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# Synthesis and characterisation of telechelic regioregular head-to-tail poly(3-alkylthiophenes)

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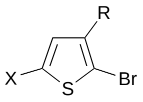
An investigation into the Stille cross-coupling reaction as an alternative synthetic route to regioregular head-to-tail poly(3-alkylthiophenes) is presented. 2-Iodo-3-alkyl-5-tri-*n*-butylstannylthiophene derivatives were made, isolated and characterised and subsequently used in Pd$^0$ catalysed cross-coupling reactions in different solvents. Short and long chain regioregular poly(3-hexylthiophenes) with over 96% head-to-tail coupling ratios between adjacent thiophene rings were obtained. The materials were analysed by gel permeation chromatography and NMR spectroscopy. Polymers with varying degrees of polymerisation were obtained depending on the conditions used. End group analysis has shown that polymers, functionalised with both iodo and tri-*n*-butyltin end groups can be obtained under certain reaction conditions. Preliminary homocoupling reactions were also conducted.

There has been a great deal of interest in the study of organic conjugated polymers over the last few years in view of their potential applications in a number of areas of molecular electronics. The structure of these rigid rod macromolecules plays an important role in determining their physical properties.[1]

Among these materials, polythiophenes have attracted significant interest in view of their environmental stability in both neutral and oxidised states. The physical properties of poly(3-alkylthiophenes) are dramatically altered by changing the regioregularity of polymer chains. On increasing the ratio of head-to-tail coupling of adjacent monomers on poly(3-alkylthiophenes), a decrease of steric hindrance between alkyl substituents on adjacent rings is observed leading to an increase in the linearity of polymer chains and hence greater conjugation along the polymer backbone. Lower band gap polymers are thus obtained. This was established by McCullough *et al.*[2] and Riecke *et al.*[3] who demonstrated the effect of regiochemical control on the properties of such materials. Enhanced conductivities (one to two orders of magnitude greater) are observed from doped head-to-tail regioregular poly(3-alkylthiophenes) when compared with conductivity values of regioirregular polymers.

Synthetic strategies for the preparation of regioregular head-to-tail poly(3-alkylthiophenes) so far reported in the literature involve nickel catalysed Grignard cross-coupling reactions using 2-bromo-3-alkyl-5-bromomagnesiothiophene **1**[2] and 2-bromo-3-alkyl-5-bromozinciothiophene **2**[3] derivatives. In such reactions the intermediate species are made *in situ* and subsequently polymerised. Good head-to-tail ratios are obtained from such syntheses providing that a strict kinetic control is observed since at high temperatures in the presence of nickel catalysts intermediates **1** and **2** can isomerise to 2-bromomagnesio-3-alkyl-5-bromothiophene and 2-bromozincio-3-alkyl-5-bromothiophene, respectively, by a series of transmetallation–reductive eliminations followed by oxidative addition. Reproducibility in molecular mass distributions of the resulting polymers in the nickel catalysed cross-coupling polymerisation of intermediates **1** is linked to their freedom from starting materials (2-bromo-3-alkylthiophene). Trace amounts of unreacted 2-bromo-3-alkylthiophene monomers still present at the polymerisation stage should contribute to chain termination. Reproducibility in the percentages of head-to-tail coupling of the resulting polymers in the nickel catalysed cross-coupling polymerisation of **2** is also linked to their freedom from starting materials (2,5-dibromo-3-alkylthiophene) since these should lead to random couplings of thiophene rings and coupling defects. In a recent communication,[4] McCullough *et al.* reported the preparation of a regioregular oxazoline functionalised polythiophene using a modified Stille coupling reaction involving 2-bromo-3-[2-4,5-dihydro-(4,4-dimethyloxazol-2-yl)ethyl]-5-trimethylstannylthiophene as intermediate.



**1** X = MgBr
**2** X = ZnBr

In this paper, we present our findings on the potential use of 2-iodo-3-alkyl-5-tri-*n*-butylstannylthiophene derivatives as intermediates in Stille type cross-coupling reactions[5] for the preparation of telechelic regioregular head-to-tail poly(3-alkylthiophenes).

