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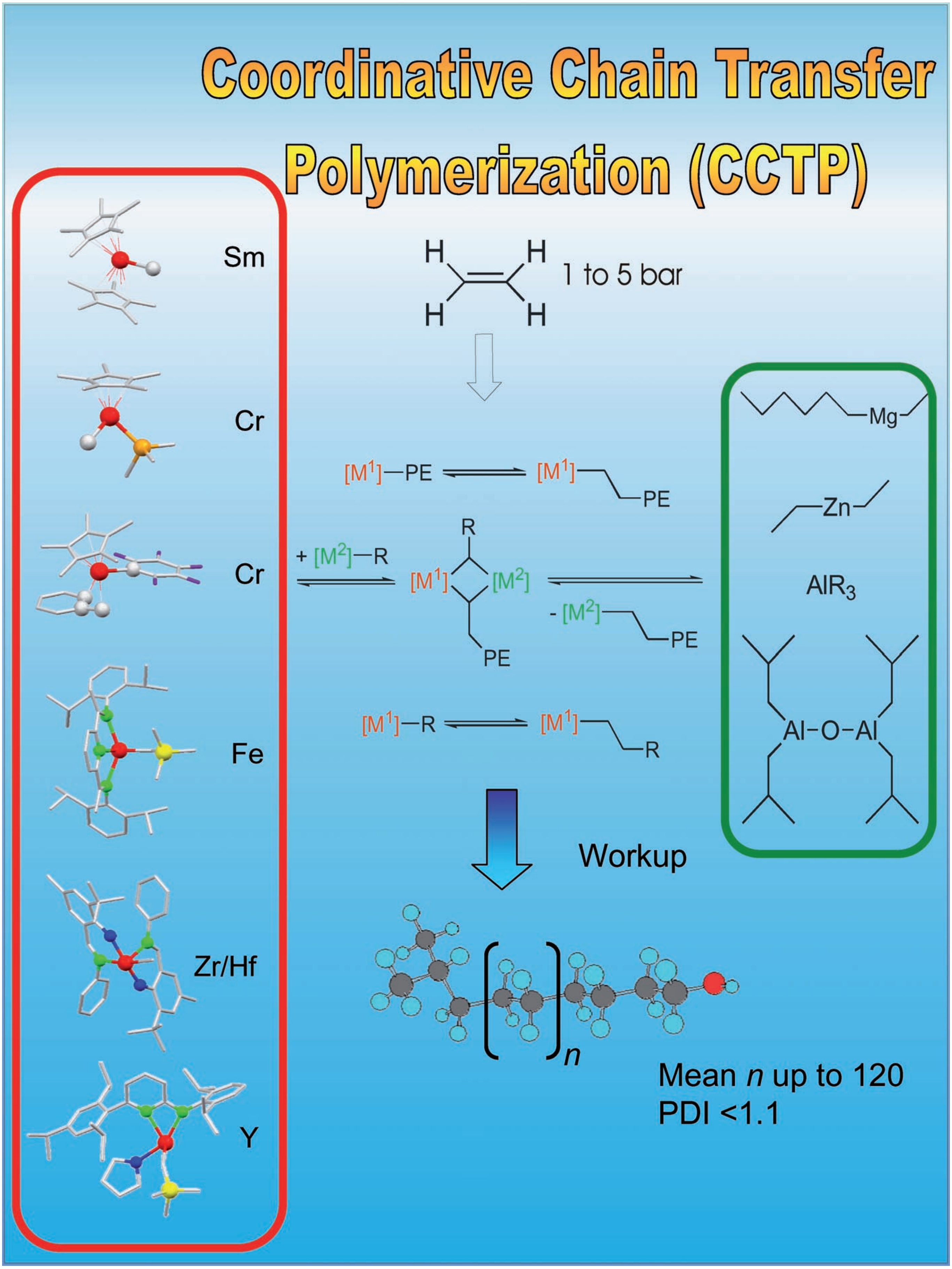

How to Polymerize Ethylene in a Highly Controlled Fashion?

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Abstract: Very fast, reversible, polyethylene (PE) chain transfer or complex-catalysed “Aufbaureaktion” describes a “living” chain-growing process on a main-group metal or zinc atom; this process is catalysed by an organo-transition-metal or lanthanide complex. PE chains are transferred very fast between the two metal sites and chain growth takes place through ethylene insertion into the transition-metal- or lanthanide-carbon bond—coordinative chain-transfer polymerisation (CCTP). The transferred chains “rest” at the main-group or zinc centre, at which chain-termination processes like β-H transfer/elimination are of low significance. Such protocols can be used to synthesise very narrowly distributed PE materials ($M_w/M_n < 1.1$ up to a molecular weight of about 4000 g mol^{-1}) with differently functionalised end groups. Higher molecular-weight polymers can be obtained with a slightly increased M_w/M_n, since diffusion control and precipitation of the polymers influences the chain-transfer process. Recently, a few transition-metal- or lanthanide-based catalyst systems that catalyse such a highly reversible chain-growing process have been described. They are summarised and compared within this contribution.

