

Direct Copolymerization of Propene and Ethene-based Macromers to Produce Long Chain Branched Syndiotactic Polypropene

S. Rulhoff, W. Kaminsky*

Summary: Copolymers of propene and ethene-based macromers have been prepared in a direct copolymerization. First macromers in a range of 3000–11600 g/mol were synthesized by varying the polymerization temperature and ethene concentration with the metallocene catalyst $[(\text{CH}_3)_2\text{CCp}_2]\text{ZrCl}_2/\text{MAO}$. These vinyl terminated ethene oligomers were copolymerized with propene by C_s symmetric catalyst $[\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})]\text{ZrCl}_2$ to a long-chain branched syndiotactic polypropylene. The LCB-sPP was separated from the bimodal product by a fractional crystallization with p-xylene and 2 - ethoxy ethanol at 130 °C. A detailed analysis of the purified copolymer was given by GPC, DSC and ^{13}C NMR spectroscopy.

Keywords: copolymerization; long-chain branching; macromer; metallocene; syndiotactic polypropylene

Introduction

Recent advances in metallocene catalyst technology make olefinic copolymers with a high homogeneous insertion of comonomer units and a small molecular weight distribution possible^[1–5]. The development has focused on copolymers of ethene with different higher α -olefins^[6–8]. The technology allows a broad property range by varying the length and content of the comonomer from a thermoplastic behavior like HDPE to an elastomeric behavior. The major development to change polymer behavior of polypropylene has been done by including different pattern of irregularities affecting the tacticities, but copolymers of iso-, syndio- or atactic polypropylenes have been received less intention.

Henschke et al. studied the copolymerization of propene with different α -olefins from 1-butene up to 1-hexadecene using

$\text{Et}(\text{Ind})_2\text{HfCl}_2/\text{MAO}$ ^[9]. Also R. Quijada et al. and Poon has copolymerized propene and 1-hexene or 1-octene with different C_2 - and C_s - symmetric zirconocenes/MAO catalysts^[10,11]. Their results show that there is only a slight decrease of reactivity by increasing the comonomer length, but on the other hand the thermal behavior of these materials is affected substantially with an increasing content of side chains in the polymer. The percentage of incorporated comonomer in the prepared copolymers influences directly the melting temperature; the material properties changes from a crystalline isotactic to an amorphous structured copolymer. Besides the effects of short-chain branches in polypropylene copolymers, long-chain branches has not developed because of the difficulties in synthesis of α -olefinic macromers and the extraction of the long-chain branched copolymer from bimodal product. Only a small amount of long-chain branches in polyethene gives the material a better processing behavior because of a slower crystallization without changing the macroscopic profile.

In this work vinyl terminated macromers were synthesized with the metallocene

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

Fax: +49 40 42838 6008

E-mail: kaminsky@chemie.uni-hamburg.de

catalyst $[\text{Me}_2\text{C}(\text{Cp})_2]\text{ZrCl}_2/\text{MAO}$, thereby β -H elimination is the dominating termination reaction. The molecular weight of these ethene-based oligomers was varied from 3 000 to 11 600 g/mol with a narrow molecular weight distribution. These macromers were copolymerized directly with propene by the C_s – symmetric metallocene $[\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})]\text{ZrCl}_2$ to long-chain branched syndiotactic copolymers.

Experimental Procedures

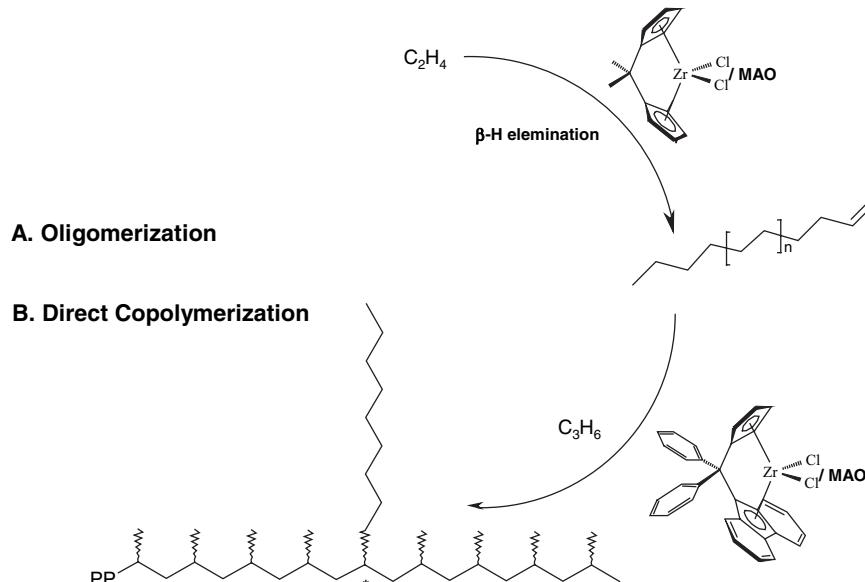
In scheme 1 is shown the direct copolymerization of propene and ethene-based macromers in detail. In a first polymerization circle the macromer was prepared by the metallocene catalyst $[\text{Me}_2\text{C}(\text{Cp})_2]\text{ZrCl}_2/\text{MAO}$ (1) ^[12]. The oligomerization procedure was aborted after consumption of 4.5 L ethene by removing the monomer. The reaction solution was degased from ethene, evacuated and rinsed several times with argon. After the desired copolymerization temperature was reached the propene pressure was adjusted. The copolymerization was

