Heteronuclear, Monomer-Selective Zn/Y Catalyst Combines Copolymerization of Epoxides and CO₂ with Group-Transfer Polymerization of Michael-Type Monomers

Alina Denk,[‡] Sebastian Kernbichl,[‡] Andreas Schaffer, Moritz Kränzlein, Thomas Pehl, and Bernhard Rieger*

WACKER-Chair of Macromolecular Chemistry, Catalysis Research Center, Technical University Munich, Lichtenbergstr. 4, 85748 Garching, Germany

Content

1.	Synthesis procedures	2
2.	NMR spectra of CH-bond activation	7
3.	Mononuclear catalysts in P2VP and PCHC polymerization	8
4.	MALDI-MS of oligomeric P2VP synthesized with catalyst 3	. 10
5.	Polymerization procedures	, 11
6.	In situ ATR-IR spectrum of the CHO/CO ₂ copolymerization with catalyst 3	. 12
7.	ESI- and MALDI-MS of oligomeric PCHC synthesized with catalyst 3	. 13
8.	NMR spectrum of catalyst 3 pressurized with CO ₂	. 14
9.	GPC traces of P2VP/PCHC and PIPOx/PCHC terpolymers	. 15
10.	NMR after extraction/washing of an artificial P2VP/PCHC blend with methanol	. 21
11.	NMR after extraction/washing of a P2VP/PCHC terpolymer with methanol	. 22
12.	GPC after extraction/washing of a P2VP/PCHC terpolymer with methanol	. 23
13.	DSC Analysis of P2VP/PCHC terpolymer	. 24
14.	TGA of P2VP/PCHC and PIPOx/PCHC terpolymers	. 25
15.	ESI-MS of oligomeric PIPOx synthesized with catalyst 3	. 26
16.	DSC Analysis of PIPOx/PCHC terpolymer	. 26
17.	NMR spectra of P2VP/PCHC and PIPOx/PCHC terpolymers	. 27

1. Synthesis procedures

General

All reactions containing air- and/or moisture sensitive compounds were carried out under dry argon 4.6 (99.996%, Westfalen AG) using standard Schlenk or glovebox techniques. Toluene was dried with a solvent purification system (SPS) MB SPS-800 of the company M. Braun and stored over molecular sieve under argon atmosphere. Commercially available chemicals were purchased from Sigma-Aldrich, ABCR, TCI Chemicals or the central administration of materials of the Technical University of Munich and, unless otherwise specified, used without further purification. The compounds $1,^1$ 3-((2,6dimethylpyridin-4-yl)oxy)propan-1-ol² and Cp₂Y(CH₂TMS)(thf)³ were synthesized according to procedures from literature. Monomers were dried and purified prior to polymerization. Cyclohexene oxide was dried over NaH and purified by distillation. The monomers 2-vinylpyridine and 2isopropenyl-2-oxazoline were dried over CaH₂ and purified by distillation. NMR-measurements (¹H, ¹³C) were carried out on the spectrometers AV-400 and AV-500 Cryo of the company Bruker. Deuterated solvents were purchased from Sigma-Aldrich and for substances susceptible to hydrolysis stored over molecular sieves and under argon. The chemical shifts (δ) are given in parts per million (ppm) and are calibrated to the signals of the deuterated solvents. Mass spectra were carried out either on a Varian 500-MS with electron spray ionization (ESI) in acetonitrile using positive ionization mode at 70 eV or on a Bruker Daltonics ultraflex TOF/TOF with matrix assisted laser desorption ionization (MALDI). For MALDI-MS measurements the polymer sample is dissolved in dichloromethane and mixed with a saturated solution of α -cyano-4-hydroxycinnamic acid in a 0.1 vol% solution of trifluoroacetic acid in water/acetonitrile. The instrument has been calibrated with a protein standard in the same matrix as the sample prior to use. Gel permeation chromatography experiments were carried out at a PL-GPC 50 of the company Agilent with DMF (HPLC grade, 2.17 g/L LiBr) as solvent and PMMA calibration standards. Absolute molar masses of P2VP aliquots were determined via concentration measurement with a two-angle light scattering, viscosimetry and refractive index detection (dn/dc = 0.149 mL/g). Elemental analysis measurements were performed by the microanalytical laboratory of the Inorganic-chemical Institute of the Technical University Munich. In situ ATR-IR measurements were performed under argon atmosphere using a Mettler Toledo MultiMax Pressure system.

