Polymer Chemistry

Accepted Manuscript

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Polymer Chemistry

PAPER

Highly functionalisable polythiophene phenylenes

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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The synthesis and properties of novel conducting polymer monomers, and their polymers, based on poly(thiophene phenylenes) (PThP) is described. These polymers contain a range of functional groups useful for further polymer modification and design and can be obtained using both electropolymerisation and chemical oxidative polymerisation. Further modification of a chemically polymerised PThP was validated using 'click' chemistry from azide containing side chains and also by grafting of polystyrene by Activator ReGenerated by Electron Transfer Atom Transfer Radical polymerisation (ARGET-ATRP) from an ATRP initiating sites on the polymer. The complimentary and orthogonal nature of 'click' chemistry and ATRP grafting was established. The polymers were characterised by ^{1}H NMR, UV-Vis spectroscopy and cyclic voltammetry. Electrochemical analysis showed that the functionalised polymers retain excellent electroactivity.

Introduction

Since their discovery,[1] electrically conducting polymers (ECP) have been used in a number of applications, ranging from light emitting diodes, photovoltaics, corrosion inhibitors, biosensors, drug delivery and other biomedical applications.[2] However, in spite of numerous significant advances in the field of applications of ECPs, there is still a substantial gap to fill in terms of synthesis of ECPs with advanced functionalities and processability.

Side-chain functionalization in ECP materials has been traditionally limited to short-chains[3] mainly as means of improving the material's solubility[4] and bearing recognition sites for sensing, with examples in polyaniline (PANI), polypyrrole (PPy), PTh (polythiophene) and poly(3,4-ethylenedioxythiophene) (PEDOT).[5–11] To date, functionalization with larger polymeric side chains has been fairly limited.[12] Recent research by us[5,13–16] and others[17–20] on grafting of ECPs with polymeric side chains provides a versatile and generalised approached to modification of ECPs' properties. The grafted brushes can be used to alter, and tailor, the polymer properties to specific needs.[21] In our previous work we utilised atom transfer radical polymerisation (ATRP), a method of controlled radical polymerisation (CRP) developed by Matyjaszewski, for 'grafting from' an electrode-surface confined ECP.[5,13–15,22,23]

Other versatile modification approach to functionalised ECPs is the use of 'click' chemistry[24], a high yielding reaction characterised by robustness to various functional groups.[25]

In this work, we describe the synthesis and properties of novel ECP monomers based on thiophene phenylenes, that carry versatile functional sites, and their polymers. We demonstrate their derivatisations in solution that produce organic solvent soluble ECPs amenable to further functionalization. The methodology provides a convenient route to designer ECPs. Poly(thiophene phenylene) (PThP) was chosen as the ECP backbone, due to its advantages over polythiophene, such as reduced oxidation potential, easy of termonomer synthesis and versatility in derivatisation. We present here the synthesis of a range of functionalised PThPs and showcase their electrochemical properties. Moreover, we demonstrate that a further, double functionalization by both 'click' chemistry and ATRP grafting can be performed on the same PThP polymer backbone. In particular, grafting of the polymer brushes by Activator ReGenerated by Electron Transfer Atom Transfer Radical Polymerisation (ARGET-ATRP) from PThPs is demonstrated before and after performing 'click' functionalization chemistry. The obtained polymers are soluble in a range of solvents, well preserve the electrochemical properties of the parent ECP and possess new functionalities brought by the grafted side chains.

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

2. Experimental

2.1 General Methods

2-Thiopheneboronic acid pinacol ester (97%), hydroquinone (99%), 3-bromopropanol (97%), potassium tert-butoxide (98%), tert-butyldimethylsilyl chloride (97%), phenylacetylene was purchased from AK Scientific and used as received. Triethylene glycol monomethyl ether (95%), hydroquinone bis(2-hydroxyethyl) ether (95%), palladium chloride, PMDETA, ascorbic acid, SPhos, hex-1-yne, mercury acetate, anisole, copper (II) chloride, 4-dimethylaminopyridine, 2-bromo propanoyl bromide, copper (II) sulphate pentahydrate, tin(II) ethylhexanoate, lithium perchlorate and sodium azide was purchased from Sigma-Aldrich and used as received. Nuclear magnetic resonance was carried out on a Bruker 300 MHz or 400 MHz with samples prepared in $CDCl_3$, DMSO-d_6 or MeOD. All melting points were measured using Reicher-Kofler block and are uncorrected.

2.2 Synthesis

2.2.1 Synthesis of 2,2'-(2,5-bis(2-(2-methoxyethoxy)ethoxy)-1,4-phenylene)dithiophene monomer (TGThP) 1.

The procedure to synthesise the monomer TGThP **1** is outlined in Figure 1 and in detail in the Supporting Information.

2-(2-(2-Methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate **6**. To a solution containing of 2-(2-(2-methoxyethoxy)ethoxy)ethanol (2.00 g, 12.0 mmol) and tosyl chloride (2.29 g, 10.94 mmol) in 10 mL dry $CH2Cl_2$ under an atmosphere of nitrogen at 0 °C, Et_3N (3.06 mL, 21.9 mmol) was added dropwise. The solution was warmed to room temperature and stirred for 18 h. The reaction was then quenched with addition of water (10 mL) and the organic layer separated. The aqueous phase was extracted with CH_2Cl_2 (20 mL) and the combined extracts washed with brine (10 mL), dried ($MgSO_4$) and solvent removed *in vacuo*. The crude product was purified by flash chromatography (3:1, ethyl acetate, hexanes) to yield *title product* **6** (2.63 g, 86%) as a red oil. R_f = 0.2, 3:1 ethyl acetate, hexanes. ^{1}H NMR (400 MHz; $CDCl_3$) 2.45 (3H, s, Ar-CH_3), 3.37 (3H, s, OCH_3), 3.51-3.70 (10H, m, OCH2), 3.59 (3H, s, Ar-CH_3) 4.14-4.19 (2H, m, OCH_2),), 7.36 (2H, d, *J* = 8.0 Hz, 3-H and 5-H), 7.79 (2H, d, *J* = 8.0 Hz, 2-H and 6-H); ^{13}C NMR (100 MHz; $CDCl_3$) 21.6, 59.6, 68.7, 69.2, 70.5, 70.6, 70.8, 71.9, 128.0, 129.8, 133.1, 144.8. The ^{1}H NMR and ^{13}C NMR in agreement with literature.[26]

1,4-Bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene **9**. To a solution of tosylate **6** (2.86 g, 9.00 mmol) and hydroquinone **5** (0.33 g, 3.00 mmol) in ethanol (30 mL) at 0 °C, ^{t}BuOK (1.01 g, 9.00 mmol) was added and the resulting mixture was heated at 70 °C for 24 h. The reaction was then cooled to room temperature and quenched with water (10 mL) and extracted with CH_2Cl_2 (3 x 30 mL). The combined extracts were washed with brine (30 mL), dried (Na_2SO_4) and solvent removed *in vacuo*. The crude product was purified using flash chromatography (3:1, ethyl acetate, hexanes) to yield the *title product* **9** (0.591 g, 49%) as a red oil. R_f = 0.5, (2:1 ethyl acetate, hexanes), ^{1}H NMR (400 MHz; $CDCl_3$) 3.38 (6H, s, OCH_3), 3.56-3.59 (4H, m, OCH_2), 3.69-3.73 (4H, m, OCH_2), 3.79-3.83 (4H, m, OCH_2), 4.02-4.08 (4H, m, OCH_2), 6.82 (4H, s, Ar-H); ^{13}C NMR (100 MHz; $CDCl_3$) 59.0 (CH_3), 66.0 (OCH_2), 66.8 (OCH_2), 70.6 (OCH_2), 71.9 (OCH_2), 115.6 (CH), 153.0 (C-1 and C-4). The ^{1}H NMR and ^{13}C NMR were in agreement with literature values.[16]

1,4-Diiodo-2,5-bis(2-(2-methoxyethoxy)ethoxy)benzene **13**. To a solution of diether **9** (0.71 g, 1.77 mmol) and iodine (1.79 g, 7.09 mmol) in CH_2Cl_2 (20 mL), mercury acetate (2.26 g, 7.09 mmol) was added and the resulting solution was stirred at room temperature for 5 h. The mixture was then diluted with CH_2Cl_2 (20 mL) filtered through celite, washed with sat. $Na_2S_2O_3$ (20 mL), sat. $NaHCO_3$ (20 mL), water (20 mL), brine (20 mL), dried (Na_2SO_4) and solvent removed in vacuo to yield *title product* **13** (0.782 g, 76%) as an orange oil, which was used without further purification. R_F = 0.5, (3:1 ethyl acetate, hexanes), ^{1}H NMR (400 MHz; $CDCl_3$) 3.38 (6H, s, OCH_3), 3.55-3.57 (4H, m, OCH_2), 3.64-3.70 (8H, m, OCH_2), 3.86-3.89 (4H, m, OCH_2), 4.09- 4.11 (4H, m, OCH_2), 7.23 (4H, s, Ar-H); ^{13}C NMR (100 MHz; $CDCl_3$) 59.1, 69.6, 70.3, 70.5, 70.6, 70.8, 71.2, 72.0, 86.4, 123.6, 153.1. The ^{1}H and ^{13}C NMR data were in agreement with literature values.[27]

