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ARTICLE

ipso-Arylative polymerization as a route to π-conjugated polymers: Synthesis of poly(3-hexylthiophene)

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ipso-Arylative cross-coupling with two 3-hexylthiophene derivatives, 5-bromo-4-hexylthiophen-2-yl)diphenylmethanol and 2-(5-bromo-4-hexylthiophen-2-yl)propan-2-ol, has been used to prepare poly(3-hexylhiophene) (P3HT) as a model conjugated polymer. P3HT with number-average molecular weights ranging from 8–20 kg/mol ($Đ$ 1.4–2.2) was prepared from 5-bromo-4-hexylthiophen-2-yl)diphenylmethanol with a Pd(OAc)$_2$/PCy$_3$/Cs$_2$CO$_3$ catalyst system. Only oligomerization of 2-(5-bromo-4-hexylthiophen-2-yl)propan-2-ol ($M_n \approx 3$ kg/mol) was observed under similar conditions. Studies with model compounds suggest that side reactions involving end-group loss limit ultimate molecular weights.

Introduction

π-Conjugated semiconducting polymers have been studied for use as materials for applications including organic photovoltaics, organic light emitting diodes,[1-3] and organic thin-film transistors.[4, 5] While living polymerization methods have been developed for specific polymers, notably poly(3-hexylthiophene) derivatives,[6-12] the majority of conjugated polymers are prepared in a step-growth fashion by palladium-catalyzed coupling methods, such as Stille cross-coupling[13, 14] or Suzuki-Miyaura cross-coupling,[15, 16] because these methods can generally be applied to a wide range of reactants. Besides those two classic aryl-aryl cross-coupling reactions, palladium-catalyzed polymerizations with other classes of monomers, including unfunctionalized monomers (by CH activation) [17-24] and aurylated monomers,[25] have been studied.

ipso-Arylative cross-coupling polymerizations use organic leaving groups (carboxylic acids,[20, 26-28], silanolates,[29-31] triflates,[20, 32] diaryl or dialkylcarbinol groups) instead of the inorganic groups used in Suzuki-Miyaura cross-coupling reactions (boric acids and esters) and Stille cross-coupling (organostannanes). In addition to diphenylcarbinol groups, which are lost as benzophenone, dialkylcarbinols such as dimethylcarbinol, which is lost as acetone, and di-*tert*-butyl carbinol, which leaves as di-*tert*-butyl ketone, have been reported as leaving groups in the palladium-catalyzed arylation[33, 34] and allylation[35, 36] of aryl halides. We have previously found *ipso*-arylative coupling of bis(diphenylcarbinol)-substituted thiophene, selenophene, and tellurophene units to dibromoarenes to be an effective route to the synthesis of conjugated molecules and macromolecules, with the properties of the resulting polymers indistinguishable from those prepared by Stille and Suzuki-Miyaura coupling methods.[38, 39] Extending *ipso*-arylative polymerization from the existing AA + BB monomer polymerization strategies to the polymerization of AB monomers has the potential to enable the development of chain polymerization mechanisms that could lead to better controlled polymerization.

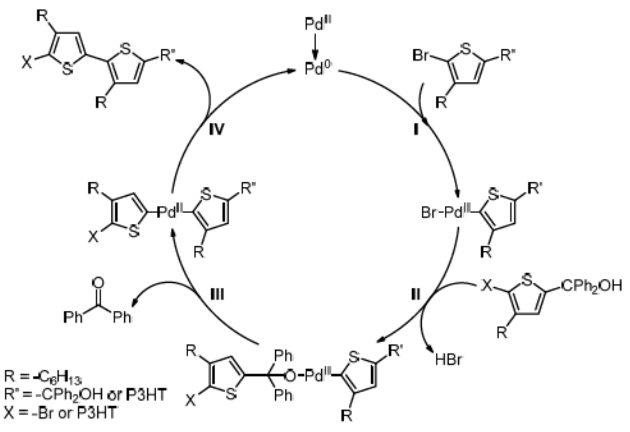

Fig. 1 Catalytic cycle for ipso-arylative cross-coupling polymerization (adapted from Bour, et al.).[37]

The mechanism of *ipso*-arylative cross-coupling reaction is believed to comprise four key steps (Fig. 1):[37] (I) oxidative addition of bromothiophene to active Pd(0) species, (II) formation of a palladium alkoxide by addition of carbinol to the thienyl palladium halide species with loss of hydrobromide, (III) formation of the dithienyl palladium by extrusion of the carbinol leaving groups as a ketone, and (IV) reductive elimination of the new dithienyl species with regeneration of the Pd(0) catalyst.

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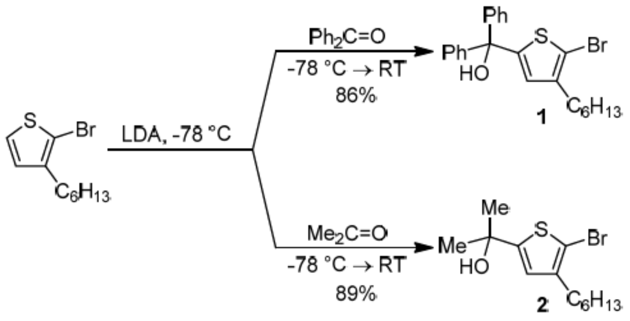
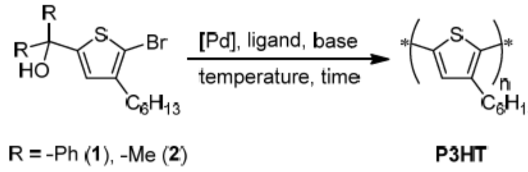
To investigate the efficacy of *ipso*-arylative cross-coupling as a general strategy for the preparation of conjugated polymers, we have explored the polymerization of carbinol-functionalized 3-hexylthiophene derivatives to poly(3-hexylthiophene) (P3HT), a widely studied π-conjugated polymer, as a model for the synthesis of other conjugated polymers. To use *ipso*-arylative cross-coupling with an AB monomer to synthesize P3HT, the thiophene ring of the monomer needs to be substituted with both a diphenylcarbinol (or dimethylcarbinol) substituent and a halide substituent. To this end, (5-bromo-4-hexylthiophen-2-yl)diphenylmethanol (**1**) and 2-(5-bromo-4-hexylthiophen-2-yl)propan-2-ol (**2**) have been synthesized (Scheme 1) and their polymerization has been attempted under a range of reaction conditions (different palladium sources, ligands, solvents, concentrations, and temperatures; Scheme 2). The purified polymers have been characterized by ^{1}H NMR, GPC, and MALDI-TOF. Reactions of non-polymerizable model compounds (2-bromo-3-hexylthiophene (**3**) and (4-hexylthiophen-2-yl)diphenylmethanol (**4**)) under optimized polymerization conditions were conducted to study side reactions that appear to result in the loss of bromide and carbinol end-groups during polymerization, thereby limiting polymer molecular weights.

Results and Discussion

The monomers (5-bromo-4-hexylthiophen-2-yl)diphenylmethanol (**1**), with benzophenone as the leaving group, and 2-(5-bromo-4-hexylthiophen-2-yl)dimethylmethanol (**2**), with acetone as the leaving group, were synthesized by deprotonation of 2-bromo-3-hexylthiophene (**3**) followed by addition of either benzophenone (for **1**) or acetone (for **2**) (Scheme 1). Briefly, bromothiophene **3** was slowly added to lithium diisopropylamide (LDA) to deprotonate the 5-position of the thiophene ring, and then a solution of benzophenone or acetone in THF was added. Both monomers were isolated in high yields (85-90%). Because of difficulties in removing unreacted benzophenone, benzophenone (0.8 equiv. relative to **3**) was used as the limiting reagent in the synthesis of diphenylcarbinol **1**, which minimized the amount of residual benzophenone and increased the purity of **1**. For the synthesis of dimethylcarbinol monomer **2**, the ease with which residual acetone could be removed allowed the use of bromothiophene **3** as the limiting reagent.



Scheme 1



Scheme 2 General polymerization scheme. Asterisks indicate varied end groups.

A range of conditions were examined for the polymerization of monomers **1** and **2** (Scheme 2). In a typical polymerization procedure, monomer **1** or **2**, precatalyst ($Pd(OAc_2)$, PEPPSI-*i*Pr, or $Pd(CNPh)_2Cl_2$), ligand (PCy_3, PPh_3, tBu_3P, or 1,3-bis-(2,6-diisopropylphenyl)imidazolinium chloride (IPr·HCl)), and base (Cs_2CO_3 or CsF) were mixed in *o*-xylene under nitrogen and the resulting mixtures were stirred and heated at the specified temperature (80-170 °C) for 24-96 h. For each polymerization, the crude polymerization mixture was allowed to cool to room temperature and precipitated in methanol. The resulting solid was collected by filtration, then extracted sequentially with methanol, to afford a low molecular weight fraction, and chloroform, to isolate a higher molecular weight fraction.

Polymerization of diphenylcarbinol monomer 1

Ligands. The effect of different ligands on the polymerization of diphenylcarbinol monomer **1** with $Pd(OAc)_2$ (2 mM) and Cs_2CO_3 (0.15 M) for 72 h was examined (Table 1: entries 1-7). PCy_3 and PPh_3 are regularly used in *ipso*-arylative cross-coupling reactions.[40] NHC ligands (such as IPr·HCl) and tBu_3P have been reported to promote chain-growth behavior in Suzuki-Miyaura coupling polymerizations of borylated arenes and heteroarenes.[41, 42] The NHC/Pd complex [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl)-palladium(II) dichloride (PEPPSI-iPr) has also been reported to promote chain-growth behavior in some palladium-catalyzed polymerizations of stannylated and aurylated aryl monomers.[25, 43]

Of the phosphine ligands examined, PCy_3 resulted in P3HT with significantly higher molecular weight (M_n = 8.3 kg/mol) and yield (58% for $CHCl_3$ fraction) than the other ligands (Table 1: entries 1-3). PCy_3 has been reported to more effectively

Table 1. Effect of ligand on polymerization of **1**[a]

Entry	T (°C)	Ligand[b]	M_n (kg/mol)[c]	$Đ$[c]	$CHCl_3$ Fraction Yield (%)[d]
1	170	PCy_3	8.3	1.4	58
2	170	PPh_3	5.6	1.5	6
3	170	tBu_3P	3.0	2.4	12
4[e]	80	PEPPSI-iPr	9.1	1.5	25

[a] **1** (0.1 M), $Pd(OAc)_2$ (2 mM), ligand (6 mM), and Cs_2CO_3 (0.15 M) heated in *o*-xylene for 72 h; [b] Polymerizations with the ligands IPr·HCl (170 °C), JohnPhos (140 °C), RuPhos (140 °C and 80 °C), XPhos (140 °C and 80 °C) did not result in the formation of any isolable polymer upon precipitation of the $CHCl_3$ fraction into methanol; [c] number-average molecular weight (M_n) and dispersity ($Đ$) of polymer in $CHCl_3$ fraction were estimated by GPC in THF with polystyrene standards; [d] yield of the isolated chloroform fraction based on 100 % conversion; [e] **1** (0.5 M), PEPPSI-iPr (2.5 mM), and Cs_2CO_3 (1 M) in *o*-xylene at 80 °C for 72 h.

promote C-C (C$_{sp3}$ (carbinol)-C$_{sp2}$ (thienyl-5C) in this case) cleavage in *ipso*-arylative coupling reactions (Fig. 1: III) than PPh$_3$, which would accelerate the polymerization.[34, 40] During the initial screening of other phosphine ligands (RuPhos, JohnPhos, and XPhos) at 140 °C, no isolable polymer resulted upon attempted precipitation of the polymerization mixtures, suggesting that these ligands may not suitable for *ipso*-arylative polymerization, so higher temperatures were not investigated (Table 1). RuPhos and XPhos were also screened at a lower temperature (80 °C), but no isolable polymer was obtained after precipitation of the polymerization mixtures with these ligands (Table 1).

With analogous Pd-catalyzed Suzuki-Miyaura condensation polymerization systems, ligands such as *t*Bu$_3$P[41] and *N*,*N'*-bis(isopropyl)imidazol-2-ylidene (IPr)[42] have been found to contribute to controlled polymerizations under certain conditions. With monomer **1**, no evidence of controlled chain-growth polymerization was observed with either *t*Bu$_3$P ($Đ > 2$) or IPr·HCl activated with Cs$_2$CO$_3$[44] (no polymer isolated) (Table 1: entries 3 and 4). In the polymerizations with *t*Bu$_3$P[41] and NHC,[42] even uncontrolled polymerization was not observed, which may suggest that *t*Bu$_3$P and NHC do not promote the *ipso*-arylative coupling reaction effectively under the conditions examined. While the use of PEPPSI-IPr[25, 43] (2.5 mM, 0.5 mol%) as a catalyst resulted in polymer with a molecular weight (M_n = 9.1 kg/mol) comparable to that produced with PCy$_3$, though in a lower yield (25%), the lack of any reduction in dispersity ($Đ$ = 1.5) suggested no improvement in control over the polymerization with this catalyst system (Table 1: entry 4). The use of a higher concentration of PEPPSI-IPr (5 mM, 1 mol%) did not result in any isolable polymer after precipitation in methanol.

Monomer concentration, temperature, and time. Increasing monomer concentration can increase polymerization rates, but can reduce rates at higher conversions if solution viscosity becomes too high. Catalyst solubility can also be reduced at higher monomer concentrations. Higher temperatures and longer polymerization times may accelerate the decomposition of palladium catalysts and promote the occurrence of side reactions. [45-47] To further optimize polymerization conditions, polymerizations were conducted with PCy$_3$ as the ligand at four different temperatures (80, 100, and 140 °C, in addition to the 170 °C run described in Table 1, entry 1) and three different monomer concentrations ([**1**] = 0.1, 0.3, or 0.5 M) in an effort to further increase molecular weights and reduce dispersities (Table 2).

