Facile synthesis of poly(3-hexylthiophene)-*block*-poly(ethylene oxide) copolymers *via* Steglich esterification

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1. Materials

Bromohexane (98%), Mg turnings (98%), 3-bromothiophene (97%), *tert*-butylmagnesium chloride (^{*t*}BuMgCl, 1 M solution in tetrahydrofuran, THF), 1,3-bis(diphenylphosphino)propane nickel(II) chloride [Ni(dppp)Cl₂], *N*-bromosuccinimide (NBS, 99%), allylmagnesium bromide (1 M solution in diethyl ether), 9-borabicyclo(3.3.1)nonane (9-BBN, 0.5 M solution in THF), NaOH solution (10 M), hydrogen peroxide (33% in distilled H₂O), 1,3-dicyclohexylcarbodiimide (DCC) (99%), 4-dimethylaminopydridine (DMAP) (99%), poly(ethylene oxide) methyl ether [PEO, CH₃(OCH₂)_n-OH, $M_n \sim 650$ and 2500) were purchased from Sigma Aldrich and used without further purification. Chromium (VI) oxide (CrO₃) (99.5%), from Acros Organics, and conc. H₂SO₄ (95-98%), THF (HPLC), chloroform (HPLC), acetone, methanol and hexane, from Fisher scientific, were all used as received. Monomer, 2,5-dibromo-3-hexylthiophene (M1), was synthesised according to the literature procedure.¹

2. Characterisation

The monomer and polymer structures in CDCl₃ were characterised by NMR spectroscopy using a Bruker Avance Spectrometer at 300 MHz for ¹H and at 75 MHz for ¹³C. ¹H NMR Spectroscopy was further used as an absolute method of determining M_n and the resultant degrees of polymerisation of the polymers (quoted throughout the manuscript) have been calculated from these values accordingly. Relative M_n and dispersity (M_w/M_n , D) were measured by Gel Permeation Chromatography (GPC) (flow rate 1 ml/min, 40 °C) using a Varian GPC spectrometer, comprising three PL gel 5 µm 300 x 7.5 mm mixed-C columns and a degassed THF eluent system containing triethylamine (2 % v/v) and BHT (0.05 % w/v). The samples were calibrated with narrow polystyrene standards (M_p range = 162 to 6 035 000 g/mol) and analysed using PL Cirrus software (version 2.0) supplied by Agilent Technologies. Fourier transform infrared (FTIR) spectra of all the samples were obtained using attenuated total reflectance (ATR) on a Thermo Nicolet 380 FTIR spectrophotometer over the range

4000-500 cm⁻¹ for 32 scans with a resolution of 4 cm⁻¹ and the spectra were analysed using Omnic software. Scanning Electron Microscopy with Energy Dispersive X-ray Analysis (SEM-EDXA) with a Link system AN10000 and Cambridge Scanning Electron Microscope Stereoscan S90 was used to verify the metal content of our polymers. Matrix Assisted Laser Desorption Ionisation Spectroscopy with Time of Flight detection Mass Spectroscopy (MALDI-ToF MS) measurements were performed at the University of Birmingham, UK, on a MALDI micro MX technologies using dithranol as the matrix.

3. Synthetic procedures

Scheme S1. New synthetic route for P3HT-*b*-PEO diblock copolymers via esterification.



All reactions were performed under nitrogen using either flame-dried or oven-dried glassware.

Synthesis of allyl-terminated regioregular poly(3-hexylthiophene) (allyl-P3HT)²

In a dry, three neck round bottomed flask, flushed with nitrogen, 2,5-dibromo-3-hexylthiophene (**M1**, 7.3 g, 22.3 mmol) was dissolved in anhydrous THF (40 ml) and stirred under nitrogen for 15 minutes. Afterwards, *tert*-butylmagnesium chloride (22.3 ml, 22.3 mmol, 1 M in THF) was added *via* syringe under nitrogen and the reaction mixture was stirred at room temperature for 2.5 h. The solution was further diluted with 160 ml, of dried THF, then Ni(dppp)Cl₂ (0.151 g, 0.278 mmol) was added in one portion and the reaction mixture stirred for 45 minutes at room temperature. Allyl magnesium bromide (18 ml, 18 mmol, 1 M in THF) was then added *via* syringe to the reaction mixture and stirred for an additional 45 minutes at room temperature. Finally, the crude polymer product was precipitated into methanol (800 ml), filtered into an extraction thimble and then purified by sequential soxhlet extractions with methanol, hexane and chloroform. The polymer was isolated from the chloroform with a G₄ crucible, dried overnight under vacuum and finally stored under inert atmosphere, protected from light. ¹H NMR (300 MHz, CDCl₃, ppm): $\delta = 6.98$ (s, 1nH), 5.98 (m, 1H), 5.11 (t, 2H), 3.49 (d, 2H), 2.80 (t, 2nH), 1.70 (m, 2nH), 1.34-1.43 (m, 6nH), 0.91 (t, 3nH), $M_n \sim 8500$ g mol⁻¹ (¹H NMR). GPC: $M_n = 9500$ g/mol; D = 1.11.