2,2'-(2,5-Bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-1,4-phenylene)dithiophene (TGThP) **1**

To a solution of aryl diiodide **13** (0.300 g, 0.416 mmol) in ^{n}butanol (3 mL), thiophene boronate (0.231 g, 1.10 mmol), $Pd(OAc)_2$ (0.010 g, 4.46 µmol), SPhos (0.038 g, 0.093 mmol) and K_3PO_4 (0.292 g, 1.38 mmol) was added. The mixture was placed under an atmosphere of nitrogen, degassed by freeze-thaw-cycling, sealed and heated at 110 °C in a pressure tube for 20 h. The resulting mixture was then cooled, diluted with CH_2Cl_2 (10 mL), filtered through a silica plug and solvent removed *in vacuo*. The crude product was purified by flash chromatography (3:1, ethyl acetate, hexanes) to yield *title product* **1** (0.151 g, 58%) as a brown oil. R_F = 0.4 (2:1 ethyl acetate, hexane), IR ν_{max} (neat)/cm^{-1} 3671, 2972, 2882, 1453, 1353, 1102; ^{1}H NMR (400 MHz; $CDCl_3$) 3.36 (6H, s, OCH_3), 3.53 (4H, m, OCH_2), 3.64 (4H, m, OCH_2), 3.69 (4H, m, OCH_2), 3.75 (3H, m, OCH_2), 3.93 (OCH_2), 4.24 (4H, m, OCH_2), 7.09 (2H, dd, *J* = 5.1, 3.6 Hz, 4-H), 7.28 (2H, s, 3'-H and 6'-H), 7.32 (2H, dd, *J* = 3.6, 1.2 Hz, 5-H), 7.55 (2H, dd, *J* = 5.1, 1.2 Hz, 3-H); ^{13}C NMR (100 MHz; $CDCl_3$) 59.0 (CH_3), 69.2 (OCH_2), 69.8 (OCH_2), 70.6 (OCH_2), 70.7 (OCH_2), 70.9 (OCH_2), 71.9 ($ArOCH_2$), 113.67 (C-3' and C-6'), 123.4 (C-

2' and C-5'), 125.6 (C-5), 125.7 (C-3), 126.9 (C-4), 139.0 (C-2), 149.4 (C-1' and C-4'). HRMS (EI) found (MK^+) 605.1649. $C_{28}H_{38}KO_8S_2$ requires 605.16

2.2.2 Synthesis of 2,2'-(2,5-dimethoxy-1,4-phenylene)dithiophene (MeThP) 2

The procedure to synthesise the monomer MeThP **2** is outlined in Figure 1 and in detail in the Supporting Information.

1,4-Diiodo-2,5-dimethoxybenzene **12**. Following the procedure by Ko *et al*,[28] a solution of H_5IO_6 (2.92 g, 12.5 mmol) in methanol (25 mL) was stirred for 10 min, then iodine (6.38 g, 25.0 mmol) was added to the mixture. 1,4-Dimethoxybenzene **8** (2.70 g, 20.0 mmol) was added and the mixture was then heated at 70 °C for 4 h. The mixture was then poured into a solution of $Na_5S_2O_3$ (5.00 g, 31.6 mmol) in water (50 mL). The solution was filtered and the precipitate was washed with methanol (20 mL), dissolved in CH_2Cl_2 (20 mL) filtered and the filtrate was evaporated *in vacuo* to afford the *title product* **12** as a white solid (7.52 g, 97%). ^{1}H NMR (400 MHz; $CDCl_3$) 3.82 (6H, s, CH_3), 7.19 (2H, s, Ar). The ^{1}H NMR data was in agreement with literature values.[28]

2,2'-(2,5-Dimethoxy-1,4-phenylene)dithiophene (MeThP) **2**. To a solution of 1,4-diiodo-2,5-dimethoxybenzene **8** (0.16 g, 0.416 mmol) in ^{n}butanol (3 mL), thiophene boronate (0.23 g, 1.10 mmol), $Pd(OAc)_2$ (0.010 g, 4.46 µmol), SPhos (0.038 g, 0.093 mmol) and K_3PO_4 (0.29 g, 1.38 mmol) was added. The mixture was placed in an atmosphere of nitrogen, degassed by freeze-thaw-cycling, sealed and heated at 110 °C in a pressure tube for 20 h. The resulting mixture was diluted with CH_2Cl_2 (10 mL) filtered through a silica plug and solvent removed *in vacuo*. The crude product was purified by flash chromatography (9:1, hexanes, ethyl acetate) to yield *title product* **2** (0.54 g, 90%) as a yellow solid. Mp = 58-60 °C, R_f = 0.7 (4:1, hexanes ethyl acetate), IR ν_{max} (neat)/cm^{-1} 3340, 3093, 2993, 2939, 2829, 1533, 1393, 1289, 1039; ^{1}H NMR (400 MHz; $CDCl_3$); 3.93 (6H, s, OCH_3), 7.10 (2H, dd, *J* = 5.1, 4.1 Hz, 4-H), 7.25 (2H, s, 3'-H and 6'-H), 7.33 (2H, dd, *J* = 4.1, 1.1 Hz, 5-H), 7.35 (2H, dd, *J* = 5.1, 1.1 Hz, 3-H); ^{13}C NMR (100 MHz; $CDCl_3$) 36.5 (CH_3O), 112.0 (C-3' and C-6'), 123.0 (C-2' and C-5'), 125.5 (C-5), 125.7 (C-3), 126.9 (C-4), 139.0 (C-2), 150.0 (C-1' and C-4'). HRMS (EI) found (MH^+) 303.0497. $C_{16}H_{15}O_2S_2$ requires 303.0508.

2.2.3 Synthesis of 2,2'-(2,5-bis(3-azidopropoxy)-1,4-phenylene)dithiophene 3

The procedure to synthesise the monomer AzThP **3** is outlined in Figure 1 and in detail in the Supporting Information. Care must be taken when handling with azide containing compounds as low molecular weight azide is known to be explosive. Suzuki reaction to form **3** was altered to milder condition to take into account of the potential hazard.

3-Azidopropan-1-ol. To a solution of 3-bromopropan-1-ol (1.00 g, 7.08 mmol) in water (10 mL) at 0 °C, sodium azide (0.94 g, 14.2 mmol) was added. The mixture was stirred and heated to 80 °C for 24 h, cooled to room temperature, extracted with ethyl acetate (3 x 20 mL). The combined extracts were dried (Na_2SO_4) and the solvent removed *in vacuo*. The crude product was purified by flash chromatography (4:1, hexanes, ethyl acetate) to yield the *title product* (0.65 g, 89%) as a colourless liquid. R_f = 0.3 (4:1 hexanes, ethyl acetate), ^{1}H NMR (400 MHz; $CDCl_3$) 1.81 (2H, qi, *J* = 6.5 Hz, 2-H), 3.41 (2H, t, *J* = 6.5 Hz, 3-H), 3.69 (2H, t, *J* = 6.5 Hz, 1-H); ^{13}C NMR (100 MHz; $CDCl_3$) 31.4, 48.2, 59.2. The ^{1}H NMR and ^{13}C NMR was in agreement with literature values.[29]

3-Azidopropyl 4-methylbenzenesulfonate **7**. To a solution of 3-azidopropan-1-ol (1.38 g, 13.5 mmol) and tosyl chloride (2.84 g, 15.0 mmol) in CH_2Cl_2 (30 mL) at 0 °C under an atmosphere of nitrogen, Et_3N (3.70 mL, 27.0 mmol) was added. The solution was warmed to room temperature and stirred for 18 h. The reaction was then quenched with water (30 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The combined extracts were washed with brine (30 mL), dried ($MgSO_4$) and solvent removed *in vacuo*. The crude product was purified with flash chromatography (9:1, hexanes, ethyl acetate) to yield the *title product* **7** (3.20 g, 93%) as a pale yellow oil. R_f = 0.4 (4:1 hexanes, ethyl acetate), ^{1}H NMR (400 MHz; $CDCl_3$) 1.88 (2H, qi, *J* = 8.7 Hz, 3-H), 2.45 (3H, s, CH_3), 3.37 (2H, t, *J* = 8.7 Hz, 3-H), 4.10 (2H, t, *J* = 8.7 Hz, 1-H), 7.36 (2H, d, *J* = 8.0 Hz, 3'-H and 5'-H), 7.79 (2H, d, *J* = 8.0 Hz, 2'-H and 6'-H); ^{13}C NMR (100 MHz; $CDCl_3$) 21.6, 28.4, 47.3, 67.1, 127.9, 129.9, 132.8, 145.1. The ^{1}H NMR and ^{13}C NMR was in agreement with literature values.[29]

