Propene Polymerization with Catalyst Mixtures Containing Different *ansa*-Zirconocenes: Chain Transfer to Alkylaluminum Cocatalysts and Formation of Stereoblock Polymers

Susanna Lieber and Hans-Herbert Brintzinger*

Fachbereich Chemie, Universität Konstanz, D-78457 Konstanz, Germany

Received April 20, 2000; Revised Manuscript Received September 19, 2000

ABSTRACT: Substantial transfer of growing polypropyl chains to methylalumoxane and trimethylaluminum occurs with the highly substituted, isospecific zirconocene catalyst $Me_2Si(2\text{-}Me\text{-}4\text{-}^tBu\text{-}C_5H_2)_2ZrCl_2$/MAO, while little if any such chain transfer is observed for the more open isospecific catalyst $Me_2Si(2\text{-}MeInd)_2ZrCl_2$/MAO, for aspecific $H_4C_2(Flu)_2ZrCl_2$/MAO, and for syndiospecific $Ph_2C(Cp)FluZrCl_2$/MAO. Propene polymerization with MAO-activated mixtures of $Me_2Si(2\text{-}MeInd)_2ZrCl_2$ and $H_4C_2(Flu)_2ZrCl_2$ gives completely separable mixtures of the isotactic and atactic polymers characteristic for each of the individual catalysts. MAO-activated mixtures of $Me_2Si(2\text{-}Me\text{-}4\text{-}^tBu\text{-}C_5H_2)_2ZrCl_2$ and $H_4C_2(Flu)_2ZrCl_2$, however, give polypropene mixtures that contain, besides isotactic and atactic polymers, polymer fractions in which isotactic and atactic polypropene chain segments are inseparably linked. While clear evidence for isotactic−syndiotactic stereoblock formation was not obtained, some polymeryl exchange between isospecific and syndiospecific catalyst sites in MAO-activated mixtures of $Me_2Si(2\text{-}Me\text{-}4\text{-}^tBu\text{-}C_5H_2)_2ZrCl_2$ and $Ph_2C(Cp)$-$FluZrCl_2$ is indicated by increased stereoerror frequencies in some fractions of the polymer product mixture obtained by temperature-rising elution fractionation. Structural prerequisites for an efficient transfer of growing polymer chains between different types of catalyst centers are discussed.

Introduction

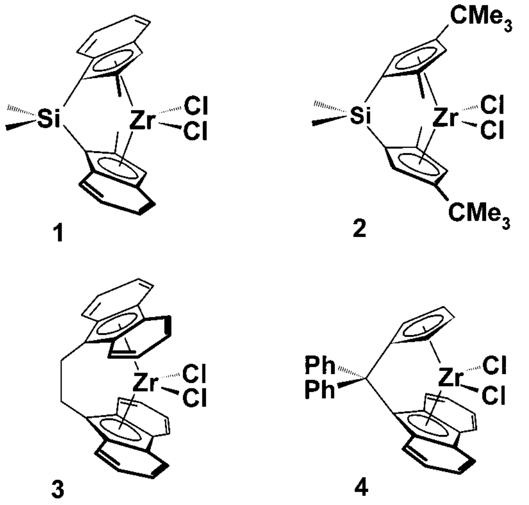
The possibility to obtain polyolefins with an otherwise unattainable architecture, i.e., with adjoining chain segments of distinctly different stereoregularities, has recently been investigated in several laboratories, since stereoblock polymers of this sort promise to be useful as thermoplastic elastomers or as heterophase compatibilizers.[1−3] It has been established in principle that such stereoblock polyolefins can be generated by using in-situ mixtures of metallocene catalysts with different stereoselectivities.[2,3] It is not clear at present, however, which circumstances—which types of dissolved or supported metallocene catalysts and cocatalysts—favor or suppress their formation, respectively, nor is it established which elementary reaction steps are involved in the prerequisite transfer of a growing polymer chain from one type of metallocene catalyst to another.

To elucidate the underlying structure−property relations and reaction sequences, we have studied propene polymerizations using the four zirconocene complexes **1**−**4** (Scheme 1), in conjunction either with methylalumoxane (MAO) or with triisobutylaluminum (Al^iBu_3) and triphenylcarbenium tetrakis(perfluorophenyl borate) (trityl borate) as activating agents. These catalysts were first studied individually with regard to their tendency toward alkyl−polymeryl exchange with the respective alkylaluminum activators and then pairwise with respect to their capability to generate polymers with a stereoblock structure.

Results and Discussion

Polymeryl Exchange with Alkylaluminum Cocatalysts. Transfer of a Zr-bound polypropyl chain to an Al center of the cocatalyst in exchange for an Al-bound methyl group is recognized by the occurrence of saturated isopropyl end group units in the hydrolyzed polymer product instead of the normally observed *n*-propyl and isopropenyl (or isobutenyl) groups,[4,5] which arise from termination of chain growth by β-H transfer. By studying the effects of TMA added to the reaction mixture, we have tried to determine to which degree this type of polymeryl transfer is associated with the TMA content of the MAO activator. Saturated isopropyl chain ends are also expected to form when Zr-bound polypropyl chains are exchanged against the Al-bound isobutyl groups of an Al^iBu_3/trityl borate activator and were thus looked for as an indication for the occurrence of this conceivable exchange reaction, which has not been observed so far with metallocene catalysts.[6]

Scheme 1



The isospecific catalyst $Me_2Si(2\text{-}MeInd)_2ZrCl_2$ (**1**) produces, in the presence of MAO, isotactic polypropene with rather high molar mass ($P_n \approx 900$). ^{13}C NMR spectra of these polymers indicate the presence of only 2-propenyl and *n*-propyl end groups, while isopropyl end groups are not detectable (Table 1).[7] Addition of TMA

10.1021/ma000691j CCC: $19.00

Table 1. Tacticities, End Group Distributions, and Degrees of Polymerization, P_n, of Polypopenes Obtained with Complexes 1−4 in the Presence of Different Activators[a]

run	cocatalyst[b]	catalyst[c]	[Al]:[Zr]	activity[d]	mmmm[e]	rrrr[e]	*n*-propyl[e]	propenyl[e]	isopropyl[e]	allyl[e]	isobutenyl[e]	P_n[f]
1	MAO	**1**	1500	1300	93		50	50				900
2	TIBA/TB	**1**	1500	2700	91		50	50				1200
3	MAO	**2**	2000	1000	99		40	19	25		16	150
4	MAO/TMA	**2**	3500	3300	96		2	0	96		2	50
5	TIBA/TB	**2**	2000	5000	98		52	38	0		10	363
6	MAO	**3**	1000	1200	1	10	25	25	25	25		300
7	MAO/TMA	**3**	2000	500	2	10	22	22	33	23		250
8	TIBA/TB	**3**	1650	2100	2	10	34	38	14	14		540
9	MAO	**4**	2800	1200		79	n.o.	n.o.	n.o.	n.o.	n.o.	800
10	MAO/TMA	**4**	3800	600		80	n.o.	n.o.	n.o.	n.o.	n.o.	500
11	TIBA/trityl	**4**	2800	3000		80	n.o.	n.o.	n.o.	n.o.	n.o.	870

