

Supporting Information

Self-Assembly of a Novel Alternant Amphiphilic Poly(OPE-alt-TEO) Copolymer: From Nanowires to Twist Fibrillar Architectures with Molecular Dimensions

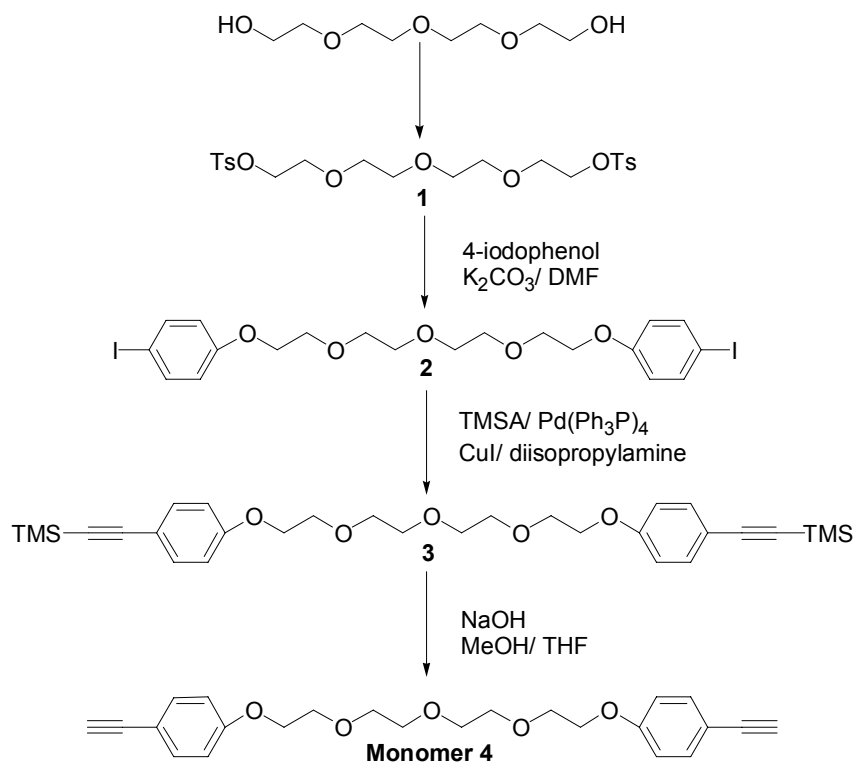
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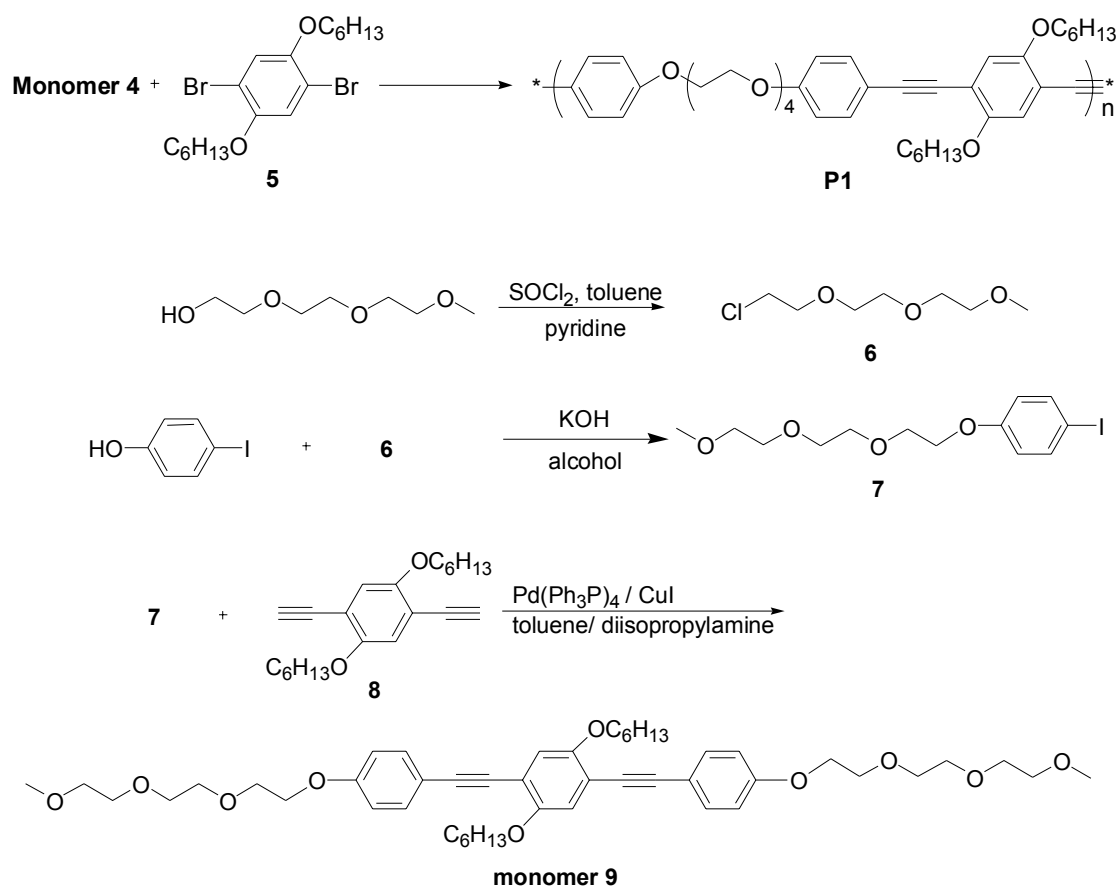
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SCHEME 1S. Synthetic route of P1 and model compound.





