Supporting Information


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Experimental Information
All reagents were purchased from TCI, Sigma-Aldrich, J&K Scientific and Acros Organics and used without further purification. Isopropylmagnesiumchloride lithium chloride complex was titrated before use according to the procedure by Love et al.\textsuperscript{1} Reagent grade solvents were dried by a solvent purification system MBRAUN SPS 800 (columns with activated alumina).\textsuperscript{1}H NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. \textsuperscript{13}C-NMR-spectra were measured on a Bruker Avance 600 MHz-spectrometer. Size exclusion chromatography (SEC) measurements were carried out on a Shimadzu 10A GPC system. The column is a PLgel 5 μm mixed-D type column, and the detection system consists of a
differential refractometer and a UV–vis spectrophotometer. The GPC system is calibrated toward polystyrene standards (purchased from Polymer Laboratories). Before measuring, the polymers are dissolved in THF (c ≈ 1 mg/mL) and filtered over a pore size of 0.2 μm. UV–vis measurements were performed on a Varian 400 Scan. Fluorescence spectra were recorded on an Edinburgh Instruments LLS980 Steady-State spectro-fluorimeter. Excitation was done with a 450W xenon lamp and the emission was measured with an extended red-sensitive photomultiplier. All fluorescence spectra were absorption corrected by dividing the obtained emission values by the absorption values obtained at the wavelength of excitation. The samples were measured in quartz cuvettes with an optical pathway of 1 cm. Compounds 1, 4, 9, 4, 10 and 3-octyloxythiophene were prepared according to literature procedures.

Synthesis of the monomers

**Synthesis of 2.** N-bromosuccinimide (4.80 mmol, 0.854 g) was added to a stirred solution of 1 (4.80 mmol, 1.67 g) in THF at 0°C. The resulting solution was stirred at 0°C for 1 hour. An aqueous solution of Na₂S₂O₃ was then added and the product was extracted with Et₂O. The organic layers were washed with NaHCO₃ and dried on MgSO₄. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO₂, heptane/DCM 8/2). The product was obtained as a slightly yellow, viscous oil, which polymerizes rapidly upon standing at room temperature. The product needs to be stored at -18°C. Yield: 0.591 g (8%) ¹H-NMR (CDCl₃, 300 MHz) δ (ppm) = 7.13 (d, J=5.3Hz, 1H), 7.05 (s, 1H), 6.98 (d, J=5.3 Hz, 1H), 4.12 (t, 2H), 1.80-1.24 (m, 20H), 0.88 (t, 3H)

**Synthesis of 5.** N-bromosuccinimide (4.39 mmol, 0.782 g) was added to a stirred solution of 4 (4.36 mmol, 2.79 g) in THF at 0°C. The resulting solution was stirred at room temperature for 2 hours. An aqueous solution of Na₂S₂O₃ was then added and the product was extracted with Et₂O. The organic layers were washed with NaHCO₃ and dried on MgSO₄. The solvent was removed under reduced pressure and the crude product was purified by column
chromatography. (SiO₂, heptane/DCM 8/2) The product was obtained as a slightly yellow, viscous oil. Yield: 0.591 g (20%) \(^1\)H-NMR (CDCl₃, 300 MHz) \(\delta\) (ppm) = 7.18 (m, 2H), 7.11 (m, 1H), 6.68 (s, 2H), 4.00 (dd, 6H), 1.88-1.72 (m, 6H), 1.54-1.42 (m, 6H), 1.40-1.22 (m, 24H), 0.89 (m, 9H); \(^{13}\)C-NMR (CDCl₃, 150 MHz) \(\delta\) (ppm) = 153.9, 143.4, 141.7, 136.8, 134.7, 123.8, 116.4, 115.5, 115.4, 112.2, 109.9, 102.0, 73.7, 69.4, 31.9, 31.8, 30.4, 29.6, 29.4, 29.4, 29.3, 29.3, 26.1, 26.1, 22.7, 22.7, 14.1, 14.1 MS (ESI) (m/z): 718.2

