Copolymerization of Ethene with Cyclic and Other Sterically Hindered Olefins

Walter Kaminsky*, Inken Beulich, Michael Arndt-Rosenau

Institut für Technische und Makromolekulare Chemie, Universität Hamburg
Bundesstrasse 45, 20146 Hamburg, Germany

SUMMARY: Sterically hindered olefins like norbornene, dimethanooctahydronaphthalene (DMON), 4-methylpentene, and 3-methylbutene can be copolymerised with ethene by metallocene/MAO catalysts. Different C_2-, C_s- and C_1-symmetric and *meso*-zirconocenes were used. Only isolated and alternating norbornene sequences but no norbornene blocks are formed by substituted $[Me_2C(Cp\text{-}R)(Flu)]ZrCl_2$ catalysts. The alternating microstructure leads to melting points up to 270°C for ethene-norbornene copolymers and up to 380°C for the semi-crystalline alternating copolymer of ethene and DMON. Other sterically hindered olefins such as 3-methylpentene build more blocky structures with high glass transition temperatures. The mechanism for the insertion reaction of the different catalysts is discussed.

Introduction

Metallocene/methylaluminoxane (MAO) catalysts can be used to polymerise and copolymerise strained cyclic olefins such as cyclobutene, cyclopentene, norbornene, DMON and other sterically hindered olefins[1-6]. While polymerisation of cyclic olefins by Ziegler-Natta catalysts is accompanied by ring opening[7], homogeneous metallocene[8], nickel [9,10] or palladium[11,12] catalysts achieve exclusive double bond opening polymerisation.

Homopolymerisation of cyclic olefins via ring opening polymerisation by means of metathesis (ROMP)[13] results in elastomeric materials. The metallocene homopolymers feature two chiral centers per monomer unit and therefore are ditactic. The cycloolefins may be divided into achiral, monocyclic and prochiral, polycyclic types. Polymerisation of both types by chiral metallocenes may yield tactic, crystalline homopolymers[14]. The melting points of these homopolymers are extremely high, for instance 400°C for polycyclopentene, and in most cases decomposition occurs before melting. Atactic homopolymers of cyclic olefins are produced by non-chiral metallocenes such as Cp_2ZrCl_2. They have a high glass transition temperature and are not elastomers. While the atactic polymers can be dissolved in hydrocarbon solvents at least to some extent, tactic polymers are hardly soluble.

© WILEY-VCH Verlag GmbH, D-69469 Weinheim, 2001 CCC 1022-1360/00/$ 17.50+.50/0

Tactic poly(cycloolefins) are not processible due to their high melting points but by copolymerisation of these cyclic olefins with ethylene or α-olefins cycloolefin copolymers (COC) can be produced, representing a new class of thermoplastic amorphous materials[15-17]. Early attempts to produce such copolymers were made using heterogeneous $TiCl_4/AlEt_2Cl$ or vanadium catalysts, but first significant progress was made by utilizing metallocene catalysts for this purpose. They are about ten times more active than vanadium systems and by careful choice of the metallocene, the comonomer distribution may be varied from statistical to alternating. Furthermore the glass transition temperature can be varied over a wide range by selection of the appropriate cycloolefin and its degree of incorporation into the polymer chain. Statistical copolymers become amorphous at comonomer incorporations beyond 10 – 15 mol% cycloolefin.

COCs are characterized by excellent transparency and very high, long-life service temperatures. They are soluble, chemically resistant and can be melt-processed. Due to their high carbon/hydrogen ratio, these polymers feature a high refractive index, e.g. 1.53 for ethylene-norbornene copolymer at 50 mol% norbornene incorporation. Their stability against hydrolysis and chemical degradation, in combination with their stiffness lets them become desirable materials for optical applications, e.g. for compact discs, lenses, optical fibers and films[15]. The first commercial COC plant run by Ticona GmbH with a capacity of 30,000 tons a year commenced production in September 2000 and is located in Oberhausen, Germany.

The first metallocene-based COC material was synthesized from ethene and cyclopentene[18]. While homopolymerisation of cyclopentene results in 1,3-enchainment of the monomer units[19], isolated cyclopentene units are incorporated into the ethylene-cyclopentene copolymer chain by 1,2-insertion. Ethylene is able to compensate the steric hindrance at the α-carbon of the growing chain after and before the insertion of cyclopentene[20].

