Versatile Post-Polymerization Functionalization of Poly(p-Phenylene Vinylene) Copolymers Containing Carboxylic Acid Substituents:

Development of a Universal Method towards Functional Conjugated Copolymers

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Electronic Supplementary Information (ESI)

[6-(4-methoxy-phenoxy)-hexanoic acid ethyl ester 1]

A mixture of 4-methoxyphenol (46.36 g, 373.5 mmol), NaOBU (43.07 g, 448.2 mmol) and EtOIH (375 mL) was stirred for 1 h at room temperature under N2 atmosphere, after which ethyl 6-bromohexanoate (32.1 g, 448.2 mmol) and NaI (1.5 g, 10 mmol) were added. The resulting solution was stirred for 4 h at reflux temperature and then overnight at 50 °C under N2 atmosphere. The reaction was quenched with water (400 mL), and extracted with CH2Cl2 (3 x 200 mL). The combined organic extracts were dried over anhydrous MgSO4. Evaporation of the solvent under reduced pressure gave the crude product.

Substituents:

Phenylene Vinylene) Copolymers

Bisulfonium salt was filtered off and washed with cold diethyl ether. The precipitate was vacuum-dried over phosphorus pentoxide. 1H-NMR (CDCl3): δ = 6.89+6.88+6.84+6.82 (4s, 2H), 4.61+4.60 (2s, 2H), 3.94 (m, 2H), 3.83+3.81 (2s, 3H), 3.69+3.68 (2s, 2H), 3.65 (s, 3H), 2.44 (t, 2H), 2.33 (t, 2H), 1.79 (m, 2H), 1.71 (m, 2H), 1.52 (m, 2H), 1.23-1.30 (m, 12H), 0.85 (t, 3H). Because of the instability of 4, the oxidation of the sulfanyl-group towards 5 was done without further purification.

[6-(4-methoxy-phenoxy)-hexanoic acid methyl ester and 6-(2-chloromethyl-4-methoxy-5-octylsulfanyl)methylphenoxy)-hexanoic acid methyl ester 4]

A mixture of n-octane thiol (1.346 g, 9.2 mmol) and NaOBU (0.884 g, 9.2 mmol) in MeOH (50 mL) was stirred for 30 min at room temperature after which a clear solution was obtained. This solution was added drop wise to a solution of 3 (5 g, 9.2 mmol) in MeOH (150 mL) under N2 atmosphere. The reaction mixture was stirred for 2 h after which it was concentrated under reduced pressure at 40 °C. Subsequently, n-octane (125 mL) was added and evaporated again to remove the tetrahydrothiophene. This sequence was repeated three times. After removal of the solvents under reduced pressure, the residue was redissolved in CH2Cl2 (125 mL) and the organic layer was extracted with water (3 x 150 mL). The organic layer was dried over anhydrous MgSO4. Evaporation of the solvent under reduced pressure gave the crude product.

6-(5-chloromethyl-4-octylsulfanyl)methylphenoxy)-hexanoic acid methyl ester and 6-(2-chloromethyl-4-methoxy-5-octylsulfanyl)methylphenoxy)-hexanoic acid methyl ester 5

An aqueous (35 wt%) solution of H2O2 (1.55 g, 16 mmol) was added drop wise to a mixture of 4 (3.68 g, 8 mmol) and TeO2 (0.0768 g, 0.5 mmol) in dioxane (75 mL). To this solution, 3 droplets of concentrated HCl were added. As soon as all 4 was consumed (TLC, CH2Cl2/MeOH 19/1), 200 mL of a saturated Na2S2O3-solution was added to quench the reaction. The reaction mixture was extracted with CHCl3 (3 x 100 mL) after which the combined organic extracts were dried over anhydrous MgSO4. Evaporation of the solvent under reduced pressure gave the crude product. The pure product was obtained by column chromatography (SiO2, eluent CH2Cl2/MeOH 95/5) and afterwards mixed-solvent crystallizations from MeOH and hexane, as a colorless oil (78.6 g, 79 % yield). 1H-NMR (CDCl3): δ = 6.60 (s, 4H), 4.10 (q, 2H), 3.88 (t, 2H), 3.74 (s, 3H), 2.30 (t, 2H), 1.75 (m, 2H), 1.67 (m, 2H), 1.47 (m, 2H), 1.23 (t, 3H).