Experimental Part

Materials

1,4-Dibromo-2,5-bis-hexyloxy-benzene (**5**), and 1,4-diethynyl-2,5-bis-hexyloxy-benzene (**8**) was synthesized according to the literature procedures.¹ The solvents were dried using standard procedures. All other reagents were used as received from commercial sources.

Characterization

¹H and ¹³C NMR spectra were collected on a Varian Mercury plus 400 spectrometer with chemical shifts being referenced against TMS as the internal standard. Gel permeation chromatography (GPC) analysis was conducted with a Shimadzu LC-VP system using polystyrenes as the standard and

tetrahydrofuran (THF) as the eluent at a flow rate of 0.8 mL/min and 40°C. UV-vis absorption spectra were recorded with a Shimadzu UV-2450 VU-vis-NIR spectrophotometer. Photoluminescence spectra were performed with a Shimadzu RF-5301PC fluorescence spectrometer. Fluorescence micrographs were obtained by means of a fluorescence microscope (Olympus BX-51) with an attached Olympus digital camera. AFM experiments were performed under ambient conditions and room temperature on a Nanoscope IIIa microscope (Digital Instruments, Santa Barbara, CA) operating in a tapping-mode.

Tetra(ethylene oxide)-di(p-toluenesulfonate) (1)

(42 g, 0.22 mol) of toluenesulfonyl chloride was added dropwise to a THF solution of (19.4 g, 0.1 mol) of Tetra (ethylene glycol) monoethyl ether and (20.2 g, 0.2 mol) of triethylamine at 0°C. After stirring for 12 h, the reaction mixture was filtered and the filtrate was evaporated and the residue was then extracted with CH₂Cl₂/10%HCl and the organic layer was concentrated under reduced pressure. The crude extract was purified by silica gel column chromatography using hexane/ethyl acetate (1:1) as eluent to give the desired product as a viscous oil (47.2 g, yield 94%). ¹H NMR (CDCl₃, ppm): δ7.80 (d, 4H), 7.35 (d, 4H), 4.15 (t, 4H), 3.67 (t, 4H), 3.53 (s, 8H), 2.45 (s, 6H).

