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

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Over the past decades several new families of well-defined transition metal-based polymerization catalysts have been discovered.[1] Although these systems are generally referred to as "*single-site*" catalysts, this seems not to hold in all cases.[2] Deviations of the polydispersity (M_w/M_n) of the produced (co)-polymers from the theoretical Flory-Schulz value of 2 have been attributed to polymer precipitation and heterogenization of the catalyst giving rise to "*multiple-site*" catalysis.[2a,c−f] The copolymerization of ethene and carbon monoxide to a perfectly alternating polyketone, $[CH_2CH_2C(O)]_n$, which is catalyzed by a cationic palladium catalyst, $[L_2PdR]^+(X)^-$ (L_2 = bidentate ligand; X = weakly or noncoordinating anion; R = $[CH_2CH_2C(O)]_nOCH_3$ or $[C(O)CH_2CH_2]_nH$ ($n \geq 0$)), generally affords materials with $M_w/M_n \approx 2.5-5$.[3] This suggests that the initially *single-site* catalyst becomes a heterogeneous, *multiple-site* system during copolymerization, in line with the slurry nature of the polyketone manufacturing process. In this communication, evidence is provided from polymer end-group analysis that the running catalyst species, $[L_2PdR]^+$, exhibits two-stage kinetic behavior. This is ascribed to residence of the catalyst in two different states. Depending on the length of the growing copolymer chain R, the catalyst is either dissolved during copolymerization (at the shorter chains) or polyketone-supported (at the longer chains).

Termination during CO/ethene copolymerization proceeds via two competing mechanisms, *protonolysis*, leading to the formation of a ketone end-group (**K**; eq 1) and *alcoholysis*, giving an ester end-group (**E**; eq 2).[1h,4] After termination via protonolysis a Pd−methoxy species is obtained that gives rise to the formation of an **E** end-group at the start of the next copolymer chain it produces (eq 3), whereas after alcoholysis a Pd-hydride species is obtained, giving a **K** end-group in the next chain (eq 4).

termination pathways:

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

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

initiation pathways:

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

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

According to this two-catalytic cycle model, three types of copolymer chains may be produced, those containing: (i) both an ester and a ketone end-group (**EK**), (ii) two ester end-groups (**EE**), and (iii) two ketone end-groups (**KK**). This model also predicts the formation of equal amounts of **E** and **K** and, consequently, equal amounts of **EE** and **KK** copolymer chains.[1h,5] However, in several cases the **E**/**K** ratio in the methanol-soluble oligomer fraction (filtrate) deviated from unity (GC-analysis).[6] For example, when $Pd(bdompp)(TFA)_2$ (bdompp = 1,3-bis-(di-(*o*-methoxyphenyl)phosphino)propane) is employed as the catalyst, the **E**/**K** ratio in the filtrates of polyketone produced at 50 bar CO/ethene and 90 °C amounts to 0.14, while no oligomeric **EE**-chains are detected (see Table 1). The **E**/**K** ratio in the precipitated polyketone did not significantly deviate from unity. As the latter fraction contains the large majority (>98%) of the chains formed, the **E**/**K** ratio of the total products is about unity, indicating that chain transfer occurs in a perfect fashion, that is, only via eq 1−4. These observations suggested that the ratio in which the two-chain transfer mechanisms occur is dependent on the physical state of the catalyst.

To map this phenomenon in detail, a low-molecular weight polyketone product was produced. The product slurry (**3**) was divided into two parts. The first part (**3a**) was analyzed after drying, while the second part (**3b**) was first filtrated, affording a viscous oligomer fraction (**3b-o**) and a solid polymer fraction (**3b-p**) after workup. The **E**/**K** ratio and M_n of the fractions were determined by ^{13}C NMR (Table 2). The **E**/**K** ratio in **3b-o** amounted to 0.725 ± 0.04 and in **3b-p** to 1.185 ± 0.04. By combining these data with the M_n-values and the weight of the fractions, the **E**/**K** ratio in the parent part **3b** was calculated to amount to 1.015 ± 0.04.[7,8] So, the excess of **K** present in the oligomer fraction is fully compensated by the excess of **E** in the polymer fraction.

By virtue of the difference in mass between an **E** and a **K** end-group ($\Delta_{mass} = 2$), field desorption (FD) mass spectrometry proved a useful tool to determine the ratio of **KK**, **EK**, and **EE**-copolymers for chains longer than those observed by GC.[9] On the basis of the FD-mass spectrum of fraction **3a** (recorded and analyzed in 4-fold), the **EE**/**EK**/**KK**-ratio versus chain length

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[5] The oligomer fraction from a slurry copolymerization carried out at 45 bar and 120 °C using a Pd(dppb)-based catalyst contained equal amounts of **EE** and **KK** oligomers. See ref 1a.