[a] Reaction conditions: 1 bar propene pressure, 60 min, [Zr] = 2 μmol/L, 40 °C. [b] MAO, methylalumoxane, TIBA/TB, triisobutylaluminum and trityltetrakis(perfluorophenyl) borate ([B]:[Zr] = 10:1). [c] **1** $Me_2Si(2\text{-}MeInd)_2ZrCl_2$, **2** $MeSi(2\text{-}Me\text{-}4\text{-}{}^tBuC_2H_5)_2$, **3** $en(Flu)_2ZrCl_2$, **4** $Ph_2C(Cp)(Flu)ZrCl_2$. [d] g PP/(mmol Zr h). [e] In % of all pentads or all end groups, respectively, determined by ^{13}C NMR spectroscopy. [f] Determined by GPC.

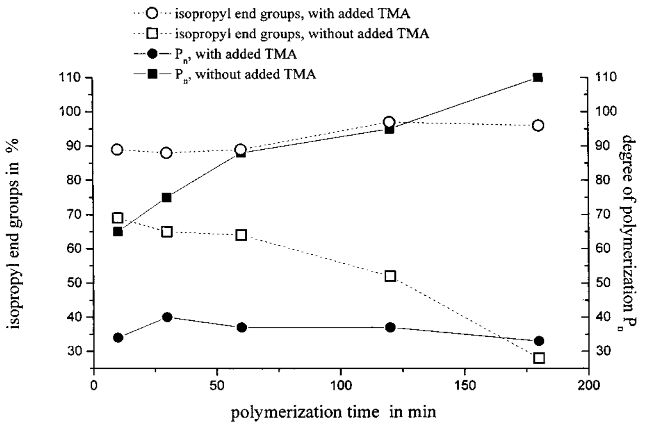


Figure 1. Changes with time of relative isopropyl end group frequencies and degrees of polymerization of polymers produced with catalyst **2**/MAO, with and without added TMA.

([TMA]:[Zr] ≈ 1000:1) results in almost complete loss of activity, such that no polymer was isolated. Apparently, TMA forms a particularly stable, inactive adduct with the zirconocenium cation derived from complex **1** and MAO.[8]

In the presence of Al^iBu_3 and trityl borate as cocatalysts, complex **1** gives isotactic polypropene with a molar mass higher than that obtained in the presence of MAO, again without detectable isopropyl end group signals. For complex **1,** no polymeryl transfer from Zr to Al centers is thus observable in the presence of either cocatalyst.

Polymerization of propene with $Me_2Si(2\text{-}Me\text{-}4\text{-}{}^tBu\text{-}C_5H_2)_2ZrCl_2$ (**2**) in the presence of excess MAO ([Al]:[Zr] = 2000:1) gives highly stereoregular (95−99% [mmmm]) and regioregular (100% 1,2-insertions) polypropene with rather low molar mass ($P_n \approx 80-150$). The ^{13}C NMR spectra of these polymers indicate rather high contents of isopropyl chain ends, i.e., a high probabilty of polymeryl transfer from Zr to Al.[9]

When such a polymerization mixture is quenched after variable times, we observe a steady decrease in the fraction of isopropyl end groups together with an increase of molar mass with time (Figure 1). These observations are explicable by the assumption that polymeryl transfer from Zr to Al centers decreases, over the reaction time considered, since the $Al-CH_3$ groups of MAO and/or its TMA content are increasingly consumed by exchange of methyl against polymeryl groups.[10]

Propene polymerization with the dimethyl derivative of complex **2** and TMA-free MAO[11] gives results similar to those obtained with “ordinary” MAO, except that the frequency of isopropyl end groups is decreased to ca. 10% and the average polymerization degree is increased to 200. Chain transfer to Al centers thus appears to be diminished here due to the reduced availability of $Al-CH_3$ groups in this catalyst system.

Addition of excess TMA ([TMA]:[Zr] ≈ 500−5000:1) on the other hand causes catalyst **2**/MAO to generate even shorter polymer chains ($P_n \approx 30-50$) with an isopropyl end group frequency of more than 95%, which now remains constant over the entire reaction period (Figure 1). In the presence of added TMA, the activity of these catalyst systems is noticeably enhanced. TMA thus not only leaves catalyst **2**/MAO unhindered,[12] but the ensuing methyl−polymeryl exchange even appears to remove slowly inserting species, which otherwise reduce the average activity of the catalyst.

Formation of polypropene with almost equal proportions of hydroxymethyl and isopropyl end groups upon exposure of the resulting reaction mixtures to dry O_2 gas likewise documents that about 90% of all polymer chains have been transferred to Al under these conditions.

When propene was polymerized with catalyst **2** in the presence of Al^iBu_3 and trityl borate, however, the resulting polymers had practically no isopropyl end groups and substantially higher molar mass ($P_n \approx 350$) than polymers produced by **2** with MAO as cocatalyst (Table 1). This indicates that little if any polymeryl transfer occurs between **2** and Al^iBu_3. Similar observations were reported by Kim et al. and by Naga et al. with related zirconocene catalysts.[13]

The bis(fluorenyl) complex **3** produces, in the presence of MAO, atactic polypropene with moderately high molar mass ($P_n \approx 300$).[14] In these polymers, *n*-propyl, 2-propenyl, allyl, and isopropyl end groups are observed in about equal proportions. Isopropyl end groups can arise here either by chain transfer from Zr to Al or by insertion of propene into a Zr−methyl bond which is generated through β-methyl transfer, a rather frequent mechanism of chain termination with this catalyst.[14] Addition of TMA to the polymerization mixture gives rise to a reduction in activity and molar mass ($P_n \approx 250$) and to an enhanced ratio (ca. 1.5:1) of isopropyl over *n*-propyl or 2-propenyl end groups. These observations indicate that polymeryl tranfer to TMA is occurring with this catalyst to a significant degree. In the presence of Al^iBu_3 and tritylborate, no indications for polymeryl transfer to Al are obtained for complex **3**.