Ethene-norbornene copolymers are most interesting for technical applications as they can be made from easily available monomers and provide glass transition temperatures up to 200°C. Table 1 presents the activities and comonomer ratios for the several applied catalysts of C_2- and C_s- symmetry. C_s-symmetric zirconocenes are more active in the copolymerisation than for the homopolymerisation of ethene. Under the chosen conditions, $[En(Ind)_2]ZrCl_2$ develops the highest activity while the highest comonomer incorporation is achieved by $[Ph_2C(Ind)(Cp)]ZrCl_2$.

Table 1. Copolymerisation of norbornene (N) and ethene by different metallocene/MAO catalysts at 30°C. Conditions: MAO/Zr = 200, c(Zr) = $5 \cdot 10^{-6}$ mol/l; p(E) = 2.00 bar, c(N) = 0,05 mol/l.

Catalyst	t [min]	Activity [kg/mol h]	Incorp. of norbornene [weight %]
Cp_2ZrCl_2	30	1200	21,4
$[En(Ind)_2]ZrCl_2$	10	9120	26,1
$[Me_2Si(Ind)_2]ZrCl_2$	15	2320	28,4
$[En(IndH_4)_2]ZrCl_2$	40	480	28,1
$[Me_2C(Flu)(Cp)]ZrCl_2$	10	7200	28,9
$[Ph_2C(Flu)(Cp)]ZrCl_2$	10	6000	27,3
$[Ph_2C(Ind)(Cp)]ZrCl_2$	15	2950	33,3

Due to different incorporation ratios of the cyclic olefin into the copolymer, the glass transition temperature can vary over a wide range which is basically independent of the applied catalyst. A copolymer containing 50 mol% of norbornene yields a material with a glass transition point of 145°C. Considering COCs of different comonomers with equal comonomer ratios, increased T_g values can be observed for the bulkier comonomer, for instance 72°C for ethene-norbornene and 105°C for ethene-DMON at comonomer mole ratio $X_{Co} = 0.30$ each.

Experimental Part

Sterically hindered olefins such as norbornene, DMON, 4-methylpentene, and 3-methylpentene (Figure 1) were copolymerised with ethene by metallocene/MAO catalysts.

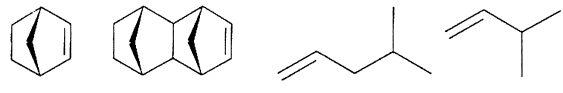

Fig. 1: Cycloolefins and α-olefins used for the copolymerisation with ethene.

For comparison, different C_1- and C_2-symmetric zirconocenes were used for the copolymerisation of the olefins. Selected C_1-symmetric zirconocenes are shown in Figure 2.

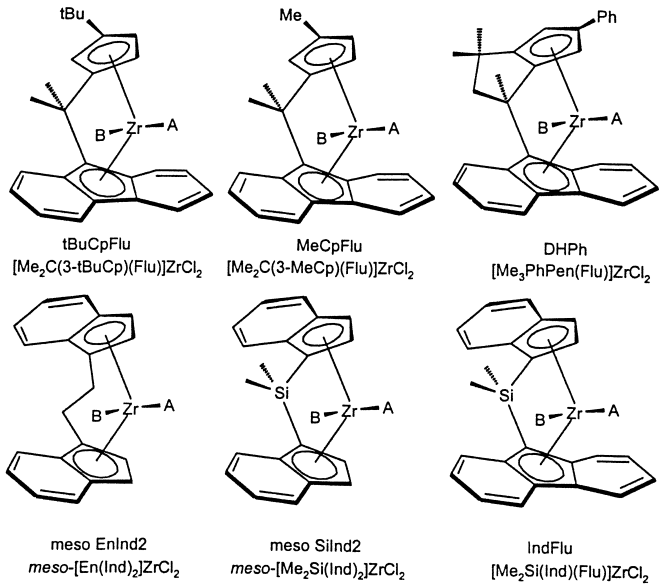

Fig. 2: Molecular structures of selected copolymerisation catalysts and their terms.

