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Synthesis of Long-Chain Branched Comp-Structured Polyethylene from Ethylene by Tandem Action of Two Single-Site Catalysts

O. Sperber* and W. Kaminsky

Institute of Technical and Macromolecular Chemistry, University of Hamburg, Bundesstrasse 45, 20146 Hamburg, Germany

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ABSTRACT: The synthesis of long-chain branched polyethylene by copolymerization of ethylene with higher α-olefins has its limitations due to commercial availabilities of pure α-olefins above carbon lengths of C30. Soga[1] and Bazan[2] have shown the possibility of inserting side chains up to a length of 60 carbons into a growing polyethylene backbone. The details of combining $[Me_2C(Cp)_2]ZrCl_2$ **(1)** and $[Me_2Si(N^tBu)(Me_4Cp)]TiCl_2$ **(2)** to obtain long-chain branched polyethylene with branch lengths up to 350 carbons as well as the copolymerization profile and purification of the product throughout the Kumagawa extraction are discussed here. Compound **1** was used in a first oligomerization step to yield a macro-comonomer. Three different methods involving conventional copolymerization, tandem polymerization, and simultaneous entry of the catalysts were examined using **2** and MAO as cocatalyst to copolymerize different macro-comonomers with ethylene.

Introduction

Highly active metallocene catalysts in conjunction with suitable cocatalysts are now used for olefin polymerization to obtain custom-made polymers with superior mechanical properties.[1−3] Development of the design of single-site catalysts provides an ever expanding field of metal−ligand combinations suitable for catalyzing the polymerization of olefins.[4] They offer a promising new way to control stereoregularity and regioregularity of the polyolefins and to produce entirely new polymeric materials.[5] This also represents a major advantage over conventional heterogeneous Ziegler−Natta catalysts, which are normally deactivated by long-chain α-olefins.[6] Because of their narrow molar mass distribution, metallocene-produced high linear polyethylene is difficult to process compared to conventional polyolefins of higher polydispersity.[7] A very small amount of long-chain branches along the polymer backbone leads to totally different properties of the polymers, which make it very interesting for industrial processings. Tandem copolymerization with two different catalysts opens the synthesis of ultra-long-chain branched polyethylene[8] with chain lengths up to 350 carbons and branching percentages up to 1.0 mol %. Such long-chain branched comp-structured polyethylene, even at very low side-chain concentration, significantly increases the viscosity, shear flow, and elasticity in extensional flow.[9] The additional interlock of long-chain branches within the polymer cluster is considered to give a very robust structure−property relationship. For example, under dynamic stress a film, made of such LCB−PE, could have a much better tearing toughness than an equivalent linear PE.

α-Olefin comonomers are commercially available as pure materials up to a chain length of approximately 30 carbons. Higher α-olefins must be synthesized. While some late-transition-metal catalysts such as the diimine ligand systems $[(2\text{-ArN}{=}\text{CMe})_2C_5H_3N]FeCl_2$/MAO[10] are able to produce low molar mass oligoethylene up to 2000 g/mol, **1**/MAO produces oligomers with an average molar mass between 800 and 4500 g/mol and a mass distribution around 2.0 depending on the chosen oligomerization conditions. These conditions are mainly high catalyst concentration, low ethylene pressure, and high oligomerization temperatures.

We have carried out the copolymerization by three different methods. First, the produced macro-comonomer was separated after the oligomerization was finished, washed, dried, and applied to a conventional copolymerization **(**copo**)** with ethylene and **2**/MAO. Second, the macro-comonomer was kept in the apparatus after the oligomerization was finished and **2** has been added in situ to the process to start a tandem-like copolymerization **(**tandem**)**. Third, a mixture of **1**, **2,** and MAO was added to the reactor simultaneously **(**simultan**)**. For all three methods (copo, tandem, simultan) the same oligomerization and copolymerization conditions were used in order to compare the reactivity and achieved product. Compound **2** was chosen because of its high tolerance toward higher α-olefins, when insert into a growing polymer backbone.[12]

Results and Discussion

The reactivity profiles of the individual catalysts **1** and **2** have been reported.[11,12] The oligomerization was carried out in solution with 5.0×10^{-6} mol of **1** in 200 mL of absolute toluene and 200 mg of MAO. With the variation of the ethylene pressure between 1.0 and 2.0 bar and a reaction temperature between 75 and 90 °C, waxy or solid oligoethylene of an average molar mass between 800 and 4500 g/mol was obtained. The according reactivity, DSC, and GPC data of some of those macro-comonomers are shown in Table 1. The average percentage of terminal double bond in the molecule was calculated by ^1H NMR spectroscopy, and the branching mole percent and side-chain type were examined by ^{13}C NMR spectroscopy.

Homopolymerization was performed as a reference to the copolymerizations using 1.0×10^{-6} mol of **2** and 200 mg of MAO in 200 mL of absolute toluene. The ethylene pressure was set between 1.0 and 2.0 bar while the reaction temperature was varied from 75 to 90 °C. Under these polymerization conditions, the average molar mass of the pure polyethylene can be adjusted between 8.0×10^4 and 5.0×10^5 g/mol. The mass distribution, DSC, GPC, and ^{13}C NMR data concerning the linearity are also presented in Table 1.

