Influence of zirconocene structure and propene intent on melt rheology of polyethene and ethene/propene copolymers

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Summary

Ethene was homo- and copolymerized in the presence of methylaluminoxane (MAO)-activated zirconocenes comprising $(Me_5CP)_2ZrCl_2$ (Cp^*) and racemic dimethylsilylene-bis[-2-methyl-indenyl]-bridged zirconocene dichloride where the ligand framework was varied by benzannelation (MBI), 4-phenyl (MPI), and 4-naphthyl (MNI) substitution. Zero shear viscosity and shear thinning of the ethene homopolymers increased as a function of the catalyst system with MNI • MPI > MBI >> Cp^* and were correlated with the presence of long chain branches formed via reinsertion of vinyl-terminated polymer chains. The ranking was confirmed using the reduced vanGurp Palmen plot (δ vs. $|G^*|/G_N^0$) being less sensitive on molecular weight for polyolefin materials. Poly(ethene-co-propene)s (EP) containing 17 and 30 wt.-% propene were long chain branched as reflected by pronounced viscosity build-up at low angular frequency and increased shear thinning at higher angular frequency, whereas with propene comonomer content exceeding 46 wt.-% EP was essentially linear.

Introduction

Single-site metallocene catalysts are well known to produce very uniform ethene homo- and copolymers with narrow molecular weight distributions of $M_w/M_n = 2$ and molecular weight independent comonomer incorporation including copolymerization of less reactive comonomers such as long-chain n-alkenes, styrene and isobutene [1,2]. Today it is well understood how the variation of the ligand substitution pattern of racemic dimethylsilylene-bridged bisindenyl zirconocenes affects propene polymerization [3,4] and ethene homo- and copolymerization [5-7]. While 2-methyl substitution accounts for increased molecular weights, benzannelation and especially 4-naphthyl- and 4-phenyl substitution promote high catalyst activities and substantially higher comonomer incorporation with respect to non-bridged metallocenes. Incorporation of short chain branches via ethene/1-olefin copoly-merization has been applied to control phase transition temperatures and mechanical properties of materials ranging from stiff thermoplastics to rubbers [5,8-10]. Much

less is known about the influence of metallocene structures on processing. In fact, many metallocene-based polyolefins were rather difficult to process and processing depended upon catalyst structure, support type, catalyst preparation, and polymerization process conditions. This is not surprising because it is well known that the melt viscosities of linear polyethenes with narrow molecular weight distributions are much less shear sensitive during processing [11].

In order to lower melt viscosity at high shear rates and to achieve a viscosity build-up at lower shear rates without sacrificing narrow molecular weight distributions, long chain branches are introduced into the polyolefin backbone. This was first demonstrated for single-site catalysts based upon half-sandwich complexes, also known as constrained geometry catalysts [12]. Due to high comonomer incorporation of such catalysts, copolymerization of polyethene vinyl end groups was proposed to afford long chain branches. Malmberg et al. [13,14] have examined the role of long chain branching in ethene polymerization using bridged bisindenyl zirconocenes such as Et[Ind]$_2$ZrCl$_2$/MAO. Recently, a positive comonomer effect on long chain branching was detected in metallocene-catalyzed ethene/eicosene copolymerization where catalyst activity, copolymer molecular weight and long chain branching increased simultaneously with increasing eicosene content for ethene-rich copolymers [14]. Here, we report the influence of both propene content and the ligand substitution pattern of dimethylsilylene-bridged bis(2-methyl-indenyl) zirconium dichloride on the rheological behavior of polyethene and ethene/propene copolymers.

Experimental

Materials

All manipulations involving air- and moisture-sensitive compounds were carried out under a dry argon atmosphere using Schlenk tube and glove box techniques. Methylaluminoxane (MAO) was provided by Witco GmbH as a 10 wt.-% solution in toluene. Toluene (Merck, p.a. > 99,7 %) was purified by passing it through a column containing A1$_2$O$_3$, refluxed and distilled over Na/K alloy prior to use. Ethene was supplied by GHC Gerling, Holz & Co. Handels-GmbH, whereas propene was obtained from BASF AG in polymerization grade. The bridged metallocenes *rac*-Me$_2$Si(2-Me-4,5-Benz-Ind)$_2$ZrCl$_2$ (MBI), *rac*-Me$_2$Si(2-Me-4-Phen-Ind)$_2$ZrCl$_2$ (MPI) and *rac*-Me$_2$Si(2-Me-4-Naph-Ind)$_2$ZrCl$_2$ (MNI) were supplied by BASF AG and the metallocene (Me$_5$CP)$_2$ZrCl$_2$ (Cp*) was delivered by Sigma-Aldrich fine chemicals.