Table 2. Propene Polymerization with Mixtures of Isospecific and Aspecific Catalysts, Reaction Conditions, and Product Fractionation[a]

									mass % of fraction			isotacticity (% mmmm) of fraction			
run	μmol **1**[c]	μmol **2**[c]	μmol **3**[c]	mmol MAO	mmol TIBA	[Al]:[Zr]	yield[d]	activity[e]	ether-soluble	hexane-soluble	in-soluble	ether-soluble	hexane-soluble	in-soluble	total
12[b]	6		19	10		400	8.5	680	65		35	2		90	24
13	6		19	10		400	6	480	63		37	2		90	19
14	6		19	10		400	6	480	60		40	2		93	23
15	6		19	20		1250	9	1125	57	5	38	2	2	95	46
16		4	6	20		2041	3.7	378	38	12	50	9	54	89	55
17		2	5	10		1428	7	610	52	14	25	7	35	76	24
18		4	4	10		1266	3	380	34	9	57	4	37	78	43
19		4	7	10		909	6.8	618	42	27	31	4	40	72	37
20		2	10	10		847	7.2	660	58	2	6.6	4	31	71	30
21		4	4	4		506	2.7	342	22	14	64	4	30	62	14
22		4	7	2	10	1034	8	690	36	17	47	6	35	45	26
23		2	10		5	471	10	1620	37	36	27	2	4	96	7
24		2	10		5	471	8	1377	68		32	3		96	8

[a] Reaction conditions: 1 bar propene pressure, 60 min, 100 mL of toluene, 40 °C. [b] Run 12: 50 mL of toluene. [c] **1**: $Me_2Si(2\text{-}MeInd)_2ZrCl_2$, **2**: $Me_2Si(2\text{-}Me\text{-}4\text{-}{}^tBuC_2H_5)_2ZrCl_2$, **3**: $en(Flu)_2ZrCl_2$. [d] In g. [e] gP/(mmol Zr h).

The C_s symmetric complex $Ph_2C(Cp)FluZrCl_2$ (**4**) finally gives polypropene with a regioregular, mostly syndiotactic (80% [rrrr]) microstructure and a rather high molar mass ($P_n \approx 800$) in the presence of MAO.[15] Addition of TMA to this catalyst system ([TMA]:[Zr] ≈ 1000:1), while resulting again in a strong reduction of activity, gives small amounts of a polymer with substantially reduced chain length ($P_n \approx 500$). Occasional transfer of Zr-bound polymer chains to Al centers is thus indicated for this catalyst system in the presence of added TMA.

With Al^iBu_3 and trityl borate as cocatalysts, complex **4** produces polypropene with similar molar mass ($P_n \approx 870$) as in the presence of MAO. This and the absence of any detectable isopropyl group signal indicates, as for **1**−**3**, that polymeryl tranfer to Al^iBu_3 does not occur in this catalyst system to any noticeable degree.

These results demonstrate that polymeryl transfer to the alkylaluminum component of the cocatalyst depends on the substitution pattern of the zirconocene complex as well as on the nature and the concentration of the alkylaluminum compound: While almost complete polymeryl transfer to excess TMA occurs with the highly substituted complex **2**, this transfer takes place with lower but finite degrees with complex **3** and probably also with **4**. No indication was obtained for this transfer reaction with complex **1** in the presence of MAO. In the presence of the Al^iBu_3−trityl borate activator, on the other hand, polymeryl transfer was observed with none of the zirconocene complexes studied. Apparently, alkyl exchange between bulky Al^iBu_3 and sterically demanding zirconocene catalysts is not able to compete with alternative chain growth termination reactions.[16]

Back-transfer of Al-bound polymeryl chains to the Zr centers of a zirconocene catalyst system has not been unequivocally established so far.[17] In catalyst systems containing two zirconocene complexes with different substitution patterns, transfer of Al-bound polymeryl chains derived from one type of zirconocene catalyst to another zirconocene with different stereoselectivity should manifest itself in the formation of polymers containing adjacent chain segments of distinctly different stereoregularity, i.e., of stereoblock polymers. We have thus studied this phenomenon in some detail.

Formation of Stereoblock Polymers with Mixtures of Different Zirconocene Catalysts. Polymerization of propene with a mixture of two differently substituted zirconocene catalysts is expected to result in the formation of the "homotactic" polymers typical for each of the catalysts, together with smaller or larger fractions (depending on the relative rates of polymeryl transfer between the two Zr centers) of polymers containing segments of different tacticities. To identify these stereoblock polymers in the resulting polymer mixture, suitable physical data of the latter have to be compared with those of a mixture containing only the homotactic polymers. Useful properties in this regard are the solubilities of the resulting polymers in different solvents, together with further separation and characterization techniques, such as gel permeation chromatography (GPC) and ^{13}C NMR.

As catalyst combinations we used first MAO-activated mixtures of the isospecific catalysts **1** and **2** with the aspecific catalyst **3**, since isotactic and atactic polypropenes are rather easily separated.[18] The polymer mixtures obtained in the following experiments were thus fractionated by Soxhlett extractions first with diethyl ether and then with hexane. ^{13}C NMR spectra were recorded for each of these fractions as well as of that insoluble in either solvent (Table 2).

Propene polymerizations with mixtures of **1** and **3** in the presence of either MAO or Al^iBu_3 and trityl borate give waxy solids. All polymers produced with these catalyst mixtures are completely separable into an atactic (ether soluble) and an isotactic (insoluble) fraction.[19] Irrespective of [Al]:[Zr] ratios and total zirconocene concentrations used, ca. 60% atactic and ca. 40% isotactic polypropene are obtained from the product mixture. The ether-soluble fraction is identical with the atactic polypropene produced by MAO-activated catalyst **3** with regard to their ^{13}C NMR pentad signal distribution, which follows Bernoulli statistics with a slight syndiotactic preference,[20] and with regard to its preponderant allyl and isopropyl end groups. The insoluble, highly isotactic fraction, on the other hand, which contains only 2-propenyl and *n*-propyl end groups, is indistinguishable from isotactic polypropene produced by MAO-activated catalyst **1** alone. Neither fraction contains, in particular, any combination of isotactic and atactic pentad patterns (Figure 2). From these results we can safely conclude that these catalyst mixtures do not form stereoblock polymers to any detectable degree.