started by injecting the second catalyst $[\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})]\text{ZrCl}_2$ (2). In both circle the ethene or propene pressure is kept constant by a Brooks Mass Flow Controller for the whole time of polymerization. The limitation of this reaction procedure is that catalyst 1 must be inactive towards polymerization of propene but its benefit is obviously a maximum of vinylic endgroups of the macromer by not handling it in between. The macromer will be separated from the bimodal product by a fractional crystallization with p-xylene and 2 - ethoxy ethanol at 130 °C (see Figure 2).

Results and Discussion

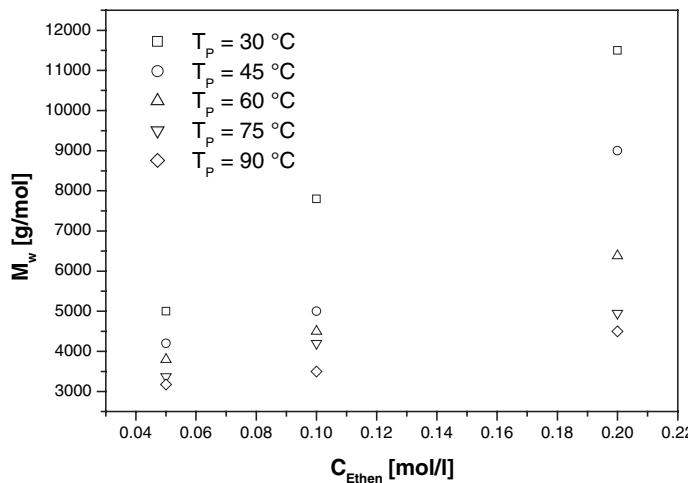
Ethene-based Macromers

Investigations of several metallocene catalysts revealed that the termination mechanism is catalyst specific. Apart from hydrogen transfer to the monomer or chain transfer to the cocatalyst the preferred termination mechanism is β -H elimination. The amount of vinylic endgroups of ethene oligomers, obtained via β -H elimination,



Scheme 1.

Scheme of the direct copolymerization.

**Figure 1.**

Adjusting the molecular weight of the macromer by varying the polymerization temperature and ethene concentration.

was determined by ^{13}C NMR measurements (139.0/114.1 ppm) and it was in range of 90–98 %.

To achieve a rheological effect of the long-chain branched polymer the side chain must be greater than the entanglement molar mass of syndiotactic polypropylene (sPP $M_e \sim 2800$ g/mol). By varying polymerization temperature and monomer concentration the molecular weight of the desired macromer can be adjusted between 3 000 and 12 000 g/mol and the polydispersity of all samples was approximately 2. In Figure 1 the adjustment of the molar masses are given for polymerization temperatures between 30 to 90 °C and an ethene concentration up to 0.2 mol/L.

Synthesis of Long-chain Branched sPP

Three macromers were selected for the copolymerization with propene as shown in Table 1. The macromer length (C214, 464 and 828 carbons) was adjusted by varying

the polymerization temperature (30, 60 and 90 °C). All copolymerizations were carried out at 45 °C with a propene concentration of 1 mol/L, and started by injection of the metallocene catalyst (2) ($1 \cdot 10^{-6}$ mol). The reaction solution was quenched with ethanol after entire consumption of 4.5 l propene. The bimodal product was stirred overnight in a solution of HCl/ethanol/water solution and washed with water and dried at 60 °C in vacuo overnight.

