Macromolecules **2008**, *41*, 4095–4101

Decisive Progress in Metallocene-Catalyzed Elastomer Synthesis

Aleksander Ostoja Starzewski,*,[†] Norbert Steinhauser,[‡] and Bruce S. Xin[§,||]

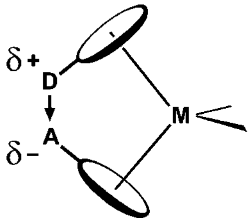
LANXESS Deutschland GmbH, 51368 Leverkusen, Germany, LANXESS Deutschland GmbH, Dormagen, Germany, and Bayer AG, Leverkusen, Germany

Received April 1, 2008; Revised Manuscript Received April 10, 2008

ABSTRACT: Within the last 2 decades a large number of metallocene/MAO copolymerization catalysts has been developed, targeting tailor-made high-quality ethylene–propylene elastomers. However, under the widely used EP(D)M solution polymerization process temperatures, conventional metallocene catalysts give only access to the lower 15% of the commercial molecular weight range, established with Ziegler–Natta catalysts, which extends to about 10^6 g/mol. The novel class of donor–acceptor metallocenes makes a quantum leap in enhancing in EP(D)M molecular weights by orders of magnitude. Thus, the full molecular weight range of tailor-made polyolefin elastomers up to ultra high molecular weights is now accessible. At lower temperatures the D–A metallocene catalyst systems approach 100% chain growth selectivity in living olefin homo- and copolymerizations.

Introduction

Donor/acceptor metallocene catalysts are characterized by the coexistence of donor (D) and acceptor (A) groups in complex sandwich structures, which may be D/A bridged or unbridged. Highly polar dative transannular D/A interactions in bridged states and Lewis basic and Lewis acidic functionalities in unbridged states are the resulting structural features, which establish unique catalytic performances in olefin polymerizations.[1]



(1)

The specific choice of the D/A bridge, the π-ligands, and the transition metal has defined the subclass of (P–B)-bridged (Flu)(Cp) zirconocenes. In ethylene homopolymerization, these (Flu)(Cp)-D/A zirconocenes exhibit ultrahigh selectivity for chain propagation (e.g., 99.999%, $M_n = 2.8 \times 10^6$ g/mol), even at elevated polymerization temperatures. They thus provide synthetic access to high performance polyethylenes in the ultrahigh molecular weight range 10^6–10^7 g/mol.[1a]

Other advanced PE metallocene catalysts have been developed with extraordinary catalyst activities.[2] Structurally different metallocenes again were successfully designed to generate high molecular weight PPs of various tacticity at process-relevant temperatures.[3] The applicability of metallocene technology to important areas of ethylene copolymers, however, is still restricted due to limited copolymer molecular weights and disadvantageous low temperature properties. For example, as yet there is no metallocene EP(D)M grade having very high molecular weight available on a commercial scale.

In ethylene copolymerizations, the material properties change dramatically with increasing amounts of comonomer incorporation from thermoplastic (medium density polyethylene MDPE and linear low density polyethylene LLDPE) via plastomeric to the domain of semicrystalline and amorphous elastomeric polyolefins (POEs).[4] Unlike natural rubber or butadiene-based synthetic elastomers, POEs consist of macromolecules with fully saturated main chains. Accordingly, they are less sensitive to oxygen, ozone, UV light, and heat and thus show a better aging resistence. The majority of these POEs (>1 million t/a) is represented by copolymers of ethylene and propylene (EPM) and—even more important—terpolymers of ethylene, propylene, and smaller amounts (2–10 wt %) of a diene, the so-called EPDM rubber. EP(D)M grades are produced using nonconjugated dienes with double bonds of different reactivity (e.g., 5-ethylidene-2-norbornene, 5-vinyl-2-norbornene, dicyclopentadiene) and are in particular suitable for peroxide, resin or sulfur vulcanization.[5]

EP(D)M elastomers, which possess especially good elastic properties even at low temperatures, have little or no crystallinity (melt enthalpy ΔH_m 20 – 0 J/g from DSC measurements), which in the case of EPM results from a statistical distribution of ca. 30–50 mol % (ca. 40–60 wt %) of propylene and 70–50 mol % (60–40 wt %) ethylene, respectively. These specialty elastomers are valuable materials for outdoor applications (e.g., automotive and construction). Glass transition temperatures (T_g) of approximately −45 °C and even down to −60 °C can be obtained with vanadium-based Ziegler–Natta catalysts in the most frequently used commercial solution process (approximately 75% of all production plants) at polymerization temperatures of 30–80 °C.[5c,d] Higher amounts of ethylene result in higher crystallinity and higher glass transition temperatures. These products, as well as those with much lower ethylene and very high propylene contents, will not be considered in this publication because of their inferior low temperature elasticity (see T_g values in Table 1, entries 1 and 4a).

