

Influence of metallocene structures on ethene copolymerization with 1-butene and 1-octene

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Abstract

Ethene/1-octene and ethene/1-butene copolymerization using various methylaluminoxane-activated metallocene catalysts, e.g. silylene-bridged substituted bisindenyl zirconocene systems and halfsandwich titanocene, was performed at 40°C in toluene. The influence of the ligand substitution on comonomer incorporation, catalyst activity, molar mass, molar mass distribution, degree of polymerization and copolymerization parameters was investigated in ethene/1-octene copolymerization at constant comonomer ratio and in ethene/1-butene copolymerization as a function of varying ethene/1-butene feed mass ratios. In ethene/1-octene copolymerization the highest comonomer incorporation was achieved with MAO-activated $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(N\text{-tert-butyl})\text{TiCl}_2$ catalyst. Best performance in terms of comonomer incorporation combined with high catalyst activity and molar mass was found for silylene-bridged bisindenylzirconocenes, where 2-methyl substitution promoted high degree of polymerization and benzannulation accounted for improved catalyst activity, comonomer incorporation and randomness of comonomer incorporation. In ethene/1-butene copolymerization at high 1-butene feed content silylene-bridged substituted bisindenyl systems showed polymerization characteristics similar to that of ethene/1-octene copolymerization. The influence of 2-methyl substitution on activity and comonomer incorporation was significant only at low 1-butene feed content. Storage moduli and glass transition temperature of the poly(ethene-co-1-butene) copolymers decreased with increasing 1-butene content. © 1998 Elsevier Science B.V.

Keywords: Ziegler–Natta catalysis; Metallocene; Ethene/1-octene copolymers; Ethene/1-butene copolymers

1. Introduction

Controlling comonomer incorporation represents one of the key features of metallocene-catalyzed polymerization processes. Most traditional Ziegler–Natta catalysts are multi-site catalysts, which produce copolymers consisting of a complex mixture of homo- and copolymers with comonomers frequently being incorporated

in the low molar mass fractions. As depicted in Fig. 1, in contrast to multi-site catalysts, single-site metallocene based catalysts afford uniform comonomer incorporation as well as narrow molar mass distribution. Also vinyl-terminated oligo(ethene) produced by β -hydride elimination, can be incorporated during ethene copolymerization to produce long-chain branches [1–8]. Few long chain branches can facilitate melt processing of ethene/1-olefin copolymers. Moreover, in addition to 1-olefins, also cycloolefins and styrene are readily copolymer-

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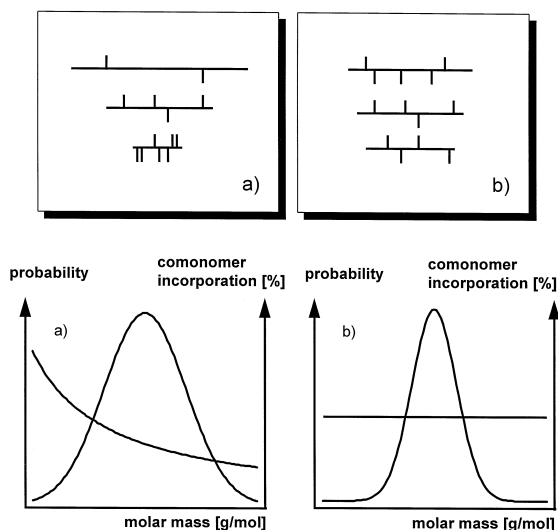


Fig. 1. Molar mass distribution and comonomer incorporation of multi-site Ziegler-Natta catalysts (a) compared to single-site metallocene based catalysts (b): (a) copolymers consisting of a complex mixture of homo- and copolymers with comonomers frequently incorporated in the low molar mass fractions, broad molar mass distribution ($M_w/M_n = 5-40$), (b) uniform comonomer incorporation, narrow molar mass distribution ($M_w/M_n \approx 2$).

ized. Several reviews describe the attractive potential of metallocene catalysts in polymer synthesis [9–12] [13–20].

Metallocene-catalyzed copolymerization can be described by means of first order Markov statistics using the copolymerization parameters r_1 and r_2 ; which correspond to the rate constant ratios $r_1 = k_{11}/k_{12}$ or $r_2 = k_{22}/k_{12}$, respectively. The copolymerization parameter r_1 indicates the rate constant ratio of comonomer 1 versus that of comonomer 2, subsequent to the insertion of comonomer 1. The product $r_1 * r_2$ reflects the distribution of the comonomers in the polymer chain, with random comonomer distribution corresponding to $r_1 * r_2 = 1$. Table 1 displays copolymerization parameters typical for copolymerizations with heterogeneous (No. 1–5) and homogeneous (No. 6–17) catalysts using different 1-olefins and polymerization temperatures.

Copolymerizations with compositions covering the entire feasible range of ethene/1-olefin or propene/1-olefin copolymers ratios were investigated as a function of metallocenes with different ligands, bridging groups and transition metal centers. [21–37] [38–42]. It is known, that monomer incorporation can be promoted by using bridged cyclopentadienyl- or indenyl-ligands. Soga et al. [43] and Fink et al. [44,45]

Table 1

Copolymerization parameters for copolymerizations with heterogeneous (No. 1–5) and homogeneous (No. 6–17) catalysts, $r_1 * r_2 > 1$ indicates preferred incorporation of one comonomer, $r_1 * r_2 = 1$ reflects random distribution of the comonomers in the polymer chain