Synthesis of hydroxypropyl-terminated P3HT (P3HT-OH)

P3HT-OH was obtained by hydrolysis of allyl-P3HT in two steps according to the literature.³ In a 250 ml flame-dried flask, allyl-P3HT (1.65 g, 0.1 mmol), was dissolved in anhydrous THF (160 ml) under nitrogen and stirred for 15 minutes. To this reaction mixture, a 0.5 M solution of 9-BBN (11 ml, 5.5 mmol) in anhydrous THF was added via a syringe under nitrogen. The reaction mixture was allowed to stir for 24 hours at 45 °C. An aqueous solution of NaOH (10 ml, 10 M) was then added to the reaction flask and was stirred for additional 15 min at 45 °C. The reaction mixture was allowed to cool to room temperature followed by slow addition of a 33% aqueous solution of hydrogen peroxide (10 ml), and the reaction mixture was again heated at 45 °C for another 24 hours. The polymer was precipitated into methanol (800 ml). The polymer was purified by soxhlet extraction with methanol and finally extracted with chloroform. The solvent was removed under reduced pressure, vacuum-dried to obtain a pure polymer which was characterised by ¹H NMR and SEC analysis. The ¹H NMR of P3HT-OH is shown in Figure S1. ¹H NMR (300 MHz, CDCl₃, ppm): $\delta = 6.98$ (s, 1nH), 3.75 (t, 2H), 2.80 (t, 2nH), 1.95 (m, 2H), 1.70 (m, 2nH), 1.34-1.43 (m, 6nH), 0.91 (t, 3nH), $M_n \sim 8500$ g mol⁻¹ (¹H NMR). GPC: $M_n = 9400$ g/mol; D = 1.11.

Synthesis of carboxylic acid-terminated monomethoxy-PEO (PEO-COOH) by Jones oxidation⁴ In a 1 l oven-dried flask, PEO_n (10 g, 13.3 mmol, 1 eq.) was dissolved in acetone (300 ml) and stirred at room temperature for approximately 10 minutes. To this solution, 85 ml Jones reagent was added at 0 °C [Jones reagent consisted of CrO₃ (6.8 g, 67 mmol, 3.8 eq.), sulfuric acid (108 ml, 1.5 M)]. After

stirring for 10 minutes, the solution was allowed to return to room temperature. Following further stirring overnight, the solid waste was filtered off, and washed with acetone (200 ml). Acetone was removed *in vacuo* to yield a viscous liquid, to which an aqueous solution of sodium hydroxide (400 ml, 0.1M) was added. Subsequently, the solution was washed with diethyl ether (3 x 100 ml). Sulfuric acid (400 ml, 0.2 M) was then added (to separate PEO-OH from PEO-COOH) and the product was extracted with dichloromethane (3 x 300 ml). All the collected organic layers were combined and dried with magnesium sulfate, filtered, and the dichloromethane removed under reduced pressure. The product (a clear viscous liquid for PEO₁₃COOH and white solids for PEO₃₀COOH and PEO₃₉COOH) and was dried under vacuum overnight. Yields were between 60 and 84 %, depending on the molecular weight of the PEO starting material. ¹H NMR (300 MHz, CDCl₃, ppm): $\delta = 9.68$ (s, 1H), 4.11 (s, 2H), 3.60 (m, 4[m-1]H), 3.33 (s, 3H). For PEO₁₃COOH, $M_n = 622$ g mol⁻¹ (¹H NMR), $M_n = 620$ g mol⁻¹ (GPC); D = 1.16 (GPC). For PEO₃₉COOH, $M_n = 1800$ g mol⁻¹ (GPC); D = 1.14 (GPC).