The zirconocenes were prepared as described in the literature[21-23]. The polymerisations were carried out under argon using a 1 l Büchi A6 Type I autoclave equipped with an additional external cooling system. For the standard experiments, the reactor was evacuated at 95°C for 1 h and charged subsequently with 200 ml toluene, 500 mg MAO from Witco, 10-20 g of the comonomer and ethene at different pressures. The cycloolefins were dried over tri-*iso*-butylaluminum and subsequently destilled. The gaseous monomers (ethene, 3-methyl-1-butene) were purified with a copper-catalyst (BASF R3-11) and dried over molecular sieves 3-4 Å. The polymerisation was started by injection of a toluenic solution of the metallocene into the reaction vessel. During the reaction, the ethene pressure was kept constant by supplying the monomer. The polymerisation was quenched by addition of 5 ml ethanol. Workup proceeded by stirring over night in diluted hydrochloric acid followed by neutralization with aqueous $NaHCO_3$ and washing with water. After phase separation the polymer was precipitated if possible. Otherwise the organic solvent was removed under reduced pressure and the obtained polymer dried in vacuo.

All ^{13}C NMR spectra of the polymers were recorded with a Bruker MSL 300 spectrometer operating at 75,47 MHz and 373 K. The polymer specimen were dissolved in perchlorobutadiene and tetrachloroethane-d_2. Molar masses and molar mass distributions were determined by size exclusion chromatography on a Waters 150-C instrument running with trichlorobenzene at 135°C employing a PL-EMD-960 evaporation light scattering detector. Additional molar mass determination was conducted by viscosimetry using an Ubbelohde viscosimeter at 30°C (Kapillare 0a, K = 0,005). Differential scanning calorimetry was performed on a Mettler-Toledo DSC 821e instrument at a heating rate of 20°C/min. To eliminate any thermal history, the samples were heated twice and only values obtained in the second run are reported herein. Molecular mass and distributions were determined by GPC on a Waters 150C instrument (trichlorobenzene, 135 °C) using polystyrene standards.

Ethene-Norbornene Copolymers

For the copolymerisation of ethene with norbornene the ethene concentration was kept constant. Table 2 contains the results using different zirconocenes of C_S- and C_1-symmetry.

Table 2. Copolymerisation of ethene-norbornene by various zirconocene/MAO catalysts at 30°C. Conditions: c(E) = 0,237 mol/l, c(Zr) = 5 µmol/l, MAO 2,5 g/l, x_N = norbornene ratio in feed, X_N = norbornene ratio in polymer, T_g = glass temperature, T_m = melting point, n.d. = not detected, n.m. = not measured.

Catalyst	x_N	X_N	Activity [kg_{Pol}/mol_{Zr} h]	M_W [g/mol]	T_g (T_m) [°C]
$[Me_2C(Cp)(Flu)]ZrCl_2$	0	0	1541	558000	(136)
	0,21	0,090	5880	178000	(7)
	0,40	0,145	5550	230000	0
	0,56	0,260	5086	114000	46
	0,80	0,371	3314	129000	92
	0,90	0,431	961	135000	111
	0,95	0,495	1785	158000	135
	0,99	0,626	2084	143000	200
$[Me_2C(3\text{-}MeCp)(Flu)]ZrCl_2$	0,19	0,073	3438	145000	n. d.
	0,37	0,150	3271	87000	3
	0,55	0,218	3926	99000	40
	0,77	0,324	4420	171000	86
	0,89	0,407	5721	252000	106 (215)
	0,94	0,438	1602	431000	118 (243)
	0,96	0,456	20	n. d.	124 (276)
$[Me_2C(3\text{-}^tBuCp)(Flu)]ZrCl_2$	0,23	0,055	1853	230000	-96
	0,43	0,080	1133	159000	-66
	0,58	0,160	296	101000	14
	0,68	0,220	355	90000	37
	0,83	0,313	437	82000	74
	0,91	0,373	205	7300	97 (242)
	0,93	0,388	142	8900	103 (255)
$[Me_2Si(Cp)(Flu)]ZrCl_2$	0,21	0,054	38957	842000	(88)
	0,40	0,123	27150	705000	-4 (44)
	0,57	0,184	30220	808000	15
	0,71	0,263	13964	950000	43
	0,79	0,323	27454	1011000	70
	0,90	0,407	14316	1123000	65
	0,95	0,467	11084	431000	129
	0,99	0,644	432	190000	133