6-(2,5-bis-chloromethyl-4-methoxy-phenoxy)-hexanoic acid 2

A solution of 1 (20 g, 75.6 mmol) and p-formaldehyde (6.2 g, 207 mmol) at 0 °C under N2 atmosphere, concentrated HCl (48.03 g, 487.5 mmol) was added drop wise. Subsequently, acetic anhydride (76.56 mmol) and NaI (1.5 g, 10 mmol) were added. The resulting solution was stirred for 4 h at reflux temperature and then overnight at 50 °C under N2 atmosphere. The reaction was quenched with water (400 mL), and extracted with CH2Cl2 (3 x 200 mL). The combined organic extracts were dried over anhydrous MgSO4. Evaporation of the solvent under reduced pressure gave the crude product.

6-(2,5-bis-chloromethyl-4-methoxy-phenoxy)-hexanoic acid methyl ester 3

To a stirred mixture of 1 (20 g, 75.6 mmol) and p-formaldehyde (6.2 g, 207 mmol) at 0 °C under N2 atmosphere, concentrated HCl (48.03 g, 487.5 mmol) was added drop wise. Subsequently, acetic anhydride (76.56 mmol) and NaI (1.5 g, 10 mmol) were added. The resulting solution was stirred for 4 h at reflux temperature and then overnight at 50 °C under N2 atmosphere. The reaction was quenched with water (400 mL), and extracted with CH2Cl2 (3 x 200 mL). The combined organic extracts were dried over anhydrous MgSO4. Evaporation of the solvent under reduced pressure gave the crude product.

6-(2,5-bis-chloromethyl-4-methoxy-phenoxy)hexanoic acid methyl ester 3

To a solution of 2 (22.24 g, 69.9 mmol) in MeOH (220 mL) tetrahydrothiophene (23.598 g, 267.6 mmol) was added. The mixture was allowed to react for 24 h at 50 °C, after which the total volume was reduced to 100 mL by evaporation at room temperature. Subsequently the product was precipitated in cold diethyl ether (1 L) after which the bissulfonium salt was filtered off and washed with cold diethyl ether. The resulting pure product was a white solid (22.24 g, 65 % yield). 1H-NMR (D2O): δ = 7.12+7.11 (2s, 2H), 4.44+4.43 (2s, 4H), 4.03 (t, 2H), 3.80 (s, 3H), 3.57 (s, 3H), 3.40 (m, 8H), 2.32 (t, 2H), 2.24 (m, 8H), 1.75 (m, 2H), 1.59 (m, 2H), 1.42 (m, 2H).

6-(5-chloromethyl-4-octylsulfanyl)methylphenoxy)-hexanoic acid methyl ester and 6-(2-chloromethyl-4-methoxy-5-octylsulfanyl)methylphenoxy)-hexanoic acid methyl ester 4

A mixture of n-octane thiol (1.346 g, 9.2 mmol) and NaOBU (0.884 g, 9.2 mmol) in MeOH (50 mL) was stirred for 30 min at room temperature after which a clear solution was obtained. This solution was added drop wise to a solution of 3 (5 g, 9.2 mmol) in MeOH (150 mL) under N2 atmosphere. The reaction mixture was stirred for 2 h after which it was concentrated under reduced pressure at 40 °C. Subsequently, n-octane (125 mL) was added and evaporated again to remove the tetrahydrothiophene. This sequence was repeated three times. After removal of the solvents under reduced pressure, the residue was redissolved in CH2Cl2 (125 mL) and the organic layer was extracted with water (3 x 150 mL). The organic layer was dried over anhydrous MgSO4. Evaporation of the solvent under reduced pressure gave the crude product.
product was obtained by column chromatography (SiO₂, eluent CH₂Cl₂) as a yellow oil (0.455 g, 78 % yield). 1H-NMR (CDCl₃): δ = 6.80 (s, 4H), 5.90 (m, 1H), 5.29 (dd, 1H), 5.21 (dd, 1H), 4.55 (dt, 2H), 3.88 (t, 2H), 3.74 (s, 3H), 2.35 (2H, 1.64-1.80 (m, 4H), 1.49 (m, 2H); 13C-NMR (CDCl₃; δ = 173.1, 153.5, 152.9, 132.1, 118.0, 115.2, 114.4, 68.1, 64.8, 55.5, 33.9, 28.1, 25.5, 24.5; Mass (GC-MS, EI): 278 [M⁺1]ₕ, [M⁺1]⁻; C₁₀H₁₆; 124 [M⁺1]⁻ - CO₂H₄; 109 [M⁺1]⁻ - CO₂H₄ - CH₂; FT-IR (NaCl, cm⁻¹): 2994, 2948, 2868, 2834, 1738 (νC=O, νC=O); 1648 (νC≡N, νC=O, νC=O), 1591, 1510, 1466, 1442, 1383, 1232, 1162, 1073, 909, 932, 825.

