

Reactor blending with early/late transition metal catalyst combinations in ethylene polymerization

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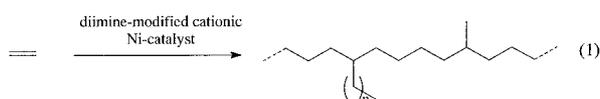
SUMMARY: Ethylene is polymerized by heterobimetallic combinations of early and late transition metal catalysts. Dual combinations of zirconocenes and cationic nickel and iron catalysts with multidentate nitrogen-donor ligands are described. Reactor blends of linear and branched ethylene homopolymers are obtained. With zirconocene / nickel complex catalyst combinations, addition of hydrogen selectively reduces the molecular weight of the linear polyethylene formed by the metallocene catalyst.

Introduction

Blending of two or more polymers is often applied to control the overall property profile of materials¹. For polyethylene resins, blending primarily aims at improving the balance of processability and mechanical properties of the final product. Important industrial applications comprise the blending of polyethylenes with different molecular weights, thus achieving broad molecular weight distributions, and the blending of homo- and copolymers with different degrees of branching and branching types.

Basically, blending is achieved by post-polymerization mixing of the different polymers, e.g., in an extruder, or, more conveniently, by directly generating the different polymers during the polymerization process ('reactor blending'). The latter technique can employ multiple reactors, generating different polymers by varying the reaction conditions in each reactor², or within a single reactor two or more polymerization catalysts can be used³. For early transition metal based metallocene or Ziegler catalysts⁴, reactor blending is well established and is applied on an industrial scale.

The polymerization of ethylene by late transition metal complexes^{5,10(c)} has received increasing interest in recent years. Lately, olefin polymerization catalysts based on cationic nickel(II) and palladium(II) complexes with bidentate diimine ligands⁶ were reported by Brookhart et al.⁷ They are highly active for ethylene polymerization, allowing for the homopolymerization to branched high molecular weight polymers (Eq. 1)^{7a,8}.



Subsequently, iron complexes with related tridentate nitrogen ligands were reported independently by different research groups⁹. They are highly active for the linear polymerization of ethylene.

Considering combinations of early and late metal catalysts in olefin polymerization, in an application related to reactor blending of different polymerization catalysts, combinations of neutral nickel(II)-based ethylene oligomerization catalysts with titanium, zirconium or chromium based polymerization catalysts have been reported¹⁰. α -Olefins, generated *in situ* by the nickel catalyst, are copolymerized with ethylene. Overall, a branched linear copolymer results employing ethylene as the sole feedstock.

The coordination chemistry of heterobimetallic complexes combining early and late transition metals has been the subject of considerable interest¹¹. Such complexes have also been applied to the polymerization of olefins¹². However, to the best of the author's knowledge no evidence for the simultaneous catalytic activity of the different metal centers has been reported for the latter reactions.

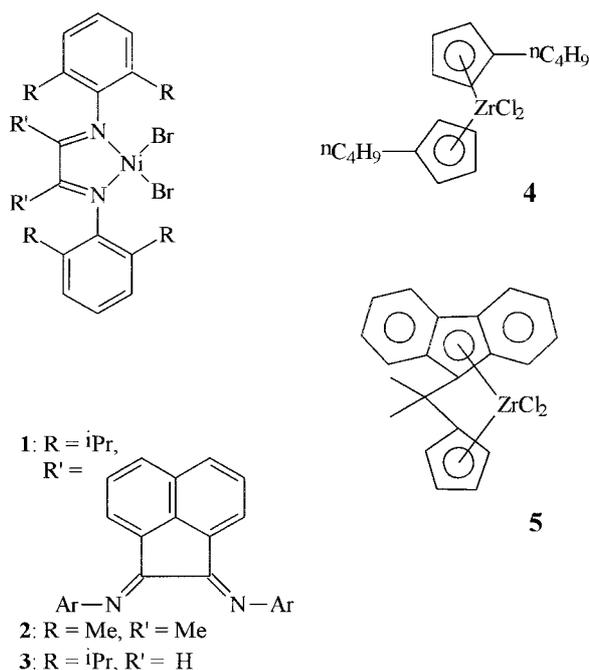
This paper now reports first results on the simultaneous polymerization of ethylene by combinations of early and late metal polymerization catalysts¹³. Hereby, reactor blends of linear and branched polyethylenes are obtained employing ethylene as the sole monomer.

