid was obtained in 85.7% yield. IR (KBr), ν (cm^{-1}): 3269 (≡C–H stretching), 2112 (C≡C stretching), 1711 (C=O stretching). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 9.1 (s, 1H, NH), 7.6

(m, 2H, aromatic protons *o* to NH), 7.5 (m, 2H, aromatic protons *m* to NH), 4.6 (s, 1H, sugar–H at 3 position), 4.4 (m, 1H, sugar–H at 5 position), 4.3 (d, 1H, sugar–H at 4 position), 4.2 (d, 2H, sugar–H at 6 position), 3.0 (s, 1H, ≡CH), 1.60, 1.58, 1.45, 1.23 {s, 12H, $[(CH_3)_2CO_2]_2$}. ^{13}C NMR (75 MHz, $CDCl_3$), δ ($CDCl_3$, ppm): 165.4 (CONH), 137.7 (aromatic carbon attached to NH), 132.9 (aromatic carbons *m* to NH), 119.1 (aromatic carbons *o* to NH), 117.9 (aromatic carbon *p* to NH), 115.1 (sugar carbon at 2 position), 110.6, 97.7 {$[(CH_3)_2\mathit{C}O_2]_2$}, 88.2 (sugar carbon at 3 position), 83.3 (Ph*C*≡), 76.8 (≡CH), 74.0, 72.1, 60.2, 29.0, 27.0, 25.5, 18.5 $[(CH_3)_4]$.

Polymerization. All the polymerization reactions and manipulations were carried out under nitrogen using either an inert-atmosphere glove box (Vacuum Atmospheres) or Schlenk techniques in vacuum-line systems except for the polymer purification, which was done in a fume hood in open atmosphere. Typical experimental procedures for the polymerization of **1** catalyzed by $[Rh(nbd)Cl]_2$ in THF/Et_3N are given below as an example.

*Poly[1,2:5,6-di-O-isopropylidene-3-O-(4-ethynylbenzoyl)-α-D-glucofuranose] (P**1**).* Into a 20 mL Schlenk tube with a side arm was added 78 mg (0.2 mmol) of **1**. The tube was evacuated under vacuum and then flushed with dry nitrogen three times through the side arm. THF (1 mL) was injected into the tube to dissolve the monomer. The catalyst solution was prepared in another tube by dissolving 4.6 mg (0.01 mmol) of $[Rh(nbd)Cl]_2$ in 1 mL of THF with 1 drop of triethylamine, which was then transferred to the monomer solution using a hypodermic syringe. The reaction mixture was stirred at room temperature under nitrogen for 24 h. The mixture was then diluted with 2 mL of THF and added dropwise to methanol (150 mL) under stirring. The precipitate was filtered and dried in a vacuum oven at room temperature to a constant weight. Yellowish fibrous polymer was obtained in 93.0% yield. M_w 604 000; M_w/M_n 8.9 (GPC; Table 1, no. 2). IR (KBr), ν (cm^{-1}): 1728 (C=O stretching). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.6 (aromatic protons *o* to C=O), 6.7 (aromatic protons *m* to C=O), 5.9 (Glu–H at 1 position), 5.6 (*Z* olefin proton), 5.4 (CO_2CH), 4.5 (Glu–H at 2 position), 4.3 (Glu–H at 4 and 5 positions), 4.0 (Glu–H at 6 position), 1.5, 1.4, 1.2 {$[(CH_3)_2CO_2]_2$}. ^{13}C NMR (75 MHz, $CDCl_3$),

δ ($CDCl_3$, ppm): 164.2 (CO_2), 146.3 (=*C*–Ph), 139.3 (aromatic carbon *p* to C=O), 132.1 (aromatic carbon attached to C=O), 129.3 (aromatic carbons *o* to C=O), 128.5 (HC=), 126.9 (aromatic carbons *m* to C=O), 112.3, 109.3 {[$(CH_3)_2CO_2]_2$}, 105.0, 83.3, 79.7, 76.8, 72.4, 67.0, 26.7, 26.1, 25.3. UV (chloroform; 1.55×10^{-4} mol/L), λ_{max} (nm)/ε_{max} (mol^{-1} L cm^{-1}): 275/1.45×10^4, 440/6.21×10^3.