4-5-chloromethyl benzylic alcohol 15

4-chloromethyl benzylic alcohol (2 g, 11.76 mmol) was dissolved in dry THF (40 mL) under N₂ atmosphere, and cooled down to 0 °C. In BF₃·THF (19.52 mL, 19.52 mmol) was added drop wise under N₂ atmosphere. The reaction was allowed to proceed for 1 h at room temperature. Water was added to quench the reaction at 0 °C and the reaction mixture was extracted with diethyl ether (3 x 150 mL). The combined organic extracts were dried over anhydrous MgSO₄. Evaporation of the solvent under reduced pressure gave the crude product. The pure product was obtained by column chromatography (SiO₂, eluent EtOAc) as a white solid (0.69 g, 83 % yield). 1H-NMR (CDCl₃; δ = 7.36 (dd, 4H), 6.79 (s, 4H), 5.10 (s, 2H), 4.56 (s, 2H), 3.87 (t, 2H), 3.74 (s, 2H), 2.37 (t, 2H), 1.65-1.78 (m, 4H), 1.48 (m, 2H); 13C-NMR (CDCl₃; δ = 170.3, 150.5, 149.9, 134.3, 133.2, 125.6, 114.2, 111.4, 65.0, 62.4, 27.8, 25.9, 22.5, 21.5; Mass (GC-MS, EI): 376 [M⁺1]⁺, 121 [M⁺1]⁻ - Cl, 107 [M⁺1]⁻ - Cl - CH₂ - CH₂; FT-IR (NaCl, cm⁻¹): 3217, 1444, 1421, 1269, 1105, 1026, 844, 834.

6-(4-methoxy-phenoxy)-hexanoic acid 4-chloromethyl-benzyl ester 16

16 was prepared following the DCC/DMAP-method described for 10 using 15 (0.80 g, 52.55 mmol) as the alcohol-functionalized molecule. The pure product was obtained by column chromatography (SiO₂, eluent CH₂Cl₂) as a yellow-white solid (0.564 g, 67 % yield). 1H-NMR (CDCl₃; δ = 7.34 (dd, 4H), 6.79 (s, 4H), 5.10 (s, 2H), 4.56 (s, 2H), 3.87 (t, 2H), 3.74 (s, 2H), 2.37 (t, 2H), 1.65-1.78 (m, 4H), 1.48 (m, 2H); 13C-NMR (CDCl₃; δ = 170.2, 150.5, 149.9, 134.3, 133.2, 125.6, 114.2, 111.4, 65.0, 62.4, 27.8, 25.9, 22.5, 21.5; Mass (GC-MS, EI): 376 [M⁺1]⁺, 121 [M⁺1]⁻ - Cl, 107 [M⁺1]⁻ - Cl - CH₂ - CH₂; FT-IR (NaCl, cm⁻¹): 3217, 1444, 1421, 1269, 1105, 1026, 844, 834.

6-(4-methoxy-phenoxy)-hexanoic acid 4-chloromethyl-benzyl ester 17

17 was prepared following the DCC/DMAP-method described for 10 using 15 (0.80 g, 52.55 mmol) as the alcohol-functionalized molecule. The pure product was obtained by column chromatography (SiO₂, eluent CH₂Cl₂) as a yellow-white solid (0.564 g, 67 % yield). 1H-NMR (CDCl₃; δ = 7.34 (dd, 4H), 6.79 (s, 4H), 5.10 (s, 2H), 4.56 (s, 2H), 3.87 (t, 2H), 3.74 (s, 2H), 2.37 (t, 2H), 1.65-1.78 (m, 4H), 1.48 (m, 2H); 13C-NMR (CDCl₃; δ = 170.2, 150.5, 149.9, 134.3, 133.2, 125.6, 114.2, 111.4, 65.0, 62.4, 27.8, 25.9, 22.5, 21.5; Mass (GC-MS, EI): 376 [M⁺1]⁺, 121 [M⁺1]⁻ - Cl, 107 [M⁺1]⁻ - Cl - CH₂ - CH₂; FT-IR (NaCl, cm⁻¹): 3217, 1444, 1421, 1269, 1105, 1026, 844, 834.