Synthesis of poly(3-hexylthiophene)-*b*-poly(ethylene oxide) (P3HT-*b*-PEO) diblock copolymers by Steglich esterification⁵

P3HT-b-PEO was synthesised by Steglich esterification of P3HT-OH and PEO-COOH. In a 100 ml flame-dried round bottomed flask, P3HT₅₁-OH (0.2 g, 0.02 mmol), PEO₁₃-COOH (0.150 g, 0.2 mmol) and 1.6 mg of 4-DMAP (0.013 mmol) were added, and the flask was degassed under vacuum and backfilled with nitrogen gas three times. 30 ml of degassed chloroform (HPLC grade) was added to the reaction mixture and the solution stirred at 50 °C for 15 minutes. Then, DCC (34 mg, 0.16 mmol) dissolved in 3 ml chloroform (HPLC grade) was added dropwise using a syringe, and the solution was stirred at 50 °C for 2 days. The reaction mixture was precipitated into methanol and the copolymer purified by soxhlet extraction with methanol to remove excess homopolymer PEO-COOH. The copolymer was isolated with chloroform, precipitated in methanol, collected by filteration and then dried in vacuo at 50 °C to give pure copolymer with yields of 65 % to 94 % (depending on the PEO molar mass, see the main manuscript). The ¹H NMR spectra of P3HT₅₁-*b*-PEO₁₃ and its corresponding precursor polymers are shown in Figure S1 and those of the P3HT₅₁-*b*-PEO₃₉ are shown in Figure S2. ¹H NMR (300 MHz, CDCl₃, ppm): $\delta = 6.98$ (s, 1nH), 4.23 (m, 2H), 3.65 (m, 4[m-1]H), 3.38 (s, 3H), 2.80 (t, 2nH), 1.70 (m, 2nH), 1.43-1.34 (m, 6nH), 0.91 (t, 3nH). For P3HT₅₁-b-PEO₁₃, $M_{\rm n} \sim 9100 \text{ g mol}^{-1}$ (¹H NMR), $M_{\rm n} = 9700 \text{ g mol}^{-1}$ (GPC); D = 1.14 (GPC). For P3HT₅₁-*b*-PEO₃₀, $M_{\rm n} \sim 9800 \text{ g mol}^{-1}$ (¹H NMR), $M_{\rm n} = 10400 \text{ g mol}^{-1}$ (GPC); D = 1.15 (GPC). For P3HT₅₁-*b*-PEO₃₉, $M_{\rm n} \sim 10200 \text{ g mol}^{-1} ({}^{1}\text{H NMR}), M_{\rm n} = 11000 \text{ g mol}^{-1} (\text{GPC}); D = 1.24 (\text{GPC}).$

4. Discussion

Figures S1 to S3 show the ¹H NMR spectra of the PEO_mOH, PEO_{m-1}COOH and P3HT_nOH building blocks alongside the final coupled diblock copolymer, P3HT-*b*-PEO, where Figure S1 comprises low molar mass PEO (750 g mol⁻¹), Figure S2 moderately higher molar mass PEO (ca. 1,300 g mol⁻¹) and Figure S3 highest molar mass PEO (ca. 2,000 g mol⁻¹). In each spectrum, the unambiguous signals have been assigned to the corresponding protons in the polymer structure. It is noteworthy that the unassigned signal at approximately 2.55 ppm arises from any regio-irregularity of the P3HT. The complete conversion of PEO-OH to PEO-COOH is confirmed by the appearance of new peaks around 9.7 ppm (carboxylic acid proton) and 4.11 ppm (two methylene protons adjacent to the carboxylic acid group) and the appropriate signal ratio (2:3) of the latter with that of the three terminal methyl protons (3.33 pm).

Further comparison of the PEO backbone methylene protons with the end-group protons (either of the aforementioned peaks at 3.33 or 4.11 ppm), show that the lower molar mass PEO comprises 14 repeat units prior to oxidation and 13 units after, and the intermediate molar mass PEO comprises 32 repeat units before and 30 units after, whereas the higher molar mass PEO comprises 55 repeat units before, and 39 following oxidation. The GPC traces (Figures S4 to S6) also reflect this; there is a minor increase in retention time for the lower molar mass PEO materials, but a much more substantial change for the highest molar mass PEO samples. This has been previously observed for various PEO functionalization reactions.⁶ On-going work is focused on the optimisation of this PEO oxidation step, using various reagents and reaction times to suppress the molar mass reduction prior to coupling to P3HT. The P3HT block length was calculated using ¹H NMR spectroscopy, from the ratio of the end group methylene protons at 3.75 ppm with the aromatic proton in the repeat unit to reveal an approximate degree of polymerisation of 51.

Formation of the block copolymers is confirmed by the presence of peaks at 4.23 ppm, 3.65 ppm and 3.38 ppm, corresponding to PEO, in the appropriate ratios when to compared with those of P3HT (showing that there is no free P3HT present). Furthermore, the GPC traces of the diblock copolymers (Figure 1, main manuscript, and Figures S7 and S8) show negligible PEO homopolymer impurity, revealing that the PEO content is covalently bound to P3HT.