Results and discussion

Initial experiments, using the combination $Cp_2ZrCl_2/1$ (Scheme 1) with methylaluminoxane (MAO) as a cocatalyst for ethylene homopolymerization, demonstrated that a metallocene and a cationic nickel diimine complex-based catalyst can be run simultaneously in one reactor.

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Scheme 1: Nickel and zirconium catalyst precursors employed



Employing a molar excess of either transition metal compound, both catalysts were found to be active, as evidenced by the formation of mixtures of linear and branched polyethylenes. The latter were partially, or even completely in some cases, dissolved in the hydrocarbon solvent used as a reaction medium, forming very viscous solutions. **1** is known^{7a,e,14)} to produce high molecular weight, highly branched polyethylene, which is well soluble in hydrocarbon solvents. Under typical polymerization conditions of the work presented here (10 atm ethylene pressure and 50 °C), a total of 59 branches/1000 methylene groups was found, $\delta = 0.877 \text{ g} \cdot \text{mL}^{-1}$.

Such a separation of the blend during the polymerization process is undesirable. In this context, considering the process types applied¹⁵⁾, the transition metal catalyzed polymerization of ethylene is commonly carried out in slurry, in gas-phase or in solution, and polymerization in bulk, i.e., supercritical ethylene, is also well known. In applications of the solution process to the production of linear ethylene homopolymers, high temperatures, usually in excess of 200 °C, are necessary to retain the polymer in solution. Such high temperatures would lead to deactivation of the nickel catalyst. Therefore, of the most common processes, gas phase- or slurry-polymerization seem favorable for reactor blending of branched with linear polyethylene.

Employing the nickel compounds **2** or **3** as precursors for the late metal component of the catalyst, reactor blends which precipitate completely^b in a hydrocarbon slurry are obtained under convenient reaction conditions, i.e., elevated temperature and moderate pressure (typically 50 or 60 °C and 10 atm of ethylene). Tab. 1 shows typical polymerization results (entries 1 to 5). Utilizing solely **2** as a catalyst precursor in the absence of an early metal catalyst, a polymer with a density of $0.910 \text{ g} \cdot \text{mL}^{-1}$ is obtained, corresponding to an overall branching of 26/1000 CH_2 . Reactor blends in the density range of 0.91 to 0.96 were prepared.

Branching analysis by ¹³C NMR spectroscopy (Tab. 2) shows the structure consisting of methyl and long chain branches, in addition to $\text{C}_{\geq 2}$ short chain branches, previously reported by Brookhart et al.^{7e)} Whereas the overall average number of branches of a reactor blend is of course dependent on the ratio of early/late metal catalyst employed, the data shown in Tab. 2 does not reveal any change in branching structure for different blend compositions. The relative ratio of the different types of branches is constant within experimental error. Thus, from this data and the molecular weight data given in Tab. 1, entries 1 to 4, no direct interaction between early and late metal centers is apparent.

Comparison of the DSC traces of reactor blends with polymers obtained using solely **2** and **5** as a catalyst precursor shows that the branched and linear fractions in the reactor blend largely cocrystallize. For the reactor blend of entry 1, $T_m = 128^\circ\text{C}$ and $\Delta H_m = 153 \text{ J} \cdot \text{g}^{-1}$ were found (branched polyethylene obtained with **2** under identical conditions: $T_m = 117^\circ\text{C}$, $\Delta H_m = 131 \text{ J} \cdot \text{g}^{-1}$; linear polyethylene obtained with **5**: $T_m = 133^\circ\text{C}$, $\Delta H_m = 188 \text{ J} \cdot \text{g}^{-1}$).

