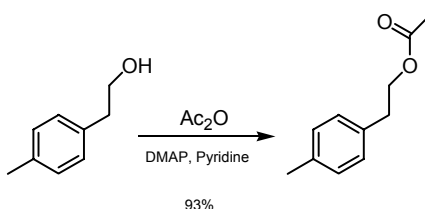


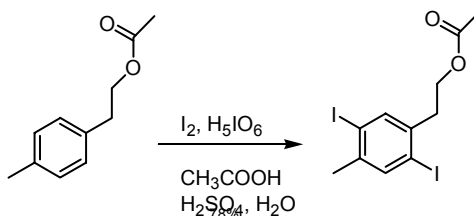
# Grafted conjugated polymers: synthesis and characterization of polyester side chain substituted poly(*paraphenyleneethynylene*s)

Yiqing Wang, James N. Wilson, Belma Erdogan and Uwe H. F. Bunz,\*

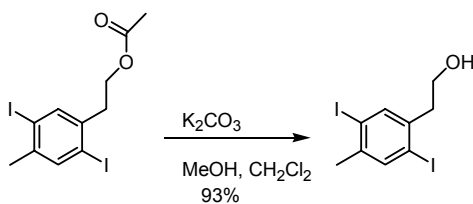
## Supplementary Material and Experimental Details



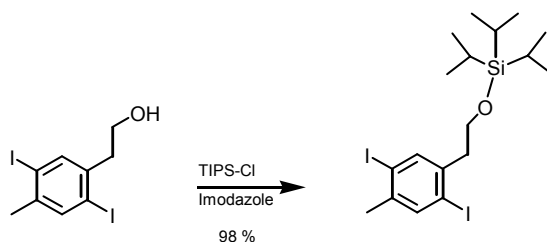
To a nitrogen-purged flask were added 4-methylphenethyl alcohol (21.2 g, 156 mmol), acetic anhydride (79.6 g, 780 mmol), pyridine (400 mL) and 4-dimethylaminopyridine (catalytic amount). The mixture was stirred at room temperature for 6 h. The solvent and excess acetic anhydride were removed in vacuo to afford the desired product as a colorless liquid. The acetate was purified by column chromatography by using hexane / dichloromethane (1:3) as an eluent. The product was obtained as a colorless oil (25.9 g, 93%). IR (KBr)  $\text{cm}^{-1}$  = 3460, 2864, 2732, 2073, 1900, 1740, 1514, 1365, 1223, 976, 908, 812, 718, 640, 606, 550.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 7.13 (s, 4H), 4.30-4.26 (t, 2H,  $J_{\text{3H,H}} = 7.0$  Hz), 2.94-2.89 (t, 2H,  $J_{\text{3H,H}} = 7.0$  Hz), 2.35 (s, 3H), 2.05 (s, 3H)  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 170.82, 135.88, 134.56, 129.04, 128.62, 64.92, 34.50, 20.87, 20.79.



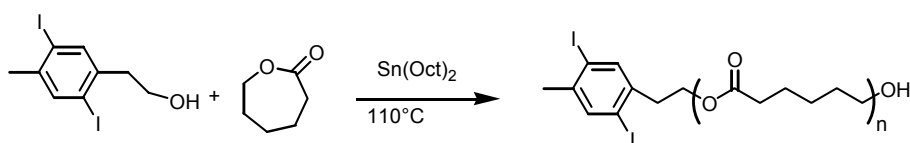
To a nitrogen purged flask, 4-methylphenethylacetate (25.0 g, 140 mmol), iodine (39.1 g, 154 mmol), periodic acid (0.639 g, 2.81 mmol), acetic acid (500 mL),  $\text{H}_2\text{O}$  (100 mL), and  $\text{H}_2\text{SO}_4$  (15.0 mL) were added. The mixture was heated to 80 °C for 3 h under  $\text{N}_2$ . The solvent was removed in vacuo. The residue was dissolved in ethylacetate and washed with  $\text{H}_2\text{O}$ , then 1N (aq)  $\text{K}_2\text{CO}_3$  and 1N (aq)  $\text{Na}_2\text{SO}_3$ . The organic phase was dried over  $\text{MgSO}_4$  and the solvent was evaporated. The resulting solid was purified by silica gel chromatography using 1:3 hexanes:dichloromethane to give the iodinated product as a colorless solid (51.7 g, 78%). Mp = 55 °C. IR (KBr)  $\text{cm}^{-1}$  = 2945, 2870, 1738, 1516, 1452, 1369, 1232, 1041, 984, 878, 802, 700, 656, 606.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 7.65 (s, 1H), 7.62 (s, 1H), 4.24-4.19 (t, 2H,  $J_{\text{3H,H}} = 7.0$  Hz), 2.98-2.94 (t, 2H,  $J_{\text{3H,H}} = 7.0$  Hz), 2.33 (s, 3H), 2.03 (s, 3H)  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 170.73, 141.76, 139.76, 139.70, 139.60, 100.76, 100.01, 63.16, 38.48, 26.90, 20.87.