Figures 2 (main manuscript), S9 and S10 show the FTIR spectra of the diblock copolymers and corresponding homopolymer precursors. As discussed in the manuscript, the expected

bands are observed, confirming the conversion of PEO-OH to PEO-COOH and production of the diblock copolymers.



Figure S1. ¹H NMR spectra of P3HT₅₁-*b*-PEO₁₃, P3HT₅₁-OH, PEO₁₃-COOH and PEO₁₄-OH.



Figure S2. ¹H NMR spectra of P3HT₅₁-*b*-PEO₃₀, P3HT₅₁-OH, PEO₃₀-COOH and PEO₃₂-OH.



Figure S3. ¹H NMR spectra of P3HT₅₁-*b*-PEO₃₉, P3HT₅₁-OH, PEO₃₉-COOH and PEO₅₅-OH.



Figure S4.GPC traces of PEO₁₄-OH and PEO₁₃-COOH.



Figure S5. GPC traces of PEO₃₂-OH and PEO₃₀-COOH.



Figure S6.GPC traces of PEO₅₅-OH and PEO₃₉-COOH.



Figure S7.GPC traces of P3HT₅₁-*b*-PEO₃₀, P3HT₅₁-OH and PEO₃₀-COOH.



Figure S8.GPC traces of P3HT₅₁-*b*-PEO₃₉, P3HT₅₁-OH and PEO₃₉-COOH.



Figure S9. IR spectra of P3HT₅₁-*b*-PEO₃₀, P3HT₅₁-OH, PEO₃₀-COOH and PEO₃₂-OH.



Figure S10. IR spectra of P3HT₅₁-*b*-PEO₃₉, P3HT₅₁-OH, PEO₃₉-COOH and PEO₅₅-OH.

Scanning Electron Microscopy with Energy Dispersive X-ray Analysis (SEM-EDXA) with a Link system AN10000 and Cambridge Scanning Electron Microscope Stereoscan S90 was used to verify the metal content of our polymers. Firstly, the three metals used across this study (chromium, magnesium and nickel) were deliberately added (at 1 wt%) to a poly(ethylene oxide) sample to identify the individual metal peaks (Figure S11). The three metal peaks are clear at 1.16 - 1.36 eV, 5.26 - 5.58 eV and 7.30 - 7.58 eV for Mg, Cr and Ni, respectively. PEO₃₀-COOH showed no chromium content (Figure S12), indicating that the facile washing purification was sufficient following Jones oxidation. Likewise, P3HT₅₁-OH showed no magnesium or nickel contaminants according to the SEM-EDXA spectrum (Figure S13). Finally, the SEM-EXDA spectrum of the P3HT₅₁-*b*-PEO₃₀ block copolymer in Figure S14 shows that there are no metal contaminants, as expected. It is noteworthy that SEM-EDXA has a lower detection limit of ca. 0.1 % for these metals.



Figure S11. SEM-EDXA spectrum of PEO containing 1 wt% Mg, Cr and Ni.



Figure S12. SEM-EDXA spectrum of PEO₃₀-COOH.



Figure S13. SEM-EDXA spectrum of P3HT₅₁-OH.



Figure S14. SEM-EDXA spectrum of P3HT₅₁-*b*-PEO₃₀.

Matrix Assisted Laser Desorption Ionisation Spectroscopy with Time of Flight detection Mass Spectroscopy (MALDI-ToF MS) measurements were performed on a MALDI micro MX technologies using dithranol as the matrix. Measurements were performed in reflection mode to determine the P3HT chain end-groups present. Two major series of peaks were observed for both P3HT₅₁-allyl (Figure S15) and P3HT₅₁-OH (Figure S16). In the case of P3HT₅₁-allyl, the major peak series belongs to P3HT + C_3H_5 + H [selected example from Figure S15: for a 35-mer, 5862 Da = (35)

 \times 166.3) + 41 + 1] and the minor peak series belongs to P3HT + C₃H₅ + Br (selected example from Figure S15: for a 37-mer, 6274 Da = (37 × 166.3) + 41 + 79.9). In the case of P3HT₅₁-OH, the major peak series belongs to P3HT + C₃H₇O + H [selected example from Figure S16: for a 36-mer, 6047 Da = (36 × 166.3) + 59 + 1] and the minor peak series belongs to P3HT + C₃H₇O + Br [selected example from Figure S16: for a 37-mer, 6292 Da = (37 × 166.3) + 59 + 79.9].



Figure S15. MALDI-ToF spectrum of P3HT₅₁-allyl, showing the presence of both hydrogen and bromine terminated chain ends.



Figure S16. MALDI-ToF spectrum of P3HT₅₁-OH, showing the presence of both hydrogen and bromine terminated chain ends.

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