1,4-Bis(3-azidopropoxy)benzene **10**. To a solution of tosylate **7** (5.63 g, 22.0 mmol) and hydroquinone **5** (0.89 g, 8.80 mmol) in ethanol (50 mL), at 0 °C under atmosphere of nitrogen, ^{t}BuOK (2.96 g, 26.4 mmol) was added and the resulting mixture was heated at 70 °C for 24 h. The mixture was then quenched with water (30 mL) and extracted with CH_2Cl_2 (3 x 40 mL). The combined extracts were then washed with brine (30 mL), dried (Na_2SO_4) and solvent removed *in vacuo*. The crude product was purified using flash chromatography to yield *title product* **10** (1.50 g, 62%) as a colourless oil. R_f = 0.6 (4:1 hexanes, ethyl acetate), ^{1}H NMR (400 MHz; $CDCl_3$) 2.03 (4H, qi, *J* = 6.6 Hz, 2-H), 3.51 (4H, t, *J* = 6.6 Hz, 3-H), 4.00 (4H, t, *J* = 6.6 Hz, 1-H), 6.83 (4H, s, Ar-H); ^{13}C NMR (100 MHz; $CDCl_3$) 28.9, 48.3, 65.2, 115.5, 153.0. HRMS (EI) found (MNa^+) 299.1230. $C_{12}H_{16}N_6NaO_2$ requires 299.1227.

1,4-Bis(3-azidopropoxy)-2,5-diiodobenzene **14** To a solution of diazide **10** (1.00 g, 3.61 mmol) in CH_2Cl_2 (20 mL), mercury acetate (5.16 g, 16.2 mmol) and iodine (4.11 g, 16.2 mmol) was added. The resulting solution was stirred for 24 h, and was then filtered through celite, washed with sat. $Na_2S_2O_3$ (20 mL), sat. $NaHCO_3$ (20 mL), water (20 mL) and brine (20

mL) and then dried (Na_2SO_4) and solvent removed *in vacuo* to yield *title product* **14** (1.31 g, 70%) as a yellow solid which was used without further purification. Mp = 74-76 °C; R_f = 0.7 (4:1 hexanes, ethyl acetate), IR ν_{max} (neat)/cm^{-1} 3355, 2963, 2937, 2166, 2092; ^{1}H NMR (400 MHz; $CDCl_3$) 2.06 (4H, qi, *J* = 6.5 Hz, 2-H), 3.60 (4H, t, *J* = 6.5 Hz, 3-H), 4.04 (4H, t, *J* = 6.5, 1-H), 7.20 (2H, s, C-2' and C-5'); ^{13}C NMR (100 MHz; $CDCl_3$) 28.7 (C-2), 48.2 (C-3), 66.8 (C-1), 86.3 (C-2' and C-5'), 122.9 (C-3' and C-6'), 132.7 (C-1' and C-4').

2,2'-(2,5-Bis(3-azidopropoxy)-1,4-phenylene)dithiophene (AzThP) **3**. To a solution of diiodide **14** (0.67 g, 1.26 mmol) in DMF (20 mL), thiophene boronate (0.64 g, 3.03 mmol), K_3PO_4 (0.80 g, 3.79 mmol), tetrakis(triphenylphosphine)palladium(0) (0.14 g, 0.13 mmol) was added and the mixture was placed under an atmosphere of nitrogen. The mixture was heated at 70 °C for 48 h, cooled to room temperature, quenched with water (20 mL) and extracted with CH_2Cl_2 (40 mL). The organic extract was then washed with brine (20 mL), dried ($MgSO_4$) and solvent removed *in vacuo*. The crude product was purified by flash chromatography (4:1 hexanes, ethyl acetate), to yield *title product* **3** (0.18 g, 32%) as a yellow-white solid. Mp = 82-84 °C; R_f = 0.4 (4:1 hexanes, ethyl acetate), IR ν_{max} (neat)/cm^{-1} 2963, 2925, 2092, 1431; ^{1}H NMR (400 MHz; $CDCl_3$) 2.15 (4H, qi, *J* = 6.3 Hz, 2''-H), 3.60 (4H, t, *J* = 6.3 Hz, 1''-H), 4.18 (4H, t, *J* = 6.3 Hz, 3''-H), 7.11 (2H, dd, *J* = 5.0, 3.5 Hz, 4-H), 7.25 (2H, s, 3'-H and 6'-H), 7.36 (2H, dd, *J* = 5.0, 1.0 Hz, 5-H), 7.48 (2H, dd, *J* = 3.5, 1.0 Hz, 3-H); ^{13}C NMR (100 MHz; $CDCl_3$) 29.0 (C-2''), 48.5 (C-3''), 66.6 (C-1''), 113.1 (C-3' and C-6'), 123.4 (C-2' and C-5'), 125.3 (C-5), 126.0 (C-3), 126.8 (C-4), 140.1 (C-2), 149.1 (C-1' and C-4'); HRMS (EI) Found (MNa^+) 463.0976. $C_{20}H_{20}N_6NaO_2S_2$ requires 463.0981.

2.2.4 Synthesis of ((2,5-di(thiophen-2-yl)-1,4-phenylene)bis(oxy))bis(ethane-2,1-diyl) bis(2-bromopropanoate) 4

The procedure to synthesise radical initiator monomer **4** is outlined in Figure 1 and in detail in the Supporting Information.

2,2'-((2,5-Diiodo-1,4-phenylene)bis(oxy))diethanol **15**. To a solution of 2,2'-(1,4-phenylenebis(oxy))diethanol **12** (3.00 g, 15.2 mmol) in methanol (20 mL) at 0 °C, iodine monochloride (9.82 g, 60.6 mmol) in methanol (10 mL) was added dropwise and the resulting mixture heated at reflux for 6 h. The mixture was then cooled to room temperature and solvent was removed *in vacuo*. The crude product was dissolved in CH_2Cl_2 (50 mL) washed with sat. $Na_sS_2O_3$ (50 mL), brine (50 mL), water (50 mL), dried ($MgSO_4$) and solvent removed *in vacuo* to yield *title product* **15** (5.01 g, 74%) as a white solid, which was used without further purification. Mp = 167-170 °C, R_f = 0.3 (1:1 hexanes ethyl acetate), ^{1}H NMR (400 MHz; DMSO-d6) 3.71 (4H, q, *J* = 5.4 Hz, 2-H), 4.00 (4H, t, *J* = 5.4 Hz, 1-H), 4.83 (2H, t, *J* = 5.4 Hz, OH), 7.39 (2H, s, Ar-H); ^{13}C NMR (100 MHz; $CDCl_3$) 59.6, 71.9, 87.1, 123.1, 152.7. The ^{1}H and ^{13}C NMR data were in agreement with literature values.[30]

2,2'-((2,5-Di(thiophen-2-yl)-1,4-phenylene)bis(oxy))diethanol. To a solution of diiodide **15** (1.17 g, 2.60 mmol) in DMF (30 mL), thiophene boronate (1.37 g, 6.51 mmol), K_3PO_4 (1.84 g, 7.81 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.29 g, 0.26 mmol) was added and the mixture was placed under an atmosphere of nitrogen. The mixture was heated at 70 °C for 48 h, cooled to room temperature, quenched with water (30 mL) and extracted with CH_2Cl_2 (3 x 30 mL). The combined extracts were washed with brine (30 mL), dried (Na_2SO_4) and solvent removed *in vacuo*. The crude product was purified by flash chromatography (3:1 hexanes, ethyl acetate), to yield *title product* (0.67 g, 71%) as a yellow solid. Mp = 145-150 °C. R_f = 0.5 (2:1 hexanes, ethyl acetate), IR ν_{max} (neat)/cm^{-1} 3209, 3071, 2926, 2856, 1536, 1488, 1402, 1281; ^{1}H NMR (400 MHz; $CDCl_3$) 4.02-4.07 (4H, m, H-2''), 4.22 (4H, t, *J* = 4.5 Hz, H-1''), 7.12 (2H, dd, *J* = 5.0, 3.8 Hz, 4-H), 7.29 (2H, s, 3'-H, 6'-H), 7.37 (2H, dd, *J* = 5.0, 0.9 Hz, 5-H), 7.49 (2H, dd, *J* = 3.8, 0.9 Hz, 3-H); ^{13}C NMR (100 MHz; $CDCl_3$) 61.5 (C-2''), 71.2 (C-1''), 113.3 (C-3' and C-6'), 123.5 (C-2' and C-5'), 125.3 (C-5), and 126.1 (C-3), 126.9 (C-4), 138.6 (C-2), 149.5(C-1' and C-4'); HRMS (EI) Found (MH^+) 363.0707. $C_{18}H_{19}O_4S_2$ requires 363.0719.