Synthesis

According to procedures reported by Suhm [9], ethene and ethene/propene copolymerization were performed in an 1.6 1 Buechi glass autoclave rinsed with 300 ml of a 0.03 mol/l Al(^{i}Bu)$_3$ solution prior to use. Typically 480 ml toluene and 6.2 ml MAO solution were fed into the glass reactor. The total volume of the reaction mixture was 0.5 1. After thermal equilibration of the reactor using two independent cooling systems for inner and outer cooling, ethene and in the case of copolymerization reactions also propene were continuously added by mass flow controllers (F-201C-FA, Bronkhorst, Nl-/261 AK Ruurlo, The Netherlands) combined with a digital readout and control system (E7000, Bronkhorst, Nl-7261 AK Ruurlo, The Netherlands). In case of ethene/propene copolymerization the mass ratio of gas

flows were adjusted with respect to the desired feed composition. The reaction

mixture was saturated with ethene or ethene/propene mixture, respectively, for 30 min by a continuous gas stream. The polymerization was started by injecting typically between 0.5 and 4.5 μmol metallocene catalyst in 10 ml toluene. The pressure of ethene/propene gas feed was kept constant during the polymerization by a pressure valve. Typically, after 30 min copolymerization was quenched by pouring the autoclave content into approximately 3.0 1 acidic methanol.

Polymer Characterization

^{1}H NMR spectra were recorded for solutions of 40 mg of polymer in 0.5 ml $C_2D_2Cl_4$ at 127 °C with a Bruker ARX 300 at 300 MHz; ^{13}C NMR spectra were recorded at 75.4 MHz with a pulse angle of 30 °, 5 s delay and at least 5000 scans. The signals were referred to $C_2D_2Cl_4$ (δ = 74.06 ppm). Size exclusion chromatography (SEC) analyses were performed at the BASF AG using polyethene standards for calibration. Differential scanning calorimetry (DSC) curves were obtained through a Perkin Elmer Series 7. The melting temperature was determined with a heating rate of 10 °C/min from -80 to 180 °C. Only the second heating curve was analyzed. The rheological measurements were performed on a stress controlled Bohlin CVO rheometer with parallel plate geometry (25 mm diameter) as reported elsewhere in detail [14]. Isothermal frequency sweeps were performed and shifted obtaining mastercurves at 170 °C. The mastercurves were extended towards low angular frequencies by means of creep measurements. The obtained creep compliance data were converted into $G^*(\omega)$ following a method described elsewhere [16, 19]. $\eta^*(\omega)$, δ, $|G^*(\omega)|$ were calculated from the extended mastercurves. The plateau moduli G_N^0 were determined by use of the vanGurp Palmen plot [16.].

Results and Discussion

Ethene and ethene/propene mixtures were polymerized at 40 °C in toluene using methylaluminoxane (MAO)-activated zirconocenes such as $(Me_5Cp)_2ZrCl_2$ (Cp^*), *rac*-Me_2Si(2-Me-4,5-Benz-Ind)$_2ZrCl_2$ (MBI), *rac*-Me_2Si(2-Me-4-Phen-Ind)$_2ZrCl_2$ (MPI), and *rac*-Me_2Si(2-Me-4-Naph-Ind)$_2ZrCl_2$ (MNI). The zirconocene structures are displayed in Fig. 1. The properties of ethene/propene copolymers prepared using ethene/propene (24 mol-% / 76 mol-%) mixtures are listed in Table 1. In accord with previous investigations on ethene/1-octene copolymerization [5,6], propene incorporation increased with MNI > MPI > MBI >> Cp*.