The material properties of EPM and EPDM result from the chemical composition of the polymer and from the catalyst selectivity under given process conditions. Selectivity controls size (molecular weight) and architecture of the formed macromolecules. The architectural selectivity of metallocene polymerization catalysts by now can be chosen out of a large and still growing variety of individual metallocene structures.[6–13] The metallocene structure determines for a given monomer feed the amount of comonomer incorporated and its distribution in a statistical, a blocky or an alternating fashion. In particular *ansa*-metallocenes allow for any amount of comonomer incorporation and thus any number of short chain branches with uniform chemical composition and branching distribution. The

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* To whom all correspondence should be addressed. E-mail: aleksander.ostoja-starzewski@uni-bayreuth.de.

[†] LANXESS Deutschland GmbH, Leverkusen, Germany.

[‡] LANXESS Deutschland GmbH, Dormagen, Germany.

[§] Bayer AG, Leverkusen, Germany.

[||] Present adress: Mitsubishi Chemical Corp., Yokohama, Japan.

10.1021/ma8007306 CCC: $40.75

Table 1. Ethylene/Propylene/ENB Terpolymerizations Using Conventional Metallocene/MAO Catalysts and a Constrained Geometry Half-Sandwich Catalyst[a]

metallocene no.	formula	T_0 [°C]	T_p [°C]	A [t/mol·h]	[η] [dL/g]	M_η [g/mol]	mol wt range	P/ENB [wt %]	T_g [°C]	H_m [J/g]
1	$[(Cp)_2ZrCl_2]$	40	40	25	0.65	33 000	low	32/5	−35	42
2	*rac*-$[C_2H_4(Ind)_2ZrCl_2]$	40	42	33	0.74	40 000	low	42/11	−50	0
3	$[Me_2C(Flu)(Cp)ZrCl_2]$	40	43	25	0.58	29 000	low	51/5	−55	0
4	$[Me_2Si(Me_4Cp)(N\text{-}tBu)TiCl_2]$									
4a		40	42	6	1.76	136 000	low	83/2	−27	0
4b		80	88	48	1.22	81 000	low	66/5	−43	0
4c		80	87	116	2.30	197 000	medium	51/2	−52	4

[a] Abbreviations used: Me, methyl; tBu, *tert*-butyl; Cp, cyclopentadienyl; Flu, fluorenyl; MAO, methylaluminoxane (cocatalyst); T_0, temperature at start of polymerization; T_p, polymerization temperature; [η], intrinsic viscosity, measured in *o*-dichlorobenzene (ODCB) at 140°C; M_η, calculated viscosity average molecular weight; solvent, toluene 100 mL, propene, 10 g; ENB, 1 g; ethene pressure, 4 bar (12 bar entry 4c), Al/Zr ratio 10000; t_p, polymerization time 30 min.

specific metallocene structure furthermore governs the regiochemistry of the comonomer incorporation (i.e., 1−2, 2−1, 1−3 propylene insertions) as well as the stereochemical microstructure by steering the probability for atactic, isotactic and syndiotactic insertions. In this respect and to overcome vanadium inherent catalyst properties (redox instability, activity decline, coloration etc.), metallocene catalysts seem to be obvious candidates for the development of advanced polymerization technologies, which can offer arrays of synthetic elastomers with fine-tuned properties in a precise differentiation, currently not accessible with the established Ziegler−Natta technology. In fact, bridged amido-cyclopentadienyl half-sandwich titanium catalysts with a constrained geometry (CGC), which are conceptually related to *ansa*-metallocenes, are already in use industrially in a homogeneous solution process for ethylene−propylene and other ethylene-1-olefin copolymers. Despite of less highly developed selectivity-directing ligand control instruments and missing C_2 and C_{2v} symmetry options to enter or delete enantioface selectivity, the modern single-site CGC technology has generated a broad range of competitive, basic materials within the steadily growing world market of EP(D)M and related matter, also by providing novel polyolefin elastomers, such as ethylene−1-octene elastomers.[14] However, there is still a gap to cover the full range of established EP(D)Ms which are currently available by conventional vanadium-based catalyst systems, and further development on a technical scale is needed.

Metallocenes, different from CGC catalysts, in combination with the highly efficient cocatalyst methylaluminoxane (MAO) for the production of ethylene−propylene or other ethylene−1-olefin elastomers in a solution process at temperatures of at least 40−70 °C are facing "the molecular weight problem" as a serious drawback.[9d] In metallocene-based copolymerizations, where the monomer feed has been adjusted to generate copolymers with similar amounts of ethylene and propylene incorporated, the catalyst selectivity for chain growth suffers more severely from competing termination and/or chain transfer reactions than in the corresponding homopolymerizations.[6−13] In fact, after more than twenty years of metallocene research the accessible molecular weight range under solution process conditions still covers only the lower 15 % of the established Ziegler−Natta molecular weight range of the commercial EP(D)M grades, which extends to about 10^6 g/mol. Slurry and gas phase polymerization processes can partly circumvent the catalyst inherent problem, but they do not give access to the full property range. In order to avoid investments for additional production plants, utilizing different processes, and due to a broader product flexibility of the homogeneous process, the search for *advanced metallocene copolymerization catalysts for the production of EP(D)M and other polyolefin elastomers* for the solution and the slurry process goes on.

