Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for the Manuscript Entitled

Stereospecific Catalytic Precision Polymerization of 2-Vinylpyridine via Rare Earth Metal-Mediated Group Transfer Polymerization with 2-Methoxyethylamino-bis(phenolate)-Yttrium Complexes

P. T. Altenbuchner,[a] F. Adams,[a] A. Kronast,[a] E. Herdtweck[b], A. Pöthig[b] and B. Rieger[a*]

Table of Contents

1 Experimental procedures

Materials and Methods.

All reactions were carried out under 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 Sigma-Aldrich, Acros Organics, or ABCR and used as received. Toluene, thf and pentane were dried using a MBraun SPS-800 solvent purification system. Hexane was dried over 3 Å molecular sieves. The precursor complexes $Ln(CH_2Si(CH_3)_3)_3(thf)_2$ (Ln = Y,Lu) and $Y(N(SiH(CH_3)_2)_2)_3(thf)_2$, $LiCH_2TMS$ and catalysts 4 and 5 are prepared according to literature procedures.[1-4] Triethylamine and 2-vinylpyridine were dried over calcium hydride and distilled prior to use.

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

NMR spectra were recorded on a Bruker AVIII-300, AVIII-500 Cryo and AVIII 900 Cryo spectrometer. Unless otherwise stated, ^{1}H- and ^{13}C-NMR spectroscopic chemical shifts δ are reported in ppm relative to δ (^{1}H) is calibrated to the residual proton signal, δ (^{13}C) to the carbon signal of the solvent. Unless otherwise stated, coupling constants J are averaged values and refer to couplings between two protons. Deuterated solvents were obtained from Sigma-Aldrich and dried over 3 Å molecular sieves.

Elemental analyses were measured at the Laboratory for Microanalysis at the Institute of Inorganic Chemistry at the Technische Universität München.

ESI-MS analytical measurements were performed with methanol, isopropanol, ethyl acetate and toluene solutions on a Varian 500-MS spectrometer.

Single Crystal X-ray Crystallography was performed in the SCXRD laboratory of the Catalysis Research Center at the Technische Universität München. Additional crystallographic information is given below.

Polymerization Procedures. To a solution of 13.5 µmol catalyst (1.0 eq.) in 2 mL solvent at room temperature, 2.7 mmol monomer (200 eq.; 27 mmol [2VP]/ 20 mL solvent) was added in one portion. The polymerization is quenched by addition of methanol. Conversion is determined by ^{1}H-NMR-spectroscopy. The polymers were precipitated by addition of the reaction mixtures to pentane (100 mL) and the solution was decanted of. Residual solvent was removed by freeze-drying from benzene (100 mL) over night.

Kinetic measurements by aliquots method. To a solution of 135 µmol catalyst in 20 mL toluene at room temperature, the corresponding amount of monomer (27 mmol, 200 eq.) was added in one portion. Aliquots were taken from the reaction solution at regular time intervals and quenched by addition of MeOH. Solvent and not polymerized monomer were removed by drying the polymers under vacuum at

60 °C overnight. For each aliquot, the conversion is determined gravimetrically and the molecular weight of the polymer is determined by GPC-MALS analysis.

Characterization of P2VP Samples. The tacticity determination of P2VP was performed by ^{13}C-NMR-spectroscopy at room temperature. Spectra for the analysis of P2VP *mm*, *mr*/*rm* and *rr* triads were recorded with a sample concentration of 15% (w/w; 75 mg/0.6 mL CD_3OD) on a AVIII 500 Cryo spectrometer and analyzed according to literature.[5] Spectra for the analysis of P2VP pentades were recorded with a sample concentration of 6% (w/w; 30 mg/0.6 mL CD_3OD) on a AVIII 900 Cryo spectrometer and analyzed according to literature.[6] Unless otherwise stated, ^{13}C-NMR-spectra are measured with 2000 scans, a relaxation delay of 4 seconds and calibrated to the *mmmm*-pentade of the aromatic quaternary carbon-atom of P2VP due to better possibility of comparison.

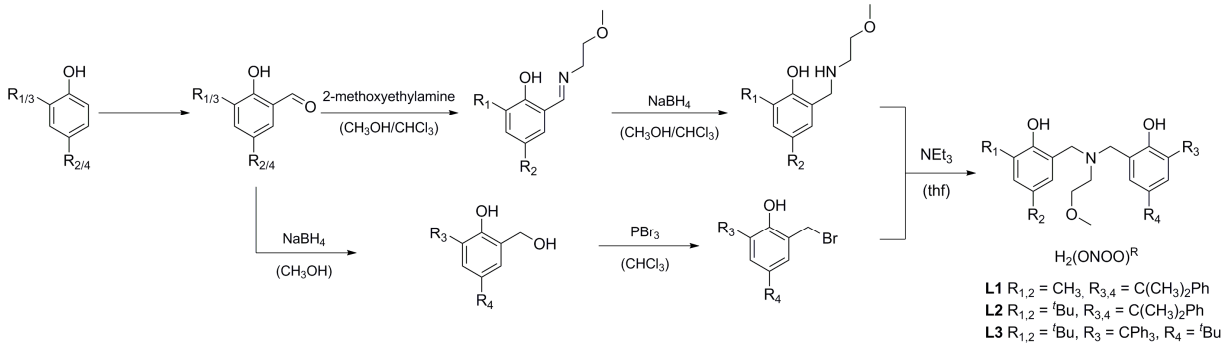
Gel permeation chromatography (GPC) was carried out with samples of 5 mg/mL concentration on a Varian LC-920 equipped with two PL Polargel columns. As eluent a mixture of THF/water (1:1; v:v), 9 g/L tetrabutylammonium bromide (TBAB) and 680 mg/L_{THF} 3,5-di-tert-butyl-4-hydroxytoluene (BHT), was used. Absolute molecular weights have been determined online by multiangle light scattering (MALS) analysis using a Wyatt Dawn Heleos II in combination with a Wyatt Optilab rEX as concentration source.

Proligand Synthesis

Synthesis of 4-(tert-butyl)-2-tritylphenol after a modified literature procedure:[7]

4-tert-butylphenol (10.0 eq.) is heated up to 111 °C and sodium metal (1.39 eq.) is added to the molten phenol. The reaction mixture is stirred till melting of the sodium and triphenylchloromethane (1.0 eq) was added. The resulting mixture is heated for 3 h at 140 °C with vigorous stirring. After cooling down to 90 °C the reaction mixture is treated with 7% $NaOH_{aq.}$ and diethylether. The organic layer is separated, washed with 7% $NaOH_{aq.}$, water and brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the crude product is recrystallized from hot ethanol. Yield: 65% (light yellow powder)

Synthesis route of formation of 2-methoxyethylamino-bis(phenolate)ligands (L_1-L_3):



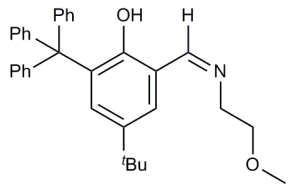
General procedure for the formylation of phenols after a modified literature procedure:[7]

The respective phenol (1.0 eq.), hexamethylenetetramine (1.0 eq.) and CF_3COOH are mixed and heated to 110 °C for 22 h and then cooled to 80 °C. 2 M HCl is added and the reaction mixture is cooled to room temperature. Chloroform is added and the organic layer is separated. The aqueous layer is extracted with chloroform two more times. The combined organic layers are washed with 2 M HCl, water and brine, separated and dried over $MgSO_4$. The solvents are evaporated and the residue is purified by recrystallization from methanol or column chromatography (SiO_2, hexane/EtOAc = 12:1).

General procedure for the synthesis of the secondary amines:

2-methoxyethylenamine (1.0 eq.) is added to a solution of the respective 2-hydroxybenzaldehyde (1.0 eq.) in methanol/chloroform (1:1, v:v). The reaction mixture is heated to reflux for 24 hours, cooled to 0 °C and $NaBH_4$ (2.1 eq.) is added in small portions. The reaction is kept at 50 °C for 48 h. After cooling to room temperature, the solution is acidified by adding concentrated HCl. All volatiles are removed under vacuum and the residue is dissolved in saturated aqueous Na_2CO_3. The aqueous layer is extracted with chloroform and the combined organic layers are dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Recrystallization from ethanol leads to the desired product.

4-(tert-Butyl)-2-(((2-methoxyethyl)imino)methyl)-6-tritylphenol



$C_{33}H_{35}NO_2$
M: 477.65

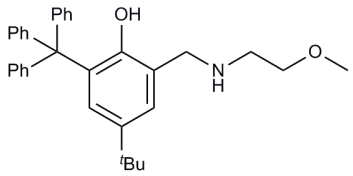
Yield: 61% (yellow powder)

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 13.37 (s, 1H, C*H*O), 8.33 (s, 1H), 7.33 (d, ^4J = 2.4 Hz, 1H, H_{arom}), 7.25 – 7.09 (m, 16H, H_{arom}), 3.63 (t, ^3J = 5.5 Hz, 2H, CH_2), 3.54 (t, ^3J = 5.5 Hz, 2H, CH_2), 3.29 (s, 3H, CH_3), 1.17 (s, 9H, ^{t}Bu).

^{13}C-NMR (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 166.7, 145.5, 133.9, 131.0, 128.3, 127.0, 126.9, 125.5, 118.0, 77.2, 71.6, 63.3, 58.9, 34.0, 31.3.

ESI-MS (toluene): 478.2 $[M]^+$.

4-(tert-butyl)-2-(((2-methoxyethyl)amino)methyl)-6-tritylphenol



$C_{33}H_{37}NO_2$
M: 479.66

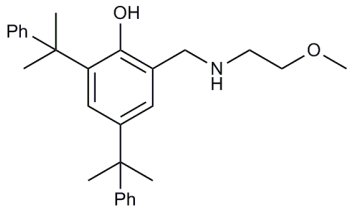
Yield: 67% (yellow powder)

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.14 – 7.09 (m, 15H, H_{arom}), 7.00 (d, ^4J = 2.4 Hz, 1H, H_{arom}), 6.83 (d, ^4J = 2.4 Hz, 1H, H_{arom}), 3.81 (s, 2H, ArCH_2), 3.21 – 3.04 (m, 5H, CH_2, CH_3), 2.46 (t, ^3J = 5.0 Hz, 2H, CH_2), 1.05 (s, 9H, *t*Bu).

^{13}C-NMR (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 154.2, 146.2, 140.1, 133.6, 131.1, 128.4, 127.7, 127.5, 127.0, 125.4, 124.3, 122.0, 71.0, 63.5, 58.9, 52.6, 47.2, 34.1, 31.6.

EA: calculated: C 82.63 H 7.73 N 2.92
found: C 83.48 H 7.92 N 2.73

2-(((2-methoxyethyl)amino)methyl)-4,6-bis(2-phenylpropan-2-yl)phenol



$C_{28}H_{35}NO_2$
M: 417.59

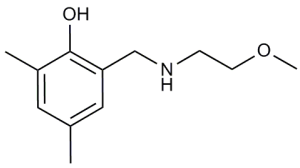
Yield: 74% (yellow powder)

^{1}H-NMR (300 MHz, $CDCl_3$, 298 K): δ (ppm) = 7.37 – 7.12 (m, 11H, H_{arom}), 6.81 (d, ^4J = 2.2 Hz, 1H, H_{arom}), 3.87 (s, 2H. ArCH_2), 3.43 (t, ^3J = 5.0 Hz, 2H), 3.26 (s, 3H, O*Me*), 2.74 (t, ^3J = 5.0 Hz, 2H), 1.69 (s, 6H, CMe_2Ph), 1.64 (s, 6H, CMe_2Ph).

^{13}C-NMR (75 MHz, $CDCl_3$, 298 K): δ (ppm) = 154.2, 151.5, 151.4, 139.9, 135.2, 128.0, 127.8, 126.9, 125.6, 125.5, 125.0, 124.9, 122.2, 70.9, 58.9, 52.8, 47.8, 42.5, 42.2, 31.2, 29.7.