((2,5-Di(thiophen-2-yl)-1,4-phenylene)bis(oxy))bis(ethane-2,1-diyl) bis(2-bromopropanoate) (BIThP) **4**. To a solution of 4-dimethylaminopyridine (0.096 g, 0.79 mmol) and bis-ethanol thiophene phenylene (0.572 g, 1.58 mmol) in CH_2Cl_2 (40 mL) at 0 °C under an atmosphere of nitrogen, Et_3N (0.66 mL, 4.49 mmol) was added dropwise followed by addition of 2-bromopropanoyl bromide (0.50 g, 2.37 mmol) dropwise. The resulting mixture was stirred at room temperature for 24 h and then quenched with water (20 mL). The organic layer was separated and then washed with brine (30 mL), sat. $NaHCO_3$ (20 mL), dried ($MgSO_4$) and solvent removed *in vacuo*. The crude product was purified by flash chromatography (3:1 hexanes, ethyl acetate) to yield *title product* **4** (0.85 g, 85%) as a yellow oil. R_f = 0.8 (3:1, hexanes, ethyl acetate); ν_{max} (neat)/cm^{-1} 3111, 2926, 1738, 1214; ^{1}H NMR (400 MHz; $CDCl_3$) 1.81 (6H, d, *J* = 7.1 Hz, CH_3), 4.32 (4H, t, *J* = 4.8 Hz, 2''-H), 4.39 (2H, q, *J* = 7.1 Hz, $CHCH_3$), 4.54-4.64 (4H, m, 1''-H), 7.10 (2H, dd, *J* = 5.3, 4.0 Hz, 4-H), 7.25 (2H, s, 3'-H, 6'-H), 7.34 (2H, dd, *J* = 5.3, 1.5 Hz, 5-H), 7.54 (2H, dd, *J* = 4.0, 1.5 Hz, 3-H); ^{13}C NMR (100 MHz; $CDCl_3$) 21.6 (CH_3), 39.8 (C-2''), 64.2 (C-1''), 67.3 ($CHCH_3$), 113.8 (C-3' and C-6'), 123.7 (C-2' and C-5'), 125.8 (C-5), 126.0 (C-3), 127.1 (C-4), 138.5 (C-2), 149.2 (C-1' and C-4'), 170.3 (CO); HRMS (EI) Found (MK^+) 668.9006. $C_{24}H_{24}Br_2KO_6S_2$ requires 668.9013.

2.2.5 General procedure for chemical polymerisation

A solution of monomer **1**, **2**, **3**, or **4** (0.20 mmol) in CH_3NO_2 (1 mL) was prepared and stirred for 10 min under an atmosphere of nitrogen at 0 °C. A solution of $FeCl_3$

(0.30 mmol) in CH_3NO_2 (1 mL) was added to the mixture dropwise and the resulting solution was stirred for 4 days at room temperature. The mixture was then quenched with water (2 mL), nitromethane removed *in vacuo*, the precipitate collected via filtration and washed with cold methanol. The products produced from all monomer polymerisation were dark green solids. The molecular weight measured was between 14,000 MW and 50,000 MW (Supporting Information, Table **S1**). The figures are similar or higher than those previously reported in the literature for similar polymers.[31]

2.2.6 General procedure for 'click' reactions

To a solution of PThPs **P3**, **P5** or **P6** (0.02 mmol) in THF (2 mL), alkyne (0.02 mmol) was added. A solution of ascorbic acid (2.00 µmol) and copper sulphate hexahydrate (2.00 µmol) in water (2 mL) was added dropwise to the polymer solution and the resulting mixture was stirred for 48 h. The mixture was extracted with ethyl acetate (3 x 10 mL) and the combined extracts washed with water (5 mL), brine (5 mL), dried (Na_2SO_4) and solvent removed *in vacuo* to give triazole polymers **P7** to **P13**. For the all alkynes used (hex-1-yne **16**, phenylacetylene **17** and propargyl *tert*-butyldimethylsilane (TBDMS) **18**) the resulting polymers were orange.

2.2.7 Grafting of styrene brushes via ARGET ATRP

Polystyrene brushes were grafted via Activators ReGenerated by Electron Transfer (ARGET) ATRP in solution as shown in Figure 4. Distilled styrene (561 mg, 5.40 mmol) was added to flask containing a solution of macroinitiator **P4**, **P5** or **P6**, toluene (10 mL) and anisole (0.50 mL). The solution was bubbled with nitrogen for 30 minutes, $Cu(II)Cl_2$ (2.00 mg, 18.0 µmol) was added, flask sealed and flushed with nitrogen. *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDTA) (3.10 mg, 18.0 µmol) was added and the solution was heated to 110 °C. A solution of tin(II) 2-ethylhexanoate in toluene (2 mL) was degassed and added to the reaction was stirred for 7 h. The reaction was stopped by opening to air and reaction allowed to be cooled to room temperature. The resulting solution was then diluted with CH_2Cl_2 (20 mL) washed with water (10 mL), dried ($MgSO_4$) and solvent removed *in vacuo* yielding macroinitiator grafted with styrene.

2.3.1 Electropolymerisation

Electropolymerisation was carried out potentiodynamically by potential cycling from +0.20 to +0.95 V (vs. Ag/AgCl (3M KCl, +0.197 V vs. SHE)at a scan rate of 100 mV s^{-1}, using CH Instruments electrochemical workstation (Model 440, CH Instruments USA). A three-electrode electrochemical cell was used, where the working electrode was BASI 0.5 mm gold coated, the counter electrode was platinum wire while the reference electrode was Ag/AgCl (3 M KCl), 0.230 V against standard hydrogen electrode (SHE). The polymerisation was carried out in 0.1 M $LiClO_4$ using 0.05 M thiophene monomer solution in acetonitrile.

2.4 Characterisation

2.4.1 Cyclic voltammetry

Cyclic voltammetry (CV) was carried by potential cycling between 0.2 and 0.75 V (vs. Ag/AgCl (3M KCl, +0.197 V vs. SHE) and by varying the scan rate between 5 mV s^{-1} to 250 mV s^{-1} in 0.1 M $LiClO_4$ solution in 4:1 H_2O:MeCN. Gold working electrode was modified with the polymer as per 2.3.1, reference electrode was Ag/AgCl (3 M KCl) and platinum wire counter electrode.

2.4.2 UV-Vis

UV-Visible spectrum was carried out using Shimadzu Spectrophotometer (Model UV-1700) on a polymer solution in CH_2Cl_2. The polymer solution was diluted to an absorbance value below 0.05 to prevent self-quenching.

2.4.3 Conductivity

The room temperature conductivity of compressed pellets was measured by a standard four-probe method using a Jandel Model RM2 instrument. The 250 mg of samples were pelletized to a diameter of 1.5 cm using a mechanical press.

2.4.4 Gel permeation chromatography

Molecular weights were determined with TDA_{max} GPC system (Polymerlabs) attached using the Polymerlabs PL50 with a UV detector (280 nm). DMF filtered through 0.02 µm PTFE membrane filter (Grace) was used as eluent with the flow rate of 1 mL min^{-1}. 100 µL of polymer solutions at concentration of 0.10 mg mL^{-1} were injected into the column. All samples were filtered through 0.22 µm PTFE syringe filters (Grace) before injection. The columns and the detectors were maintained at 35 °C. Calibration curve was plotted using polystyrene standards obtained from Sigma.

3. Results and Discussions

The synthesised thiophene phenylene 'termonomers' were designed in such a way to allow a great flexibility in manipulating of the polymer properties and to allow us to build polymers in a "Lego blocks" fashion (Figure 1 and Figure 2). For that purpose the termonomers were modified in such a way that the central heterocycle ring was chosen to be a phenylene ring with two thiophene side rings, thus creating poly[1,4-bis(2-thiophene)-p-phenylenes] (PThPs). The phenylene ring here carries a range of useful substituents, some of which provide a handle for further polymer modification. To the best of our knowledge, all polymers prepared in this work, except PMeThP **P1**,[32] are novel and not previously reported.