Keywords: Aufbaureaktion · lanthanides · main group elements · polyethylene · polymerization · transition metals

Introduction

Modern polymer chemistry means, for instance, the design of very controlled polymerisation processes allowing for the synthesis of very narrowly distributed polymers exactly tuneable with respect to their molecular weights. The accessibility of new, innovative, nanostructured and intelligent materials correlate with such highly controlled protocols. Ethylene, one of the cheapest monomers, is very difficult to handle in this regard despite the progress in the development of living olefin polymerisation catalysts and to a much smaller extent of living ethylene polymerisation catalysts.[1,2a] Transition-metal- and lanthanide-based living ethylene polymerisation catalysts are rare and are usually synthetically demanding molecules. Since they produce (by definition) one PE (PE = polyethylene) chain per catalyst molecule, such processes are relatively inefficient. Furthermore, they are usually quite active, operate preferentially at low temperatures to suppress β-H transfer/elimination and thus difficulties arise to access a specifically wanted molecular-weight (especially in the low molecular-weight range) due to very fast chain growth. Anionic polymerisation of ethylene by using *n*BuLi is another approach to synthesise well-defined PE materials, but rather limited since the presence of “protons” that are more acidic than aliphatic protons (for instance solvents like toluene or benzene) lead to chain termination, as *n*BuLi or PELi reacts with such protons. Furthermore, polymerisation proceeds slowly due to the low reactivity of ethylene in comparison to other monomers like styrene and at higher temperatures olefin elimination becomes relevant as well.[1b] Zieglers “Aufbaureaktion/Wachstumsreaktion”[2] can be understood as a high-temperature ethylene polymerisation process in which chain growth is also quite slow, but the reactivity of the initiator tolerates a broader range of functional groups. The problem of the Aufbaureaktion as a synthetic tool in terms of the production of well-defined PE materials over a large range of molecular weights is the “Verdrängungsreaktion” relevant at high temperatures. A PE−Al function reacts formally with ethylene forming a C_2H_5−Al moiety (which again can catalyse chain growth) and a 1-olefin (β-H transfer/elimination). Even at 100 °C this elimination process is fast enough with respect to the chain growth such that only about 100 insertions are feasible. Ziegler wrote: “Als wir dies erkannt hatten, schien das ”Polyäthylen-Problem“ für uns erledigt, denn wir sahen keinerlei Möglichkeiten, wie wir diese grundsätzliche Schwier-

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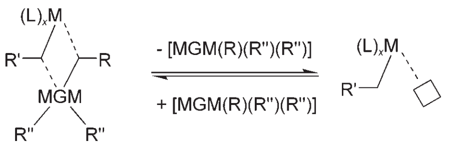
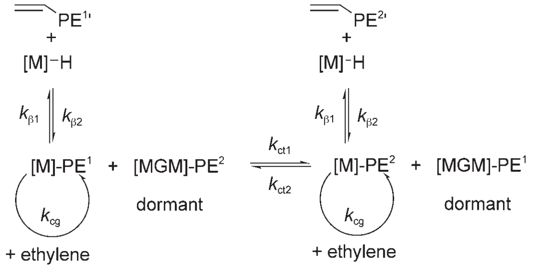
igkeit vielleicht würden überwinden können. (When we had recognised this, the "polyethylene problem“ seemed settled for us, because we did not see any possibility as to how we could eventually overcome this fundamental difficulty).”[2b] Lowering the insertion barrier should increase the rate of chain growth. A classical way to lower the activation barrier of any reaction is the introduction of a catalyst. Thus, catalysing the insertion should make the rate of insertion significantly faster and thus the “Verdrängungsreaktion” could be suppressed, that is, the use of a metal-complex-catalysed “Aufbaureaktion” or reversible and very fast PE chain transfer. Such a strategy appeared in the patent literature in the early 1990s. Samsel described a variety of metallocene-based catalysts systems that catalysed chain growth at Al alkyls.[3] A well-adjusted equilibrium between the chain-transfer state (CTS) and the chain-growing state (CGS) is the basis of such a polymerisation protocol (Scheme 1). The CTS is essentially responsible for a very fast intra- (exchange of dashed and solid lines within the CTS) and intermolecular {exchange of [MGM(R)(R″)(R″)] (MGM = main-group metal or zinc), units of the CTS} chain transfer. The CGS accomplishes the growing of a single chain. If an excess of [MGM(R)(R″)(R″)] is present, if inter- and intramolecular chain transfer are faster than chain growth and if other chain termination processes like β-H transfer/elimination could be suppressed (significantly slower than chain growth), a chain growth of all chains of all [MGM(R)(R″)(R″)] molecules with nearly the same rate is observed, giving rise to very narrowly distributed MGM-terminated PE material.



Scheme 1. Complex-catalysed “Aufbaureaktion” or very fast, reversible, PE chain transfer; left: chain-transfer state (CTS); right: chain-growing state (CGS, M = transition metal or lanthanide, MGM = main-group metal,[4] L = neutral or anionic ligand to stabilise M and to suppress β-H transfer/elimination within the needed time range).

Abstract in German: *Sehr schneller reversibler PE-Kettentransfer oder die komplexkatalysierte Aufbaureaktion beschreiben einen “lebenden” Kettenwachstumsprozess an einem Hauptgruppenmetall oder Zink, der durch einen Übergangsmetall- oder Lanthanoidkomplex katalysiert wird. Die PE-Ketten werden sehr schnell zwischen beiden Metallzentren übertragen und das Kettenwachstum findet via Ethyleninsertion in die Übergangsmetall- bzw. Lanthanoid-Kohlenstoff-Bindung statt—Koordinative Ketten-Transfer-Polymerisation (KKTP). Die übertragenen Ketten “ruhen” am Hauptgruppenmetall- bzw. Zinkzentrum wo Kettenabruchreaktionen wie die β-H-Transfer/Eliminierung kaum von Bedeutung sind. Solche Synthesevarianten können genutzt werden, um sehr eng verteilte PE-Materialien (*$M_w/M_n < 1.1$ *bis zu einem Molekulargewicht von rund 4000 g mol*$^{-1}$*) mit unterschiedlich funktionalisierten Endgruppen darzustellen. Höhermolekulare Polymer können mit einem leicht erhöhten* M_w/M_n *erhalten werden, da Diffusionskontrolle und Fällung der Polymere den Kettenübertragungsprozess beeinflussen. Kürzlich wurden einige auf Übergangsmetall- bzw. Lanthanoidkomplexen basierende Katalysatorsysteme, die ein solches hochreversibles Kettenwachstum katalysieren, beschrieben. Sie wurden im Rahmen dieses Beitrages zusammengefasst und verglichen.*