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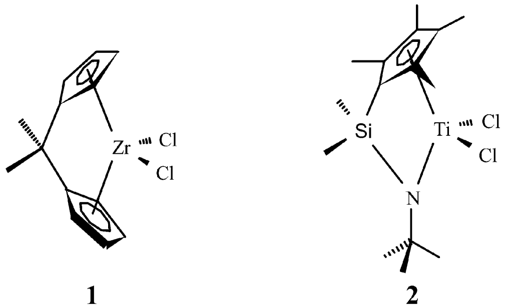
Table 1. Individual Ethylene Oligomerization and Polymerization with 1/MAO and 2/MAO[a]

entry	cat.	Al/M	activity[f]	T_m (°C)	α [%]	M_w [g/mol]	M_w/M_n	branching [mol %]	branching type	terminal double bond (%)
1	**1**[b,e]	680	19 800	111.5	29	1 200	2.3	0.41	Me, Et, minor Hex	98
2	**1**[c,e]	680	34 000	113.0	35	2 700	2.2	0.39	Me, Et, minor Hex	97
3	**1**[b,d]	680	8 000	116.9	59	3 600	2.4	0.31	Me, Et	98
4	**1**[c,d]	680	13 000	118.5	67	4 500	2.3	0.33	Me, Et	96
5	**2**[b,e]	3400	82 000	138.8	71	79 200	2.1	n.d.[g]		
6	**2**[c,e]	3400	175 000	141.3	53	189 500	2.0	n.d.		
7	**2**[b,d]	3400	31 000	138.4	58	221 600	2.0	n.d.		
8	**2**[c,d]	3400	43 000	140.4	60	490 000	2.2	n.d.		

[a] Reaction conditions: 5.0×10^{-6} mol for **1** and 1.0×10^{-6} mol for **2**, 200 mL of absolute toluene, 200 mg of MAO, polymerization time 60 min, stirrer rate 450 rpm, ethylene pressure. [b] 1.0 bar. [c] 2.0 bar, polymerization temperature. [d] 75 °C. [e] 90 °C. [f] Activity = $kg_{polymer}/[(mol_{catalyst}\ mol)/(L_{monomer}\ h)]$. [g] n.d. = not detectable; Me = methyl, Et = ethyl, Hex = hexyl; cat. = catalyst; α = crystallinity.



1 **2**

Figure 1. Structures of $[Me_2C(Cp)_2]ZrCl_2$ **(1)** and $[Me_2Si(N^t\text{-}Bu)(Me_4Cp)]TiCl_2$ **(2)**.

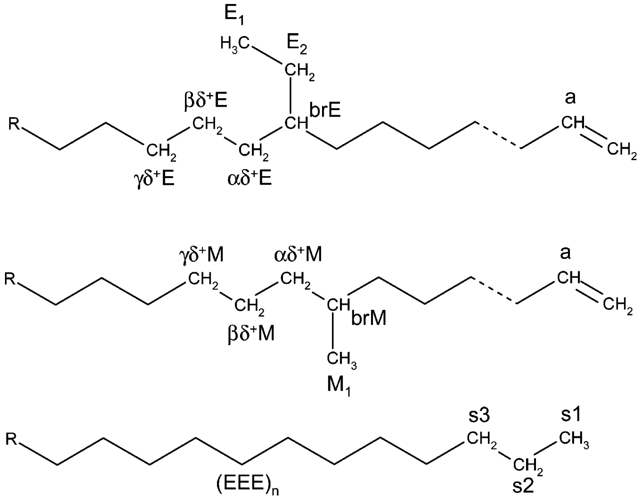


Figure 2. Nomenclature of polymer backbone and branching carbons by ^{13}C NMR.[17]

Beside the end-group signals, the ^{13}C NMR spectra of the oligomers in Figure 3 show peaks for isolated ethyl branches at 11.33, 26.77, 27.27, 30.49, 34.08, and 39.67 ppm; isolated methyl branches at 20.13, 27.43, 30.89, 33.22, and 37.54 ppm; and minor signals for isolated hexyl branches at 14.04, 27.27, 29.36, 30.46, 34.53, and 38.13 ppm.

For the polymer material obtained by **2**/MAO no branches were detectable beside the end-group peaks at 14.24, 22.92, 29.58, and 32.22 ppm (Figure 3).

To compare the three different processing methods (copo, tandem, simultan) in their reactivity and resulting polymer product, all copolymerization conditions were identical. The reaction temperature was 90 °C, the ethylene pressure was 2.0 bar, and 200 mL of absolute toluene, 400 mg of MAO, 5×10^{-6} mol of **1**, and 1×10^{-6} mol of **2** were used. The method differences are shown in Table 2.