The advantage of utilising PThP, where the central thiophene is exchanged with benzene, rather than terthiophene was threefold. Firstly, the monomers retain

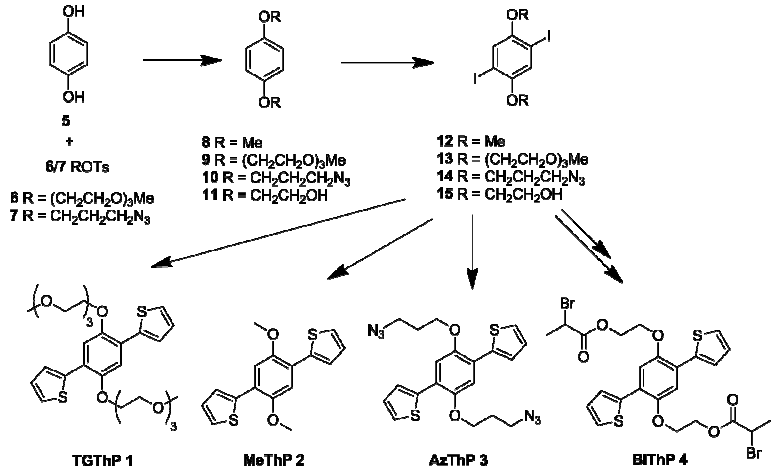

Figure 1: General synthesis pathway of monomers.

the benefit of lower oxidative potentials of terthiophenes compared to polythiophene.[33] Whilst some of thiophene derivatives, such as EDOT[34] and terthiophenes exhibit an oxidation potential that is lower than non-modified thiophene[35], the termonomers synthesized in this work undergo electropolymerisation at even lower potentials, as presented below in section 3.6. Secondly, with functionality being appended to only benzene rings the substitution is not expected to hinder α-α addition during oxidative polymerisation of the termonomers. The use of derivatised thiophenes leads to poor alignment of the aromatic rings due to steric hindrance between the substituents, which directly correlates to impairment of electrical activity.[36] Conversely, the use of thiophene phenylenes has been shown to contribute to greater regioregularity.[37] Thirdly, functionality is positioned on the every third ring, spacing out the substituted benzene rings and allowing further chemical functionalization at these sites.

Childs *et al* showed that the use of electron donating alkoxy substituents leads to better polythiophene(phenylene) and polyfuran(phenylene) conductivity, lower optical band gap and lower oxidation potential due to the increase in electron density in the π-conjugated system.[38] Steric effects of side chains also affect conductivity, where the energy barrier to attain a planar π system needed for high conjugation and conductivity increases. Planar system also allows two-dimensional charge transport through π-stacking.[39] By using ThPs substituted with alkoxy substituents we hypothesised that the prepared polymers will preserve conductivity and at the same time would allow us to easily alter the side chains by adding various functionalities without significant deviation of the main synthetic procedure.

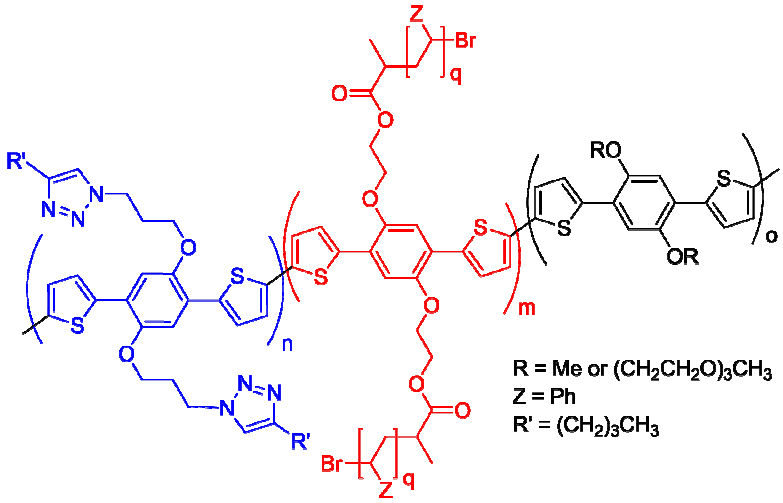

Figure 2: Examples of functionalised PThPs with 'click' and ATRP

The use of 1,4-disubstituted phenylene rings doubles the number of functional sites available per each termonomer unit (as two functional groups/side chains are added per phenylene ring), increasing density of the functional groups. For example, the dual tri-ethylene glycol side chains on the tri-ethylene glycol thiophene phenylene **1** (TGThP) were added to overcome highly hydrophobic chemical nature of thiophene polymers. Ethylene glycol chains are known to prevent non-specific protein adsorption, making the polymer a potential candidate for biomedical applications.[40]

In addition to ethylene glycol side chains, we particularly focused on adding functionalisable groups that enable further functionalization - an azide, which could be modified in labile conditions through 'click' reactions, and an ATRP initiator site, which allows for the grafting of polymeric side chain (Figure 2). The interesting aspects of the synthesized monomers are their ability to co-polymerise. The copolymer can be then easily post-polymerisation modified through both 'click' and ATRP that could be performed interchangeably, as discussed below in 3.2 – 3.4.

The synthetic procedure to obtain all of monomers was performed using a similar pathway, as outlined in Figure 1. 1,4-Hydroquinone alkylated with functional groups was subjected to iodination with subsequent Suzuki cross-coupling. MeThP **2** was synthesised starting from commercially available 1,4-dimethoxybenzene, where it was reacted following the general procedure of iodination followed by Suzuki cross-coupling to obtain monomer **2**.

For TGThP, tosylate **6** was prepared, which allowed alkylation with hydroquinone to form diether **9**, subsequent iodination and Suzuki cross-coupling to form monomer **1**.

Monomer AzThP **3** was prepared in a similar approach using tosylate **7**, which was obtained in two steps from 3-bromo-propan-1-ol. BIThP **4** was synthesised using commercially available hydroquinone bis(2-hydroxyethyl) ether, which was iodinated, followed by Suzuki cross-coupling and finally acylation with 2-bromopropionyl bromide.

3.1 Chemical polymerisation

To produce larger amounts of polymers needed for a range of experiments (and also considering any future applications of these materials) chemical polymerisation was employed, as opposed to electropolymerisation that enables the production of films of a controlled thickness but in limited quantities.

The chemical oxidative polymerisation of MeThP **2** and TGThP **1** in nitromethane using six equivalence of iron(III) p-toluenesulfonate hexahydrate as an oxidant yielded a green polymer film which was insoluble in all investigated organic solvents. The use of six equivalence $FeCl_3$ in nitromethane also led to the formation of green insoluble polymer powder. Reducing the equivalence of $FeCl_3$ to 1.5, with stirring overnight, led to the formation of a red powder, likely consisting of oligomers; however an extended time for the reaction to 4 days at room temperature yielded a green, soluble polymer. The formation of the soluble polymer with lower ratio of oxidant to monomer indicates that the higher ratios most likely formed a cross-linked polymer.[41] The highly coloured reaction mixture, due to the presence of $FeCl_3$ in CH_3NO_2, meant it was not possible to track the colour change as the reaction progressed. Eight hour polymerisation of MeThP **1** resulted in an orange polymer, whereas the polymerisation