In Fig. 2 melt viscosity data of polyethene samples prepared with MNI, MPI, MBI and Cp* with molecular weights around 200000 g/mol and with molecular weight distributions of M_w/M_n 2 are shown. Apparently, zero shear viscosity and shear thinning increased with MNI MPI > MBI > Cp*. The different degree of shear thinning is displayed more clearly in Fig. 3, where the reduced complex shear viscosity $|\eta^*|/\eta_0$ is plotted versus $\eta_0\omega$. Since the same ranking is found for incorporation of propene into the polyethene backbone, shear thinning and viscosity build-up at low frequency are highly likely to be associated with the presence of long chain branching resulting from copolymerization of ethene with vinyl-terminated

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polyethene. As a consequence, due to the very poor comonomer incorporation using Cp*, polyethene prepared with Cp* is essentially linear.

Table 1 Ethene/propene copolymerization using various MAO-actiavted zirconocenes

Metallocene	MBI	MPI	MNI	Cp*
Run No.:[a]	1	2	3	4
F [E] [mol-%] [b]	49.1	40.8	25.6	97.9
F [P] [mol-%] [b]	50.9	59.2	74.4	2.1
F [E] [wt.-%] [b]	39.2	31.5	18.6	96.9
F [P] [wt.-%] [b]	60.8	68.5	81.4	3.1
r_E [c]	5.01	3.27	2.44	256
r_P [c]	0.39	0.59	1.26	0.21
$r_E{}^*r_P$	2.0	2.0	3.1	55
Activity [d]	22200	113500	152000	40000
M_n [g/mol] [e]	91900	32000	44500	17000
M_w/M_n [e]	1.5	2.0	2.3	1.85

