- Supporting Information -

2-Methoxyethylamino-bis(phenolate)yttrium Catalysts for the Synthesis of Highly Isotactic Poly(2-vinylpyridine) by Rare-Earth Metal-Mediated Group Transfer Polymerization

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1. Experimental

1.1 General

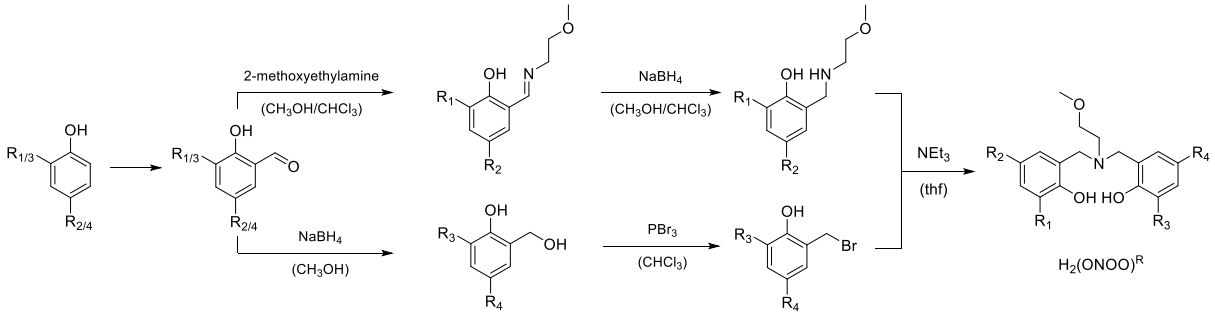
All air and moisture sensitive reactions were carried out under an argon atmosphere using standard Schlenk or glovebox techniques. All glassware was heat dried under vacuum prior to use. Unless otherwise stated, all chemicals were purchased from Acros Organics, Sigma-Aldrich, or ABCR and used as received. Dichloromethane, pentane, THF and toluene were dried using an MBraun SPS-800 solvent purification system. The precursor complex $[Y(CH_2SiMe_3)_3(THF)_2]$ was prepared following literature procedures.[1] Triethylamine and 2-vinylpyridine were dried over calcium hydride and distilled prior to use. 2-(((2-methoxyethyl)amino)methyl)-4,6-dimethylphenol and 2,4-di-*tert*-butyl-6-(((2-methoxyethyl)amino)methyl)phenol were synthesized according to literature procedures.[2]

NMR Spectra were recorded on Bruker AVIII-300 and AVIII-500C spectrometers. ^{1}H NMR spectroscopic chemical shifts δ are reported in ppm relative to the residual proton signals of deuterated solvents. Unless otherwise stated ^{13}C NMR spectroscopic chemical shifts δ are referenced to the carbon atoms of the solvent. Coupling constants *J* are given in Hertz (Hz) as averaged values and refer to couplings between protons. The following abbreviations are used to describe signal multiplicities: s (singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), br (broad signal). Deuterated solvents were obtained from Sigma-Aldrich and dried over 3 Å molecular sieves.

Quantitative elemental analyses (EA) were measured at the Laboratory for Microanalysis at the Institute of Inorganic Chemistry at the Technische Universität München. Low resolution mass spectrometry (LRMS) analytical measurements were obtained by electrospray ionization (ESI) with acetonitrile and toluene solutions on a Varian LC/MS 500-MS spectrometer. X-Ray Powder Diffraction was measured on a PANalytical Empyrean system. DSC was carried out on a Texas Instruments DSC Q2000 with a heating rate of 5 K min^{-1}. TGA was carried out on a Texas Instruments TGA Q5000 with a heating rate of 10 K min^{-1}. Gel permeation chromatography (GPC) measurements were carried out on a Varian 920-LC HPLC equipped with two PL Polargel columns.

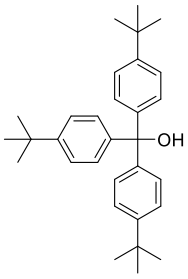
Initiator efficiency ($I^* = M_{n,calc}/M_{n,exp}$) is determined by taking aliquots during and at the end of the polymerization. I^*_t is determined for polymerization kinetics as the average initiator efficiency I^* at the maximum rate of the reaction (maximum slope of the conversion-reaction time plot).

1.2 Proligand Precursor Synthesis



Scheme S1. Proligand synthesis starting from phenols **3** and **10** for Ligands **L1-L4**.

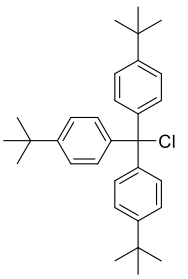
Tris(4-*tert*-butylphenyl)methanol (1)



$C_{31}H_{40}O$
428.65 g/mol

A solution of 1-bromo-4-*tert*-butylbenzene (24.4 mL, 30.0 g, 141 mmol, 3.0 eq) in dry THF (20 mL) was added dropwise to a stirred suspension of magnesium turnings (3.76 g, 155 mmol, 3.3 eq) in dry THF (200 mL). The reaction mixture was heated to initiate the reaction and stirred until the reaction subsided. A solution of diethyl carbonate (5.69 mL, 5.54 g, 46.9 mmol, 1.0 eq) in dry THF (100 mL) was added dropwise to the *Grignard* reagent and stirred for 3 h at room temperature. Ice-cold 2 M HCl (100 mL) was then poured into the reaction mixture and the organic phase was separated and washed with 2 M HCl (50 mL) and brine (50 mL). The organic phase was dried over $MgSO_4$, filtered and the solution concentrated *in vacuo*. Addition of *n*-hexane led to precipitation of **1** as colorless crystals (12.4 g, 29.0 mmol, 62%).
^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ [ppm] = 1.31 (s, 27H, $C(CH_3)_3$), 7.19 (d, ^3J = 8.5 Hz, 6H, Ar-H), 7.31 (d, ^3J = 8.5 Hz, 6H, Ar-H).
^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ [ppm] = 31.5, 34.6, 81.7, 124.8, 127.7, 144.3, 149.9.