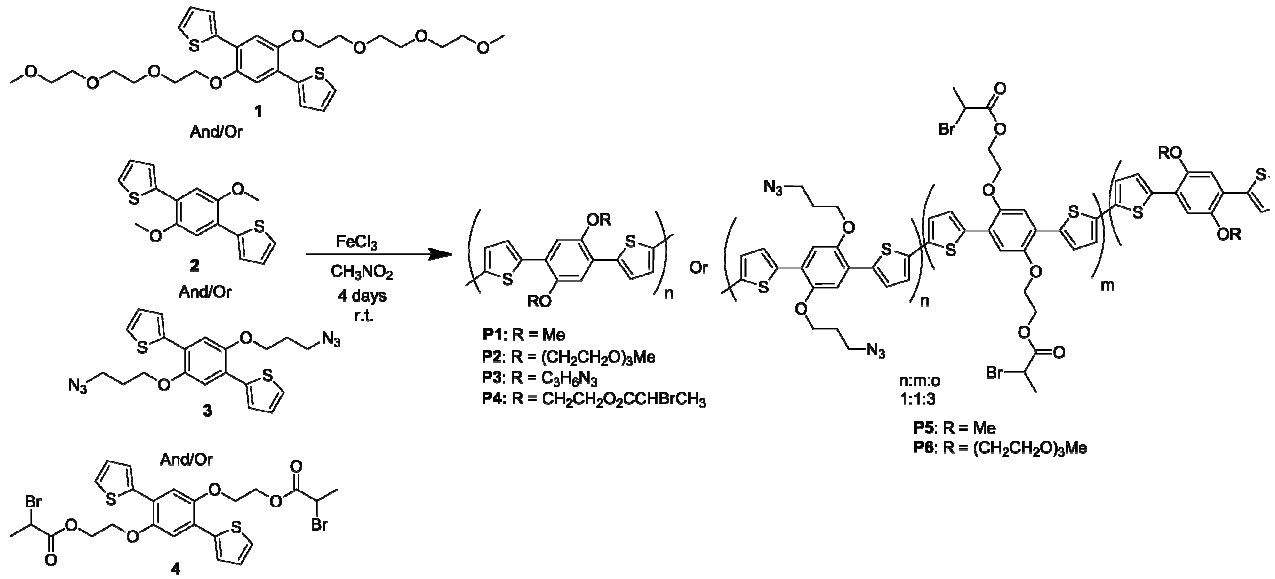

Figure 3: Reaction conditions for chemical oxidative polymerization

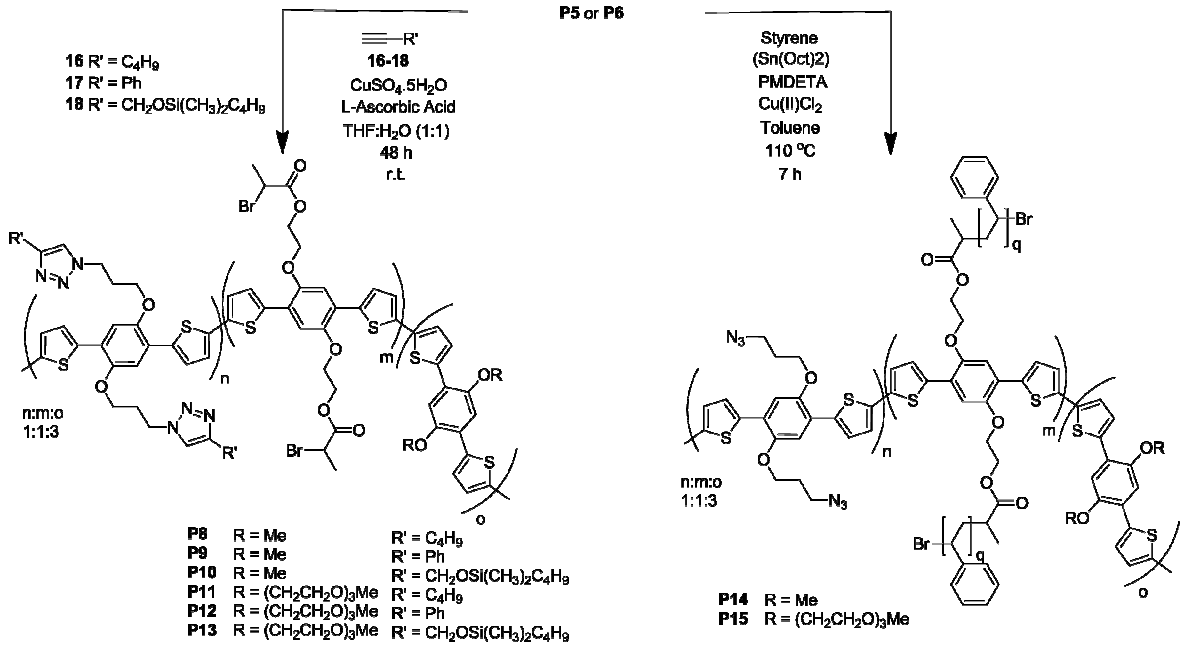

Figure 4: Functionalization of **P5** and **P6** with 'click' chemistry and ATRP of styrene, respectively

reactions that were allowed to run for 4 days resulted in a green polymer (Figure 3). All other polymerisation using these conditions resulted in the formation of green polymers. The terpolymer **P5** and **P6** were prepared using the same method as above using MeThP **2** or TGThP **1** (12.0 µmol) along with AzThP **3** (4 µmol) and BIThP **4** (4 µmol) to produce TMeThP **P5** and TTGThP **P6**. Success of polymerization of both polymers was confirmed by GPC analysis (Supporting Information, Table S1) showing M_W of between 24,000 and 36,000. ^{1}H NMR spectrum of the co(ter)polymers showed that the 3:1:1 ratio of the monomers was retained in the polymer. The yield for these reactions ranges typically from 60 to 80%.

3.2 Click chemistry

The inclusion of side chains with azides on the polymer allowed us to perform 'click' reactions via Cu^I-catalyzed Huisgen 1,3-dipolar addition of the azide and terminal alkynes.[25] The terpolymers **P3**, **P5** or **P6**, prepared by oxidative chemical polymerisation as described above, were subjected to a 'click' reaction, as described in the experiment section 2.2.6. The characterisation of the product of the click reaction was performed using NMR spectroscopy. The yields for 'click' reactions are 70 - 90% with GPC results provided in Supporting information, Table S1. There is an increase in M_n of the polymers after click reaction was performed which indicates successful addition. However, M_w decreases which we ascribe to high molecular weight polymers not dissolving in the reaction mixture and therefore the high molecular weight fraction was likely removed in the work up procedure.

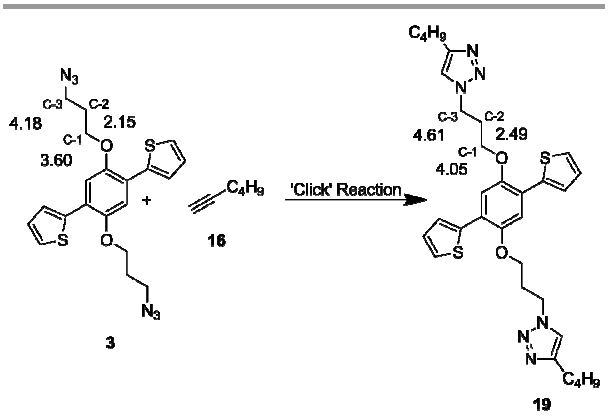

Figure 5: Chemical shift of protons in ^{1}HMR on propyl chain before and after triazole formation.

The broad H^1 NMR signals of the polymers impair differentiation between the characteristic peaks. However, ^{1}H-^{1}H correlation spectroscopy (COSY), was an effective tool to analyse the conversion of azide to triazole due to the chemical shifts of the protons on the propyl chain. The proton shifts on the propyl linker of monomer **3**, C-1, C-2 and C-3, are seen at 3.60, 2.15 and 4.18 ppm respectively (Figure 5). After 'click' reaction with hex-1-yne **16**, there is an easily observed downfield shift, in triazole **19**, of the signals to 4.05, 2.49 and 4.61 ppm respectively. When in polymeric form, the broad nature of the signals meant the shift in signals could not be easily identified. However, crosspeaks on the COSY spectrum remained well defined and the crosspeaks between C-1 and C-2, and C-3 and C-2 was used to identify the chemical shifts of the protons on the propyl linker (Supporting Information, Figure S6 – S8). It

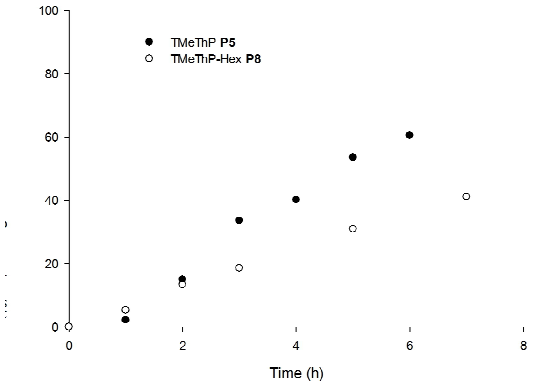

Figure 6: Plot of the conversion of styrene vs time for ARGET ATRP for TMeThP **P5** and TMeThP-Hex **P8**.

was found that this method is better suited than IR spectroscopy to characterise these polymers. Whilst the disappearance of the diagnostic azide signal, at ~2000 cm^{-1}, was observed after 'click' reactions, signals for the newly formed triazole, at ~1600 cm^{-1}, could not be observed due to overlap with others. In contrast, crosspeaks on COSY spectrum exhibit little overlapping and thus the extent of triazole conversion could be determined from the intensity of crosspeaks between signals associated with azide to those associated with triazole. The crosspeaks could also be used to clearly determine the associated signal in ^{1}H NMR despite the overlap and thus determine the integration of the corresponding peak which allows quantitative measurement of the extent of conversion.