**Synthesis of 6.** Compound 5 (0.870 mmol, 0.590 g) was dissolved in DCM and cooled down to 0°C. Iodine (0.520 mmol, 0.130 g) and iodobenzene diacetate (0.520 mmol, 0.140 g) were added and the mixture was stirred at room temperature for 4 hours. A saturated solution of Na₂S₂O₃ was added and the product was extracted with DCM. The organic layers were dried on MgSO₄ and the solvent was removed under reduced pressure. The product was filtered over a short silica plug (heptane/DCM 8/2) and isolated as a slightly yellow viscous oil. Yield: 0.43g (60%) \(^1\)H-NMR (CDCl₃, 300 MHz) \(\delta\) (ppm) = 7.26 (s, 1H), 7.12 (s, 1H), 6.62 (s, 2H), 3.99 (dd, 6H), 1.88-1.72 (m, 6H), 1.54-1.42 (m, 6H), 1.40-1.22 (m, 24H), 0.89 (m, 9H) \(^{13}\)C-NMR (CDCl₃, 100 MHz) \(\delta\) (ppm) = 153.9, 142.7, 141.5, 137.2, 134.2, 121.4, 116.1, 115.4, 110.6, 102.3, 77.2, 73.7, 71.0, 69.5, 31.9, 31.8, 30.3, 29.6, 29.4, 29.3, 29.3, 26.1, 26.1, 22.7, 22.7, 14.1; MS (ESI) (m/z): 843.0

**Synthesis of 11.** N-bromosuccinimide (5.25 mmol, 0.930 mg) was added to a solution of 4 (5.25 mmol, 3.36 g) in THF (50 ml). The solution was placed under N₂-atmosphere and shielded from light. After two hours, a solution of Na₂S₂O₃ was added and the product was extracted with diethylether. The organic layer was washed with NaHCO₃ and NaCl and dried on MgSO₄. The solvent was removed under reduced pressure and the crude product was purified using column chromatography (SiO₂, heptane/DCM 9/1). The product was isolated as an off-white solid. Yield 3.71 g (88%) Melting point: 42.1-45.4°C. \(^1\)H-NMR (CDCl₃, 300 MHz) \(\delta\) (ppm) = 7.12 (s, 2H), 6.62 (s, 2H), 3.98 (m, 6H), 1.88-1.72 (m, 6H), 1.54-1.42 (m,
6H), 1.40-1.22 (m, 24H), 0.89 (m, 9H); $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$ (ppm) = 153.9, 140.9, 137.1, 134.2, 116.2, 115.4, 110.4, 102.2, 77.2, 73.7, 69.4, 31.9, 31.8, 30.3, 29.6, 29.4, 29.3, 29.3, 26.1, 26.1, 22.7, 22.6, 14.1, 14.1; MS (ESI) (m/z): 798.1

**Synthesis of 12.** A solution of 3-octyloxythiophene (10.8 mmol, 2.28 g) in DMF (20 ml) was stirred at 0°C and $N$-chlorosuccinimide (10.2 mmol, 1.37g) in 5 ml of DMF was added dropwise. The mixture was stirred overnight at room temperature. An aqueous Na$_2$S$_2$O$_3$-solution was added and the product was extracted with ethyl acetate. The organic layer was dried on MgSO$_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO$_2$, heptane/EtOAc, 9/1) to obtain a colorless oil. Yield 1.44 g (54%) $^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$ (ppm) = 6.99 (d, 1H, 6 Hz), 6.76 (d, 1H, 6 Hz), 4.03 (t, 2H), 1.74-0.8 (m, 15H); $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$ (ppm) = 152.3, 120.6, 117.5, 108.3, 72.3, 31.8, 29.5, 29.4, 29.3, 29.2, 25.8, 22.7, 14.1; MS (ESI) (m/z): 246.2

**Synthesis of the polymers**

**Catalyst transfer condensative polymerization**

**KCTCP Polymerization of alkyl-substituted DTP.** TMPMgCl.LiCl (1.41 mmol, 1.41 ml) was cooled to -78°C and added to a N$_2$-purged flask containing compound 2 (1.41 mmol, 0.430 g) at -78°C. The mixture was stirred at -78°C for 3 hours and added to a N$_2$-purged suspension of Ni(dppp)Cl$_2$ (7.04 $\mu$mol, 3.90 mg) in 1 ml of THF. GPC of the resulting polymer can be found in Figure S 1.

**Catalyst testing.** Compound 6 (0.825 mmol, 0.697 g) was added to an oven dried flask, purged with N$_2$, diluted with dry THF and cooled to 0°C. $i$-PrMgCl.LiCl (0.825 mmol, 0.670 ml) was added, the mixture was diluted with dry THF to a total volume of 8.25 ml and the mixture is stirred at 0°C for 30 minutes.

Four different catalysts (see Table S 1) were put in four different oven dried, N$_2$-purged flasks. To flasks 1,2 and 3 were added 2 ml of the above GRIM-solution. Another 2 ml was
added to an oven dried, N₂-purged flask containing dry ZnBr₂ (0.24 mmol, 0.056 g). This mixture was stirred for 10 minutes and then added to flask 4. The remaining 0.25 ml was quenched with water for ¹H-NMR analysis of the GRIM reaction (compound 5 was formed, indicating a successful GRIM reaction).