*Poly[2,3:5,6-di-O-isopropylidene-1-O-(4-ethynylbenzoyl)-α-D-mannofuranose] (P**2**).* Yellowish fiber; yield 99.4%. M_w 776 000; M_w/M_n 5.8 (GPC; Table 2, no. 2). IR (KBr), ν (cm^{-1}): 1730 (C=O stretching). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.6 (aromatic protons *o* to C=O), 6.7 (aromatic protons *m* to C=O), 6.3 (CO_2CH), 5.7 (*Z* olefin proton), 4.9 (Man–H at 4 position), 4.8 (Man–H at 2 position), 4.4 (Man–H at 5 position), 4.0 (Man–H at 3 and 6 positions), 1.6, 1.5, 1.4, 1.3 {[$(CH_3)_2CO_2]_2$}. ^{13}C NMR (100 MHz, $CDCl_3$), δ ($CDCl_3$, ppm): 163.9 (CO_2), 146.1 (=*C*–Ph), 139.2 (aromatic carbon *p* to C=O), 132.0 (aromatic carbon attached to C=O), 129.5 (aromatic carbons *o* to C=O), 128.4 (HC=), 127.0 (aromatic carbons *m* to C=O), 113.1, 109.0 {[$(CH_3)_2CO_2]_2$}, 101.5 (CO_2CH), 85.0, 82.5, 79.2, 72.9, 66.6, 26.9, 26.0, 25.2, 24.6 [$(CH_3)_4$]. UV (chloroform; 1.00×10^{-4} mol/L), λ_{max} (nm)/ε_{max} (mol^{-1} L cm^{-1}): 278/9.18×10^3, 428/3.76×10^3.

*Poly[1,2:3,4-di-O-isopropylidene-6-O-(4-ethynylbenzoyl)-D-galactopyranose] (P**3**).* Yellowish fiber; yield 93.5%. M_w 803 000; M_w/M_n 5.9 (GPC; Table 3, no. 2). IR (KBr), ν (cm^{-1}): 1724 (C=O stretching). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.6 (aromatic protons *o* to C=O), 6.7 (aromatic protons *m* to C=O), 5.7 (*Z* olefin proton), 5.5 (Gal–H at 1 position), 4.6 (Gal–H at 3 position), 4.3 (CO_2CH_2 and Gal–H at 2 and 4 positions), 4.1 (Gal–H at 5 position), 1.44, 1.33, 1.27 {[$(CH_3)_2CO_2]_2$}. ^{13}C NMR (75 MHz, $CDCl_3$), δ ($CDCl_3$, ppm): 165.5 (CO_2), 146.1 (=*C*–Ph), 139.7 (aromatic carbon *p* to C=O), 132.1 (aromatic carbon attached to C=O), 129.3 (aromatic carbons *o* to C=O), 128.8 (HC=), 127.0 (aromatic carbons *m* to C=O), 109.5, 108.6 {[$(CH_3)_2CO_2]_2$}, 96.1, 71.1, 70.7, 70.5, 66.1 (CO_2CH_2), 63.9, 25.9, 24.9, 24.5. UV (chloroform; 7.72×10^{-5} mol/L), λ_{max} (nm)/ε_{max} (mol^{-1} L cm^{-1}): 278/8.92×10^3, 435/4.19 $\times 10^3$.

*Poly[4-(2,3:4,6-di-O-isopropylidene-2-keto-L-gulonoyloxymethyl)phenylacetylene] (P**4**).* Yellowish fiber; yield 75.4%. M_w 161 000; M_w/M_n 6.6 (GPC; Table 4, no. 2). IR (KBr), ν (cm^{-1}): (C=O stretching). ^1H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.0 (aromatic protons *m* to CH_2), 6.6 (aromatic protons *o* to CH_2), 5.7 (*Z* olefin proton), 5.0 (CO_2CH_2), 4.7 (sugar–H at 3 position), 4.2 (sugar–H at 5 position), 4.1 (sugar–H at 4 position), 4.0 (sugar–H at 6 position), 1.43, 1.33, 1.27, 1.21 {[(CH_3)$_2CO_2$]$_2$}. ^{13}C NMR (100 MHz, $CDCl_3$), δ ($CDCl_3$, ppm): 166.4 (CO_2), 142.3 (=*C*–Ph), 138.8 (aromatic carbon attached to CH_2), 134.2 (aromatic carbon *p* to CH_2), 131.4 (aromatic carbons *o* to CH_2), 127.2 (HC= and aromatic carbons *m* to CH_2), 113.7, 110.2, 97.4 {[(CH_3)$_2C$$O_2$]$_2$}, 87.4, 73.6, 72.7, 66.8 (Ph*C*H_2), 59.8, 28.8, 26.4, 25.7, 18.7 [(CH_3)$_4$]. UV (chloroform; 1.16×10^{-4} mol/L), λ_{max} (nm)/ε_{max} (mol^{-1} L cm^{-1}): 263/7.31×10^3, 413/3.62×10^3.