| No. | Catalysts | Comonomer ^a | Temperature | r_1 | r_2 | $r_1 * r_2$ |
|-----|---|------------------------|-------------|-------|-----------|-------------|
| 1 | Cp ₂ TiMe ₂ /TiCl ₃ [21] | E/P | 40 | 10.00 | 0.22 | 2.20 |
| 2 | Cp ₂ TiMe ₂ /TiCl ₃ [22] | E/B | 40 | 69 | 0.06 | 4.00 |
| 3 | Cp ₂ TiMe ₂ /TiCl ₃ | E/H | 40 | 69 | 0.03 | 2.20 |
| 4 | SiO ₂ /MgCl ₂ /TiCl ₄ /AlEt ₃ [23] | E/P | 40 | 5–10 | 0.20–0.34 | 2 (ca.) |
| 5 | SiO ₂ /MgCl ₂ /TiCl ₄ /AlEt ₃ [24,25] | E/B | 40 | — | — | 0.50–4.00 |
| 6 | Cp ₂ ZrCl ₂ [13] | E/P | 40 | 16.50 | 0.03 | 0.53 |
| 7 | Et(IndH ₄)ZrCl ₂ | E/P | 40 | 11.70 | 0.08 | 0.99 |
| 8 | i-Pr(Cp)(Flu)ZrCl ₂ | E/P | 40 | 6.70 | 0.09 | 0.65 |
| 9 | i-Pr(Cp)(Flu)ZrCl ₂ [26] | P/O | 40 | 1.72 | 0.63 | 1.02 |
| 10 | Me ₂ Si(Ind) ₂ ZrCl ₂ | P/O | 40 | 3.30 | 0.39 | 1.26 |
| 11 | Me ₂ Si(2-MeInd) ₂ ZrCl ₂ | P/O | 40 | 3.60 | 0.32 | 1.15 |
| 12 | Me ₂ Si(Benz[e]Ind) ₂ ZrCl ₂ | P/O | 40 | 2.60 | 0.37 | 0.96 |
| 13 | Me ₂ Si(2-MeBenz[e]Ind) ₂ ZrCl ₂ | P/O | 40 | 2.40 | 0.48 | 1.15 |
| 14 | Me ₂ Si(2-MeBenz[e]Ind) ₂ ZrCl ₂ [27] | E/O | 0 | 4.71 | 0.22 | 1.06 |
| 15 | Me ₂ Si(2-MeBenz[e]Ind) ₂ ZrCl ₂ | E/O | 20 | 6.45 | 0.18 | 1.14 |
| 16 | Me ₂ Si(2-MeBenz[e]Ind) ₂ ZrCl ₂ | E/O | 40 | 8.16 | 0.14 | 1.14 |
| 17 | Me ₂ Si(2-MeBenz[e]Ind) ₂ ZrCl ₂ | E/O | 60 | 10.61 | 0.10 | 1.11 |

^aE = ethene, P = propene, B = 1-butene, H = 1-hexene, O = 1-octene.

reported that the syndiospecific catalyst $\text{Me}_2\text{C}(\text{Cp})(\text{fluorenyl})\text{ZrCl}_2$ gave much higher 1-olefin incorporation with respect to isospecific and non-stereospecific catalysts. According to Kaminsky et al. substituting zirconium for hafnium appears to further improve comonomer incorporation [46]. Moreover, catalyst concentration, $[\text{Al}]/[\text{transition metal}]$ molar ratio, comonomer molar ratio in monomer feed, activators (e.g. MAO = methylaluminoxan, TIBA = triisobutylaluminium, cationic activators) used for starting the copolymerization by activating the metallocenes and also polymerization temperature influence copolymerization behavior of the metallocene-based catalysts [27,44]. Solubility of the monomers as well as the solubility of the copolymers in the solvent during copolymerization process must be taken into account when copolymerization processes are evaluated. In the case of ethene/1-butene or ethene/propene copolymerization, respectively, metallocene catalyst technology only competes successfully with the multi-center heterogeneous Ziegler–Natta catalysts provided that gas mixtures and constant monomer gas ratios in polymerization feed can be maintained during polymerization. For ethene/1-butene copolymerization it was reported by Yoon et al. that there are significant deviations from ideal behavior described by Henry's law [47].

Objective of this work was to investigate copolymerization of ethene with 1-butene and 1-octene and to compare the influence of metallocene structures, especially the indenyl ligand substitution pattern. Ethene was copolymerized with 1-octene at constant ethene/1-octene ratio (1 mol/3 mol run 1–5, 1 mol/6 mol run 6) using MAO activated $\text{rac-Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$, abbreviated as I, $\text{rac-Me}_2\text{Si}(2\text{-MeInd})_2\text{ZrCl}_2$, abbreviated as MI, $\text{rac-Me}_2\text{Si}(\text{Benz[e]Ind})_2\text{ZrCl}_2$, abbreviated as BI, $\text{rac-Me}_2\text{Si}(2\text{-MeBenz[e]Ind})_2\text{ZrCl}_2$, abbreviated as MBI, $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(N\text{-tert-butyl})\text{TiCl}_2$ abbreviated as CBT and zirconocenedichloride abbreviated as Cp_2ZrCl_2 at 40°C in toluene. For ethene copolymerizations with 1-butene using MAO

activated $\text{rac-Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$, abbreviated as I and $\text{rac-Me}_2\text{Si}(2\text{-MeBenz[e]Ind})_2\text{ZrCl}_2$, abbreviated as MBI, the role of different comonomer ratios was studied at 40°C in toluene.

2. Experimental

2.1. Polymer synthesis

All catalyst components, including toluene solvent and monomers, were handled and stored under dry argon atmosphere. $\text{Rac-Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$, $\text{Rac-Me}_2\text{Si}(2\text{-MeInd})_2\text{ZrCl}_2$, and MAO (10 wt% in toluene, $M_n = 1000$ g/mol) was obtained from Witco, Germany. $\text{Rac-Me}_2\text{Si}(\text{Benz[e]Ind})_2\text{ZrCl}_2$ was obtained from Dr. U. Stehling, University of Konstanz, $\text{rac-Me}_2\text{Si}(2\text{-MeBenz[e]Ind})_2\text{ZrCl}_2$ from BASF, $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(N\text{-tert-butyl})\text{TiCl}_2$ from Dr. F. Sernetz, University Freiburg, zirconocenedichloride and 1-octene from Aldrich, toluene from Roth, ethene from Gerling Holz, 1-butene (polymerization grade) from BASF. Toluene solvent was rectified over LiAlH_4 and refluxed and distilled over Na/K alloy prior to use, 1-octene was distilled over CaH_2 . Ethene and MAO were used without further purification, 1-butene was purified by passing through $\text{NaAl}(\text{C}_2\text{H}_5)_4$ filled columns.

Ethene/1-octene copolymerizations were performed as described elsewhere [48]. Ethene/1-butene polymerization reactions were performed in a 1.6 l Buechi glass autoclave rinsed with 300 ml of a 0.03 mol/l $\text{Al}(i\text{Bu})_3$ solution in toluene 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 l. After thermal equilibration of the reactor using two independent cooling systems for inner and outer cooling, ethene and 1-butene were continuously added by two mass-flow controller (F-201C-FA, Bronkhorst, Ruurlo) combined with a digital readout and control system (E7000, Bronkhorst, Ruurlo) using different mass ratios of gas flows.

The reaction mixture was saturated with ethene and 1-butene for 15 min by a continuous gas stream. The polymerization was started by injecting typically 2 μmol of metallocene catalyst in 10 ml toluene, equivalent to $[\text{Zr}] = 4 \mu\text{mol}/\text{l}$ and $[\text{Al}] = 80 \text{ mmol}/\text{l}$. The pressure of ethene/1-butene gas feed was kept constant during the polymerization by a pressure valve. Typically, after 60 min copolymerization was quenched by pouring the autoclave content in 3 l acidic methanol.