At the lowest monomer concentration examined ([**1**] = 0.1 M), polymerization at 140 °C produced P3HT of higher molecular weight (M_n = 11.4 kg/mol, 51% CHCl$_3$ yield) after 24 h (Table 2: entry 2) than was observed at 170 °C after 72 h (M_n = 8.3 kg/mol, Table 1: entry 1), suggesting that catalyst deactivation is an issue at the higher temperature. Polymerization at 140 °C for a longer period of time (72 h) did not result in a significant increase in molecular weight, suggesting either the loss of chain-end functional groups or catalyst decomposition (**Table 2**: entry 3). Polymerization at 120 °C resulted in comparable M_n (11.4 kg/mol) but lower apparent yield (28%, **Table 2**: entry 4). Polymerization at 100 °C produced polymers with slightly lower molecular weights (M_n = 8.8 kg/mol) and a similarly low yield (Table 2: entry 5). A polymerization temperature near 140 °C appears to provide a more optimal balance between polymerization rate, catalyst decomposition, and molecular-weight-limiting side reactions than do higher or lower temperatures.[45-47] At 80 °C, the color of the reaction solution was reddish rather than the almost black color observed for polymerizations that proceeded to higher molecular weights, which was consistent with the formation of low molecular weight species, but could also imply the involvement of Pd nanoparticles or Pd black at higher temperatures (**Table 2**: entry 6).[48]

Table 2 Effects of concentration, temperature, and time on polymerization of **1**.[a]

Entry	[**1**] (M)	T (°C)	t (h)	M_n (kg/mol)[c]	$Đ$[c]	CHCl$_3$ Fraction Yield (%)[d]
1 (*T1-1*)[b]	*0.1*	*170*	*72*	*8.3*	*1.4*	*58*
2	0.1	140	24	11.4	1.5	51
3	0.1	140	72	11.2	1.7	55
4	0.1	120	48	11.4	1.5	28
5	0.1	100	48	8.8	1.5	27
6	0.1	80	96	7.2	1.6	48
7	0.3	140	48	16.0	1.6	52
8	0.5	140	48	19.7	1.8	57
9	0.5	140	96	19.5	1.6	45
10	0.5	120	96	15.0	1.7	44
11	0.5	100	96	15.0	2.2	42
12	1.0	140	48	5.5	1.4	24

[a] Monomer **1** (1 equiv.), Pd(OAc)$_2$ (0.03 equiv.), PCy$_3$ (0.06 equiv.), and Cs$_2$CO$_3$ (1.5 equiv.) heated in *o*-xylene; [b] identical to entry 1 in Table 1. Effect of ligand on polymerization of 1[a]; [c] number-average molecular weight (M_n) and dispersity ($Đ$) of polymer in CHCl$_3$ fraction were estimated by GPC in THF with polystyrene standards; [d] yield of the isolated chloroform fraction based on 100 % conversion.

At a higher monomer concentration ([**1**] = 0.5 M), polymerization at 140 °C produced P3HT of significantly higher molecular weight (M_n = 19.7 kg/mol, 57% CHCl$_3$ yield) after 48 h (Table 2: entry 8) than at higher or lower concentrations ([**1**] = 0.1 M, 0.3 M, 1 M; **Table 2**: entries 2, 7, 12), though the molecular weight observed at [**1**] = 0.3 M was only slightly lower (M_n = 16 kg/mol; **Table 2**: entry 7). In general, at a monomer concentration of 0.5 M, much higher molecular weights (M_n up to 20 kg/mol) and somewhat larger dispersities ($Đ$ from 1.8 to 2.2) were observed at temperatures ranging from 100-140 °C (**Table 2**: entries 8-11). At higher monomer concentration ([**1**] = 1 M), only low molecular weight P3HT was collected (M_n = 5.5 kg/mol), suggesting that the ultimate molecular weight may be limited by low solubility of polymer at these concentrations (**Table 2**: entry 12). The typical regioregularity of P3HT (**Table 2**: entry 8) was 90% head-to-tail, as calculated by comparing the integrations of peaks at δ 2.81 (head-to-tail) and 2.58 ppm (head-to-head) in ^{1}H NMR spectra of the polymers (Fig S10).[49]

Base concentration. The effect of the amount of base (Cs$_2$CO$_3$), which primarily serves to neutralize HBr generated during the coupling reaction (**Fig. 1**), on the polymerization of monomer **1**

Table 3 Effect of [Cs_2CO_3] on polymerization of 1[a]

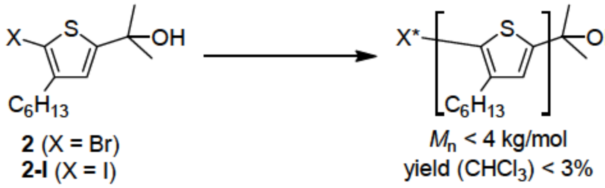
Entry	[Cs_2CO_3]/[1]	M_n (kg/mol)[b]	$Đ$[b]	$CHCl_3$ Fraction Yield (%)[c]
1 (*T2-8*)[d]	1.5	19.7	1.8	57
2	1	19.4	1.5	44
3	0.5	14.3	1.4	57

[a] **1** (0.5 M), $Pd(OAc)_2$ (15 mM), PCy_3 (30 mM), and Cs_2CO_3 heated in *o*-xylene at 140 °C for 48 h. The reaction mixture was precipitated in methanol, isolated by filtration, and then washed with methanol and hexanes in a Soxhlet apparatus before being collected with chloroform; [b] number-average molecular weight (M_n) and dispersity ($Đ$) of polymer in $CHCl_3$ fraction was estimated by GPC in THF with polystyrene standards; [c] yield of the isolated chloroform fraction based on 100 % conversion; [d] identical to Table 2: entry 8.

was also examined in an attempt to further optimize the polymerization conditions (**Table 3**). Relatively high molecular weights (M_n from 19-20 kg/mol) were observed with 1.0 or 1.5 equivalents of Cs_2CO_3 relative to monomer **1**, though the larger amount appeared to result in a slightly higher dispersity (**Table 3**: entries 1 and 2). Reduction of the base concentration to half that of monomer resulted in a reduction in M_n to 14 kg/mol (Table 3: entry 3). Substitution of CsF (1.5 equiv), which has been used to promote conversion in Suzuki-Miyaura and Stille cross-coupling,[50, 51] for Cs_2CO_3 resulted in isolation of only a small amount of oligomer after 48 h. It seems CsF neither neutralizes HBr effectively nor promotes the coupling reaction under the conditions examined.

Polymerization of dimethylcarbinol monomer 2

Monomer **2**, with a dimethylcarbinol substituent that is eliminated as acetone, was synthesized and investigated to determine if a more volatile leaving group might be beneficial for *ipso*-arylative polymerization (Scheme 3). As was done for the polymerization of diphenylcarbinol **1**, a range of ligands, temperatures, and concentrations were investigated for the polymerization of **2**, however, under the best conditions, only low molecular weight polymers (M_n = 4.4 kg/mol) were obtained in low yield (2.3%) (Table S1: entry 2). It seems that the polymerizability of monomer **2** was significantly lower than **1** due to the lower reactivity of dimethyl carbinol groups in comparison to diphenyl carbinol groups, which is likely the result of a lower rate of insertion of Pd in step II of the catalytic cycle (Fig. 1). Dimethylcarbinol methyl peaks (δ 1.68 ppm, peak h in Fig. S9) were still visible in ^1H NMR spectra of the hexane-soluble oligomer fraction after Soxhlet purification. When iodothienyl monomer **2-I** was polymerized in an attempt to increase coupling efficiency, a slightly higher molecular weight was obtained (M_n = 6.6 kg/mol; Table S1: entry 7), but the yield remained low (2.5%).



Scheme 3 Polymerization of dimethylcarbinol monomers **2** and **2-I** (see Table S1)

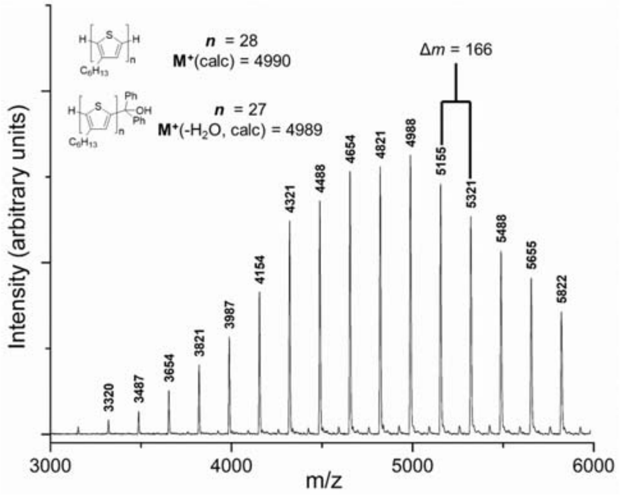


Fig. 2 MALDI-TOF for P3HT prepared by *ipso*-arylative cross-coupling polymerization of monomer **1** at 140 °C for 24 h (Table 2, entry 2).

Model studies of termination reactions.

P3HT with higher molecular weight (M_n > 20 kg/mol) has been reported to result from other palladium-catalyzed cross-coupling polymerizations.[17, 22, 42, 43] The plateau in molecular weight evolution observed at longer polymerization times for several of the polymerization conditions used with monomer **1** suggests that catalyst decomposition and/or end-group loss are limiting the ultimate molecular weight.

MALDI-TOF mass spectrometry of P3HT prepared by *ipso*-arylative polymerization of monomer **1** at 140 °C shows a single major series of peaks with a mass difference of 166 Da between peaks, corresponding to the mass of the 3-hexylthienyl repeating unit (166.28 g/mol) (Fig. 2). The *m/z* values for the peaks in this series do not match the values expected for polymers with bromide and diphenylcarbinol end groups (Fig. 3, Br-/-CPh₂OH), but can be matched to several possible end-

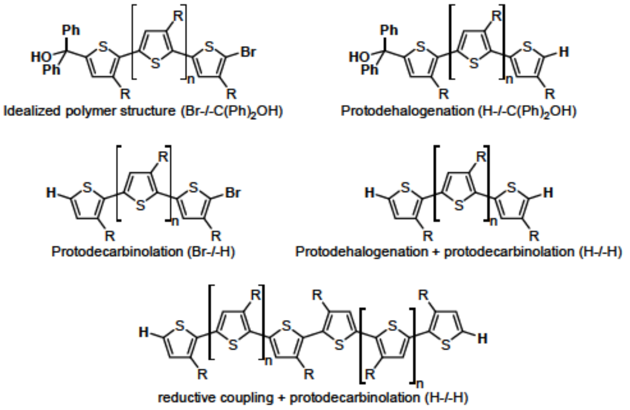


Fig. 3 Expected polymer end-groups and possible end-groups resulting from side reactions.

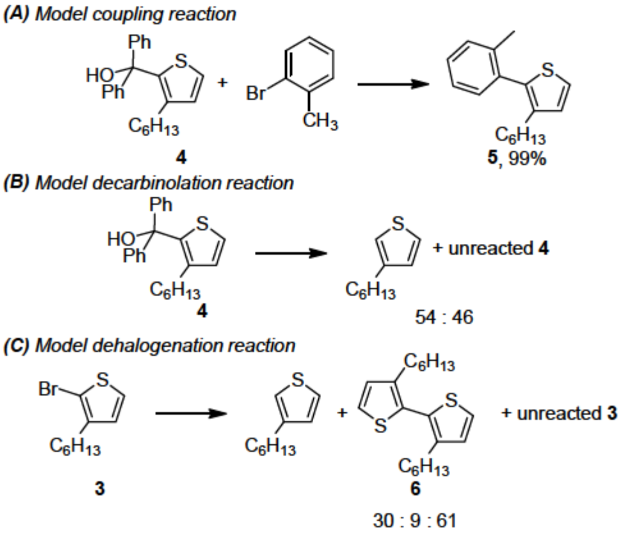
group combinations: H-/-H resulting from either protodehalogenation/protodecarbinolation or reductive coupling of thienyl halides[52] followed by protodecarbinolation at both chain ends (for DP = 31, M_{calc} = 5157 Da), or H-/-CPh_2^+ resulting from protodehalogenation and ionization through loss of hydroxide anion (for DP = 30, M_{calc} = 5156 Da) (Fig. 2). (Mass spectra for monomers **1** and **2** similarly show the major species present results from cationization through loss of hydroxide.)

The absence of diphenylcarbinol aromatic protons in ^1H NMR spectra for P3HT prepared from monomer **1** at 140 °C (Fig. S10) suggests that the major series present has protons at both termini (H-/-H). The occurrence of these side reactions which lead to the loss of end-groups under standard polymerization conditions appears to be a significant factor limiting polymer growth.

MALDI-TOF spectrograms of polymerizations of monomer **1** run at lower temperatures (80-120 °C, Fig. S12) show that the major series of peaks at each temperature corresponds to the H-/-H or H-/-CPh_2^+ series, but two minor series of peaks can be observed at the lower temperatures, neither with masses corresponding to Br-/-$C(Ph)_2OH$ end-groups. One series is 16 amu larger than the major series (M_{major}+16), which likely corresponds to either H-/-CPh_2OH (protodehalogenation) or $Ph_2(HO)C$-/-CPh_2^+ (reductive coupling) end-groups, which is supported by the presence of diphenylcarbinol aromatic protons in the ^1H NMR spectrum (7.43 and 7.35 ppm) of this polymer (Fig. S11). The second series (M_{major}+44) does not match any expected end-group combination. It is plausible that this series results from either enchainment of monomer through *ortho*-arylation, which would result in additional carbinol groups on each chain, or direct arylation of *ortho*-xylene, but further study will be necessary to identify these species.