ESI-MS (EtOAc): 418.3 $[M]^+$

2-(((2-methoxyethyl)amino)methyl)-4,6-dimethylphenol



$C_{12}H_{19}NO_2$
M: 209.29

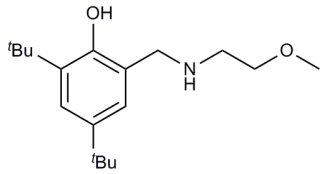
Yield: 63% (yellow powder)

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 6.89 – 6.82 (m, 1H, H_{arom}), 6.66 – 6.61 (m, 1H, H_{arom}), 3.94 (s, 2H), 3.51 (m, 2H), 3.36 (s, 3H), 2.81 (m, 2H), 2.21 (s, 3H), 2.20 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 153.9, 130.5, 127.5, 126.5, 124.9, 121.5, 71.1, 58.9, 52.4, 47.9, 20.5, 15.7.

ESI-MS (EtOAc): 210.4 $[M]^+$

2,4-di-tert-butyl-6-(((2-methoxyethyl)amino)methyl)phenol



$C_{18}H_{31}NO_2$
M: 293.45

Yield: 78% (yellow powder)

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.21 (virt. s, 1H, H_{arom}), 6.86 (d, ^4J = 2.5 Hz, 1H, H_{aron}), 3.96 (s, 2H), 3.53 (s, 2H), 3.36 (s, 3H), 2.84 (s, 2H), 1.42 (s, 9H, ^{t}Bu), 1.28 (s, 9H, ^{t}Bu).

^{13}C-NMR (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 151.7, 144.4, 141.3, 127.0, 125.9, 121.1, 67.5, 59.1, 48.5, 45.6, 35.2, 34.5, 31.6, 30.2.

ESI-MS (EtOAc): 294.6 $[M]^+$

General procedure for the synthesis of bromomethyl-compounds:[8-10]

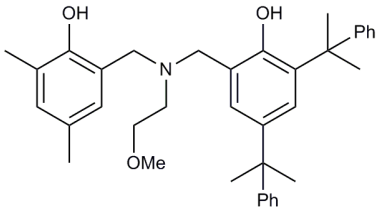
$NaBH_4$ (2.0 eq.) is slowly added to a stirred solution of the respective 2-hydroxybenzaldehyde (1.0 eq.) in methanol. The solution is stirred at room temperature for 1 h. All volatiles are removed in vacuum and the resulting residue is dissolved in water. The resulting aqueous mixture is neutralized with glacial acetic acid and extracted with CH_2Cl_2. The combined organic layers are dried with anhydrous $MgSO_4$ and concentrated to give a white solid which is immediately converted in the next step.

PBr_3 (0.5 eq.) is added to a stirred solution of 2-hydroxybenzyl alcohol (1.0 eq.) in chloroform. The mixture is stirred for 1 h at room temperature. Within 5 minutes cold water is added with vigorous stirring. The organic layer is separated and the aqueous residue is extracted with chloroform. The combined organic layers are dried with anhydrous $MgSO_4$ and concentrated *in vacuo* to yield the desired product.

General procedure for the synthesis of $H_2(ONOO)^R$:

One equivalent of the methylbromide is dissolved in tetrahydrofurane and added dropwise to a solution of one equivalent of the respective secondary amine in tetrahydrofurane. The solution is stirred for 30 minutes at room temperature before 1.5 equivalents of triethylamine are added slowly. The solution is heated up to 75 °C for 14 hours. The solid is filtered off and the solvent is removed *in vacuo*. A respective purification leads to the desired product.

$H_2(ONOO)^{Me,C(CH_3)_2Ph}$ (L1):



$C_{37}H_{45}NO_3$
M: 551.77

L1

A gradient column chromatographic purification (SiO_2, hexane / EtOAc = 12: 1 → 9: 1) yields the desired product. Yield: 64% (white powder)

DC: R_f = 0.25 (hexane/EtOAc = 20:1) [UV]

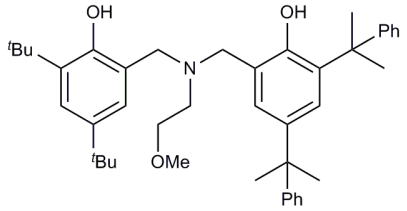
^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.33 – 7.12 (m, 11H, H_{arom}), 6.84 (s, 2H, H_{arom}), 6.57 (d, ^4J = 2.2 Hz, 1H, H_{arom}), 3.63 (d, ^2J = 3.0 Hz, 4H, ArCH_2), 3.33 (t, ^3J = 5.3 Hz, 2H, $H_{sidearm}$), 3.22 (s, 3H, O*Me*), 2.56 (t, ^3J = 5.3 Hz, 2H, $H_{sidearm}$), 2.18 (s, 6H), 1.69 (s, 6H), 1.63 (s, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 151.3, 150.2, 135.2, 128.3, 128.2, 127.9, 126.7, 125.8, 125.4, 120.9, 71.1, 58.7, 56.3, 56.0, 50.9, 42.5, 42.0, 31.0, 29.5, 20.4, 16.0.

EA: calculated: C 80.54 H 8.22 N 2.54
found: C 80.50 H 8.32 N 2.56

ESI-MS (iso-propanol): 552.5 $[M]^+$

$H_2(ONOO)^{tBu,C(CH_3)_2Ph}$ (L2):



$C_{43}H_{57}NO_3$
M: 635.93

L2

A column chromatographic purification (SiO_2, hexane / EtOAc = 12: 1) yields the desired product. Yield: 49% (white powder)

DC: R_f = 0.46 (hexane/EtOAc = 12:1) [UV]

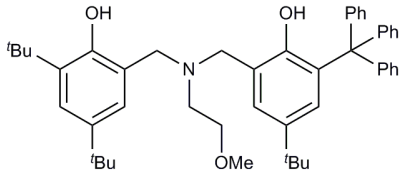
^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.37 – 7.11 (m, 12H, H_{arom}), 6.91 (d, ^4J = 2.4 Hz, 1H, H_{arom}), 6.83 (d, ^4J = 2.4 Hz, 1H, H_{arom}), 3.68 (s, 2H), 3.61 (s, 2H), 3.27 (t, ^3J = 5.4 Hz, 2H, H_{Henkel}), 3.17 (s, 3H, O*Me*), 2.59 (t, ^3J = 5.4 Hz, 2H, H_{Henkel}), 1.71 (s, 6H, C*Me*$_2$Ph), 1.64 (s, 6H, C*Me*$_2$Ph),1.42 (s, 9H, *t*Bu), 1.29 (s, 9H, *t*Bu).

^{13}C-NMR (75 MHz, $CDCl_3$, 300 K): δ (ppm) = 153.3, 151.7, 151.2, 150.2, 140.7, 140.4, 135.7, 135.4, 128.0, 127.8, 127.4, 126.7, 125.9, 125.4, 125.4, 124.8, 124.4, 123.1, 122.8, 121.6, 71.0, 58.5, 58.3, 56.0, 51.4, 42.5, 41.9, 34.9, 34.0, 31.7, 31.0, 29.6, 29.3.

EA: calculated: C 81.22 H 9.03 N 2.20
found: C 81.39 H 9.24 N 2.01

ESI-MS (iso-propanol): 636.6 $[M]^+$

$H_2(ONOO)^{tBu,tBu,CPh3}$ (L3):



$C_{48}H_{59}NO_3$
M: 698.00

L3

A gradient column chromatographic purification (SiO_2, hexane / EtOAc = 20: 1 → 11: 1) yields the desired product. Yield: 43% (white powder)

DC: R_f = 0.25 (hexane/EtOAc = 20:1) [UV]

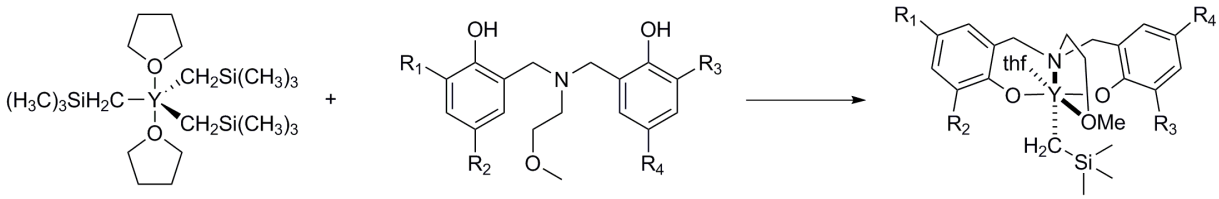
^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.17 – 7.13 (m, 6H, H_{arom}), 7.10 (m, 10H, H_{arom}), 7.06 (d, ^4J = 2.4 Hz, 1H, H_{arom}), 6.96 (d,^4J = 2.4 Hz, 1H, H_{arom}), 6.75 (d,^4J = 2.4 Hz, 1H, H_{arom}), 3.68 (s, 2H, ArCH_2), 3.55 (s, 2H, ArCH_2), 3.21 (t, ^3J = 5.6 Hz, 2H, $H_{sidearm}$), 3.07 (s, 3H, O*Me*), 2.48 (t, ^3J = 5.6 Hz, 2H, $H_{sidearm}$), 1.18 (s, 9H, ^{t}Bu), 1.04 (s, 9H, ^{t}Bu).

^{13}C-NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 153.9, 151.6, 145.2, 141.6, 140.5, 135.8, 133.2, 131.2, 128.5, 127.9, 127.6, 127.2, 126.2, 124.3, 123.8, 123.1, 121.7, 70.9, 63.4, 58.8, 58.7, 54.7, 51.3, 35.1, 34.3, 34.2, 31.8, 31.6, 29.9.

EA: calculated: C 82.60 H 8.52 N 2.01
found: C 82.58 H 8.63 N 2.00

Catalyst Synthesis

General procedure for the synthesis of $(ONOO)^{R}Y(CH_2Si(CH_3)_3)(thf)$:[4]

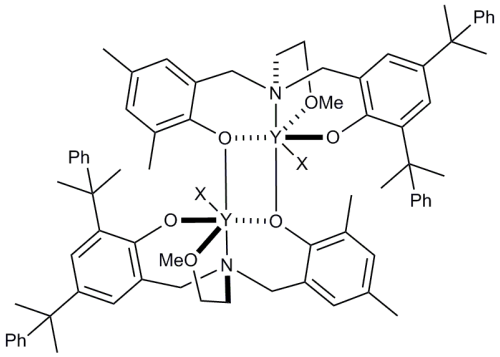


$[Y(CH_2Si(CH_3)_3)_3(thf)_2]$ $H_2(ONOO)^{R}$ $(ONOO)^{R}Y(CH_2Si(CH_3)_3)(thf)$

1 $R_{1,2} = CH_3$, $R_{3,4} = C(CH_3)_2Ph$
2 $R_{1,2} = {}^{t}Bu$, $R_{3,4} = C(CH_3)_2Ph$
3 $R_{1,2,4} = {}^{t}Bu$, $R_3 = CPh_3$
4 $R_{1,2,3,4} = {}^{t}Bu$
5 $R_{1,2,3,4} = C(CH_3)_2Ph$

One equivalent of proligand $H_2(ONOO)^{R}$ in toluene is added to a stirred solution of $Y(CH_2Si(CH_3)_3)_3(thf)_2$ in pentane at 0 °C. The resulting solution is stirred overnight at room temperature. The solvent is removed *in vacuo* and the resulting solid is washed with pentane.