2.2. Polymer analysis

$^1\text{H-NMR}$ spectra were recorded from solutions of 40 mg of polymer in 0.5 ml $\text{C}_2\text{D}_2\text{Cl}_4$ at 400 K temperature by a Bruker ARX 300 at 300 MHz; $^{13}\text{C-NMR}$ spectra at 75.4 MHz, with a 90° pulse angle, inverse gated decoupling, 5 s delay and at least 8000 scans. The signals were referenced to $\text{C}_2\text{D}_2\text{Cl}_4$ ($\delta = 74.06 \text{ ppm}$). High temperature size exclusion chromatographic (SEC) analysis of molar mass and molar mass distribution were performed at BASF. Glass temperatures were determined by means of differential scanning calorimetry (DSC) with a Perkin Elmer Series 7 from the heating curve at a heating rate of 20 K/min. Dynamical mechanical analysis were performed in a Rheometrics Solid Analyzer (RSA II) with dual cantilever bending geometry using a dynamic temperature ramp with a heating rate of 2 K/min, 0.1% strain and a frequency of 6.28 rad/s. The measurements used test specimens ($2 \times 6 \times 60 \text{ mm}$) which were melted in vacuum at 140°C in a pressing form. The test specimens were compression molded and cooled down to room temperature within 30 min.

3. Results and discussion

3.1. Ethene / 1-octene copolymerization

For studying the effects of different types of ligands and especially indenyl ligand substitu-

tion pattern ethene was copolymerized with 1-octene at constant ethene/1-octene feed molar ratios (1 mol/3 mol run 1–5, 1 mol/6 mol run 6, Table 2). Typically, copolymerization was performed in toluene at 40°C in the presence of the metallocenes, displayed in Fig. 2, which were activated with methylaluminoxane (MAO) using $[\text{Zr}] = 2 \mu\text{mol}/\text{l}$ and $[\text{Al}] = 40 \text{ mmol}/\text{l}$ with $[\text{Al}]/[\text{Zr}] = 20000/1$.

Incorporation of 1-octene, catalyst activity, molar mass, molar mass distribution, degree of polymerization, copolymerization parameters and $r_{\text{O}} * r_{\text{E}}$, are listed in Table 2 for the different metallocenes. Average catalysts molar activities A_{m} were calculated from the number of inserted monomer units per total monomer concentration, catalyst concentration and polymerization time according to Eq. (1).

$$A_{\text{m}} = \frac{n_{\text{G}}}{[\text{M}]_{\text{G}} * n_{\text{Zr}} * t};$$

$$n_{\text{G}} = \sum_i n_i;$$

$$[\text{M}]_{\text{G}} = \sum_i [\text{M}]_i \quad (1)$$

A_{m} is molar activity, n_{G} is total number of inserted monomers, $[\text{M}]_{\text{G}}$ is the total concentration of monomer, n_{Zr} is mol of metallocene, n_i is mol of inserted monomer i , $[\text{M}]_i$ is concentration of monomer i in polymerization medium, t is polymerization time.

According to runs 1–4 (Table 2) the 2-methyl substitution of benzindenyl (MBI) and benzannelation of the indenyl ligand (BI) accounted for reduced catalyst activity but promoted formation of higher molar mass copolymers.

As displayed in Fig. 3 the CGT catalyst (run 5) showed the lowest activity in comparison to the other systems using the above mentioned polymerization conditions. The Cp_2ZrCl_2 system was more active with respect to CGT and MBI but less active than I, MI or BI, respectively.

In the series I and BI, benzannelation adversely affected molar mass, whereas benzannelation of the 2-methyl-substituted metal-

Table 2

Ethene/1-octene copolymerization performed at 40°C in toluene using metallocenes, as displayed in Fig. 2, at constant monomer molar feed ratio

| | Metallocene, Run No. ^a | | | | | |
|---|-----------------------------------|---------|-----------|---------|---------|---------------------------------------|
| | I, 1 | MI, 2 | BI, 3 | MBI, 4 | CGT, 5 | Cp ₂ ZrCl ₂ , 6 |
| F[E] (mol%) ^b | 88.2 | 88.6 | 80.6 | 77.8 | 56.9 | 86.2 |
| F[O] (mol%) ^b | 11.8 | 11.4 | 19.4 | 22.2 | 43.1 | 13.8 |
| F[E] (wt%) ^b | 65.1 | 65.9 | 50.9 | 46.7 | 24.5 | 61.0 |
| F[O] (wt%) ^b | 34.9 | 34.1 | 49.1 | 53.3 | 75.5 | 39.0 |
| r _E | 18.9 | 19.5 | 10.7 | 10.1 | 4.1 | 32.8 |
| r _O | 0.014 | 0.013 | 0.076 | 0.118 | 0.290 | 0.05 |
| r _E * r _O | 0.27 | 0.25 | 0.81 | 1.20 | 1.19 | 0.17 |
| Activity ^c | 1 598 000 | 894 000 | 1 667 000 | 596 000 | 34 000 | 708 900 |
| M _n ^d (g/mol) | 90 800 | 140 000 | 77 700 | 172 000 | 126 900 | 25 000 |
| M _w /M _n ^d | 1.6 | 1.8 | 1.6 | 1.8 | 2.3 | 2.5 |
| P _n ^e | 2390 | 3720 | 1750 | 3690 | 1970 | 630 |
| T _g ^f (°C) | -48.9 | -45.9 | -57.1 | -58.5 | -63.3 | -50.4 |

^aP_E = 2 bar, run 1–5 [E] = 0.2 mol/l = 25 mol%, [O] = 0.6 mol/l = 75 mol%, run 6 [E] = 0.2 mol/l = 25 mol%, [O] = 1.2 mol/l, [Zr] = 2 μmol/l run 1–4, [Zr] = 20 μmol/l run 5, [Zr] = 5 μmol/l run 6, [Al] = 40 mmol/l, [Al]/[Zr] = 20.000, 40°C, solvent: toluene.

^bDetermined by ¹³C-NMR.

^c(mol_{inserted monomer units})/(mol/l_{total monomer conc} mol_{metallocene} h_{polymerization time}).

^dDetermined by GPC using polystyrene standards.

^eDegree of polymerization.

^fdetermined by DSC, heating rate 20 K/min.

locenes (MI versus MBI, Table 2 and Fig. 4), slightly improved molar mass. The molar mass of the poly(ethene-co-1-octene) copolymer obtained with MAO activated Cp₂ZrCl₂ catalyst was only M_n = 25 000 g/mol, even at low 1-octene incorporation. Interestingly, as shown in Fig. 4, molar mass of the copolymer obtained with CGT was nearly as high as that of the copolymer produced with MBI (cf: M_n = 126 900 g/mol CGT versus 172 000 g/mol MBI, Table 2), however 1-octene incorporation doubled when CGT was used.