Polymerizations with MAO-activated mixtures of complexes **2** and **3**, on the other hand, yield gooey product mixtures which cannot be separated into atactic and isotactic polymers by fractionating extraction. Apart

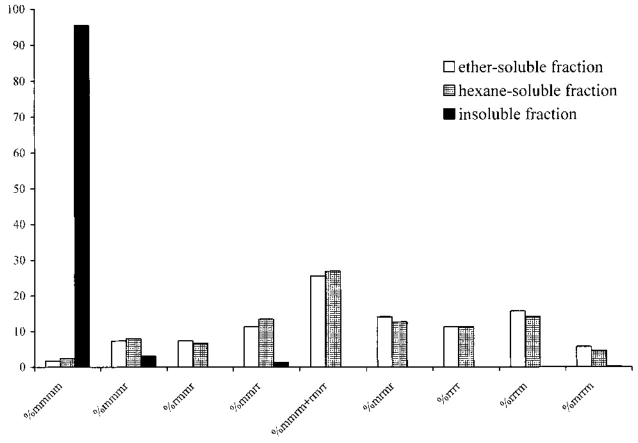


Figure 2. Pentad distributions of individual fractions of polypropene produced with a MAO-activated mixture of catalyst **1** and **3** (run 15).

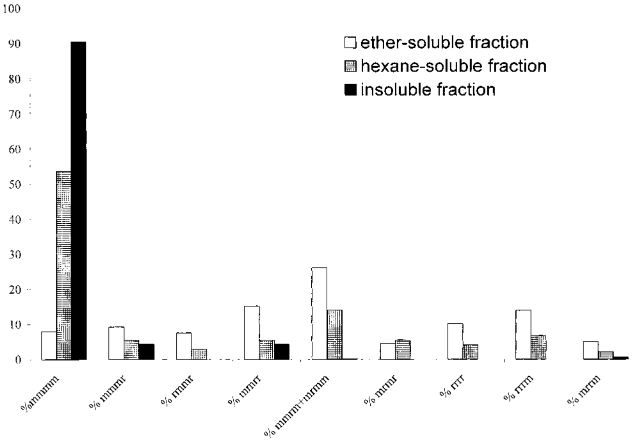


Figure 3. Pentad distributions of individual fractions of polypropene produced with a MAO-activated mixture of catalysts **2** and **3** ([Al]:[Zr] = 1300:1, run 16).

from an ether-soluble, atactic fraction and an insoluble, mainly isotactic fraction, one obtains also ca. 10% of a hexane-soluble fraction which shows both isotactic and atactic pentad signal patterns in its ^{13}C NMR (Figure 3) and is thus likely to consist of chains containing adjoining isotactic and atactic stereoblocks.

When the MAO excess is reduced to [Al]:[Zr] ≈ 500:1, the product mixture contains, apart from about 20% of ether-soluble, atactic polymer, about 20% hexane-soluble and 60% insoluble polymer. In both of these fractions, the mmmm-pentad intensity is rather low, 30% and 60%, respectively. Here, even the insoluble fraction thus appears to contain substantial amounts of atactic chain segments (Figure 4).

To test whether the relatively short isotactic chains produced by catalyst **2**/MAO are co-extracted by hexane together with the atactic product of catalyst **3**/MAO, we blended the isotactic and atactic polymers, prepared with each of these two catalysts individually, by their dissolution in hot xylene and subsequent coprecipitation with cold methanol. When this blend was subjected to the fractionation procedure described above, the atactic material was completely removed by extraction with diethyl ether, while all of the isotactic polymer remained in the insoluble fraction, such that no detectable amounts of polymer were found in the hexane extract.

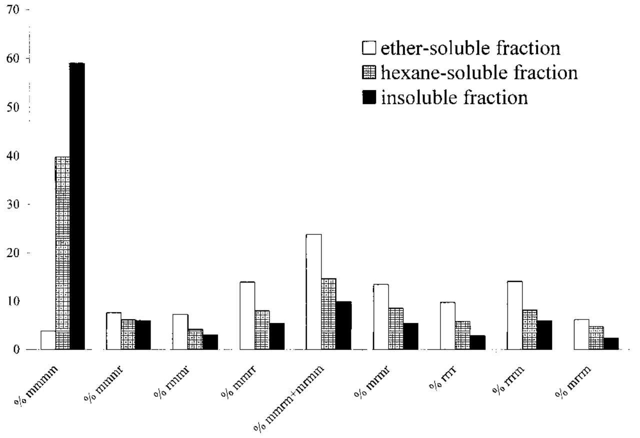


Figure 4. Pentad distributions of individual fractions of polypropene produced with a MAO-activated mixture of catalysts **2** and **3** ([Al]:[Zr] = 500:1, run 21).

The pentad distributions of the ether-soluble and insoluble fractions show that the polymer blend is completely separated into atactic and isotactic polypropenes, unlike the product mixture obtained by using catalysts **2** and **3** simultaneously in the presence of MAO. In this latter case, the polymer fraction isolated from the hexane extract thus appears to be the searched-for isotactic–atactic stereoblock polymer. This fraction amounts to about 10% of the total polymer produced under the reaction conditions used. Under MAO-“starved” conditions (runs 21 and 22) even larger fractions of the product mixture appear to consist of isotactic–atactic stereoblock polymer.

When Al^{i}Bu$_3$ and trityl borate are used, however, instead of MAO, to activate a mixture of catalysts **2** and **3**, the resulting polymer mixture is separable again into atactic and isotactic polypropene by extraction with ether and hexane: The soluble fraction is a viscous oil with the atactic pentad distribution typical of catalyst **3**, while the insoluble fraction is highly isotactic (96% [mmmm], $P_n \approx 300$) and has only the 2-propenyl and *n*-propyl end groups characteristic for polypropene produced by catalyst **2** in the presence of Al^{i}Bu$_3$ and trityl borate (vide supra). In the presence of this activator, catalysts **2** and **3** are thus not capable of forming any detectable amounts of stereoblock polymers.

For the catalyst systems described above, the occurrence of a stereoblock polymer fraction in the polymer product mixtures appears to follow the propensity of the respective catalyst components for polymeryl exchange with the alkylaluminum cocatalyst: Irrespective of the cocatalyst used, catalyst **1** did not yield any indications for polymeryl transfer between Zr and Al centers and is, accordingly, not capable of generating, together with catalyst **3,** any detectable amounts of isotactic–atactic stereoblock polymers. Instead, only the “homotactic” polymers typical for each individual catalyst arise from these catalyst mixtures. The same is true for catalysts **2** and **3** in the presence of Al^{i}Bu$_3$ and trityl borate, with which neither of these catalysts shows any signs of polymeryl exchange.