As the polymerization temperature is increased from 100 to 140 °C, the relative intensity of the minor series of peaks decreases (Fig. S12: B, C, and D), suggesting that higher reaction temperature, while resulting in higher molar masses, may promote protodehalogenation/protodecarbinol-ation or reductive coupling[52]/protodecarbinolation to produce chains with proton end-groups (H-/-H). At a lower temperature (80 °C), longer reaction times may also favor the formation of proton end-groups (H-/-H).

To confirm the MALDI-TOF MS end group assignments, model compounds **3** and **4** were subjected to standard polymerization conditions (Scheme 4). Control reaction **A** was designed to allow investigation of side reactions that can occur during *ipso*-arylative coupling between a monofunctional carbinol and a monofunctional aryl halide (Scheme 4). 2-Hydroxydiphenylmethyl-3-hexylthiophene (**4**, 0.1 M), a model for the diphenylcarbinol chain end, and 2-bromotoluene (0.1 M) were mixed with $Pd(OAc)_2$ (3 mM), PCy_3 (6 mM), and Cs_2CO_3 (0.15 M) in *o*-xylene and heated for 24 h at 140 °C. The resulting mixture was concentrated and dissolved in $CDCl_3$. In the ^1H NMR spectrum of the resulting solution, the near quantitative conversion of the two precursors to 3-hexyl-2-(*o*-tolyl)thiophene (**5**) with no protodecarbinolation was observed.



Scheme 4 Model coupling reactions: reactant(s) (0.1 M each), $Pd(OAc)_2$ (0.03 M), PCy_3 (0.06 M), and Cs_2CO_3 (0.15 M) in *o*-xylene, 140 °C, 24 h.

Control reaction **B** was designed to determine the extent of protodecarbinolation during standard coupling conditions in the absence of an aryl halide (Scheme 4). Carbinol **4** was heated for 24 h at 140 °C without aryl halide, but otherwise under the same conditions as reaction **A**. The formation of 3-hexylthiophene (~54%, multiplets at δ 7.25 ppm and 6.95 ppm), the product resulting from protodecarbinolation, and benzophenone (43%, triplets at δ 7.51 and 7.63 ppm, doublet at δ 7.85 ppm) was observed by ^1H NMR, in addition to unreacted **4** (~46%, doublets at δ 7.13 and 6.98 ppm, multiplets at δ 7.35 and 7.42 ppm) (Fig. 4: Spectrum B). In a reaction carried out under the same conditions as reaction **B**, but in the absence of palladium catalyst and phosphine, only unreacted **4** was observed by ^1H NMR, confirming that the catalyst system plays

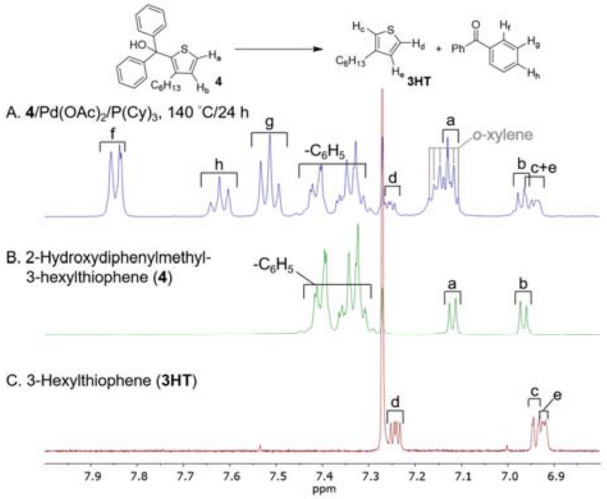


Fig. 4 ^1H NMR spectra ($CDCl_3$, solvent peak at 7.26 ppm) for control reaction **B** (Scheme 2): (A) Reaction mixture after 2-hydroxydiphenylmethyl-3-hexylthiophene (**4**) (0.1 M) was heated with $Pd(OAc)_2$ (3%), PCy_3 (6%), Cs_2CO_3 (1.5 equiv.) in o-xylene at 140 °C for 24 h; (B) model compound **4**; (C) 3-hexylthiophene.

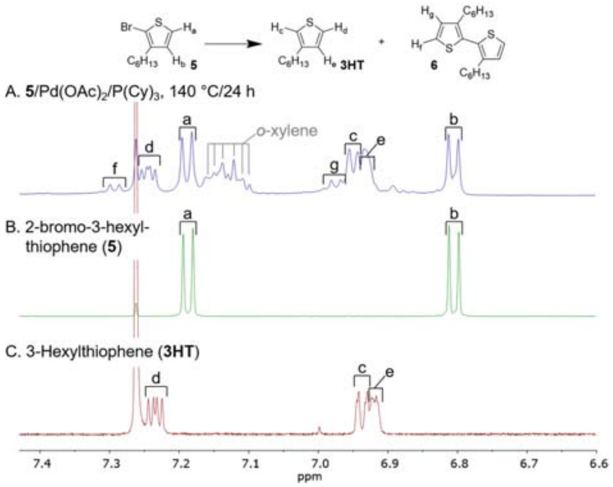


Fig. 5 ^{1}H NMR spectra ($CDCl_3$, solvent peak at 7.26 ppm) for control reaction **C** (Scheme 2): (A) crude product mixture resulting from reaction of 2-bromo-3-hexylthiophene (**5**) (0.1 M) with $Pd(OAc)_2$ (3%), PCy_3 (6%), Cs_2CO_3 (1.5 equiv.) in o-xylene at 140 °C for 24 h; (B) 2-bromo-3-hexylthiophene (**5**); (C) 3-hexylthiophene.

an important role in the protodecarbinolation reaction.

Together, control reactions **A** and **B** suggest that protodecarbinolation during polymerization is more likely to occur at higher conversions where the concentration of aryl halides is low, which is consistent with the finding that carbinol end group loss appears to increase at higher temperatures and longer polymerization times. While it has previously been reported that protodecarbinolation in *ipso*-arylative cross-coupling reactions with molecular substrates can be minimized by the use of PCy_3 rather than bulkier phosphines,[53] these results suggest that it can occur to a sufficient extent during polymerization to limit the ultimate molecular weights that can be realized.Control reaction **C** was used to examine the possibility of protodehalogenation under *ipso*-arylative coupling conditions. 2-Bromo-3-hexylthiophene (**3**, 0.1 M), $Pd(OAc)_2$ (3 mM), PCy_3 (6 mM), and Cs_2CO_3 (0.15 M) in *o*-xylene were heated for 24 h at 140 °C. The resulting mixture was concentrated and dissolved in$CDCl_3$. In the ^{1}H NMR spectrum of this solution (Fig. 4), 56% of **3** remained unchanged, 28% had been reduced to 3-hexylthiophene (Fig. 5: Spectrum A, peaks c, d, and e), and 16% had dimerized to 3,3'-dihexyl-2,2'-bithiophene (**6**), likely through Ullman-like reductive coupling,[54, 55] resulting 61:30:9 ratio of unreacted **5**, the dehalogenated product 3-hexylthiophene, and dimer **6**.

Palladium-catalyzed dehalogenation of aryl halides has been purposefully carried out in the presence of primary or secondary alcohols[56, 57] or under a hydrogen atmosphere.[58, 59] Uncontrolled dehalogenation of aryl halides has also been reported as an undesired side reaction in palladium-catalyzed cross-coupling reactions in the absence of alcohols or a hydrogen atmosphere, though the mechanism is unclear.[60, 61] In the *ipso*-arylative polymerization of **1**, the mechanism of dehalogenation of bromothiophene is still unclear, but it may be related to the formation of other palladium species or palladium black since similar undesired end groups (-H) have also been observed in other palladium-catalyzed cross-coupling polymerizations.[25, 55]

Based on the model reactions (Scheme 4), protodehalogenation, protodecarbinolation, and reductive coupling reactions occur more slowly than *ipso*-arylative cross-coupling, suggesting that these termination reactions are only significant at higher monomer conversions. The occurrence of protodecarbinolation and dehalogenation side reactions, as evidenced by ^{1}H NMR spectra of the products of control reactions **B** and **C** (Fig. 4 and Fig. 5) and MALDI-TOF MS of polymerizations at different temperatures, would explain the increase in proton end groups rather than the expected diphenylcarbinol or bromide end groups on P3HT prepared by *ipso*-arylative coupling.

Conclusions

ipso-Arylative cross-coupling reactions have been applied to the preparation of P3HT. The chemical structures of those polymers have been analyzed by ^{1}H NMR and MALDI-TOF and the polymer molecular weights have been estimated by SEC. Ligand-screening studies showed that PCy_3 is more suitable for producing higher molecular weights than other phosphine ligands. Diphenylcarbinol monomer **1** has been successfully polymerized over a wide range of temperatures (80-140 °C) to number-average molecular weights up to 20 kg/mol. Dimethylcarbinol monomer **2** showed lower polymerizability than **1** under the same conditions and mostly formed oligomers ($M_n \approx 3$ kg/mol).

The occurrence of side reactions that limit molecular weight in the polymerization of diphenylcarbinol **1** have been studied with model compounds. The loss of both bromide and diphenylcarbinol groups under polymerization conditions has been observed in the model compounds by ^{1}H NMR and in polymers by end-group analysis with MALDI-TOF, suggesting that P3HT prepared by *ipso*-arylative polymerization of **1** is terminated with protons on both ends during the course of the polymerization, suggesting that the growth of polymer chains is ultimately halted by the loss of active end-groups. These results suggest that, without further optimization of *ipso*-arylation coupling methods, that the use of this method as a general route to π-conjugated polymers is likely to be limited to cases where its advantages over complementary methods (e.g., monomer stability, lack of tin by-products) are clear.

Experimental Section

Materials

All reactions were carried out in oven-dried glassware under a nitrogen atmosphere. Anhydrous and anaerobic solvents were purchased from commercial sources. *N*-Bromosuccinimide was recrystallized from hot water. Other starting materials were purchased from commercial sources and used without further purification.

Characterization

^1H NMR and ^{13}C NMR spectra were collected on a 400 MHz NanoBay Bruker spectrometer or a 500 MHz Bruker Avance III Console with CD_2Cl_2 or $CDCl_3$ as the solvent at room temperature and referenced to either dichloromethane (5.35 ppm for ^1H NMR and 54.0 ppm for ^{13}C NMR) or chloroform (7.26 ppm for ^1H NMR and 77.2 ppm for ^{13}C NMR) peaks. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were acquired with a Bruker AutoFlexII equipped with a nitrogen laser (λ = 337 nm). Time-of-flight mass analysis were performed in the reflectron mode over an *m/z* range 1000–9000 Da. Polymer solutions in chloroform (4 mg/mL) and matrix (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) solutions in chloroform (25 mg/mL) were mixed in a 1:2 v/v ratio. The mixed solution (1 µL) was applied to a stainless steel target and air-dried. High resolution mass spectra were obtained on Agilent LC-MSD consisting an 1100 HPLC and a G1956A mass spectrometer. All size-exclusion chromatography (SEC) data were acquired at 40 °C with THF (HPLC grade, J.T. Baker) as the eluent at a flow rate of 1.0 ml/minute. The SEC consisted of a K-501 pump (Knauer), a K-3800 Basic Autosampler (Marathon), 2 × PLgel 5 μm Mixed-D columns (300 × 7.5 mm, rated for linear separations at polymer molecular weights from 200 to 400,000 g/mol, Polymer Laboratories), a CH-30 Column Heater (Eppendorf), a PL-ELS 1000 Evaporative Light Scattering Detector (Polymer Laboratories), and a PL Datastream unit (Polymer Laboratories). Narrow polydispersity polystyrene standards with molecular weights from 580-377,400 g/mol (EasiCal PS-2, Polymer Laboratories) were used to construct a calibration curve for data analysis.

Synthetic Procedures

(5-Bromo-4-hexylthiophen-2-yl)diphenylmethanol (1). Lithium diisopropylamide (LDA) solution (6.0 ml, 1.5 M in THF, 9.0 mmol) was injected into anhydrous THF (20 ml) in a nitrogen-filled glovebox, then the flask containing the LDA solution was removed from the glovebox and cooled under nitrogen to -78 °C in an acetone/liquid nitrogen bath. 2-Bromo-3-hexylthiophene (2.0 g, 8.1 mmol) was dissolved in anhydrous THF (20 ml). The 2-bromo-3-hexlythiophene solution was added to the LDA solution with a syringe pump (40 ml/h) at -78 °C. Then the mixture was allowed to stir for 15 min before a solution of benzophenone in THF (10 ml, 0.65 M, 6.5 mmol) was slowly injected by syringe. The mixture was stirred for 1 h at -78 °C and then allowed to warm up to room temperature overnight. The reaction mixture was neutralized by the addition of aqueous HCl (1 M, 10 ml). The organic layer was separated and the aqueous layer was extracted with chloroform (3 x 40 ml). The chloroform extracts and the first organic layer were combined and dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure. The crude product was purified by gravity chromatography (SiO_2, hexanes/ethyl acetate 100:0 to 95:5 as a gradient) to give **1** as a viscous orange liquid (2.4 g, 86%). ^1H NMR (400 MHz, $CDCl_3$, Fig. S1) δ 7.40 – 7.31 (m, 10H, -Ph), 6.46 (s, 1H, thienyl 3-H), 2.53 – 2.44 (m, 2H, thiophene-CH_2-), 1.53 (t, 2H, thiophene-CH_2CH_2-), 1.38 – 1.22 (m, 6H, -$(CH_2)_3CH_3$), 0.96 – 0.82 (m, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, Fig. S2) δ 151.4, 146.1, 141.8, 128.3, 128.0, 127.8, 127.4, 109.4, 80.3, 31.7, 29.83, 29.76, 29.0, 22.8, 14.3.; ESI-MS HRMS (positive ion mode) (m/z) $[M+H-H_2O]^+$ calcd. for $C_{23}H_{25}OBrOS+H-H_2O$, 413.0758; found, 413.0759.