(1) Reiter, M.; Vagin, S.; Kronast, A.; Jandl, C.; Rieger, B., A Lewis acid β -diiminato-zinc-complex as all-rounder for co- and terpolymerisation of various epoxides with carbon dioxide. *Chemical Science* 2017, 8 (3), 1876-1882.

(2) Wang, Q.; Chen, S.; Liang, Y.; Dong, D.; Zhang, N., Bottle-Brush Brushes: Surface-Initiated Rare Earth Metal Mediated Group Transfer Polymerization from a Poly(3-((2,6-dimethylpyridin-4-yl)oxy)propyl methacrylate) Backbone. *Macromolecules* 2017, *50* (21), 8456-8463.

(3a) Hultzsch, K. C.; Voth, P.; Beckerle, K.; Spaniol, T. P.; Okuda, J., Single-Component Polymerization Catalysts for Ethylene and Styrene: Synthesis, Characterization, and Reactivity of Alkyl and Hydrido Yttrium Complexes Containing a Linked Amido–Cyclopentadienyl Ligand.

Organometallics 2000, *19* (3), 228-243; (b) Salzinger, S.; Soller, B. S.; Plikhta, A.; Seemann, U. B.; Herdtweck, E.; Rieger, B., Mechanistic Studies on Initiation and Propagation of Rare Earth Metal-Mediated Group Transfer Polymerization of Vinylphosphonates. *J Am Chem Soc* 2013, *135* (35), 13030-13040.

Synthesis of catalyst 3'

In a glovebox 52.1 mg (288 μ mol, 1.0 eq.) 3-((2,6-dimethylpyridin-4-yl)oxy)propan-1-ol are dissolved in 1.0 mL toluene and a solution of 200 mg (288 μ mol, 1.0 eq.) **1** in 1.0 mL toluene is added. Immediate precipitation of a light-yellow solid can be observed, which is separated from the supernatant solution by decantation. Complex **3'** in form of a light-yellow solid is dried under vacuum (yield: 61%).





Figure S1. ¹H NMR spectrum of complex 3' in benzene-d₆.





Figure S2. ¹³C NMR spectrum of a saturated solution of complex **3'** in benzene-d₆ (due to the low solubility of the complex the signals of Pyr-C^{Ar}-O, CF₃, BDI-C^{Ar}, C-CF₃, CH-C-CF₃ and CH₂-O are not visible in the spectrum).

EA: [%] calculated: C 58.79, H 5.78, N 5.88

found: C 60.06, H 6.13, N 5.67

Synthesis of catalyst 3

In a vial 6.00 mg (8.39 μ mol, 1.0 eq.) **3'** and 3.18 mg (8.39 μ mol, 1.0 eq.) Cp₂Y(CH₂TMS)(thf) are suspended in 1.2 mL toluene and stirred at room temperature for four hours. The resulting solution of the dinuclear complex **3** is used directly for a polymerization reaction.





Figure S3. ¹H NMR spectrum of complex 3 in benzene-d₆.





Figure S4. ¹³C NMR spectrum of complex 3 in benzene-d₆.

EA: [%] calculated: C 58.54, H 5.82, N 4.18

found: C 57.45, H 5.48, N 4.17

2. NMR spectra of CH-bond activation



Figure S5. ¹H NMR spectra of the CH-bond activation of complex 3' over four hours in benzene-d₆.

3. Mononuclear catalysts in P2VP and PCHC polymerization

Cp₂Y(thf)(CH₂TMS) in the copolymerization of cyclohexene oxide/CO₂

In the glovebox 40.8 μ mol (1.0 eq.) Cp₂Y(thf)(CH₂TMS) are dissolved in 4.0 g toluene and transferred into a handheld autoclave together with 20.4 mmol (500 eq.) cyclohexene oxide. The reaction mixture is pressurized with 30 bar CO₂ and stirred at 40 °C. After 17 hours no generation of PCHC product could be observed.



Figure S6. ¹H NMR spectrum of the reaction of CHO and CO₂ with catalyst 2 after 17 hours with no visible polymerization in benzene-d₆.