Synthesis of the triazoles was more efficient for TMeThP **P5** and TTGThP **P6** in comparison to PAzThP **P3**, and led to complete conversion from azide to triazole as judged from the absence of the proton signals associated with the propyl azide side chain. Incomplete conversion of azide in **P3** is likely due to the closer proximity of the numerous azide sites, leading to steric hindrance from the formed triazole groups. Spacing out of the azide groups with non-functionalised methoxy or tri-ethylene glycol PThP units led to greater rate of conversion, with crosspeaks associated with azide side chain undetectable in COSY spectrum, indicating almost complete conversion to triazole. The use of hex-1-yne **16** demonstrated the feasibility of the click reaction with the prepared terpolymers, whilst reactions with TBDMS protected propargyl alcohol **17** and phenylacetylene **18** demonstrated that the reaction is also compatible with other alkynes; the crosspeaks associated with azide side chain were undetectable in all 'click' reactions performed with the above alkynes on **P5** or **P6**, indicating complete, or close to complete, conversion. The performed reactions show that a variety of compounds could be easily grafted to the polymers using 'click' chemistry methodologies to provide a simple and versatile route to conducting polymers with complex architecture, chemistry and designer multi-functionality.

The UV-vis spectrum of TMeThP **P5** and TTGThP **P6** are presented in Supporting Information, Figure S12. Absorption peak at around 430 nm, which corresponds to the π–π* transition seen in terthiophenes, was observed.[13] TMeThP-Hex **P8** also showed absorption at around 430 nm confirming that the presence of the triazole does not affect the core backbone of the TMeThP **P6** polymer. It was noticed that in PAzThP **P3**, the adsorption peak was broader than that of the other investigated polymers.

3.3 Atom-Transfer Radical Polymerisation

The use of Activators ReGenerated by Electron Transfer (ARGET) ATRP was chosen due to the robustness of the procedure, with the additional benefit of being more environmentally friendly then conventional ATRP.[42] The grafting of styrene as model polymer brushes was carried out *via* $Cu(II)Cl_2$ catalyst with PMDETA as ligand and tin ethylhexanoate as the reducing agent.

The monomer conversion was determined from the concentration of the residual monomer using NMR spectroscopy, with anisole as the internal standard. The grafting of polystyrene using ARGET ATRP of both TMeThP **P5** and TMeThP-Hex **P8** as the macroinitiator to form TMeThP-Sty **P14** and TMeThP-HexSty **P16** respectively was studied. The propagation of side chain for both macroinitiator was linear with time, indicating controlled, uniform grafting of styrene (Figure 6), but the initiation was slow or delayed. This may be due to steric hindrance of neighbouring side chains initially, which is alleviated as the chain propagates. An additional aliquot was analysed at 24h and it showed no sign of any residual styrene (by NMR analysis) for both macroinitiator. We observed that the grafting occurred at a faster rate with the non-triazole-containing macroinitiator TMeThP **P5**, where it reached 50% monomer conversion in less than 5 h (Figure 6), whereas TMeThP-Hex **P8** had not reached 50% conversion in 7 h. This indicates there may be some steric effects from neighbouring triazoles, reducing accessibility of the styrene monomer to the initiator site, however, grafting still proceeds. GPC results for TMeThP-Sty **P14** are provided in Supporting Information, Table S1 and Figure S5. The yield for these reaction ranges from 40-50%.

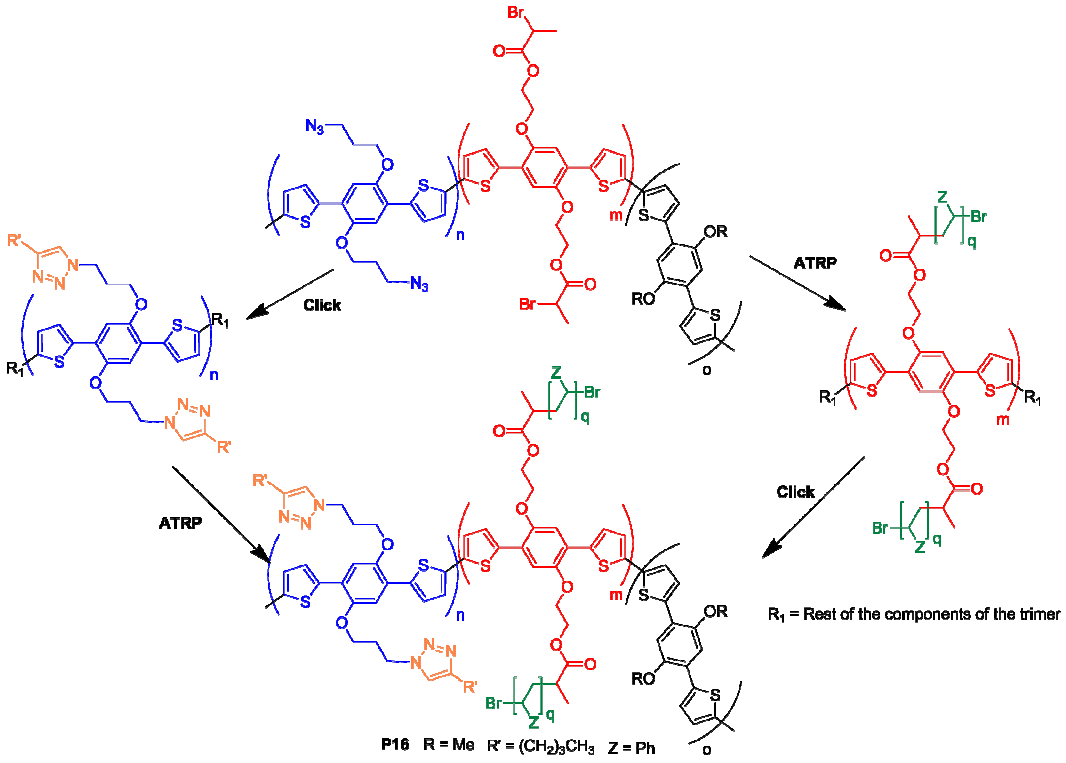

Figure 7: Dual functionalization of 'click' and ATRP could be performed interchangeably

3.4 Dual functionalization: ATRP grafting followed by 'click' chemistry

In addition to demonstrating grafting of polymer brushes by ATRP chemistry after performing 'click' chemistry, as described in the previous section, we further explored the possibility of performing the two functionalization chemistries in *vice versa* (Figure 7). Here, we investigate if 'click' chemistry can also be effectively performed in the presence of an ATRP grafted side chains. Such flexibility in functionalization chemistries would open up new possibilities towards functionalised conducting polymers. In order to demonstrate the possibility, short brush of 15 units of styrene were first grafted onto the polymer **P5**, followed by cycloaddition reaction of hex-1-yne **16**. Through analysis of the easily obtain COSY NMR spectrum, the change in the crosspeaks could be seen, consistent with that seen in 'click' reactions discussed above (Supporting Information, Figure S9). This result confirms that addition of alkynes is possible even after ATRP grafting. This route may be of particular significance where the alkyne group contains functionalities incompatible with ATRP conditions, thus showcasing the versatility of the functionalization possible.

3.5 Conductivity

Bulk resistance of a selection of the synthesized polymers was measured by pressing the polymer into pellets and the measuring conductivity using a four point probe. Polymers which had been subjected to click reactions were re-doped, due to the use of ascorbic acid, which likely reduced these polymers. The bulk resistances measured are shown in Table 1. The results show that the incorporation of different substitutions, as well as post-polymerisation modification does not necessarily eliminate the conductivity. The exceptions are polystyrene brushes grafted polymers (TMeThP-Sty **P9** and TMeThP-HexSty **P10**) where the bulk resistance could not be measured; the reason being the presence of stiff, glassy and insulating polystyrene that dominates the overall polymer properties in dry state.

3.6 Electrochemistry

We further wished to investigate another approach to the synthesis of the functionalised PThPs by means of electropolymerisation. This would also allow

Monomer	Bulk Resistivity (ρ) (ohms-cm)
TMeThP **P5**	42540
TMeThP-Hex **P8**	140400
TTGThP **P6**	458800
TMeThP-Sty **P9**	Cannot be measured
TMeThP-HexSty **P14**	Cannot be measured

Table 1: Four-point measurements on pressed pellets.

