Chain End-Groups Reveal Two Stages for Palladium-Based Polyketone Catalyst Species

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Supporting information

1. Experimental procedures and data

General

All operations involving preparation of catalyst systems and synthesis of palladium complexes were carried out under an atmosphere of dry nitrogen. All reagents were used as supplied by manufacturers: methanol (p.a.) from Merck, palladium acetate from Acros, trifluoroacetic acid (>98%, abbreviated as HTFA) from Merck-Schuchardt, 1,3-bis(diphenylphosphino)propane (dppp) from Strem, and CO, ethene and CO/ethene (50:50) from Hoekloos. 1,3-bis(di(o-methoxyphenyl)phosphino)propane (bdompp) was synthesised according to a standard procedure.[1] The complexes $Pd(dppp)(TFA)_2$ and $Pd(bdompp)(TFA)_2$ were synthesised along the lines of a standard procedure.[2]

$^{13}C\{^1H\}$ NMR spectra of polyketone materials were measured in HFIPA/C_6D_6 on a Varian AMX-500 apparatus operating at 125.77 MHz, applying a Pulse Delay time of 30 sec.

Field Desorption (FD) mass spectra were obtained with a Jeol HX110 magnetic sector mass spectrometer with a combined EI/FI/FD source, fitted with a 10 μm tungsten wire FD-

emitter containing carbon needles with an average length of 30 μm, using emitter currents of 0-15 mA.

Matrix Assisted Laser Desorption Ionization Spectroscopy Time-of-Flight (MALDI-TOF) mass spectroscopy was carried out using a PerSeptive Biosystems Voyager-DE-RP MALDI-TOF mass spectrometer. A 337 nm UV Nitrogen laser producing 2 ns pulses was used in the linear and reflection mode. The samples were prepared by dissolving a sample of product 3a in hexafluoro-isopropylalcohol (HFIPA) in a concentration of about 3 mg/ml. This solution was mixed with a 1:1 mixture of Dithranol (1,8,9-anthracenetriol) and HFIPA and with a saturated solution of NaI in HFIPA, on a 1:1:1 basis. Of this solution a 1 μl droplet was spotted on the golden sample plate, giving approximately 1 μg of sample.

Copolymer molecular weights determined using a Size Exclusion Chromatographic system comprising: a Beckman 112 SDM pump, a Waters 717 plus autosampler, kept at 10 °C, a Croco-Cil column oven, kept at 35 °C, two Phenogel SEC columns in series (types: 5 μm, mixed bed & 5 μm, 500 Å; Phenomex) and a UV absorbency frequency detector (195 nm) and /or a refractive index (RI) detector. Hexafluoroiisopropanol containing 0.01 M Ammonium trifluoroacetate was used as diluent and mobile phase.

Gas chromatographic analysis was performed on a HP 5890 gas chromatograph equipped with a Chrompack 50 m CP-sil-5 capillary column (ϕ = 0.53 mm) and an FID-detector. Retention times (in min) of low molecular weight co-oligomers of CO and ethene:

EE: $CH_3O[C(O)CH_2CH_2]_{n-1}C(O)OCH_3$, 6.55, 10.57, 13.92, 16.73 for n = 2-5, respectively,

EK: $CH_3CH_2[C(O)CH_2CH_2]_{n-1}C(O)OCH_3$, 7.06, 10.98, 14.29, 17.10 for n = 2-5, respectively,

KK $CH_3CH_2[C(O)CH_2CH_2]_{n-1}C(O)CH_2CH_3$, 7.45, 11.38, 14.66, 17.49 for n = 2-5, respectively.