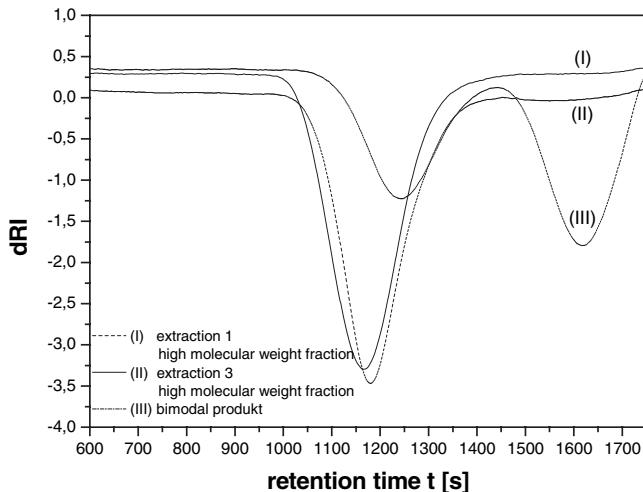
Extraction

J. Kong et al. reported on the solution fractionation of different polyethene types conducted by the stepwise control of temperature and the amount of precipitant.^[13] This fractionation is a successful technique to separate polyolefins samples according to their molecular weight and their molecular weight distribution in a high molecular fraction I ($M_w > 100.000$ g/mol) and a low molecular weight fraction II

Table 1.

Macromers used in the direct copolymerization

No	T_p [°C]	C_{ethene} [mol/L]	macromer carbons	M_w macromer [g/mol]	PDI	T_m [°C]	T_c [°C]
1	90	0.1	214	3000	2.4	120.0	107.9
2	60	0.1	464	6500	1.8	118.4	105.1
3	30	0.2	828	11600	1.5	113.2	100.4

**Figure 2.**

SEC controlled separation of LCB sPP (macromer $M_w = 3000$ g/mol) from the bimodal product by a fractional crystallization with p-xylene and 2 - ethoxy ethanol at 130°C .

($M_w < 15.000$ g/mol). The macromer in this study was separated from the bimodal product by a stepwise solution fractionation with p-xylene and 2 - ethoxy ethanol at $120-130^\circ\text{C}$. The purity of the isolated high molecular weight fraction I was controlled by size exclusion chromatograph (SEC) measurements. Figure 2 shows the results of the SEC controlled separation of LCB sPP (macromer $M_w = 3000$ g/mol) from the bimodal product (III) by a fractional crystallization. The sample (II) presented the high molecular fraction after the first run and there was still some macromer detected. The long-chain branched copolymer was finally purified after the third extraction (I). In comparison to the bimodal product the molar masses were shifted by every succeeded fractionation run to

higher masses because the lower parts of the fraction was washed out.

Resulting Copolymers

The comonomer incorporation was determined by ^{13}C NMR spectroscopy. The detection of the characteristic branching carbon analogues at the investigated short-chain branched copolymers was not possible due to the resolution problems, but in comparison to long-chain branched polyethenes the methylene group signal of the side chain (~ 30 ppm) was separated from the backbone. By analyzing these methylene groups the incorporation of the ethene-based macromer into the syndiotactic polypropylene backbone ($\delta(\text{CH}_3) = 20.27$ ppm, $\delta(\text{CH}) = 28.33$ ppm, $\delta(\text{CH}_2) = 47.09$ ppm) could be determined. So it was possible to

Table 2.

Resulting syndiotactic copolymer in dependence of the macromer length

No.	macromer carbons	feed c_{macromer} [mol/L]	copolymer X_{macromer} [mol%]	copolymer X_{macromer} [wt%]	$C^*/1000_{\text{backbone}}$	M_w [g/mol]	MWD	T_m [$^\circ\text{C}$]
1	—	—	—	—	—	380000	2.1	130.0
2	214	0.0017	0.062	4.23	0.309	178000	1.6	113.0
3	464	0.0007	0.012	1.82	0.060	256000	1.5	118.3
4	828	0.0004	0.002	0.60	0.011	356000	1.7	124.9