## Results and Discussion

The use of 2-iodo-3-alkyl-5-tri-*n*-butylstannylthiophene derivatives as intermediate monomers in palladium(0) catalysed cross-coupling reactions for the production of regioregular head-to-tail poly(3-alkylthiophenes) presents several advantages. A major advantage in using these intermediates is their kinetic, air and moisture stability. This permits their separation and purification from undesired residual starting materials. Another advantage in using these derivatives is the possibility of preparing telechelic polymer chain fragments that could be involved in the synthesis of 3-functionalised polythiophene block copolymers with different substituents on respective blocks since both iodo and tri-*n*-butyltin groups can, in principle, be retained at the chain ends of polymers after reaction work-up and polymer separation, as opposed to synthetic schemes involving the use of intermediates **1** or **2**, and where the Grignard ends of polymer chains are hydrolysed at the work-up stage.

2-Iodo-3-hexyl-5-tri-*n*-butylstannylthiophene **3** was targeted as a model monomer in these reactions in view of the wealth of data on poly(3-hexylthiophenes) available in the literature. It was made by selective iodination of 3-hexylthiophene at the 2-position using iodine with mercury(II) oxide in benzene, followed by selective lithiation of the resulting 2-iodo-3-hexylthiophene at the 5-position with lithium diisopropylamide (LDA) and reaction with tri-*n*-butyltin chloride at low tempera-

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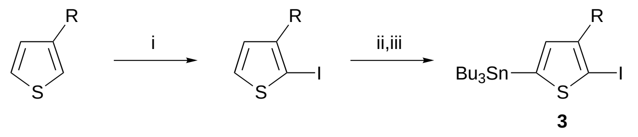
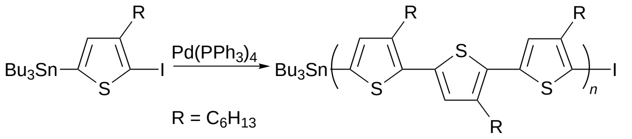


**Scheme 1** *Reagents and conditions*: i, $I_2$, HgO; ii, LDA; iii, $Bu_3SnCl$



**Scheme 2**

tures. The resulting materials from these reactions are always found to contain trace amounts of the staring material (2-iodo-3-hexylthiophene). These are removed by evaporation *in vacuo*, to leave the desired product in quantitative yields (see Scheme 1).

Monomer **3** is kinetically stable and can be handled in an air and water atmosphere without degradation. NMR analysis of the product shows exclusive functionalisation at the 5-position on the thiophene ring. $^1H$ NMR analysis also shows $^3J$ coupling of the proton at the 4-position on thiophene rings with naturally abundant tin isotopes with nuclear spins ($^{117}Sn$ and $^{119}Sn$) [Fig. 1(*a*)].

The new 2-iodo-3-hexyl-5-tri-*n*-butylstannylthiophene derivative is then used as monomer in palladium(0) cross-coupling catalysed reactions leading to highly regioregular poly(3-hexylthiophenes) with head-to-tail coupling ratios exceeding 96%. (see Scheme 2). The resulting polymers are readily soluble in methylene chloride, chloroform and THF.

## Solvents effects on the reaction

Polymerisation reactions were carried out in different solvents under the same conditions for set periods of time (18 h). Cross-coupling reactions proceed in all three solvents used, tetrahydrofuran, toluene and 1,2-dichloroethane at reflux temperatures. It is found that in all solvents used, selective head-to-tail regiochemical coupling of monomers is observed. However, polymers with different molecular masses are obtained in each case. GPC analysis results from these experiments are shown in Table 1.

The work up procedure of the polymers obtained from reactions carried out in toluene and 1,2-dichloroethane, presented in Table 1, involved precipitation of polymers in methanol at the end of reactions, followed by washing with methanol several times at room temperature. The materials obtained are then extracted with hexane at room temperature allowing separation of the polymer into two fractions; the hexane insoluble fractions (which have the higher molecular masses) and those separated from the hexane extracts by precipitation in methanol (lower molecular mass fractions). Upon Soxhlet extraction of the high molecular mass fractions with methanol for 24 h and then a further Soxhlet extraction with hexane for 24 h, materials with higher average molecular masses and lower polydispersities are obtained (Table 2). Experiments in 1,2-dichloroethane for longer periods of time (66 h) where the resulting polymers are subjected to the same work up procedure are also presented in Table 2.