2,5-Diiodo-4-methylphenethylacetate (50.0 g, 116 mmol) was dissolved in dichloromethane (65 mL). After addition of MeOH (1.5 L) and  $\text{K}_2\text{CO}_3$  (161 g, 1.16 mol), the mixture was stirred at room temperature for 16 h. The solvent was evaporated and the resultant solid was transferred into funnel and washed with  $\text{H}_2\text{O}$ . Recrystallized from hexane, the product was obtained as a colorless solid (41.9 g, 93%). Mp = 118 °C. IR (KBr)  $\text{cm}^{-1}$  = 3273, 2950, 2874, 1439, 1371, 1342, 1163, 1041, 1018, 995, 876, 781, 704, 654, 606.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 7.66-7.65 (d, 2H), 3.83-3.79 (t, 2H,  $J_{\text{3H,H}}$  = 6.8 Hz), 2.93-2.88 (t, 2H,  $J_{\text{3H,H}}$  = 6.8 Hz), 2.33 (s, 3H), 1.42 (bs, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  = 141.65, 140.39, 139.86, 139.76, 100.91, 100.23, 62.02, 42.49, 26.93.



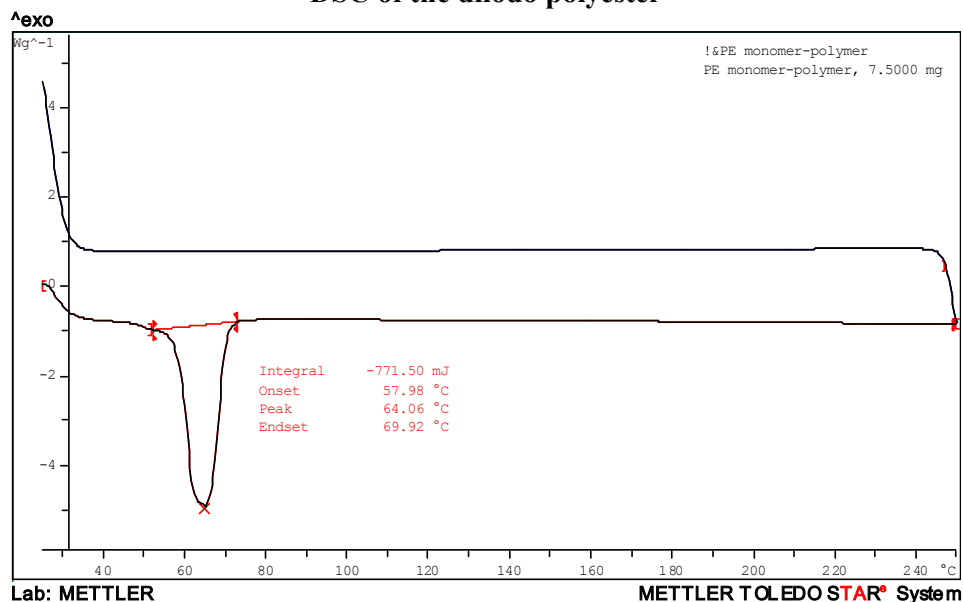
2,5-Diiodo-4-methylphenethyl alcohol (2.00 g, 5.16 mmol), chlorotriisopropylsilane (3.96 g, 20.7 mmol), and imidazole (0.975 g, 15.5 mmol) were placed into a pressure tube and capped. The tube was placed in a household microwave oven (Emerson, 600 W) and irradiated for 4 x 1 minute pulses. The progress of the reaction was monitored by TLC. The reaction mixture was separated by flash column chromatography (hexane/ethyl acetate, 80:20) and excess chlorotriisopropylsilane was removed by vacuum distillation. The silyl ether was obtained as a light yellow oil. Yield 2.75 g (98%). IR: 2939.3, 2889.2, 2862.2, 1506.3, 1461.9, 1446.5, 1379.0, 1365.5, 1247.9, 1188.1, 1103.2, 1068.5, 1012.6, 996.2, 921.9, 881.4, 746.4, 680.8, 657.7.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  = 7.71 (s, 1H), 7.65 (s, 1H), 3.83(t, 2H,  $J_{\text{3H,H}}$  = 6.9 Hz), 2.88(t, 2H,  $J_{\text{3H,H}}$  = 6.9 Hz), 2.34 (s, 3H), 1.55-0.99 (m, 21H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 141.47, 141.43, 140.69, 139.74, 100.87, 100.35, 62.81, 43.18, 27.16, 18.24, 12.16.