Degrees of polymerization (P_n in Table 1) show the same trends as molar masses. Benzannulation of indenyl ligand accounts for much larger decay than benzannulation of the 2-methyl-substituted indenyl ligand. Lowest degree of polymerization was observed for Cp₂ZrCl₂.

As is apparent in Table 2 and Fig. 5, at ethene/1-octene 1 mol/3 mol molar ratio, 2-methyl substitution did not affect 1-octene incorporation, whereas benzannulation of both in-

denyl and 2-methyl-substituted indenyl ligand almost doubled molar content of 1-octene.

This is in accord with earlier observations by Schneider for propene/1-octene copolymerization [49]. When comparing I with MI or BI with MBI, the 1-octene content of the copolymer increased from 12 to 19 mol% or 11 to 22 mol%, respectively. All four catalysts (cf. runs 1–4, Table 2 and Fig. 5) give much lower incorporation with respect to that of 43 mol% 1-octene content observed for CGT (cf. run 5, Table 2 and Fig. 5). When 1-octene incorporation is taken into account, the CGT catalyst was exceptional with regard to producing copolymers with highest 1-octene incorporation without sacrificing high molar mass. With 13 mol% 1-octene incorporated the MAO activated Cp₂ZrCl₂ gave lowest incorporation of 1-octene, considering the high ethene/1-octene molar ratio of 1 mol/6 mol.

The effect of benzannulation (run 1–4, Table 2) is also reflected by the copolymerization parameters (Table 2). The diad sequence distri-

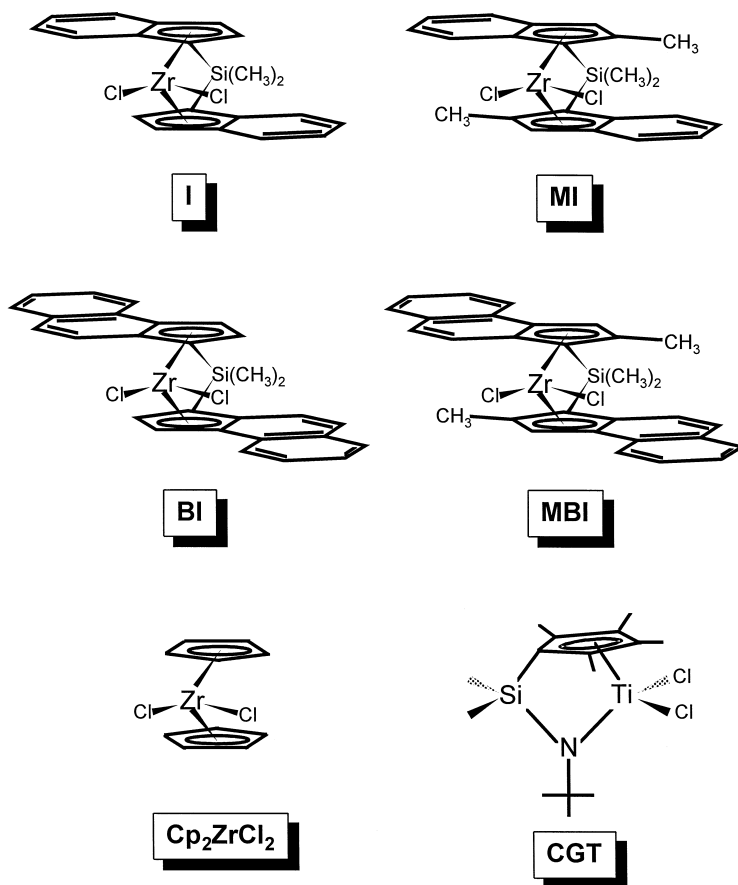


Fig. 2. Methylaluminoxane-activated metallocene catalysts, e.g. silylene-bridged substituted bisindenyl zirconocene systems and half-sandwich titanocene. $rac\text{-Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$, abbreviated as I, $rac\text{-Me}_2\text{Si}(2\text{-MeInd})_2\text{ZrCl}_2$, abbreviated as MI, $rac\text{-Me}_2\text{Si}(\text{Benz}[e]\text{Ind})_2\text{ZrCl}_2$, abbreviated as BI, $rac\text{-Me}_2\text{Si}(2\text{-MeBenz}[e]\text{Ind})_2\text{ZrCl}_2$, abbreviated as MBI, $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(N\text{-tert-butyl})\text{TiCl}_2$ abbreviated as CBT and zirconocenedichloride abbreviated as Cp_2ZrCl_2 .

bution was used for the calculation of the r -parameters (Eqs. (2) and (3)) according to Uozumi and Soga [43].

$$r_E = 2 * \frac{D_{EE}}{D_{EO}} * \frac{[O]}{[E]} \quad (2)$$

$$r_O = 2 * \frac{D_{OO}}{D_{EO}} * \frac{[E]}{[O]} \quad (3)$$

r_E , r_O are r -parameters of ethene and 1-octene, D_{EE} , D_{EO} , D_{OO} are monomer-diads along the polymer chain. [O], [E] are 1-octene and ethene concentrations, respectively.

Both r_E and r_O are very similar for I and MI (cf. $r_E = 18.9$ and $r_E = 19.5$, Table 2) or BI and

MBI (cf. $r_E = 10.7$ and $r_E = 10.1$, Table 2), respectively, whereas those of Cp_2ZrCl_2 clearly indicate that this system is much less effective in ethene copolymerization. According to copolymerization parameters, CGT promoted 1-octene incorporation. (cf. $r_E = 32.8$ Cp_2ZrCl_2 and $r_E = 4.1$ CGT, Table 2). Benzannulation in contrast to 2-methyl-substitution significantly changed copolymerization parameters, increasing r_O and decreasing r_E . Only for the benzannulated systems BI, MBI and CGT catalyst $r_E * r_O$ approach 1, as expected for random 1-octene incorporation. Therefore, 2-methyl-substitution of indenyl ligand favors molar mass build-up, whereas benzannulation promotes

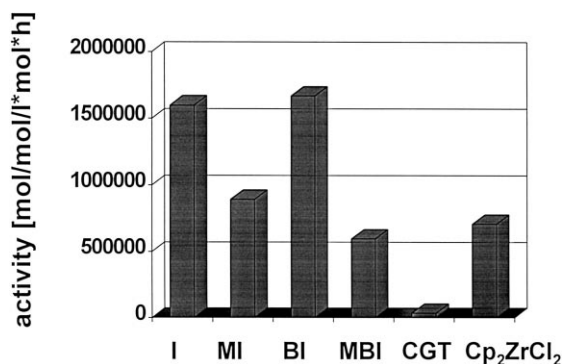


Fig. 3. Molar activity of methylaluminoxane-activated metallocene catalysts in ethene/1-octene copolymerization at constant comonomer ratio.

higher 1-octene incorporation and random distribution of 1-hexyl short-chain branches, resulting from random 1-octene incorporation into the poly(ethene) chain. Increasing 1-octene content accounted for lowering glass transition temperatures of the resulting poly(ethene-co-1-octene). Glass temperature was found, as listed in Table 2, to be -63°C for poly(ethene-co-1-octene), containing 43 mol% 1-octene and -49°C containing 12 mol% 1-octene.

