# 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), NaO*t*Bu (43.07 g, 448.2 mmol) and EtOH (375 mL) was stirred for 1 h at room temperature under $N_2$ 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 $N_2$ atmosphere. The reaction was quenched with water (400 mL), and extracted with $CH_2Cl_2$ (3 x 200 mL). The combined organic extracts were dried over anhydrous $MgSO_4$. Evaporation of the solvent under reduced pressure gave the crude product as a brown oil. The pure product was obtained, by column chromatography ($SiO_2$, eluent $CH_2Cl_2$/MeOH 95/5) and afterwards mixed-solvent crystallizations from MeOH and hexane, as a colorless oil (78.6 g, 79 % yield). $^1$H-NMR ($CDCl_3$): δ = 6.80 (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**

To a stirred mixture of **1** (20 g, 75.6 mmol) and *p*-formaldehyde (6.2 g, 207 mmol) at 0 °C under $N_2$ atmosphere, concentrated HCl (48.03 g, 487.5 mmol) was added drop wise. Subsequently, acetic anhydride (76.56 g, 756 mmol) was added at such a rate that the temperature did not exceed 70 °C. After the addition was complete, the resulting solution was stirred at 60 °C for 10 h after which it was cooled down to room temperature and poured into water (200 mL). The resulting precipitate was filtered off, redissolved in $CH_2Cl_2$ (200 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent under reduced pressure gave the crude product. The pure carboxylic acid was obtained by crystallization from EtOAc as a white solid (22.42 g, 89 % yield). $^1$H-NMR ($CDCl_3$): δ = 6.89+6.88 (2s, 2H), 4.61+4.60 (2s, 4H), 3.97 (t, 2H), 3.83 (s, 3H), 2.39 (t, 2H), 1.81 (m, 2H), 1.72 (m, 2H), 1.58 (m, 2H).

**Bis-tetrahydrothiophenium salt of 6-(2,5-bis-chloromethyl-4-methoxy-phenoxy)-hexanoic acid methyl ester 3**

To a solution of **2** (22.24 g, 69.9mmol) in MeOH (220 mL) tretrahydrothiophene (23.598 g, 267.6mmol) 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 (22.84 g, 65 % yield). $^1$H-NMR ($D_2O$): 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-methoxy-2-octylsulfanylmethyl-phenoxy)-hexanoic acid methyl ester and 6-(2-chloromethyl-4-methoxy-5-octylsulfanylmethyl-phenoxy)-hexanoic acid methyl ester 4**

A mixture of *n*-octane thiol (1.346 g, 9.2 mmol) and NaO*t*Bu (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 $N_2$ 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 $CH_2Cl_2$ (125 mL) and the organic layer was extracted with water (3 x 150 mL). The organic layer was dried over anhydrous $MgSO_4$. Evaporation of the solvent gave the crude product, as a yellow oil. $^1$H-NMR ($CDCl_3$): δ = 6.90+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-(5-chloromethyl-4-methoxy-2-octylsulfinylmethyl-phenoxy)-hexanoic acid methyl ester and 6-(2-chloromethyl-4-methoxy-5-octylsulfinylmethyl-phenoxy)-hexanoic acid methyl ester 5**

An aqueous (35 wt%) solution of $H_2O_2$ (1.55 g, 16 mmol) was added drop wise to a mixture of **4** (3.68 g, 8 mmol) and $TeO_2$ (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, $CH_2Cl_2$/MeOH 19/1), 200 mL of a saturated $Na_2S_2O_3$-solution was added to quench the reaction. The reaction mixture was extracted with $CHCl_3$ (3 x 100 mL) after which the combined organic extracts were dried over anhydrous $MgSO_4$. Evaporation of the solvent under reduced pressure gave the crude product. The pure product was obtained by column chromatography ($SiO_2$, eluent $CH_2Cl_2$/MeOH 19/1), followed by another column chromatography ($SiO_2$, eluent EtOAc) as a white-yellow solid (1/1 mixture of regio-isomers; 2.36 g, 54 % yield). $^1$H-NMR ($C_7D_8$): δ = 6.88+6.76+6.72+6.67 (4s, 2H), 4.51+4.50 (2s, 2H), 3.91+3.89+3.86+3.84 (2dd, 2H), 3.47 (t, 2H), 3.39+3.38 (2s, 3H), 3.29 (s, 3H), 2.32 (m, 2H), 2.09 (t, 2H), 1.47-1.70 (m, 6H), 1.10-1.30 (m, 12H), 0.9 (t, 3H).