The equilibrium between CTS and CGS is crucial for such a process. Very strong coordination of [M−R′(L)$_x$] (M = transition metal) at [MGM(R)(R″)(R″)] leads to virtually no chain growth, since the concentration of CGS is too low. A very low overall activity is observed. Furthermore, very strong binding may give rise to the growth of only one chain or at least a significant broadening of the molecular-weight distribution, since chains grow indifferently. On the other hand, if this equilibrium is shifted to the extreme right-hand side (CGS dominates) chain transfer to [MGM(R)(R″)(R″)] becomes unlikely and a classic ethylene polymerisation process is observed in which [MGM(R)(R″)(R″)] acts only as a scavenger, and chain terminations like β-H transfer/elimination are of relevance. Very fast, reversible, chain transfer is illustrated by Scheme 2 and can be viewed as degenerative transfer polymerisation.[5] Chain transfer is much faster than chain growth ($k_{ct1} \approx k_{ct2} > k_{cg}$). MGM is a main-group metal or zinc and is essentially inert in terms of chain termination other than chain transfer and thus acts as a dormant state. Chain-termination processes other than chain transfer to MGM have to be suppressed as well for [M]-PE by either very fast reinsertion ($k_{\beta1} < k_{\beta2}$) or very slow β-H transfer/elimination ($k_{\beta1}$) with regard to the rate of chain growth (k_{cg}).



Scheme 2. Complex-catalysed “Aufbaureaktion” or very fast, reversible, chain transfer with $k_{cg} < k_{ct1} \approx k_{ct2}$. Other chain termination processes like β-H transfer/elimination are suppressed either $k_{\beta1} < k_{\beta2}$ or $k_\beta < k_{cg}$. [M] = transition or f-element metal moiety and [MGM] metal moiety preferentially main group metals or zinc.

Pioneering work of Mortreux and co-workers describe such an approach using Mg as MGM and [SmCp*$_2$] as [M(L)$_x$] (Cp* = pentamethylcyclopentadienyl).[6] Since 1996 a variety of transition-metal- and lanthanide-based catalyst systems have been described. Advantages and disadvantages of lanthanide- versus transition-metal-based systems in terms of the synthesis of well-defined PE materials are discussed.

Lanthanide-Based Catalyst Systems

Mortreux and co-workers used $[SmCl_2Cp^*_2Li(OEt_2)_2]$[7] (**1**), which is relatively easy to synthesise and to handle for an organo–lanthanide complex, as a precursor compound to generate the CGS by activation with dialkyl magnesium (*n*Bu-Mg-Et) compounds. Reactions can be carried out at elevated temperatures (80 °C), which provides a good solubility of the Mg-terminated polymers during the polymerisation process (Table 1).

Table 1. Selected polymerisation results accomplished with **1**/*n*Bu-Mg-Et at 80 °C, di-*n*-hexylmagnesium was used for run 8 (ethylene pressure 1 bar).

	Mg/Sm	t [min]	Activity [$kg\,mol^{-1}\,h^{-1}$]	M_n [$g\,mol^{-1}$]	PDI
1	10	5	564	1870	1.2
2	20	5	396	690	1.3
3	50	5	348	400	1.3
4	50	8.3	398	580	1.2
5	50	20.3	328	900	1.2
6	50	31	298	1300	1.3
7	1000	1480	37	460	1.1
8	134	9	–	336	1.11
9	50	41	438	1530	4.0

After precipitation of the polymer materials, the reversibility of the chain transfer is lowered accompanied with a broadening of the PDI (run 9, Table 1, PDI = poly dispersity index = M_w/M_n). Furthermore, classic polymerisation by using samarocene[8] involving β-H transfer/elimination to some extent leads to additional broadening. Activities with Mg/Sm ratios ranging from 10–50 are around 400 $kg_{polymer}\,mol_{cat}^{-1}\,h^{-1}$. Polydispersities reached for these experiments (runs 1–6, Table 1) are between 1.2 and 1.3. Very narrowly distributed polymers (PDI = 1.1) were synthesised up to a molecular weight of about 500 $g\,mol^{-1}$ (approximately 15 insertions). A high Mg/Sm ratio (1000) led to a low activity of about 40 $kg_{polymer}\,mol_{cat}^{-1}\,h^{-1}$ (Table 1, run 7). The equilibrium between CTS and CGS is shifted towards the CTS with increased Mg/Sm ratio, concentration of CGS is lowered and thus a reduction of the activity of the system is observed. Nevertheless, a high amount of polymer was produced and the long-term catalyst stability is excellent. The transfer efficiency of the catalyst system is very high, for instance run 7. Despite the high Mg to Sm ratio all Mg–alkyl functionalities have been extended (N_{exptl}/N_{theor} = 1.01). The experimental chain number (N_{exptl}) in mol was calculated from the yield of polymer divided by M_n and N_{theor} (theoretically expected chain number) which equals the number of metal–alkyl bonds available for chain extension.[6] If the temperature rises to 100 °C β-H transfer/elimination becomes an issue even before the polymers precipitate and α-olefin byproducts are produced in significant amounts. PE-Mg-PE′ is an initiator for the polymerisation of polar monomers like ε-caprolactone (80 °C) or acrylates (−78 °C) and allows for the synthesis of block copolymers directly with an overall PDI of less than 1.3. Furthermore, a large variety of products are accessible from PE-Mg-PE′.[9] A range of structural model complexes of the CTS and CGS of the Sm/Mg catalyst system have been described. Considering the classic $[SmCp^*_2(alkyl)]$ polymerisation catalyst as the CGS, the X-ray crystal structure analysis of $[SmCp^*_2Me(thf)]$[10] (Figure 1) could be considered as a model of the CGS. No structural data exist on bimetallic complexes of samarium and magnesium alkyls. The closest model of the CTS is $[SmCp^*_2AlEt_4]$[11] (Figure 1).