3.2. Ethene / 1-butene copolymerization

Ethene was copolymerized with 1-butene in toluene at 40°C in the presence of MAO-activated MBI, and MAO-activated I, using $[\text{Al}]/[\text{Zr}] = 20000/1$, in order to study the in-

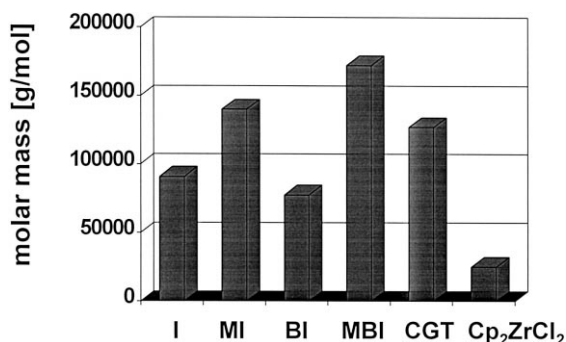


Fig. 4. Molar mass of poly(ethene-co-1-octene) copolymers using methylaluminoxane-activated metallocene catalysts at constant comonomer ratio.

fluence of varying ethene/1-butene feed mass ratios on ethene/1-butene copolymerization. Experimental results and reaction conditions of the copolymerization runs are summarized in Table 3 (MBI catalyst) and in Table 4 (I catalyst).

Incorporation of 1-butene was calculated according to $^1\text{H-NMR}$ (Tables 3 and 4), and $^{13}\text{C-NMR}$ spectroscopy data (Tables 5 and 6 and Fig. 6) [50]. In ethene/1-octene copolymerization the evaluation of $^{13}\text{C-NMR}$ spectroscopy data was achieved via integration of significant regions of the easy soluble poly(ethene-co-1-octene) copolymers containing more than 10 mol% 1-octene. Incorporation as determined by $^1\text{H-NMR}$ spectroscopy was in good agreement with that obtained from $^{13}\text{C-NMR}$'s spectroscopy.

In ethene/1-butene copolymerization $^1\text{H-NMR}$ determined comonomer incorporation differed from $^{13}\text{C-NMR}$ determined comonomer incorporation due to a lack of significant regions useful for integration.

Determination of monomer sequences was more difficult for high molar mass copolymers with high ethene content, due to their low solubility in the $\text{C}_2\text{D}_2\text{Cl}_4$ solvent. The comparison of copolymer incorporation determined with $^1\text{H-NMR}$ (Table 3) data and $^{13}\text{C-NMR}$ data (Table 6) showed a deviation of 3 mol% in relation to

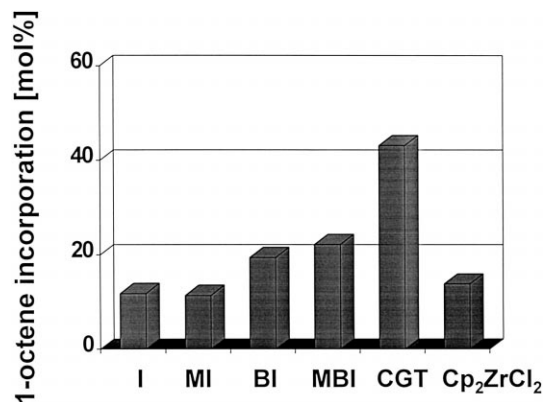


Fig. 5. Incorporation of 1-octene using methylaluminoxane-activated metallocene catalysts in ethene/1-octene copolymerization at constant comonomer ratio.

Table 3

Ethene/1-butene copolymerization performed at 40°C in toluene using *rac*-Me₂Si(2-Me-Benz[e]Ind)₂ZrCl₂/MAO (MBI) at various 1-butene mass feed contents

| | Metallocene, Run No. | | | | | | | |
|--|----------------------|-----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| | MBI, 7 | MBI, 8 | MBI, 9 | MBI, 10 | MBI, 11 | MBI, 12 | MBI, 13 | MBI, 14 |
| 1-Butene content (mass%) ^a | 10 | 17 | 33 | 50 | 66 | 83 | 90 | 100 |
| [MBI] ^b | 1 | 1 | 1 | 1 | 4 | 4 | 8 | 40 |
| <i>F</i> [E] (mol%) ^b | 94.2 | 88.8 | 80.9 | 64.7 | 43.9 | 34.5 | 22.2 | 0 |
| <i>F</i> [B] (mol%) ^c | 5.8 | 11.2 | 19.1 | 35.3 | 56.1 | 65.9 | 77.8 | 100 |
| <i>F</i> [E] (wt%) ^c | 88.9 | 79.8 | 67.8 | 47.8 | 30.4 | 18.4 | 12.5 | 0 |
| <i>F</i> [B] (wt%) ^c | 11.1 | 20.2 | 32.2 | 52.2 | 69.6 | 81.6 | 87.5 | 100 |
| <i>M</i> _n ^d | 128000 | 121900 | 107900 | 82800 | 62400 | 63500 | 82100 | 46700 |
| <i>M</i> _w / <i>M</i> _n ^d | 2.4 | 2.5 | 2.3 | 2.4 | 2.4 | 2.4 | 2.4 | 2.8 |
| <i>T</i> _m ^e | 103.7 | — | — | — | — | — | — | 97.7 |
| <i>T</i> _g ^f | n.d./n.d. | n.d./n.d. | −50.6/ −49.5 | −55.4/ −57.9 | −51.3/ −45.5 | −40.6/ −41.4 | −36.7/ −39.5 | −25.4/ −15.2 |
| <i>P</i> _n ^g | 4300 | 3900 | 3200 | 2200 | 1450 | 1300 | 1600 | 800 |
| Activity (kg/mol h) ^h | 265300 | 113600 | 74400 | 74100 | 12300 | 5300 | 3800 | 290 |

^a *P*_g = 2 bar, 1-butene content in gas mixture.^b MBI catalyst concentration (μmol/l).^c Determined by ¹H-NMR.^d Determined by GPC using poly(ethene) standards.^e Determined by DSC, heating rate 20 K/min.^f Determined by DSC, heating rate 20 K/min and DMA.^g Degree of polymerization.^h Determined according to Eq. (4).