Results and Discussion

To visualize the established metallocene performance, we report EPDM test results obtained from comparable experiments in the relevant temperature window for three prototypic ziconocenes of distinctely differing structure and symmetry and for a bridged amido-cyclopentadienyl half-sandwich titanium catalyst in Table 1. The MAO-activated unbridged metallocene bis(cyclopentadienyl)zirconium dichloride (PE catalyst, C_{2v} symmetry) has the highest ethylene selectivity (ethylene contents 63%) of the four catalysts. (entry 1) The accordingly low propylene incorporation of 32% results in high crystallinity (H_m = 42 J/g) due to crystallizing oligoethylene sequences and in a relatively high glass transition temperature $T_g = -35$ °C. The intrinsic viscosity of 0.65 dL/g corresponds to a calculated viscosity average molecular weight of only 33,000 g/mol. The covalently bridged *rac*-ethylene−bis(indenyl)zirconocene (i-PP catalysts, C_2 symmetry) allows for a higher incorporation of propylene (42%) and ENB. The terpolymer is amorphous with a low T_g of −50 °C. Again, the molecular weight $M_\eta = 40\,000$ g/mol is low (entry 2).

The isopropylidene−(fluorenyl)(cyclopentadienyl)zirconocene (s-PP catalysts, C_s symmetry) further improves propylene incorporation to 50% and lowers the T_g to −55 °C. The molecular weight, however, is only 29 000 g/mol. (entry 3). The situation changes significantly when using the dimethylsilylene-bridged *tert*-butylamidotetramethylcyclopentadienyltitanium constrained geometry catalyst. The M_η improves to 136 000 g/mol with an extremely high propylene incorporation of 83%, which is detrimental to the glass transition temperature ($T_g = -27$ °C) and thus not desired. (entry 4a) At this polymerization temperature (42 °C), the catalyst activity is only 6 t/mol·h. A high catalyst activity however is obtained at 88 °C. (entry 4b) By raising the ethylene pressure from 4 to 12 bar (entry 4c) an EPDM of proper composition, low crystallinity, low T_g, and of at least medium molecular weight of 197 000 g/mol is obtained.

Throughout this publication the catalyst performance is classified according to six molecular weight ranges, based on viscosity average molecular weights M_η. Sometimes the classification is based on GPC data (denoted in Table 2 as GPC) assuming that M_η is lower than the reported weight average molecular weight M_w.

EP(D)M molecular weight ranges, used for classification, are as follows.

1. very low: for molecular weights below 10 000 g/mol
2. low: for molecular weights below 150 000 g/mol
3. medium: for molecular weights between
150 000 and 300 000 g/mol (2)
4. high: for molecular weights above
300 000 g/mol up to 500 000 g/mol
5. very high: for molecular weights above 500 000 g/mol
6. ultrahigh: for molecular weights of 1 000 000 g/mol and more

Table 2. Insufficient Molecular Weight Capabilities of Conventional Zirconocene/MAO Catalysts for Ethylene−Propylene Co- and Terpolymerizations in Solution[a]

metallocene no.	formula	POE	T_p [°C]	mol wt range of M_η	refs
1	$[(Cp)_2ZrX_2]$ X = Cl, Me	EP(D)M	50, 20	low	6a, 8a, 9a
2	$[(Ind)_2ZrCl_2]$	EPM	50	low (GPC)	8a
3	$[Me_2Si(Cp)_2ZrCl_2]$	EPDM	30	very low	6e
4	*rac*-$[Me_2C(3\text{-}tBu\text{-}Cp)_2ZrCl_2]$	EPM	50	low	7d, g
5	*rac*-$[C_2H_4(H_4Ind)_2ZrCl_2]$	EPM	50	low	7f, i, 8a
6	*rac*-$[C_2H_4(Ind)_2ZrCl_2]$	EP(D)M	50, 40	low	6b, 7g, 8a, 9c, 13
7	*rac*-$[Me_2Si(Ind)_2ZrCl_2]$	EPDM	70	low	8f
8	*rac*-$[Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2ZrCl_2]$	EPM	50, 70	low	7g, 9d
9	*rac*-$[Me_2Si(2\text{-}Me\text{-}4\text{-}Naph\text{-}Ind)_2ZrCl_2]$	EPM	30	low (GPC)	6f
10	$[Me_2Si(Flu)_2ZrCl_2]$	EPM	50	low	7f
11	$[C_2H_4(Flu)_2ZrCl_2]$	EP(D)M	70	low	8f
12	$[Ph_2C(Flu)(Cp)ZrCl_2]$	EPDM	30	low	6e
13	$[Me_2Si(Flu)(Cp)ZrCl_2]$	EPDM	30	low	6e
14	$[Me_2C(Flu)(Cp)ZrCl_2]$	EP(D)M	60, 30	low	6c, e
15	$[Me_2C(Flu)(3\text{-}Me\text{-}Cp)ZrCl_2]$	EP(D)M	60, 30	low	6c, e
16	$[Me_2C(Flu)(3\text{-}tert.Bu\text{-}Cp)ZrCl_2]$	EP(D)M	60, 30	low	6c, e
17	$[Me_2C(Flu)(3\text{-}Ph\text{-}Cp)ZrCl_2]$	EPDM	30	low	6e
18	$[(4\text{-}Me\text{-}Ph)_2C(2,7\text{-}tBu_2Flu)(Cp)ZrCl_2]$	EPM	30	low	6h
19	$[C_2H_4(Flu)(Ind)ZrCl_2]$	EPM	−40	very low (GPC)	11a
20	$[Me_2C(Flu)(Ind)ZrCl_2]$	EPM	0	very low (GPC)	12c
21	$[Me_2Si(Flu)(Ind)ZrCl_2]$	EPM	45, 0	low	6g, 12c
22	$[Ph_2Si(Flu)(Ind)ZrCl_2]$	EPM	45, 0	low	6g
23	$[Ph_2Si(Me_8H_8dibenzoFlu)(2\text{-}Me\text{-}Ind)ZrCl_2]$	EPM	45	low (GPC)	6g