2-(5-Bromo-4-hexylthiophen-2-yl)propan-2-ol (2). LDA solution (6.0 ml, 1.5M in THF, 9.0 mmol) was injected into anhydrous THF (20 ml) in a nitrogen-filled glovebox. The flask containing the LDA solution was removed from the glovebox and cooled under nitrogen to -78 °C in an acetone/liquid nitrogen bath. A solution of 2-bromo-3-hexylthiophene (2.0 g, 8.1 mmol) in anhydrous THF solvent (20 ml) was prepared and slowly added to the LDA solution with a syringe pump (40 ml/h) at -78 °C. Then the mixture was stirred for 15 min before a solution of acetone in THF (10.0 ml, 1.22 M, 12.2 mmol) was slowly injected by syringe at -78 °C. The mixture was stirred for 1 h at -78 °C and then allowed to warm up to room temperature overnight with stirring. The reaction mixture was neutralized by addition of aqueous HCl (1 M, 10 ml). The organic layer was separated and the aqueous layer was extracted with chloroform (3 x 40 ml). The chloroform fractions and the first organic layer were combined and dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure. The crude product was purified by gravity chromatography (hexanes/ethyl acetate 90:10 to 75:25 as a gradient) to give **2** as a viscous orange liquid (2.2 g, 89%). ^1H NMR (400 MHz, $CDCl_3$, Fig. S3) δ 6.65 (s, 1H, thienyl 3-H), 2.56 – 2.46 (m, 2H, thiophene-CH_2-), 1.96 (s, 1H, -OH), 1.62 (s, 6H, -C(OH)$(CH_3)_2$), 1.56 (m, 2H, thiophene-CH_2CH_2-), 1.32 (s, 6H, -$(CH_2)_3$-CH_3), 0.90 (s, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, Fig. S4) δ 153.8, 141.8, 123.1, 107.3, 76.9, 71.7, 32.1, 31.8, 29.88, 29.86, 29.1, 22.8, 14.3; ESI-MS HRMS (positive ion mode) (m/z) $[M+H-H_2O]^+$ calcd. for $C_{13}H_{21}BrO_5S+H-H_2O$, 289.0443; found, 289.0445.

(3-Hexylthiophen-2-yl)diphenylmethanol (4). 2-Bromo-3-hexylthiophene (1 g, 4.05 mmol) was dissolved in anhydrous THF (10 ml) in a Schlenk flask. The flask was cooled to -78 °C in an acetone/liquid nitrogen bath. *n*-Butyl lithium (2.66 ml, 1.60 M, 4.25 mmol) was injected by syringe into the flask dropwise. Then the mixture was stirred for 30 min and a solution of benzophenone in THF (10 ml, 0.365 M, 3.65 mmol) was injected by syringe slowly at -78 °C. The mixture was stirred for 1 h at -78 °C and then allowed to warm up to room temperature overnight with stirring. The mixture was neutralized by addition of aqueous 1M HCl (5.0 ml). The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 x 10 ml). The dichloromethane fractions and the first organic layer were combined and dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure. The crude product was purified by gravity chromatography (SiO_2, hexanes/ethyl acetate 95:5) to give **4** as a viscous orange liquid (779 mg, 55%). ^1H NMR (400 MHz, $CDCl_3$, Fig. S7) δ 7.39 (dd, 4H, -Ph), 7.36 – 7.29 (m, 6H, -Ph), 7.11 (d, 1H, thienyl-4H), 6.96 (d, 1H, thienyl-3H), 2.97 (s, 1H, -OH), 2.30 (t, 2H, thiophene-CH_2-), 1.38 – 1.25 (m, 2H, thiophene-CH_2-CH_2-), 1.25 – 1.14 (m, 2H, -CH_2-CH_2-CH_2-), 1.14 – 1.03 (m, 4H, -$(CH_2)_2$-CH_3), 0.83 (t, 3H, -CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, Fig. S8) δ 146.4, 144.6, 140.7, 130.152, 130.151, 127.9, 127.5, 123.3, 79.8, 31.6, 30.1, 29.6, 29.3, 22.6, 14.2; ESI-MS HRMS (positive ion mode) (m/z) $[M+H-H_2O]^+$ calcd. for $C_{23}H_{26}OS+H-H_2O$, 333.1671; found, 333.1674.

General Polymerization Procedure. **Monomer** (0.5 M), palladium acetate (15 mM), tricyclohexylphosphine (30 mM), and cesium carbonate (1 M) in *o*-xylene were loaded in a pressure tube with a magnetic stirbar in a nitrogen-filled glovebox. The sealed pressure tubes were removed from the glovebox and clamped in a preheated silicon oil bath. After polymerization, the solution was allowed to cool to room temperature and precipitated by addition to an excess of stirred methanol. The precipitated polymer was collected by filtration and purified by sequential Soxhlet extraction with hexanes, to afford a low molecular weight fraction, and chloroform, to afford the higher molecular weight fraction.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1. V. Jankus, M. Aydemir, F. B. Dias and A. P. Monkman, *Adv. Sci.*, 2016, **3**, 1500221.
2. Guangru Li, Zhi-Kuang Tan, Dawei Di, May Ling Lai, Lang Jiang, Jonathan Hua-Wei Lim, Richard H. Friend and N. C. Greenham, *Nano Lett.*, 2015, **15**, 2640-2644.
3. R. Trattnig, L. Pevzner, M. Jäger, R. Schlesinger, M. V. Nardi, G. Ligorio, C. Christodoulou, N. Koch, M. Baumgarten, K. Müllen and E. J. W. List, *Adv. Funct. Mater.*, 2013, **23**, 4897-4905.
4. B. Sun, W. Hong, Z. Yan, H. Aziz and Y. Li, *Adv. Mater.*, 2014, **26**, 2636-2642, 2613.
5. Y. He, W. Hong and Y. Li, *J. Mater. Chem. C*, 2014, **2**, 8651-8661.
6. A. Yokoyama, R. Miyakoshi and T. Yokozawa, *Macromolecules*, 2004, **37**, 1169-1171.
7. R. Tkachov, V. Senkovskyy, H. Komber, J.-U. Sommer and A. Kiriy, *J. Am. Chem. Soc.*, 2010, **132**, 7803-7810.
8. R. Miyakoshi, A. Yokoyama and T. Yokozawa, *J. Am. Chem. Soc.*, 2005, **127**, 17542-17547.
9. R. S. Loewe, S. M. Khersonsky and R. D. McCullough, *Adv. Mater.*, 1999, **11**, 250-253.
10. K. Okamoto and C. K. Luscombe, *Polym. Chem.*, 2011, **2**, 2424-2434.
11. Z. J. Bryan and A. J. McNeil, *Macromolecules*, 2013, **46**, 8395-8405.
12. K.-B. Seo, I.-H. Lee, J. Lee, I. Choi and T.-L. Choi, *J. Am. Chem. Soc.*, 2018, **140**, 4335–4343.
13. J. Linshoeft, E. J. Baum, A. Hussain, P. J. Gates, C. Nather and A. Staubitz, *Angew. Chem. Int. Ed.*, 2014, **53**, 12916-12920.
14. X. Yin, F. Guo, R. A. Lalancette and F. Jäkle, *Macromolecules*, 2016, **49**, 537-546.
15. B. Li, Z. Guan, W. Wang, X. Yang, J. Hu, B. Tan and T. Li, *Adv. Mater.*, 2012, **24**, 3390-3395.
16. G. He, L. Kang, W. Torres Delgado, O. Shynkaruk, M. J. Ferguson, R. McDonald and E. Rivard, *J. Am. Chem. Soc.*, 2013, **135**, 5360-5363.
17. T. Bura, J. T. Blaskovits and M. Leclerc, *J. Am. Chem. Soc.*, 2016, **138**, 10056-10071.
18. P. D. Homyak, Y. Liu, J. D. Harris, F. Liu, K. R. Carter, T. P. Russell and E. B. Coughlin, *Macromolecules*, 2016, **49**, 3028-3037.
19. J. Kuwabara, T. Yasuda, N. Takase and T. Kanbara, *ACS Appl. Mater. Interfaces*, 2016, **8**, 1752-1758.
20. N. Rodriguez and L. J. Goossen, *Chem. Soc. Rev.*, 2011, **40**, 5030-5048.
21. A. E. Rudenko and B. C. Thompson, *J. Polym. Sci., Part A: Polym. Chem.*, 2015, **53**, 135-147.
22. A. E. Rudenko, C. A. Wiley, J. F. Tannaci and B. C. Thompson, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 2660-2668.
23. Q. Wang, M. Wakioka and F. Ozawa, *Macromol. Rapid Commun.*, 2012, **33**, 1203-1207.
24. A. Yokooji, T. Satoh, M. Miura and M. Nomura, *Tetrahedron*, 2004, **60**, 6757-6763.
25. S.-L. Suraru, J. A. Lee and C. K. Luscombe, *ACS Macro Lett.*, 2016, **5**, 533-536.
26. P. Forgione, M. C. Brochu, M. St-Onge, K. H. Thesen, M. D. Bailey and F. Bilodeau, *J. Am. Chem. Soc.*, 2006, **128**, 11350-11351.
27. L. J. Goossen, N. Rodriguez, B. Melzer, C. Linder, G. Deng and L. M. Levy, *J. Am. Chem. Soc.*, 2007, **129**, 4824-4833.
28. W. I. Dzik, P. P. Lange and L. J. Gooßen, *Chem. Sci.*, 2012, **3**, 2671.
29. S. E. Denmark, R. C. Smith, W.-T. T. Chang and J. M. Muhuhi, *J. Am. Chem. Soc.*, 2009, **131**, 3104-3118.
30. S. A. Tymonko, R. C. Smith, A. Ambrosi and S. E. Denmark, *J. Am. Chem. Soc.*, 2015, **137**, 6192-6199.
31. S. E. Denmark and A. Ambrosi, *Org. Process Res. Dev.*, 2015, **19**, 982-994.
32. T. Ishiyama, Y. Itoh, T. Kitano and N. Miyaura, *Tetrahedron Lett.*, 1997, **38**, 3447-3450.
33. M. Iwasaki, Y. Araki, S. Iino and Y. Nishihara, *J. Org. Chem.*, 2015, **80**, 9247-9263.
34. Y. Terao, H. Wakui, T. Satoh, M. Miura and M. Nomura, *J. Am. Chem. Soc.*, 2001, **123**, 10407-10408.
35. R. Wakabayashi, D. Fujino, S. Hayashi, H. Yorimitsu and K. Oshima, *J. Org. Chem.*, 2010, **75**, 4337-4343.
36. M. Iwasaki, S. Hayashi, K. Hirano, H. Yorimitsu and K. Oshima, *Tetrahedron*, 2007, **63**, 5200-5203.
37. J. R. Bour, J. C. Green, V. J. Winton and J. B. Johnson, *J. Org. Chem.*, 2013, **78**, 1665-1669.
38. Y. S. Park, Q. Wu, C. Y. Nam and R. B. Grubbs, *Angew. Chem. Int. Ed.*, 2014, **53**, 10691-10695.
39. Y. S. Park, T. S. Kale, C. Y. Nam, D. Choi and R. B. Grubbs, *Chem. Commun.*, 2014, **50**, 7964-7967.
40. Y. Terao, H. Wakui, M. Nomoto, T. Satoh, M. Miura and M. Nomura, *J. Org. Chem.*, 2003, **68**, 5236-5243.
41. K. Kosaka, Y. Ohta and T. Yokozawa, *Macromol. Rapid Commun.*, 2015, **36**, 373-377.
42. A. Sui, X. Shi, H. Tian, Y. Geng and F. Wang, *Polym. Chem.*, 2014, **5**, 7072-7080.
43. Y. Qiu, J. Mohin, C. H. Tsai, S. Tristram-Nagle, R. R. Gil, T. Kowalewski and K. J. Noonan, *Macromol. Rapid Commun.*, 2015, **36**, 840-844.
44. H. Lebel, M. K. Janes, A. B. Charette and S. P. Nolan, *J. Am. Chem. Soc.*, 2004, **126**, 5046-5047.
45. P. W. van Leeuwen, *Appl. Catal., A*, 2001, **212**, 61-81.