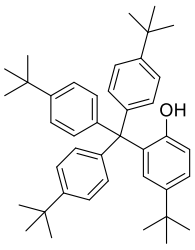
Tris(4-*tert*-butylphenyl)methyl chloride (2)



$C_{31}H_{39}Cl$
447.09 g/mol

To a vigorously stirred solution of **1** (12.4 g, 29.0 mmol, 1.0 eq) in dry toluene (30 mL) was added freshly distilled acetyl chloride (5.18 mL, 5.69 g, 72.6 mmol, 2.5 eq). The reaction mixture was heated under reflux for 30 min. After the solution was allowed to cool down to ambient temperature, *n*-hexane (40 mL) was added and the flask was left at 4 °C overnight. The resulting precipitate was filtered and dried under vacuum to afford **2** as a beige powder (10.0 g, 22.4 mmol, 77%).
^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ [ppm] = 1.33 (s, 27H, $C(CH_3)_3$), 7.16 (d, ^3J = 8.6 Hz, 6H, Ar-H), 7.31 (d, ^3J = 8.6 Hz, 6H, Ar-H).
^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ [ppm] = 31.5, 34.7, 81.8, 124.6, 129.5, 142.7, 150.6.

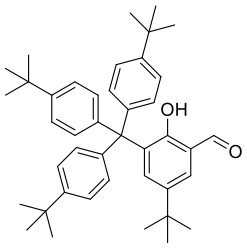
4-*tert*-Butyl-2-(tris(4-*tert*-butylphenyl)methyl)phenol (3)



$C_{41}H_{52}O$
560.85 g/mol

To molten 4-*tert*-butylphenol (33.7 g, 224 mmol, 10.0 eq) was added sodium metal (722 mg, 31.4 mmol, 1.4 eq) at 110 °C with vigorous stirring. **2** (10.0 g, 22.4 mmol, 1.0 eq) was added to the melt of phenolate and the resulting mixture was heated to 145 °C for 3 h. The reaction mixture was treated with 7% aqueous NaOH (67 mL) and Et_2O (77 mL) after cooling down to 80 °C. The organic layer was separated and the aqueous phase extracted with Et_2O (3 × 34 mL). The combined organic phases were washed with 7% aqueous NaOH (3 × 34 mL), distilled water (34 mL) and brine (34 mL). After drying over anhydrous $MgSO_4$ and filtration, the solvent of the amber solution was removed *in vacuo*. Recrystallization of the crude product from ethanol yielded **3** as colorless crystals (9.99 g, 17.8 mmol, 79%).
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 1.12 (s, 9H, $C(CH_3)_3$), 1.32 (s, 27H, $C(CH_3)_3$), 4.41 (s, 1H, Ar-OH), 6.78 (d, ^3J = 8.3 Hz, 1H, Ar-H), 6.86 (d, ^4J = 2.5 Hz, 1H, Ar-H), 7.13 (d, ^3J = 8.5 Hz, 6H, Trit-H), 7.22 (dd, ^4J = 2.4 Hz, ^3J = 8.3 Hz, 1H, Ar-H), 7.31 (d, ^3J = 8.5 Hz, 6H, Trit-H).
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 31.5, 31.5, 34.3, 34.5, 61.8, 117.0, 124.7, 125.3, 128.1, 130.8, 133.0, 141.3, 142.5, 149.5, 152.2.
LRMS (ESI, MeCN): m/z = 584.2 [$(M+Na)^+$].
EA [%]: calculated: C 87.80 H 9.35; found: C 87.94 H 9.43

5-*tert*-Butyl-2-hydroxy-3-(tris(4-*tert*-butylphenyl)methyl)-benzaldehyde (4)



$C_{42}H_{52}O_2$
588.86 g/mol

A mixture of **3** (9.96 g, 17.8 mmol, 1.0 eq), hexamethylenetetramine (2.74 g, 19.5 mmol, 1.1 eq) and trifluoroacetic acid (100 mL) was heated at 110 °C under reflux for 40 h. Subsequently the warm reaction mixture was poured into vigorously stirred 2 M HCl (250 mL). The cold mixture was extracted with chloroform (3 × 125 mL) and the combined organic layers were washed with 2 M HCl (3 × 75 mL), distilled water (175 mL) and brine (100 mL). After drying over $MgSO_4$ and filtration, the solvent was removed under reduced pressure. Silica gel column chromatography (*n*-hexane:EtOAc = 30:1) was utilized to purify the residue and afford **4** as a white powder (6.65 g, 11.3 mmol, 64%).

TLC: R_f = 0.19 (silica gel, *n*-hexane:EtOAc = 30:1, [UV]).