**Table 1** Comparison of molecular mass distributions of poly(3-hexylthiophenes), UV–VIS data and yields of polymerisation in different solvents for reactions run for 18 h

| entry | solvent | $M_W$ | $M_N$ | polydispersity | $\lambda_{max}$/nm (CHCl$_3$) | yield (%) |
|---|---|---|---|---|---|---|
| 1 | toluene | 9992 | 7366 | 1.36 | 447 | 50 |
| 2 | | 2659[b] | 2239 | 1.19 | 430 | 20 |
| 3 | $CH_2ClCH_2Cl$ | 13 711 | 7977 | 1.72 | 448 | 54 |
| 4 | | 4198[b] | 3538 | 1.48 | 434 | 17 |
| 5 | THF | 2315 | 1409 | 1.64 | 391 | <10 |
| 6 | toluene[a] | 7693 | 4220 | 1.82 | 439 | 40 |

[a] Reaction carried out with monomer **3** contaminated with trace amounts of 2-iodo-3-hexylthiophene. [b] Fractions that are soluble in hexane at room temperature, separated by precipitation with methanol.

**Table 2** Comparison of molecular mass distributions of poly(3-hexylthiophenes) after soxhlet extraction with methanol and then hexane. UV–VIS data and times of polymerisation in different solvents.

| entry | solvent | $M_W$ | $M_N$ | polydispersity | $\lambda_{max}$/nm (CHCl$_3$) | *t*/h |
|---|---|---|---|---|---|---|
| 1 | toluene | 19 732 | 16 118 | 1.22 | 449 | 18 |
| 2 | $CH_2ClCH_2Cl$ | 16 625 | 11 517 | 1.44 | 449 | 18 |
| 3 | $CH_2ClCH_2Cl$ | 14 484 | 10 889 | 1.33 | 449 | 66 |

Results in Table 1 show in the first instance that the rate of these polymerisation reactions is slower than that of polymerisation reactions involving 2-bromo-3-alkyl-5-bromomagnesiothiophene or 2-bromo-3-alkyl-5-bromozinciothiophene intermediates, where reactions occur at room temperature or lower and where higher molecular mass materials are obtained.[2,3] This is presumably due to a lower rate of halogen exchange between tin and palladium as compared to that between magnesium and nickel, zinc and nickel or zinc and palladium.

Results in Table 1 also reveal that higher molecular mass materials are obtained from reactions carried out in toluene and 1,2-dichloroethane, when compared to materials obtained from reactions carried out in THF which are mainly composed of long regioregular oligomeric chains.

Table 1 also shows results of polymerisations carried out with monomer **3** when contaminated with trace amounts of starting material (2-iodo-3-hexylthiophene) (entry 6). Lower molecular mass polymers are obtained in lower yields as compared to experiments run with purified monomer **3** under the same conditions This is explained by chain termination reactions caused by the presence of 2-iodo-3-hexylthiophene. NMR analysis indicates that the head-to-tail regioregularity of these polymers is, however, still maintained.

In experiments run in toluene, the solubility of the growing polymer chains plays an important role on the extent of polymerisation and could be a limiting factor on chain growth. Indeed, in polymerisations carried out in toluene, precipitation of part of the polymer is observed before the end of the experiment. 1,2-Dichloroethane was chosen as an alternative solvent in view of its enhanced solvation power as compared to toluene. However, as shown in Table 2, a maximal degree of polymerisation of around 67 is not surpassed even after extended reaction periods (66 h).

## Spectroscopic studies

NMR studies in chloroform on these materials explain a number of these findings. $^1H$ NMR spectra of monomer **3** and polymers with varying degrees of polymerisation from reactions in toluene are shown in Fig. 1.

Fig. 1(*d*) shows the spectrum of the polymer with the highest average molecular mass in these experiments (DP = 97, entry 1, Table 2). It reveals a single chemical environment for the aromatic protons of the thiophene rings on the backbone of the polymer ($\delta_H$ 6.97) and essentially a single chemical environment for the methylene groups attached directly to the thiophene rings ($\delta_H$ 2.80), with a small trace (<4%) of another triplet in a different environment at $\delta_H$ 2.58, suggesting a homogeneous structure for the polymer and >96% head-to-tail coupling along the backbone. It is worth noting at this stage that no signals from tri-*n*-butyltin end groups are