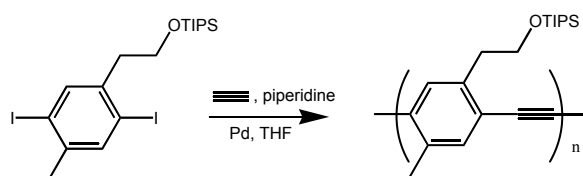
An oven-dried Schlenk flask cooled under nitrogen was charged with 2,5-diiodo-4-methylphenethylalcohol (2.00 g, 5.16 mmol),  $\epsilon$ -caprolactone (11.8 g, 103 mmol), and tin(II)-2-ethylhexanoate (127 mg, 313  $\mu\text{mol}$ ). The flask was heated to 110°C while stirring. The reaction was stopped after 12 h. The viscous product was diluted with chloroform (10 mL), then precipitated

into 300 mL of methanol. The diiodo-polyester was obtained as a colorless solid. Yield 6.56 g, 48%. GPC (vs. polystyrene standards in chloroform):  $M_n = 2400$ ,  $M_w/M_n = 1.3$  IR: 2941.2, 2893.0, 2866.0, 1722.3, 1683.7, 1652.9, 1506.3, 1471.6, 1456.2, 1394.4, 1294.1, 1244.0, 1190.0, 1107.1, 1045.3, 962.4, 933.5, 877.6, 840.9, 731.0, 709.8.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.67$  (s, 1H), 7.63 (s, 1H), 4.24 (t,  $J_{3\text{H,H}} = 6.8$  Hz, 2H), 4.05 (t,  $J_{3\text{H,H}} = 6.8$  Hz, 38H), 3.64 (t,  $J_{3\text{H,H}} = 6.6$  Hz, 2H), 2.98 (t,  $J_{3\text{H,H}} = 6.8$  Hz, 2H), 2.30 (t,  $J_{3\text{H,H}} = 7.5$  Hz, 40H), 1.68-1.60 (m, 80H), 1.41-1.33 (m, 40H)  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 173.73$ , 173.54, 173.29, 141.91, 139.91, 139.87, 139.82, 100.76, 100.03, 64.54, 64.14, 63.95, 63.10, 62.62, 38.64, 34.23, 34.12, 33.95, 33.82, 33.34, 28.53, 28.35, 28.18, 26.96, 25.93, 25.53, 25.31, 24.98, 34.69, 24.58, 24.39.