In the presence of MAO, however, to which they both transfer their polymeryl chains, catalysts **2** and **3** do give significant fractions of an additional polymer, which evidently contains isotactic and atactic stereoblocks. This additional hybrid polymer amounts to about 10–30% of the total product mixture, depending on the activation protocol followed. These results indicate that polymeryl chains are transferred not only to MAO in

Table 3. Tacticities and Molecular Weights of TREF Fractions of Polypropene Produced with a MAO-Activated Mixture of Isospecific Catalyst 2 and Syndiospecific Catalyst 4[a]

elution temp	40 °C	70 °C	75 °C	80 °C	85 °C	total
mass percentage[b]	20	52	17	8	3	100
mmmm[c]	33	37	83	88		73
mmmr[c]	3	6	3	2		2
rmmr[c]	1	4	1	0		0
mmrr[c]	5	6	5	4		2
mrmm + rrmr[c]	6	3	1	0		1
mrmr[c]	1	1	0	0		0
rrrr[c]	41	25	6	4		18
rrrm[c]	6	8	0	0		3
mrrm[c]	4	6	1	2		1
mass distribution	bimodal	bimodal	monomodal	monomodal	monomodal	bimodal
$M_n(1)$	4000	5500	6900	7551	9150	
$M_n(2)$	64000	95300				

[a] [**2**]:[**4**]:[Al] = 1:1:3000 in toluene at 40 °C. [b] Fraction of polypropene eluted at the respective temperature. [c] Integral percentage, determined by ^{13}C NMR spectroscopy.

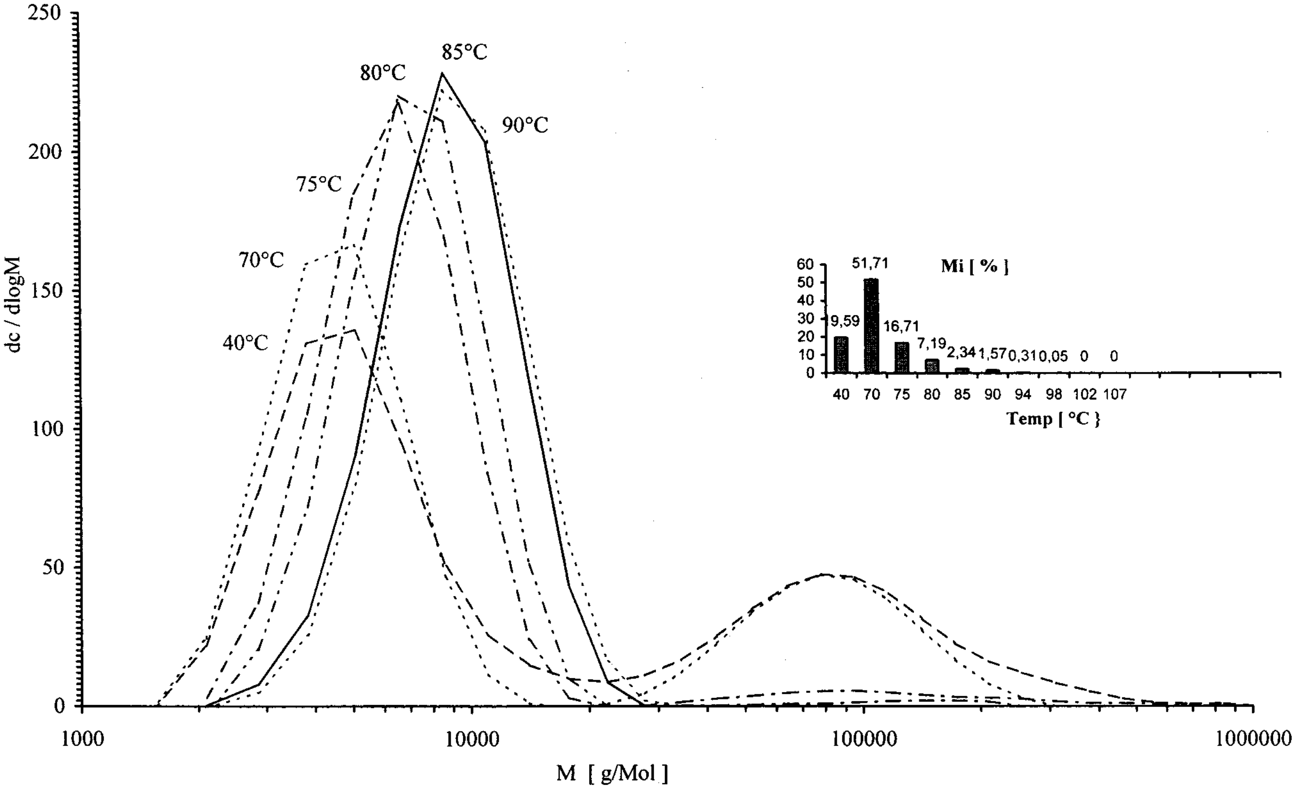


Figure 5. GPC curves of TREF fractions of polypropene produced with a MAO-activated mixture of catalysts **2** and **4**.

these reaction systems but also back to the zirconocene catalysts, as will be discussed in more detail below.

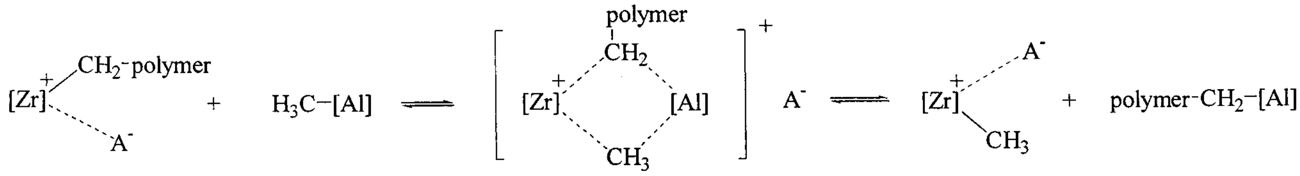
These observations raise the question whether stereoblock polymers can also be obtained with MAO-activated mixtures of the isospecific catalyst **2** and the syndiospecific catalyst **4**. For the latter, the evidence for polymeryl exchange, as described above, was not quite clear-cut in that addition of TMA reduced the chain length, but end groups could not be identified. Unfortunately, evidence for the formation of stereoblock polymers in such a mixed catalyst system is also difficult to establish, since the isotactic und syndiotactic products of the individual catalyst cannot be so easily separated from each other and from purported stereoblock hybrids by direct extraction as was the case for the isotactic and atactic polymers considered above.