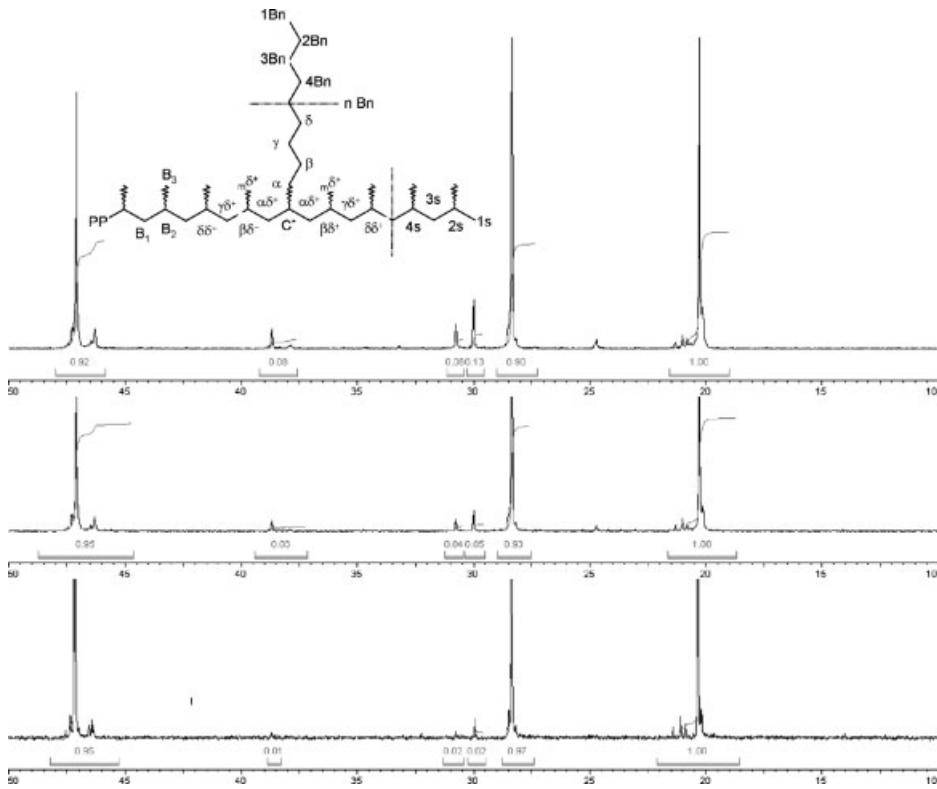


Figure 3.

^{13}C NMR spectra of a long-chain branched sPP with different comonomer length ((1) $M_w = 3.000$ g/mol; (2) $M_w = 6.500$ g/mol; (3) $M_w = 11.600$ g/mol).

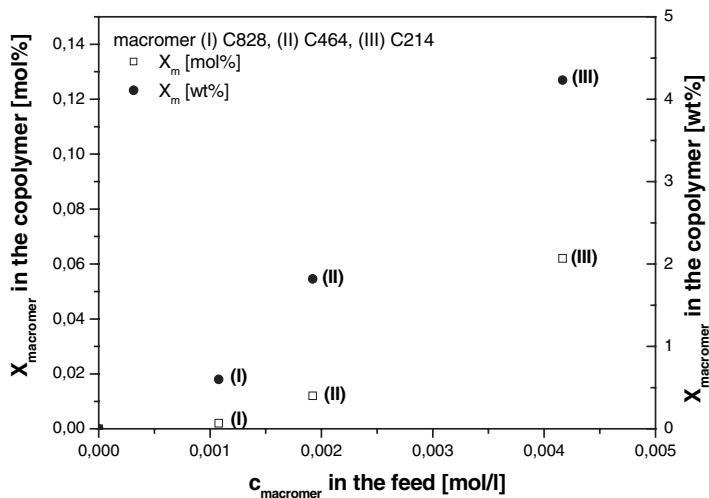
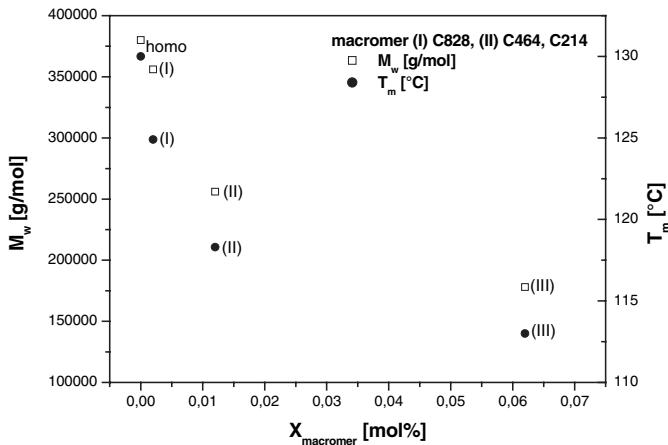


Figure 4.

Comonomer incorporation in dependence of macromer concentration in the feed and their length.