<u>$[(ONOO)^{Me,C(CH_3)_2Ph}Y(X)]_2$ (1):</u>



1 $X = CH_2Si(CH_3)_3$
1a $X = N(SiH(CH_3)_2)_2$

<u>*Catalyst 1:*</u>

Synthesis led to a dimeric structure. Yield: 56% (white powder)

^{1}H-NMR (500 MHz, C_6D_6, 300 K): δ (ppm) = 7.44 (d, ^{4}J = 2.5 Hz, 2H, H_{arom}), 7.37 – 7.30 (m, 8H, H_{arom}), 7.20 (t, ^{3}J = 7.6 Hz, 4H, H_{arom}), 7.12 – 7.06 (m, 6H, H_{arom}), 6.97 (d, ^{4}J = 2.5 Hz, 2H, H_{arom}), 6.95 (t, ^{3}J = 7.6 Hz, 2H, H_{arom}), 6.74 (d, ^{4}J = 2.3 Hz, 2H, H_{arom}), 6.61 (d, ^{4}J = 2.3 Hz, 2H, H_{arom}), 4.96 (d, ^{2}J = 12.7 Hz, 2H, CH_2Ar), 4.71 (d, ^{2}J = 12.7 Hz, 2H, CH_2Ar), 3.18 (d, ^{2}J = 12.7 Hz, 2H, CH_2Ar), 2.74 (d, ^{2}J = 12.7 Hz, 2H, CH_2Ar), 2.45 (s, 6H, O*Me*), 2.39 – 2.21 (m, 4H, H_{Henkel}), 2.20 (s, 6H), 2.14 (s, 6H), 2.12 – 2.08 (m, 4H, H_{Henkel}), 1.84 (s, 6H), 1.77

(s, 6H), 1.69 (s, 6H), 1.69 (s, 6H), 0.27 (s, 18H, H_{TMS}), -0.91 (dd, ^{2}J = 11.2 Hz, $^{2}J_{H,Y}$ = 3.1 Hz, 2H, CH_2TMS), -1.00 (dd, ^{2}J = 11.2 Hz, $^{2}J_{H,Y}$ = 3.1 Hz, 2H, CH_2TMS).

^{13}C-NMR (126 MHz, C_6D_6, 300 K): δ (ppm) = 160.8 (d, $^{2}J_{C,Y}$ = 3.4 Hz), 153.8, 152.1, 151.6, 137.3, 136.5, 133.4, 129.5, 129.3, 129.2, 128.8, 127.5, 127.2, 126.5, 125.7, 125.6, 125.0, 124.2, 73.0, 64.6, 63.3, 60.8, 49.7, 43.0, 42.7, 31.5 (d, $^{1}J_{C,Y}$ = 11.3 Hz), 31.2, 28.9, 26.9, 26.5, 20.6, 17.6, 5.3.

EA: calculated: C 67.84 H 7.50 N 1.93
found: C 67.87 H 7.35 N 2.02

Catalyst 1a:

Monomeric structure (333 K):

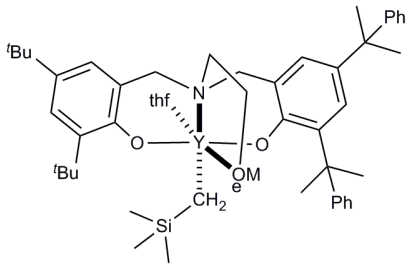
^{1}H-NMR (300 MHz, THF-d_8, 333 K): δ (ppm) = 7.28 – 6.93 (m, 11H, H_{arom}), 6.79 (d, ^{4}J = 2.5 Hz, 1H, H_{arom}), 6.77 – 6.76 (m, 1H, H_{arom}), 6.59 (m, 1H, H_{arom}), 4.80 (m, 2H, Si-*H*), 3.84 (d, ^{2}J = 12.6 Hz, 1H, CH_2Ar), 3.67 (d, ^{2}J = 12.6 Hz, 1H, CH_2Ar), 3.36 (m, 2H), 3.29 (s, 3H, OCH_3), 3.07 (d, ^{2}J = 12.9 Hz, 1H, CH_2Ar), 2.66 – 2.45 (m, 2H), 2.30 (br s, 1H), 2.12 (s, 3H), 2.11 (s, 3H), 1.82 (s, 3H), 1.65 - 1.63 (m, 9H), 0.19 (d, ^{3}J = 3.1 Hz, 6H, Si-CH_3), 0.15 (d, ^{3}J = 3.1 Hz, 6H, Si-CH_3).

^{13}C-NMR (101 MHz, THF-d_8, 333 K): δ (ppm) = 161.9 (d, $^{2}J_{C,Y}$ = 2.5 Hz), 161.4 (d, $^{2}J_{C,Y}$ = 2.5 Hz), 153.5, 153.0, 136.3, 136.2, 132.0, 129.6, 129.2, 128.9, 128.5, 128.4, 128.0, 127.5, 127.3, 127.2, 126.0, 125.9, 125.8, 125.2, 125.0, 123.5, 123.3, 73.6, 63.7, 63.3, 61.6, 51.2, 43.4, 43.0, 31.7, 31.6 (d, *J* = 1.6 Hz), 29.8 , 20.6 , 17.4 , 4.1, 4.0.

For dimeric structure ($C_{82}H_{114}N_4O_6Si_4Y_2$):

EA: calculated: C 63.87 H 7.45 N 3.63
found: C 63.95 H 7.45 N 3.58

(ONOO)$^{t\text{Bu,C(CH}_3)_2\text{Ph}}$Y(CH$_2$Si(CH$_3$)$_3$)(thf) (2):



$C_{51}H_{74}NO_4SiY$
M: 882.15

2

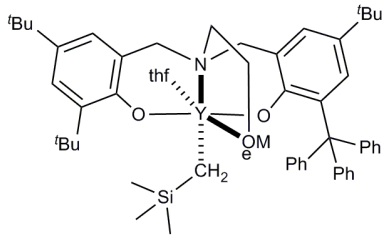
Yield: 47% (white powder)

^{1}H-NMR (300 MHz, C_6D_6, 300 K): δ (ppm) = 7.68 (d, ^4J = 2.6 Hz, 1H, H_{arom}) 7.58 (d, ^2J = 2.6 Hz, 1H, H_{arom}), 7.50 (d, ^3J = 7.5 Hz, 2H, H_{arom}), 7.46 – 7.40 (m, 2H, H_{arom}), 7.25 – 7.18 (m, 4H, H_{arom}), 7.11 (t, ^3J = 7.5 Hz, 1H, H_{arom}), 7.00 (d, ^4J = 2.6 Hz, 1H, H_{arom}), 6.97 (t, ^3J = 7.5 Hz, 1H, H_{arom}), 6.88 (d, ^4J = 2.6 Hz, 1H, H_{arom}), 3.63 – 3.28 (m, 6H, ArCH_2+H_{THF}), 2.72 (s, 3H), 2.64 (m, 2H, ArCH_2), 2.49 – 2.37 (m, 2H), 2.16 – 2.10 (m, 1H), 2.07 (s, 3H), 2.02 (m, 1H), 1.80 (m, 18H), 1.45 (s, 9H), 1.14 – 1.05 (m, 4H, H_{THF}), 0.49 (s, 9H, H_{TMS}), -0.55 – -0.65 (m, 2H, CH_2TMS).

^{13}C-NMR (126 MHz, C_6D_6, 300 K): δ (ppm) = 161.6 (d, $^2J_{C,Y}$ = 2.4 Hz), 161.2 (d, $^2J_{C,Y}$ = 2.3 Hz), 136.7, 136.5, 136.2, 136.1, 128.5, 128.4, 128.3, 128.1, 127.9, 127.3, 126.4, 125.9, 125.8, 125.6, 124.5, 124.4, 124.3, 124.0, 73.9, 71.3, 64.6, 64.2, 61.2, 49.0, 42.7, 42.6, 35.6, 34.4, 34.2, 32.4, 32.3, 31.7 (d, $^1J_{C,Y}$ = 14.9 Hz), 30.4, 28.2, 25.2, 25.0, 24.9, 22.7.

EA: calculated: C 69.44 H 8.46 N 1.59
found: C 68.99 H 8.48 N 1.61

(ONOO)$^{t\text{Bu}\ t\text{Bu,CPh}_3}$Y($CH_2Si(CH_3)_3$)(thf) (3):



$C_{56}H_{76}NO_4SiY$
M: 944.22

3

Yield: 45% (white powder)

^{1}H-NMR (500 MHz, C_6D_6, 300 K): δ (ppm) = 7.63 (d, ^4J = 2.6 Hz, 1H, H_{arom}), 7.59 (d, ^4J = 2.6 Hz, 1H, H_{arom}), 7.58 – 7.53 (m, 7H, H_{arom}), 7.18 (d, J = 2.6 Hz, 1H, H_{arom}), 7.14 (t, ^3J = 7.6 Hz, 4H, H_{arom}), 7.05 (d, ^2J = 2.6 Hz, 1H, H_{arom}), 6.99 (t, ^3J = 7.6 Hz, 4H, H_{arom}), 3.66 (d, ^2J = 12.4 Hz, 1H, C$H_a$$H_b$Ar), 3.59 (d, ^2J = 12.4 Hz, 1H, C$H_a$$H_b$Ar), 3.52 – 3.37 (m, 4H, H_{THF}), 2.91 – 2.78 (m, 2H), 2.77 (s, 3H, O*Me*), 2.62 – 2.55 (m, 1H), 2.52 – 2.44 (m, 1H), 2.40 – 2.31 (m, 1H), 2.02 – 1.94 (m, 1H), 1.77 (s, 9H, *t*Bu), 1.46 (s, 9H, *t*Bu), 1.37 (s, 9H, *t*Bu), 1.16 (br s, 4H, H_{THF}), 0.30 (s, 9H, H_{TMS}), -1.05 (dd, $^2J_{H,Y}$ = 3.2 Hz, ^2J = 10.9 Hz, 1H, CH_2TMS), -1.29 (dd, $^2J_{H,Y}$ = 3.4 Hz, ^2J = 10.9 Hz, 1H, CH_2TMS).

^{13}C-NMR (126 MHz, C_6D_6, 300 K): δ (ppm) = 161.6 (d, $^2J_{C,Y}$ = 19.4 Hz), 136.6, 136.4, 136.1, 134.8, 131.8, 130.3, 128.1, 127.9, 127.4, 126.9, 125.3, 124.4, 74.0, 71.4, 65.0, 64.6, 64.3, 61.7, 49.6, 35.7, 34.4, 34.2 (d, $^1J_{C,Y}$ = 3.7 Hz), 32.3, 32.1, 30.5, 25.0, 22.7, 14.3, 4.9, 1.4.

EA: calculated: C 71.24 H 8.11 N 1.48
found: C 70.98 H 8.32 N 1.60

2 Crystallographic data of Complex 1a

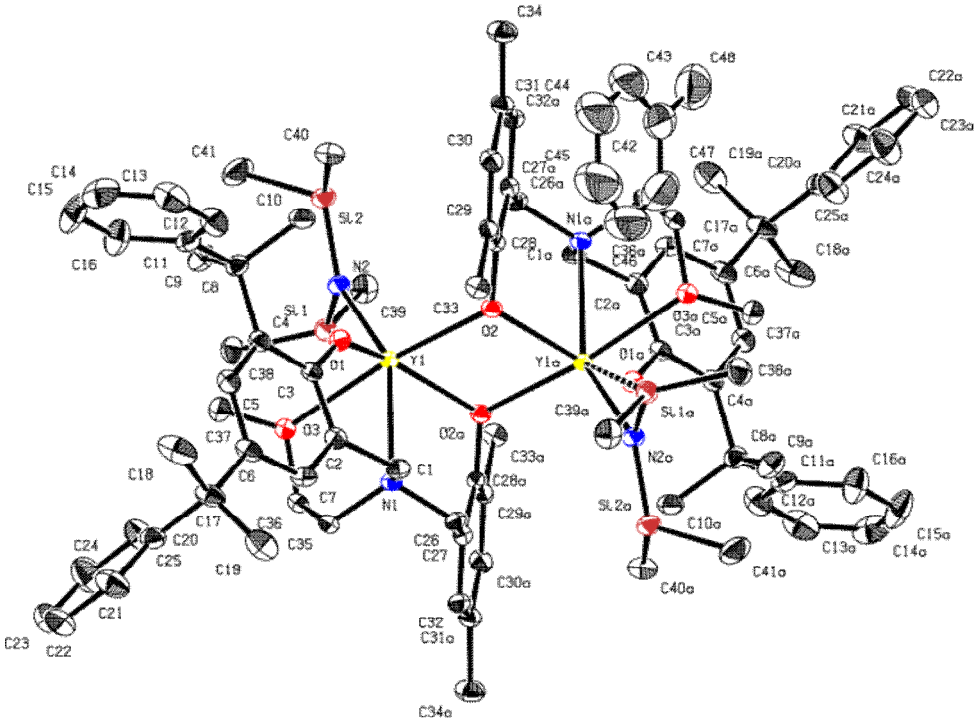


Figure S 1 ORTEP structure of complex 1a with 50% thermal ellipsoid. All H-atoms have been omitted for clarity. Selected bond distances [Å] and angles [deg]: Y(1)-O(1), 2.1181(18); Y(1)-O(2), 2.2883(19); Y(1)-O(3), 2.4661(19); Y(1)-N(1), 2.593(2); Y(1)-N(2), 2.280(2); Y(1)-Si(1), 3.2238(2); Y(1)-O(2a), 2.3170(18); O(1)-Y(1)-O(2), 94.92(7); O(1)-Y(1)-O(3), 85.17(7); O(2)-Y(1)-O(3), 172.89(7); O(1)-Y(1)-N(1), 78.20(7); O(1)-Y(1)-N(2), 105.11(8); O(1)-Y(1)-O(2a), 146.58(7); O(2)-Y(1)-N(1), 105.58(7); O(2)-Y(1)-N(2), 105.07(7); O(2)-Y(1)-O(2a), 70.24(6); N(1)-Y(1)-N(2), 148.74(8); O(3)-Y(1)-N(1), 67.45(7); O(3)-Y(1)-N(2), 81.72(7); O(2a)-Y(1)-O(3), 105.98(6); O(2a)-Y(1)-N(1), 77.45(7); O(2a)-Y(1)-N(2), 107.61(7); Y(1)-O(2)-Y(1a), 109.76(7).