Separation of the long-chain branched polyethylene appeared to be difficult due to the remaining amount of waxy and solid comonomer in the product. Because of the better solubility of the oligomeric material, a Kumagawa extraction was done to separate and pure the copolymers. A Soxhlet apparatus was used with organic solvents varying in polarity and boiling point. The solvent sequence was diethyl ether, *n*-hexane, *n*-hexane/cyclohexane (50:50), cyclohexane, *n*-heptane, toluene/*n*-heptane (50:50), toluene. Each washing step was carried out for 170 h before the residue LCB−polyethylene was dried and used for further analyses. The GPC diagrams in Figure 4 show that the copolymer was isolated completely. Here an oligomer with an average molar mass of M_w = 2700 g/mol has been inserted into a growing linear PE backbone. The individual linear PE material has an average molar mass of M_w = 216 400 g/mol. The resulting comp-PE shows no further byproduct, the mass distribution M_w/M_n is 2.1, and the average molecular mass M_w = 179 700 g/mol appears to be slightly lower than for the according linear PE.

By integrating the long-chain branching signals in the ^{13}C NMR spectra at 38.15, 34.54, 30.47, and 27.27 ppm and comparing them with the methylene carbon signal at 29.98 ppm, the mole percent of long-chain branches can be estimated. In the case of the LCB−PE in Figure 5 with a M_w of 179 704 g/mol the material consists of 0.38 mol % long-chain branches with a side-chain average molar mass of 2700 g/mol, which is a branching length of averagely 200 carbons. This 0.38 mol % corresponds to approximately 17.8 wt % of the material being side chains.

Comparison of the three processing methods (copo, tandem, simultan) shows that the conventional copolymerization and the tandem process produce similar material (Table 3). The reactivity and insertion percent of long chains are slightly higher for the tandem copolymerization, which means that the isolation/purification/drying step is not necessary. For the simultaneous copolymerization, the reactivity is higher but the long-chain insertion is lower than with the other two methods. This is presumably because the macrocomonomer concentration is low at the beginning of the reaction and increases with time. This also means that the side-chain distribution is not homogeneous in the copolymer. Also, the length of the side chains can only be estimated knowing the individual performance of **1**/MAO. However, with two active species in the reactor, the oligomer product may differ from the material synthesized separately.

Therefore, all further copolymerizations were done by the tandem reaction. Oligomerization and polymerization temperature as well as the ethylene pressure were varied to encompase side-chain length range between C70 and C350 and the PE backbone length range between 6000 and 75 000 carbons. Copolymerization

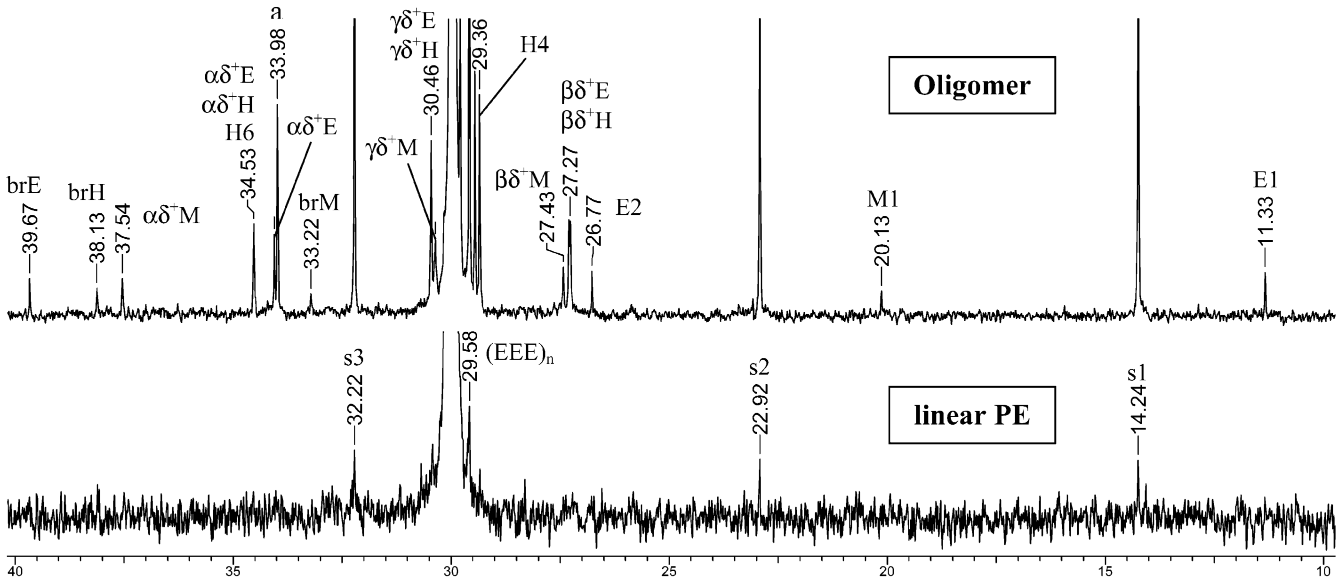


Figure 3. ^{13}C NMR spectra of an oligomeric macro-comonomer obtained by **1**/MAO with an average molar mass M_w of 2700 g/mol (entry 2) and a linear PE obtained by **2**/MAO with an average mass M_w of 189 500 g/mol (entry 6).