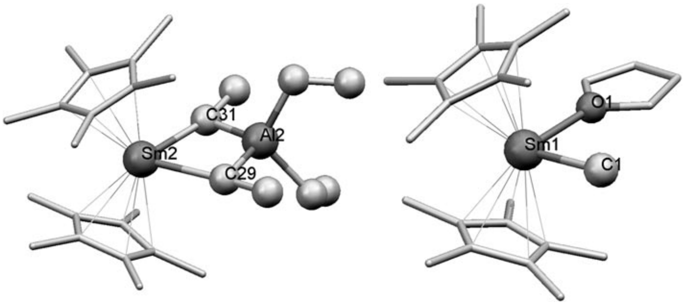


Figure 1. Molecular structures determined by X-ray crystal structure analysis of model complexes of the CTS (left) and the THF stabilised CGS (right) of the Sm/Mg catalysts system

The main disadvantage of the Sm/Mg catalyst system is the accessibility of relatively low molecular-weight spectrum if very low polydispersity (< 1.1) is required. Furthermore, the activity is low under the conditions needed to produce very narrowly distributed polymers. These disadvantages are essentially connected with a rather weak interaction/coordination of the Mg alkyls with the CTS, a rather low activity of neutral organo–lanthanide compounds and/or the side reactions caused by β-H transfer/elimination. Recently, organo–lanthanide cations were introduced and it was observed that they can polymerise ethylene with high activity.[12] Such cations should provide an enhanced Lewis acidity in comparison to neutral lanthanide alkyls and thus strongly bind a variety of main-group alkyls. Consequently, reversible chain transfer to aluminium was observed for organo–yttrium cations.[13] Such cations are accessible in high yield by treating $[Y(CH_2SiMe_3)_3(thf)_2]$[14] with one equivalent of sterically demanding aminopyridines, for instance, (2,6-diisopropylphenyl)-[6-(2,4,6-triisopropylphenyl)pyridin-2-yl]-amine (**2**, Ap*-H), which leads to $[YAp^*(CH_2SiMe_3)_2(thf)]$ (**3**). The dialkyl **3** reacts smoothly with a variety of ammonium borates for instance $[Me_2(C_6H_5)NH]^+[B(C_6H_5)_4]^-$. The abstraction of one of the alkyl functions leads to organo–yttrium cations, such as $[YAp^*(CH_2SiMe_3)(THF)_3]^+[B(C_6H_5)_4]^-$ (**4**). The cation of **4** (the molecular structure is shown in Figure 2) is a THF-stabilised model of the CGS of the Y^+/Al catalyst system.

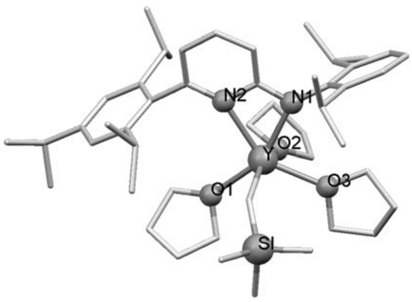


Figure 2. Molecular structure of the cation of **4**, THF stabilised CGS of the Y^+/Al catalyst system.

The Y^+/Al catalyst system shows high to very high activities if the Al/Y ratio is lower than 100. Polymerisations were done with 5 bar of ethylene pressure. In accordance with Scheme 2 increasing ethylene pressure should enhance β-H transfer/elimination. At 80 °C and after 15 min of polymerisation reaction time, very narrowly distributed polymers can be obtained (Table 2, runs 6 and 7). $N_{\text{exptl}}/N_{\text{theor}}$ for run 6, for instance, is 1.3. Two available aluminium–carbon chains per Al were considered. This assumption might be questionable, since the very low PDI value indicates a highly efficient chain transfer. Molecular weights above 3600 $g\,mol^{-1}$ (about 129 insertions) can be accessed maintaining a PDI < 1.1. Gel-permeation chromatography (GPC) data describe the behaviour of the catalyst system around the precipitation point. Extending the time of run 6 (Table 2, Figure 3), leads to a bimodal distribution in which one peak still shifts to higher molecular weights, most likely the precipitated phase, and one remains essentially at its molecular weight. The precipitated phase could be considered as the precipitated CGS continuing to polymerise in a nearly living fashion. Similar polymerisation behaviour is seen by the increase in the polymerisation temperature from 30 to 100 °C and by applying a constant polymerisation time (15 min, runs 1–4, Table 2). Alumoxanes and aluminium alkyls can be used within the Y^+/Al catalyst system, but lower activities are observed for aluminium alkyls (Table 2, runs 7–10). Aluminium alkyl compounds most likely coordinate stronger than alumoxanes.[15,16] Thus the equilibrium between CTS and CGS is shifted to higher CTS concentrations resulting in lowering of over all efficiency. The coordination chemistry of aluminium alkyls and neutral lanthanide alkyls is well documented. Such a rich coordination chemistry is not described for alumoxanes most likely because they bind much more weakly to lanthanide alkyls.[15,16]