Table 4

Ethene/1-butene copolymerization performed at 40°C in toluene using *rac*-Me₂Si(Ind)₂ZrCl₂/MAO (I) at various 1-butene mass feed contents

| | Metallocene, Run No. | | | | | | | |
|--|----------------------|-------|-------|-------|-------|-------|-------|-------|
| | I, 15 | I, 16 | I, 17 | I, 18 | I, 19 | I, 20 | I, 21 | I, 22 |
| 1-Butene content (mass%) ^a | 10 | 17 | 33 | 50 | 66 | 83 | 90 | 100 |
| [I] ^b | 1 | 1 | 1 | 1 | 1 | 5 | 5 | 20 |
| <i>F</i> [E] (mol%) ^c | 95.7 | 91.5 | 80.3 | 69.1 | 59.5 | 49.2 | 34.6 | 0 |
| <i>F</i> [B] (mol%) ^c | 4.3 | 8.5 | 19.7 | 30.9 | 40.5 | 50.8 | 65.4 | 100 |
| <i>F</i> [E] (wt%) ^c | 91.9 | 84.4 | 67.0 | 52.8 | 42.4 | 32.6 | 20.9 | 0 |
| <i>F</i> [B] (wt%) ^c | 8.1 | 15.6 | 33.0 | 47.2 | 57.6 | 67.4 | 79.1 | 100 |
| <i>M</i> _n ^d | 76300 | 95600 | 82300 | 59600 | 28600 | 22500 | 22100 | 5830 |
| <i>M</i> _w / <i>M</i> _n ^d | 3.6 | 2.5 | 2.4 | 2.2 | 2.1 | 2.0 | 2.8 | 2.1 |
| <i>T</i> _m ^e | 100.3 | 79.9 | — | — | — | — | — | 100.6 |
| <i>T</i> _g ^f | n.d. | n.d. | −54.9 | −66.2 | −64.5 | −58.2 | −47.2 | −25.9 |
| <i>P</i> _n ^g | 2600 | 3100 | 2500 | 1600 | 700 | 530 | 470 | 100 |
| Activity (kg/mol h) ^h | 20600 | 22500 | 26600 | 33600 | 53300 | 50000 | 8700 | 8500 |

^a *P*_g = 2 bar, 1-butene content in gas mixture.^b I catalyst concentration (μmol/l).^c Determined by ¹H-NMR.^d Determined by GPC using poly(ethene) standards.^e Determined by DSC, heating rate 20 K/min.^f Determined by DSC, heating rate 20 K/min.^g Degree of polymerization.^h Determined according to Eq. (4).

Table 5

¹³C-NMR integration of significant regions, as displayed in Fig. 6, for ethene/1-butene copolymers synthesized with MBI catalyst

| | Run. No. | | | | | | |
|----------------|----------|---------|--------|---------|---------|--------|--------|
| | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
| H ^a | 4.0549 | 7.25 | 0.81 | 1.1195 | 8.5277 | 5.8717 | 4.4415 |
| F | 0 | 1.9077 | 0 | 0.1173 | 1.5787 | 1.7356 | 1.6617 |
| E | 3.5119 | 12.8294 | 2.376 | 2.0107 | 9.7410 | 7.837 | 7.2007 |
| D | 8.5266 | 54.3794 | 13.435 | 35.4429 | 0.8425 | 1.2842 | 3.7296 |
| C | 6.2824 | 20.7536 | 3.763 | 3.1118 | 10.2495 | 8.5191 | 7.3036 |
| B | 0 | 1 | 0 | 0 | 1 | 1 | 1 |
| A | 1.068 | 9.5843 | 1.1504 | 1.1175 | 8.9940 | 7.1339 | 5.5373 |

^a Values of integration of ¹³C-NMR's significant regions as displayed in Fig. 6.

1-butene incorporation. The distribution sequences of the ethene/1-butene copolymers and ¹³C-NMR determined comonomer incorporation using MBI are listed in Table 6.

Molar mass and molar mass distribution were measured by means of size exclusion chromatography. Copolymer melting temperatures T_m were determined by means of DSC, glass transition temperatures by DSC and additionally the MBI series by dynamical–mechanical measurements (DMA). In Tables 3 and 4 the influence of different comonomer ratios on the metallocenes MBI and I such as catalyst activities, molar masses, melting and glass transition temperatures are listed.

Average catalysts activities A were calculated using the mass of produced copolymers, polymerization time and amount of metallocene used for copolymerization (Eq. (4)).

$$A = \frac{m_p}{n_{Zr} * t}; \quad (4)$$

A is activity, m_p is the yield of poly(ethene-co-1-butene) copolymer, n_{Zr} is mol of metallocene, t is polymerization time.

Since the solubilities of ethene and 1-butene are not available for mixed gas feeds, in contrast to ethene/1-octene copolymerization, molar activities were not calculated.

Highest catalyst activities, 265000 kg/mol h were observed at 10 mass% 1-butene content using MBI (cf. Table 3 and Fig. 7). Reduced

ethene content in the gas feed accounted for significantly reduced activities approaching only 290 kg/mol h for poly(1-butene). This decay is in accord with earlier observations in ethene/1-hexene and 1-octene copolymerization. Using I as catalyst, maximum activity 53300 kg/mol h was found at a 1-butene content of 66 mass% in gas mixture, decreasing drastically towards 8700 kg/mol h at 90 mass% 1-butene and 20600 kg/mol h at 10 mass% 1-butene content. In contrast to MBI, the I catalyst system remained more active than MBI at higher 1-butene content in the gas feed, (compare run 11–14, MBI series, with run 19–22 I series, Tables 3 and 4, Fig. 7). Only at low 1-butene feed content the average catalyst activ-