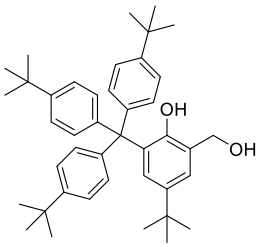
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 1.16 (s, 9H, $C(CH_3)_3$), 1.31 (s, 27H, $C(CH_3)_3$), 7.09 (d, ^3J = 8.6 Hz, 6H, Trit-H), 7.25 (d, ^3J = 8.5 Hz, 6H, Trit-H), 7.33 (d, ^4J = 2.5 Hz, 1H, Ar-H), 7.43 (d, ^4J = 2.5 Hz, 1H, Ar-H), 9.86 (s, 1H, CHO), 11.13 (s, 1H, Ar-OH).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 31.2, 31.5, 34.3, 34.4, 62.1, 120.2, 124.1, 128.8, 130.6, 136.0, 136.7, 141.4, 142.1, 148.5, 158.8, 197.0.

LRMS (ESI, MeCN): m/z = 612.2 [(M+Na)$^+$].

EA [%]: calculated: C 85.67, H 8.90; found: C 85.59, H 9.05.

4-*tert*-Butyl-2-hydroxymethyl-6-(tris(4-*tert*-butylphenyl)methyl)phenol (5)



$C_{42}H_{54}O_2$
590.88 g/mol

To a suspension of **4** (3.10 g, 5.26 mmol, 1.0 eq) in methanol (100 mL) was added sodium borohydride (398 mg, 10.5 mmol, 2.0 eq) in small portions. After the reaction mixture was stirred at room temperature for 1 h, the solvent was removed under reduced pressure. The residue was redissolved in distilled water (150 mL) and neutralized with glacial acetic acid. The aqueous phase was extracted with chloroform (3 × 100 mL) and the combined organic layers were dried over anhydrous $MgSO_4$. After filtration, the solvent was removed *in vacuo* to yield **6** as a white powder (3.09 g, 5.23 mmol, 99%). The product was utilized in the next step without further purification.

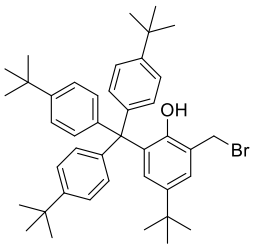
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 1.11 (s, 9H, $C(CH_3)_3$), 1.31 (s, 27H, $C(CH_3)_3$), 2.45 (br s, 1H, CH_2OH), 4.64 (s, 2H, CH_2), 4.86 (s, 1H, Ar-OH), 6.84 (d, ^4J = 2.4 Hz, 1H, Ar-H), 7.11 (d, ^3J = 8.5 Hz, 6H, Trit-H), 7.19 (d, ^4J = 2.4 Hz, 1H, Ar-H), 7.30 (d, ^3J = 8.5 Hz, 6H, Trit-H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 31.5, 31.5, 34.3, 34.5, 61.8, 63.5, 124.7, 125.0, 127.8, 127.9, 130.7, 133.2, 141.3, 142.2, 149.5, 150.6.

LRMS (ESI, MeCN): m/z = 614.2 [(M+Na)$^+$].

EA [%]: calculated: C 85.37, H 9.21; found: C 79.31, H 8.63.

2-Bromomethyl-4-*tert*-butyl-6-(tris(4-*tert*-butylphenyl)methyl)phenol (6)



$C_{42}H_{53}BrO$
653.77 g/mol

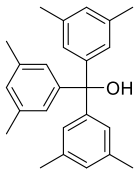
To a solution of **5** (3.06 g, 5.18 mmol, 1.0 eq) in chloroform (100 mL) was added phosphorus tribromide (0.25 mL, 701 mg, 2.59 mmol, 0.5 eq). After the reaction mixture was stirred at room temperature for 1 h, iced water (40 mL) was added over 5 min. The resulting phases were separated and the aqueous phase was extracted with chloroform (3 × 25 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo* to afford **7** as a white powder (3.39 g, 5.18 mmol, quantitative yield).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 1.11 (s, 9H, $C(CH_3)_3$), 1.31 (s, 27H, $C(CH_3)_3$), 4.53 (s, 2H, CH_2), 4.77 (s, 1H, Ar-OH), 6.87 (d, ^4J = 2.4 Hz, 1H, Ar-H), 7.10 (d, ^3J = 8.6 Hz, 6H, Trit-H), 7.25 (d, ^4J = 3.0 Hz, 1H, Ar-H), 7.30 (d, ^3J = 8.6 Hz, 6H, Trit-H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 31.1, 31.4, 31.5, 34.3, 34.5, 61.9, 124.3, 124.8, 126.6, 129.2, 130.7, 133.7, 141.0, 142.4, 149.7, 150.7.

LRMS (ESI, MeCN): m/z = 677.1 [(M+Na)$^+$].

Tris(3,5-dimethylphenyl)methanol (7)



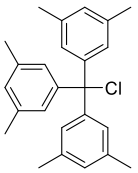
$C_{25}H_{28}O$
344.49 g/mol

A solution of 1-bromo-3,5-dimethylbenzene (18.4 mL, 25.0 g, 135 mmol, 3.0 eq) in dry THF (20 mL) was added dropwise to a stirred suspension of magnesium turnings (3.61 g, 149 mmol, 3.3 eq) in dry THF (200 mL). The reaction mixture was heated to initiate the reaction and stirred until the reaction subsided. A solution of diethyl carbonate (5.46 mL, 5.32 g, 45.0 mmol, 1.0 eq) in dry THF (100 mL) was added dropwise to the *Grignard* reagent and stirred for 3 h at room temperature. Ice-cold 2 M HCl (100 mL) was then poured into the reaction mixture and the organic phase was separated and washed with 2 M HCl (50 mL) and brine (50 mL). The organic phase was dried over $MgSO_4$, filtered and the solution concentrated *in vacuo*. Addition of *n*-hexane led to precipitation of **8** as colorless crystals (7.96 g, 23.1 mmol, 51%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ [ppm] = 2.27 (s, 18H, CH_3), 2.68 (s, 1H, OH), 6.88 (s, 6H, Ar-H), 6.91 (s, 3H, Ar-H).