[a] Abbreviations used: POE, polyolefin elastomer; Me, methyl; Ph, phenyl; Naph, naphthyl; Cp, cyclopentadienyl; Ind, indenyl; Flu, fluorenyl; MAO, methylaluminoxane; T_p, polymerization temperature; M_η, calculated viscosity average molecular weight.

Table 2 lists a rich variety of metallocene structures reported in the literature, which have been studied under MAO-activation as copolymerization catalysts at polymerization temperatures between 40 and 70 °C. Some have been tested at lower temperatures. All of these zirconocene catalysts produce only low or very low molecular weight EP(D)M in the relevant temperature range, when the polymer composition had a propylene content of 40−60 wt %.

Medium, high, very high and ultra high molecular weights are not accessible at all.[15]

However, in particular, these tough elastomers are necessary for heavy duty applications, wherever outstanding resilience and compression sets, high tear resistence, high tensile strength, and low abrasion are needed.

The insufficiencies of metallocene/MAO catalysts for the purpose defined above include unbridged as well as covalently bridged metallocene structures with cyclopentadienyl, indenyl, fluorenyl, and heterocyclic ligands with or without additional ring substituents, with various covalent transannular bridges and with C_1, C_2, C_{2v}, or C_s symmetry.

Fluorenyl−metallocenes, in principle, are attractive development candidates for novel copolymerization catalyst technologies due to their potential for a tunable stereo- and sequence-control. Fluorenyl metallocene structures have been designed for *alternating* ethylene−propylene copolymerizations and thus for high (i.e., equimolar) comonomer incorporation. The inherently high proportions of alternating EPE and PEP monomer sequences coincide with depressed molecular weights. Some of these catalysts produce very low molecular weight materials at polymerization temperatures as low as 0 °C even down to −40 °C.[11a,12c] β-H transfer from the last inserted propylene unit to complexed ethylene has been suggested to be responsible for the severe molecular weight decrease, specific for EP copolymerizations.[12c] The other side reactions known from ethylene and propylene homopolymerizations i.e. β-H-transfers from the growing chain to the active metal center or to coordinated monomer, and β-methyl transfer from last inserted propylene unit to the active metal center or to coordinated monomer and chain transfer to aluminum (MAO) may also compete with chain growth. Fan and Waymouth have shown that MAO-activated $[Me_2Si(Flu)(4,7\text{-}Me_2Ind)ZrCl_2]$ in liquid propylene (slurry polymerization) suppresses these side reactions, forming a highly alternating high molecular weight EPM at 0 °C.[12d]

Symmetry and geometry constraints and the well-developed conventional ligand, bridge and substituent toolbox for PE and PP metallocene catalysts so far are inadequate to meet the molecular weight requirements for elastomers. Obviously, other structural features are needed.

We have therefore investigated the D/A metallocenes **1**, **2**, and **3** with respect to elastomer syntheses at low, medium, and high polymerization temperatures. The most important findings are reported in the following section.

Chart 1

$(Flu)Et_2PBEt_2(Cp)ZrCl_2$, **1**

$(Flu)Et_2PBPh_2(Cp)ZrCl_2$, **2**

$(Flu)Et_2PB(C_6F_5)_2(Cp)ZrCl_2$, **3**

In a *propylene homopolymerization* experiment at −8 to −6 °C the MAO-activated C_1-symmetric P/B-(fluorenyl)(cyclopentadienyl)zirconocene **3** (Al/Zr = 1000) generates *elastomeric* PP with enhanced syndiotacticity (*rr* triads 52%), having a glass transition at 0 °C. The catalyst efficiently suppresses all chain growth terminating reactions and the PP molecular weight increases linearly with time. The polydispersity is relatively small and remains at M_w/M_n = 1.5−1.6 during the whole polymerization. The amount of polymer formed per mol of metallocene based on yield (e.g., 591 kg PP/mol Zr after 1 h) resembles the number average molecular weight M_n (e.g., 531 000 g/mol PP for the polymer isolated after 1 h) obtained from high temperature GPC measurements. (Figure 1) The approximate numerical coincidence suggests a high activation efficiency, so that the number of macromolecules formed is approximately equimolar to the amount of metallocene catalyst applied. Each macromolecule carries one metallocene fragment attached to the growing end of the chain, which remains active and attached throughout the chosen polymerization time of 1 h. The observations reflect the scenario of a living olefin insertion polymerization with an initiation efficiency close to 1. [16] The PP molecular weight grows with a rate of