Copolymerization of carbon monoxide and ethylene (exp. 1,2)

Copolymerizations were carried out in a 2.2 L stainless steel autoclave. The autoclave was loaded with 1 L of methanol and 16.2 g of Carilon EP (terpolymer of CO/ethylene/propylene with mp 225 °C and LVN=1.8) and was pressurised with 50 bar of dry nitrogen. After 5 min the pressure was released carefully and the mixture heated to 90 ° C. The autoclave was first charged with 24 bar of ethylene and subsequently with carbon monoxide up to 50 bar (thus affording a 24/24 bar mixture of ethylene/CO as the autogeneous pressure of methanol at 90 °C is about 2 bar). Next, 0.03 μmol (≡ 3.2 mg [Pd]) of catalyst, $Pd(dppp)(TFA)_2$ or $Pd(bdompp)(TFA)_2$ dissolved in 15 ml of acetone was injected. Polymerization was continued for 1 hr, after which period the pressure was released carefully and the autoclave cooled to ambient temperature. The copolymer was filtered off, washed with methanol and dried overnight in a vacuum oven at 70 °C. Yield: for $(Pd(dppp)(TFA)_2$: 24.3 g copolymer (7.6 kg·(g Pd·h)$^{-1}$), M_n = 12,000, and for $(Pd(bdompp)(TFA)_2$: 40.3 g copolymer (12.6 kg·(g Pd·h)$^{-1}$), M_n=33,000. The polymer products were analysed by $^{13}C\{^1H\}$-NMR in HFIPA/C_6D_6 (9/1) on a Varian AMX-500, applying a Pulse Delay time of 30 sec., to achieve quantitative end group analysis. $^{13}C\{^1H\}$NMR (solvent HFIPA/C_6D_6): δ 217.2, $CH_3CH_2C(O)$-; δ 211-214, -$[CH_2CH_2C(O)]_n$-; δ 176.4, $CH_3OC(O)$-; δ 52.0 $CH_3OC(O)$-; δ 35-37, -$[CH_2CH_2C(O)]_n$-; δ 27.5 $CH_3CH_2C(O)$-; δ 6.4 $CH_3CH_2C(O)$-. The $^{13}C\{^1H\}$-NMR data indicated that in both samples the **E/K** end group ratio did not deviate from 1 (the data were corrected for the use of Carilon EP). The filtrate of both runs were concentrated under reduced pressure and the

composition (in terms of **KK** : **EK** : **KK**) of the low MW oligomers (containing up to 5 CO-moieties) determined by gas chromatographic analysis (see manuscript, Table 1).

Copolymerization of carbon monoxide and ethylene at low pressure (exp. 3)

The 2.2 L autoclave was loaded with 1 L of methanol and was pressurised with 50 bar of dry nitrogen. After 5 min the pressure was released carefully and the mixture heated to 78 ◦ C. The autoclave was first charged with 2 bara of ethylene and subsequently with carbon monoxide up to 4 bara (thus affording a 1/1 bar mixture of ethylene/CO). Next, 0.03 mmol of catalyst and 0.12 mmol of trifluoroacetic acid in 20 ml of acetone was injected (followed by rinsing the injection system with 15 ml of acetone. Polymerization was continued for 4 hr, after which period the pressure was released carefully and the autoclave cooled to ambient temperature. The copolymer slurry was collected and divided into two parts. The solvent of the first part was removed under vacuum (!), and the product dried overnight in a vacuum oven at 70 ◦C. Yield: 5.01 g polyketone (containing both oligomeric and polymeric material (SP-16b; entry 3a).

The second part was filtered, affording two fractions: a methanol fraction containing the low MW cooligomers (SP-16c; entry 3b-o) and a polymer residue (SP-16a; entry 3b-p). The solvent of the oligomer fraction was removed under vacuum and the product dried overnight under vacuum, and the polymer residue was dried overnight in a vacuum oven at 70 ◦C. Yield: 0.23 g of CO/ethylene oligomers (entry 3b-o) and 3.68 g of CO/ethylene copolymer (entry 3b-o).