Compound 1a adopts a dimeric structure in the solid state with a distorted octahedral-environment at both yttrium-centers as also found in a similar structure analyzed by Carpentier and co-workers.[11] Both complexes are THF-free complexes and each metal center is coordinated by an amido-ligand and a tetradentade 2-methoxyethylamino-bis(phenolate)-ligand. The dimeric structure originates from the insufficient bulkiness of the methyl-group as an ortho-substituent. The oxygen(phenolate)-atoms O(2) and O(2a) are able to form two µ-bridges between the two metal centers (Y(1)-Y(1a) = 3.767 Å) which leads to a planar Y(1)O(2)Y(1a)O(2a) metallacycle.

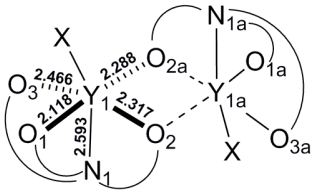


Figure S 2 Metallacycle Y(1)O(2)Y(1a)O(2a) originated from µ-bridges of the oxygen-atoms between the two metal centers. Selected bond distances are marked.

In this metallacycle the opposite bonds have the same lengths (Y(1)-O(2) = Y(1a)-O(2a), 2.2883(19); Y(1)-O(2a) = Y(1a)-O(2), 2.3170(18)) which leads to a high symmetrical rhombic-structure with bond angles of O(2)-Y(1)-O(2a) = O(2)-Y(1a)-O(2a) = 70.24° and Y(1)-O(2)-Y(1a) = Y(1)-O(2)-Y(1a) = 109.76°. This metallacycle is also found in the dimeric structure of Carpentier et al., with slightly different Y-(µ-O)-bond lengths ((Y(1)-O(1), 2,380(3); O(4)-Y(2), 2.381(3); Y(1)-O(4), 2.247(3); Y(2)-O(1), 2.344(3) which lead to a trapezoid-structure. The present close Y-Si contact of 3.224 Å already resemble Y-Si σ-bond distances suggesting an interaction in the solid state. Due to the close Y(1)-Si(1) distance of 3.224 Å (an interaction between these two centers is suggested. In addition, the relatively short Y-H distances of 2.875 Å show an interaction which leads to a formation of a four-membered Y(1)-N(2)-Si(1)-H(1)-ring with small torsional angles of -8°.The Si(1)-N(2)-Si(2) bond angle of 117.65(13) is not – as expected for Y-H-Si-agostic interaction- widened, because of an unsymmetrically interaction only on one site of the initiator.[4, 11-14]

Crystal data

$C_{82}H_{114}N_4O_6Si_4Y_2 \cdot 2(C_7H_8)$	$F(000) = 916$
$M_r = 1726.22$	
Triclinic, P	$D_x = 1.265$ Mg m^{-3}
Hall symbol: -P 1	
$a = 10.7741$ (3) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 13.3826$ (4) Å	Cell parameters from 9916 reflections
$c = 16.2750$ (5) Å	$\theta = 2.5$–$25.4°$
$\alpha = 82.3193$ (16)°	$\mu = 1.38$ mm^{-1}
$\beta = 83.5313$ (13)°	$T = 120$ K
$\gamma = 77.9230$ (13)°	Fragment, colourless
$V = 2265.39$ (12) Å^3	0.51 × 0.18 × 0.10 mm
$Z = 1$	

Data collection

Bruker APEX-II CCD diffractometer	8250 independent reflections
Radiation source: fine-focus sealed tube	7301 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.038$
Detector resolution: 16 pixels mm^{-1}	$\theta_{max} = 25.4°$, $\theta_{min} = 1.9°$
phi– and ω–rotation scans	$h = -12 \quad 12$
Absorption correction: multi-scan *SADABS*, Bruker, 2008b	$k = -16 \quad 16$
$T_{min} = 0.539$, $T_{max} = 0.874$	$l = -19 \quad 19$
39534 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier

	map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.040$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.114$	$w = 1/[\sigma^2(F_o^2) + (0.0662P)^2 + 2.1916P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
8250 reflections	$\Delta\rho_{max} = 1.20$ e Å^{-3}
525 parameters	$\Delta\rho_{min} = -0.62$ e Å^{-3}
0 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

3 High-temperature ^{1}H-NMR-spectroscopy of complex 1a

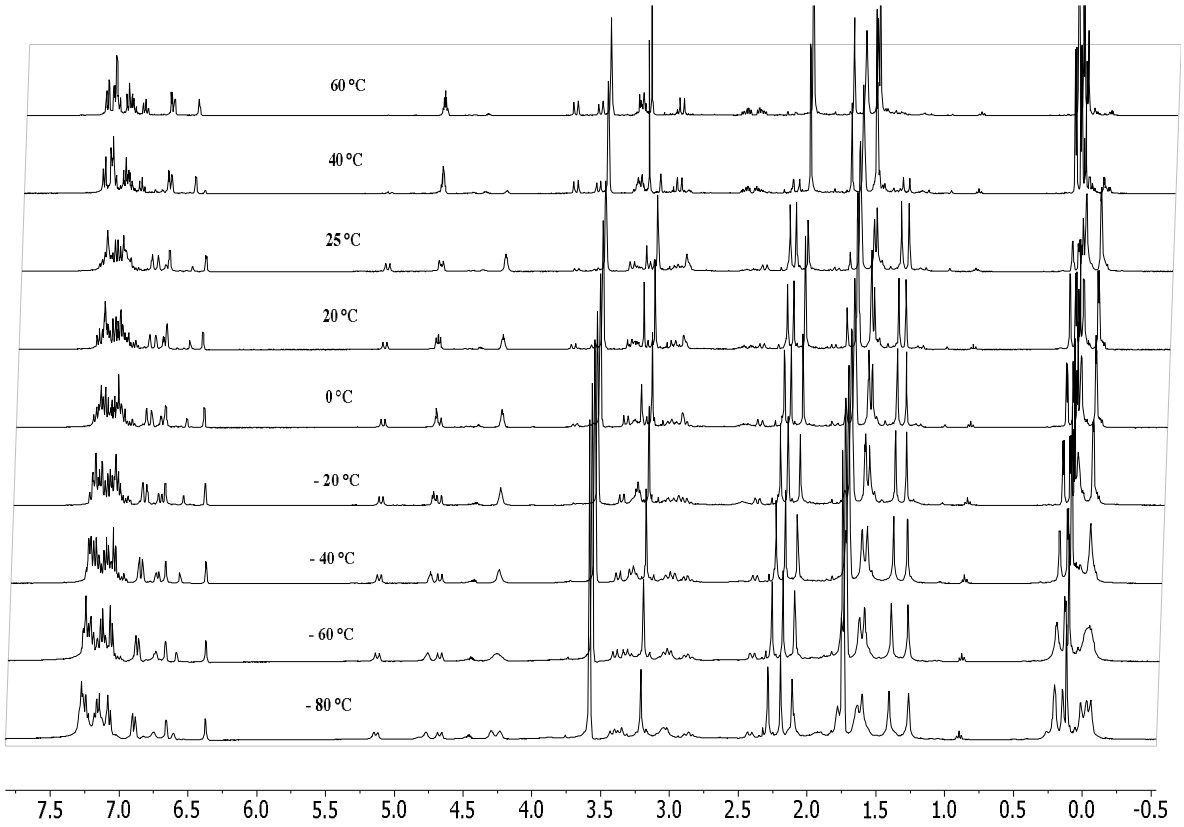


Figure S 3 ^{1}H NMR spectra of catalyst 1a at different temperatures (-80 °C-60 °C) in THF-d_8. Dissociation process at ~40 °C.

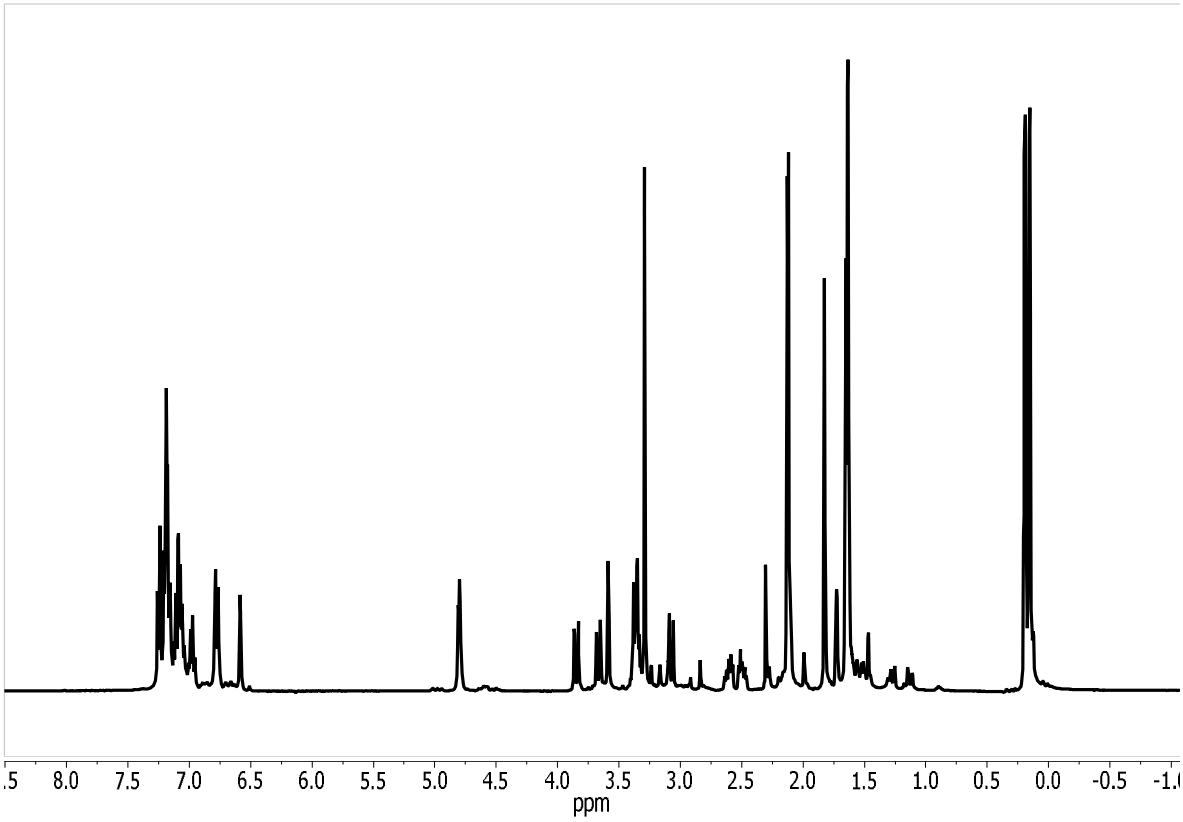


Figure S 4 ^{1}H NMR spectra of catalyst 1a at 60 °C in THF-d_8.