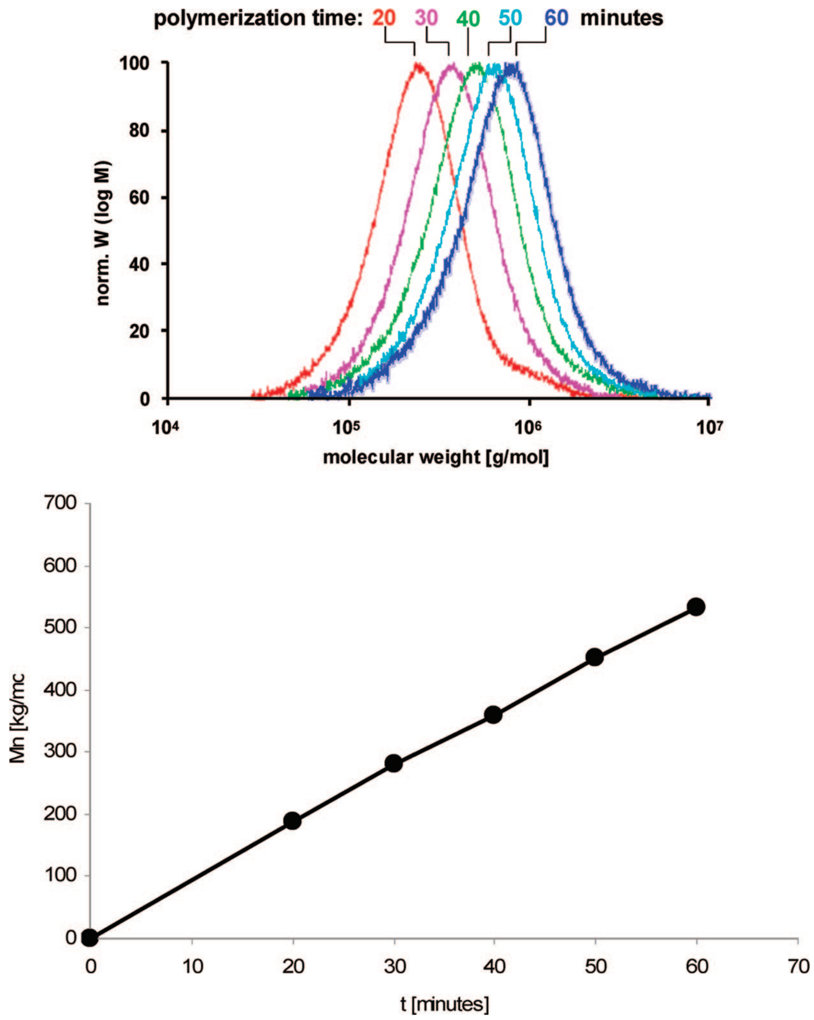

Figure 1. (a) Time-dependent GPC curves of elastomeric polypropylene using MAO-activated [(Flu)$Et_2PB(C_6F_5)_2$(Cp)$ZrCl_2$] (**3**) as polymerization catalyst. (b) Number average molecular weight (M_n) as a function of polymerization time.

approximately 9 kg/min and reaches M_n = 280 000 g/mol, M_η = 390 000 g/mol, and M_w = 407 000 g/mol after 30 min and M_n = 531 000 g/mol, M_η = 768 000 g/mol, and M_w = 856 000 g/mol after 60 min.

An EPM elastomer with E/P composition of 50/50 wt % is obtained with the same catalyst from 50 g of propylene in 500 mL of toluene and 4 bar of ethylene (total pressure 5.2 bar) at 0 to 11 °C. This EP copolymerization performs with an even higher propagation rate, resulting in an extremely fast molecular weight build up of ca. 40 kg/min into the ultrahigh molecular weight range in a living fashion. M_η values of 608 000 (M_n = 402 000), 1 216 000, and 1 858 000 g/mol are obtained after 10, 20, and 30 min, respectively.