Table 2. Selected polymerisation results accomplished with 3/TIBAO, ammonium borate: $[R_2N(CH_3)H]^+[B(C_6F_5)_4]^-$ ($R = C_{16}H_{31}$–$C_{18}H_{35}$), Y/B = 1/1.1, pressure: 5 bar, polymerisation time: 15 min, PDI is given for the main fraction if a bimodal distribution with a main fraction > 95 % was observed (run 1), other aluminium alkyls than TIBAO were used for the runs 8–10. Bimodal distributions were observed for runs 2, 3 and 5, since the polymerisations exceed the precipitation point.[a]

	Al/Y	T [°C]	Activity [$kg\,mol^{-1}\,h^{-1}$]	M_n [$g\,mol^{-1}$]	PDI
1	20	30	200	1500	1.3
2	20	50	1000	4000	19.1
3	20	80	5360	20781	3.2
4	20	100	4040	11142	1.4
5	5	80	5400	38304	2.3
6	50	80	1880	3614	1.09
7	100	80	840	1390	1.05
8 (TOAO)	100	80	760	2345	1.1
9 (TIBA)	100	80	400	n.d.	n.d.
10 (TOA)	100	80	200	n.d.	n.d.

[a] TIBAO = tetra-*iso*-butyl alumoxane, TIBA = tri-iso-butyl aluminium, TOAO = tetraoctyl alumoxane, TOA = trioctyl aluminium.

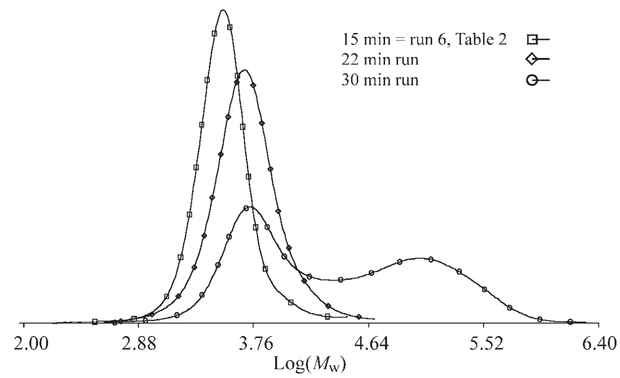


Figure 3. GPC data around the precipitation point, run 6 (Table 2) and at extended times.

Transition-Metal-Based Catalyst Systems

Reports on transition-metal-based catalyst systems can be divided into, reports on single-catalyst systems[17,18,19] and systematically accomplished studies, in which one CGS was investigated with regard to a variety of main-group alkyls[20] and vice versa.[21] Systems identified by the authors as very fast, reversible, PE chain-transfer catalysts are only taken for discussion. We do not review on chain transfer in general within this contribution.

Reports on single-catalyst systems: $[CrCp^*(Me)_2(PMe_3)]$ (**5**), a previously prepared and characterised compound,[22] has been used as a CGS after activation by methylaluminoxane (MAO), $B(C_6F_5)_3$ or perflouroaryl borates;[17] TMA and TEA (TM/EA = trimethyl/ethyl aluminium) act as the main-group alkyls. Selected results of the Cr^+/Al catalyst system are shown in Table 3.

The Cr^+/Al catalysts system was essentially used to produce oligomers. No *PDI* data were reported. Distributions of the oligomerisations reported in Table 3 vary by a factor of 2 as judged by GC data. If no transfer reagent was present, polymeric materials were produced. Activation of **5**

Table 3. Selected oligomerisation results of the Cr^+/Al catalyst system based on **5** (RT, 30 min polymerisation time, pressure 1 bar).

	Al/Cr	Activator	Al alkyl	Activity [kg mol^{-1} h^{-1}]	M_n[b] [g mol^{-1}]	PDI
1	1000	MAO	MAO[a]	278	240	n.d.
2	380	$B(C_6F_5)_3$	TMA	152	212	n.d
3	380	$B(C_6F_5)_3$	TEA	154	198	n.d

[a] MAO (MAO = methyl alumoxane) itself is not involved in the chain transfer only free TMA contained in MAO. [b] Data were estimated from published GC data.

with one equivalent of $B(C_6F_5)_3$ resulted in an organo chromium cation which was characterised by X-ray analysis (Figure 4)and can be considered as a model of the CGS of the Cr^+/Al catalyst system.

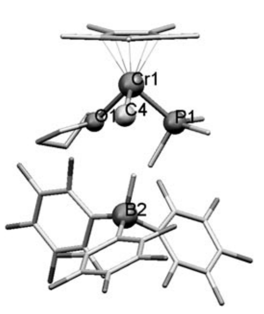


Figure 4. Molecular structure of the CGS of the Cr^+/Al catalyst system.

Chromium-based CGSs do not necessarily have to be cations. $[CrCp^*(C_6F_5)(C_7H_7)]$ (**6**, for the molecular structure see Figure 5) transfers PE very fast and reversibly to aluminium alkyls. Selected polymerisation results are summarised in Table 4.[19]

The THF-stabilised derivative of **6** was also able to accomplish very fast PE chain transfer. In the absence of TEA no oligo- or polymerisation activity was observed. THF removal by TEA is a requirement to generate the CGS. Both chromium systems were used to produce rather low molecular-weight materials and no PDI data were provided. Polymer/oligomer distributions observed for the chromium-based systems (GC data) are indicative of a mixture of a Poisson and a Schulz–Flory distribution.

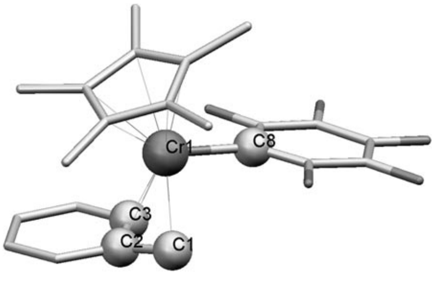


Figure 5. Molecular structure of **6** the CGS of the Cr/Al catalyst system.