We have thus tried to separate the polypropene products, which were obtained with mixtures of catalysts **2** and **4** in the presence of MAO,[21] by subjecting them to temperature-rising elution fractionation (TREF).[22] Even by this method, which is known to separate polyolefins primarily according to increasing crystallinity,[23] only a partial separation was achieved (Table 3, Figure 5).

Gel permeation chromatography (GPC) of each of the TREF fractions (Figure 5) revealed that the three fractions extracted at 75, 80, and 85 °C, which comprised 26% of the product mass, consisted predominantly of short chains with $M_n \approx 7000-9000$ g/mol, typical for polypropene produced with catalyst **2**/MAO. In accord with this, these last three fractions give rise to ^{13}C NMR spectra with essentially isotactic pentad signal distributions ([mmmm] > 80%), together with only minor syndiotactic contributions ([rrrr] < 6%) and will not be considered further.

The first two fractions, which were extracted at 40 and 70 °C and amounted to 71% of the total polymer mass, however, had bimodal molar mass distributions

Scheme 2



with probability maxima around $M_n \approx 4000-6000$ and around $M_n \approx 65\,000-95\,000$ g/mol, which are typical for the polypropenes produced, under the conditions used, by catalysts **2** and **4**, respectively. These two fractions give rise to the mmmm and rrrr pentad signals, typical for isotactic and syndiotactic polypropenes, respectively, in comparable intensities, as expected from their bimodal molar mass distributions. Remarkably, all error pentads occur much more frequently in the ^{13}C NMR spectra of these two fractions than would be expected for any mixture of isotactic and syndiotactic polypropenes produced by the MAO-activated catalyst **2** and **4** individually (Table 3).

It has been pointed out by Przybyla and Fink that an increased incidence of stereoerror pentads, in particular of mmmr, mmrr, and rrrm pentads, is expected to arise from junctions of isotactic and syndiotactic stereoblocks in a polypropene chain.[3] A diminuation of the mmmm/mmmr and rrrr/rrrm ratios below those determined for products of the isotactic and syndiotactic catalysts by themselves has thus been proposed by these authors as an indicator for the formation of stereoblock polymers by a catalyst mixture. By this criterion, the TREF fractions eluted at 40 and 70 °C (Table 3) would appear to contain significant proportions of stereoblock polymers.

Increased frequencies are observed, however, also for error pentads such as mrmr, mrmm, and rmrr, which are not associated with junctions of extended isotactic and syndiotactic blocks. While this might indicate that small amounts of atactic polymer are produced, e.g., by some degradation product of one of the zirconocene species, the increased frequencies of these random-error pentads might also be due to a particularly high rate of polymeryl exchange between Zr and Al centers (vide infra). For MAO-activated mixtures of catalysts **2** and **4**, formation of isotactic−syndiotactic stereoblocks under the conditions used can thus be neither excluded nor confirmed with similar certainty as for the isotactic−atactic stereoblock polymers discussed above.[24]

Conclusions

From the results presented above, we can conclude that formation of stereoblock polymers in a mixture of zirconocene catalysts with different stereoselectivities is contingent upon an efficient polymeryl exchange between the Zr catalyst centers and the Al centers of the cocatalyst: Where this exchange is found to occur with significant rates for each of the individual catalysts, clear evidence is obtained for the formation of stereoblock polymers in the catalyst mixture, whereas in the absence of alkyl−polymeryl exchange, i.e., for all catalyst systems activated with trityl tetrakis(perfluorophenyl borate) and Al^iBu_3 as well as for catalyst **1**/MAO, no evidence for stereoblock formation is obtained.[25]

This raises the question why this exchange is quite efficient for some of the catalysts, in particular for **2**/MAO, while it is undetectable in others. Since electronic factors are unlikely to affect the exchange of alkyl and polymeryl residues between Zr and Al centers to any substantial degree,[26] steric effects must be controlling the extent to which this exchange occurs, in kinetic and/or in thermodynamic terms.

The only reasonable pathway for such an exchange involving an Al−CH_3 species appears to be the formation of alkyl-bridged, heterobimetallic cations of the type represented in Scheme 2. The strongly inactivating effects of excess TMA on the more open zirconocene catalysts **1**/MAO, **3**/MAO, and **4**/MAO suggest that rather stable heterobimetallic cations are formed in these cases.[8] Due to ample formation of this reaction intermediate, exchange of alkyl and polymeryl residues between Zr and Al centers is thus likely to be relatively fast. That it is found to occur only to a minimal degree, if at all, with these open zirconocene catalysts must thus be due to unfavorable thermodynamics, i.e., to an equilibrium constant much smaller than unity for the exchange reaction represented in Scheme 2.

The opposite appears to be the case for the highly substituted catalyst **2**/MAO: Here, the absence of any inhibition by TMA suggests that heterobimetallic cations are practically absent.[12] Alkyl−polymeryl exchange between Zr and Al centers is thus presumably slower here than with the other catalysts, becoming fast only in the presence of excess TMA. Thermodynamics, on the other hand, appears to favor in this case the transfer of bulky polymeryl chains from sterically encumbered Zr to rather “free” Al centers in exchange for sterically less demanding CH_3 groups.

In reaction systems containing different zirconocene catalysts, the extent and direction of Al-mediated polymeryl transfer would thus appear to be controlled by their respective degrees of ligand substitution, such that polymer chains are preferentially transferred from the more hindered to the more open complex species.[27] This view would be supported by the observation that the rather open catalyst **1**/MAO does not transfer polymeryl chains to **3**/MAO, while **2**/MAO acts as an effective source of polymeryl chains vis-à-vis other catalysts.

In terms of polymeryl transfer kinetics, the most highly substituted complex appears to be rate limiting for this reaction sequence. In cases where a sufficient concentration of Al−polymeryl species has accumulated, their exchange with a particularly open zirconocene catalyst might become quite fast, possibly even comparable to the rate of olefin insertion. Whether such a fast polymeryl exchange is indeed the cause for the occurrence of random types of stereoerrors in the polymers obtained with mixtures of the MAO-activated catalysts **2** and **4** remains to be clarified. Particularly valuable in this regard would be NMR data on longer stereosequences in these polymers.