When the MAO-activated D/A Metallocene **3** is applied at industrially relevant EP(D)M solution process temperatures, it produces in co- and terpolymerization runs high-quality EPM and EPDM elastomers with high activity (nonliving) in the desired *high* molecular weight range. The EPM reaches within 30 min M_η = 484 000 g/mol at 48 °C. Replacing the pentafluorophenyl substituents in **3** by less electron withdrawing phenyl-substituents on the boron atom in **2**, the catalyst turns out to be even more selective for elastomer chain growth. The EPM molecular weight M_η obtained at ca. 45 °C of 769 000 g/mol, i.e., nearly *doubled* relative to that of the elastomer obtained with **3** thus entering the *very high* molecular weight range. In order to identify the minimal structural requirements for high chain growth selectivity, we have diminished steric effects and deleted possible phenyl-pi-interactions in utilizing the diethylboranyl derivative **1**. Surprisingly, this structurally much simpler D/A metallocene structure even *triples* the high molecular weight obtained with **3**. With 1 400 000 g/mol obtained at 46 °C the *ultra high* molecular weight range is accessible with (diethylphosphinofluorenyl)(diethylboranylcyclopentadienyl)-zirconocene dichloride catalyst system **1**/MAO. (Table 3, entries 1−3) Slightly higher molecular weights are obtained for the terpolymers EPDM. (Table 3, entries 4−6) Terpolymerization performed at ca. 65 °C give access to medium and high molecular weights (Table 3, entries 7−9).

The molecular weight data obtained with **1**, **2** and **3** at ca. 45 and 65 °C (Table 3) document a remarkable steering power provided only by the acceptor substituents in the modular D/A metallocene architecture. The newly established metallocene-EP(D)M molecular weight level from 239 000 g/mol to 1.4 million g/mol at relevant solution process polymerization temperatures is unprecedented with metallocene catalysts. By using other D/A metallocenes, the ligand controlled molecular weight range exceeds 10^4−10^6 g/mol. Raising or lowering the polymerization temperature or adding hydrogen as molecular weight regulator further extends this range. Advanced tools for tailoring EP elastomers are now on hand. By using two D/A-derivatives such as [(Flu)Et_2PBPh_2(Cp)$ZrCl_2$] (**2**) and [(Cp)Et_2PBCl_2(Cp)$ZrCl_2$] (**4**) in the same reactor, it is possible to generate a targeted molecular weight distribution. An example for a bimodal EPM molecular weight distribution is given in Figure 2.

Table 3. D/A Metallocene/MAO-Catalyzed Ethylene Co- and Terpolymerizations[a]

entry	D/A	POE	T_0 [°C]	T_p [°C]	A [t/mol Zr·h]	[η] [dL/g]	M_η [g/mol]	mol wt range	P/ENB [wt %]	T_g [°C]	H_m [J/g]
1	**1**	EPM	40	46	25	9.2	1 400 000	ultrahigh	45/0	−56	14
2	**2**	EPM	40	45	82	6.0	769 000	veryhigh	57/0	−55	8
3	**3**	EPM	40	48	46	4.4	484 000	high	65/0	−51	0
4	**1**	EPDM	40	42	22	9.3	1 418 000	ultrahigh	34/3	−48	20
5	**2**	EPDM	40	46	49	7.1	949 000	veryhigh	51/4	−49	5
6	**3**	EPDM	40	43	59	4.7	536 000	veryhigh	60/5	−49	0
7	**1**	EPDM	60	65	23	3.9	416 000	high	40/5	−51	10
8	**2**	EPDM	60	64	28	3.3	326 000	high	49/5	−49	3
9	**3**	EPDM	60	65	42	2.6	239 000	medium	45/5	−49	4

[a] Abbreviations used: MAO, methylaluminoxane(cocatalyst); T_p, polymerization temperature; [η], intrinsic viscosity, measured in *o*-dichlorobenzene (ODCB) at 140°C; M_η, calculated vicosity average molecular weight; solvent, toluene; ethylene pressure, 4 bar; propene, 10 g; ENB, 5-ethylidene-2-norbornene, 2 g; Al/Zr ratio, 10 000; t_p, polymerization time 30 min.

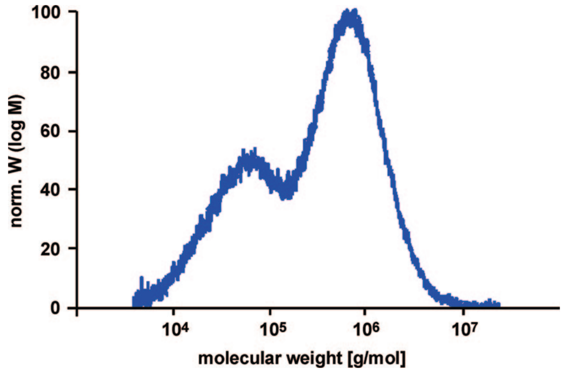

Figure 2. Bimodal EPM molecular weight distributions obtained at 50 °C with two MAO-activated D/A metallocenes [(Flu)Et_2PBPh_2(Cp)$ZrCl_2$] (**2**) and [(Cp)Et_2PBCl_2(Cp)$ZrCl_2$] (**4**).