Table 2 continued

Catalyst	x_N	X_N	Activity [kg_{Pol}/mol_{Zr} h]	M_W [g/mol]	T_g (T_m) [°C]
$[Me_2Si(Ind)(Flu)]ZrCl_2$	0,21	0,028	332	360000	(124)
	0,42	0,088	370	n. d.	(127)
	0,59	0,107	170	182000	40 (124)
	0,80	0,257	70	135000	21 (126)
	0,91	0,216	86	57000	82 (129)
$[Me_3PhPen(Flu)]ZrCl_2$	0	0	n.m.	660000	n. d. (135)
	0,20	0,046		657800	n. d. (98)
	0,37	0,094		537700	n. d. (66)
	0,54	0,159		593900	2
	0,79	0,280		757900	65
	0,91	0,380		930600	93

Of the catalysts subject to this investigation, $[Me_2Si(Cp)(Flu)]ZrCl_2$ turned out to be the most active one providing high molecular weights coming along with good comonomer ratios in the polymer. The observed glass transition temperatures are about average while the highest transition temperatures are achieved by $[Me_2C(Cp)(Flu)]ZrCl_2$.

Surprisingly, in some cases the molecular weights increase with the norbornene ratio in polymer chain which is remarkably illustrated by the catalyst system $[Me_2C(3\text{-}MeCp)(Flu)]ZrCl_2$/MAO. The lowest molecular weight of 87,000 g/mol is found for a feed composition of $x_N = 0.37$ and $x_E = 0.63$ going up to 431,000 g/mol at $x_N = 0.94$.

$[Me_3PhPen(Flu)]ZrCl_2$ produces for $x_N = 0.37$ copolymers with $X_N = 0.09$, a melting point of 66 °C and a molecular weight of 538,000 g/mol. At $X_N = 0,91$ the observed molecular weights reach a maximum of 930,000 g/mol.

As it might be expected, the glass transition temperatures of the copolymers depend on its microstructure and norbornene content. At about $X_N = 0.14$, a glass transition temperature of 0°C is found and increases for statistically distributed copolymers to 200°C. A copolymer with $X_N = 0.50$ has a glass transition temperature of about 145°C.

In addition, *meso*-ansa-zirconocenes were used as catalysts for the ethene-norbornene copolymerisation. The experimental results can be seen in Table 3.

Table 3. Copolymerisation of ethene with norbornene by different *meso*-ansa-zirconocenes at 30°C. c(E) = 0,237 mol/l, c(Zr) = 5 µmol/l, MAO 2,5 g/l, x_N = norbornene ratio in feed, X_N = norbornene ratio in polymer, T_g = glass temperature, T_m = melting point, n.d. = not detected.

Catalyst	x_N	X_N	Activity [kg_{Pol}/mol_{Zr} h]	M_W [g/mol]	T_g (T_m) [°C]
meso -[$Me_2Si(Ind)_2$]$ZrCl_2$	0	0	2778	4400	(108)
	0.31	0.096	654	12600	(86)
	0.49	0.170	260	200000	2 (118)
	0.70	0.299	27	222000	77
meso -[$En(Ind)_2$]$ZrCl_2$	0.40	0.41	1971	221000	(102)
	0.49	0.57	688	210000	2 (65)
	0.90	0.253	180	245000	51
	0.98	0.387	7	81400	n. d.
meso -[$Me_2Si(IndH_4)_2$]$ZrCl_2$	0.45	0.068	1356	107000	(99)
	0.71	0.155	992	66000	-2 (58)
	0.89	0.331	290	70000	115

The activities of the catalyst systems [$Me_2Si(Ind)(Flu)$]$ZrCl_2$/MAO, *meso*-[$Me_2Si(Ind)_2$]$ZrCl_2$ /MAO, *meso*-[$En(Ind)_2$]$ZrCl_2$/MAO and *meso*-[$Me_2Si(IndH_4)_2$]$ZrCl_2$/MAO and the molar masses of the obtained polymers are low. The formation of norbornene block sequences is remarkable considering the generally poor incorporation of norbornene by these systems. Multimodal molar mass distributions are found for the products of [$Me_2Si(Ind)(Flu)$]ZrCl, meso-[$Me_2Si(Ind)_2$]$ZrCl_2$ and meso-[$Me_2Si(IndH_4)_2$]$ZrCl_2$.