The products SP-16a-c were analysed by $^{13}C\{^{1}H\}$-NMR in HFIPA/C_6D_6 (9/1) on a Varian AMX-500, applying a Pulse Delay time of 30 sec., to achieve quantitative end group analysis; based on these data n_{av} ($n_{average}$ = average no. of CO-moieties per chain), M_n and **E/K** were determined. $^{13}C\{^{1}H\}$NMR (solvent HFIPA/C_6D_6): δ 217.2, $CH_3CH_2C(O)$-; δ 211-

214, -[$CH_2CH_2C(O)]_n$-; δ 176.4, $CH_3OC(O)$-; δ 52.0 $CH_3OC(O)$-; δ 35-37, -[$CH_2CH_2C(O)]_n$-; δ 27.5 $CH_3CH_2C(O)$-; δ 6.4 $CH_3CH_2C(O)$-. The ratio of **KK**, **EK** and **KK**-copolymers present in SP-16b (entry 3a) was determined by FD-MS (Table 1), and the MWD was determined by MALDI-TOF (Table 2).

References:

1. Budzelaar, P.H.M.; van Doorn, J.A.;Meijboom, N. *Recl. Trav. Chim. Pays-Bas* **1991**, *110*, 420.

2. See e.g.: a. Stephenson, T.A.; Morehouse, S.M.; Powell, A.R.; Heffer, J.P.; Wilkinson, G.; *J. Chem. Soc.* **1965**, 3632; b. Dekker, G.P.C.M.; Elsevier, C.J.; Vrieze, K.; van Leeuwen, P.W.N.M. *Organometallics* **1992**, *11*, 1598-1603; c. Luo, H.-K.; Kou, Y.; Wang, X.-W.; Li, D.-G. *J. Mol. Catal. A: Chem.* **2000**, *151*, 91-113.

Table 1. Ratio of EE, EK, KK (%) vs. n
(sample: Kramer4.109254.1 en 2 (SP16b+c))[a,b]

n	KK	EK	EE
6	21.0	72.0	7.0
7	21.5	72.0	6.5
8	22.7	72.2	5.1
9	24.4	69.7	5.9
10	22.6	70.9	6.5
11	23.8	70.5	5.7
12	23.1	72.9	4.8
13	21.9	70.8	7.3
14	21.9	68.9	9.2
15	18.4	69.0	12.6
16	21.7	65.5	12.8
17	20.9	65.8	13.3
18	19.7	66.6	13.7
19	18.9	64.0	17.1
20	19.0	61.4	19.6
21	20.5	63.2	16.3
22	25.8	57.1	17.1
23	23.7	54.1	22.2
24	20.8	63.4	15.8
25	19.8	61.0	19.2

[a] Determined by FD-mass spectrometry; n = number of C(O)-moieties in copolymer chain.

[b] The relative intensities of the [R'-($CH_2CH_2C(O)$]$_{n-2}$-R")·Na^+]-isotopes (**KK**: R' = R" = $C(O)CH_2CH_3$, **EK:** R' = $C(O)CH_2CH_3$, R" = $C(O)OCH_3$; **EE:** R' = R" = $C(O)OCH_3$; n=6-25) were determined (corrections were made for the presence of ^{13}C-isotopes of the **KK** and **EK** chains underneath the main (^{12}C) isotopic peaks of the **EK** and **EE**-chains). The **KK/EE/EK** end group ratio vs. copolymer chain length (n) given in Table 1, corresponds to the average result of four independent spectra recorded for sample 3a,

Table 2. Molecular weight distribution of polyketone as determined by MALDI-TOF (entry 3).

n[a]	Relative intensity MALDI-signal (N_n)	log N_n (intensity)
5	45	1.653213
6	54.6	1.737193
7	52	1.716003
8	61	1.78533
9	61.2	1.786751
10	63.3	1.801404
11	61	1.78533
12	62.5	1.79588
13	58.5	1.767156
14	55.5	1.744293
15	58	1.763428
16	51	1.70757
17	42.3	1.62634
18	41	1.612784
19	38.2	1.582063
20	31	1.491362
21	29	1.462398
22	25.5	1.40654
23	23.5	1.371068
24	18.5	1.267172
25	16.5	1.217484
26	14	1.146128
27	11.7	1.068186
28	10.8	1.033424
29	9.3	0.968483
30	7.5	0.875061
31	6.8	0.832509
32	5.6	0.748188
33	5	0.69897
34	4.4	0.643453
35	3.7	0.568202