Tetra(ethylene oxide)-di(4-iodobenzene)-ether (2) ²

4-iodophenol (4.38 g, 19.9 mmol) was added to a solution of K₂CO₃ (4.12 g, 29.85 mmol) in DMF (50 mL) and stirred at 60 °C for 15 min under N₂. To the resulting yellow solution was added **1** (5 g, 9.95 mmol). The mixture was stirred at 60 °C for 48h. Upon addition of 500 mL of water, the phases were separated and the aqueous phase was extracted with chloroform. The combined organic phases were extracted with small amounts of diluted NaOH solution and washed several times with brine. After drying over Na₂SO₄, the solvent was evaporated. The crude extract was purified by silica gel column chromatography using hexane/ethyl acetate (1:1) as eluent to give the desired product as white powder (5.65 g, yield 95%). ¹H NMR (CDCl₃, ppm): δ7.52 (d, 4H), 6.67 (d, 4H), 4.06 (t, 4H), 3.82 (t, 4H), 3.68

(m, 8H). ^{13}C NMR (100 MHz, CDCl_3): δ 67.76 (- CH_2 -), 69.84 (- CH_2 -), 70.89 (- CH_2 -), 71.07 (- CH_2 -), 83.19 (aromatic), 117.27 (aromatic), 138.40 (aromatic), 158.90 (aromatic).

Tetra(ethylene oxide)-di[4-((trimethylsilyl)ethynyl)benzene]-ether (3)³

To a mixture of **2** (1 g, 1.67 mmol), tetra(triphenylphosphine)palladium(0) (77 mg, 0.067 mmol), and copper (I) iodide (13 mg, 0.067 mmol) in diisopropylamine (15 ml) was added (trimethylsilyl)acetylene (0.5 g, 5.0 mmol) under a nitrogen atmosphere. The reaction was stirred overnight under nitrogen at 70°C. Then the residue was treated with water and extracted with chloroform. After the extract was dried over anhydrous Na_2SO_4 , the solvent was evaporated. The residue was purified by column chromatography on silica gel with ethyl acetate/hexane (8:2) to give **3** as a pale yellow syrup. Yield: 0.67 g (74%). ^1H NMR (CDCl_3 , ppm): δ 7.39 (d, 4H), 6.82 (d, 4H), 4.07 (t, 4H), 3.84 (t, 4H), 3.73 (m, 8H), 0.24 (s, 18H). ^{13}C NMR (100 MHz, CDCl_3): δ 0.01 (- SiCH_3), 67.60 (- CH_2 -), 69.76 (- CH_2 -), 70.80 (- CH_2 -), 71.03 (- CH_2 -), 92.37 (-Ar-C \equiv C-), 105.08 (-Ar-C \equiv C-) 114.34 (aromatic), 115.28 (aromatic), 133.33 (aromatic), 158.85 (aromatic).

Tetra(ethylene oxide)-di(4-diynylbenzene)-ether (4)

To a solution of **3** (1 g, 1.86 mmol) in methanol (25 mL) and tetrahydrofuran (25 mL) was added NaOH (0.2 g, 5 mmol). After stirring at room temperature for 3.5 h, the reaction mixture was filtered, and the solvent was removed under vacuum. The residue was treated with water and extracted with chloroform, and the extracts were dried over anhydrous Na_2SO_4 . After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel with ethyl acetate/hexane (8:2) to give **4** as a pale yellow solid. Yield: 0.66 g (90%). ^1H NMR (CDCl_3 , ppm): δ 7.39 (d, 4H), 6.85 (d, 4H), 4.11 (t, 4H), 3.84 (t, 4H), 3.70 (m, 8H), 2.99 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 67.69 (- CH_2 -), 69.84 (- CH_2 -), 70.10 (- CH_2 -), 71.08 (- CH_2 -), 76.03 (-Ar-C \equiv C-), 83.84 (-Ar-C \equiv C-), 114.20 (aromatic), 114.80 (aromatic), 133.77 (aromatic), 159.37 (aromatic).

General Procedure for the Preparation of poly [1,4-Bis(phenylethynyl)-2,5-bis(hexyloxy)benzene-alt-tetra(ethylene oxide)] (P1)

1,4-Bibromo-2,5-bis(hexyloxy)benzene (**5**) (0.131 g, 0.30 mmol), monomer **4** (0.118 g, 0.30 mmol) were polymerized for **P1** by using the Sonogashira cross coupling reaction in the presence of 5% (PPh₃)₄Pd and 5% CuI in the 24 ml solution of diisopropylamine/THF(1:3) at 60 °C for 1 days. The polymer was precipitated in hexane twice, filtered, and dried under vacuum at room temperature. Gel permeation chromatography analysis (mobile phase: THF, polystyrene standards) indicates that M_n of the polymer is 16800, and its polydispersity is 2.9. ¹H NMR (CDCl₃, ppm): δ 7.45 (br, 4H), 7.07-6.85 (m, 6H), 4.13-3.69 (m, 20H), 1.82 (br, 4H), 1.52-1.34 (m, 12H), 0.90 (br, 6H).