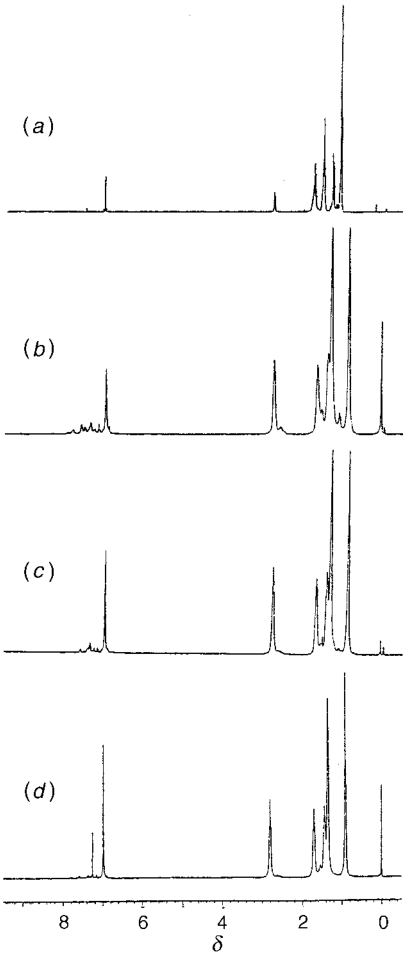


**Fig. 1** $^1$H NMR spectra of (*a*) monomer **3**, (*b*) poly(**3**) (degree of polymerisation *ca.* 13, entry 2, Table 1), (*c*) poly(**3**) (degree of polymerisation *ca.* 44, entry 1, Table 1) and (*d*) poly(**3**) (degree of polymerisation *ca.* 97, entry 1, Table 2)

observed, suggesting that they are hydrolysed in the work up to isolate the polymer. Fig. 1(*c*) shows the spectrum of the parent polymer before Soxhlet extraction with methanol and hexane, which has a lower average molecular mass (DP = 44, entry 1, Table 1). Similar features to those of the higher molecular mass polymer are observed. However, in addition to peaks discussed above, there are additional background signals in the aromatic region originating from hydrogens on thiophene rings at the chain ends on shorter polymeric chains. It is also possible to distinguish signals from tri-*n*-butyltin end groups from the $^1$H spectra with signals occurring at $\delta_H$ 1.12 and 1.58. These are attributed respectively to hydrogens on α-carbons and γ-carbons on butyl groups of tin residues, while hydrogens from β-carbons are masked under six methylene hydrogens from hexyl substituents at $\delta_H$ 1.38 and methyl hydrogens from the tin residues also masked under the methyl groups of hexyl substituents at $\delta_H$ 0.92. This shows that tri-*n*-butyltin end groups are preserved on polymer chains and are only cleaved if the polymer is subjected to treatment with refluxing methanol as in the case of the previous polymer after Soxhlet extraction with hot methanol. Fig. 1(*b*) shows the spectrum of an even lower molecular mass polymer (oligomer) (DP = 13, entry 2, Table 1). The intensity of the additional signals at the aromatic region beside the main peak at $\delta_H$ 6.97 is greater. Similarly, the intensity of signals attributed to tri-*n*-butyltin end groups is also greater. Polymers with low molecular masses display, in addition to signals at $\delta_H$ 2.80, intense signals at $\delta_H$ 2.58. These additional signals do not correspond to coupling defects and regioirregular chains since these would be duplicated in longer polymeric chains isolated from the same reaction mixture. The signals most probably originate from methylene groups directly attached to thiophene rings close to the chain ends.