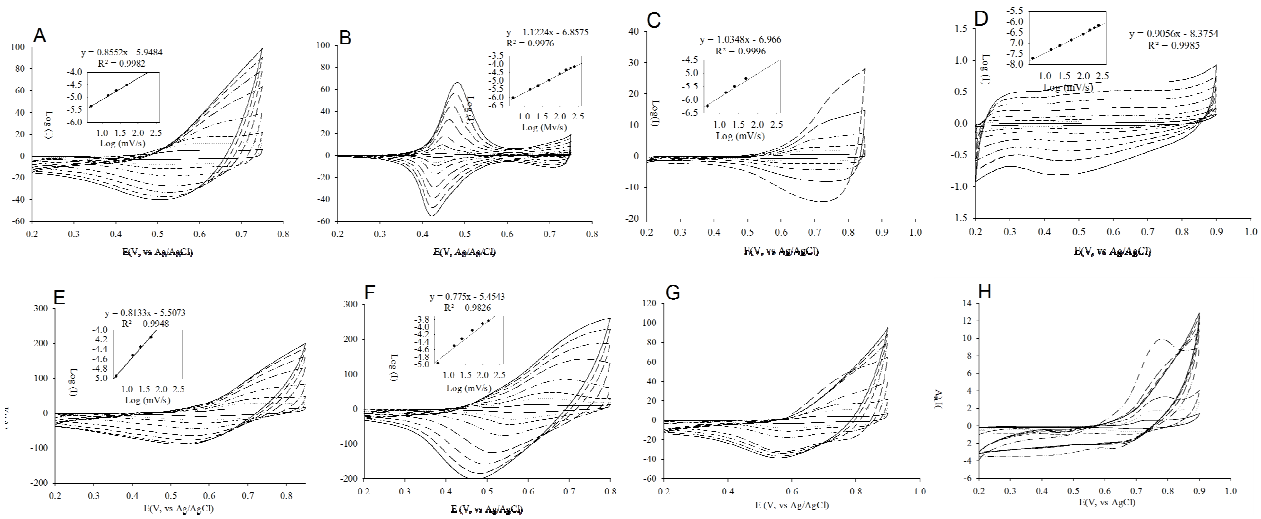

Figure 8: voltammogramsat scan rates between 5 mV s^{-1} to 250 mV s^{-1} in monomer-free solution 0.1 M $LiClO_4$ in 4:1 (H_2O:MeCN) for: **A**: PMeThP **P1**, **B**: TGThP **P2**, **C**: PAzThP **P3**, D: PBIThP **P4**, **E**: TMeThP **P5**, **F**: TTGThP **P6**, **G**: TMeThP-Hex **P8**, **H:** TMeThP-HexSty **P15**; Inset: Linear dependence of log of scan rate over log of current at the oxidation peak.

electrochemical characterisation of the electropolymerised polymers, as well as of post-chemical polymerisation functionalised polymers, described above. Cyclic voltammetry experiments were performed on the polymers, both electropolymerised on a gold electrode, and chemically polymerised and drop-casted on a gold electrode.

Monomers of **1**, **2**, **3** and **4** were electropolymerised using the method described in section 2.3.1. Electropolymerisation cyclic voltammogrammes of the four monomers - MeThP **2**, TGThP **1**, AzThP **3** and BIThP **4 -** are presented in Figure S10 of the Supporting Information. All four monomers have electropolymerisation potentials in the range 0.8-0.95 V (vs. Ag/AgCl). The cyclic voltammetry (CV) scans of the resultant polymers (**P1**, **P2**, **P3** and **P4** respectively) were recorded in monomer-free solutions. Due to the high solubility of the polymers in acetonitrile the CVs were recorded in a solution of 0.1 M $LiClO_4$ in 4:1 H_2O:MeCN.

Cyclic voltammogrammes of PMeThP **P1** at different scan rates in 0.1 M $LiClO_4$ in 4:1 H_2O:MeCN electrolyte are shown in Figure 8A. The oxidation peak of the polymer can be seen at 0.65 V and the corresponding reduction peak at 0.48. At high scan rate, the redox wave is broader and poorly defined. In the case of PTGThP **P2**, the oxidation and reduction peaks (Figure 8B) occur at 0.48 V and 0.41 V respectively; at significantly lower potentials than observed from electropolymerisation voltamogramme (Figure S10). The CVs of PTGThP **P2** presented in Figure 8B show characteristics of nearly reversible redox behaviour. The lower redox potential of PTGThP **P2** when compared to PMeThP **P1**, may be explained by enhanced compatibility (and swellability) of the polymer in the mixed solvent, facilitating the polymer redox reaction. The lower solubility of PMeThP **P1** in the mixed solvents also leads to the formation of a dense compact film slowing the diffusion of ions and charge transport.[43] CV scans of PAzThP **P3** indicate strong capacitive behaviour with broad oxidation and reduction waves with peaks appearing at 0.74 V and 0.69 V, respectively (Figure 8C). The values of the currents are the lowest for this polymer pointing to less polymer deposition at the electrode. This polymer is highly hydrophobic, similar to that of PMeThP **P1** discussed above, likely forming a thin dense film. The oxidation and reduction peaks for PBIThP **P4** are found at relatively low potentials of 0.54 V and 0.45 V, respectively, (Figure 8D).

Chemically prepared polymers **P5** and **P6** were also characterised using cyclic voltammetry and the results are discussed below. The terpolymers were dissolved in dichloromethane and drop-casted on gold electrodes. The solvent was allowed to evaporate in open air and the polymer at the electrode was blown dry using N_2. The CVs obtained from electropolymerised (Supporting Information **S11)** and chemically polymerised terpolymers (Figure 8E and 8F) were slightly different. Such differences may originate from inherent differences in morphology due to the differences in film preparation.[44,45] For TMeThP **P5** the oxidation and reduction peaks at faster scan rates (e.g. >150 mV s^{-1}) had both oxidation and reduction values moved to slightly higher potentials than the 0.64 V and 0.55 V, respectively, obtained at 15 mV s^{-1} scan rate. This is likely related to the morphology of the polymer film (Figure 8E). The CV of chemically synthesised TGThP **P2** differed slightly to the CV of the electropolymerised film (compare Figure 8F to 8B). Here, the oxidation and reduction peaks are found at 0.68 V and 0.46 V (for 50 mV s^{-1} scan rate), respectively, in contrast to 0.70 V and 0.61 V

(at 50 mV s^{-1}) found in the CV of the electrochemically prepared film. Again, the difference is likely due to difference in films morphology (density), but also to possible differences in the polymer chain lengths and exact polymer topology (i.e. presence of any branching, cross-linking etc.).

In order to confirm that the additional triazoles does not affect the electrochemistry, CV experiments on TMeThP **P5** clicked with hex-1-yne (TMeThP-Hex) **P8** were performed. From the voltamogramme in Figure 8G, the polymer oxidation peaks are clearly present at the lower scan rates. The shape of the voltamogramme is similar to that of TMeThP **P5** and PMeThP **P1** where at higher scan rates the peaks are not well defined. The oxidation and reduction peak at 50 mV s^{-1} scan rate are at 0.76 V and 0.58 V respectively. These values are similar to those of chemically polymerised TMeThP **P5** (0.73 V and 0.59 V), indicating electroactivity of the polymers with triazole present remains similar to the native polymer. Similar to other polymers with methoxy side chains, at high scan rate, the redox wave is broad. Therefore, grafting did not hinder the electrochemistry of the resulting polymer.

Interestingly, the polymer with grafted polystyrene side chains still displayed reasonable electroactivity, as seen in Figure 8H. At higher scan rate (>50 mV s^{-1}) the polystyrene grafted chains hinder the ions diffusion and charge transfer, as expected.

4.0 Conclusion

We have demonstrated the synthesis of a range of novel conducting polymer monomers and their polymers that have functionalities amenable to further functionalization. Specifically, we synthesised functionalised poly[1,4-bis(2-thiophene)-p-phenylenes] (PThPs) with an azide, an ATRP initiating site, a methoxy group and a triethylglycol group. The monomers carrying different side chain functionality could be easily ter-polymerised to form terpolymers carrying multiple functionalities. We have shown that, through the use of functionalisable azide side chain and radical polymerization initiating side chains, synthesized PThPs can be further, post-polymerisation, functionalized, exemplified here by 'click' addition of hex-1-yne **16** and ATRP of styrene. Moreover, the side chain modified PThP polymers retain electroactivity after such modifications. In addition to chemical oxidative polymerisation, we have shown that the functionalised PThPs can be easily prepared electrochemically. Cyclic voltammetry experiments demonstrated excellent electroactivity of the polymers that have relatively well defined oxidation/reduction peaks in the potential range from 0.4 to 0.75 V.

The developed methodology of co(ter)polymerising variously functionalised monomers provides a general route to versatile functionalization of 'designer' conjugated polymers. Such an approach leads to conjugated polymers that can be easily processable (e.g. via solution processing routes) and opens new and exciting opportunities for that class of polymeric materials in a range of applications, including thin film flexible electronic devices and biomedical uses.

Acknowledgement

This work was supported by grant from the Ministry of Business, Innovation and Employment, New Zealand (9146-3701426). The authros thank Assoc. Prof. S. Moratti from the University of Otago, New Zealand, for the help with performing GPC measurements.

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Graphical Abstract

Highly functionalisable polythiophene phenylenes

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