The investigation of the copolymer's microstructure and the determination of the insertion mechanism, both by means of ^{13}C NMR spectroscopy studies, is of special importance. A complete assignment of the resonances for isolated and alternating sequences in ethene-norbornene copolymers was accomplished (Figure 3, Table 4)[24].

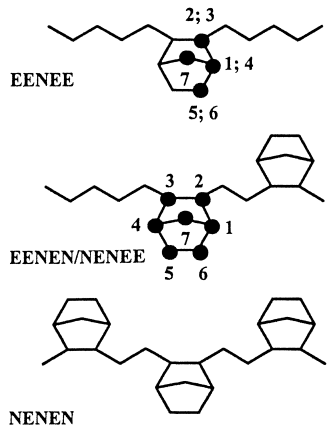

Fig. 3: Selected pentads of ethene-norbornene copolymers and indication of the carbon atoms.

Table 4. Chemical shift of the norbornene carbon atoms and pentads of the ethene block and alternating ethene-norbornene copolymers synthesized by [Me_2C(3-*tert*-BuCp)(Flu)] $ZrCl_2$/MAO.

$^{13}C\delta$ (ppm)	Carbon (see Fig. 3)	Sequences
48.05	C2, C3	mm NENEN + 0.5 m EENEN/NENEE = 0.5 m ENEN/NENE
47.35	C2, C3	EENEE + 0.5 m EENEN/NENEE = 0.5 EENE/ENEE
42.37	C1, C4	mm NENEN
42.20	C1, C4	0.5 m EENEN/NENEE
41.89	C1, C4	EENEE + 0.5 m EENEN/NENEE = 0.5 EENE/ENEE
33.32	C7	mm NENEN
33.22	C7	m NENEE/EENEN
33.15	C7	EENEE

The signals of the several carbon atoms in the ^{13}C NMR spectra are assigned on a triad level basis, partly also at tetrad and pentad level by comparison of the experimental data and the distribution of n-ads calculated with parameters representing an alternating mechanism. The microstructure of alternating ethene-norbornene copolymers is illustrated in Figure 4.

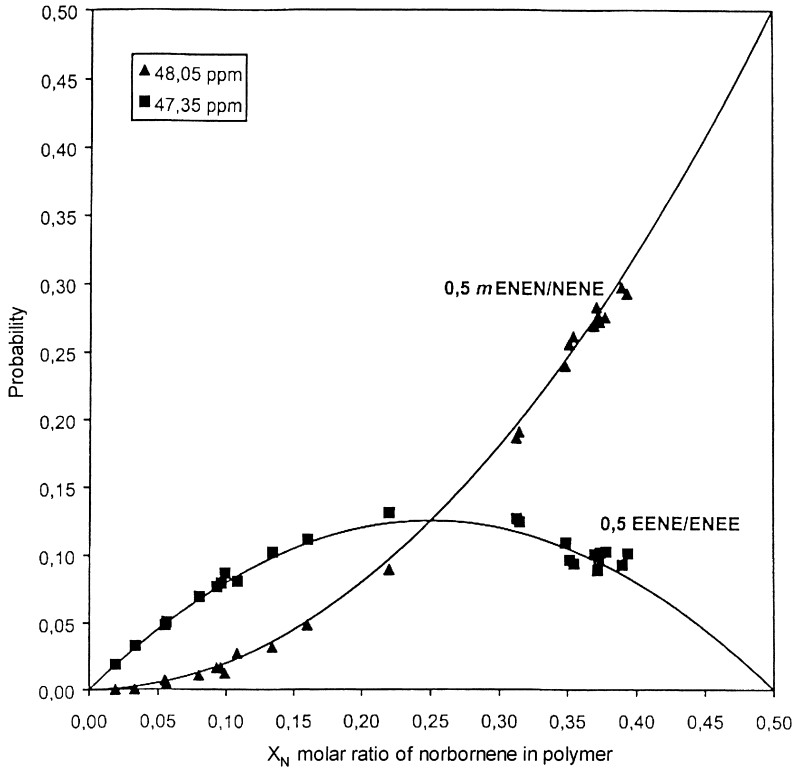

Fig. 4: Copolymerisation of ethene/norbornene in toluene at 30°C by [Me_2C(3-tert-BuCp)(Flu)]$ZrCl_2$/MAO. Comparison of the experimental measured tetrads of the ^{13}C NMR spectra with calculated lines by an alternating model (lines) (see Table 4).