46. R. H. Crabtree, *Chem. Rev.*, 2014, **115**, 127-150.
47. I. P. Beletskaya and A. V. Cheprakov, *Chem. Rev.*, 2000, **100**, 3009-3066.
48. D. Astruc, *Inorg. Chem.*, 2007, **46**, 1884-1894.
49. T.-A. Chen, X. Wu and R. D. Rieke, *J. Am. Chem. Soc.*, 1995, **117**, 233-244.
50. S. P. Mee, V. Lee and J. E. Baldwin, *Chem. Eur. J.*, 2005, **11**, 3294-3308.
51. S. W. Wright, D. L. Hageman and L. D. McClure, *J. Org. Chem.*, 1994, **59**, 6095-6097.
52. D. D. Hennings, T. Iwama and V. H. Rawal, *Org. Lett.*, 1999, **1**, 1205-1208.
53. Y. Terao, M. Nomoto, T. Satoh, M. Miura and M. Nomura, *J. Org. Chem.*, 2004, **69**, 6942-6944.
54. C. H. Woo, B. C. Thompson, B. J. Kim, M. F. Toney and J. M. Fréchet, *J. Am. Chem. Soc.*, 2008, **130**, 16324-16329.
55. F. Lombeck, H. Komber, S. I. Gorelsky and M. Sommer, *ACS Macro Lett.*, 2014, **3**, 819-823.
56. O. Navarro, H. Kaur, P. Mahjoor and S. P. Nolan, *J. Org. Chem.*, 2004, **69**, 3173-3180.
57. J. Chen, Y. Zhang, L. Yang, X. Zhang, J. Liu, L. Li and H. Zhang, *Tetrahedron*, 2007, **63**, 4266-4270.
58. X. Yuan, G. Sun, H. Asakura, T. Tanaka, X. Chen, Y. Yuan, G. Laurenczy, Y. Kou, P. J. Dyson and N. Yan, *Chem. Eur. J.*, 2013, **19**, 1227-1234.
59. R. Nakao, H. Rhee and Y. Uozumi, *Org. Lett.*, 2005, **7**, 163-165.
60. J. Yin and S. L. Buchwald, *J. Am. Chem. Soc.*, 2000, **122**, 12051-12052.
61. X. Zhang, A. Liu and W. Chen, *Org. Lett.*, 2008, **10**, 3849-3852.

ipso-Arylative polymerization as a route to π-conjugated polymers: Synthesis of poly(3-hexylthiophene)

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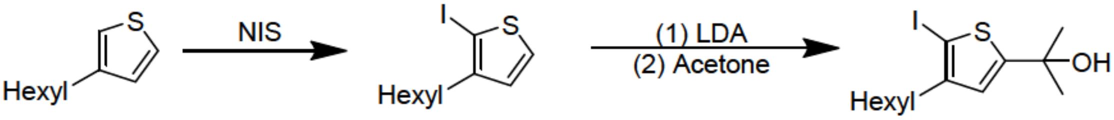
Supporting Information
Synthetic Procedures



7 (77 %)

2-I (34 %)

3-Hexyl-2-iodothiophene (7).[1] 3-Hexylthiophene (3.11 g, 18.5 mmol) was dissolved in AcOH (25 ml) and $CHCl_3$ (25 ml) in a flask wrapped with aluminum foil at room temperature, then *N*-iodosuccinimide (4.37 g, 19.4 mmol) was poured into the flask in 5 portions over 30 min. The mixture was allowed to stir overnight at room temperature. The solution was neutralized by cooling the flask in an ice bath and slowly adding aqueous 2M KOH (100 mL). The organic layer was separated in a separatory funnel and the aqueous layer was extracted with dichloromethane (3 x 50 ml), then the first organic fraction and dichloromethane fractions were combined and washed with saturated $NaHCO_3$(aq) (100 ml). The organic layer was dried over with anhydrous Na_2SO_4 and filtered, then the collected solution was concentrated and purified with chromatography (SiO_2, hexanes) to afford 7 as a reddish transparent liquid (4.2 g, 77%). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.38 (d, 1H, thienyl 4-H), 6.76 (d, 1H, thienyl 3-H), 2.57 (t, 2H, thiophene-CH_2), 1.57 (m, 2H, thiophene-CH_2-CH_2-), 1.33 (m, 4H, -$(CH_2)_2$-CH_3), 0.91 (t, 3H, -CH_3).

2-(4-Hexyl-5-iodothiophen-2-yl)propan-2-ol (2-I). LDA solution (11.1 ml, 1.5M in THF, 16.7 mmol) was injected into anhydrous THF (20 ml) in a nitrogen-filled glovebox. The flask containing LDA solution was removed from glovebox and cooled to -78 °C in an acetone/liquid nitrogen bath. Compound 7 (4.2 g, 14.4 mmol) was dissolved in anhydrous THF (20 ml) in a flask. The solution of 7 was slowly added to the LDA solution with a syringe pump (40 ml/h) at -78 °C. Then the mixture was stirred for 15 min and a solution of acetone in THF (10 mL, 2.88 M, 28.8 mmol) was slowly injected by syringe at -78 °C. The mixture was stirred for 1 h at -78 °C and then allowed to warm up to room temperature overnight with stirring. The mixture was neutralized by addition of aqueous 1M HCl (20 ml). The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 x 40 ml). The dichloromethane fractions and the first organic layer were combined and dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure. The crude product was purified by gravity chromatography (SiO_2, hexanes/ethyl acetate 95:5 to 78:15 as a gradient) to give 2-I as a viscous orange liquid (1.7 g, 34%). ^1H NMR (500 MHz, Chloroform-*d*) δ 6.60 (s, 1H, thienyl 3-H), 2.47 (t, 2H, thiophene-CH_2-), 1.62 – 1.57 (m, 6H, -COH(CH_3)$_2$), 1.54 (q, *J* = 7.4 Hz, 2H,-CH_2-CH_2-), 1.37 – 1.30 (m, 6H, -(CH_2)$_3$-CH_3), 0.90 (t, 3H, -CH_3) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 147.1, 123.1, 72.6, 71.8, 32.8, 32.2, 31.9, 30.2, 29.2, 22.9, 14.4; ESI-MS HRMS (positive ion mode) (m/z) $[M+H-H_2O]^+$ calcd. for $C_{13}H_{21}IOS+H-H_2O$, 335.0325; found, 335.0325.

Polymerization of dimethylcarbinol monomer 2. Monomer **2** was equipped with a dimethylcarbinol group on the 5-position instead of a diphenylcarbinol group. Polymerization of monomer 2 was examined with two different catalysts and several ligands in attempts to optimize the polymerization: $Pd(OAc)_2$ was paired with PCy_3, PPh_3, *t*-Bu_3P and $Pd(CNPh)_2Cl_2$ was paired with (*p*-$CF_3Ph)_3P$.[2] As was observed for the polymerization of monomer 1, significantly higher molecular weights for the chloroform fraction were found with PCy_3 as a ligand than with other ligands (Table S1, but fraction yields were exceedingly low (< 3%), indicating that mostly oligomers (M_n < 3 kg/mol) were afforded. As was found for the polymerization of the diphenylcarbinol-functionalized monomer, increasing the polymerization concentration from 0.1 M to 0.5 M led to an increase in the molecular weight and total yield of oligomers, from 55 to 79% (Table S1: entry 1 vs entry 6).

The *ipso*-arylative coupling of triphenylmethanol and bromobenzene has been reported to proceed to higher conversion than that between 2-phenylpropan-2-ol and phenyl bromide with PCy_3 or PPh_3 as the added ligand,[3] which is in agreement with the observed higher reactivity of monomer **1** as compared to monomer **2**. When polymerizations of monomer **2** with PCy_3 were conducted at lower temperatures (80 - 100 °C), polymer/oligomer precipitate was not observed in the first precipitation into methanol. The dimethylcarbinol group of P3HT of hexanes fraction in entry **1** was observed in ^{1}H NMR (peak h in Figure S9). This might be explained by the lower reactivity of dimethylcarbinol as compared to diphenylcarbinol groups in coupling reaction.

Table S1 Polymerization of monomer **2**

			$CHCl_3$ fraction (Polymer)			Hexanes Fraction (oligomers)		
Entry	Pd/Ligand	*T* (°C)	M_n (kg/mol)[c]	$Đ$[c]	yield (%)[d]	M_n (kg/mol)[c]	$Đ$[c]	yield (%)[d]
1[a]	$Pd(OAc)_2/PCy_3$	170	4.6	1.7	Trace	2.8	2.5	55
2[a]	$Pd(OAc)_2/PPh_3$	170	4.4	3.8	2.3	2.7	3.5	57
3[a]	$Pd(OAc)_2$/*t*-PBu_3	170	0.5	5.2	2.3	0.7	2.2	22
4[b]	$Pd(CNPh)_2Cl_2$/ (*p*-$CF_3Ph)_3P$	170	2	1.5	2.3	1.5	1.3	23
5[b]	$Pd(OAc)_2/PCy_3$	140	5.7	1.3	trace	3.8	1.5	41
6[b]	$Pd(OAc)_2/PCy_3$	170	5.3	2.0	trace	2.2	1.6	79
7[f]	$Pd(OAc)_2/PCy_3$	170	6.6	2.5	2.5	2.4	4.4	28
8[b]	$Pd(OAc)_2/PCy_3$	100	N/A[g]	N/A	N/A	N/A	N/A	N/A
9[b]	$Pd(OAc)_2/PCy_3$	80	N/A[g]	N/A	N/A	N/A	N/A	N/A

[a] Monomer **2** (0.1 M), $Pd(OAc)_2$ (2 mM), Ligand (6mM), and Cs_2CO_3 (0.15 M) heated in *o*-xylene for 48 h; [b] Monomer (0.5 M), $Pd(OAc)_2$ (15 mM), PCy_3 (30 mM), and Cs_2CO_3 (0.75 M) heated in *o*-xylene; [c] number-average molecular weight (M_n) and dispersity ($Đ$) of polymers in chloroform fraction were estimated by GPC in THF with polystyrene standards; [d] yield of chloroform fraction based on 100 % conversion; [e] No polymer was collected in Soxhlet extraction with chloroform; [f] **2**-**I** was used with conditions described in footnote [b]; [g] oligomer/polymer was not observed after precipitation in methanol.

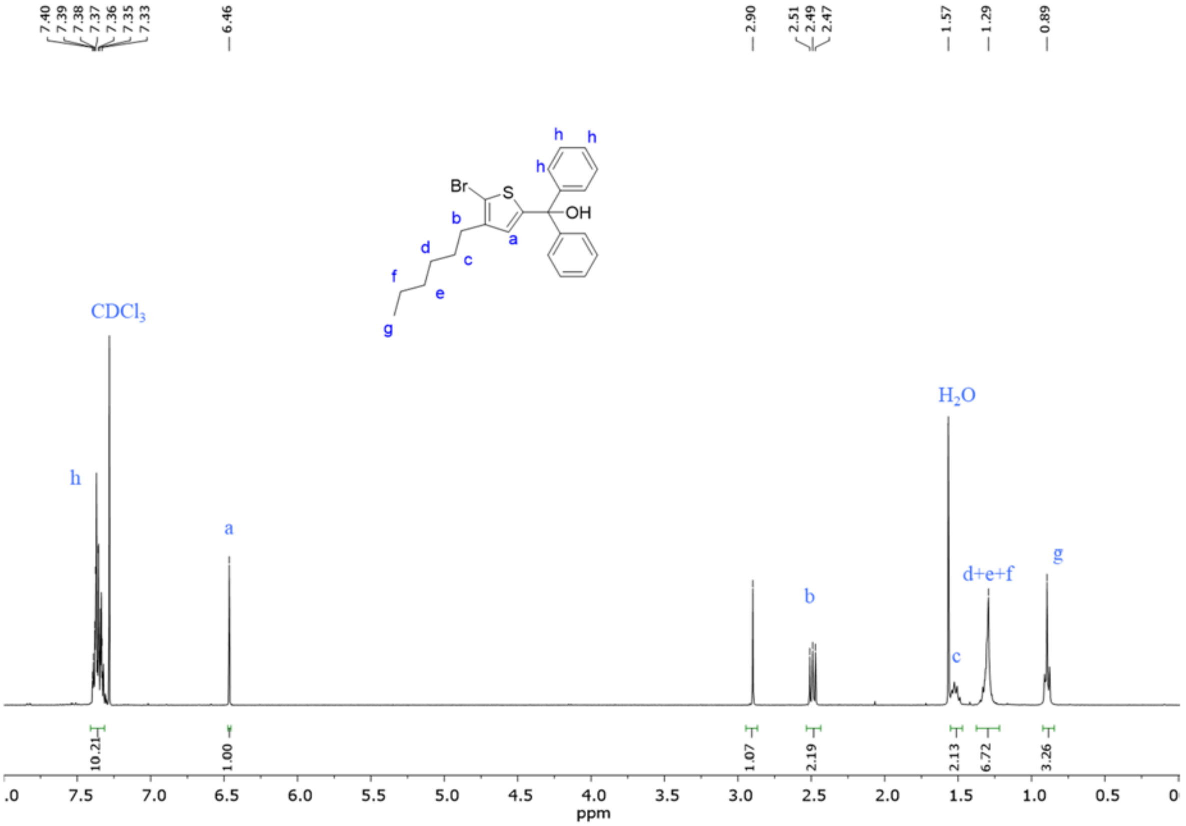


Figure S1 ^{1}H NMR of **1** in CDCl$_3$.