Addition of hydrogen is a well known and widely applied means of controlling polymer molecular weight with Ziegler-systems or in metallocene catalyzed ethylene polymerization. With metallocene **4**, under the standard reaction conditions, addition of 0.2 atm initial partial pressure of H_2 results in a strong decrease of molecular weight (Tab. 1, entries 6 and 7). Correspondingly, the density increases from a value typical for ultra high molecular weight polyethylene to a value typical of high density polyethylene. Running the system **2/4** (entries 8 and 9) under hydrogen pressure resulted in a significant decrease in average molecular weight of the reactor blend, relating to an increase in melt flowability, as anticipated. To probe hydrogen reactivity of the late metal catalyst separately, **2** was run under the conditions of entry 3, Tab. 1 in the presence of hydrogen. Adding up to 45 mmol H_2 , correspond-

^b In typical polymerization experiments with **2**, the content of ethylene polymers or oligomers dissolved in the hydrocarbon diluent was determined by evaporating the liquid phase obtained after filtration from the polymer product during the standard workup procedure. With toluene as a reaction medium, ca. 0.3 g/L (corresponding to ca. 1% relative to polymer yield) were found. Using aliphatic hydrocarbons as the reaction medium, somewhat higher amounts of solubles were found.

Tab. 1. Polymerization results^{a)}

Entry No.	Reaction conditions					Polymer yield/g	Polymer properties				
	Catalyst	$n(1)$ μmol	$n(2)$ μmol	H ₂ added mmol	reaction time/min		density g · mL ⁻¹	η_{red} mL · g ⁻¹	$10^{-4} \cdot \bar{M}_v^b$ g · mol ⁻¹	branches/ 1000 CH ₂ ^{c)}	MVI (21,6 kg) in mL/10 min
1	2/5	28.8	12.4	–	30	193	0.932	293	24	10 ^{c)}	/
2	2/5	27.8	3.9	–	30	125	0.918	259	20	22 ^{c)}	/
3	2	28.6	–	–	56	102	0.910	287	23	26 ^{c)}	/
4	5	–	8.7	–	53	107	0.953	275	23	<0.5	/
5	3/5	33.3	6.2	–	50	138	0.931	191	13	/	/
6	4	–	1.1	–	30	87	0.938	856	97	/	<1
7	4	–	1.0	15 (0.2 atm)	50	150	0.963	132	8	/	250
8	2/4	28.6	0.9	–	35	158	0.928	521	52	/	<1
9	2/4	15.4	0.9	30 (0.5 atm)	45	74	0.949	274	22	/	30
10	6	7.8	–	–	55	80	0.968	215	16	<0.5	170
11	2/6	19.2	15.9	–	55	231	0.949	399	36	8 ^{c)}	18
12	6/4	5.0	0.5	–	35	184	0.961	372	33	/	10

^{a)} Reaction temperature: 60 °C (entries 1 and 2: 50 °C; entry 10: 70 °C); 10 atm ethylene pressure (entry 10: 8 atm); reaction medium: toluene (entries 1, 2, 4, and 5) or aliphatic hydrocarbons (entry 3 and 6 to 12); cocatalyst: MAO (34 mmol; entries 3, 4, 6, 7, and 10: 17 mmol). / = not determined.

^{b)} Calculated using relationships for linear polyethylene: $[\eta] = K \cdot M_v^a$ with $K = 0.067$ mL/g and $a = 0.67$; $[\eta]$ extrapolated via $\log(\eta_{\text{red}}/[\eta]) = 0.139$ mL/g · $c \cdot [\eta]$.

^{c)} Determined by ¹³C NMR. Average branching of entire polymer (blend) composition.

Tab. 2. Branching structure of polymers

Entry no. in Tab. 1.	Total branching/ 1000 CH ₂ ^{a)}	Branches/1000 CH ₂ (relative to total)				
		methyl	ethyl	propyl	butyl	long chain ^{b)}
1	9.7	7.0 (72%)	0.7 (7%)	/ ^{c)}	/ ^{c)}	2.0 (21%)
2	22.2	14.8 (67%)	1.7 (8%)	1.1 (5%)	1.5 (7%)	3.1 (14%)
3	26.4	17.8 (67%)	1.5 (6%)	1.4 (5%)	1.1 (4%)	4.6 (17%)

^{a)} Average branching of entire polymer (blend) composition.

^{b)} Amyl and higher branches.

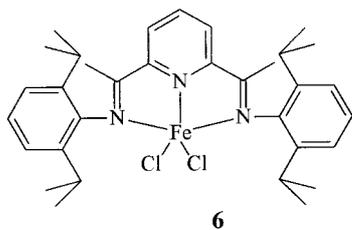
^{c)} /: not determined, i. e., below quantification limit.

ing to a partial pressure of ca. 0.7 atm H₂, no strong effect on the molecular weight was found^c, and a polymer with a MVI of ca. 1 mL/10 min (21.6 kg) is obtained. Thus, addition of hydrogen selectively controls the early metal catalyst component in this system.