^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ [ppm] = 21.7, 83.2, 126.7, 128.6, 136.5, 143.7.

Tris(3,5-dimethylphenyl)methyl chloride (8)



$C_{25}H_{27}Cl$
362.93 g/mol

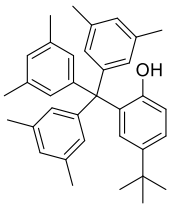
To a vigorously stirred solution of **7** (7.96 g, 23.1 mmol, 1.0 eq) in dry toluene (25 mL) was added freshly distilled acetyl chloride (4.12 mL, 4.54 g, 57.8 mmol, 2.5 eq). The reaction mixture was heated under reflux for 30 min. After the solution was allowed to cool down to ambient temperature, *n*-hexane (35 mL) was added and the flask was left at 4 °C overnight. The resulting precipitate was filtered and dried under vacuum to furnish **9** as colorless crystals (6.44 g, 17.7 mmol, 77%).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 2.29 (s, 18H, CH_3), 6.88 (s, 6H, Ar-H), 6.95 (s, 3H, Ar-H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 21.6, 82.2, 127.7, 129.5, 137.1, 145.6.

EA [%]: calculated: C 82.73, H 7.50, Cl 9.77; found: C 82.23, H 7.45, Cl 9.30

4-*tert*-Butyl-2-(tris(3,5-dimethylphenyl)methyl)phenol (9)



$C_{35}H_{40}O$
476.69 g/mol

To molten 4-*tert*-butylphenol (25.7 g, 171 mmol, 10.0 eq) was added sodium metal (550 mg, 23.9 mmol, 1.4 eq) at 110 °C with vigorous stirring. **8** (6.20 g, 17.1 mmol, 1.0 eq) was added to the formed phenolate and the resulting mixture was heated at 145 °C under reflux for 3 h. The reaction mixture was treated with 7% aqueous NaOH (52 mL) and Et_2O (60 mL) after cooling down to about 80 °C. The organic layer was separated and the aqueous phase extracted with Et_2O (3 × 26 mL). The combined organic phases were washed with 7% aqueous NaOH (3 × 26 mL), distilled water (26 mL) and brine (26 mL). After drying over anhydrous $MgSO_4$ and filtration, the solvent of the amber solution was removed *in vacuo*. Recrystallization of the crude product from ethanol yielded **10** as colorless crystals (5.72 g, 12.0 mmol, 70%).

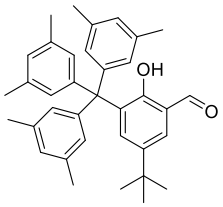
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 1.18 (s, 9H, $C(CH_3)_3$), 2.24 (s, 18H, CH_3), 4.52 (s, 1H, Ar-OH), 6.73 (d, ^3J = 8.2 Hz, 1H, Ar-H), 6.81 (s, 6H, Trit-H), 6.86 (s, 3H, Trit-H), 7.16 (d, ^4J = 2.4 Hz, 1H, Ar-H), 7.20 (dd, ^{4}J = 2.4 Hz, ^3J = 8.3 Hz, 1H, Ar-H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 21.8, 31.6, 34.3, 62.7, 117.1, 125.0, 128.3, 128.3, 128.9, 132.6, 137.0, 142.2, 144.6, 152.4.

LRMS (ESI, MeCN): m/z = 500.2 [$(M+Na)^+$].

EA [%]: calculated: C 88.19, H 8.46; found: C 88.09, H 8.57.

5-*tert*-Butyl-2-hydroxy-3-(tris(3,5-dimethylphenyl)methyl)benzaldehyde (10)



$C_{36}H_{40}O_2$
504.70 g/mol

To a suspension of **9** (6.00 g, 12.6 mmol, 1.0 eq), anhydrous magnesium chloride (2.64 g, 27.7 mmol, 2.2 eq) and paraformaldehyde (831 mg, 27.7 mmol, 2.2 eq) in dry THF (70 mL) was added dropwise freshly distilled triethylamine (1.76 mL, 1.27 g, 12.6 mmol, 1.0 eq). The resulting reaction mixture was heated under reflux for 3 d. Subsequently the mixture was allowed to cool down to room temperature and diluted with distilled water (30 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL) and the combined organic phases were washed with distilled water (75 mL) and brine (2 × 75 mL). After drying over anhydrous $MgSO_4$ and filtration, the solvent was removed *in vacuo*. Silica gel column chromatography (*n*-pentane/Et_2O = 40/1) and subsequent recrystallization from ethanol were utilized to purify the residue and afford **11** as colorless crystals (3.67 g, 7.27 mmol, 58%).

TLC: *R*f = 0.23 (silica gel, *n*-pentane:Et_2O = 40:1, [UV]).

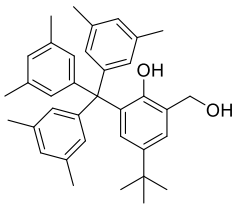
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 1.26 (s, 9H, $C(CH_3)_3$), 2.23 (s, 18H, CH_3), 6.80 (s, 3H, Trit-H), 6.89 (s, 6H, Trit-H), 7.41 (d, ^4J = 2.4 Hz, 1H, Ar-H), 7.77 (d, ^4J = 2.4 Hz, 1H, Ar-H), 9.83 (s, 1H, CHO), 11.22 (s, 1H, Ar-OH).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 21.8, 31.2, 34.3, 63.0, 120.2, 127.3, 128.5, 128.7, 135.4, 136.3, 137.1, 141.3, 145.2, 158.8, 196.9.