Statistically distributed ethene-norbornene copolymers can be produced by application of the C_s-symmetric metallocenes [Me_2C(Cp)(Flu)]$ZrCl_2$/MAO and [Me_2Si(Cp)(Flu)]$ZrCl_2$/MAO.

Microstructure analysis of the these copolymers revealed norbornene diblocks as well as isolated and alternating sequences. The ^{13}C NMR resonance signal assignments of norbornene diblock sequences have been achieved by comparison with signals observed for a reference sample. This reference system compared alternating copolymers and the model compounds norbornene hydrodi- and –trimers with *rac*- and *meso*-bonded norbornene units.

With respect to [Me_2C(3-*tert*-BuCp)(Flu)]$ZrCl_2$ and [Me_3PhPen(Flu)]$ZrCl_2$ the C_1-symmetric catalyst [Me_2C(3-MeCp)(Flu)]$ZrCl_2$ incorporates norbornene slightly better. Exclusively isolated and alternating norbornene sequences but no norbornene blocks are formed by [Me_2C(3-tert-BuCp)(Flu)]$ZrCl_2$. Polymers containing more than 47 mol% of norbornene, as produced by [Me_2C(3-MeCp)(Flu)]$ZrCl_2$, feature norbornene blocks. At x_N = 0.998 norbornene in the feed copolymers reach norbornene contents of up to 60 mol%. The molar masses of the copolymers produced by [Me_2C(3-*tert*-BuCp)(Flu)]$ZrCl_2$ are significantly lower than average values in this study**.** The alternating microstructure leads to melting points in a range from 240 to 273 °C with 0.40 < X_N < 0.47. At even higher values for X_N, the crystallinity is disturbed by norbornene blocks. In comparison, copolymers which are produced by [Me_2C(3-^{t}BuCp)(Flu)]$ZrCl_2$/MAO show melting points up to 320 °C at 50 mol% norbornene in the polymer.

The mechanism by which ethene-norbornene copolymerisation proceeds depends on the employed metallocene. While a chain migratory insertion with both coordination sites is implied by the derived parameter set r_E^A = 3.08, r_N^A = 0, r_E^B = 500 and r_N^B = 0 for the *tert*-butyl substituted system [Me_2C(3-*tert*-BuCp)(Flu)]$ZrCl_2$ at 30 °C, monomers insert only on one site in case of the methyl substituted catalyst at low norbornene excesses, i.e. x_N < 0.93 and X_N < 0.46, according to the parameters r_E = 3.3 and r_N = 0.001. At even higher norbornene ratios in the feed, e.g. 0.93< x_N < 0.98, norbornene blocks are formed which can be explained by a change in the mechanism. The insertion mechanism of the copolymerisation proceeds under control of the penultimate monomer unit in case of the C_S-symmetric metallocenes [Me_2C(Cp)(Flu)]$ZrCl_2$ and [Me_2Si(Cp)(Flu)]$ZrCl_2$, i.e. it can be described by a 2nd order Markovian model. Ethene is inserted three times faster than norbornene. No higher blocks than diblocks are formed, in agreement with the parameters calculated for [Me_2C(Cp)(Flu)]$ZrCl_2$: r_{EE} = 2.40, r_{NE} = 4.34, r_{EN} = 0.03 and r_{NN} = 0.00. This result easily explains the maximum X_N = 0.66 referring to a feed ratio of x_N = 0.98.

Of all investigated *meso*-compounds only *meso*-[En$(Ind)_2$]$ZrCl_2$ forms monomodal molar mass distributions as expected for a single site catalyst. The copolymerisation parameters of the 1st order Markovian model are calculated to r_E = 18.1 and r_N = 0.007. We conclude that, compared to other systems, norbornene is inserted poorly.