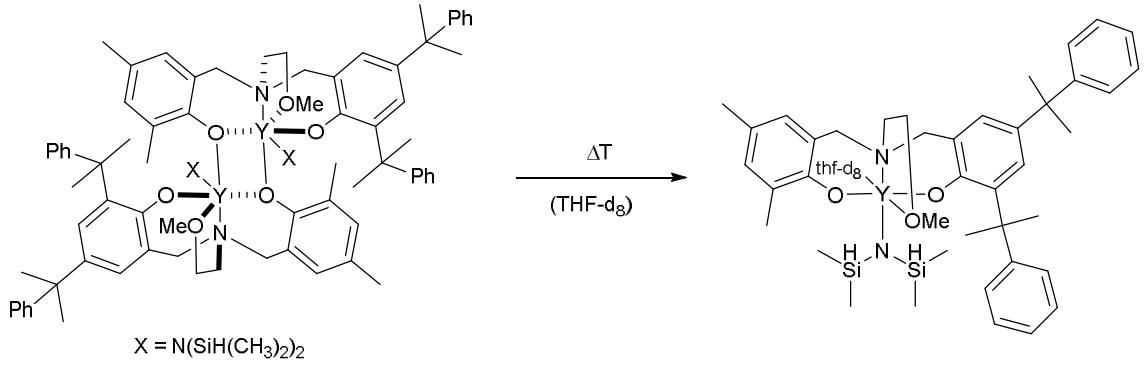


Figure S 5 Dissociation of complex 1a in THF-d_8 at elevated temperatures..

4 Kinetic investigations

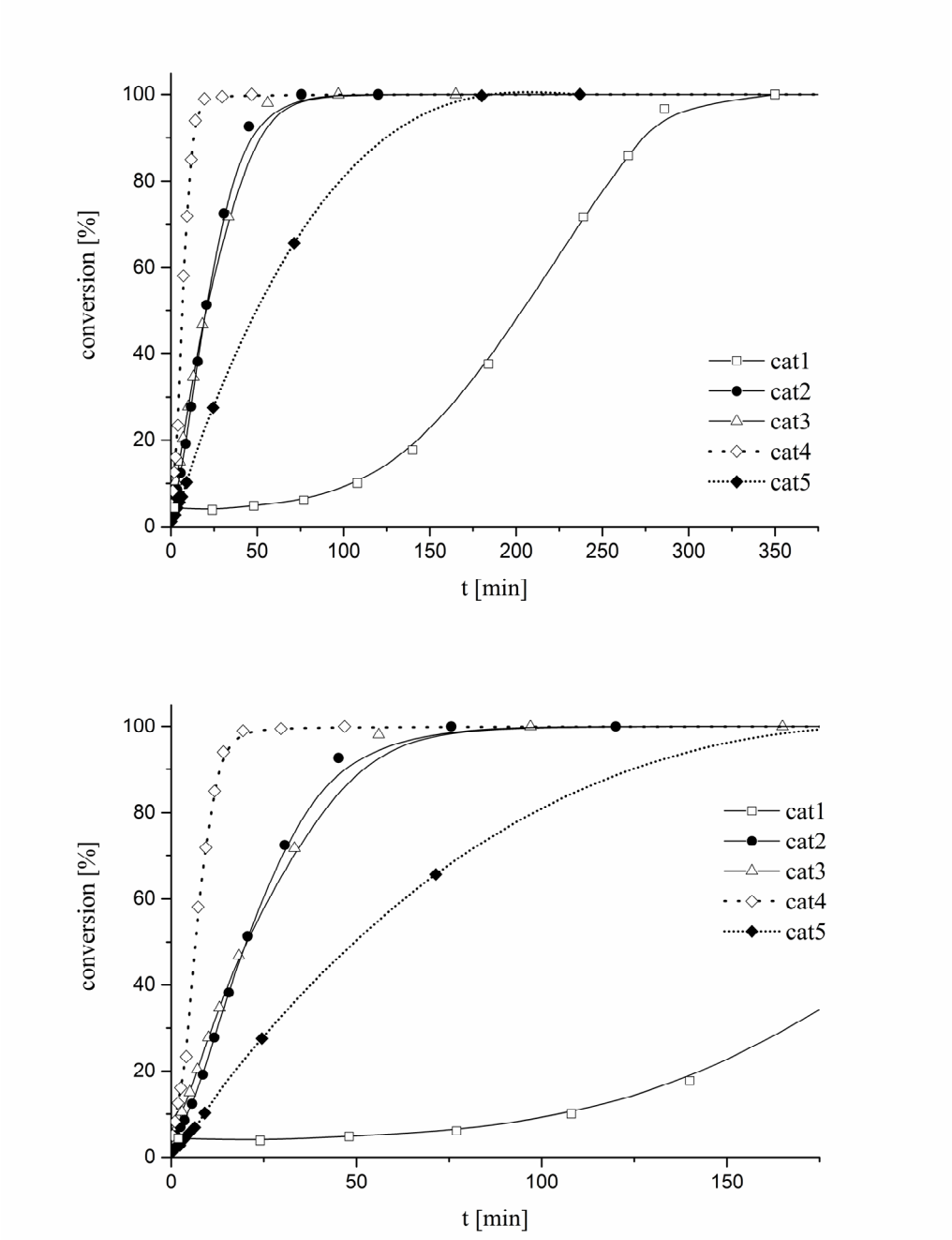


Figure S 6 Catalytic activity of catalyst 1 (square), 2 (circle), 3 (triangle), 4 (diamond, dotted), and 5 (diamond, short dotted) (catalyst 135 µmol, 2VP 27 mmol, toluene 20 mL, T = 25 °C) (table 1).

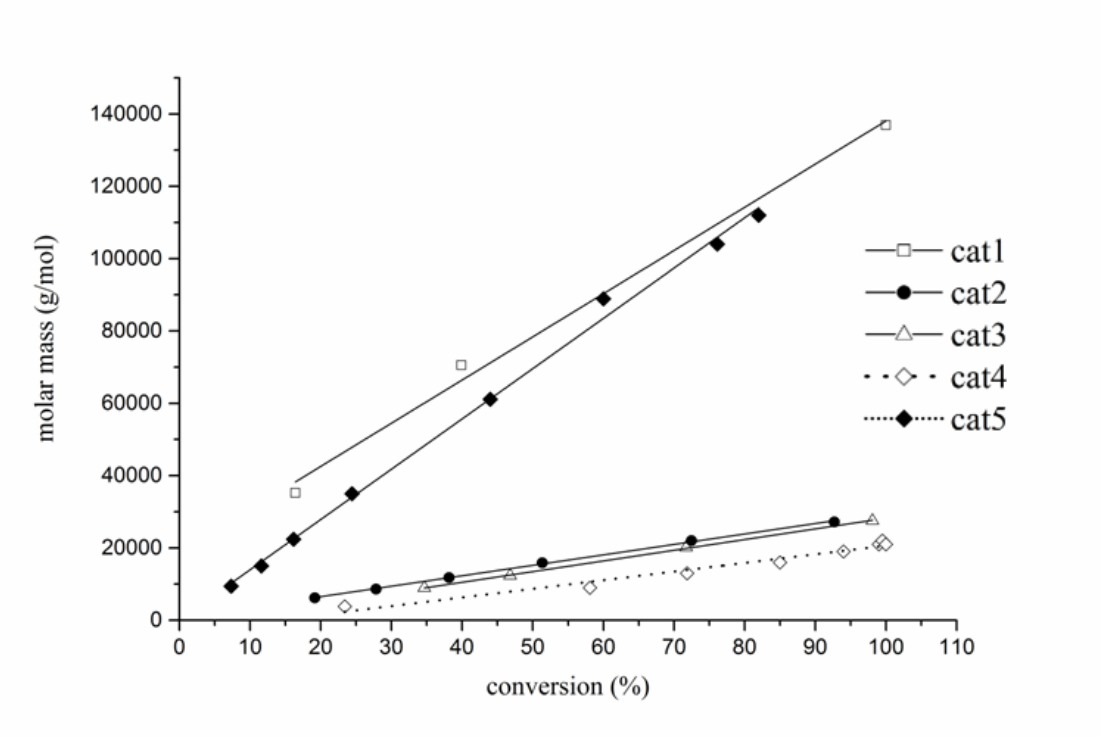


Figure S 7 Linear growth of the absolute molecular weight (M_n) for catalyst 1-5 (determined by GPC-MALS) as a function of monomer conversion (determined gravimetrically) (table 1).

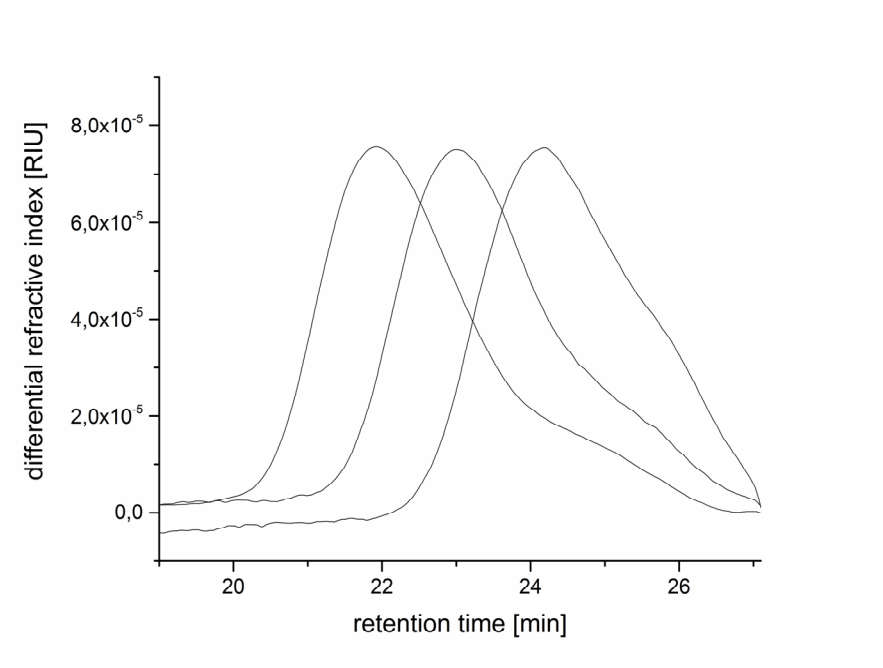


Figure S 8 GPC traces of P2VP produced with catalyst 1 (table 1, entry 1).

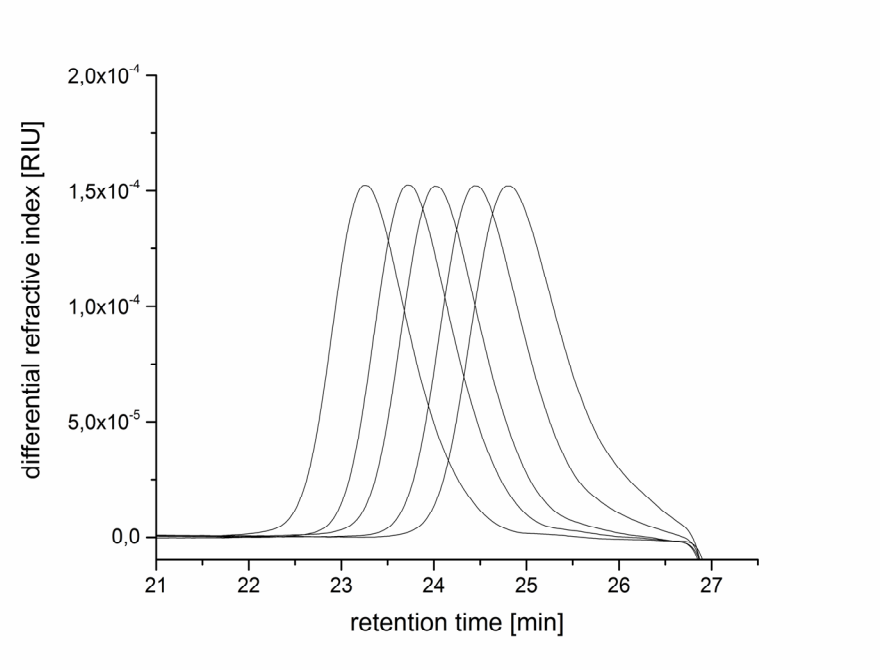


Figure S 9 GPC traces of P2VP produced with catalyst 2 (table 1, entry 2).