LRMS (ESI, MeCN): m/z = 527.4 [$(M+Na)^+$].

EA [%]: calculated: C 85.67, H 7.99; found: C 85.73, H 8.17.

4-*tert*-Butyl-2-hydroxymethyl-6-(tris(3,5-dimethylphenyl)methyl)phenol (11)



$C_{36}H_{42}O_2$
506.72 g/mol

To a suspension of **10** (2.60 g, 5.15 mmol, 1.0 eq) in methanol (100 mL) was added sodium borohydride (390 mg, 10.3 mmol, 2.0 eq) in small portions. After the reaction mixture was stirred at room temperature for 2 h, the solvent was removed under reduced pressure. The residue was redissolved in water (125 mL) and neutralized with glacial acetic acid. The aqueous phase was extracted with chloroform (3 × 75 mL) and the combined organic layers were dried over anhydrous $MgSO_4$. After filtration, the solvent was removed *in vacuo* to yield **12** as a white powder (2.58 g, 5.09 mmol, 99%). The product was utilized in the next step without further purification.

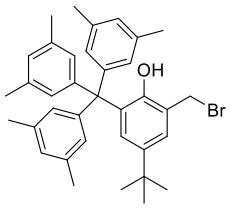
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 1.19 (s, 9H, $C(CH_3)_3$), 2.24 (s, 18H, CH_3), 4.63 (s, 2H, CH_2), 6.80 (s, 6H, Trit-H), 6.87 (s, 3H, Trit-H), 7.15 (d, ^4J = 2.5 Hz, 1H, Ar-H), 7.18 (d, ^4J = 2.5 Hz, 1H, Ar-H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 21.8, 31.6, 34.4, 62.7, 63.6, 124.7, 128.3, 128.9, 132.9, 136.3, 137.0, 142.0, 144.5, 145.2, 150.8.

LRMS (ESI, MeCN): m/z = 529.4 [$(M+Na)^+$].

EA [%]: calculated: C 85.33, H 8.35; found: C 85.04, H 8.99.

2-Bromomethyl-4-*tert*-butyl-6-(tris(3,5-dimethylphenyl)methyl)phenol (12)



$C_{36}H_{41}BrO$
569.91 g/mol

To a solution of **11** (2.58 g, 5.09 mmol, 1.0 equiv.) in chloroform (100 mL) was added phosphorus tribromide (0.24 mL, 689 mg, 2.55 mmol, 0.5 eq). After the reaction mixture was stirred at room temperature for 1 h, iced water (40 mL) was added over 5 min. The resulting phases were separated and the aqueous phase was extracted with chloroform (3 × 25 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was recrystallized from acetonitrile to afford **13** as colorless crystals (2.60 g, 4.56 mmol, 90%).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ [ppm] = 1.18 (s, 9H, $C(CH_3)_3$), 2.24 (s, 18H, CH_3), 4.52 (s, 2H, CH_2), 6.78 (s, 6H, Trit-H), 6.88 (s, 3H, Trit-H), 7.14 (d, ^4J = 2.4 Hz, 1H, Ar-H), 7.23 (d, ^4J = 2.5 Hz, 1H, Ar-H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ [ppm] = 21.8, 31.5, 31.5, 34.3, 62.8, 125.1, 126.2, 128.4, 129.0, 129.4, 133.4, 137.1, 142.1, 144.1, 151.0.

LRMS (ESI, MeCN): m/z = 593.2 [$(M+Na)^+$].

EA [%]: calculated: C 75.91, H 7.26; found: C 76.08, H 7.28.

2. Kinetic Investigations

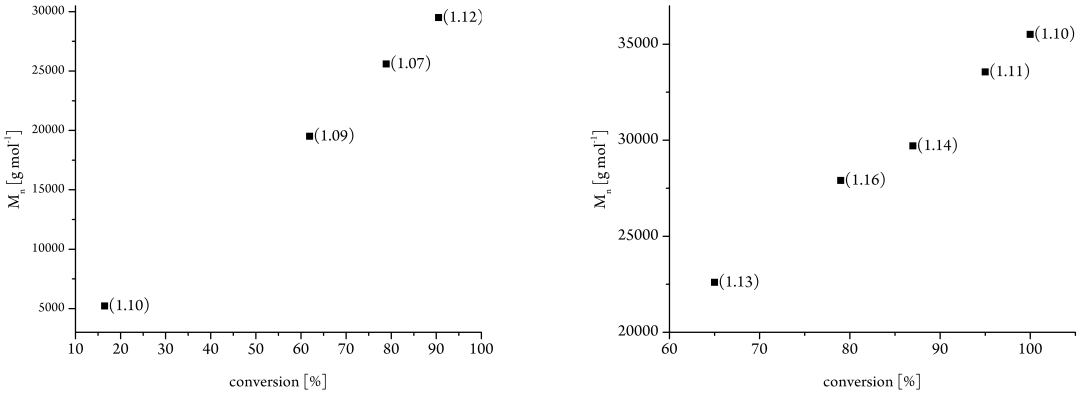


Figure S1. Linear growth of the absolute molecular weight (M_n) as a function of monomer conversion (determined gravimetically) and the corresponding PDIs. Left: catalyst **1**, right: catalyst **2**.