*Poly[4-(2,3:4,6-di-O-isopropylidene-2-keto-L-gulonoylamino)phenylacetylene] (P**5**).* Yellowish fiber; yield 70.7%. M_w 32 700; M_w/M_n 3.1 (GPC; Table 5, no. 2). IR (KBr), ν (cm^{-1}): (C=O stretching). ^1H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.7 (NH), 7.3 (aromatic protons *o* to NH), 6.5 (aromatic protons *m* to NH), 5.8 (*Z* olefin proton), 4.7 (sugar–H at 3 position), 4.3 (sugar–H at 4 and 5 positions), 4.2 (sugar–H at 6 position), 1.5, 1.3 {[(CH_3)$_2CO_2$]$_2$}. ^{13}C NMR (75 MHz, $CDCl_3$), δ ($CDCl_3$, ppm): 164.4 (CONH), 140.1 (=*C*–Ph), 136.1 (aromatic carbon attached to NH), 127.1 (HC= and aromatic carbons *m* and *p* to NH), 119.5 (aromatic carbons *o* to NH), 114.2, 110.6, 97.4 {[(CH_3)$_2C$$O_2$]$_2$}, 88.2, 73.8, 72.4, 59.8, 28.7, 27.1, 25.8, 18.5 [(CH_3)$_4$]. UV (chloroform; 1.04×10^{-4} mol/L), λ_{max} (nm)/ε_{max} (mol^{-1} L cm^{-1}): 290/1.07×10^4, 403/3.15×10^3.

Ketal Hydrolysis. The hydroxyl groups of the sugar pendants of P**1** and P**3**–P**5** could be deprotected in aqueous trifluoroacetic solution with minor side reactions.[4] A typical procedure for the hydrolysis is given below: 0.2 g (~0.5 mM) of a polymer was dissolved in 2 mL of THF (for P**5**, a small amount of DCM was added because it is not completely soluble in THF). The solutions were cooled to ~0 °C, into which, 8 mL of a CF_3CO_2H/H_2O mixture (7:1 by volume) was dropped slowly under stirring. The resultant mixture was stirred at room temperature and quenched at different time intervals by pouring

them into 500 mL of deionized water. The solid was collected by filtration and dried under vacuum for 2 days. Degree of hydrolysis (DH) of the polymer was calculated from its ^{1}H NMR spectral data according to the following equation:

$$\text{DH (\%)} = [1 - (A_{Me}/12)/(A_{Ar+Vi}/5)] \times 100\% \quad (1)$$

where A_{Me} is the integral of the resonance of the protons of methyl group and A_{Ar+Vi} is the integral of the resonance of the aromatic and vinyl protons.

Cell Culture. A THF solution of P**3** with a concentration of 1 mg/mL was prepared, which was further diluted 1000 times by the culture medium. The biological effect of P**3** on the living cells was studied using HeLa cells. The cells were cultured in Dulbecco's modified Eagle's medium (DMEM; Gibco) supplemented with 10% fetal bovine serum (Gibco), 1% penicillin/streptomycin/amphotericin (PSA) antibiotic mixture (Gibco), 1% L-glutamine (Gibco) at 37 °C in a 5% CO_2 atmosphere. The cells were harvested at 80–90% confluency and were subcultured onto 24-well plates at a concentration of ~10^4 cells/well. Different amounts of P**3** were added to the 24-well plates 5 h after the cells were seeded. The well without adding polymer solution was served as control. After incubation for three days, the cells were stained with trypan blue and counted with a hemocytometer (HBG, Germany).

Statistic significance was determined by the analysis of variance using *t*-test. All data were reported as mean ± standard deviation. The mean values of each group were compared with the control. $P \leq 0.05$ was considered statistically significant; $p \leq 0.01$ was considered outstanding.

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