Catalyst 3' in the polymerization of 2-vinylpyridine

In a glovebox 2.80 μ mol (1.0 eq.) **3'** are dissolved in 1.2 mL C₆D₆ and mixed with 280 μ mol (100 eq.) 2-vinylpyridine. The reaction mixture is stirred at room temperature for five hours without observable generation of P2VP product.



Figure S7. ¹H NMR spectra of the reaction of 2VP with 3' after over five hours without polymerization in benzene-d₆.

4. MALDI-MS of oligomeric P2VP synthesized with catalyst 3



Figure S8. MALDI-MS of oligomeric P2VP synthesized with catalyst 3.

5. Polymerization procedures

Sequential terpolymerization of cyclohexene oxide, and CO₂ with 2-vinylpyridine or 2isopropenyl-2-oxazoline

In a glovebox 8.39 μ mol (1.0 eq.) **3'** is used for the CH-bond activation with 8.39 μ mol (1.0 eq.) Cp₂Y(thf)(CH₂TMS) in 1.2 mL toluene. After four hours the reaction mixture is transferred into a handheld autoclave together with 2-vinylpyridine or 2-isopropenyl-2-oxazoline and stirred again for the respective time at room temperature. Cyclohexene oxide is added, the reaction mixture is pressurized with 30 bar CO₂ and stirred at 40 °C. The CO₂ pressure is released and the resulting product is precipitated from *n*-pentane and dried under vacuum.

One-pot terpolymerization of 2-vinylpyridine or 2-isopropenyl-2-oxazoline, cyclohexene oxide, and CO2

In a glovebox 8.39 μ mol (1.0 eq.) **3'** is used for the CH-bond activation with 8.39 μ mol (1.0 eq.) Cp₂Y(thf)(CH₂TMS) in 1.2 mL toluene. After four hours the reaction mixture is transferred into a handheld autoclave together with 2-vinylpyridine or 2-isopropenyl-2-oxazoline and cyclohexene oxide and stirred at room temperature. After conversion of the Michael-type monomer, the reaction mixture is pressurized with 30 bar CO₂ and stirred at 40 °C. The CO₂ pressure is released and the resulting product is precipitated from *n*-pentane and dried under vacuum.

6. In situ ATR-IR spectrum of the CHO/CO₂ copolymerization with catalyst 3

In a glovebox 20.4 μ mol (1.0 eq.) **1** is dissolved in 4.0 g toluene and transferred into a steel autoclave together with cyclohexene oxide. The reaction mixture is pressurized with 30 bar CO₂ and stirred at 40 °C with *in situ* IR monitoring.

In a glovebox 9.38 μ mol (1.0 eq.) **3'** is used for the CH-bond activation with 9.38 μ mol (1.0 eq.) Cp₂Y(thf)(CH₂TMS) in 2.0 mL toluene. After four hours the reaction mixture is transferred into a steel autoclave together with cyclohexene oxide. The reaction mixture is pressurized with 30 bar CO₂ and stirred at 40 °C with *in situ* IR monitoring.



Figure S9. Relative intensity of the absorption of the C=O stretching bond in PCHC at 1750 cm⁻¹ measured via *in situ* ATR-IR spectroscopy during the CHO/CO₂ copolymerization with catalysts 1 (black) and 3 (red).

7. ESI- and MALDI-MS of oligomeric PCHC synthesized with catalyst 3



Figure S10. ESI-MS of oligomeric PCHC synthesized with catalyst 3 (signals at 74.1 and 124.1 m/z are artefacts from the spectrometer).



Figure S11. MALDI-MS of oligomeric PCHC synthesized with catalyst 3.

8. NMR spectrum of catalyst 3 pressurized with CO₂



Figure S12. ¹H-NMR spectra of complex 3 prior and after pressurization with 9 bar CO₂ in benzene-d₆.

9. GPC traces of P2VP/PCHC and PIPOx/PCHC terpolymers



Figure S13. GPC trace of a PCHC copolymer (table 1, entry 1).



Figure S14. GPC trace of a PCHC copolymer (table 1, entry 2).





Figure S15. GPC traces of a P2VP aliquot (table 1, entry 3).



Figure S16. GPC traces of a P2VP/PCHC terpolymer (table 1, entry 3).