Table 2. Copolymerization Methods (copo, tandem, simultan) and Their Entry Sequences

Copolymerization (copo)	Tandem-polymerization (tandem)	Simultaneous-polymerization (simultan)
$[Me_2C(Cp)_2]ZrCl_2$ / MAO toluene, 90 °C, 2.0 bar ethylene ↓ macro-comonomer isolated and pured ↓ $[Me_2Si(^{tert}Butyl\text{-}amido)(Me_4Cp)]TiCl_2$ MAO, toluene, 90 °C, 2.0 bar ethylene $X_{macrocomonomer}$: 0.25 ↓ Comp-PE / macro-comonomer separation (Kumagawa-extraction)	$[Me_2C(Cp)_2]ZrCl_2$ / MAO toluene, 90 °C, 2.0 bar ethylene ↓ monomer consumption byi ≈ 0 ml /min. $X_{macrocomonomer} \approx 0.25$ ↓ *in situ* $[Me_2Si(^{tert}Butyl\text{-}amido)(Me_4Cp)]TiCl_2$ MAO, toluene, 90 °C, 2.0 bar ethylene ↓ Comp-PE / macro-comonomer separation (Kumagawa-extraction)	$[Me_2Si(^{tert}Butyl\text{-}amido)(Me_4Cp)]TiCl_2$ and $[Me_2C(Cp)_2]ZrCl_2$ / MAO toluene, 90 °C, 2.0 bar ethylene ↓ Comp-PE / macro-comonomer separation (Kumagawa-extraction)

conditions, results, and copolymerization diagram are given in Table 4 and Figure 6.

The melting point (T_m) and crystallinity (α) of the synthesized LCB−PE shown in Figure 7 decrease by increasing the side-chain percentage. The side-chain length shows little difference in this behavior. Both T_m and α drop down to approximately 90% compared to the linear material synthesized separately but seem to converge toward a tangent value in the observed mole percent area.

