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Supporting Information

Synthesis of conjugated copolymers by combining different coupling reactions

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Reagents and instrumentation

All reagents were purchased and used without further purification. Reagent grade solvents were dried by a solvent purification system MBRAUN SPS 800 (columns with activated alumina). All monomers were synthesized according to literature procedures.^{1–4}

All ¹H-NMR spectra were recorded on a Bruker Avance 300 MHz or 600 MHz spectrometer. A Shimadzu 10A GPC system was used for the Size exclusion chromatography (SEC) measurements. The column is a PLgel 5µm mixed-D type column and the signal is detected using a differential refractometer and a UV-vis spectrophotometer. The system is calibrated towards polystyrene standards (from Polymer Laboratories). Before injection in the SEC apparatus, the polymer samples were dissolved in THF and filtered over a pore size of 0.2 µm. The GC-MS spectra were recorded using a Thermo Finnigan Trace GC and ITQ 9000 Mass Spectrometer.

Grignard compatibility test

2-bromo-3-butyl-5-iodothiophene (0.200 mmol, 69.0 mg) and the other monomer under consideration (0.200 mmol) were put in separate flasks under argon atmosphere and dissolved in dry THF. The Grignard metathesis was started by adding *i*PrMgCl·LiCl (0.200 mmol, 0.160 mL, 1.25 M) to the first flask. After stirring for 30 minutes, both flasks were combined and left to stir for 5 minutes. Subsequently, this mixture was cannulated to a flask containing benzaldehyde (0.400 mmol, 42.0 mg) in dry THF. After 2 hours, the reaction mixture was analyzed using GC-MS.⁵

	Yield 1	Yield 2
Mg + Zn	52%	48%
Mg + Sn	30%	27%
Mg + Au	0%	0%

Copolymerization

Procedure

The monomers under consideration (0.200 mmol each), each with a different organometallic group and either a hexyl or butyl side-chain, were put in separate flasks under argon atmosphere and dissolved in dry THF. After dissolution of the monomers, they were mixed for 5 minutes. Subsequently, this mixture was cannulated to a solution of the PdPEPPSI-IPr catalyst (5.70 μ mol, 3.88 mg) in THF. A part of the polymerization mixture was quenched at low conversion (~10%) with acidified THF. The time of this quench was dependent on the combination used and was determined beforehand. The remainder of the polymerization mixture was allowed to reach full conversion, after which it was also quenched with acidified THF. The polymers were then precipitated in methanol and filtered off. After washing with methanol, a ¹H NMR spectrum was measured of all polymers. The composition of these polymers at low and full conversion was determined via integration of the signals from the CH₃-chain end of the butyl and hexyl side-chains.⁵



Figure S1: example of a ¹H NMR spectrum of a hexyl- and butylthiophene copolymer, showing the signals arising from the CH₃-chain ends of the side-chains.

MALDI-ToF analysis

MALDI-ToF was also considered to analyze the polymer structure of the obtained copolymers. However, it was found that this technique does not provide additional information in this specific case. First of all, MALDI-ToF is only capable of determining the composition of the polymer, it does not give information on the monomer sequence. Hence, it does not provide additional information compared to ¹H NMR. Furthermore, the limited ionization of high molar mass polymers limits the applicability of MALDI-ToF for this research. To get information on the polymer sequence, it would be possible to perform a MALDI-ToF analysis at different conversions. However, a certain degree of polymerization (at least 5) is required at low conversion (~10%) to be able to perform a proper analysis. This means that the polymer would have a much higher degree of polymerization at full conversion (around 50 assuming a controlled chain growth polymerization). These polymer chains are far too long for proper analysis by Maldi-Tof, as exemplified by the spectrum below. (Maldi-Tof of polymer N°6, as defined below)



Figure S2: MALDI-ToF analysis of copolymer N°6 (as defined below). Determination of the polymer composition is possible, but only for the low molar mass fraction of the polymer.

Data

Different combinations

	Au	Sn	В	Zn
Mg	1	2	/	3
Zn	4	5	/	
В	6	7		
Sn	8			

|--|

N° combination	Low	conversion	High conv	version	$\overline{M_n}$	P
N combination	DP	% hexyl	DP	% hexyl	(kg/mol)	D
1	5	53	35	54	11	1.2
2	7	51	54	53	18	1.4
3	6	49	66	50	31	1.6
4	8	50	38	51	12	1.2
5	10	57	67	58	32	1.5
6	6	45	66	48	34	1.6
7	9	49	34	50	12	1.6
8	6	71	74	50	35	1.7

In combinations 1,4, 6 and 8, the gold functionalized monomer is always the one with the hexyl side-chain. In combinations 2 and 5, the tin functionalized monomer bears the the hexyl side-chain, while the boron-functionalized monomer is equipped with the hexyl side-chain in combination 7. For combination 3, the hexyl side-chain is located on the organozinc monomer. These data are averages of at least 2 polymerizations. Combination 3 is examined in more detail in a previous research article and combination 8 is analyzed further via a Lewis-Mayo plot as described below.⁵ The increase in DP for all combinations shows that the polymer continues to grow, while the difference in % hexyl allows to determine the polymer structure. It is observed that the % hexyl monomer hardly changes between low and high conversion for combinations 1-7, meaning that a random incorporation of both monomers takes place. However, for combination 8, there is a clear difference in % hexyl monomer between the low and high conversion, meaning that a gradient is obtained.