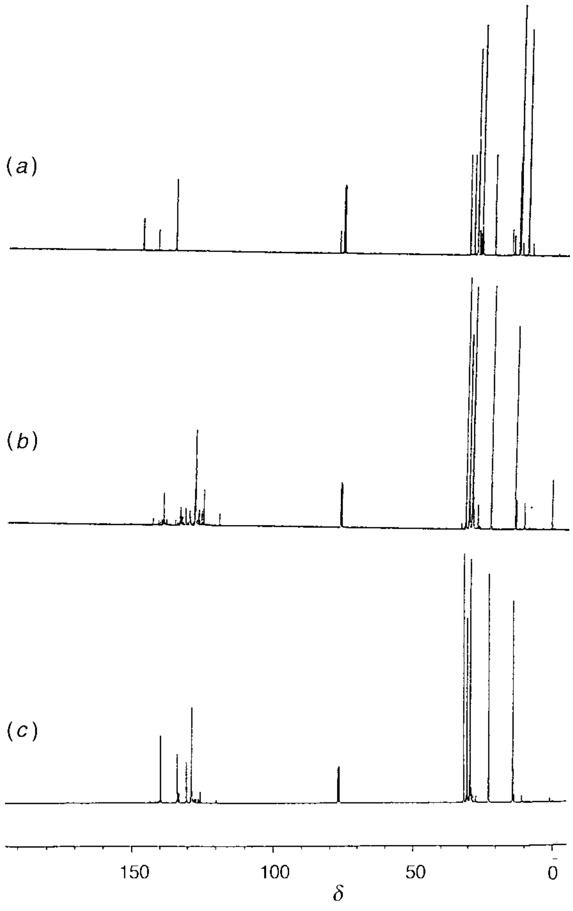


**Fig. 2** $^{13}$C NMR spectra of (*a*) monomer **3**, (*b*) poly(**3**) (degree of polymerisation *ca.* 13, entry 2, Table 1) and (*c*) poly(**3**) (degree of polymerisation *ca.* 44, entry 1, Table 1)

$^{13}$C NMR spectra of monomer **3** as well as those of polymers in entries 1 and 2 in Table 1 are shown in Fig. 2. Fig. 2(*c*) shows the spectrum of the polymer in entry 1, Table 1 (DP = 44). It essentially reveals four carbon environments for the thiophene rings with additional background signals originating from carbon on thiophene rings at the chain ends on shorter polymeric chains suggesting a homogeneous structure of the polymer and *ca.* >96% selective head-to-tail coupling along the backbone. Signals from butyl groups on tin residues are distinctly observed at $\delta_C$ 10.86, 13.54, 27.19 and 28.90. Fig. 2(*b*) shows the spectrum of a lower molecular mass polymer (oligomer) (DP = 13, entry 2, Table 1). The peak pattern in the aromatic region shows a multitude of peaks in view of the shorter length of thiophene chains. Both intensity and multiplicity of signals attributed to tri-*n*-butyltin end groups (centred at the same chemical shifts) are increased, reflecting a wide distribution of oligomers of different lengths.

NMR analysis of polymers prepared in 1,2-dichloroethane also reveal that highly regioregular head-to-tail materials are formed. However, end group analysis of the polymers shows the absence of signals from tri-*n*-butyltin residues even prior to Soxhlet extraction with methanol (entries 3 and 4, Table 1) suggesting their cleavage as reactions proceed. This also explains the similarity in molecular mass distributions and polydispersities between materials obtained after reaction times of 18 and 66 h, respectively (entries 2 and 3, Table 2).

NMR analysis of materials obtained from reactions in THF, reveals a mixture of oligomers (DP = 6, entry 5, Table 1). Signals from tri-*n*-butyltin groups are still apparent suggesting that the cross-coupling polymerisation proceeds at very low

**Table 3** Homocoupling of telechelic polymers

| | $M_W$ | $M_N$ | polydispersity | $\lambda_{max}{}^{b}$/nm ($CHCl_3$) |
|---|---|---|---|---|
| starting polymer[a] | 2999 | 2312 | 1.58 | 424 |
| final polymer | 8867 | 4765 | 1.86 | 439 |

[a]Polymer obtained from reaction in THF after 66 h at reflux temperature. [b]UV–VIS spectra were recorded on samples of initial and final reaction mixtures and were found to be concordant with spectra of isolated materials.

rates in the solvent and pointing to a kinetic effect rather than to the cleavage of end groups during the reaction. This is supported by data from reactions carried out in the same solvent for longer periods of time (66 h) and where a degree of polymerisation of around 14 is achieved. NMR analysis also shows regioregular head-to-tail coupling of adjacent monomers in these materials, together with conservation of tin end groups on the polymers formed.

Absorption spectra on these polymers in chloroform, show maximum absorptions at $\lambda_{max}$ between 424 nm for low molecular mass polymers and 449 nm for higher molecular mass polymers (Tables 1, 2 and 3). The increase in $\lambda_{max}$ is shown to be proportional to the chain length of polymers and hence to the extent of electronic delocalisation.

### Homocoupling of telechelic polymers

Preliminary investigations on the potential use of short telechelic polymer chains in the preparation of block copolymers were also conducted. Homocoupling of telechelic polymer chains was demonstrated upon treatment of polymers with a low degree of polymerisation (DP ~ 14, starting polymer, Table 3) with catalytic amounts of $Pd(PPh_3)_4$ in refluxing toluene (Scheme 3).