Table 4. Selected polymerisation results of the Cr/Al catalyst system (RT, polymerisation time 15 min, pressure 1 bar).

	Al/Cr (TEA)	Activity [kg mol^{-1} h^{-1}]	M_n [g mol^{-1}]	PDI
1	90	211	476	n.d.
2	135	155	252	n.d
3	180	41	n.d.	n.d.

2,6-Bis[1-(2,6-diisopropylphenyl)imino)ethyl]pyridineiron(II) dichloride (**7**) activated with MAO efficiently transfers PE to diethyl zinc (Table 5).[18] GPC data are indicative that the precipitation point at room temperature is close to 1000 g mol^{-1}. Run 2 (Table 5) essentially leads to a typical "after precipitation GPC" curve, that is, a bimodal distribution in which one peak is nearly identical to the peak obtained from run 3 and a second higher molecular weight peak of "heterogeneously" grown polymer. In contrast to all catalyst systems described above, increasing the Zn/Fe ratio does not result in lowering of activity. An N_{exptl}/N_{theor} ratio of 1.00 was observed for run 3 indicative of chain extension of all available Zn–alkyl functionalities. On the other hand, the TMA/MAO concentration (introduced during the activation procedure) is constant and Al alkyls may become involved in the chain-transfer process (See detailed discussion below.). Structural data (X-ray crystal structure analysis; Figure 6) of the CGS of the $Fe^+/Al–Zn$ catalyst system were reported by Chirik and co-workers recently.[23]

Table 5. Selected polymerisation results of the $Fe^+/Al-Zn$ catalyst system (100 equiv MAO, RT, 30 min polymerisation time, pressure 1 bar).

	Zn/Fe	Activity [kg mol^{-1} h^{-1}]	M_n [g mol^{-1}]	PDI
1	0	1204	10000	19.2
2	100	1944	3000	36.8
3	500	1405	700	1.1

The $Fe^+/Al–Zn$ catalyst system was restricted to the synthesis of rather low molecular-weight polymers, mainly because the studies were performed at room temperature and hence the precipitation point was reached rather soon. In the presence of Ni complexes, PE_2Zn chain-transfers to

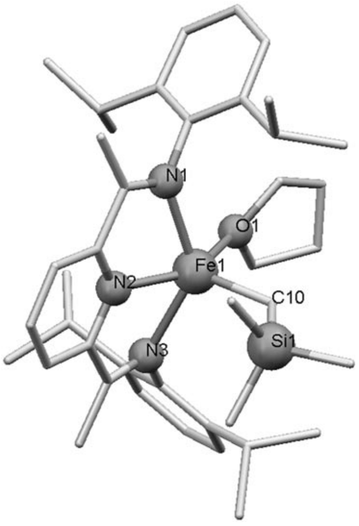


Figure 6. Molecular structure of the THF stabilised CGS of the $Fe^+/Al-Zn$ catalyst system.

nickel at which β-H transfer/elimination takes place rapidly and Poisson distributed α-olefins are obtained.[18]

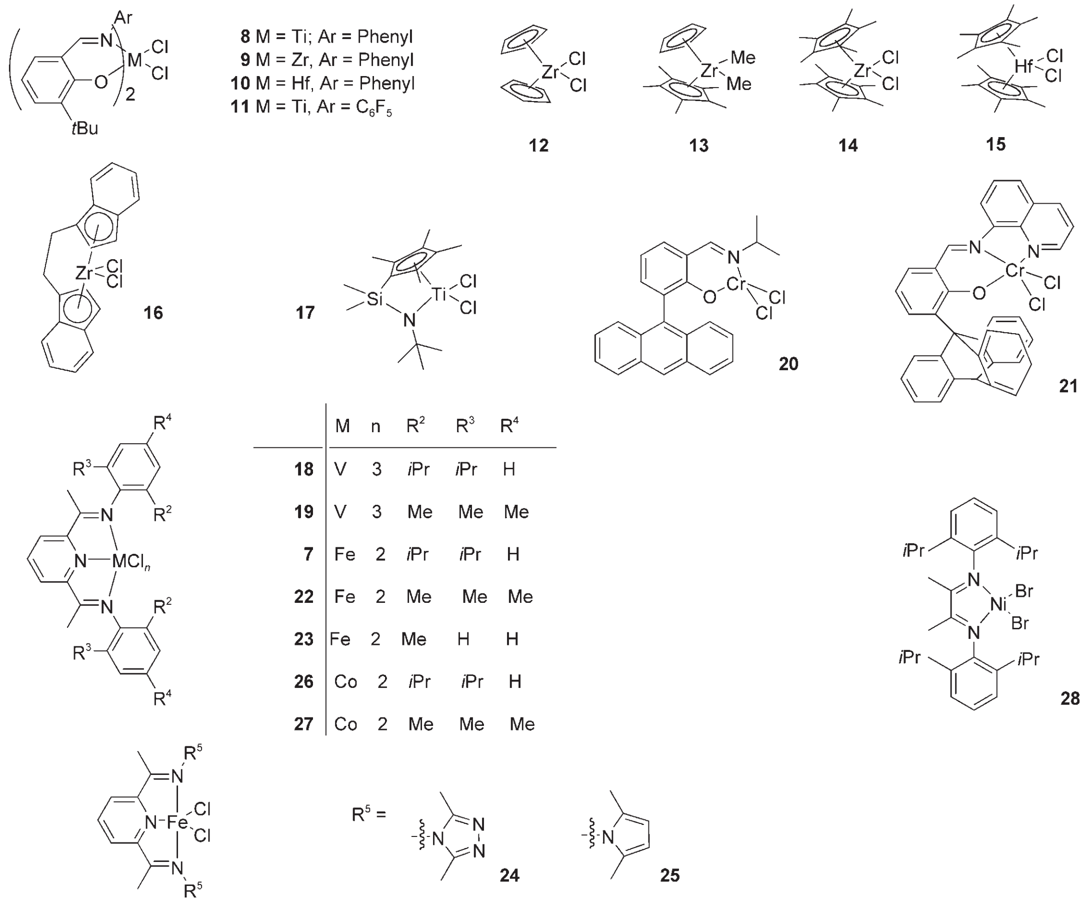
Systematic studies concerning the main group alkyl and CGS: The Fe$^+$/Al–Zn catalyst system was systematically investigated with regard to the variation of the MGM (Table 6).[20] This excellent study shows how difficult it is to find the right combination of CGS and MGM. The CGS based on bis(imino)pyridine iron complex **7** essentially transfers PE chains very fast and reversibly to zinc and gallium alkyls. No efficient transfer or no transfer at all (polymerisation data match with run 1, Table 6) is observed with Al, Li Mg, B, Sn and Pb alkyls. Inefficient transfer observed for trialkyl aluminium compounds might be tuneable to some extent by manipulating the equilibrium between CGS and CTS. Me_2AlCl, *n*BuLi, $(nBu)_2Mg$ and Et_3B irreversibly poison the CGS and suppress all polymerisation. Gallium alkyls such as Me_3Ga, Et_3Ga and $(nBu)_3Ga$ mediate the necessary reversibility. Such gallium alkyls might be considered, in general, to act in a similar fashion as diethyl zinc in a very fast chain-transfer scenario. The Fe$^+$ CGS based on **7** is limited in terms of the MGM to Zn and Ga.