**6-(4-methoxy-phenoxy)-hexanoic acid 9**

A solution of **1** (4 g, 15 mmol) and MeOH (200 mL) was heated to 50°C after which a solution of KO*t*Bu (4.213 g, 37.5 mmol) in water (4 mL) was added. After overnight stirring at 50 °C the reaction mixture was cooled down to room temperature and a 1 N HCl-solution was added until pH 6. Water was added and the reaction mixture was extracted with $CH_2Cl_2$ (3 x 150 mL). The combined organic extracts were dried over anhydrous $MgSO_4$. Evaporation of the solvent under reduced pressure gave the crude product. The pure carboxylic acid was obtained by crystallization from hexane as a white solid (3.26 g, 65 % yield). $^1$H-NMR ($CDCl_3$): δ = 6.80 (s, 4H), 3.89 (t, 2H), 3.74 (s, 3H), 2.37 (t, 2H), 1.64-1.80 (m, 4H), 1.50 (m, 2H); $^{13}$C-NMR ($CDCl_3$): δ = 179.4, 153.5, 152.9, 115.2, 114.4, 68.1, 64.0, 55.5, 33.7, 28.9, 25.4, 24.3; Mass (GC-MS, EI): 238 $[M+1]^+$, 124 $[M+1]^+$ - $C_7O_2H_{10}$, 109 $[M+1]^+$ - $C_7O_2H_{10}$ - $CH_3$; FT-IR (NaCl, $cm^{-1}$): 3041, 3014, 2949, 2901, 2872, 2838, 1721, 1701 ($\nu_{C-O}$), 1591, 1513, 1475, 1456, 1449, 1428, 1407, 1392, 1307, 1249, 1223, 1232, 1203, 1174, 1109, 1051, 1038, 1008, 908, 825.

**6-(4-methoxy-phenoxy)-hexanoic acid allyl ester 10**

**9** (0.5 g, 2.1 mmol) was dissolved in dry $CH_2Cl_2$ (20 mL) and cooled down to 0 °C. The alcohol-functionalized reagent, *i.e.* allylalcohol (0.304 g, 5.25 mmol) and N,N'-dicyclohexylcarbodiimide (DCC) (0.476 g, 2.31 mmol) were added. Subsequently 4-(N,N'-dimethylamino)pyridine (DMAP) (0.050 g, 0.42 mmol) in dry $CH_2Cl_2$ was added drop wise over a period of 15 minutes under $N_2$ atmosphere. The reaction was allowed to proceed for 1 h at 0 °C and for an additional 24 h at room temperature. Filtering off dicyclohexylurea (DCU) gave the crude product. The pure

product was obtained by column chromatography ($SiO_2$, eluent $CH_2Cl_2$) as a yellow oil (0.455 g, 78 % yield). $^1$H-NMR ($CDCl_3$): δ = 6.80 (s, 4H), 5.90 (m, 1H), 5.29 (dq, 1H), 5.21 (dq, 1H), 4.55 (dt, 2H), 3.88 (t, 2H), 3.74 (s, 3H), 2.35 (t, 2H), 1.64-1.80 (m, 4H), 1.49 (m, 2H); $^{13}$C-NMR ($CDCl_3$): δ = 173.1, 153.5, 152.9, 132.1, 118.0, 115.2, 114.4, 68.1, 64.8, 55.5, 33.9, 28.9, 25.5, 24.5; Mass (GC-MS, EI): 278 $[M+1]^+$, 155 $[M+1]^+$ - $C_7O_2H_7$, 124 $[M+1]^+$ - $C_9O_2H_{14}$, 109 $[M+1]^+$ - $C_9O_2H_{14}$ - $CH_3$; FT-IR (NaCl, $cm^{-1}$): 2994, 2943, 2868, 2834, 1738 ($\nu_{C-O}$), 1648 ($\nu_{C=C}$), 1591, 1510, 1466, 1442, 1383, 1232, 1162, 1107, 1039, 990, 932, 825.