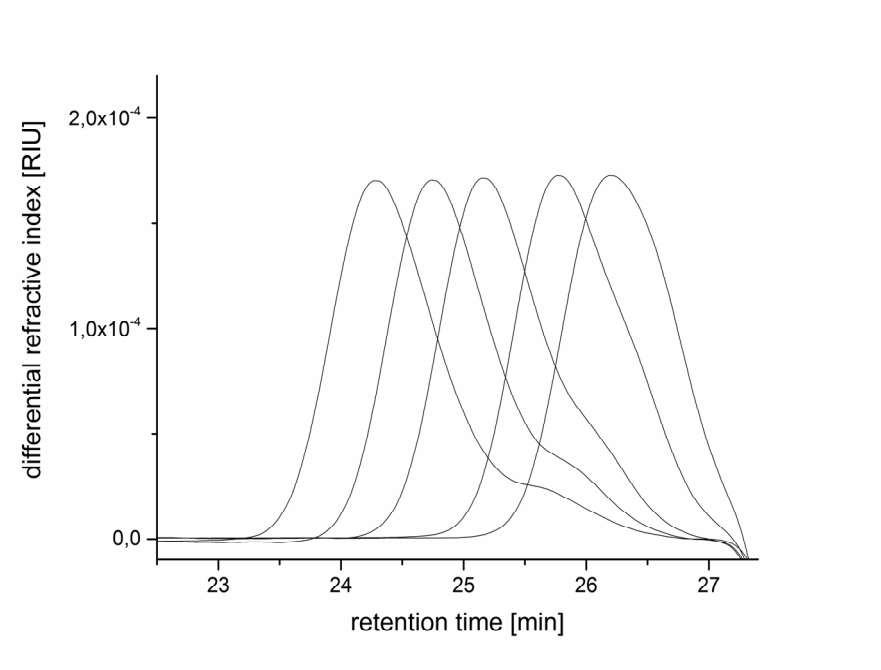


Figure S 10 GPC traces of P2VP produced with catalyst 3 (table 1, entry 3).

5 NMR-Analysis of P2VP

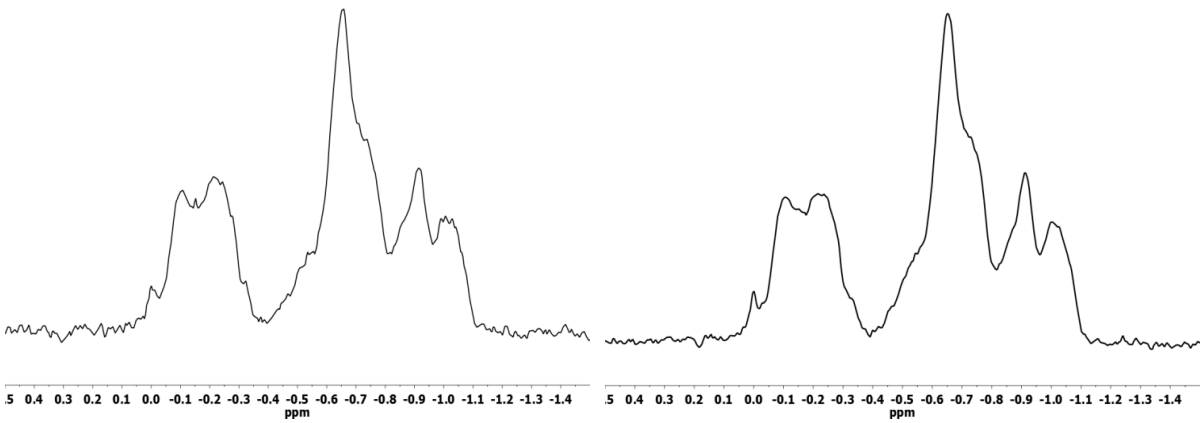


Figure S 11 Aromatic quarternary ^{13}C NMR resonances of P2VP produced with catalyst 4 (left) and 5 (right). Calibration on *mmmm*-pentade (126 MHz, Cryo, 2000 scans, CD_3OD, table 1, entry 4 and 5).

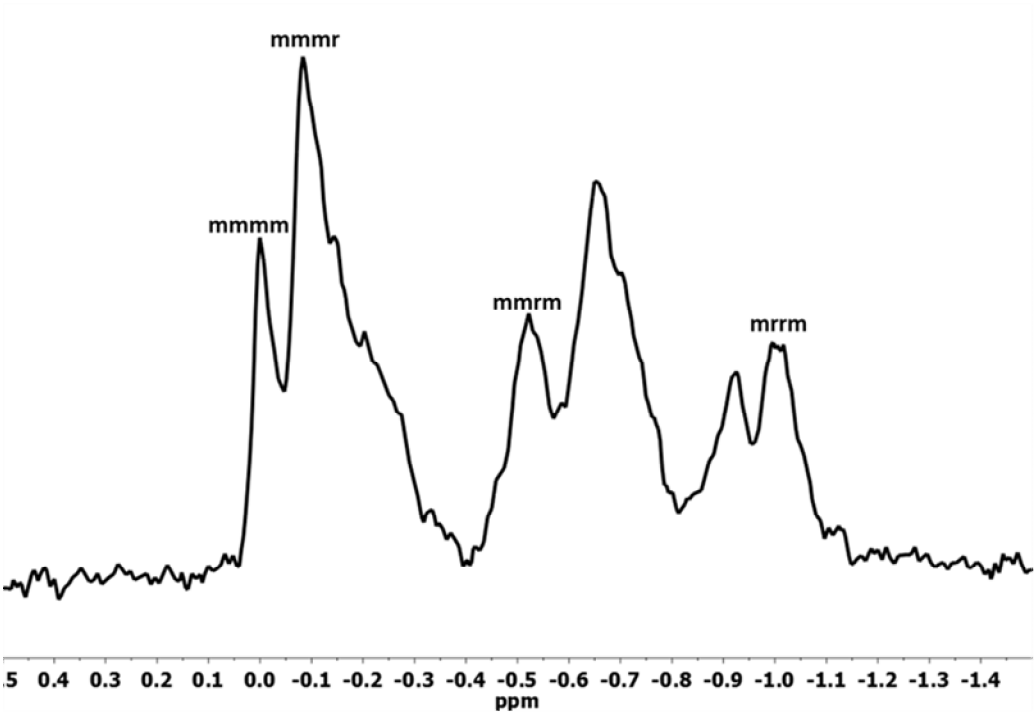


Figure S 12 Aromatic quarternary ^{13}C NMR resonance of P2VP produced with catalyst 1. Calibration on *mmmm*-pentade (126 MHz, Cryo, 2000 scans, MeOD, table 1, entry 1).

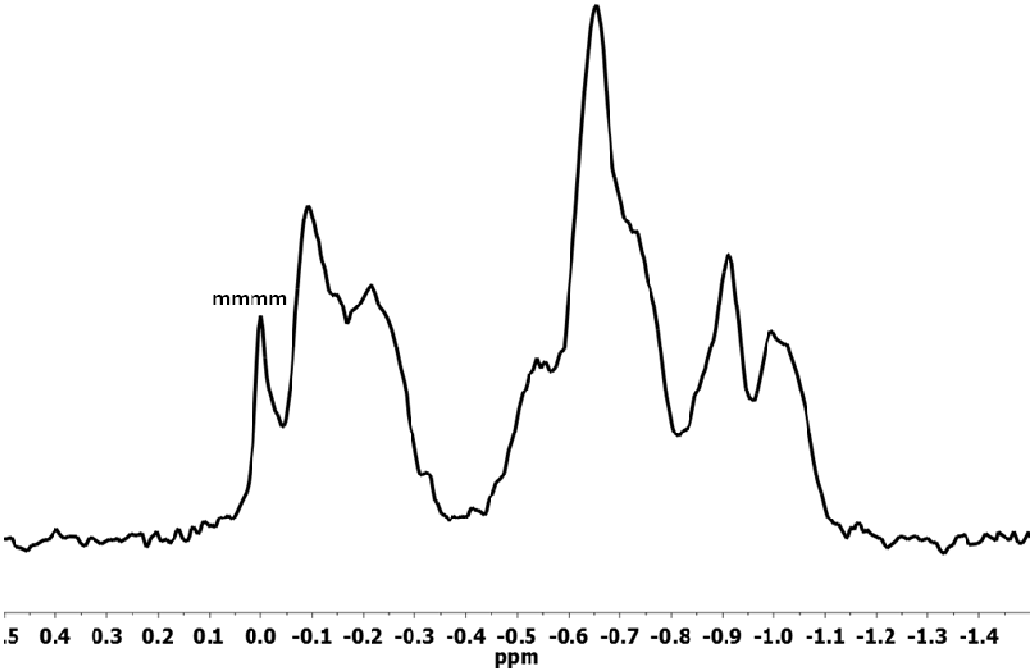


Figure S 13 Aromatic quarternary ^{13}C NMR resonance of P2VP produced with catalyst 2. Calibration on *mmmm*-pentade (126 MHz, Cryo, 2 000 scans, CD_3OD, table 1, entry 2).

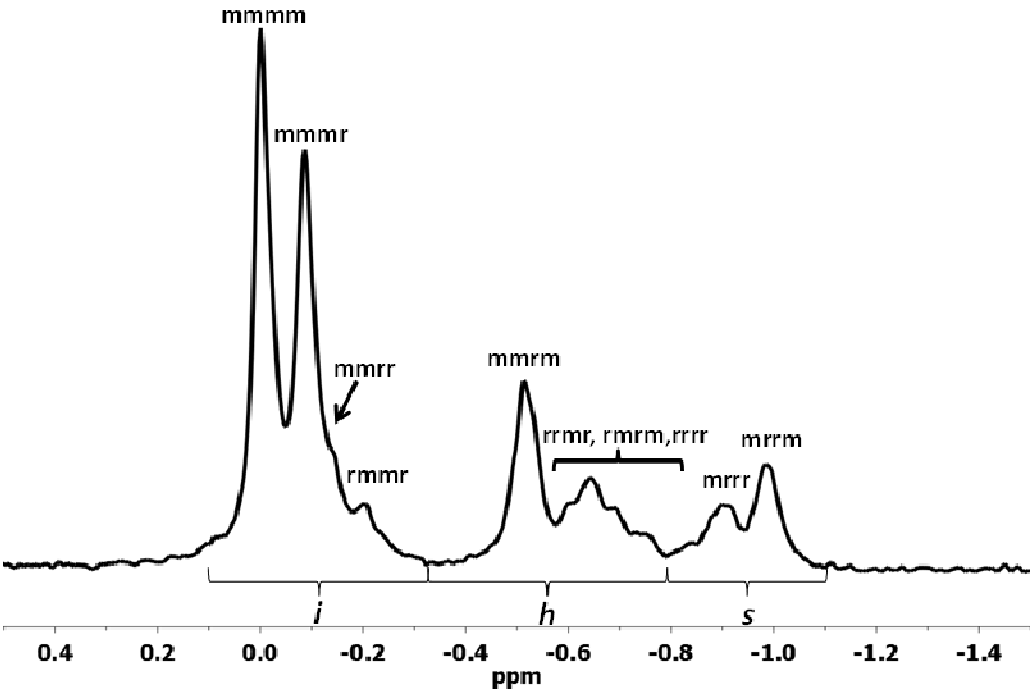


Figure S 14 Aromatic quarternary ^{13}C NMR resonance (i,h,s :proportions of isotactic, heterotactic and syndiotactic triad) of P2VP produced with catalyst 3 (226 MHz, Cryo, 1 000 scans, relaxations delay: 2 seconds, 30 mg/0.6 mL CD_3OD, table 1, entry 3).