Reactor blends were also prepared with heterogeneous catalysts, obtained by adding toluene solutions of the metal halide catalyst precursors to a commercially available silica adsorbed MAO (MAO-S). For blends, as well as for polymers obtained solely with late metal catalysts, total branching is lowered in comparison to polymerization with homogeneous catalysts, and the branching structure appears to be slightly altered (e. g. **2**/MAO-S: 16 branches/1000 methylene groups; Me: 77%, Et: 7%, Pr: 4%, Bu: 3%, C_{≥5} branches: 8% vs. 26 branches with **2**/MAO in entry 3, Tab. 1).

In addition to the nickel-based late metal catalysts, iron catalyst **6** was also employed for reactor blending. **6** has been reported very recently⁹⁾ to polymerize ethylene in a strictly linear fashion. Thus, combination with a nickel catalyst could again result in reactor blends of linear and branched polyethylenes, and combination with a metallocene could be suitable for *in situ* production of blends of linear polyethylenes of different molecular weights or crystallinities. Results are given in Tab. 1, entries 10 to 12 (cf. comparative entries 3 and 6). Densities, molecular weights and, for the combination of the two late metal catalysts, the overall branching observed (8/1000 methylene groups; Me: 68%, Et: 7%, Pr, Bu: below quantification limit, C_{≥5} branches: 25%) are indicative of both catalysts being active, as anticipated.

^c Unexpectedly, the data available indicates a moderate *increase* in molecular weight in the presence of hydrogen. Further investigations on this effect are necessary.



In conclusion, cationic olefin polymerization catalysts based on late transition metals are compatible with early metal metallocene catalysts. Running both catalysts in the same reaction medium simultaneously, no strong interaction between the early and late metal centers is evident from the data presented. Reactor blends of branched and linear polyethylenes are obtained, employing ethylene as the sole monomer. Addition of hydrogen can selectively control the molecular weight of the polymer formed by the metallocene catalyst component.

Experimental part

Materials and analytical procedures

Catalyst precursors were obtained commercially or similar to literature procedures^{7a,9b}). All compounds employed gave satisfactory elemental analyses. MAO activator was obtained as a 10% solution in toluene from Witco; for heterogeneous catalysts silica-supported MAO-S with 23 wt.-% aluminium was used (Witco TA02794). Catalyst precursors and solutions were handled under nitrogen or argon atmosphere, employing standard Schlenk or drybox technique. Dry solvents purged with argon or nitrogen prior to use were employed. As an aliphatic hydrocarbon solvent, Exxsol (Exxon) with a boiling range of 100 to 120 °C was used.

NMR spectra of the polymers were obtained on a Bruker MSL-300 (¹³C: 75 MHz) at 90 °C in tetrachloroethane-*d*₂/hexachlorobutadiene. Branching was determined according to ref.¹⁶) DSC traces were obtained on a Mettler DSC820 at heating rates of 10 °C · min⁻¹. Data reported are second heats. Solution viscosities were determined on an Ubbelohde viscosimeter at 135 °C in decalin, at concentrations of 0.1 g · dL⁻¹. Densities were determined in a density gradient column on samples cut from sheets pressed in the melt. Melt flow indices were determined at 190 °C according to ISO1133.

Polymerization procedure

For activation of the catalyst precursors, the early and late metal halide were each weighed into a flask. MAO was added (typically 10 mL) to both flasks, and the resulting solutions were briefly stirred and then transferred to the polymerization reactor.

Polymerization experiments were carried out in a mechanically stirred 5 L pressure reactor equipped with an external heating/cooling jacket. The clean reactor was flushed with nitrogen, and was then charged with 3.5 L of solvent. The solvent was saturated by brief stirring under ethylene pressure, the pressure was released and the reactor was charged with the above catalyst solutions under stirring. Optionally, a specified amount of hydrogen was then added from a pressure chamber of known volume. A constant ethylene pressure was applied, and the reactor was rapidly brought to the desired temperature. After the specified reaction time, the reaction was stopped by releasing the ethylene pressure and by rapid cooling.

The polymer slurry was filtered, and the product was washed by stirring with acidified methanol and twice with acetone to remove residual cocatalyst^d. The product was dried in a vacuum oven at 50 °C.

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