Table 6

¹³C-NMR analysis of ethene/1-butene copolymers synthesized with MBI catalyst

| | Run No. | | | | | | |
|-------------------------------|---------|-------|--------|-------|-------|-------|-------|
| | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
| $k(\text{EEE})^a$ | 17.238 | 6.064 | 24.636 | 3.706 | 1.631 | 0.513 | 0.305 |
| $k(\text{BEE} + \text{EEB})$ | 1.936 | 2.613 | 10.215 | 2.228 | 0.935 | 0.517 | 0.466 |
| $k(\text{BEB})$ | 0.000 | 0.000 | 1.000 | 0.000 | 1.000 | 1.000 | 1.000 |
| $k(\text{EBE})$ | 0.984 | 1.387 | 8.017 | 2.771 | 0.441 | 0.947 | 0.930 |
| $k(\text{EBB} + \text{BBE})$ | 0.117 | 0.000 | 1.908 | 0.000 | 1.662 | 1.736 | 1.579 |
| $k(\text{BBB})$ | 0.000 | 0.000 | 0.000 | 1.284 | 0.409 | 2.092 | 5.595 |
| $T(\text{EEE})^b$ | 0.850 | 0.603 | 0.538 | 0.371 | 0.268 | 0.075 | 0.031 |
| $T(\text{BEE} + \text{EEB})$ | 0.095 | 0.260 | 0.223 | 0.223 | 0.154 | 0.076 | 0.047 |
| $T(\text{BEB})$ | 0.000 | 0.000 | 0.022 | 0.000 | 0.165 | 0.147 | 0.101 |
| $T(\text{EBE})$ | 0.049 | 0.138 | 0.175 | 0.277 | 0.073 | 0.139 | 0.094 |
| $T(\text{EBB} + \text{BBE})$ | 0.006 | 0.000 | 0.042 | 0.000 | 0.273 | 0.255 | 0.160 |
| $T(\text{BBB})$ | 0.000 | 0.000 | 0.000 | 0.129 | 0.067 | 0.307 | 0.567 |
| $D(\text{EE})^c$ | 0.898 | 0.732 | 0.650 | 0.483 | 0.204 | 0.113 | 0.054 |
| $D(\text{EB})$ | 0.099 | 0.268 | 0.329 | 0.389 | 0.451 | 0.452 | 0.299 |
| $D(\text{BB})$ | 0.003 | 0.000 | 0.021 | 0.129 | 0.345 | 0.435 | 0.647 |
| $F[\text{E}] \text{ mol}\%^d$ | 94.7 | 86.5 | 81.4 | 67.7 | 42.9 | 33.9 | 20.4 |
| $F[\text{B}] \text{ mol}\%$ | 5.3 | 13.5 | 18.6 | 32.3 | 57.1 | 66.1 | 79.6 |

^a $k(\text{EEE})$, $k(\text{BEE} + \text{EEB})$, $k(\text{BEB})$, $k(\text{EBE})$, $k(\text{EBB} + \text{BBE})$, $k(\text{BBB})$ = triad ratio constants determined according to [50].

^b $T(\text{EEE})$, $T(\text{EEB} + \text{BEE})$, $T(\text{EBE})$, $T(\text{EBB} + \text{BBE})$, $T(\text{BEB})$, $T(\text{BBB})$ = triad distribution determined according to [50].

^c $D(\text{EE})$, $D(\text{EB})$, $D(\text{BB})$ = diad distribution, determined from triad distribution.

^dEthene incorporation determined from diad distribution.

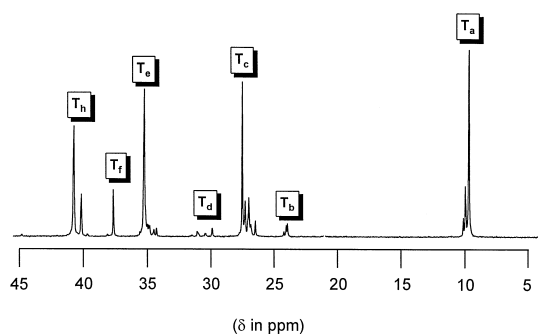


Fig. 6. ^{13}C -NMR spectrum of ethene/1-butene copolymer $T_a - T_h$ = significant regions for integration [50].

ities of the MBI-series are substantially lower with respect to those of I. 2-methyl substitution, which accounted for reduced catalyst activities in ethene/1-octene or propene/1-octene copolymerization at high 1-octene feed content, influenced ethene/1-butene copolymerization in a similar way. Interestingly, ethene/1-butene copolymer activities of MBI were higher than those of I when 1-butene feed content was below 50 mass% (compare run 7–10, MBI series, with run 15–18 I series, Table 3 and Fig. 7). However, at a 1-butene content of 66 mass% activity of I increased and surpassed that of the MBI system, (compare run 11–14 MBI series with run 19–22 I series, Table 4 and Fig. 7).

MBI catalyst gave markedly improved copolymer molar masses and degrees of polymerization of the copolymers over the entire gas

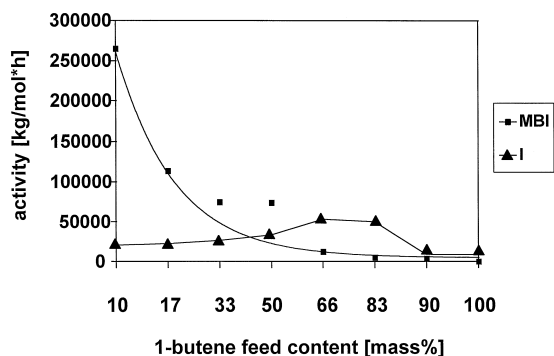


Fig. 7. Activity of methylaluminoxane-activated MBI and I catalysts in ethene/1-butene copolymerization as a function of 1-butene feed content.

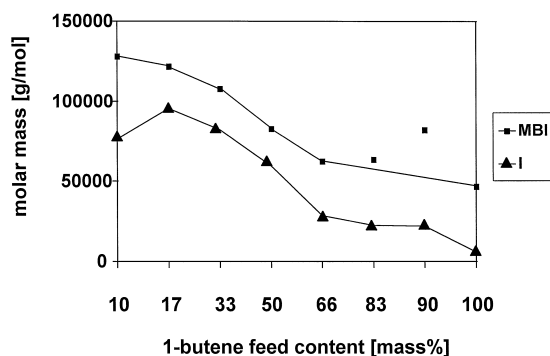


Fig. 8. Molar mass of poly(ethene-co-1-butene) copolymers as a function of 1-butene feed content using methylaluminoxane-activated MBI and I catalysts in ethene/1-butene copolymerization.

composition range. Especially at 1-butene feed content exceeding 50 mass%, 2-methyl substitution of the benzindenyl ligand promoted molar mass build up (compare run 10–14, MBI series with 19–22, I series, Table 4 and Fig. 8).

Independent of the metallocene type (I or MBI), molar mass distribution remained narrow, indicating both, the presence of one type of catalytically active center and constant concentrations of the 1-olefins during the entire polymerization process.