**6-(4-methoxy-phenoxy)-hexanoic acid 3-phenylprop-2-ynyl ester 11**

**11** was prepared following the DCC/DMAP-procedure described for **10** using 3-phenyl-2-propyn-1-ol (0.693 g, 5.25 mmol) as the alcohol-functionalized molecule. The pure product was obtained by column chromatography ($SiO_2$, eluent $CH_2Cl_2$) as a white-yellow solid (0.604 g, 82 % yield). $^1$H-NMR ($CDCl_3$): δ = 7.42 (m, 2H), 7.30 (m, 3H), 6.80 (s, 4H), 4.89 (d, 2H), 3.88 (t, 2H), 3.74 (s, 3H), 2.40 (t, 2H), 1.65-1.81 (m, 4H), 1.50 (m, 2H); $^{13}$C-NMR ($CDCl_3$): δ = 169.8, 150.5, 150.0, 128.7, 125.6, 125.1, 118.9, 112.2, 111.4, 83.2, 79.8, 65.0, 52.6, 49.5, 30.8, 25.8, 22.4, 21.4; Mass (GC-MS, EI): 352 $[M+1]^+$, 124 $[M+1]^+$ - $C_{15}O_2H_{16}$, 115 $[M+1]^+$ - $C_{13}O_4H_{17}$, 109 $[M+1]^+$ - $C_{15}O_2H_{16}$ - $CH_3$; FT-IR (NaCl, $cm^{-1}$): 3655, 3463, 3055, 2937, 2968, 2834, 2473, 2337, 2237, 2118 ($\nu_{\equiv CH}$), 2061, 1978, 1887, 1732 ($\nu_{C-O}$), 1593, 1572, 1510, 1471, 1455, 1385, 1349, 1233, 1107, 1033, 955, 825, 758, 692.

**6-(4-methoxy-phenoxy)-hexanoic acid 2-(2-methyl-acryloyloxy)-ethyl ester 12**

**12** was prepared following the DCC/DMAP-procedure described for **10** using 2-hydroxyethyl-methacrylate (0.682 g, 5.25 mmol) as the alcohol-functionalized molecule. The pure product was obtained by column chromatography ($SiO_2$, eluent $CH_2Cl_2$) as a yellow oil (0.672 g, 91 % yield). $^1$H-NMR ($CDCl_3$): δ = 6.80 (s, 4H), 6.10 (dd, 1H), 5.56 (dd, 1H), 4.32 (m, 4H), 3.88 (t, 2H), 3.74 (s, 3H), 2.35 (t, 1H), 1.92 (s, 3H), 1.63-1.78 (m, 4H), 1.48 (m, 2H); $^{13}$C-NMR ($CDCl_3$): δ = 173.4, 167.1, 153.7, 153.1, 135.9, 126.0, 115.3, 114.6, 68.2, 62.4, 61.9, 55.7, 34.0, 29.0, 25.6, 24.6, 18.2; Mass (GC-MS, EI): 350 $[M+1]^+$, 124 $[M+1]^+$ - $C_{12}O_4H_{18}$, 113 $[M+1]^+$ - $C_{13}O_4H_{17}$, 109 $[M+1]^+$ - $C_{12}O_4H_{18}$ - $CH_3$; FT-IR (NaCl, $cm^{-1}$): 3045, 2947, 2867, 2834, 1740 ($\nu_{C-O}$), 1722 ($\nu_{C-O}$), 1637, 1591, 1509, 1464, 1455, 1377, 1320, 1297, 1232, 1155, 1107, 1039, 945, 825.