### DSC of the diiodo polyester



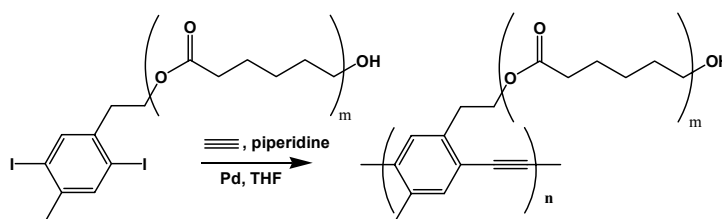
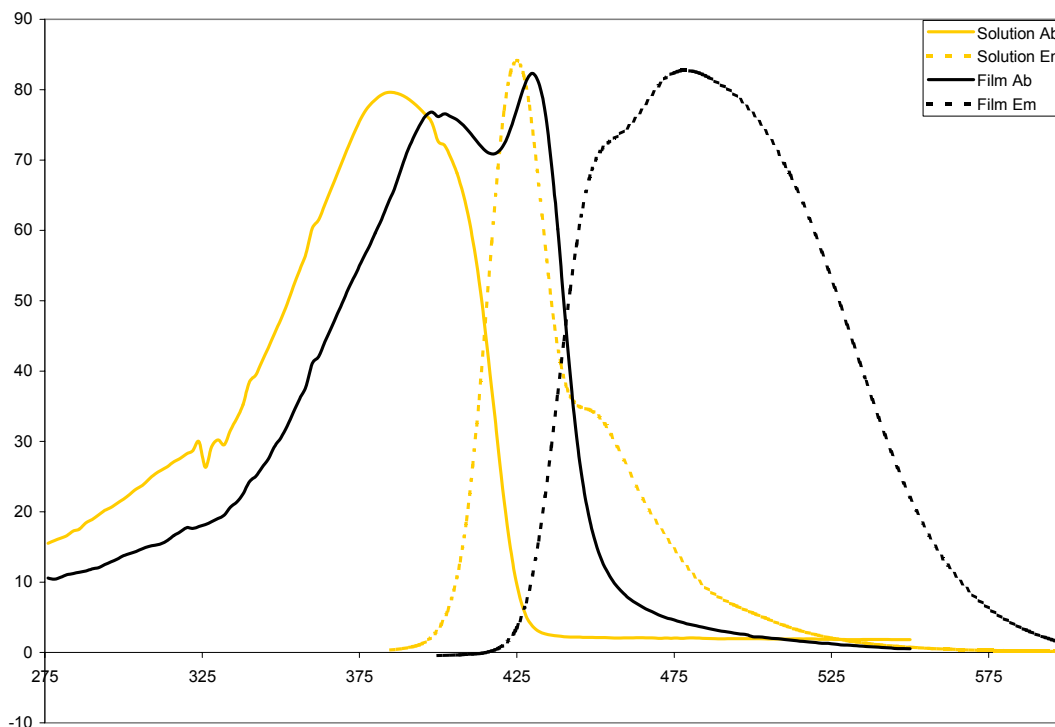
13.3 kJ/mol repeat



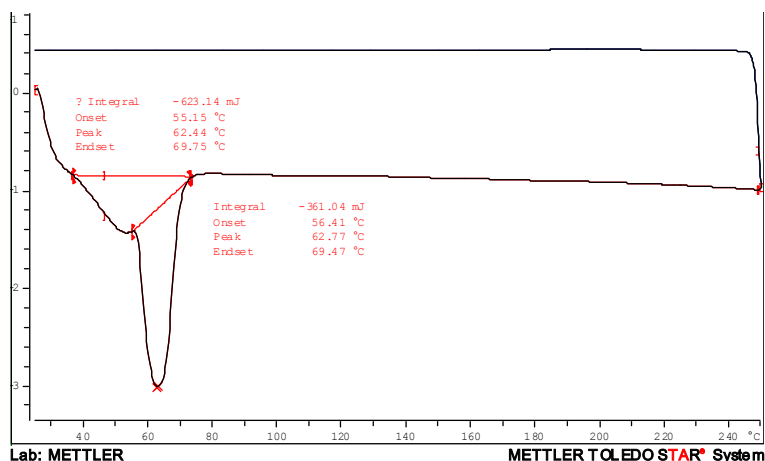
A Schlenk flask of known volume (37 mL) was charged with the triisopropylsilylether of 2,5-diiodo-4-methylphenethyl alcohol (0.761 g, 1.39 mmol), THF (1.5 mL), piperidine (1.5 mL),  $(\text{PPh}_3)_2\text{PdCl}_2$  (2.0 mg, 2.8  $\mu\text{mol}$ , 0.2 mol%), and  $\text{CuI}$  (1.0 mg, 5.3  $\mu\text{mol}$ , 0.4 mol%). The flask was degassed by three freeze-pump-thaw cycles. The acetylene gas (34 mL, 1.4 mmol) was added through the purged sidearm by a balloon. The reaction was allowed to stir at room temperature for 48 h during which time the reaction mixture solidified. The reaction mixture was filtered over a small volume of silica ( $\sim 10$  mL) on a fritted funnel with hexane as solvent. The hexane was evaporated, the polymer re-dissolved and precipitated into methanol. A bright yellow polymer (0.414 g, 98%) was obtained. GPC (vs. polystyrene standards in chloroform):  $M_n = 37200$ ,  $M_w/M_n = 3.9$ . IR: 2941.2, 2891.1, 2864.1, 2194.8, 1504.4, 1461.9, 1360.9, 1103.2, 1070.4, 1012.6, 996.2, 918.1, 883.3, 742.5, 680.8, 569.6.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 7.45 (2H, term. Ph-H), 7.42-7.36