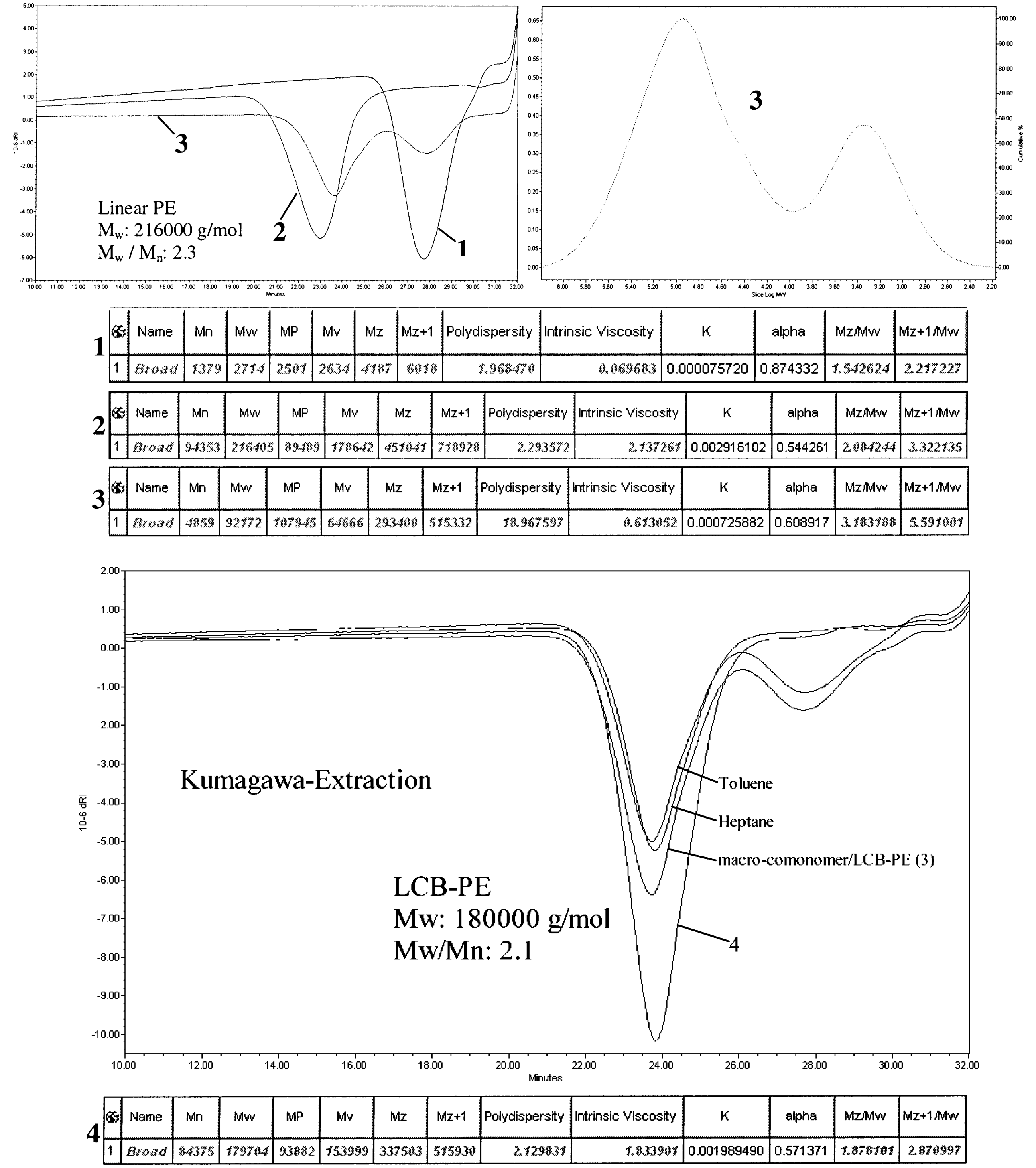
Summary and Conclusion

With the reaction conditions used in this study, we have shown the possibility of inserting side chains into a linear polyethylene backbone up to a branching length of about 350 carbons, with mole percentages to 1.0%. The backbone length can be varied from 6000 to 35 000 carbons. Furthermore, the use of two single-site metallocenes within a tandem-type copolymerization basically offers a practical way for industrial application to produce even high molecular weight linear PE with very low amounts of long-chain branching. Using **1**/MAO to synthesize terminal double-bonded oligomers as macro-comonomers for the second step, adding **2** in situ to the oligomerization to initiate the copolymerization leads to homogeneous material compared to the simultaneous entry. However, one big lack is the purification and high yield loss that comes with isolation methods like the Kumagama extraction. For an industrial use of tandem-type copolymerizations to obtain LCB−PE with well-defined long-chain branches, the isolation method still needs much improvement. A second need of continuing research in this field is the finding of a proper analysis method for long-chain branches. Even now, no certain statement can be made about the actual microstructure of such branched copolymers. By synthesizing defined oligomeric α-olefins and using them as macro-comonomers for the copolymerization to LCB−PE, the length and braching weight distribution are

Table 3. Comparison of the Three Methods (copo, tandem, simultan) for the Copolymerization of Oligoethylene Macro-comonomers and Ethylene Using 1, 2/ MAO, 75 °C Polymerization Temperature, 2.0 bar Ethylene Pressure, and 1.0 h Reaction Time

	copolymerization (copo)	tandem polymerization (tandem)	simultaneous polymerization (simultan)
side-chain length *n*(carbons)	140	140	n.d.[a]
side-chain M_w [g/mol]	1960	1960	n.d.
side-chain M_w/M_n	2.1	2.1	n.d.
mol %	0.48	0.52	0.42
wt %	12.73	12.67	n.d.
LCB−PE M_w [g/mol]	588 400	546 400	616 500
LCB−PE length *n*(carbons)	42 000	39 000	44 000
LCB−PE M_w/M_n	2.2	2.1	2.2

[a] n.d. = not detectable.



1

	Name	Mn	Mw	MP	Mv	Mz	Mz+1	Polydispersity	Intrinsic Viscosity	K	alpha	Mz/Mw	Mz+1/Mw
1	*Broad*	1379	2714	2501	2634	4187	6018	1.968470	0.069683	0.000075720	0.874332	1.542624	2.217227

2

	Name	Mn	Mw	MP	Mv	Mz	Mz+1	Polydispersity	Intrinsic Viscosity	K	alpha	Mz/Mw	Mz+1/Mw
1	*Broad*	94353	216405	89489	178642	451041	718928	2.293572	2.137261	0.002916102	0.544261	2.084244	3.322135

3

	Name	Mn	Mw	MP	Mv	Mz	Mz+1	Polydispersity	Intrinsic Viscosity	K	alpha	Mz/Mw	Mz+1/Mw
1	*Broad*	4859	92172	107945	64666	293400	515332	18.967597	0.613052	0.000725882	0.608917	3.183188	5.591001

4

	Name	Mn	Mw	MP	Mv	Mz	Mz+1	Polydispersity	Intrinsic Viscosity	K	alpha	Mz/Mw	Mz+1/Mw
1	*Broad*	84375	179704	93882	153999	337503	515930	2.129831	1.833901	0.001989490	0.571371	1.878101	2.870997

Figure 4. GPC data of the individual oligomerization (**1**) and polymerization (**2**) products and the chromatograms of the LCB–PE/oligomer mixture (**3**) and purified LCB–PE (**4**).