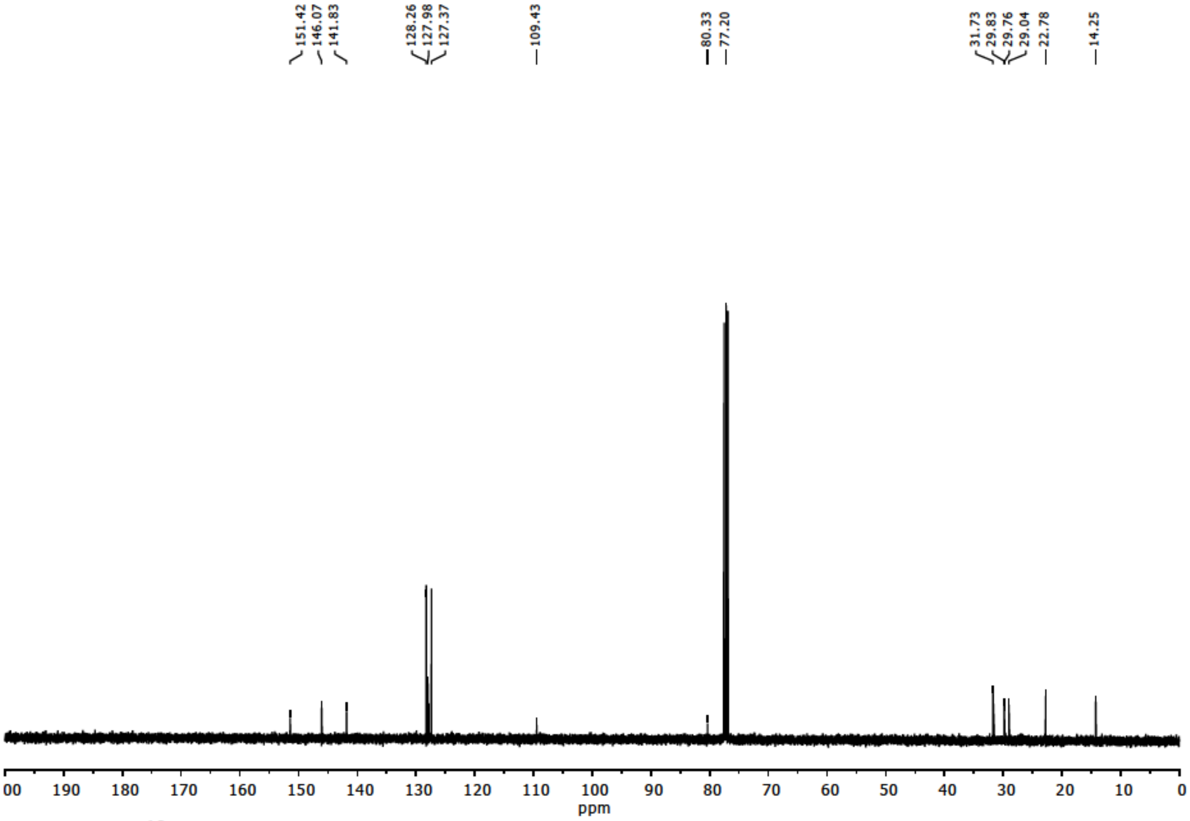


Figure S2 ^{13}C NMR of **1** in CDCl$_3$.

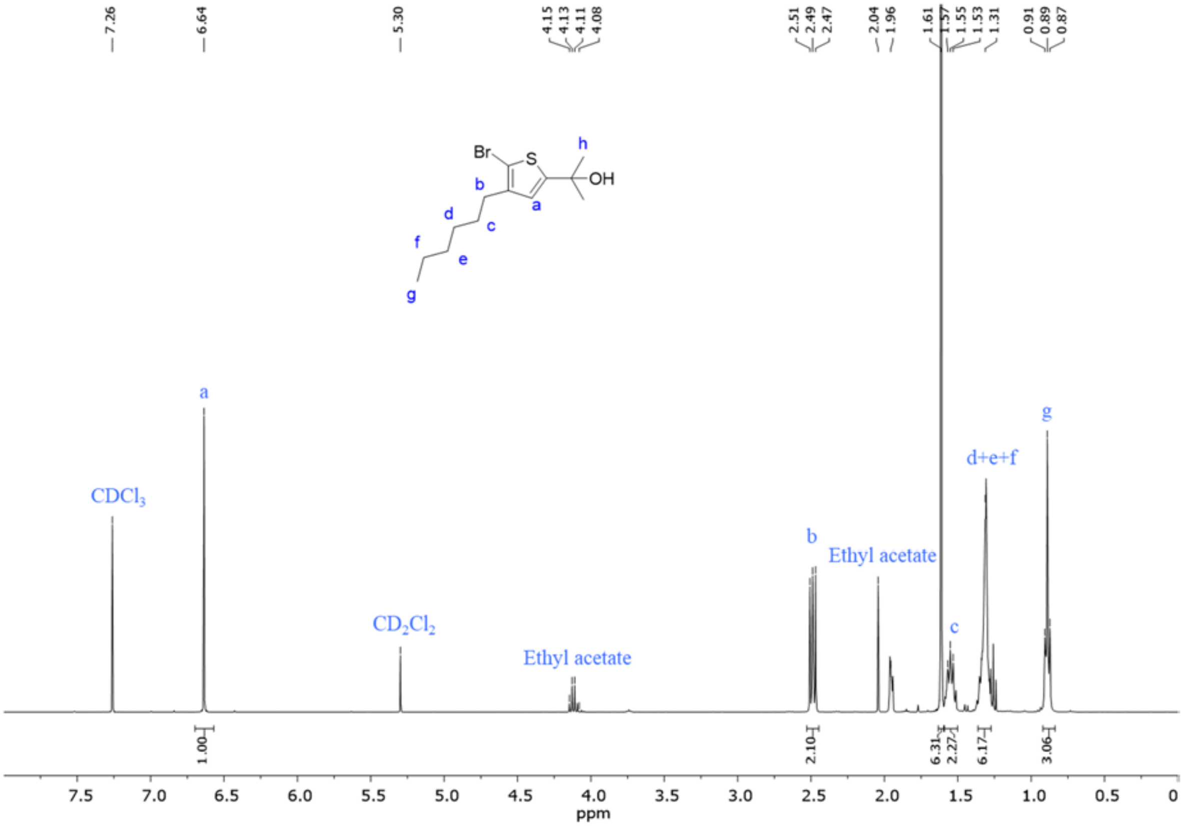


Figure S3 ^{1}H NMR of **2** in CDCl$_3$.

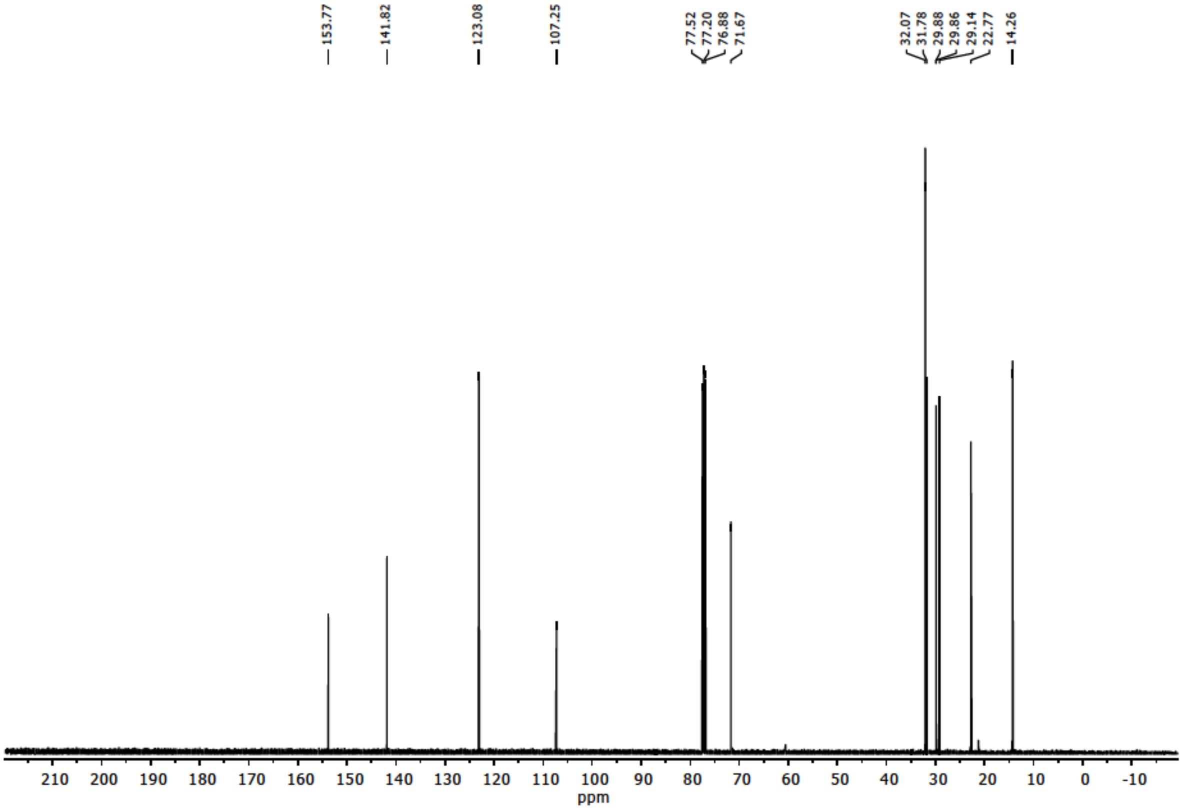


Figure S4 ^{13}C NMR of **2** in CDCl$_3$.

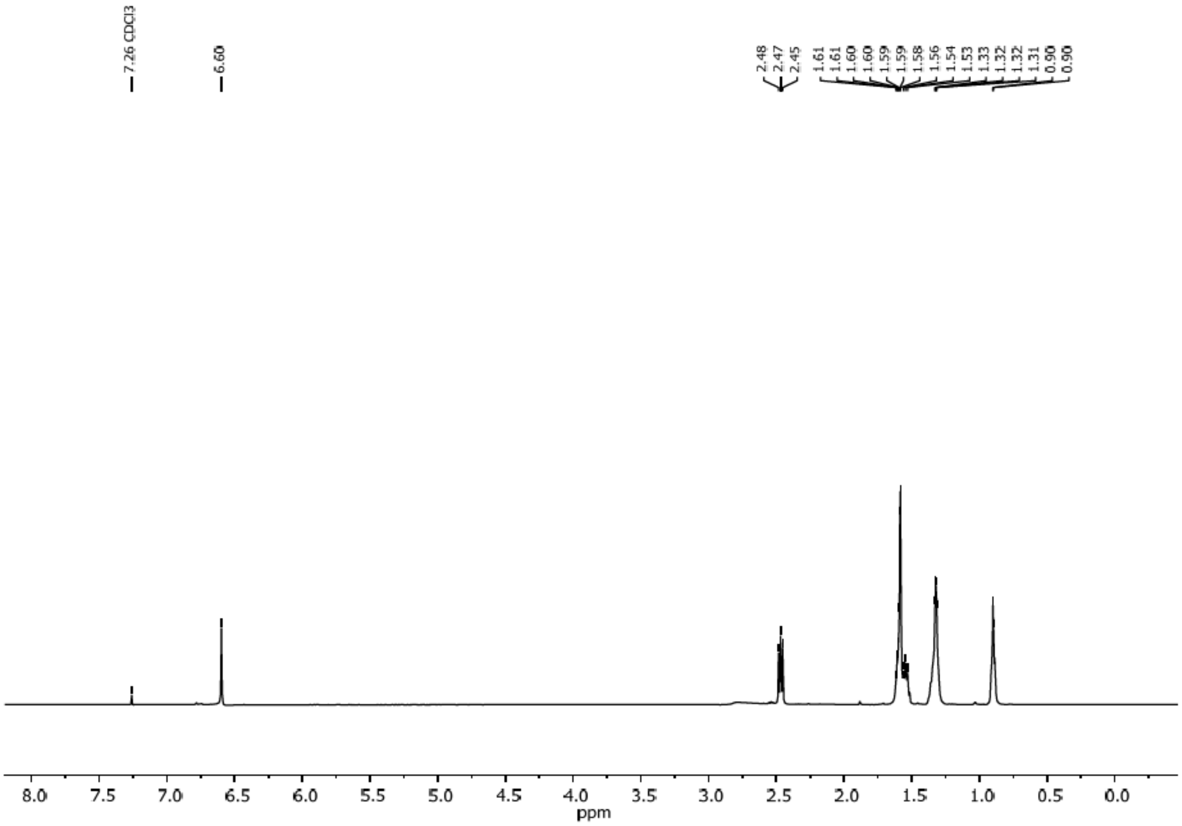


Figure S5 ^{1}H NMR of **2-I** in $CDCl_3$.

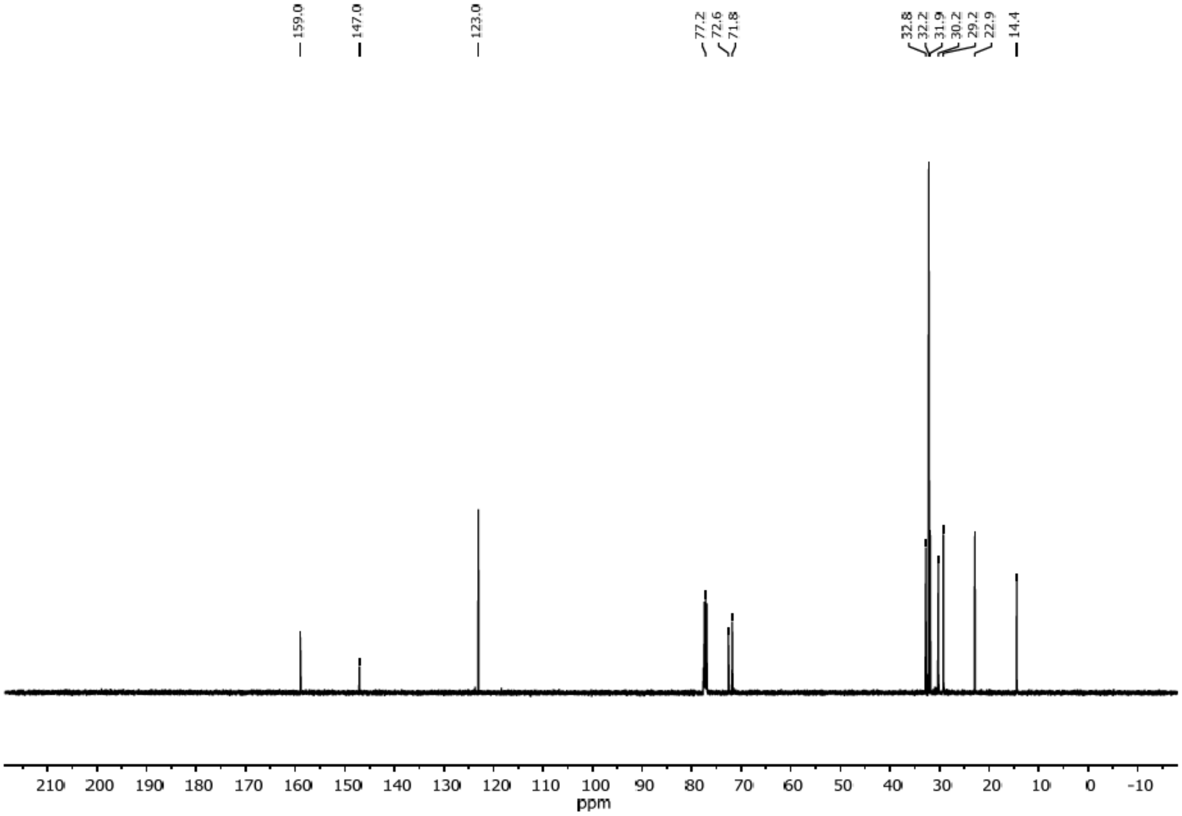


Figure S6 ^{13}C NMR of **2-I** in $CDCl_3$.