Conclusions

In summary, fluorenyl-cyclopentadienyl D/A metallocene catalysts with highly polar phosphorus−boron bridging moieties exhibit outstanding performance in polyolefin elastomer synthesis, as they impose extreme selectivity for chain propagation in homo-, co-, and terpolymerizations.

At lower temperatures they suppress all chain terminating reactions and approach 100% selectivity in favor of monomer insertion. Accordingly, they can be used as catalysts for the living olefin insertion polymerization with a good activation and initiation efficiency. Any desired molecular weight can be obtained by simply adjusting the polymerization time.

At higher polymerization temperatures D/A metallocenes prove to be highly efficient MAO activated copolymerization catalysts for the synthesis of designed very low, low, medium, high, very high and even ultrahigh molecular weight elastomers. The modular D/A metallocene catalyst system provides tools for tailored molecular weight distributions (MWD). The herein described catalysts **2** and **3** feature outstanding molecular weight capabilities in conjunction with enhanced comonomer incorporation. The combination with a second metallocene catalyst, selective for the medium or low molecular weight range and with lower comonomer reactivity alters—in a predictable way—the MWD together with the chemical composition distribution. The latter will be reversed (i.e., higher comonomer incorporation at high molecular weight) relative to Ziegler−Natta systems.[9a] Thus, new and interesting property/processing material profiles may be tailored from the chemical variability of the D/A metallocene concept without the need for multistage process technology.[17]

The described catalytic features are not limited to propylene copolymerizations, but are also beneficial for the synthesis of new low-T_g polyolefin elastomers such as ethylene-hexene elastomers (EHM) with glass transition temperatures down to − 65 °C.

Experimental Section

The D/A metallocenes **1**, **2**, and **3** were prepared according to the procedure described in ref 1a by reacting zirconium tetrachloride with the corresponding diorganylboranyl−trimethylsilylcyclopentadiene, forming the acceptor half-sandwich complex 1-diorganylboranylcyclopentadienylzirconium trichloride, which is converted into the D/A metallocene by reaction with 9-diethylphosphinofluorenyllithium.

The D/A metallocene **4** was prepared according to the procedure described in ref 1f.

Living Polymerization of Propene. A dry, oxygen-free, mechanically stirred 1.4 L V4A steel autoclave, provided with jacket cooling, was charged with 600 g of toluene at 20 °C, and 200 g of propene was subsequently added via a pressure lock. At an internal temperature of −8 °C and an internal pressure of 2.8 bar, the catalyst was added via a pressure lock. The catalyst employed comprised 15 × 10^{-6} mol of [(flu)$Et_2PB(C_6F_5)_2$(cp)$ZrCl_2$] (**3**) and 9.9 mL of a 10% solution of MAO in toluene (15 mmol of Al). The Al/Zr ratio was 1000. During the polymerization, samples were taken at various times and analyzed using HT-GPC. The polymer formed in each case was precipitated in ethanol, stirred with ethanol/hydrochloric acid 90/10, filtered, washed with ethanol, and dried to constant weight at 80 °C in a vacuum drying oven.

after 20 min
at a reactor temperature of −7 °C
GPC (universal calibration)
M_w = 285 kg/mol
M_n = 186 kg/mol
PD = 1.53
after 30 min
at a reactor temperature of −7 °C
GPC (universal calibration)
M_w = 407 kg/mol
M_n = 280 kg/mol
PD = 1.45
after 40 min
at a reactor temperature of −7 °C:
GPC (universal calibration)
M_w = 559 kg/mol
M_n = 358 kg/mol
PD = 1.56
after 50 min
at a reactor temperature of −6 °C:
GPC (universal calibration)
M_w = 694 kg/mol
M_n = 450 kg/mol
PD = 1.54
after 60 min
at a reactor temperature of −6 °C:
GPC (universal calibration)
M_w = 856 kg/mol
M_n = 531 kg/mol PP
PD = 1.61
yield: 8.86 g (4.43% conversion)
calculated catalyst activity:591 kg PP/mol Zr and 1 h.

The observed linear increase in molecular weight (M_n) with polymerization time indicates a living polymerization (Figure 1).

Living Copolymerization of Ethene with Propene. A dry, oxygen-free, mechanically stirred 1.4 L V4A steel autoclave provided with jacket cooling was charged with 500 mL of toluene at 20 °C, and 50 g of propene were subsequently added via a pressure lock. At an internal temperature of 0 °C, the pressure was increased from 1.4 to 5.4 bar by means of ethene. The catalyst was added via a pressure lock. The catalyst employed comprised 7 $\times 10^{-6}$ mol of $[(\mathrm{flu})\mathrm{Et_2PB(C_6F_5)_2(cp)ZrCl_2}]$ and 4.62 mL of a 10% solution of MAO in toluene (7 mmol of Al). During the polymerization, samples were taken at various times and analyzed. The polymer formed in each case was precipitated in ethanol, stirred with ethanol/hydrochloric acid 90/10, filtered, washed with ethanol and dried to constant weight at 80 °C in a vacuum drying oven and the limiting viscosity and the composition were determined.