3. Microstructure Analysis

3.1 ^{13}C NMR spectra

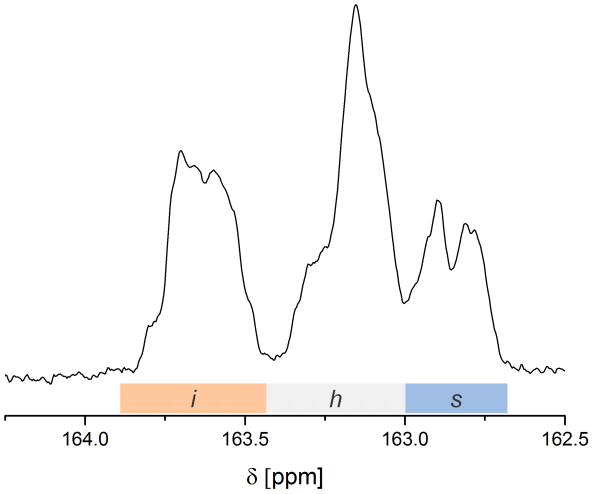


Figure S2. Aromatic quaternary ^{13}C NMR resonances (*i*, *h*, *s* proportions for *isotactic*, *heterotactic*, and *syndiotactic* triads) of poly(2-vinylpyridine) (30 mg of P2VP in 0.6 mL of CD_3OD for catalyst **5**. ([2VP]:[Cat.] = 200:1, [M] = 2.7 mmol, 2 mL of toluene, 25 °C)).

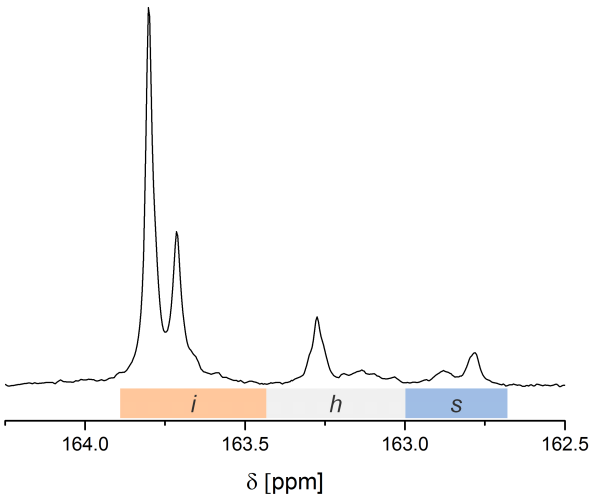


Figure S3. Aromatic quaternary ^{13}C NMR resonances (*i*, *h*, *s* proportions for *isotactic*, *heterotactic*, and *syndiotactic* triads) of poly(2-vinylpyridine) (30 mg of P2VP in 0.6 mL of CD_3OD for catalyst **1**. ([2VP]:[Cat.] = 200:1, [M] = 2.7 mmol, 2 mL of toluene, 25 °C)).

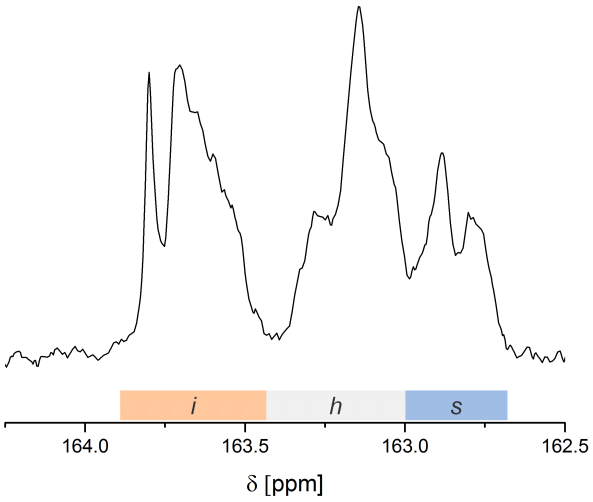


Figure S4. Aromatic quaternary ^{13}C NMR resonances (*i*, *h*, *s* proportions for *isotactic*, *heterotactic*, and *syndiotactic* triads) of poly(2-vinylpyridine) (30 mg of P2VP in 0.6 mL of CD_3OD for catalyst **2**. ([2VP]:[Cat.] = 200:1, [M] = 2.7 mmol, 2 mL of toluene, 25 °C)).

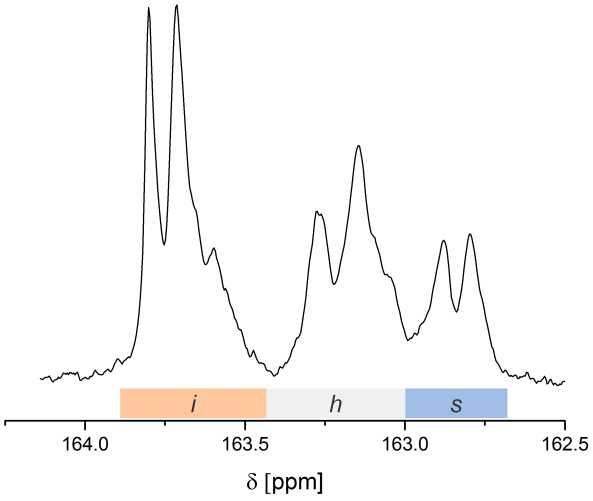


Figure S5. Aromatic quaternary ^{13}C NMR resonances (*i*, *h*, *s* proportions for *isotactic*, *heterotactic*, and *syndiotactic* triads) of poly(2-vinylpyridine) (30 mg of P2VP in 0.6 mL of CD_3OD for catalyst **3.** ([2VP]:[Cat.] = 200:1, [M] = 2.7 mmol, 2 mL of toluene, 25 °C)).