Figure S17. GPC traces (RI) of a P2VP aliquot (blue) and the corresponding P2VP/PCHC terpolymer (black, table 1, entry 3).

Table 1, entry 4



Figure S18. GPC traces of a P2VP aliquot (table 1, entry 4).



Figure S19. GPC traces of a P2VP/PCHC terpolymer (table 1, entry 4).



Figure S20. GPC traces (RI) of a P2VP aliquot (blue) and the corresponding P2VP/PCHC terpolymer (black, table 1, entry 4).

Table 1, entry 5



Figure S21. GPC traces of a P2VP aliquot (table 1, entry 5), the absolute molar mass was calculated via ¹H NMR spectroscopy.



Figure S22. GPC traces of a P2VP/PCHC terpolymer (table 1, entry 5).



Figure S23. GPC traces (RI) of a P2VP aliquot (blue) and the corresponding P2VP/PCHC terpolymer (black, table 1, entry 5).

Table 1, entry 6



Figure S24. GPC traces of a PIPOx aliquot (table 1, entry 6), the absolute molar mass was calculated via ¹H NMR spectroscopy.



Figure S25. GPC traces of a PIPOx/PCHC terpolymer (table 1, entry 6).



Figure S26. GPC traces (RI) of a PIPOx aliquot (blue) and the corresponding PIPOx/PCHC terpolymer (black, table 1, entry 6).





Figure S27. GPC traces of a PIPOx aliquot (table 1, entry 7), the absolute molar mass was calculated via ¹H NMR spectroscopy



Figure S28. GPC traces of a PIPOx/PCHC terpolymer (table 1, entry 7).



Figure S29. GPC traces (RI) of a PIPOx aliquot (blue) and the corresponding PIPOx/PCHC terpolymer (black, table 1, entry 7).

10. NMR after extraction/washing of an artificial P2VP/PCHC blend with methanol



Figure S30. ¹H NMR spectra in chloroform-d of the methanol phase (1) and the remaining solid (2) of an artificial P2VP/PCHC blend $(M_n(P2VP) = 22 \text{ kg/mol}, M_n(PCHC) = 33 \text{ kg/mol})$ after extraction/washing with methanol.

11. NMR after extraction/washing of a P2VP/PCHC terpolymer with methanol



Figure S31. NMR spectra of a P2VP/PCHC terpolymer (table 1, entry 4) prior (4) and after washing with methanol (3-1) in chloroform-d.

12. GPC after extraction/washing of a P2VP/PCHC terpolymer with methanol



Figure S32. GPC traces (RI) of a P2VP/PCHC terpolymer (table 1, entry 4) prior (black) and after washing with methanol (orange, remaining solid and green, methanol phase).



13. DSC Analysis of P2VP/PCHC terpolymer

Figure S33. DSC measurement of PCHC (1), P2VP (2) and a P2VP/PCHC terpolymer (table 1, entry 3) (3).

14. TGA of P2VP/PCHC and PIPOx/PCHC terpolymers



Figure S34. TGA of a P2VP/PCHC (table 1, entry 3) and a PIPOx/PCHC terpolymer (table 1, entry 6).

15. ESI-MS of oligomeric PIPOx synthesized with catalyst 3



Figure S35. ESI-MS of oligomeric PIPOx synthesized with catalyst 3 (the signal at 112.15 m/z is the mass of the protonated monomer).



16. DSC Analysis of PIPOx/PCHC terpolymer

Figure S36. DSC measurement of PIPOx homopolymer (1) and of a PIPOx/PCHC terpolymer (table 1, entry 6) (2).

17. NMR spectra of P2VP/PCHC and PIPOx/PCHC terpolymers



Figure S37. ¹H NMR spectrum of a P2VP/PCHC terpolymer (table 1, entry 5) in chloroform-d.



Figure S38. ¹³C NMR spectrum of a P2VP/PCHC terpolymer (table 1, entry 5) in chloroform-d.



Figure S39. ¹H NMR spectrum of a PIPOx/PCHC terpolymer (table 1, entry 6) in chloroform-d.



Figure S40. ¹³C NMR spectrum of a PIPOx/PCHC terpolymer (table 1, entry 6) in chloroform-d.