Polymers with a higher degree of polymerisation (DP ~ 28, final polymer, Table 3) and increased maximum absorptions ($\lambda_{max} = 439$ nm) resulted.

## Conclusions

An investigation into the use of 2-iodo-3-alkyl-5-tri-*n*-butylstannylthiophene derivatives as intermediates in $Pd^0$ Stille cross-coupling polymerisation for the production of regioregular head-to-tail poly(3-alkylthiophenes) was undertaken in three different solvents. Reactions in THF afforded low molecular mass materials with a degree of polymerisation up to 14 with no sign of cleavage of tin end groups. Reactions in 1,2-dichloroethane led to highly regioregular (>96% head-to-tail ratio) polymers with a degree of polymerisation up to 70. However, tri-*n*-butyltin end groups are cleaved during reactions in this solvent. Reactions in toluene also afford highly regioregular head-to-tail poly(3-akylthiophenes) with >96% head-to-tail coupling ratios with a degree of polymerisation up to 97. Careful work-up of these materials in methanol and hexane at room temperature allows separation of polymers with preservation of both iodo and tri-*n*-butyltin end groups. Treatment of these polymers with methanol at elevated temperatures leads to the cleavage of tin end groups.

Preliminary homocoupling reactions of telechelic polymer chains were successful and yielded polymers with higher molecular masses.

An important possible application of materials made in the present study, especially those functionalised with both iodo and tri-*n*-butyltin end groups, is in the preparation of polythiophene multi-block copolymers with different substituents on alternating blocks.

## Experimental section

NMR spectra were recorded using a JEOL GSX400 spectrometer (400 MHz, $^1H$ and 100.5 MHz, $^{13}C$). *J* Values are in Hz. UV–VIS spectra were recorded using a Unicam 8700 spectrophotometer. IR spectra were obtained using a Nicolet 205 FTIR. The gel permeation chromatography (GPC) system comprised a Waters 510 pump coupled *via* a Rheodyne injection port to Polymer Laboratories columns. A Waters 410 differential refractometer was used to detect molecular mass fractions eluting from the columns. The data were manipulated using Polymer Laboratories GPC software operating under Microsoft Windows 3.11. Calibration of the columns was carried out using polystyrene standards. All samples were run in tetrahydrofuran (THF). The flow rate was set to 1 ml $min^{-1}$ and toluene was added as a flow rate marker.

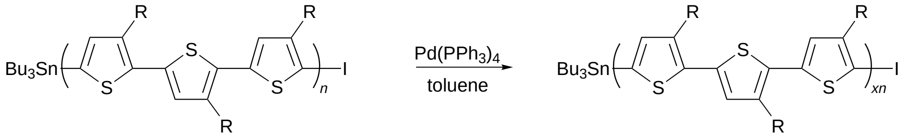
Toluene and benzene were distilled over sodium. THF and diethyl ether were distilled over sodium–benzophenone, 1,2-dichloroethane was dried and distilled over $CaH_2$. Diisopropylamine was dried and distilled over sodium hydroxide. 3-hexylthiophene[6] and $Pd(PPh_3)_4$[7] were made according to literature procedures. Tri-*n*-butyltin chloride was obtained commercially and used without further purification.

### 2-Iodo-3-hexylthiophene

To a solution of 3-hexylthiophene (2 g, 11.88 mmol) in benzene (20 $cm^3$) at 0 °C was added, in small portions, mercury(II) oxide (2.57 g, 11.88 mmol, yellow crystals) and iodine (3.02 g, 11.90 mmol) over 40 min. The mixture was stirred at room temp. for 1 h, and the orange precipitate was filtered off and washed with diethyl ether. The filtrate and washings were combined and washed with aqueous sodium thiosulfate and dried over magnesium sulfate. Solvent was removed by rotary evaporation and the residue distilled *in vacuo* (88 °C at 0.5 mmHg) to give a colourless oil (Yield 2.00 g; 57%). $\delta_H$ ($CDCl_3$, $SiMe_4$) 0.89 (t, *J* 7, 3H), 1.31 (m, 6H), 1.56 (m, 2H), 2.54 (t, *J* 7, 2H), 6.74 (d, *J* 5, 1H), 7.36 (d, *J* 5, 1H). $\delta_C$ ($CDCl_3$, $SiMe_4$) 13.99 (1C), 22.49 (1C), 28.78 (1C), 29.89 (1C), 31.52 (1C), 31.99 (1C), 73.86 (1C), 127.83 (1C), 130.16 (1C), 147.04 (1C).