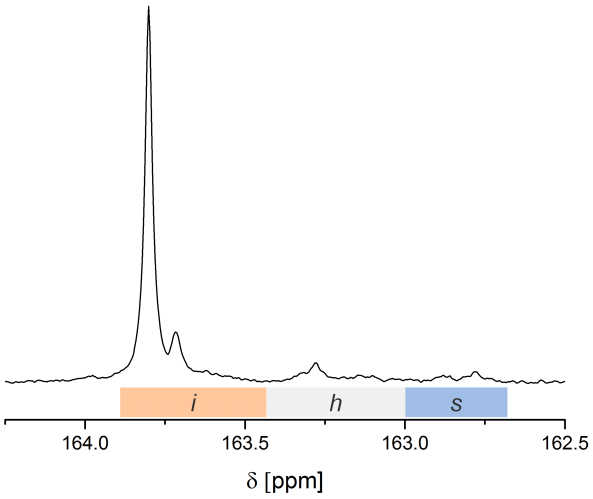


Figure S6. Aromatic quaternary ^{13}C NMR resonances (*i*, *h*, *s* proportions for *isotactic*, *heterotactic*, and *syndiotactic* triads) of poly(2-vinylpyridine) (30 mg of P2VP in 0.6 mL of CD_3OD for catalyst **4**. ([2VP]:[Cat.] = 200:1, [M] = 2.7 mmol, 2 mL of toluene, 25 °C)).

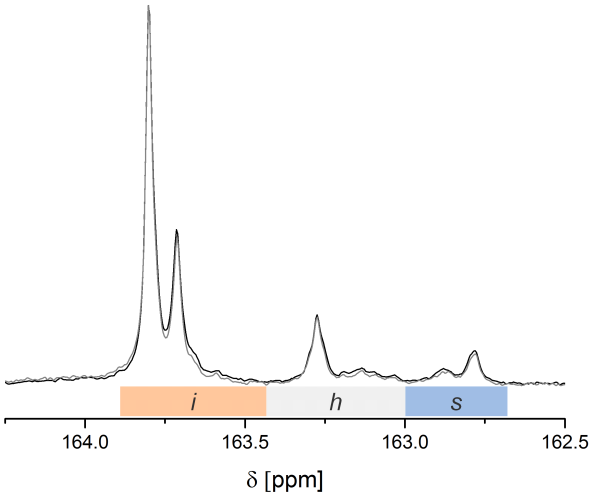


Figure S7. Aromatic quaternary ^{13}C NMR resonances (*i*, *h*, *s* proportions for *isotactic*, *heterotactic*, and *syndiotactic* triads) of poly(2-vinylpyridine) (30 mg P2VP in 0.6 mL of CD_3OD for catalysts **1**. ([2VP]:[Cat.] = 200:1, [M] = 2.7 mmol, 2 mL of toluene, 25 °C: black, 50 °C: grey)).

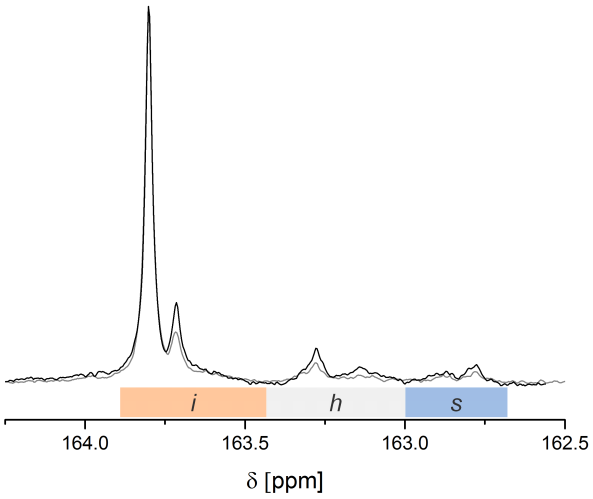


Figure S8. Aromatic quaternary ^{13}C NMR resonances (*i*, *h*, *s* proportions for *isotactic*, *heterotactic*, and *syndiotactic* triads) of poly(2-vinylpyridine) (30 mg P2VP in 0.6 mL of CD_3OD for catalysts **4**. ([2VP]:[Cat.] = 200:1, [M] = 2.7 mmol, 2 mL of toluene, 25 °C: black, 50 °C: grey)).

3.2 Theoretical Investigations

- P_m is the probability of meso linkages between monomer units and is determined by ^{13}C NMR spectroscopy.
- Theoretical triad distributions are calculated using the following correlations:

Probability of prochiral monomer addition via *re* or *si* side of the catalyst, where $P_m = m = \sigma + (1 - \sigma)^2$ and $P_r = 1 - P_m$