[a] n = number of C(O)-moieties in copolymer chain

2. Mathematical expressions for the calculation of EE, EK, KK, E/K and EE/KK

- for short chains (n<12: so, to those terminating in the homogeneous phase).
- Assumption: all catalyst species that terminate, both in the homogeneous phase and in the heterogeneous phase, become homogeneous again, prior to producing a new copolymer chain.

Consider chain transfer to take place *via* eq. 1-4 exclusively:

Termination via protonolysis: T_p:

$$[L_2Pd(CH_2CH_2C(O)R]^+ + MeOH \rightarrow [L_2Pd\text{-}OMe]^+ + CH_3CH_2C(O)R \ \mathbf{(K)} \quad (1)$$

Termination via alcoholysis: T_a:

$$[L_2Pd(C(O)CH_2CH_2C(O)R]^+ + MeOH \rightarrow [L_2Pd\text{-}H]^+ + MeOC(O)CH_2CH_2C(O)R \ \mathbf{(E)} \quad (2)$$

Initiation pathways:

$$[L_2Pd\text{-}OMe]^+ + CO \rightarrow [L_2Pd(C(O)OMe)]^+ + CH_2{=}CH_2 \rightarrow [Pd(CH_2CH_2C(O)OMe)]^+ \ \mathbf{(E)} \quad (3)$$

$$[L_2Pd\text{-}H]^+ + CH_2{=}CH_2 \rightarrow [L_2Pd(CH_2CH_3)]^+ + CO \rightarrow [L_2Pd(C(O)CH_2CH_3)]^+ \ \mathbf{(K)} \quad (4)$$

Consider 3 equations with 3 independent variables.

$T_{hom} + T_{het} = 1$

$T_{a,hom} + T_{p,hom} = 1$

$T_{a,het} + T_{p,het} = 1$

in which:

T_{hom} : degree to which termination takes place in the homogeneous phase
T_{het} : degree to which termination takes place in the heterogeneous phase
$T_{a,hom}$: degree to which alcoholysis takes place in the homogeneous phase
$T_{p,hom}$: degree to which protonolysis takes place in the homogeneous phase
$T_{a,het}$: degree to which alcoholysis takes place in the heterogeneous phase
$T_{p,het}$: degree to which protonolysis takes place in the heterogeneous phase

than **EE**, **KK** and **EK** (in %) can be derived from the equations::

$$\mathbf{EE} = \{(T_{het}/(T_{het}+T_{hom}))*T_{p,het} + (T_{hom}/(T_{het}+T_{hom}))*T_{p,hom}\}*T_{a,hom}*100\ \%$$

$$\mathbf{KK} = \{(T_{het}/(T_{het}+T_{hom}))*T_{a,het} + (T_{hom}/(T_{het}+T_{hom}))*T_{a,hom}\}*T_{p,hom}*100\ \%$$

$$\mathbf{EK} = [\{(T_{het}/(T_{het}+T_{hom}))*T_{p,het} + (T_{hom}/(T_{het}+T_{hom}))*T_{p,hom}\}*T_{p,hom} + \{(T_{het}/(T_{het}+T_{hom}))*T_{a,het} + (T_{hom}/(T_{het}+T_{hom}))*T_{a,hom}\}*T_{a,hom}]*100\ \%.$$

and the E/K ratio can be derived from the equation:

$$\mathbf{E/K} = (2*\mathbf{EE}+\mathbf{EK})/(2*\mathbf{KK}+\mathbf{EK})$$