Table 4. Some Sample LCB–Polyethylenes Obtained by Tandem Copolymerization Using 1, 2, and MAO at the Same Polymerization Conditions[a]

entry	ethylene press. [bar]	T_P [°C]	activity[b]	T_m [°C]	α [%]	M_w [g/mol]	M_w/M_n	branching [mol %] ([wt %])	branching M_w [g/mol]	branching M_w/M_n
1	0.5	90	65 130	124.5	44	83 000	2.1	0.69 (7.09)	980	2.2
2	1.0	90	83 100	124.7	49	101 000	2.2	0.51 (8.83)	1200	2.1
3	2.0	90	125 100	125.3	49	130 000	2.1	0.38 (17.69)	2700	2.1
4	0.5	75	19 300	125.1	55	140 000	2.3	0.42 (18.95)	3100	2.2
5	1.0	75	33 000	124.4	56	170 000	2.2	0.33 (22.62)	3600	2.1
6	2.0	75	57 200	124.6	59	244 000	2.1	0.28 (27.75)	4500	2.1

[a] Reaction conditions: 5.0×10^{-6} mol for **1** and 1.0×10^{-6} mol for **2**; method is tandem copolymerization, 200 mL of absolute toluene, 200 mg of MAO, polymerization time 60 min, stirrer rate 450 rpm. **2** has been injected in situ when $X_{\text{macro-comonomer}}$ has reached 0.25 relative to the solvents ethylene concentration. The monomer consumption for the oligomerization at this time was about 0 mL of ethylene. [b] Activity: $\text{kg}_{\text{polymer}}/[(\text{mol}_{\text{catalyst 2}}\ \text{mol})/(\text{L}_{\text{monomer}}\ \text{h})]$; T_P = copolymerization temperature; α = crystallinity.

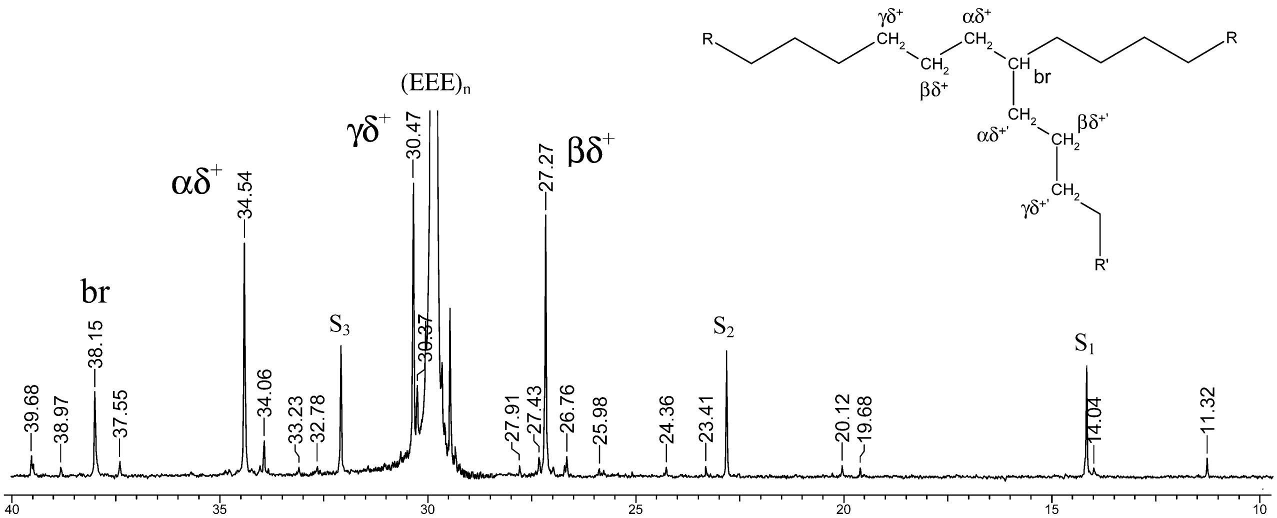


Figure 5. ^{13}C NMR spectra of a long-chain branched PE ($M_w = 179\,704$ g/mol) obtained by a tandem copolymerization with the entry of **1** and **2** using MAO, 200 mL of absolute toluene, 90 °C polymerization temperature, and 2.0 bar ethylene pressure.

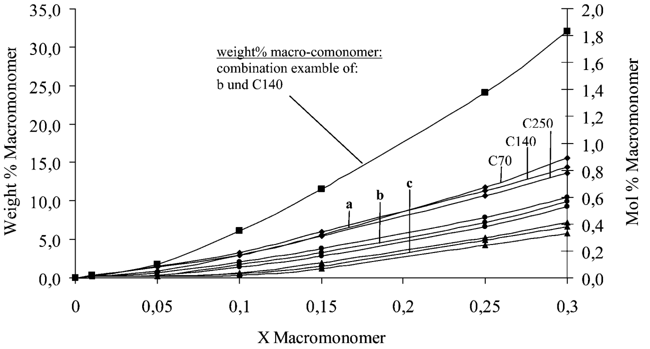


Figure 6. Copolymerization diagram of comp-PE samples with a backbone length of 7000 (a), 12 000 (b) and 35 000 (c) carbons and side-chain lengths between C70 and C250 carried out by tandem copolymerization using **1**, **2**, and MAO.