(a) P_E=2bar, [E]=0.12 mol/l = 24 mol%, [P]=0,39 mol/l = 76 mol%, run 1 [Zr] = 2µmol/l, run 2 [Zr]= 0,375µmol/l, run 3 [Zr] = 1.0 µmol/l run 4 [Zr]= 3µmol/l, run 1 Al/Zr = 10000, run 2 and 3 Al/Zr = 30000, run 4 Al/Zr = 20000, 40°C, solvent: toluene. (b) determined by ^{13}C-NMR. (c) Determined by Uozumi-Soga equation: r_E, r_P = copolymerization parameter of ethene (E) and propene (P). (d) [kg$_{polymer}$ / mol$_{Zr}$ * h$_{polymerization time}$] (e) Determined by means of SEC.
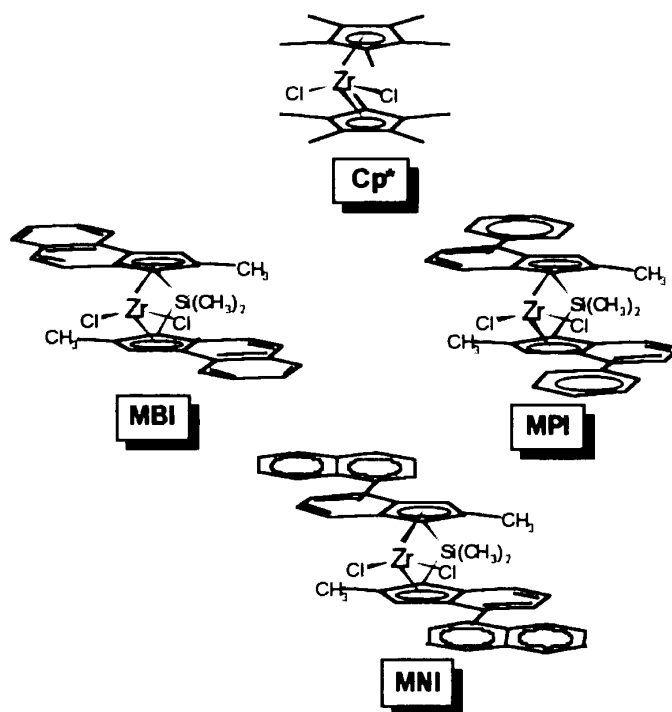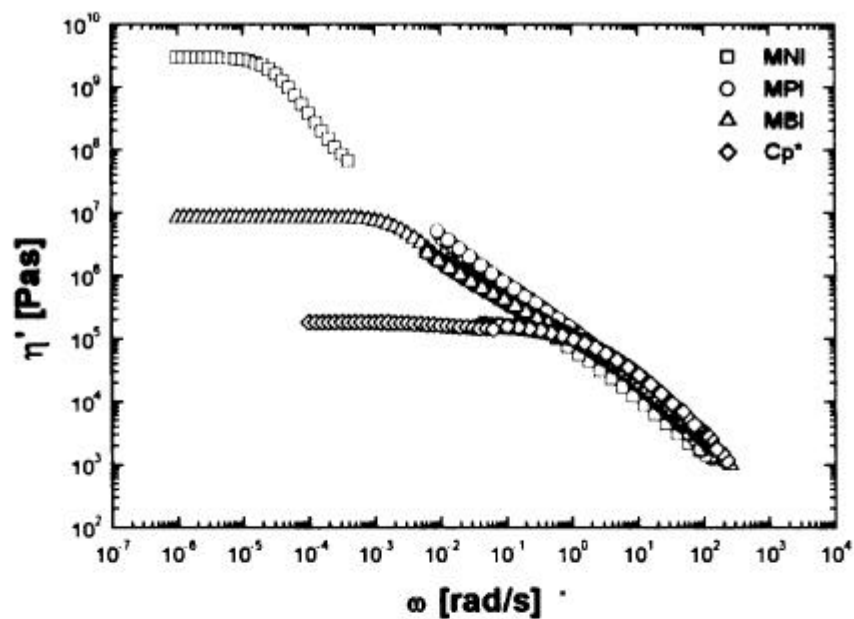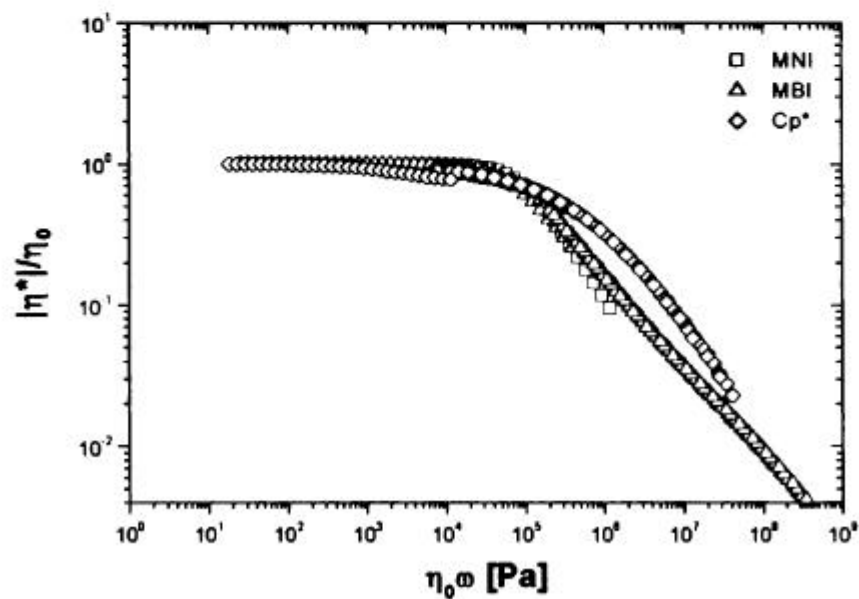

Fig. 1 Zirconocene catalyst structures

Fig. 2 Melt viscosity of polyethenes, prepared with various zirconocene catalyst systems, as a function of angular frequency (M_n: (MNI) 189 kg/mol, (MPI) = 300 kg/mol, (MBI), 217 kg/mol, (Cp*) = 160 kg/mol; Mw/Mn $\Box$ 2).