Ethene-DMON Copolymers

Ethene was copolymerised with dimethanooctahydronaphthaline (DMON) by $[Me_2C(3\text{-}MeCp)(Flu)]ZrCl_2$ and $[Me_2C(3\text{-}\textit{tert}\text{-}BuCp)(Flu)]ZrCl_2$ to form high melting alternating copolymers at low activities (Table 5).

Table 5. Copolymerisation of ethene-DMON by $[Me_2C(3\text{-}MeCp)(Flu)]ZrCl_2$/MAO (I) and $[Me_2C(3\text{-}\textit{tert}\text{-}BuCp)(Flu)]ZrCl_2$/MAO (II) catalyst at 30°C, c(E) = 0.018 mol/l, X_{DMON} = 0.995, c(Zr) = 100 µmol/l, VR = 50 ml, c(MAO) = 4 g/l, solvent: toluene.

Catalyst	t_{Pol} [h]	Activity [kg_{Pol}/mol_{Zr} h]	X_{DMON}	M_W [g/mol]	T_g (T_m) [°C]
I	8	1.3	0.40	530000	134 (377)
II	24	0.4	0.44	580000	143 (380)

The copolymers obtained are semi-crystalline, showing an alternating structure and melting points up to 380 °C. This means a 60 °C increase with respect to previously discussed ethene-norbornene copolymers.

Ethene-Branched Olefin Copolymers

The copolymerisation of ethene was investigated with other sterically hindered olefins such as 4-methyl-1-pentene or 3-methyl-1-butene as well. Table 6 gives details on the polymerisation conditions, activities and selected polymer properties.

Table 6. Copolymerization of ethene-(4-methyl-pentene) (4MP) by different metallocene/MAO catalysts at 30 °C, c(E) = 0,02-0,237 mol/l, c(MAO) = 2,5 g/l, c(Zr) = 5-50 µmol/l, solvent: toluene, a = amorphous.

Catalyst	x_{4MP}	X_{4MP}	Activity [kg_{Pol}/mol_{Zr} h]	M_W [g/mol]	T_g (T_m) [°C]
$[Me_2C(3\text{-}tert\text{-}BuCp)(Flu)]ZrCl_2$	0.20	0.006	20700	270000	(119)
	0.39	0.025	7160	163000	(107)
	0.58	0.077	4350	68000	-26 (91)
	0.79	0.177	2210	78000	-35 (60)
	0.89	0.408	3820	79000	-25 (a)
	0.98	0.976	556	20900	(180)
$[Me_2C(3\text{-}MeCp)(Flu)]ZrCl_2$	0.59	0.12	9450	85000	- 39 (57)
	0.77	0.226	4640	95000	-45 (a)
	0.90	0.412	2620	38000	-33 (a)
	0.95	0.494	2260	37000	-27 (a)
	0.98	0.629	1870	31000	-15 (a)
$[Me_2Si(Ind)(Flu)]ZrCl_2$	0.60	0.080	1550	98000	-36 (63)
	0.72	0.203	4040	73000	-46 (a)
	0.9	0.325	5690	59000	-40 (a)
	0.95	0.401	4260	36000	-35 (a)
	0.98	0.489	1420	35000	-28 (a)

The copolymerisation of ethene and dimethanooctahydronaphthalene (DMON) by $[Me_2C(3\text{-}tert\text{-}BuCp)(Flu)]ZrCl_2$/MAO and $[Me_2C(3\text{-}MeCp)(Flu)]ZrCl_2$/MAO results in semi-crystalline alternating copolymers with melting points around 380°C, as discussed in the previous paragraph. Ethene-(4-methylpentene) copolymers produced by $[Me_2C(3\text{-}MeCp)(Flu)]ZrCl_2$/MAO display a tendency to alternating sequences. Their composition may reach up to X_N = 0.60 4-methylpentene at x_N = 0.98 in the feed. Copolymers produced by $[Me_2Si(Ind)(Flu)]ZrCl_2$/MAO are even more alternating. If the polymerisation temperature is decreased, the fraction of alternating sequences in the copolymers produced by $[Me_2Si(Ind)(Flu)]ZrCl_2$ rises to 76% of X_{4MP} = 0.44, the total comonomer incorporation,

yielding an over all degree of alternation of 33%. In contrast to the foregoing ethene-norbornene copolymers these copolymers are not crystalline, probably due to a low stereoselectivity of this catalyst. Poly-(4-methyl-pentenes) prepared with this metallocene catalyst also show a comparingly low melting point ranging from 180 to 220°C in dependence of the polymerisation temperature and the part of alternating structures, due to low stereoregularity.