The lack of polymeryl exchange observed in the presence of Al^iBu_3 and trityl borate would be explicable by the unfavorable effects of the bulky alkyl groups on both the kinetics and the thermodynamics of the exchange reaction indicated in Scheme 2. Extensions of these studies underway in our laboratory concern the search for alkyl transfer agents more efficiently than the hitherto employed methyl-Al species and for reaction systems that contain selected zirconocene representatives together with other transition metal catalysts.

Experimental Section

All reactions were performed under argon using Schlenk line techniques or under nitrogen in a glovebox. Solvents were dried prior to use by refluxing over and distilling from sodium. Deuterated solvents were dried over 4 Å molecular sieves. $\mathrm{Me_2Si(2\text{-}Me\text{-}4\text{-}{}^tBu\text{-}C_5H_2)_2ZrCl_2}$[28] and $\mathrm{en(Flu)_2ZrCl_2}$[14] were synthesized according to literature procedures. A 25% solution of MAO in toluene was donated by CK WITCO. $\mathrm{[Ph_3C][B(C_6F_5)_4]}$ was obtained as gift from BASF AG and $\mathrm{Ph_2C(Flu)CpZrCl_2}$ and $\mathrm{Me_2Si(2\text{-}MeInd)_2ZrCl_2}$ from Axiva GmbH. All other chemicals were purchased from commercial suppliers and used without further purification.

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AC 250 (250 MHz) or Bruker Avance 600 (600 MHz) instruments. Polymer ^{13}C NMR spectra were recorded at 150 MHz in $\mathrm{CD_2Cl_4}$ solution at 100 °C with an acquisition time of 3.2 s. Temperature-rising elution fractionations (TREF) were performed in the analytical laboratories of BASF AG and at the Materialforschungszentrum Freiburg.

Propene Polymerization with 2/MAO. A Schlenk vessel was charged with toluene (100 mL) and MAO solution (3 mL). The mixture was thermostated at 40 °C and saturated with the monomer to 1 bar. In another vessel, 2 mL of a toluene solution of complex **2** (2 μmol) and 2 mL MAO solution were combined and incubated for 20 min. The polymerization was started by adding the catalyst/MAO solution to the reaction vessel. Propene pressure was kept at 1 bar with a mass flow detector. The reaction was stopped after variable times, by adding an acidic methanol solution, and stirred overnight. The precipitated polymer was collected by filteration, washed several times with methanol, and dried in vacuo. Evaporation of the methanol−toluene solution did not yield any additional polymer; no significant amounts of atactic polypropene had thus been formed.

Propene Polymerization with Added TMA. The reaction mixture was prepared as described above. Variable amounts of TMA were added to the toluene−MAO solution before saturation with propene. All other steps were performed analogously.

To obtain hydroxy-end-capped polypropene, the propene supply was turned off, and dry synthetic air was bubbled through the unhydrolyzed reaction mixture, while maintaining it at 0 °C with an external ice bath. After 1 h, the mixture was treated with an acidic methanol solution and stirred overnight. The precipitated polymer was collected by filtration, washed with methanol, and dried.

Propene Polymerization with Complex 2 and $\mathrm{Al^iBu_3}$/Trityl Borate as Cocatalyst. A Schlenk vessel was charged with toluene (50 mL), triisobutylaluminum (0.5 mmol), and 2 mL of a solution of complex **2** (2 μmol). The mixture was thermostated at 40 °C and saturated with the monomer to 1 bar. To start the polymerization, 5 mL of a solution of trityl borate in toluene (20 μmol) was added. The reaction was stopped after 30 min by adding an acidic methanol solution. The precipitated polymer was collected by filtration, washed several times with methanol, and dried in vacuo.

Polymerization of Propene with Complexes 1, 3, or 4 and MAO as Cocatalyst. A Schlenk vessel was charged with toluene (100 mL) and MAO solution (3 mL). The mixture was thermostated at 40 °C and saturated with propene to 1 bar. In another vessel, 2 mL of a solution of the zirconocene complex used (2 μmol) and 2 mL of MAO solution were combined and incubated for 20 min. To start the polymerization, the zirconocene/MAO solution was added to the reaction vessel. The propene pressure was kept at 1 bar with a mass flow detector. The reaction was stopped after 30 or 60 min polymerization time with an acidic methanol solution and stirred overnight. The precipitated polymer was filtered, washed, and dried at 90 °C.

Propene Polymerization with MAO-Activated Mixtures of Two Zirconocene Complexes. In a Schlenk vessel, 100 mL of toluene and 3 mL of MAO solution were combined, thermostated to 40 °C, and saturated with propene to a pressure of 1 bar. In a second vessel, toluene solutions of the two zirconocene complexes were combined in the reported ratios and incubated with 2 mL of MAO solution. Polymerizations were started by addition of the zirconocene/MAO solution to the reaction vessel. After 30 or 60 min the polymerization was stopped, by adding an acidic methanol solution, and stirred overnight. The precipitated polymer was collected by filtation, washed with methanol, and dried. The toluene/methanol solution was extracted with toluene and water. The organic layer was separated and dried with $\mathrm{Na_2SO_4}$, and the solvent was removed in vacuo. The residue was subjected to fractionation together with the precipitated polymer product.

Preparation of Polymer Blends. Variable amounts of isotactic and atactic polypropene were suspended in xylene and refluxed for ca. 30 min. The homogeneous solution was then cooled with an ice bath and the polymer precipitated with ice-cold methanol. The solid polymer was collected by filtration, washed with methanol, and dried at 90 °C.

Polymer Fractionations. The dried polymer products were filled into a Soxhlett apparatus and extracted with ether and hexane for a minimum of 3 h each. The solvent was removed in vacuo and the remaining polymer dried at 60 °C.

Acknowledgment. We thank Dr. Dieter Lilge and Dr. Jürgen Suhm (BASF AG), Klaus Hauschild, Eric Kaminsky, and Professor Gerhard Fink (Max-Planck-Institut für Kohlenforschung), and Jonas Scherble and Professor Rolf Mülhaupt (Materialforschungs-Zentrum Freiburg) for help with analytical determinations, interpretations, and discussions. Gifts of chemicals were kindly donated by BASF AG, CK-Witco, and Axiva GmbH. Financial support of this work by BASF AG, BMBF, and Universität Konstanz is gratefully acknowledged.