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This behavior is confirmed by the reduced Van Gurp-Palmen plot in Fig.4, which is in particular for polyolefin materials less sensitive on molecular weight as described elsewhere in more detail [16,17]. Based on this plot a level of long chain branching can be derived from a minimum at $|G^*|/G_N^0$ values below 1 as long as bimodality can be excluded [18]. Here, a low δ in minimum accounts for a high long chain branching density. As apparent from Fig. 4, the catalyst ranking with respect to branching density is in accordance with that derived from copolymerization parameters.
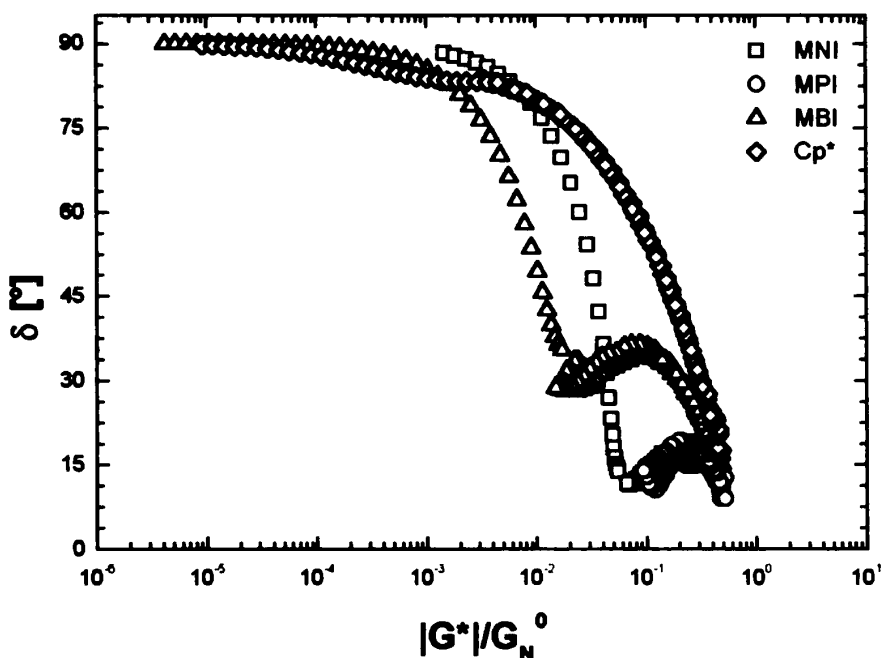

Fig. 4 Van Gurp-Palmen plot for polyethenes prepared with various zirconocene catalyst systems. G_N^0 for Polyethene was taken from the literature [20] .

Similar to metallocene-catalyzed ethene/eicosene copolymerization [15], long chain branch formation is also affected by the incorporation of propene comonomer. Ethene/propene copolymers were prepared using MAO-activated MBI (Table 2). As shown in Fig. 5 and Fig. 6, propene-rich copolymers give poor shear thinning and show moderate zero shear viscosities, whereas ethene-rich copolymers, containing less than 30 wt.-% propene, and polyethene exhibit drastically reduced melt viscosities with increasing angular frequency and high shear viscosities at low frequency. This again can be correlated with copolymerization of vinyl end groups. At high propene content, no vinyl end groups are formed because chain termination is likely to occur after inserting propene, thus producing vinylidene- and vinylene-type

end groups. The higher degree of shear thinning of EP30 compared to ethene homopolymer can be explained similar to ethene/eicosene copolymerization by a positive comonomer effect.

Table 2 Poly(ethene-co-propene)s prepared with MAO-activated MBI[a)].

Polymer	EP00	EP30	EP46	EP50	EP60	EP75	EP84
f [P] [mol-%][b)]	0	58	64	71	77	92	94
F [E] [mol-%][c)]	100	76.3	64.0	59.6	49.1	31.9	22.9
F [P] [mol-%][c)]	0	23.7	36.0	40.4	50.9	68.1	77.1
F [P] [wt.-%][c)]	0	31.8	45.7	50.4	60.8	76.2	83.5
M_n [kg/mol][d)]	222	105	35	40	92	78	50
M_w/M_n [d)]	2.7	1.7	2.1	2.2	1.5	1.5	1.9

(a) p_{total} = 2.0 bar, 40 °C, Al/Zr = 10000/1, c_{MBI} = 2.0 µmol/l, (for EP84, c_{MBI} = 4.0 µmol/l). (b) Propene content in the feed. (c) Ethene (E) and Propene (P) incorporation determined by means of ^{13}C NMR spectroscopy. (d) Molecular weight and molecular weight distribution determined by means of high-temperature SEC using polyethene and polypropene standards, respectively.