(bm, 2H), 3.94 (bs, 2H), 3.07 (bs, 2h), 2.47 (bs, 3H).  $^{13}\text{C}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 138.39, 138.00, 133.69, 123.36 (broad—2 carbons), 93.58, 63.77, 37.99, 20.53, 18.24, 12.22.

Optical Spectra

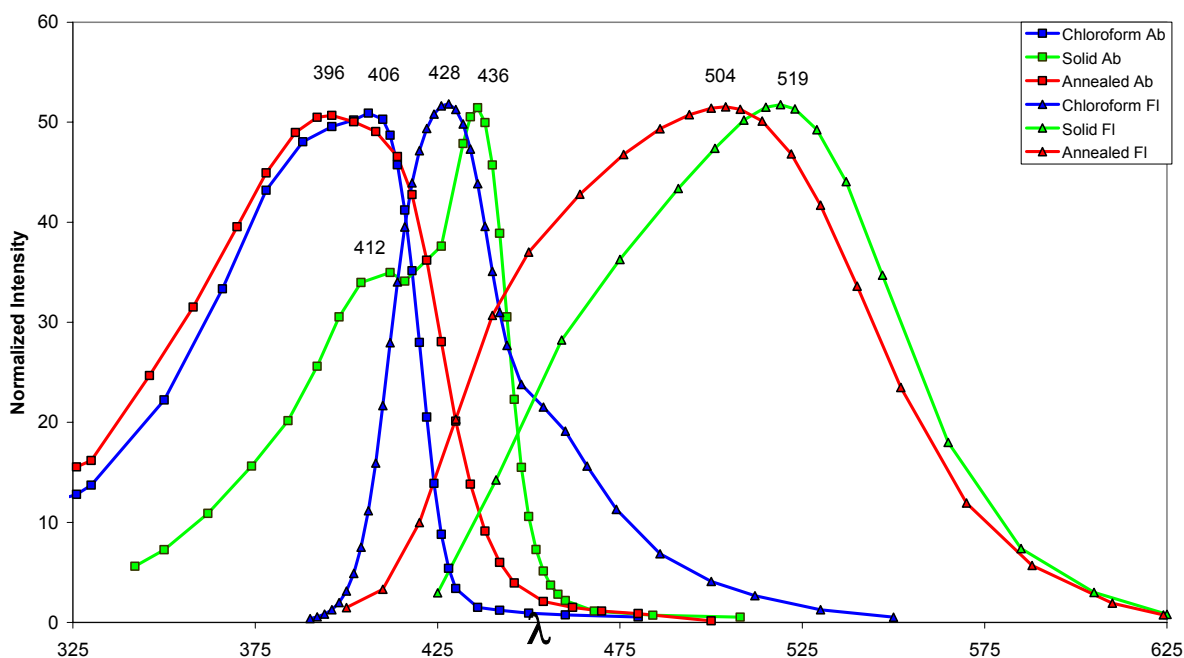


The diiodo polyester (3.29 g, 1.39 mmol) was combined with piperidine (1.5 mL), THF (1.5 mL),  $(\text{PPh}_3)_2\text{PdCl}_2$  (2.0 mg, 2.8  $\mu\text{mol}$ , 0.2 mol%), and  $\text{CuI}$  (1.0 mg, 5.3  $\mu\text{mol}$ , 0.4 mol%) in a Schlenk flask (37 mL). Acetylene gas (34 mL, 1.4 mmol) was added through the purged side arm with a balloon. The reaction solidified after 36 h. The resultant polymer was filtered over a cotton plug using dichloromethane as a solvent before precipitating into methanol. The polymer was collected over a fritted funnel, re-dissolved in dichloromethane and precipitated again. A bright yellow polymer was obtained (2.31 g, 77 % yield). GPC (vs. polystyrene standard in chloroform): 336,000  $M_n$  vs polystyrene standards. Repeat = 2400 g/mol,  $P_n = 140$ ,  $M_w/M_n = 5.3$  IR: 2941.2, 2864.1, 1718.5, 1419.5, 1363.6, 1292.2, 1238.2, 1174.6, 1047.3, 960.5, 933.5, 840.9, 732.9, 709.8.