known. However, the detection and quantification of unknown long-chain branched material need other ways of ^{13}C NMR measurements that allow to detect more than only six carbons around the branching point. Right now, there exist strong efforts for example on solid-state ^{13}C NMR modification[13] combined with rheological measurements to enable the detection and microstructure analysis even of long-chain branching above a branching carbon length of C6. Such PE with well-defined long-chain branching, as it was obtained in this study, could also be used as standard material to establish and calibrate new methods in this field. Still some research is to be done concerning the separation of the copolymer material from the macro-comonomer. The comonomer itself is a waxy and solid which makes the isolation of the solid LCB-*co*-polymer difficult. Every attempt of fractional crystallization has failed, and so far the Kumagawa extraction seems to be the easiest way of isolating the product with the lack of drastic loss of material due to its partial solubility in the used extraction solvents.

The simultaneous copolymerization tangented in this paper and reported previously[8,9] for lower molar mass branching also offers a promising way to produce long-chain branched PE, but still there is a lot of research to do to find and understand the kinetics of a possible quasi-balance between the monomer/oligomer ratio during the copolymerization. Our future interest lies in synthesizing larger amounts of LCB−PE within the scale, PE backbone, and branching length presented in this paper. These materials shall help to establish new methods for the analysis of long-chain branches and the research in material properties of this LCB-*co*-polymers in comparison to homogeneous PE. Our focus lies on the dependence of different branching mole percentage relative to different branching and backbone length and their influence in mechanical properties of these materials.

Experimental Section

General Data. Toluene was received from Merck with a purity of ≥99.5%. It was stored for several days over potassium hydroxide, filtered, distilled, degassed in vacuo afterward, and

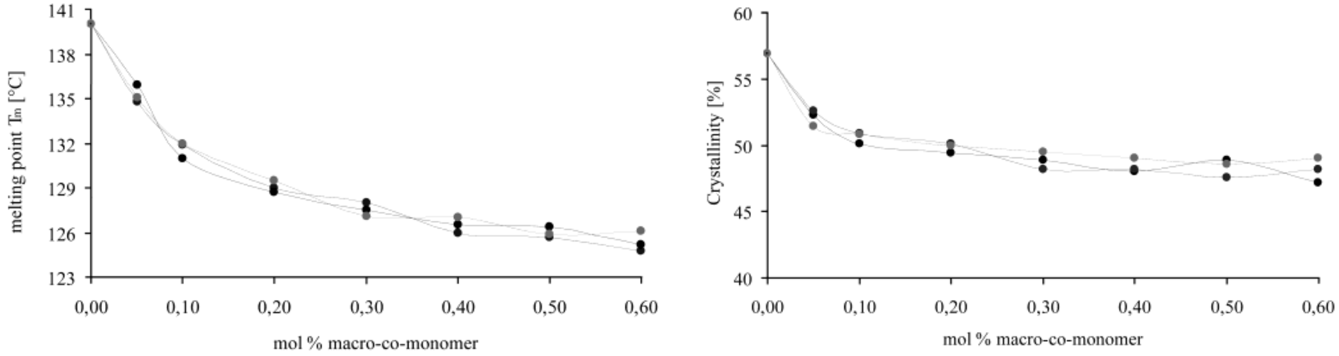


Figure 7. Melting point (T_m) and crystallinity (α) diagram of the comp-PE samples with a backbone length of 12 000 carbons and side-chain lengths between C70 and C250 carried out by tandem-*co*-polymerization using **1**, **2**, and MAO. For comparison, the course of the individual linear PE with a M_w of 12 000 g/mol by using **2**/MAO only is also shown.

purified using two washing columns, one filled with molecular sieve 4 Å and one filled with the BASF catalyst R3-11. The catalyst dimethylsilylene(2,3,4,5-tetramethyl-1-η^5-cyclopentadienyl)(*tert*-butylamido)titanium dichloride, $[Me_2Si(N^tBu)(Me_4Cp)]TiCl_2$, and cocatalyst methylaluminoxane (MAO) were supplied by Crompton, Polymer Chemicals Group. Isopropylidenebis(cyclopentadienyl)zirconium dichloride, $[Me_2C(Cp)_2]ZrCl_2$ (purity ≥99%), was supplied from Boulder Scientific. MAO was condensated and dried, and the solid MAO was redissolved in toluene with a concentration of 100 mg/mL. The solution was used within 3 weeks to avoid self-condensation effects of the MAO. The monomer ethylene was supplied by Linde with a purity of ≥99.8%. To free the gas from oxygen and minor sulfur contamination, it was washed using two columns filled with molecular sieve 10 Å and the BASF catalyst R3-11. Argon was used as inert gas and supplied by Linde with a purity of ≥99.996%, which was further washed with an oxisorb cartridge from Messer Griesheim before used.