**Figure 5.**

Melting behavior and molecular weight characteristics of the copolymer in dependence of incorporated comonomer.

calculate the amount of branches in the backbone analogous to polyethenes in C^{*}/1000 (without CH₃-groups). The copolymer characteristics was shown in Table 2. The stereoregularity of the syndiotactic polypropylene backbone decreased with increasing comonomer content in the copolymer.

The increasing comonomer incorporation with decreasing macromer length is depicted in Figure 3. However the increasing incorporation is established partially by the greater comonomer concentration in the feed; but the increase in dependence of the macromer length is much greater than the increase of the macromer concentration. The molecular weight fraction in the copolymer (2) with 0.062 mol% of macromer with 214 CH₂-groups is about 4.23 wt%, while the incorporation of 0.002 mol% comonomer with 828 carbons complies 0.6 wt%. The long-chain branching in the sPP copolymers shown in Table 2 is corresponds to 0.309 to 0.011 branches at 1000 carbons as is in well known for long-chain branched polyethenes.

The molar mass of the macromer/propene copolymer ranges from 356 000 g/mol to 176 000 g/mol. In comparison to the syndiotactic homopolymer the molar mass decreases from 380 000 g/mol with an increasing content of long-chain branching

in the copolymer. As expected for metallocene catalysis the molecular weight distribution is about 2.

There is a strong dependence of the melting behavior on the ratio of macromer in the copolymer. Furthermore the melting temperature is dependant on the stereoregularity and molar mass of the copolymer. The melting temperature decreases from 130.0 °C for the homopolymer to 113.1 °C at a content of 0.062 mol% macromer (214 carbon side chain).

Conclusions

Three ethene-based α -olefinic macromers ($M_w = 3\,000, 6\,500, 11\,600$ g/mol) were synthesized using the catalytic system $[\text{Me}_2\text{C}(\text{Cp})_2\text{ZrCl}_2]/\text{MAO}$ by varying the polymerization temperature and afterwards they were in-situ copolymerized with propene by a C_s symmetric metallocene catalyst $[\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2]$ to a long-chain branched syndiotactic copolymer. Macromer incorporation up to 0.062 mol% which complies with 4.23 wt% are detected by ¹³C NMR spectroscopy. The comonomer content in the copolymer effects the melting behavior as well as the molar mass of the copolymer.

Acknowledgement: We thank the Deutsche Forschungs Gesellschaft (DFG) for supporting these studies.

- [1] Kaminsky, W. *Journal of the Chemical Society-Dalton Transactions* **1998**, (9), 1413–1418.
- [2] Alt, H. G.; Köppl, A. *Chem. Rev.* **2000**, 100, 1205–1222.
- [3] Coates, G. W. *Chem. Rev.* **2000**, 100, 1233–1252.
- [4] Scheins, J.; Kaminsky, W. (eds), *Metallocene-based Polyolefins.*; Wiley & Sons: Chichester, I + II, **2000**; Vol. I + II.
- [5] Seraidaris, T.; Kaminsky, W.; Seppala, J.; Lofgren, B. *Macrom. Chem. Phys.* **2005**, 206, (13), 1319–1325.
- [6] Kaminsky, W.; Piel, C. *Journal of Molecular Catalysis A - Chemical* **2004**, 213, (1), 15–19.
- [7] Kaminsky, W.; Piel, C.; Scharlach, K. *Macrom. Symp.* **2005**, 226, 25–34.
- [8] Bianchini, C.; Frediani, M.; Giambastiani, G.; Kaminsky, W.; Meli, A.; Passaglia, E. *Macromolecular Rapid Communications* **2005**, 26, (15), 1218–1223.
- [9] Arnold, M.; O. Henschke; Knorr, J. *Macromol. Chem. Phys.* **1996**, 197, 563–573.
- [10] Quijada, R.; Guevara, J. L.; Galland, G. B.; Rabagliati, F. M.; Lopez-Majada, J. M. *Polymer* **2005**, 46, 1567–1574.
- [11] Poon, B.; Rogunova, M.; Hiltner, A.; Baer, E.; Chum, S. P.; Galeski, A.; Piorkowska, E. *Macromolecules* **2005**, 38, 1232–1243.
- [12] Sperber, O.; Kaminsky, W. *Macromolecules* **2003**, 36, (24), 9014–9019.
- [13] Kong, J.; Fan, X.; Jia, M. *J. Appl. Polym. Sci.* **2004**, 93, 2542–2549.