**6-(4-methoxy-phenoxy)-hexanoic acid prop-2-ynyl ester 13**

**13** was prepared following the DCC/DMAP-procedure described for **10** using propargylalcohol (0.304 g, 5.25 mmol) as the alcohol-functionalized molecule. The pure product was obtained by column chromatography ($SiO_2$, eluent $CH_2Cl_2$) as a white-yellow solid (0.429 g, 74 % yield). $^1$H-NMR ($CDCl_3$): δ = 6.80 (s, 4H), 4.65 (d, 2H), 3.88 (t, 2H), 3.74 (s, 3H), 2.44 (t, 1H), 2.37 (t, 2H), 1.65-1.80 (m, 4H), 1.49 (m, 2H); $^{13}$C-NMR ($CDCl_3$): δ = 172.6, 153.5, 152.9, 115.2, 114.4, 77.6, 74.6, 68.0, 55.5, 51.6, 33.7, 28.8, 25.4, 24.4; Mass (GC-MS, EI): 276 $[M+1]^+$, 153 $[M+1]^+$ - $C_7O_2H_7$, 124 $[M+1]^+$ - $C_9O_2H_{12}$, 109 $[M+1]^+$ - $C_9O_2H_{12}$ - $CH_3$; FT-IR (NaCl, $cm^{-1}$): 3286 ($\nu_{\equiv CH}$), 2997, 2942, 2867, 2834, 2118 ($\nu_{\equiv CH}$), 1742 ($\nu_{C-O}$), 1591, 1510, 1466, 1442, 1381, 1232, 1155, 1107, 1037, 937, 825.

**6-(4-methoxy-phenoxy)-hexanoic acid 1-phenylsulfanylmethyl-1H-[1,2,3] triazol-4-ylmethyl ester 14**

**13** (0.250 g, 0.90 mmol) was dissolved in degassed THF (25 mL) under $N_2$ atmosphere. The azide-functionalized reagent, *i.e.* azidomethyl phenyl sulfide (0.297 g, 1.80 mmol) and distilled N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) (0.016 g, 0.09 mmol) were added. The solution was again degassed for 5 min and purified Cu(I)Br (0.013 g, 0.09 mmol) was added under a continuous $N_2$ flow. After overnight stirring at 50 °C the reaction mixture was filtered over $Al_2O_3$ and washed with THF and $CH_2Cl_2$. The pure product was obtained by column chromatography ($SiO_2$, eluent $CH_2Cl_2$) as a white solid (0.246 g, 62 % yield). $^1$H-NMR ($CDCl_3$): δ = 7.57 (s, 1H), 7.28 (s, 5H), 6.77 (s, 4H), 5.56 (s, 2H), 5.14 (s, 2H), 3.84 (t, 2H), 3.72 (s, 3H), 2.31 (t, 2H), 1.59-1.78 (m, 4H), 1.44 (m, 2H); $^{13}$C-NMR ($CDCl_3$): δ = 173.2, 153.6, 153.1, 143.4, 132.1, 131.8, 129.5, 128.7, 123.3, 115.4, 114.6, 68.1, 57.4, 55.6, 53.7, 33.9, 28.9, 25.6, 24.5; Mass (GC-MS, EI): 441 $[M+1]^+$, 318 $[M+1]^+$ - $C_7O_2H_7$, 176 $[M+1]^+$ - $C_7O_2H_7$ - $C_8O_2H_{14}$, 123 $[M+1]^+$ - $C_{16}O_2N_3SH_{20}$, 109 $[M+1]^+$ - $C_{16}O_2N_3SH_{20}$ - $CH_2$; FT-IR (NaCl, $cm^{-1}$): 3001, 2942, 2867, 2834, 1735 ($\nu_{C-O}$), 1584, 1510, 1466, 1440, 1390, 1232, 1158, 1108, 1044, 825.

**4-chloromethyl benzyl alcohol 15**

4-chloromethyl benzoic acid (2 g, 11.76 mmol) was dissolved in dry THF (40 mL), under $N_2$ atmosphere, and cooled down to 0 °C. 1N $BH_3$·THF (19.52 mL, 19.52 mmol) was added drop wise under $N_2$ 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 $MgSO_4$. Evaporation of the solvent under reduced pressure gave the crude product. The pure product was obtained by column chromatography ($SiO_2$, eluent EtOAc) as a white solid (0.691 g, 38 % yield). $^1$H-NMR ($CD_3OD$): δ = 7.36 (dd, 4H), 4.62 (s, 2H), 4.60 (s, 2H); $^{13}$C-NMR ($CD_3OD$ + $CDCl_3$): δ = 142.2, 137.4, 129.3, 127.7, 64.4, 46.4; Mass (GC-MS, EI): 156 $[M+1]^+$, 121 $[M+1]^+$ - Cl, 107 $[M+1]^+$ - Cl - $CH_2$, 91 $[M+1]^+$ - Cl - $CH_2$ - O; FT-IR (NaCl, $cm^{-1}$): 3217, 1444, 1421, 1262, 1195, 1025, 1013, 844, 834.