It is well known that the catalysts displayed in Fig. 1 give very poor incorporation of internal double bonds. Therefore, in the absence of vinyl end groups, linear propene-rich copolymers are formed.
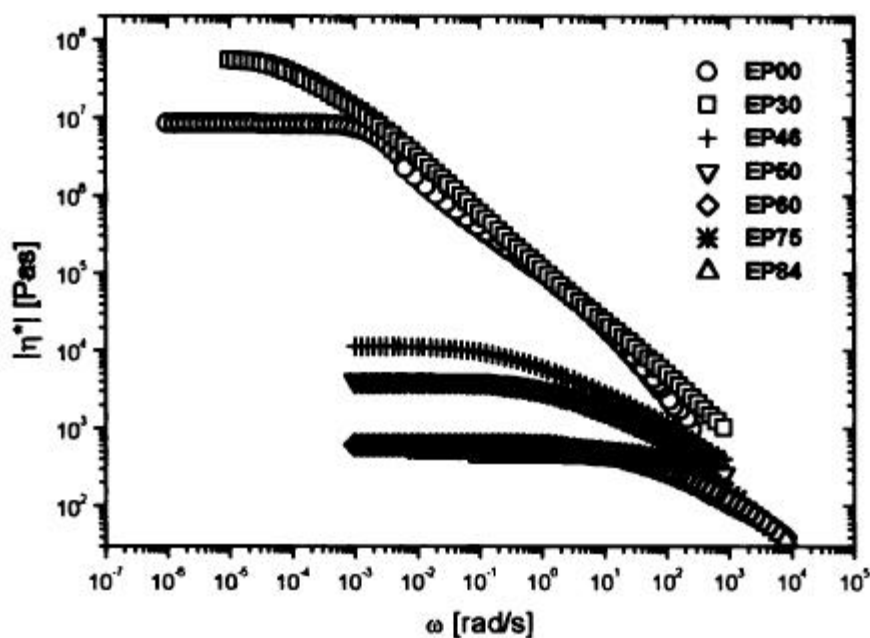

Fig. 5 Melt viscosities of poly(ethene-co-propene) (EP) as a function of angular frequency and propene content (the number behind EP denotes the propene content in wt.-%).
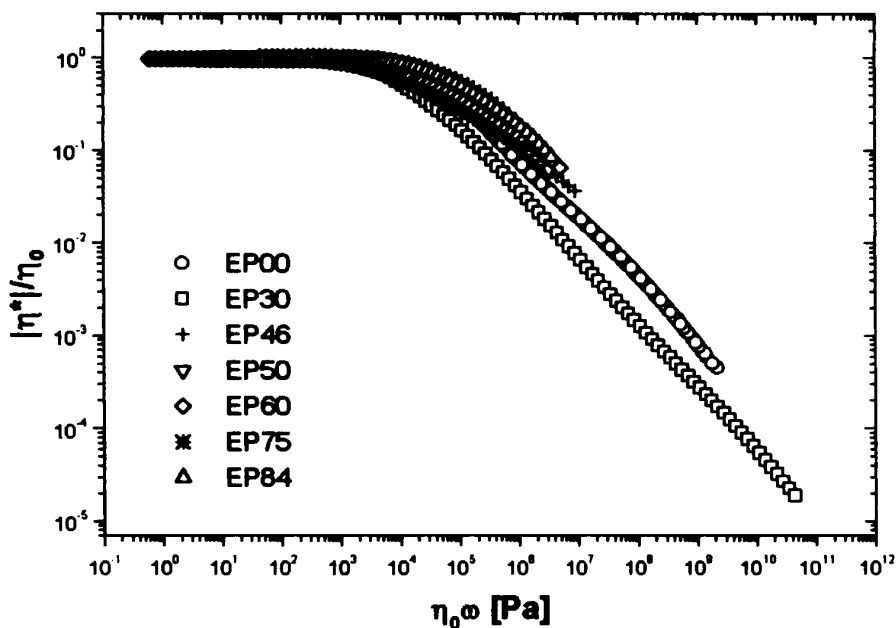
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Fig. 6 Shear thinning plot of EP copolymers prepared with MBI.

Conclusion

The comparison of zirconocene catalysts in ethene homo- and copolymerization provides strong experimental evidence that both short and long chain branching are affected by the reactivity of zirconocenes toward 1-olefin incorporation, as reflected by the same ranking of MNI ð MPI > MBI >> Cp*. In the absence of copolymerizable vinyl end groups, linear copolymers are formed with poor shear thinning due to the absence of long chain branching. The variation of long chain branching as a function of catalyst and process conditions offers attractive opportunities for improving melt processability without affecting molecular weight distributions. This is of particular interest for manufacturing of tailor-made polyolefins with novel combinations of attractive mechanical properties, controlled crystallization, and easy processability.

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