Gibson and co-workers described a comparative investigation of highly active ethylene polymerisation catalysts (across the transition series) with regard to very fast chain transfer towards zinc. Pre-catalysts summarised in Scheme 3 were activated with MAO and used as CGS.[21]

Nine out of nineteen transition-metal complexes listed in Scheme 3 show catalytic polymerisation characteristics indicative of chain transfer to Zn. Polymerisation details of these complexes are listed in Table 7. Complexes **7**, **9**, **10**,

Table 6. Polymerisation results of **7** activated with MAO (100 equiv) in the presence of a variety of alkyl reagents (RT, polymerisation time 30 min, Bu = butyl, pressure 1 bar).

	MGM	MGM/FE	Activity [kg mol^{-1} h^{-1}]	M_n [g mol^{-1}]	PDI
1	none	0	1500	10000	19
2	TMA	500	1000	490	69
3	TEA	380	1100	1500	263
4	TOA	500	800	1100	39
5	TIBA	1000	2000	3100	129
6	$(iBu)_2AlH$	500	94	2600	3.7
7	Me_2AlOEt	1000	1000	21000	5
8	Me_2AlCl	500	0		
9	*n*BuLi	500	0		
10	$(nBu)_2Mg$	500	60	n.d.	n.d.
11	Et_3B	500	60	n.d.	n.d
12	Me_3Ga	520	1160	400	1.2
13	Me_4Sn	560	360	4400	12.2
14	Et_4Pb	500	900	10000	6.4
15	Et_2Zn	500	1400	700	1.1



	M	n	R^2	R^3	R^4
18	V	3	*i*Pr	*i*Pr	H
19	V	3	Me	Me	Me
7	Fe	2	*i*Pr	*i*Pr	H
22	Fe	2	Me	Me	Me
23	Fe	2	Me	H	H
26	Co	2	*i*Pr	*i*Pr	H
27	Co	2	Me	Me	Me

Scheme 3. Complexes used to catalyse chain growth on zinc after activation with 100 equiv of MAO.

Table 7. Polymerisation results of the transition-metal complexes listed in Scheme 3 that catalyse chain growing on zinc (RT, polymerisation time 30 min, ethylene pressure 1 bar).

	Precatalyst	Zn/metal	Activity [$kg\,mol^{-1}\,h^{-1}$]	M_n [$g\,mol^{-1}$]	PDI
1	**9**	0	1600	5500	23.0
2	**9**	550	1700	1000	1.1
3	**10**	0	800	7000	9.4
4	**10**	550	900	800	1.1
5	**13**	0	700	100000	3.3
6	**13**	520	1700	1100	16.0
7	**13**	2100	1700	600	1.5
8	**20**	0	220	14000	11.1
9	**20**	550	650	400	1.5
10	**21**	0	1800	900	2.0
11	**21**	550	1400	500	1.2
12	**7**	0	1500	10000	19.1
13	**7**	550	1400	700	1.1
14	**22**	0	2000	4700	9.6
15	**22**	440	2000	1000	1.1
16	**26**	0	800	3300	3.2
17	**26**	550	500	1500	1.9
18	**27**	0	700	900	2.2
19	**27**	550	500	1000	1.2

and **22** initiate reversible and very fast chain transfer to zinc, if activated with 100 equivalents of MAO. Time-dependent chain growth (Poisson distribution) was observed and chain-growth efficiency was very high, since N_{exptl}/N_{theor} values of around 1 were observed. Structural data (X-ray analysis) of the CGS or the CTS of the catalysts systems based on **9** and **10** are not documented.[24] Complexes **13**, **20**, **21**, **26** and **27** transfer PE to zinc with rather small PDI values. The distribution of the polymers accessible with these catalysts are in between Schulz–Flory and Poisson distribution, which means chain transfer is essentially not fast enough to meet the requirements discussed in Scheme 2. Some of these catalysts, for instance **21**, show other chain terminations like β-H transfer/elimination.