The polymerization mixtures were stirred at room temperature for 30 minutes and then terminated with acidified THF for GPC analysis. GPC chromatograms can be found in Figures S2-S5.

Table S1. Used catalysts and amounts

<table>
<thead>
<tr>
<th>Catalyst*</th>
<th>Amount (µmol)</th>
<th>Amount (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Ni(dppp)Cl₂</td>
<td>2.7</td>
<td>1.5</td>
</tr>
<tr>
<td>2 Ni(dppe)Cl₂</td>
<td>2.7</td>
<td>1.4</td>
</tr>
<tr>
<td>3 Ni(NHC)(iPr)Cl₂</td>
<td>2.7</td>
<td>2.1</td>
</tr>
<tr>
<td>4 Pd PEPPSI-iPr</td>
<td>2.7</td>
<td>1.8</td>
</tr>
</tbody>
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*Ni(dppp)Cl₂: [1,2-Bis(diphenylphosphino)propane]dichloronickel(II), Ni(dppe)Cl₂: [1,2-Bis(diphenylphosphino)ethane]dichloronickel(II), Ni(NHC)(iPr)Cl₂: [1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]triphenylphosphine]dichloronickel(II)

Catalyst association experiment
Compound 11 (0.100 mmol, 79.8 mg) and Ni(dppp)Cl₂ (1.00 µmol, 0.50 mg) were brought under N₂-atmosphere and dissolved in 1ml of dry THF. The resulting suspension was cooled to 0°C. A solution of 2-thienyl magnesiumbromide (1M, 0.1ml, 0.100 mmol) was then added and the resulting mixture was stirred overnight at room temperature. Water was then added and the products were extracted with diethylether. The solvent was removed under reduced pressure and a ¹H-NMR spectrum of the resulting compound was taken. The aromatic region of this NMR is visible in Figure S 13. It is clear that only a small fraction of compound 11 underwent reaction.
Lewis acid catalyzed polymerizations

11 (0.33 mmol, 0.26 g) was dissolved in 2 ml of anhydrous solvent (either o-DCB, DCM, toluene or THF) under N₂-atmosphere. The corresponding Lewis acid (see Table 1) was also dissolved in 2 ml of anhydrous solvent and added. Reaction temperature and times can be found in Table 1. After polymerization, the polymers were precipitated in methanol and a few drops of hydrazine monohydrate were added.

SnCl₄ catalyzed polymerization

A solution of 11 (0.40 mmol, 0.32 g) in o-DCB was brought under N₂-atmosphere. The solution was heated to 120°C and SnCl₄ (0.04 mmol, 1.7M, 0.24 ml) was added. The reaction was stirred at 120°C for 36 hours. The polymer was then precipitated in MeOH and a few drops of hydrazine hydrate were added. The precipitate was filtered in a Soxhlet thimble and purified using a Soxhlet extraction with acetone and chloroform. The chloroform fraction was concentrated and precipitated in MeOH. The precipitate was filtered over a glass sintered filter and dried under vacuum. It was isolated as a purple solid. Yield: 0.18g (56%)

Study of transfer and termination of the SnCl₄ catalyzed reaction

11 (0.73 mmol, 0.58g) was dissolved in 7 ml of o-DCB under N₂-atmosphere. The solution was heated to 120°C and SnCl₄ (0.2 ml) was added via syringe. At regular intervals, 0.2 ml of solution was taken out via syringe and quenched by addition of a few drops of water and N₂H₄. These samples were then analyzed via GPC.

End capping of the Lewis acid catalyzed polymerization

A solution of SnCl₄ (16.5 µmol, 0.2 ml)in o-DCB was added to 11 (0.33 mmol, 0.10 g) dissolved in 2 ml of anhydrous o-DCB under inert atmosphere at 120°C. The resulting mixture was stirred at 120°C for 24h, after which it was cannulated to a suspension of sodium (4-trimethylsilyl)phenolate (0.50 mmol, 94.1 mg). The mixture was stirred overnight. The polymer was then precipitated in MeOH and a few drops of hydrazine hydrate were added. The resulting precipitate was filtered in a Soxhlet thimble and purified using a Soxhlet
extraction with acetone and chloroform. The chloroform fraction was concentrated under vacuum and precipitated in MeOH. The product was then filtered and dried. It was isolated as a purple solid. Yield: 15%