1-Chloro-2-[2-(2-methoxy-ethoxy)-ethoxy]-ethane (6)

To a solution of compound 2-[2-(2-methoxy-ethoxy)-ethoxy]-ethanol (8.87 g, 54.0 mmol) in dry toluene (100 mL) containing a few drops of pyridine was slowly added thionyl chloride (15.9 mL, 218 mmol) at 0 °C. The mixture was stirred at 0 °C for 1 h and then at room temperature for 2 h. The excess of thionyl chloride and toluene was removed under reduced pressure. The yellow oil obtained was used without further purification.

1-Iodo-4-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-benzene (7)

4-Iodo-phenol (2 g, 9.1 mmol), KOH (1.27 g, 22.75 mmol) were mixed in 15 mL alcohol, and the reaction mixture was heated at 50°C under a nitrogen atmosphere for 0.5h. Monomer **6** (1.66 g, 9.1 mmol) was dissolved in alcohol (5 mL) and added to the mixture, and heating was continued at 60°C for 10h. The solution was diluted with water and extracted with chloroform. The extracted organic layer was washed with water two times and concentrated in a vacuum. The white residue was purified by column chromatography on silica gel with ethyl acetate/hexane (1:1) to give **7** as a white liquid. Yield:

2.6 g (80%). ^1H NMR (CDCl_3 , ppm): δ 7.45-7.42 (d, 2H), δ 6.60-6.58 (d, 2H), 4.00-3.97 (t, 2H), 3.75-3.72 (t, 2H), 3.88-3.85 (t, 2H), 3.75-3.73 (t, 2H), 3.69-3.64 (m, 4H), 3.56-3.54 (t, 2H), 3.27 (s, 3H).

1,4-Bis-hexyloxy-2,5-bis-(4-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-phenylethynyl)-benzene (9, model compound)

To a mixture of **8** (0.5 g, 1.53 mmol), tetra(triphenylphosphine)palladium(0) (34.6 mg, 0.03 mmol), and copper (I) iodide (6 mg, 0.03 mmol) in diisopropylamine (15 ml) was added **7** (1.68 g, 4.59 mmol) under a nitrogen atmosphere. The reaction was stirred overnight under nitrogen at 70°C. Then the residue was treated with water and extracted with chloroform. After the extract was dried over anhydrous Na_2SO_4 , the solvent was evaporated. The residue was purified by column chromatography on silica gel with ethyl acetate/hexane (1:1) to give **9** as a pale yellow powder. Yield: 0.91 g (74%). ^1H NMR (CDCl_3 , ppm): δ 7.45-7.43 (d, 4H), 6.98 (s, 2H), 6.89-6.87 (d, 4H), 4.16-4.13 (t, 4H), 4.03-3.98 (t, 4H), 3.88-3.85 (t, 4H), 3.75-3.73 (t, 4H), 3.69-3.64 (m, 8H), 3.56-3.54 (t, 4H), 3.376 (s, 6H), 1.87-1.80 (m, 4H), 1.55-1.51 (m, 4H), 1.36-1.34 (m, 8H), 0.90-0.87 (t, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 14.30 (- CH_3), 22.88 (- CH_2 -), 25.97 (- CH_2 -), 29.55 (- CH_2 -), 31.85 (- CH_2 -), 59.29 (-O- CH_3), 67.66 (- CH_2 -O-), 69.82(- CH_2 -O-), 69.88 (- CH_2 -O-), 70.82 (- CH_2 -O-), 70.90 (- CH_2 -O-), 71.08 (- CH_2 -O-), 72.15 (- CH_2 -O-), 84.97 (- $\text{C}\equiv\text{C}$ -), 94.97 (- $\text{C}\equiv\text{C}$ -), 114.12, (aromatic), 114.81, (aromatic), 117.00 (aromatic), 128.20 (aromatic), 133.20 (aromatic), 153.68 (aromatic), 159.04 (aromatic).

References.

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