Interestingly, an increase in the Zn/metal ratio does not reduce the overall catalytic activity of any of the catalysts. This behaviour differs drastically from transfer processes involving Al or Mg alkyls. It seems at this stage that diethyl zinc does not behave differently, but that different transfer mechanisms are involved for diethyl zinc and TMA (which is a part of MAO) mixtures. TMA/MAO is constant regarding its concentration and may determine the equilibrium between CTS and CGS in these very fast, reversible, chain-transfer processes and thus the overall efficiency/activity. TMA could be involved in the transfer process, for instance as primary transfer alkyl that exchanges alkyl chains in a catalytic or non-catalytic fashion with zinc alkyls. Chain transfer of **7** activated with MAO to aluminium alkyls is well documented.[25]

Conclusions and Perspectives

Chain growth on main-group metal or zinc alkyls catalysed by transition-metal or lanthanide complexes displays a highly efficient way to synthesis PE material in a very controlled fashion: narrowly distributed (PDI < 1.1) and with a molecular weight of choice up to 4000 $g\,mol^{-1}$.

Criteria for very fast, reversible, chain transfer are very narrow molecular-weight distributions < 1.1 up to the precipitation point,[13] linear time-dependent chain growth during which β-H transfer/elimination is suppressed giving rise to Poisson distributed polymers.[21]

Only a few systems have been described that meet these requirements so far: the Sm/Mg system based on **1**, the Y^+/Al system based on **3**, the Zr^+ or Hf^+/Al–Zn system based on **9** and **10** and the Fe^+/Al–Zn based on **7** or **22**. For the catalyst systems based on **5** and **6**, not enough data are available to evaluate the potential of these catalyst systems.

A comparison of the catalyst systems at this stage is difficult, since many open questions remain. The lanthanide-based catalyst systems operate at 80 °C and also at higher ethylene pressure. According to Scheme 2 β-H transfer/elimination becomes much more relevant at higher monomer concentrations. At elevated temperatures the solubility of the growing PE chains are better and thus narrowly distributed polymers with significantly higher molecular weight (by a factor of four) can be synthesised (Y^+/Al catalyst system). Furthermore, the borate activation procedure avoids unwanted side reactions that may arise during the MAO activation procedure, since alumoxanes and TMA may become involved in the chain-transfer process. The introduction of a second transfer reagent also has advantages; for instance, the remaining overall activity with increased concentration of the reagent. The Sm/Mg catalyst system does not need to be activated at all (besides alkylation). For the lanthanide-based catalyst systems, the nature of the CGS is known in detail and the coordination chemistry of neutral Ln alkyls and Al alkyls is well described.[15,16] Alumoxanes, Al, Mg, Ga and Zn alkyls have been described to mediate very fast chain transfer. No CGS has been described yet for which more than two of these alkyls work efficiently. Systematic studies are only known for the Fe-based catalyst system. They have shown that only zinc and Ga alkyls match. A better understanding of the nature of the main-group metals with regard to the ability to mediate reversible and fast chain transfer would be interesting. The most suited system to do so is the catalyst system based on **3**, since it already covers alumoxanes and Al alkyls. It is also important to gain more insight into the unusual Zn effect (MAO-activated systems) in comparison to Al and Mg in terms of not lowering the overall activity by increasing the Zn to CGS ratio.

Organic and materials chemistry resulting from the well-defined PE materials is rich.[1b,26] In addition, higher molecular weight PE blocks are now accessible from the Y^+/Al catalyst system. Mg alkyls directly initiate a variety of consecutive reactions that lead to narrowly distributed block copolymers and end-group functionalisations.[6,9] Thus Mg is an interesting metal to use in the transfer reactions. In terms of the polymerisation chemistry, direct copolymerisation processes should be possible in a reversible, chain-transfer scenario by means of simultaneous addition of two monomers; however, this possibility has not yet been explored much yet. Coordinative chain-transfer polymerisation (CCTP) could be combined with chain shuttling[27] in many ways. CCTP catalyst systems are ideally suited for chain shuttling protocols. Diblocks of PE and stereo-controlled PP should be accessible through a combination of very fast, reversible, chain transfer and selective PP chain extension should be accessible through chain-shuttling polymerisation. Ln-based CGS became poisoned by propylene addition via allyl formation and thus PP chain enhancement by a second catalyst could become dominating. If only propylene is fed after addition of the second catalyst pure diblocks might be obtained. Other industrial applications of CCTP catalyst systems besides chain shuttling seem possible since Zieglers Aufbaureaktion is still a protocol of industrial relevance.

The scope of the lanthanide-based catalyst systems seem to be boarder (temperature and pressure range as well as the nature of the MGM) and thus at this stage more suited to produce well-defined PE materials. It can be addressed essentially to Ln-specific functionalities like large and tuneable size of the metal centres in combination with a high Lewis acidity both allow for the specific binding between the CGS and the main-group alkyl; this seems to be the prerequisite for a very fast, reversible, chain transfer. To make the Ln-based protocols more accessible it would be helpful to search for starting complexes that are not based on difficult to handle homoleptic silylalkyls. The number of efficient CCTP catalyst systems is still low and lots of research is necessary to find new catalyst systems. Once more, the fine tuning of ligand environments of polymerisation catalysts in order to adjust reaction rates is the key step for further development of CCTP catalysts. Of major relevance is high-temperature stability as this leads to better polymer solubility und high-pressure catalyst performance, since unwanted side reactions like β-H transfer/elimination may become more relevant with increasing pressure (and temperature). The Y^+/Al catalyst system seems to be suited to work highly controlled at higher ethylene pressures and at high temperatures. Reports on CCTP experiments at ethylene pressure higher than 1 bar are rare.

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