GPC traces of the different polymers







Figure S3: GPC traces of all the copolymers (combinations 1-9 as defined in the table)

Controlled character of the 2-bromo-3-hexyl-5-(trimethyltin)thiophene polymerization Procedure

2-bromo-3-hexyl-5-(trimetheyltin)thiophene (0.200 mmol, 82.0 mg) was put under argon atmosphere and dissolved in THF (1.5 mL). A drop of tridecane was added as internal reference for the GC-Ms analysis. A quench was taken of the monomer solution, after which the remainder was cannulated to a solution of PdPEPPSI-IPr (5.00 μ mol, 3.39 mg) in THF (0.5 mL) at 60°C. The polymerization proceeded at 60°C while quenches were taken regularly, which were analyzed using GC-MS and SEC to obtain the conversion and \overline{M}_n , respectively.

Data

Time (min)	<i>ln</i> ([M]°/[M])
0	0.00
10	0.18
30	0.64
60	1.00
120	1.87

Conversion (%)	$\overline{M}_n(kg/mol)$
0	0.0
16	7.4
47	23
63	51
85	48

Lewis-Mayo analysis for the gold-tin combination

Procedure

(5-bromo-4-hexylthiophen-2-yl)(tri-*tert*-butylphosphine)gold(I) (0.200 mmol, 129 mg) and 2-bromo-3-butyl-5-(trimethyltin)thiophene (0.200 mmol, 76.4 mg) were put in separate flasks under argon atmosphere and dissolved in dry THF (2.5 mL). The monomers were subsequently mixed in 4 different ratios by combining 1, 0.75, 0.5 and 0.25 mL of one solution with 0.25, 0.5, 0.75 and 1 mL of the other, respectively. After stirring for 5 minutes, the monomer mixtures were cannulated to four flasks under argon atmosphere containing the PdPEPPSI-IPr catalyst (1.40 μ mol, 0.970 mg) in dry THF. The polymerizations were performed at 60°C and were quenched with acidified THF at low conversion (approximately after 6 minutes). The polymer was subsequently precipitated in methanol and filtered off. After washing with methanol, an ¹H NMR was recorded. Again, the composition of the polymer was determined via integration of the signals from the CH₃-chain end of the butyl and hexyl side-chains.

Data

f _A	FA	± err
0.00	0.00	0.00
0.20	0.14	0.02
0.40	0.21	0.02
0.50	0.29	0.01
0.60	0.41	0.07
0.80	0.55	0.02
1.00	1.00	0.00

¹H NMR of the 50/50 copolymer



Figure S4: ¹H NMR spectrum (400 MHz, CDCl₃) of the copolymer synthesized by mixing the gold-functionalized monomer with a hexyl side-chain and the stannylated monomer with a butyl side-chain in a 1/1 ratio.

¹H NMR spectra of the mixed organometallic compounds



Figure S5: ¹H NMR (600 MHz, THF-*d8*) of the Grignard and gold monomers and their mixture. The interaction between the two compounds is clearly visible. In the mixture, 1.5 equivalents of the Grignard monomer were used compared to the aurylated compound to account for protonation of the Grignard monomer.



Figure S6: ¹H NMR (600 MHz, THF-*d8*) of the organozinc and organogold monomer, and their mixture. In this case, no interaction is observed between the compounds. In the mixture, 1.7 equivalents of the organozinc compound was used compared to the aurylated compound to account for protonation of the organozinc functionality.



Figure S7: ¹H NMR (600 MHz, THF-*d8*, measured at 328K) of the boronic ester and gold thiophene compound, their mixture (both compounds in a 1-1 ratio), and the mixture together with the PdPEPPSI-IPr catalyst. There is no sign of interaction between these compounds.



Figure S8: ¹H NMR (600 Mhz, THF-*d8*, measured at 328K) of the boronic ester and trimethyltin thiophene compound, their mixture (both compounds in a 1-1 ratio), and the mixture together with the PdPEPPSI-IPr catalyst. There is no sign of interaction between these compounds.



Interaction between the stannylated monomer and AuPtBu₃Br

Figure S9: ¹H NMR (300 MHz, THF-*d8*) spectra of the stannylated monomer in combination with AuPtBu₃Br. No interaction is observed between these compounds, even after prolonged mixing at 60°C.

Copolymers synthesized with CsF or at lower temperature

The same procedures were followed as described above, with either 2 equivalents of CsF that were added to the monomer mixture or the polymerization being performed at 40°C instead of 60°C.

N° combination	Low	Low conversion High conversion		version	$\overline{M_n}$	ъ
N combination	DP	% hexyl	DP	% hexyl	(kg/mol)	U
Au + B with CsF	4	58	68	56	37	1.6
B + Sn with CsF	11	70	36	53	12	1.6
Au + Sn with CsF	5	77	58	57	28	1.7
$Au + B$ at $40^{\circ}C$	6	48	14	46	4.6	1.2
$B + Sn at 40^{\circ}C$	9	73	16	59	4.9	1.2
$Au + Sn at 40^{\circ}C$	5	69	10	62	4.0	(1.7)

GPC traces of the polymers









Figure S11: GPC traces of the copolymers synthesized at 40°C