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

**16** was prepared following the DCC/DMAP-procedure described for **10** using 15 (0.820 g, 5.25 mmol) as the alcohol-functionalized molecule. The pure product was obtained by column chromatography ($SiO_2$, eluent $CH_2Cl_2$) as a white-yellow solid (0.564 g, 67 % yield). $^1$H-NMR ($CDCl_3$): δ = 7.34 (dd, 4H), 6.79 (s, 4H), 5.10 (s, 2H), 4.56 (s, 2H), 3.87 (t, 2H), 3.74 (s, 3H), 2.37 (t, 2H), 1.65-1.78 (m, 4H), 1.48 (m, 2H); $^{13}$C-NMR ($CDCl_3$): δ = 170.2, 150.5, 149.9, 134.3, 133.2, 125.6, 125.4, 112.2, 111.4, 65.0, 62.4, 42.7, 27.8, 25.9, 22.5, 21.5; Mass (GC-MS, EI): 376 $[M+1]^+$, 139 $[M+1]^+$ - $C_{13}O_4H_{17}$, 124 $[M+1]^+$ - $C_{14}O_2ClH_{17}$, 109 $[M+1]^+$ - $C_{14}O_2ClH_{17}$ - $CH_3$; FT-IR (NaCl, $cm^{-1}$): 2997, 2945, 2867, 2834, 1736 ($\nu_{C-O}$), 1591, 1508, 1465, 1443, 1384, 1352, 1289, 1232, 1158, 1107, 1038, 977, 825.

**6-(4-methoxy-phenoxy)-hexanoic acid 4-((N,N-diethyldithiocarbamate)methyl)-benzyl ester 17**

A mixture of **16** (0.200 g, 0.53 mmol), sodium diethyldithiocarbamate trihydrate (0.120 g, 0.53 mmol) in THF (20 mL) was stirred overnight at room temperature. Evaporation of the solvent under reduced pressure gave the crude product. The pure product was obtained by column chromatography ($SiO_2$, eluent $CH_2Cl_2$) as a yellow oil (0.156 g, 60 % yield). $^1$H-NMR ($CDCl_3$): δ = 7.34 (dd, 4H), 6.79 (s, 4H), 5.06 (s, 2H), 4.52 (s, 2H), 4.01 (q, 2H), 3.86 (t, 2H), 3.73 (s, 3H), 3.71 (q, 2H), 2.37 (t, 2H), 1.65-1.78 (m, 4H), 1.48 (m, 2H), 1.24 (2t, 6H); $^{13}$C-NMR ($CDCl_3$): δ = 194.9, 173.4, 153.7, 153.1, 136.2, 135.2, 129.5, 128.7, 115.4, 114.6, 68.2, 65.8, 55.7, 49.5, 46.7, 41.7, 34.2, 29.0, 25.6, 24.7, 12.5, 11.6; Mass (DIP-MS, EI): 489 $[M+1]^+$, 340 $[M+1]^+$ - $C_5S_2NH_{11}$, 148 $[M+1]^+$ - $C_{21}O_4H_{25}$, 124 $[M+1]^+$ - $C_5S_2NH_{11}$ - $C_{14}O_2H_{16}$; FT-IR (NaCl, $cm^{-1}$): 3453, 3044, 2935, 2870, 2833, 2059, 1738 ($\nu_{C-O}$), 1732, 1615, 1591, 1508, 1488, 1465, 1443, 1417, 1380, 1355, 1269, 1233, 1158, 1206, 1107, 1070, 1038, 1010, 985, 918, 825.].