[6] Polyketone oligomers are soluble in methanol up to $n \approx 10$. GC could be used to analyse oligomers up to $n = 5$; n refers to the number of C(O) units in the copolymer chain.

[7] The masses of the end-groups were taken into account in the calculation of the M_n values.

[8] The small deviation between the **E**/**K** ratios found for **3a** (1.080 ± 0.04) and **3b** (1.015 ± 0.04) is attributed to the slurry nature of the original product (**3**), hampering splitting into two parts of exactly equal composition.

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Table 1. **E**/**K** Ratio in Polyketone Oligomer Fractions[a]

entry	catalyst	*T*, °C	rate	**EE**	**EK**	**KK**	**E**/**K**
1	Pd(bdompp)(TFA)$_2$	90	12.8	0	25	75	0.14
2	Pd(dppp)(TFA)$_2$	90	7.5	7	48	45	0.45

[a] Experiments were carried out at 90 °C, 50 bar CO/ethene (1/1) in methanol; [Pd] = $3.5 \cdot 10^{-5}$ M; t = 1 h; rate in kg copolymer·(g Pd·h)$^{-1}$. The **EE**, **EK**, and **KK** ratio was determined by GC, and averaged for $n = 3-5$.[6]

Table 2. Data of a Low-Molecular Weight Polyketone[a]

entry[b]	weight, g	n_{av}[c]	M_n[c]	n[d]	**E**/**K** ratio[c]
3a	5.01	31.3	1840 ± 200		1.080 ± 0.04
3b-p	3.68	38.1	2220 ± 200	≥9−11	1.185 ± 0.04
3b-o	0.23	4.6	343 ± 20	≤9−11	0.725 ± 0.04

[a] Reaction conditions: catalyst: Pd(bdompp)(TFA)$_2$/HTFA (1:4); methanol, T = 78 °C, t = 4 h, P = 4.5 bar (CO/ethene = 1). [b] The product was divided into two parts (**3a**,**b**). Part **3a** was analyzed as such, while part **3b** was filtrated, affording an oligomer fraction (**3b-o**) and a polymer fraction (**3b-p**). [c] n_{av} (average number of CO units/chain), M_n and **E**/**K** were determined by $^{13}C\{^1H\}$ NMR in HFIPA/C_6D_6. [d] Determined by FD-MS.

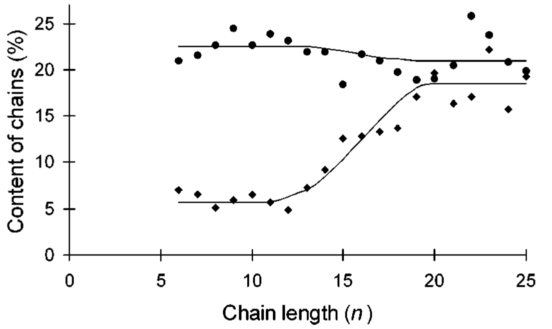

Figure 1. **EE** (◆) and **KK** (●) content[9] as a function of the polyketone chain length, *n*,[6] as determined by FD-MS (entry **3a**). The **EK** content was omitted for clarity; **EK** (%) = 100 − (**EE** + **KK**).

could be accurately determined in the mass-range of 400−1200 ($n \approx 5-20$).[6] Above masses of about 1500 ($n \approx 25$), the method became too insensitive to analyze the individual copolymer chains. It was found that the **E**/**K** ratio, as derived from the FD-mass data, gradually increased with *n*, indicating a gradual change of the ratio to which the two-chain transfer mechanisms occur.

A better insight into this change is obtained by comparing the ratio between content of **EE**, **EK**, and **KK**-chains at individual chain length *n* (Figure 1). For short chains ($n < 13$) the ratio **EE**/**KK** is about 0.25, while for longer chains ($n > 20$) it is close to 1.[10] This shows that the ratio to which the two possible termination reactions, alcoholysis and protonolysis, occur, alters when the copolymer chain attached to an individual catalytic palladium center has reached a length of about 13−20 [$CH_2CH_2C(O)$] units. This points to the transition of the running catalyst species from the homogeneous into heterogeneous phase over this range of chain lengths.[11] Under mild conditions (20 °C, 1 bar CO/ethene), the running catalyst species were found to nucleate after about 6 min, when the average chain length amounted to $n \approx 11$.[12] This corresponds nicely to the chain length at which the running catalyst species, [Pd(bdompp)R]$^+$, start to precipitate under the above-mentioned process conditions.