Synthesis of PDTP-P3AOT block copolymer
A solution of SnCl$_4$ (50 µmol, 0.6 ml) in $\alpha$-DCB was added to 11 (0.80 mmol, 0.64 g) dissolved in 6 ml of anhydrous $\alpha$-DCB under inert atmosphere at 120°C. The resulting mixture was stirred for 36h at 120°C. 2.5ml was then removed to obtain a GPC of the first block. 12 (0.40 mmol, 0.10 g) was dissolved in 5ml of $\alpha$-DCB and added to the polymerization. The mixture was then stirred for an additional 36 hours after which the polymer was precipitated in MeOH. A few drops of hydrazine hydrate were added to dedope the polymer and the polymer was filtered in a Soxhlet thimble. It was purified by Soxhlet extraction with acetone and chloroform. The chloroform fraction was concentrated and precipitated in MeOH. It was then filtered and dried under reduced pressure. The block copolymer was obtained as a dark purple solid. Yield: 32%

Synthesis of P3AOT-PDTP block copolymer
A solution of SnCl$_4$ (8.3 µmol, 0.1 ml) in $\alpha$-DCB was added to 12 (0.19 mmol, 47.5 mg) dissolved in 2 ml of $\alpha$-DCB under inert atmosphere at 120°C. The resulting mixture was stirred for 36h at 120°C. 1 ml was then removed to obtain a GPC of the first block. 11 (8.0 µmol, 0.06 g) was dissolved in 2ml of $\alpha$-DCB and added to the polymerization. The mixture was then stirred for an additional 36 hours after which the polymer was precipitated in MeOH. A few drops of hydrazine hydrate were added to dedope the polymer and the polymer was filtered in a Soxhlet thimble. It was purified by Soxhlet extraction with acetone and chloroform. The chloroform fraction was concentrated and precipitated in MeOH. It was then filtered and dried under reduced pressure. The resulting polymer was obtained as a dark purple solid. Yield: 35%
Figure S1. GPC trace of the polymerization using Ni(dppp)Cl₂ after C-H functionalization with TMPMgCl.LiCl.

Figure S2. GPC trace of the KCTCP polymerization with Ni(dppp)Cl₂.
Figure S3. GPC trace of the KCTCP polymerization with Ni(dppe)Cl₂.

Figure S4. GPC trace of the KCTCP polymerization with Ni(NHC)(iPr)Cl₂.
Figure S 5. GPC trace of the KCTCP polymerization with Pd PEPPSI-iPr.

Figure S 6. GPC-trace of the ‘polymer’ formed during the $^{31}$P-NMR experiment.
Figure S 7. Polymerization of 11 in o-DCB using SnCl$_4$.

Figure S 8. Polymerization of 11 in toluene using SnCl$_4$. 
Figure S 9. Polymerization of 11 in DCM using SnCl$_4$.

Figure S 10. Polymerization of 11 in o-DCB using triflic acid.
Figure S 11. Polymerization of 11 in THF using AlCl$_3$.

Figure S 12. GPC trace of the first block (PDTP) and entire block copolymer (PDTP-P3AOT).

NMR spectra
All spectra were recorded in CDCl$_3$ with 0.1 v/v TMS, 300 MHz.
NMR-spectrum of the catalyst association experiment

Figure S 13. $^1$H-NMR spectrum of the catalyst association experiment. Peaks at 7.12 and 6.62 ppm correspond to starting compound 11.

NMR spectrum of the end capped polymer

Figure S 14. $^1$H-NMR spectrum of the end capped polymer. The peak of TMS-group is at 0.07 ppm.
NMR spectra of compounds 2, 5, 6, 11 and 12.

Figure S15. $^1$H-NMR spectrum of compound 2

Figure S16. $^1$H-NMR spectrum of compound 5

Figure S17. $^{13}$C-NMR spectrum of compound 5
Figure S 18. $^1$H-NMR spectrum of compound 6

Figure S 19. $^{13}$C-NMR spectrum of compound 6

Figure S 20. $^1$H-NMR spectrum of compound 11
Figure S 21. $^{13}$C-NMR spectrum of compound 11

Figure S 22. $^1$H-NMR spectrum of compound 12

Figure S 23. $^{13}$C-NMR spectrum of compound 12
**Figure S 24. **$^1$H-NMR of PDTP

$^1$H-NMR was also measured at higher field strength (600 MHz) and higher temperature (55°C) to obtain narrower and better resolved peaks. However, this did not seem to improve the spectrum.

**Figure S 25. **$^1$H-NMR of PDTP-P3AOT
Figure S 26. $^1$H-NMR of PDTP-P3AOT in CDCl$_3$ at 55°C. Measured on a 600 MHz spectrometer.

MALDI-ToF

Figure S 27. MALDI-ToF spectrum of the end capped polymer
Figure S 28. Fluorescence spectra of PDTP and PDTP with added P3AOT.

References