Incorporation of 1-butene, depicted in Fig. 9, at the same 1-butene feed content varying from 50 to 90 mass% was higher for MBI with

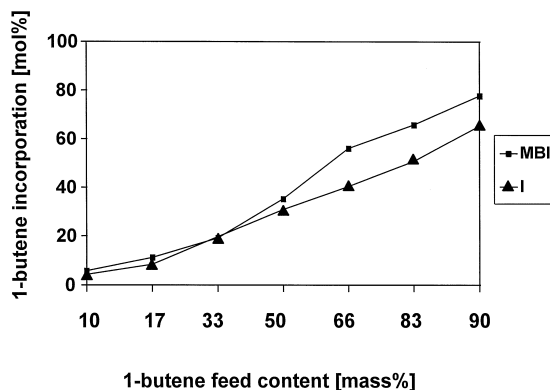


Fig. 9. Incorporation of 1-butene as a function of 1-butene feed content using methylaluminoxane-activated MBI and I catalysts in ethene/1-butene copolymerization.

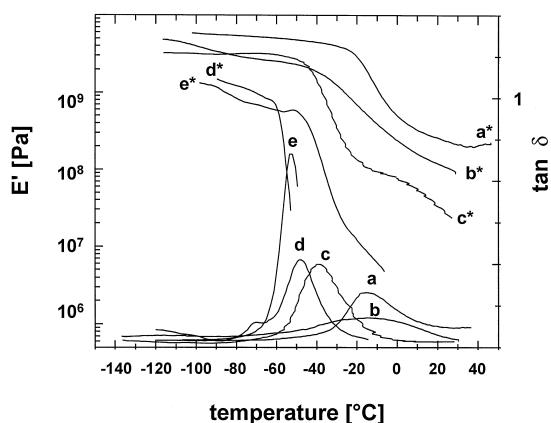


Fig. 10. Glass transition temperature (T_g) and storage modulus (E') of poly(ethene-co-1-butene) copolymers synthesized with methylaluminoxane-activated MBI as a function of 1-butene content: (a) isotactic poly(1-butene), (b) 12 mass% ethene (88 mass% 1-butene), (c) 12 mass% 1-butene (88 mass% ethene), (d) 32 mass% 1-butene (68 mass% ethene), (e) 50 mass% 1-butene.

respect to that of I. With decreasing 1-butene feed content (cf. Fig. 9) below 50 mass% 1-butene incorporation was not promoted. In fact, 1-butene incorporation was identical for I and MBI system below 50 mass% 1-butene feed content.

Fig. 10 displays the glass transition temperatures T_g and storage moduli E' as a function of temperature. The $\tan \delta$ maximum, representing T_g , was very broad for the copolymers with low 1-butene incorporation (Fig. 10b) and for poly(1-butene) (Fig. 10a), as reported in literature [51]. With increasing 1-butene content $\tan \delta$ maxima became sharper (Fig. 10c–e) and T_g values became comparable to those determined by DSC-measurements.

With increasing 1-butene content of the copolymer, T_g declined in the MBI series reaching the minimum of about -55°C at 50 mass% 1-butene incorporation. Storage moduli E' at -80°C decreased with increasing comonomer content. Highest E' was found for poly(1-butene) (Fig. 10a*). Copolymers containing 12 mass% 1-butene displayed nearly the same modulus as the copolymer containing 12 mass% ethene, (Fig. 10b*–c*). With comonomer content of 1-butene increasing to 32 mass% modu-

lus decreased (Fig. 10d*). At 50 mass% 1-butene content (Fig. 10e*) modulus of the poly(ethene-co-1-butene) copolymer reached a minimum value.

T_g values of the copolymers obtained with I depended on comonomer incorporation in a similar way. With increasing ethene content T_g decreased to -66°C at a 1-butene incorporation of 47 mass%. At identical 1-butene comonomer incorporation of I and MBI of 50 mass% T_g differences are mainly due to the different molar masses of the poly(ethene-co-1-butene) copolymers. Melting temperatures of the poly(ethene-co-1-butene) copolymers were only detectable for low 1-butene content ($< 10\text{ mol}\%$), typically in range of 100°C (run 7, 15, Tables 3 and 4) and 80°C (run 17, Table 4). With increasing 1-butene content all copolymers were rendered amorphous.

4. Conclusion

Metallocene catalyzed copolymerization of ethene with 1-butene or 1-octene, respectively, was primarily dependent on metallocene structures and ethene/1-olefin ratio. Highest 1-octene incorporation was found for MAO-activated halfsandwich titanocene CGT. In the family of silylene-bridged bisindenyl zirconocenes, benzannelation clearly promoted random incorporation of 1-octene. This result was in accord with recent force field modelling studies by Schneider and Prosenec [52], where benzannelation accounted for substantially lower differences of activation energy of 1-octene insertion subsequent to ethene insertion or ethene subsequent to 1-octene, respectively. Although 2-methyl substitution did not affect randomness, it improved copolymer molar mass at the expense of catalyst activity. For ethene/1-butene copolymerization the ethene/1-butene feed mass ratio played an important role. Below 50 mass% 1-butene in comonomer feed, MBI catalyst activity was substantially higher with respect to I,

whereas above 50 mass% 1-butene feed content, I was more active than MBI. A similar trend was observed for 1-butene incorporation. Below 50 mass% 1-butene content 1-butene incorporation was almost identical for MBI and I. At 1-butene mass feed content exceeding 50 mass% 1-butene, however, MBI promoted 1-butene incorporation with respect to I. In accord with ethene/1-octene copolymerizations, independent of 1-butene mass feed content, MBI-based catalyst always afforded markedly higher molar masses of the resulting poly(ethene-co-1-butene) copolymers with respect to those prepared by I-based catalyst. At low 1-butene content (< 10 wt%), the poly(ethene-co-1-butene) copolymers prepared with MBI were semicrystalline materials. The incorporation of 1-butene reduced crystallinity. At 1-butene content > 10 wt% up to 90 wt% poly(ethene-co-1-butene) copolymers were rendered amorphous and highly flexible with glass temperatures T_g and storage moduli E' decreasing with increasing 1-butene content with respect to poly(1-butene). Controlled incorporation of 1-butene into poly(ethene) with the MBI catalyst demonstrated an efficient route to highly diversified, poly(ethene-co-1-butene) copolymers with narrow molar mass distribution via metallocene catalysis.

The influence of 1-butene feed content must be further elucidated by taking into account possible deviation of local 1-butene concentration which can not be calculated by Henry's law [47]. Although the influence of 1-butene solubility is not yet fully understood, the narrow molar mass distribution clearly indicates the presence of single catalytically active sites. In conclusion, both silylene-bridged bisindenyl zirconocenes, especially those being benzannelated and 2-methyl substituted, as well as halfsandwich titanocenes offer attractive synthetic potential to prepare copolymers covering the entire feasible composition range. This is very attractive, both in view of industrial application as well as in view of better understanding the influence of copolymer microstructures and molar mass on copolymer properties and blend behavior.

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