Homopolymerization. Polymerizations were carried out in a 500 mL Büchi autoclave reactor. The apparatus was controlled of its denseness by putting it under a pressure of 4 bar. If the pressure was constant for 24 h, the reactor was dried for 1.5 h under vacuum at 105 °C, cooled to room temperature, and flushed several times with argon. Toluene (200 mL) and MAO were introduced into the reactor under an argon atmosphere; the solution was then kept under constant stirring at 450 rpm and heated to the polymerization temperature ±2 °C, and ethylene pressure was adjusted. After saturation the catalyst dissolved in toluene was injected with a Hamilton gastight syringe to start the polymerization. Ethylene pressure and reactor temperature were monitored and kept constant throughout the polymerization. Consumption of ethylene was followed continuously using a mass flow controller connected to a computer. The polymerization was stopped by closing the monomer supply and injecting 15 mL of ethanol to the reactor. The polymer product was than poured into 400 mL of ethanol/H_2O/HCl, stirred overnight, filtered, washed with $NaHCO_3/H_2O$, H_2O, and dried under vacuum at 60 °C for 24 h. To keep the terminal double bond from shifting the oligomer product was poured into 400 mL of ethanol/H_2O/NaOH and stirred overnight, the organic phase was separated and washed with H_2O, the solvent was removed under vacuum, and the oligomer was than also dried under vacuum at 60 °C for 24 h. With this procedure, 5.17 g of linear HDPE ($M_w = 79\,200$ g/mol, $T_m = 138.8$ °C, $\alpha = 71\%$, $M_w/M_n = 2.1$) was obtained, using 90 °C, 200 mL of toluene, 200 mg of MAO, 1×10^{-6} mol of $[Me_2Si(N^tBu)(Me_4Cp)]TiCl_2$, 1.0 bar of ethylene, and 60 min reaction time as polymerization condition.

Copolymerization. All copolymerizations were carried out in a 500 mL Büchi autoclave reactor with toluene as solvent. To the reactor 200 mL of toluene and 400 mg of MAO were introduced, the solution was than kept under constant stirring at 450 rpm and heated to the copolymerization temperature, and ethylene pressure was adjusted. During the whole copolymerization ethylene pressure and reactor temperature were monitored and kept constant. For the conventional copolymerization the according oligomeric macro-comonomer was added to the dry reactor, toluene and MAO were introduced, and the solution was stirred and heated to copolymerization temperature. After the solution was saturated with ethylene, **2** dissolved in toluene was injected to initiate the copolymerization. For the tandem copolymerization a conventional oligomerization was done using **1** dissolved in toluene after the reactor was set with toluene, MAO, stirring, temperature, and ethylene pressure. The ethylene pressure and reactor temperature were monitored and kept constant. After a monomer consumption of about 0 mL/min ethylene **2** dissolved in toluene was added to the reactor to start the copolymerization. The simultaneous copolymerization was carried out by injecting a mixture of **1** and **2** after the reactor was set. Results and conditions to this three copolymerization methods can be found in Tables 2 and 3.

Polymer Characterization. ^{13}C NMR spectra were measured with a Bruker Avance 400 Ultrashield at 100.13 MHz. In each case, 300−400 mg of polymer or oligomer was dissolved in hexachlorobutadiene in a 10 mm tube. As lock solvent and reference substance 1,1,2,2-tetrachlorethane-d_2 was added to broadband decoupling. Waltz-16 and Igated spectra were measured at 100 °C and evaluated with the Bruker WIN NMR program 5.0. The pulse angle was 60°, the pulse delay 5 s, the acquisition time 0.65 s, that sweep frequency 25 125 Hz, the number of the data points by spectrum 32K, and the number of the scans 16K. The absolute concentration of the polymer solutions did not exceed 15% in order to avoid concentration dependences in the considered resonance field.[14] We used the nomenclature of Carman[15] for the different carbon atoms, evaluated, and identified the carbon signals according to specifications of Randall.[17]

Gel permeation chromatography (GPC) was carried out with a Waters GPC 2000 Alliance system equipped with a refractive index detector and a set of three columns, Styragel HT type (HT3, HT4, HT6). The particle size for each column was 10 μm, and the pore sizes were 10^3 Å (HT3), 10^4 Å (HT4), and 10^6 Å (HT6). 1,2,4-Trichlorobenzene was used as solvent. The analysis were performed at 140 °C and 1.0 mL/min. The columns were calibrated with narrow molecular mass distribution polystyrene standards. The sample concentration was 1 mg/mL and the injection volume 215 μL.

Differential scanning calorimetric analyses (DSC) were carried out on a Mettler Toledo DSC 821^e connected to a cooling system. As calibration standard indium with a melting point of 156.61 °C was used. The polymer sample mass ranged from 2 to 3 mg, and aluminum pans were used. The DSC curves were recorded at a heating rate of 10 °C/min. The cooling rate was 10 °C/min. Melting point T_m and crystallinity α were calculated using the second heating phase and integrating the according signal using literature known melt enthalphy for PE ($\Delta H_{ideal} = 293$ J/g).[16]

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References and Notes

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