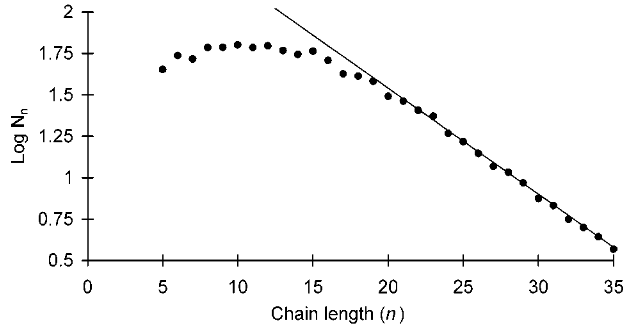

Figure 2. MWD of polyketone from MALDI-TOF (entry **3a**).

A MALDI-TOF spectrum of sample **3a** supports, although qualitatively, the two-stage model described above (Figure 2). Instead of a regular Flory-Schulz MW-distribution, the number of copolymer chains with a chain length of below $n \approx 18$ stays below the trend-line fitted for the higher MW-part ($\alpha = 0.936$), indicating $(k_{t,a} + k_{t,p})/k_p$ to increase upon heterogenization of the individual catalyst species.[13] On the basis of the current data, it cannot be determined whether $k_{t,a} + k_{t,p}$ increases, k_p decreases, or both. The drastically altered termination kinetics is a reflection of the fact that the deposited catalyst sites strongly experience the surface of the polyketone support in close proximity. Further study is required to elucidate the underlying molecular processes of this intriguing phenomenon.

The **EE**/**EK**/**KK** data are consistent with a catalytic two-phase system, in which termination in the homogeneous phase occurs predominantly via protonolysis, whereas termination in the heterogeneous phase occurs via both protonolysis and alcoholysis.[14] The ratio to which the two-chain transfer mechanisms occur in the *heterogeneous phase* can be deduced from the end-group ratio in the chains terminated in the *homogeneous phase*. For example, employing Pd(bdompp)(TFA)$_2$ as the catalyst at 90 °C and 50 bar CO/ethene (entry 1), protonolysis (eq 1) and alcoholysis (eq 2) occur in a ratio of about 25:75 in the heterogeneous phase.

In conclusion, we have shown that during CO/ethene copolymerization under slurry process conditions, the running palladium-based catalyst species occur in two physically and kinetically different states, depending on the copolymer chain length.[15]

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Supporting Information Available: Experimental procedures and data, and mathematical expressions (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[9] The given data correspond to amount of the mono-Na$^+$ adducts of the **EE**, **EK**, and **KK**-chains. Besides mono-Na$^+$ adducts, also H$^+$ adducts and dehydrated ($-nH_2O$) chains are observed in the FD-mass spectra. The intensities of the **EK** and **EE** peaks were corrected for the coinciding ^{13}C-isotopes of the lighter **KK** and **EK** chains, respectively.

[10] On the basis of the ^{13}C NMR spectrum of fraction **3b**, the **EE**/**KK** should approach 1.185 ± 0.04 at high *n*, rather than become about 1. This deviation is probably due to the relatively large error in the amount of **EE** oligomers, as determined by FD-MS, especially at higher *n*, due to their coincidence with the corresponding **EK** containing two ^{13}C isotopes.

[11] It should be noted that the beginning of the transition at $n \approx 13$ is much more clear-cut than the end of the transition at $n \approx 20$, due to the diminished sensitivity of the FD-mass spectrometry technique at higher masses.

[12] These experiments were performed employing (bdompp)Pd(CH$_3$)(TFA) as the catalyst instead of Pd(bdompp)(TFA)$_2$, to overcome the otherwise slow initiation. Reaction conditions: a 1:1 CO/ethene mixture was slowly bubbled through a solution of catalyst in methanol; [Pd]=1.05 mM. Samples were taken at regular time intervals, quenched on solid CO$_2$, and analyzed.

[13] $K_{t,a}$, $k_{t,p}$ and k_p refer to the rate of alcoholysis (eq 2), the rate of protonolysis (eq 1), and the rate of propagation, respectively.

[14] If alcoholysis had occurred selectively in the heterogeneous phase and both protonolysis and alcoholysis in the homogeneous phase, the number of **KK** chains would have dropped substantially above $n = 20$.

[15] Propagation kinetics in solution have been determined by: (a) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 4746. (b) Shultz, C. S.; Ledford, J.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **2000**, *122*, 6351.