Table S 1 Triad- and pentade-assignment of the aromatic quarternary ^{13}C NMR resonance of P2VP produced with catalyst 3.[a] chemical shifts are stated as positive values and calibrated on the *mmmm*-pentade (table 1, entry 3).

		chemical shift [ppm][a]	proportions
triad-splitting	i (mm)	0.00-0.38	0.61
	h (mr)	0.38-0.80	0.26
	s (rr)	0.80-1.11	0.13
pentade-splitting	mmmm	0.00	
	mmmr	0.09	
	mmrr	0.14	
	rmmr	0.20	
	mmrm	0.51	
	rrmr		
	rrrr	0.64-0.81	
	rmrm		
	mrrr	0.90	
	mrrm	0.98	

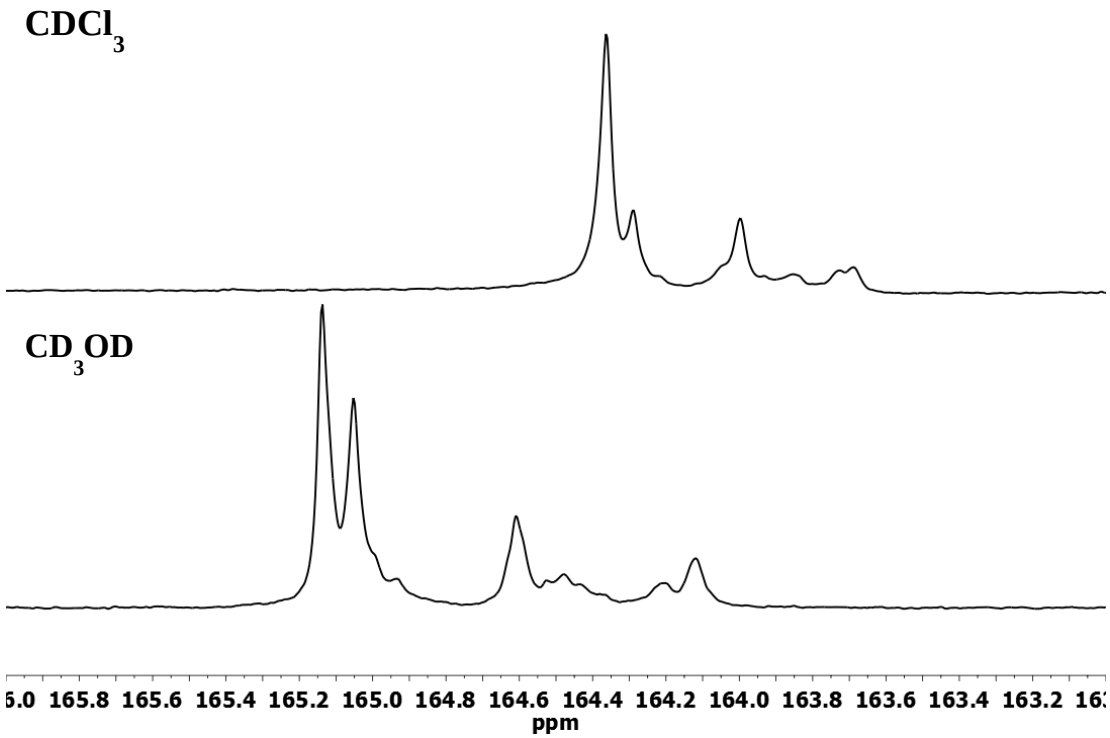


Figure S 15 ^{13}C-NMR-spectra of the quaternary carbon atom of P2VP produced by catalyst 3 measured in $CDCl_3$ (top) and CD_3OD (bottom) (126 MHz, Cryo, 2 000 scans). Spectra in $CDCl_3$ show different chemical shifts, intensities and coupling constants.

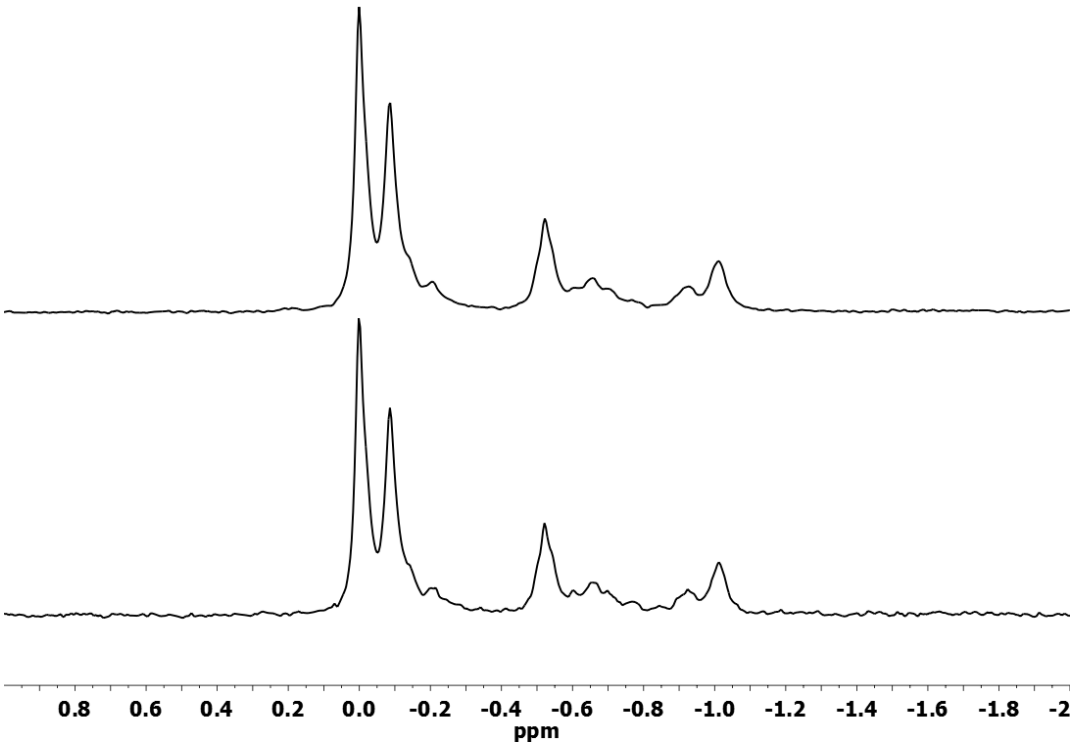


Figure S 16 ^{13}C-NMR-spectra of the quaternary carbon atom of P2VP produced by catalyst 3 measured in CD_3OD with a concentration of 30 mg/0.6 mL (top) and 15 mg/mL (bottom) (126 MHz, Cryo, 4 000 scans). Lower concentrations led to an increased signal-to-noise ratio, but without a better pentade resolution.

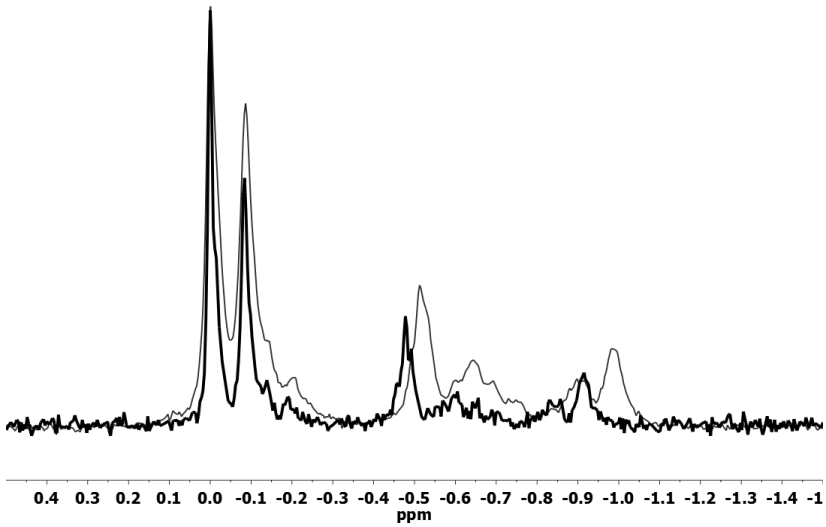


Figure S 17 ^{13}C-NMR-spectra of the quaternary carbon atom of P2VP produced by catalyst 3 measured in CD_3OD at 40 °C (black, 75 mg/0.6 mL; 72 MHz, 12 000 scans, relaxation delay: 3.5 sec, CD_3OD) and at room temperature (gray, 30 mg/0.6 mL; 226 MHz, Cryo, 2 000 scans, relaxation delay: 2 sec, CD_3OD). High temperature measurements led to incomparable chemical shifts, but with a better splitting of *mmmm*- and *mmmr*-pentade. A higher signal-to-noise ratio is observed due to a weaker magnetic field.

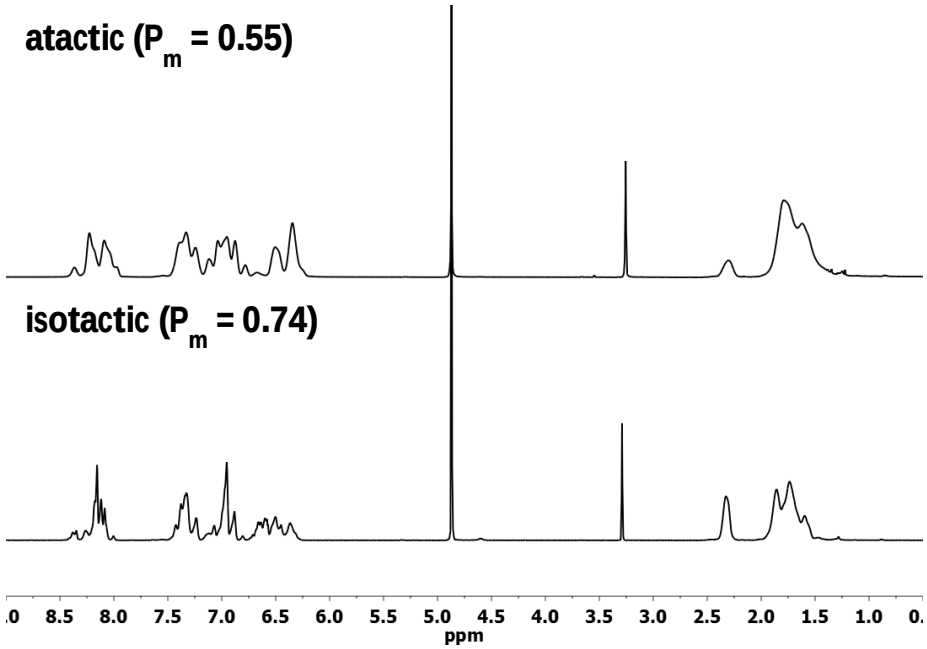


Figure S 18 ^{1}H-NMR-spectra of atactic and isotactic P2VP produced by catalysts 3 (bottom) and 4 (top) (500/900 MHz, Cryo, CD_3OD)