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 7.41 (bs), 4.36 (bs, 2H), 4.04 (bt,  $J_{3\text{H,H}} = 6.6$  Hz, 38H), 3.62 (bs, 2H), 2.94 (bs, 2H), 2.28 (bt,  $J_{3\text{H,H}} = 7.4$  Hz, 40H), 1.62 (bm, 80H), 1.36 (bm, 40H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 173.69, 173.50, 13.8.32, 136.73, 133.40, 132.84, 123.85, 123.18, 93.18, 92.54, 65.15, 64.09, 63.05, 62.55, 34.06, 32.27, 28.29, 25.47, 25.25, 24.52, 20.29.



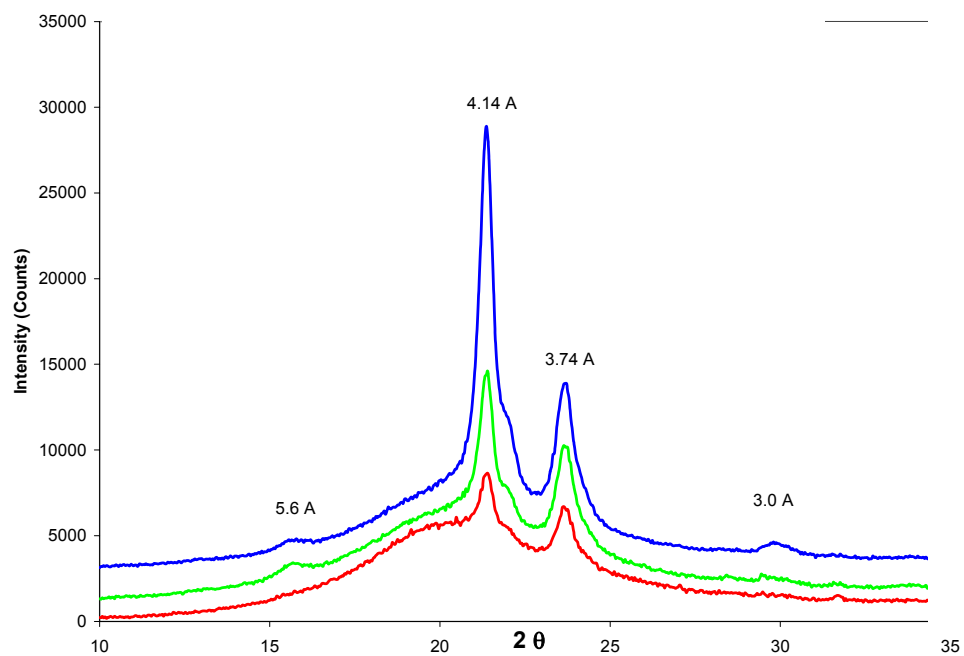
Total Curve: 216 kJ/mol repeat  
 Peak Curve: 124 kJ/mol repeat

### Optical Spectra



### XRD

Samples were prepared for powder XRD (Rigaku D\Max-2100 Powder X-Ray Diffractometer, Bragg-Bretano geometry, Cu K $\alpha$  radiation). All samples utilized the same plate to maintain a consistent background and sample thickness. The samples were run at a step of  $0.04^\circ 2\theta$  from  $5^\circ$  to  $42^\circ 2\theta$ . The precipitated PE-PPE was packed into the well and pressed smooth with a glass slide to obtain the plot for “packed aggregates”. A concentrated chloroform solution of the polymer was layered onto the sample holder. This gelatinous sample was run under identical conditions to obtain the “gel” plot. This gel was then annealed at  $100^\circ\text{C}$  for 4h to produce the plot for “annealed gel”.



X-ray diffraction of different polyester substituted PPEs. Red: Gel phase. Green: Pristine powder. Blue annealed powder.