References and Notes

(1) Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267*, 217. Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 11586. Petoff, J. L. M.; Bruce, M. D.; Waymouth, R. M.; Masood, A.; Lal, T. K.; Quan, R. W.; Behrend, S. J. *Organometallics* **1997**, *16*, 5909. Bruce, M. D.; Coates, G. W.; Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 11174. Carlson, E. D.; Krejchi, M. T.; Shah, C. D.; Terakawa, T.; Waymouth, R. M.; Fuller, G. C. *Macromolecules* **1998**, *31*, 5343. Bruce, M. D.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 2707. Hu, Y.; Krejchi, M. T.; Shah, C. D.; Myers, C. L.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 6908. Hu, Y.; Carlson, E. D.; Fuller, G. G.; Waymouth, R. M. *Macromolecules* **1999**, *32*, 3334.

(2) Chien, J. C. W.; Iwamoto, Y.; Rausch, M. D.; Wedler, W.; Winter, H. H. *Macromolecules* **1997**, *30*, 3447. Chien, J. C. W.; Iwamoto, Y.; Rausch, M. D. *J. Polym. Sci., Part A* **1999**, *37*, 2439.

(3) Przybyla, C.; Fink, G. *Acta Polym.* **1999**, *50*, 77.

(4) Resconi, L.; Bossi, S.; Abis, L. *Macromolecules* **1990**, *23*, 4489. Resconi, L.; Camurati, I.; Sudmijer, O. *Top. Catal.* **1999**, *7*, 145.

(5) Formation of ^{13}C-labeled Al-polymeryl species by exchange with a $\mathrm{Cp_2Zr}$-polymeryl intermediate: Tritto, I.; Donetti, R.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1999**, *32*, 264.

(6) Polymeryl exchange between $\mathrm{Al^iBu_3}$ and Fe catalysts: Small, B. L.; Brookhart, M. *Macromolecules* **1999**, *32*, 2120.

(7) Spaleck, W.; Antberg, M.; Rohrmann, J.; Winter, A.; Bachmann, B.; Kiprof, P.; Behm, J.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1347.

(8) NMR evidence for the formation of inactive TMA adducts of $Me_2Si(Ind)_2ZrMe^+$: Bochmann, M.; Lancaster, S. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1634.

(9) Rieger, B.; Reinmuth, A.; Röll, W.; Brintzinger, H. H. *J. Mol. Catal.* **1993**, *82*, 67. Röll, W.; Brintzinger, H. H.; Rieger, B.; Zolk, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 279.

(10) If the MAO used contains an estimated 10% of TMA, about 2 mmol of TMA is present in the reaction mixture. After 30 min, an estimated 0.8 mmol of isopropyl-terminated chains has been produced, such that almost half of the initially present TMA has been consumed and the probability of polymeryl exchange with a Me-Al unit is accordingly diminished.

(11) Carvill, A.; Tritto, I.; Locatelli, P.; Sacchi, M. C. *Macromolecules* **1997**, *30*, 7056.

(12) Formation of a heterobimetallic TMA adduct was not observed in ^{1}H NMR experiments with $[Me_2Si(2\text{-}Me\text{-}4\text{-}^tBu\text{-}C_5H_2)_2ZrMe^+][MeB(C_6F_5)_3^-]$ and TMA.

(13) Naga, N.; Mizunuma, K. *Polymer* **1998**, *39*21, 5059. Kim, I. *J. Appl. Polym. Sci.* **1999**, *71*, 875. Kim, I.; Zhou, J. M. *J. Polym. Sci., Part A* **1999**, *37*, 1071. Kim, I.; Jordan, R. F. *Polym. Bull.* **1997**, *39*, 325. Kim, I. *J. Macromol. Sci. Pure Appl. Chem.* **1998**, *A35*, 293. Kim, I.; Choi, C. S. *J. Polym. Sci., Part A* **1999**, *37*, 1523.

(14) Resconi, L.; Jones, R. L.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 998.

(15) Razavi, A.; Atwood, J. L. *J. Organomet. Chem.* **1993**, *459*, 117.

(16) No alkyl exchange was detected in ^{1}H NMR studies on reaction systems containing the dimethyl derivatives of complexes **1** or **2** together with Al^iBu_3 ([Al]:[Zr] 20:1).

(17) Al-mediated polymeryl transfer between the R and S isomers of a racemic zirconocene catalyst is expected to enhance the formation of stereoerrors of the mmrm type compared to a reaction system containing only one of the catalyst enantiomers. Experimental results in this regard are controversial: Reinmuth, A. Dissertation Universität Konstanz, 1992; p 115. Song, W.; Yu, Z.; Chien, J. C. W. *J. Organomet. Chem.* **1996**, *512*, 131. Song, W.; Chien, J. C. W. *J. Organomet. Chem.* **1998**, *558*, 223. Busico, V.; Brita, D.; Caporaso, L.; Cipullo, R.; Vacatello, M. *Macromolecules* **1997**, *30*, 3971. Busico, V.; Cipullo, R. *J. Organomet. Chem.* **1998**, *558*, 219.

(18) Pasquon, I. *Pure Appl. Chem.* **1967**, *15*, 465.

(19) A small hexane-soluble fraction gave the same atactic pentad distribution as the ether fraction.

(20) Bovey, F. A. *Acc. Chem. Res.* **1968**, *1*, 175.

(21) The polymer products are slightly sticky powders of homogeneous appearance.

(22) Soares, J. B. P.; Hamielec, A. E. *Polymer* **1995**, *36*, 1639.

(23) With some effects being probably due also to increasing molar masses, cf. ref 22.

(24) Przybyla and Fink (ref 3) used SiO_2-supported rather than homogeneously dissolved metallocene catalysts, which might have different reactivities.

(25) Direct transfer of polymeryl chains between different Zr centers is not likely to contribute to the formation of stereoblock polymers by a mixture of catalysts, since changes in the zirconocene concentration did not influence the polymer microstructure (cf. run 12). NMR studies on solutions of $(C_5H_5)_2Zr(^{13}CH_3)_2$ and $Me_2Si(2\text{-}Me\text{-}4\text{-}^tBu\text{-}C_5H_2)_2Zr(CH_3)_2$ did not show any transfer of the labeled methyl group between these complexes either.

(26) In this respect, methyl-polymeryl exchange between Zr and Al differs from methyl-Cl exchange, which is strongly affected by differences in Zr electron deficiencies: Beck, S.; Brintzinger, H. H. *Inorg. Chim. Acta* **1998**, *270*, 376.

(27) Similar observations were made in studies with different allyl-zirconocene complexes: Lieber, S.; Prosenc, M. H.; Brintzinger, H. H. *Organometallics* **2000**, *19*, 377.

(28) Wiesenfeldt, H.; Reinmuth, A.; Barsties, E.; Evertz, K.; Brintzinger, H. H. *J. Organomet. Chem.* **1989**, *369*, 359.

MA000691J