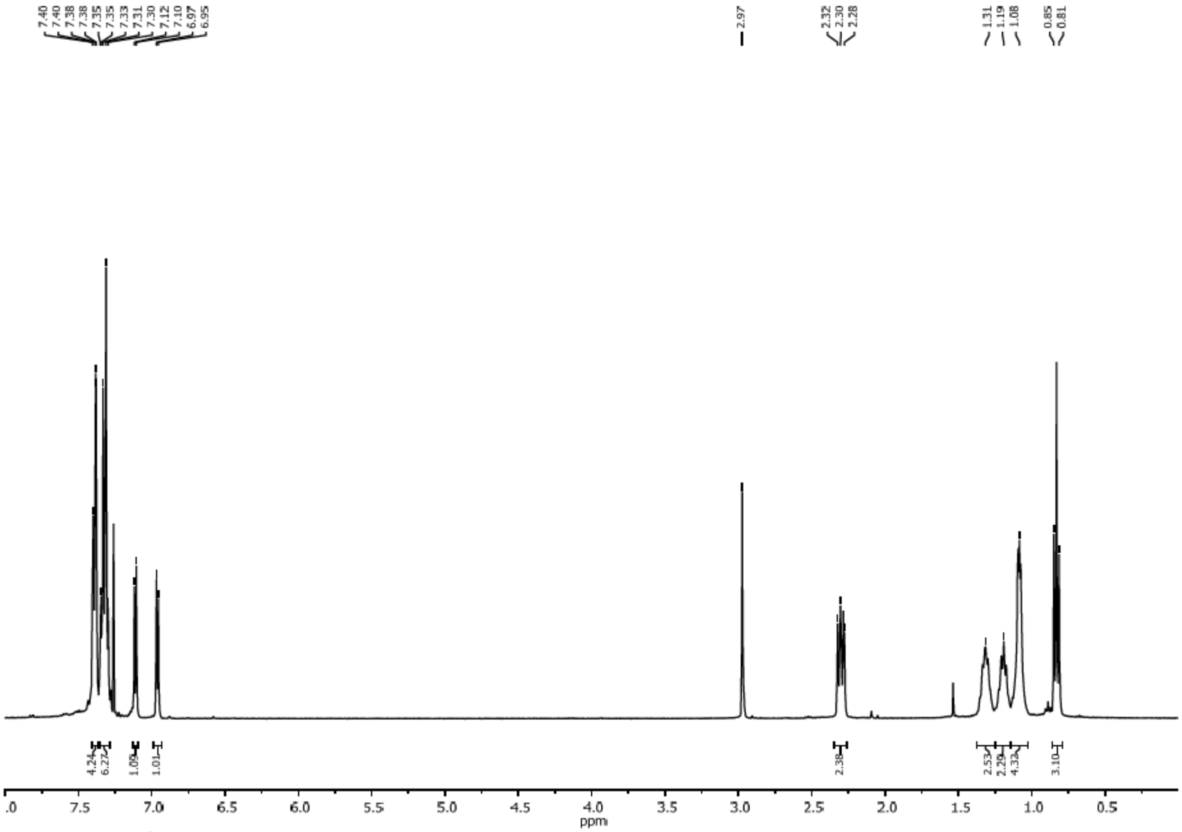


Figure S7 ^{1}H NMR of model diphenylcarbinol **4** in CDCl₃.

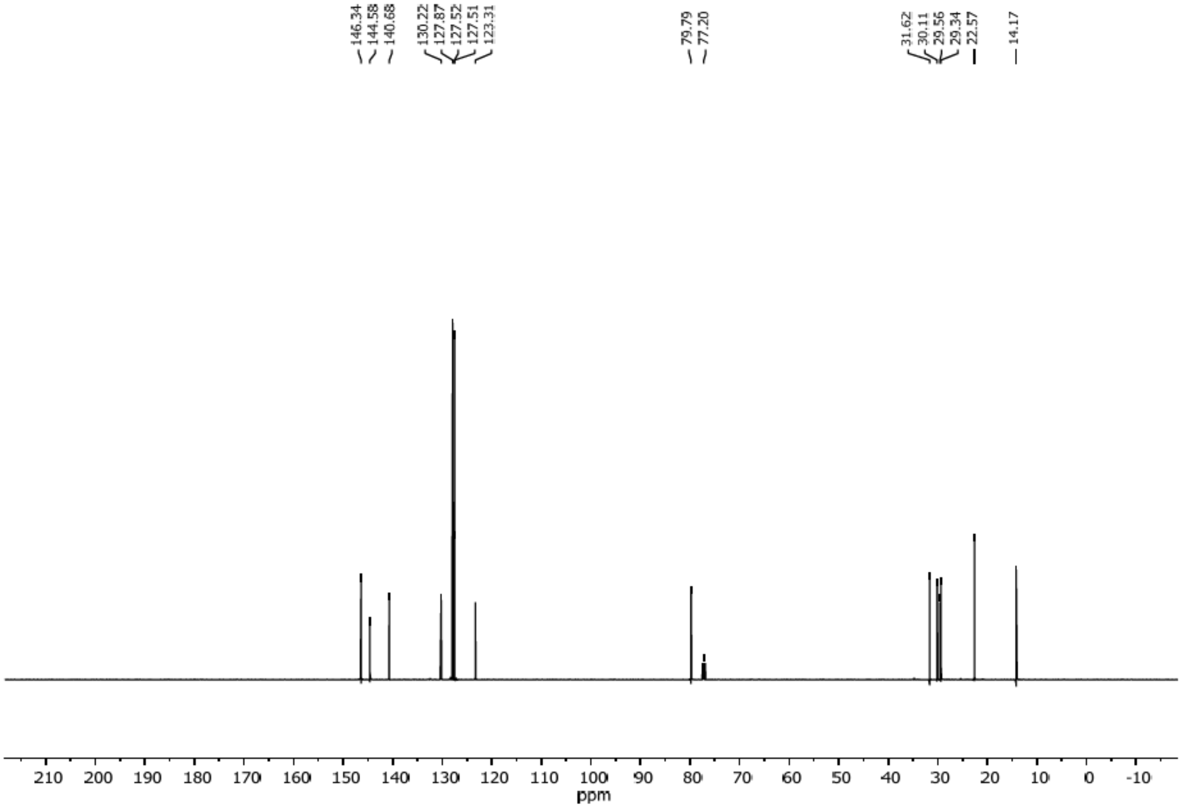


Figure S8^{13}C NMR of model diphenylcarbinol **4** in CDCl₃.

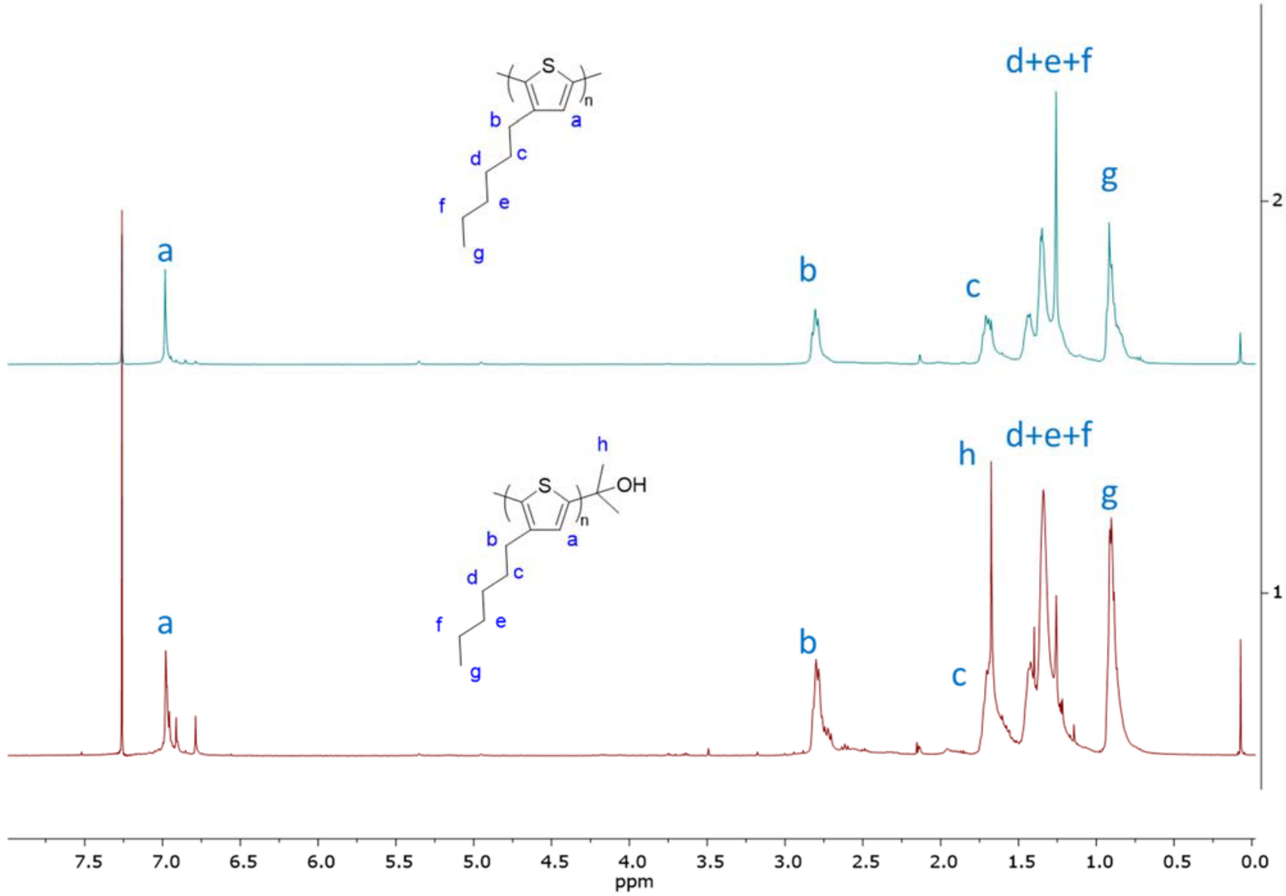


Figure S9. ^{1}H NMR spectra of chloroform-soluble (top) and hexanes-soluble (bottom) fractions of P3HT prepared from monomer **2** (Table S1, entry 1).

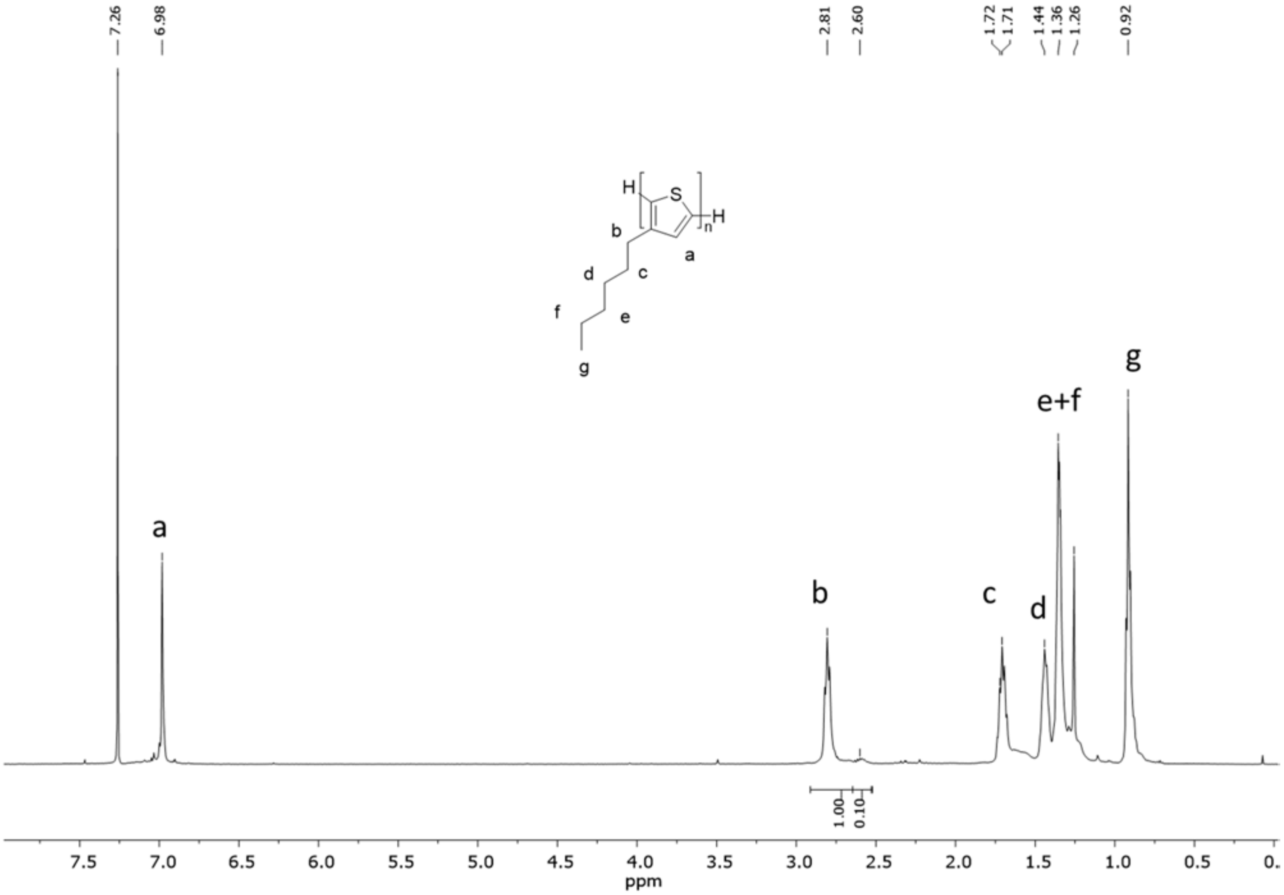


Figure S10 ^{1}H NMR of P3HT prepared by polymerization of monomer **1** (0.5 M) at 140 °C for 48 h (Table 2: entry 8).