$$mm = P_m^2$$

$$mr = P_m P_r$$

$$rr = P_r^2$$

4. Thermoanalysis

4.1 DSC

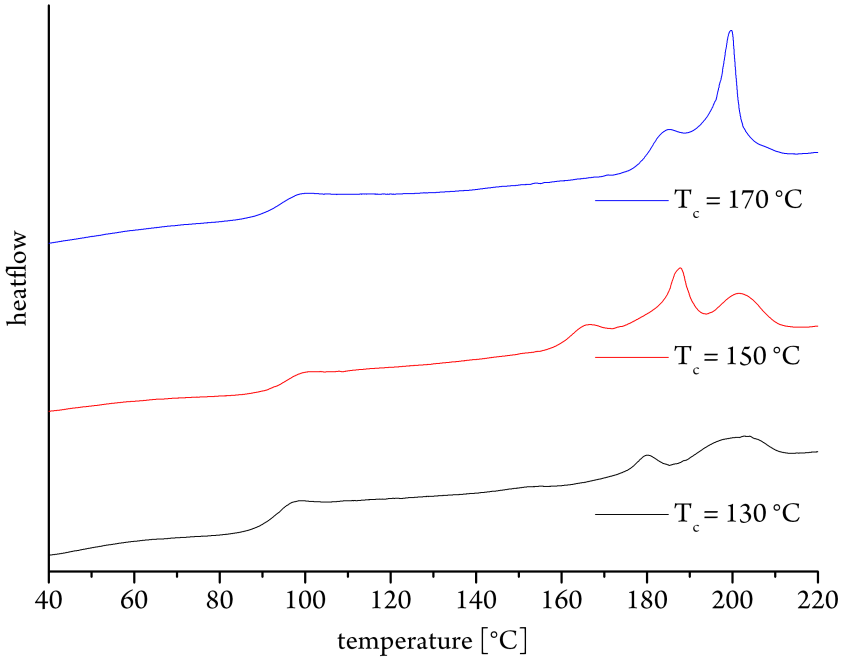


Figure S9. DSC curves of crystallized P2VP samples at different crystallization temperatures T_c for 150 min (catalyst **4,** [2VP]:[Cat.] = 200:1, [M] = 2.7 mmol, 2 mL toluene, 25 °C).

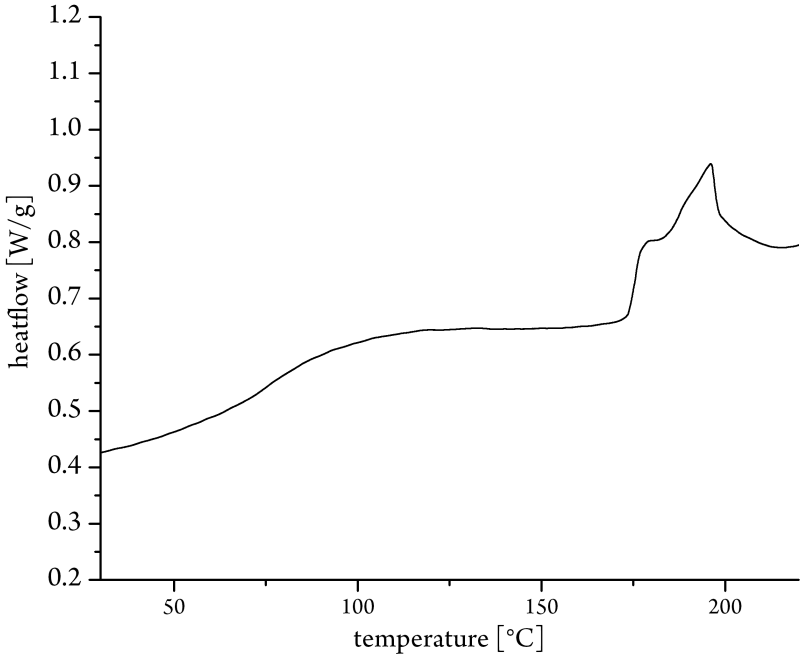


Figure S10. DSC curves of crystallized P2VP samples at a T_c = 130°C for 16 h (catalyst **1,** [2VP]:[Cat.] = 200:1, [M] = 2.7 mmol, 2 mL of toluene, 25 °C).

4.2 TGA

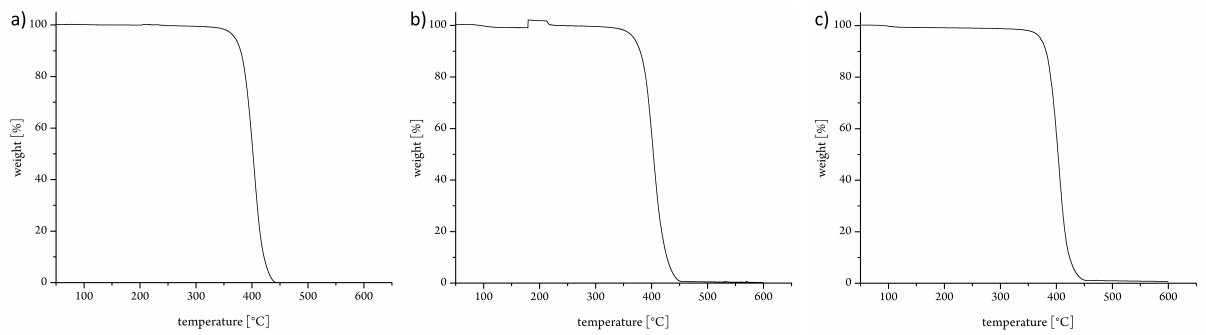


Figure S11. TGA curves of atactic (a), highly *isotactic* amorphous (P_m = 0.92, b), and highly *isotactic* crystallized P2VP (P_m = 0.92, T_c = 170 °C, crystallization time 150 min, c).

5. Literature

[1] K. C. Hultzsch, P. Voth, K. Beckerle, T. P. Spaniol, J. Okuda, *Organometallics* **2000**, *19*, 228-243.

[2] P. T. Altenbuchner, F. Adams, A. Kronast, E. Herdtweck, A. Pöthig, B. Rieger, *Polym. Chem.* **2015**, *6*, 6796-6801.