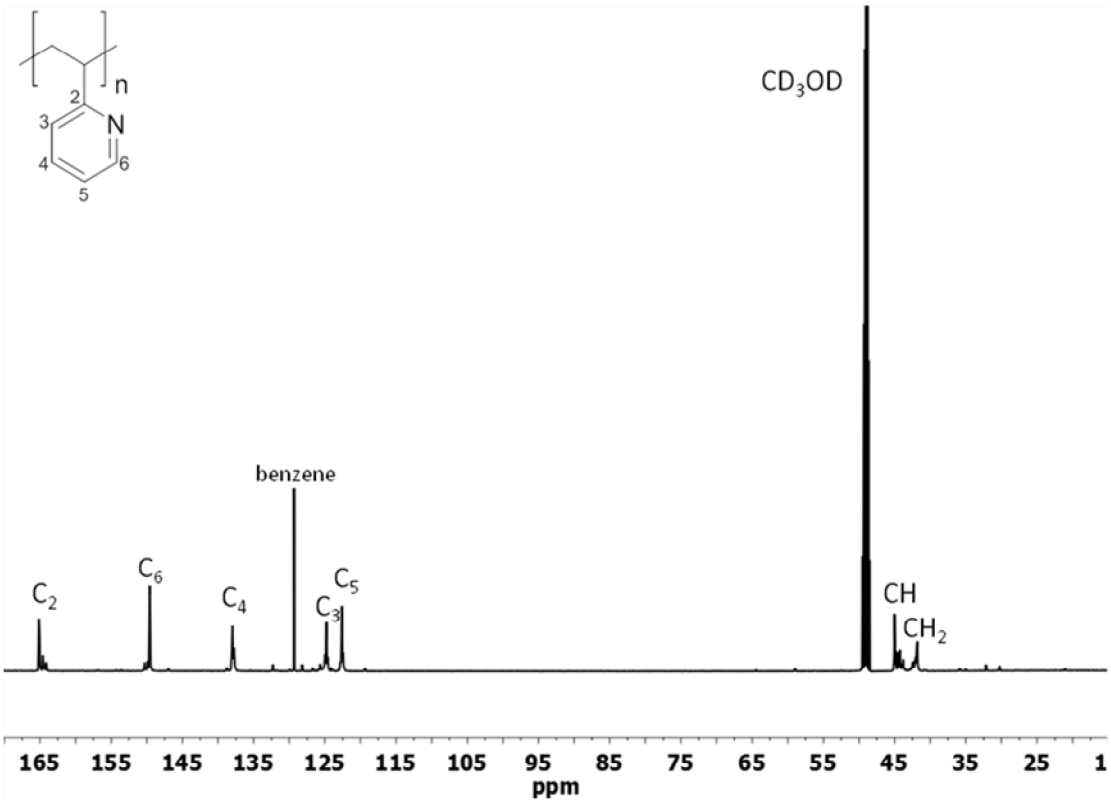


Figure S 19 ^{13}C-NMR-spectra of isotactic P2VP produced by catalysts 3 (500 MHz, Cryo, CD_3OD). Assignment according to Matsumoto and coworkers [15]

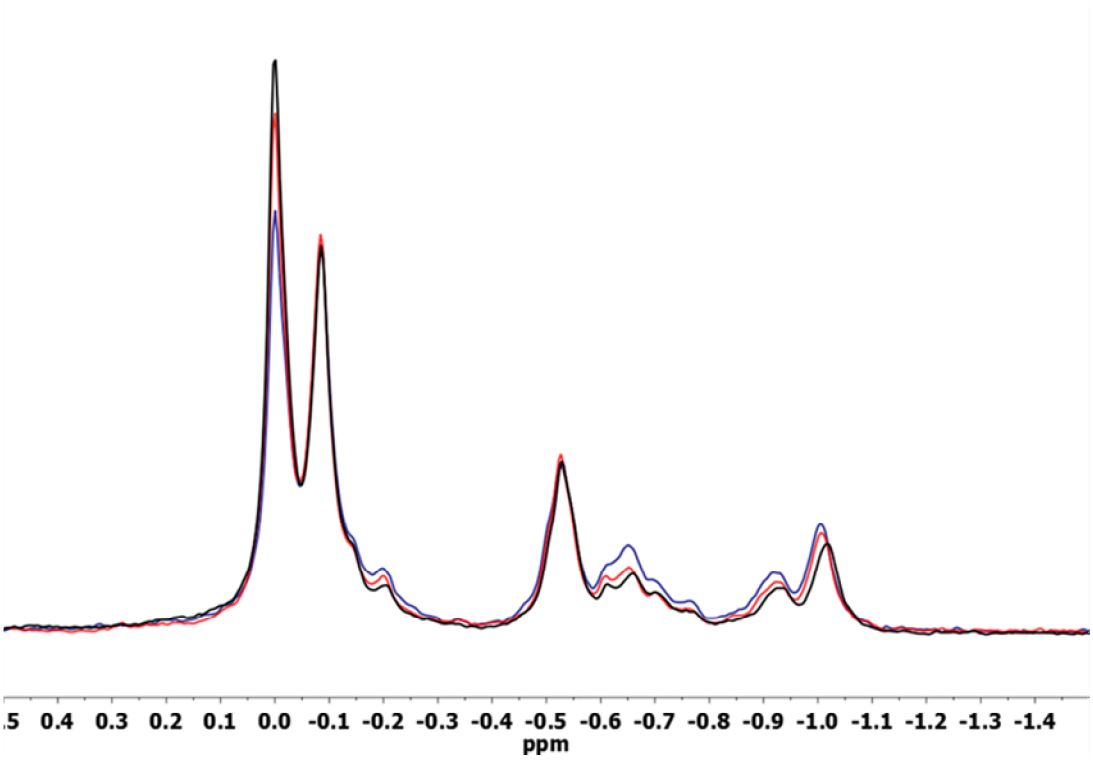


Figure S 20 ^{13}C-NMR-spectra of the quaternary carbon atom of P2VP produced by catalyst 3 in toluene (black), thf (blue) and dichloromethane (red) measured in CD_3OD at room temperature (75 mg/0.6 mL; 226 MHz, Cryo, 2 000 scans, relaxation delay: 2 sec, CD_3OD).

6 Mechanistic investigations and polymerization data

Table S 2 Experimental and calculated triad distributions in the aromatic quaternary ^{13}C resonance for mechanistic investigations.[a]

Catalyst	triad distributions							B[d]	E[e]	σ[f]
	experimental values				theoretical values[c]					
	i (mm)	h (mr)	s (rr)	P_m[b]	i	h	s			
1	0.44	0.37	0.19	0.63	0.45	0.37	0.18	2.44	1.03	0.755
2	0.35	0.43	0.22	0.57	0.36	0.43	0.21	1.67	1.02	0.687
3	0.61	0.26	0.13	0.74	0.61	0.26	0.13	4.69	1.00	0.846
4	0.34	0.43	0.23	0.55	0.32	0.45	0.23	1.69	1.07	0.658
5	0.31	0.45	0.24	0.54	0.34	0.44	0.22	1.47	1.07	0.673

Table S 3 Experimental and calculated triad distributions in the aromatic quaternary ^{13}C resonance for mechanistic investigations of P2VP produced with catalyst 3 in different solvents and at different temperatures.[g]

Entry	Solvent	Temp.	triad distributions							B[d]	E[e]	σ[f]
			experimental values				theoretical values[c]					
			i (mm)	h (mr)	s (rr)	P_m[b]	i	H	s			
1	thf	rt	0.59	0.27	0.14	0.73	0.59	0.27	0.14	4.53	1.04	0.839
2	CH_2Cl_2	rt	0.63	0.24	0.13	0.75	0.63	0.25	0.12	5.68	1.08	0.854
3	toluene	-30 °C	0.57	0.29	0.14	0.72	0.58	0.28	0.14	3.80	0.97	0.831
4	toluene	50 °C	0.58	0.27	0.15	0.72	0.58	0.28	0.14	4.72	1.11	0.831
5	pyridine	rt	-	-	-	-	-	-	-	-	-	-

[a] 75 mg P2VP in 0.6 mL CD_3OD; NMR AV500C; ^{13}C NMR resonances of poly(2-vinylpyridine) produced with catalyst 1-5, at 25 °C, ([Cat]:[2VP] =1:200, [2VP] = 27 mmol, 20 mL toluene).

[b] Pm is the probability of *meso* linkages between monomer units and is determined by ^{13}C NMR spectroscopy:

$$P_m = mm + 0.5mr$$

[c] Theoretical triad distributions calculated for enantiomorphic site control model:

$$mm = m^2 = 1 - 3\sigma(1-\sigma)$$

$$mr = m(1-m) = 2\sigma(1-\sigma)$$

$$rr = (1-m)^2 = \sigma(1-\sigma)$$

[d] Bernoulli model triad test B:

$$B = \frac{4(mm)(rr)}{(mr)^2}$$

With B = 1 for chain end control.

[e] Enantiomorphic site control triad test E:

$$E = \frac{2(rr)}{(mr)}$$

With E = 1 for enantiomorphic site control.

[f] Probability of prochiral monomer addition *via re* or *si* side of the catalyst:

$$P_m = m = \sigma^2 + (1-\sigma)^2$$

[g]75 mg P2VP in 0.6 mL CD_3OD; NMR AV500C; ^{13}C NMR resonances of poly(2-vinylpyridine) produced with catalyst 3, at given temperature, ([Cat]:[2VP] =1:200, [2VP] = 2.7 mmol, 2.0 mL solvent).

Table S 4 REM-GTP of 2VP with catalyst 3 at various reaction conditions.[a]

Entry	Solvent	Temp [°C]	Time [h]	Conversion [%]	$M_{n,calc}$ ($x10^4$) [g/mol][b]	$M_{n,exp}$ ($x10^4$) [g/mol]	M_w/M_n	I^* [c]	P_m[d]
1	THF	25	2.0	10	0.22	3.3	1.14	0.06	0.73
2	THF	25	24w	>99	2.1	9.2	1.15	0.22	0.73
3	CH_2Cl_2	25	2.0	>99	1.9	4.6	1.07	0.41	0.75
4	toluene	-30	26	6	0.11	0.43	1.30	0.26	0.72
5	toluene	50	0.75	>99	2.2	3.9	1.07	0.57	0.72
6	toluene	25	1.6	>99	2.0	3.3	1.06	0.60	0.74

[a] Reactions performed with [2VP] = 2.7 mmol, [2VP]/[Cat] = 200/1, in 2.0 mL solvent, conversions determined by gravimetry and $M_{n,exp}$ determined by GPC-MALS. [b] $M_{n,calc}$ = M x (([M]/[Cat]) x conversion). [c] I^* at the end of the reaction. [d] P_m is the probability of *meso* linkages between monomer units and is determined by ^{13}C NMR spectroscopy.

7 References

1. P. T. Altenbuchner, B. S. Soller, S. Kissling, T. Bachmann, A. Kronast, S. I. Vagin and B. Rieger, *Macromolecules*, 2014, 47, 7742-7749.
2. K. C. Hultzsch, P. Voth, K. Beckerle, T. P. Spaniol and J. Okuda, *Organometallics*, 2000, 19, 228-243.
3. G. D. Vaughn, K. A. Krein and J. A. Gladysz, *Organometallics*, 1986, 5, 936-942.
4. C.-X. Cai, L. Toupet, C. W. Lehmann and J.-F. Carpentier, *J. Organomet. Chem.*, 2003, 683, 131-136.
5. M. Brigodiot, H. Cheradame, M. Fontanille and J. P. Vairon, *Polymer*, 1976, 17, 254-256.
6. D. K. Dimov and T. E. Hogen-Esch, *Macromolecules*, 1995, 28, 7394-7400.
7. A. I. Kochnev, I. I. Oleynik, I. V. Oleynik, S. S. Ivanchev and G. A. Tolstikov, *Russ. Chem. Bull.*, 2007, 56, 1125-1129.
8. Y.-L. Wong, L. H. Tong, J. R. Dilworth, D. K. P. Ng and H. K. Lee, *Dalton Transactions*, 2010, 39, 4602-4611.
9. S. Barroso, S. R. M. M. de Aguiar, R. F. Munhá and A. M. Martins, *Journal of Organometallic Chemistry*, 2014, 760, 60-66.
10. M. Konkol, M. Nabika, T. Kohno, T. Hino and T. Miyatake, *Journal of Organometallic Chemistry*, 2011, 696, 1792-1802.
11. M. Bouyahyi, N. Ajellal, E. Kirillov, C. M. Thomas and J.-F. Carpentier, *Chemistry*, 2011, 17, 1872-1883.
12. J. Eppinger, M. Spiegler, W. Hieringer, W. A. Herrmann and R. Anwander, *Journal of the American Chemical Society*, 2000, 122, 3080-3096.
13. W. A. Herrmann, J. Eppinger, M. Spiegler, O. Runte and R. Anwander, *Organometallics*, 1997, 16, 1813-1815.
14. A. Amgoune, C. M. Thomas, T. Roisnel and J.-F. Carpentier, *Chemistry*, 2005, 12, 169-179.
15. K. Matsuzaki, T. Kanai, T. Matsubara and S. Matsumoto, *Journal of Polymer Science: Polymer Chemistry Edition*, 1976, 14, 1475-1484.