### 2-Iodo-3-hexyl-5-tri-*n*-butylstannylthiophene

To a solution of diisopropylamine (6.50 g, 64.21 mmol) in diethyl ether (100 $cm^3$) was added *n*-butyllithium (32 $cm^3$ of 1.6 M solution in hexanes, 51.2 mmol) at room temp. After 30 min stirring at room temp., the resulting LDA solution was cooled to −80 °C. A solution of 2-iodo-3-hexylthiophene (15.00 g, 51.00 mmol) in diethyl ether (100 $cm^3$) was cooled to −80 °C and added at the same temperature to the LDA solution and the temperature allowed to rise slowly to −40 °C, whereupon it was stirred for 1 h. The solution was then cooled to −80 °C and tri-*n*-butyltin chloride (16.6 g, 51.00 mmol) added. The mixture was allowed to warm to room temp. overnight and was then poured onto ice, The products were then extracted into diethyl ether (3 × 100 $cm^3$) and washed



**Scheme 3**

with water ($2 \times 100$ cm$^3$), saturated aqueous copper sulfate (100 cm$^3$), saturated sodium hydrogen carbonate (100 cm$^3$) and water again (200 cm$^3$). The diethyl ether extracts were dried over magnesium sulfate and the solvent removed by rotary evaporation to leave an orange–red oil. NMR analysis of the residual oil revealed trace amounts of starting material (2-iodo-3-hexylthiophene). These were removed on heating the oil under high vacuum leaving the title product as a red oil (Yield 25.58 g, 86%). $\delta_H$ ($CDCl_3$, $SiMe_4$) 1.15 (m, 12H), 1.34 (m, 6H), 1.58 (m, 12H), 1.82 (m, 8H), 2.82 (t, *J* 8, 2H), 7.04 (s, 1H). $\delta_C$ ($CDC_{13}$, $SiMe_4$) 10.79 (1C), 13.50 (1C), 13.95 (1C), 22.48 (1C), 27.09 (1C), 28.76 (1C), 28.84 (1C), 29.99 (1C), 31.52 (1C), 31.58 (1C), 77.20 (1C), 136.10 (1C), 142.31 (1C), 147.86 (1C).

### Polymerisation procedure

In a typical polymerisation reaction, monomer **3** (3.00 g, 5.14 mmol) was solubilised in the appropriate dry distilled solvent (50 cm$^3$). The solution was then deoxygenated, the catalyst (178 mg, 0.154 mmol, 3 mol%) added under inert atmosphere, and the solution refluxed for set periods of time with stirring. At the end of the reaction, the solution was poured onto methanol (300 cm$^3$). The polymer was filtered off and washed with methanol until the washings were colourless.

Extraction of the polymer with hexane at room temp. allowed the separation of the polymer into two fractions; the hexane insoluble fractions (which have the higher molecular masses) and those separated from the hexane extracts by precipitation in methanol.

For experiments reported in Table 2, separation of the polymers was accomplished through Soxhlet extraction with methanol for 24 h, then hexane for 24 h, of either crude polymers or those with a high molecular mass described above, and afforded higher molecular mass materials.

### Homocoupling of telechelic polymers

To 0.22 g ($9.25 \times 10^{-2}$ mmol) of telechelic poly(**3**) (DP ~ 14, prepared as described above using THF as a solvent at reflux for 66 h) in toluene (50 cm$^3$) was added $Pd(PPh_3)_4$ (21 mg, $1.85 \times 10^{-2}$ mmol) under inert atmosphere and the solution refluxed for 18 h with stirring. At the end of the reaction, the solution was poured onto methanol (300 cm$^3$). The polymer was filtered off and washed with methanol until the washings were colourless and dried *in vacuo*. (Yield 0.20 g; 96%). UV–VIS spectra were recorded on samples of initial and final reaction mixtures and were found concordant with spectra of isolated materials [starting polymer $\lambda_{max}$ ($CHCl_3$) = 424 nm, final polymer $\lambda_{max}$ ($CHCl_3$) = 439 nm].

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