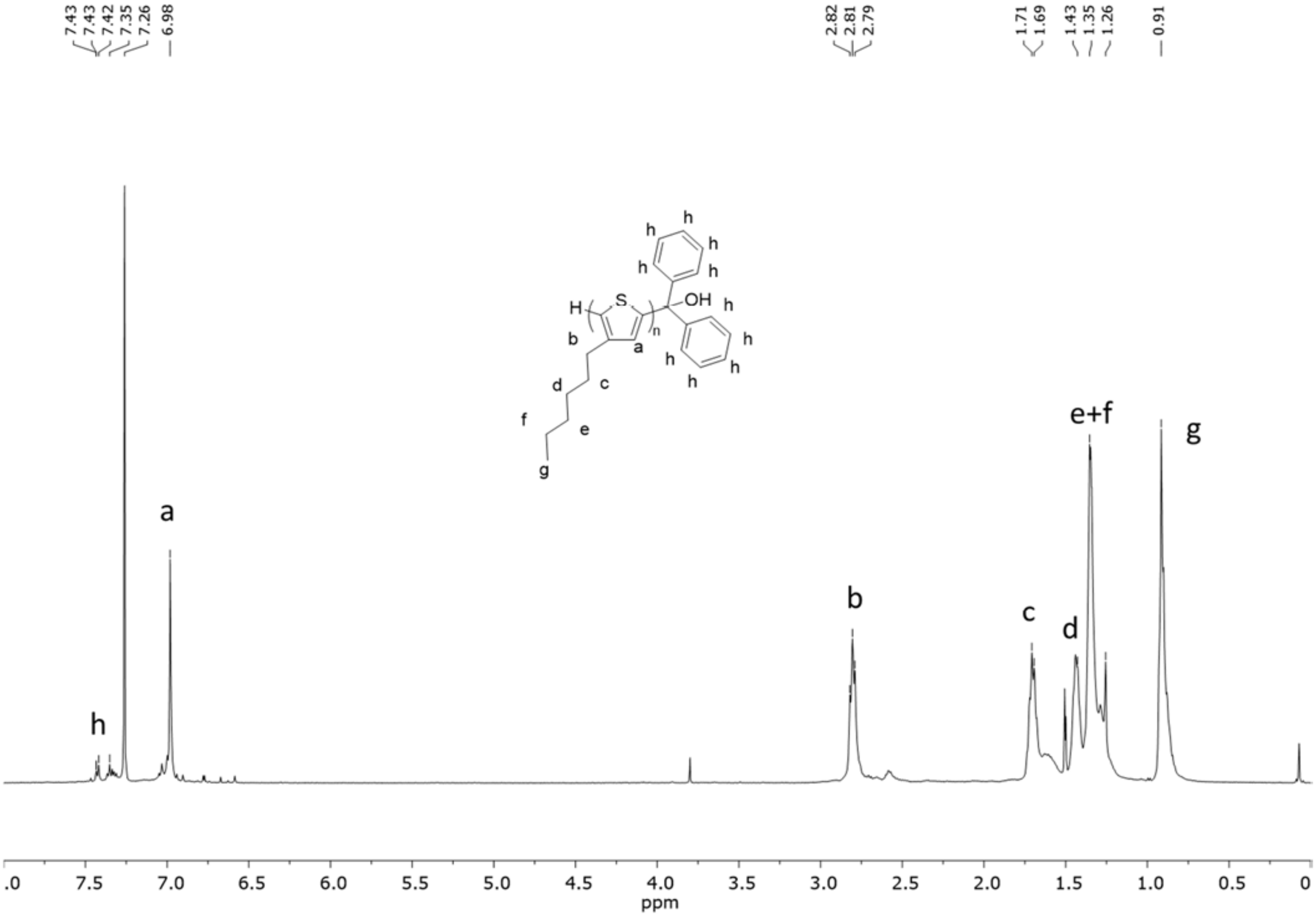


Figure S11. ^{1}H NMR of P3HT prepared by polymerization of monomer **1** (0.1 M) at 100 °C for 48 h (Table 2: entry 5).

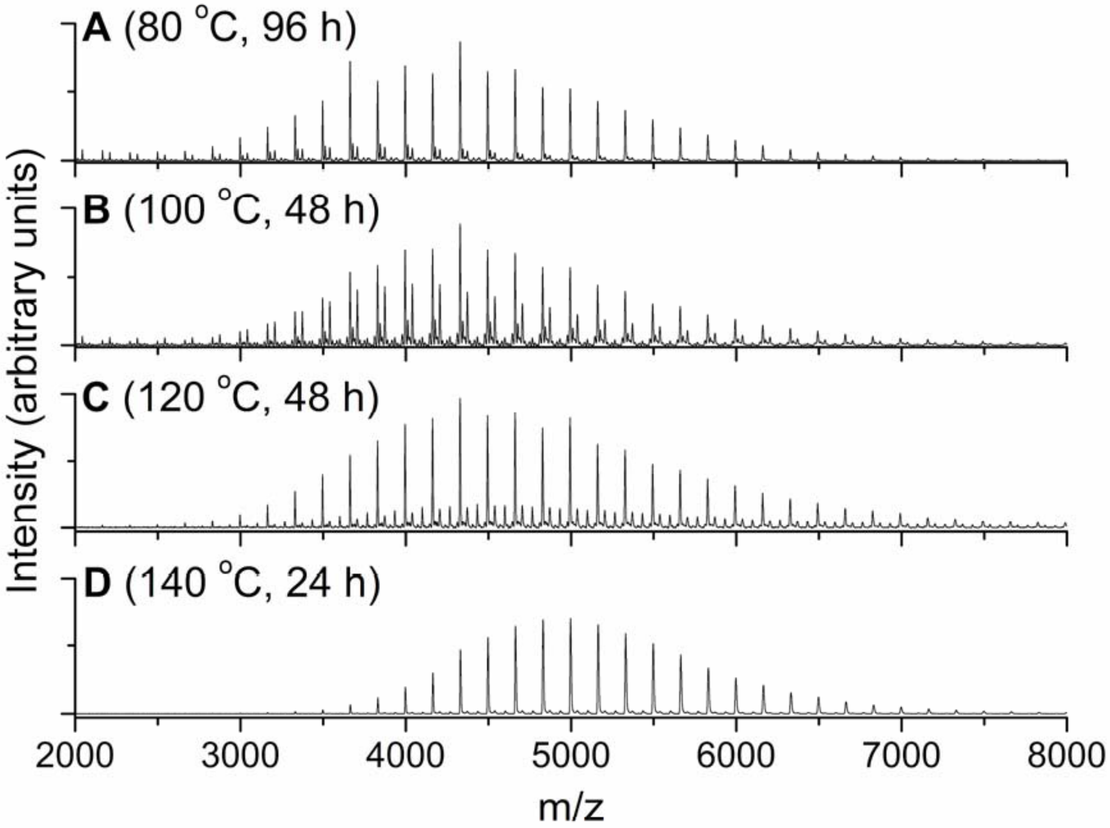


Figure S12. MALDI-TOF mass spectrograms of P3HT resulting from *ipso*-arylative polymerization of monomer **1** at A) 80 °C for 4 days (Table 2, entry 6), B) 100 °C for 2 days (Table 2, entry 5), C) 120 °C for 2 days (Table 2, entry 4), D) 140 °C for 1 day (Table 2, entry 2). Major peaks (M_{major}) at each temperature correspond to series with either H-/-H or H-/-$C(Ph)_2^+$ endgroups (Fig. 3). The end-groups that give rise to the most abundant minor series of peaks at lower temperatures (M_{major}+44) have not yet been identified. They do not match to expected masses for the expected Br-/-$C(Ph)_2OH$ or Br-/$C(Ph)_2OH$ endgroups or any other expected species. It is plausible that this series results from either enchainment of monomer through *ortho*-arylation, which would result in additional carbinol groups on each chain, or direct arylation of *ortho*-xylene, but further study will be necessary to identify these species. The second most abundant minor series (M_{major}+16) is likely to arise from either H-/-CPh_2OH or $Ph_2(HO)C$-/-CPh_2^+ end-groups.

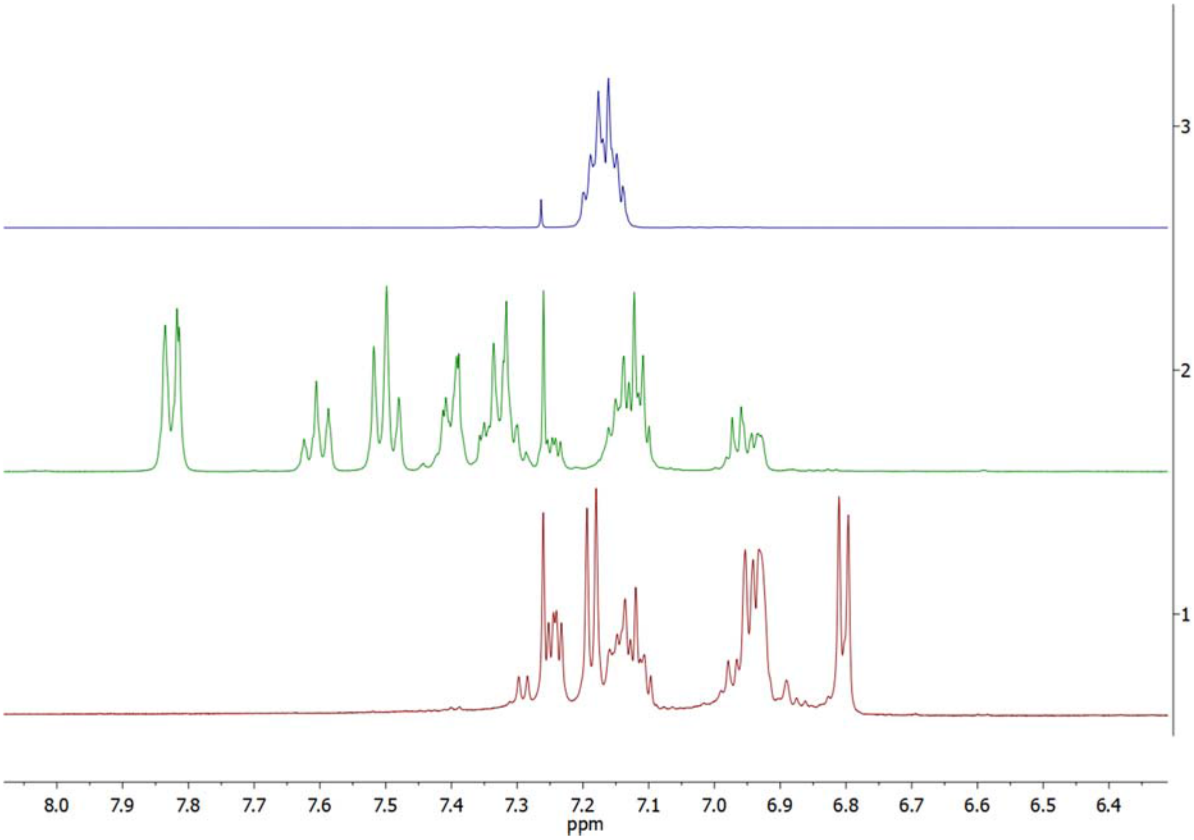


Figure S13. Comparison of ^{1}H NMR of *o*-xylene, reaction **B**, and reaction **C** (from top to bottom).

References

1. R. Tkachov, V. Senkovskyy, H. Komber and A. Kiriy, *Macromolecules*, 2011, **44**, 2006-2015, doi: 10.1021/ma102724y.
2. M. Iwasaki, Y. Araki, S. Iino and Y. Nishihara, *J. Org. Chem.*, 2015, **80**, 9247-9263, doi: 10.1021/acs.joc.5b01693.
3. Yoshito Terao, Hiroyuki Wakui, Tetsuya Satoh, Masahiro Miura and M. Nomura, *J. Am. Chem. Soc.*, 2001, **123**, 10407-10408, doi: 10.1021/ja016914i.