Polymer sample after 10 min at a reactor temperature of 0 °C.

Intrinsic viscosity in *o*-dichlorobenzene at 140 °C: $[\eta] = 5.11$ dL/g corresponding to a calculated mean molar mass $M_\eta = 608$ kg/mol.
FTIR
propene: 50% by weight
ethene: 50% by weight
GPC (universal calibration)
$M_w = 646$ kg/mol
$M_n = 402$ kg/mol
PD = 1.61

Polymer sample after 15 min at a reactor temperature of 2.5 °C.

Intrinsic viscosity in *o*-dichlorobenzene at 140 °C: $[\eta] = 7.15$ dL/g, corresponding to a calculated mean molar mass $M_\eta = 975$ kg/mol
FTIR
propene: 50% by weight
ethene: 50% by weight

Polymer sample after 20 min at a reactor temperature of 5 °C:

Intrinsic viscosity in *o*-dichlorobenzene at 140 °C: $[\eta] = 8.37$ dL/g, corresponding to a calculated mean molar mass $M_\eta = 1216$ kg/mol
FTIR
propene: 50% by weight
ethene: 50% by weight

Single Site Copolymerization of Ethene and Propene at 45 °C. A 100 mL sample of dry toluene, which had been distilled under inert gas, and 10 g of propene were placed in a dry, oxygen-free 300 mL V4A steel autoclave. At an internal temperature of 40 °C, the pressure was increased from 3 to 5 bar by means of ethene. The catalyst employed comprised 1×10^{-7} mol of $[(\mathrm{flu})\mathrm{Et_2PBPh_2(cp)ZrCl_2}]$ and 1×10^{-3} mol MAO as a 10% solution of MAO in toluene (1 mmol of Al). The catalyst was added via a pressure lock and the pressure was increased from 5 to 7 bar. The polymerization temperature increased from 40 to 45 °C and was kept at this temperature throughout the polymerization, which was stopped after 30 min.

The polymer formed was stirred with ethanol/hydrochloric acid 90/10, filtered, washed with ethanol and dried to constant weight at 80 °C in a vacuum drying oven.
Polymer yield
4.1 g
Catalyst activity
82.0 tons of EPM/mol Zr and 1 h
FTIR
propene: 57% by weight
ethene: 43% by weight
Intrinsic viscosity in *ortho*-dichlorobenzene at 140 °C: $[\eta] = 6.04$ dL/g, corresponding to a calculated mean molar mass $M_\eta = 769$ kg/mol, derived from $[\eta] = \mathrm{k}M^{\alpha}$ where $k = 4.00 \cdot 10^{-4}$ dL/g and $\alpha = 0.710$
DSC (second heating)
glass transition temperature: $T_g = -54$ °C
melting temperature: $T_m = -20$ °C
enthalpy of fusion: $H_m = 8$ J/g

Dual Site Copolymerization of Ethene and Propene. A 100 mL sample of dry toluene, which has been distilled under inert gas, and 100 mg of undried montmorillonite K 10 (Fluka), which has been degassed in a high vacuum (10 min/10^{-3} bar) and stored under argon, and 0.3 mL of a 1 M TIBA solution in toluene (=0.3 mmol of triisobutylaluminum) were introduced into a dry, oxygen-free 300 mL V4A steel autoclave, and 10 g of propene was condensed in. At an internal temperature of 50 °C, the pressure of 3.5 bar was increased to 6 bar with ethene. The catalyst used was a mixture of 3.5×10^{-7} mol of $[(\mathrm{flu})\mathrm{Et_2PBPh_2(cp)ZrCl_2}]$, 1.5×10^{-7} mol of $[(\mathrm{cp})\mathrm{Et_2PBCl_2(cp)ZrCl_2}]$, and 0.099 mL of 10% MAO solution in toluene (0.15 mmol of Al, Al/Zr = 300). The catalyst was added via a pressure lock, and the pressure was increased from 6 to 8.5 bar with ethene. The polymerization at 50 °C was terminated after 30 min.

The polymer formed was washed by stirring with ethanol/hydrochloric acid 90/10, filtered, washed with ethanol, and dried in a vacuum drying cabinet at 80 °C to constant weight.
Polymer yield
3.55 g
Catalyst activity
14.2 tons of EP rubber per mol of Zr and 1 h
Intrinsic viscosity in *o*-dichlorobenzene at 140 °C: $[\eta] = 4.88$ dL/g
The GPC analysis (universal calibration) shows a copolymer with a bimodal molecular weight distribution (Figure 2).
component 1 (64% by weight)
$M_w(1) = 1617$ kg/mol $M_n(1) = 890$ kg/mol
component 2 (36% by weight)
$M_w(2) = 152$ kg/mol
$M_n(2) = 68$ kg/mol

Acknowledgment. This work is dedicated to Professor Dr. Helmut G. Alt (University of Bayreuth). The authors thank the LANXESS Deutschland GmbH and the LANXESS Buna GmbH for releasing this manuscript for publication.

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MA8007306