Surprisingly, ethene-(4-methylpentene) copolymers produced by [Me_2C(3-*tert*-BuCp)(Flu)]$ZrCl_2$/MAO are blocky and have glass transition temperatures which are higher than those of alternating copolymers with comparable comonomer contents. Polymers with a very high 4-methylpentene content show melting points around 200°C.

Ethene-(4-methylpentene) copolymerisation with [Me_2C(3-*tert*BuCp)(Flu)]$ZrCl_2$ is described best by a 1st order Markovian statistic with $r_E = 25.73$ and $r_{4MP} = 0.27$. The product of the parameters $r_E \cdot r_{4MP} = 6.9$ indicates a tendency to form blocky copolymers. On the other hand, the copolymers produced by [Me_2C(3-MeCp)(Flu)]$ZrCl_2$ are corresponding to an alternating mechanism on both sites of the catalyst with $r_E^A = 4.92$, $r_{4MP}^A = 0.20$, $r_E^B = 30$ and $r_{4MP}^B = 0.01$. These values propose the insertion of ethene to be more likely on the catalyst's substituted site B. The probability of 4-methylpentene block formation even at high monomer contents is quite low. The copolymerisation of ethene with 4-methylpentene by [Me_2Si(Ind)(Flu)]$ZrCl_2$ is considered to proceed via an alternating mechanism with $r_E^A = 6.85$, $r_{4MP}^A = 0.010$, $r_E^B = 77.5$ and $r_{4MP}^B = 0.003$. In this case, statistics describe the insertion of ethene to be even more favoured on site B and the formation of comonomer blocks is less probable.

The tendency to form alternating copolymers by [Me_2C(3-MeCp)(Flu)]$ZrCl_2$ and [Me_2Si(Ind)(Flu)]$ZrCl_2$ is also shown for the ethene-(3-methylbutene) copolymerisation. At maximum contents of $x_{3MB} = 0.98$ in the feed incorporation values of up to $X_{3MB} = 0.36$ are observed. With respect to the ethene-(4-methylpentene) copolymerisation, the alkyl branch in position 3 gives rise to decrease of the comonomer incorporation and formation of comonomer blocks.

During the copolymerisation of ethene with 3-methylbutene, ethene inserts 88 times faster than 3-methylbutene in the case of [Me_2C(3-MeCp)(Flu)]$ZrCl_2$ with its parameters calculated

to r_E = 88.0 and r_{3MB} = 0.001 and still 20 times faster in the case of [Me_2Si(Ind)(Flu)]$ZrCl_2$ featuring parameters of r_E = 20.74 and r_{3MB} = 0.003.

References

1. W. Kaminsky, *Macromol. Chem. Phys*. **197**, 3907 (1996)
2. M. Arndt, W. Kaminsky, *Macromol. Symp.* **95**, 167 (1995)
3. W. Kaminsky, A. Bark, R. Steiger, *J. Mol. Catal.* **74**, 109 (1992)
4. W. Kaminsky, R. Steiger, *Polyhedron* **7**, 2375 (1988).
5. W. Kaminsky, A. Bark, M. Arndt, *Makromol. Chem., Macromol. Symp.* **47**, 83 (1991)
6. N. Herfert, P. Montag, G. Fink, *Makromol. Chem.* **94**, 3167 (1993)
7. J. Boor, *Ziegler-Natta Catalysis and Polymerizations*, AP press, New York, **1979**.
8. W. Kaminsky, M. Arndt, *Adv. Polym. Sci.* **127**, 143 (1997)
9. T.J. Demming, B.M. Novak, *Macromolecules* **26**, 7089 (1993)
10. B.L. Goodall, D.A. Barnes, G.M. Benedict, L.H. McIntosh, L.F. Rhodes, *Polym. Mater. Sci. Eng.* **76**, 56 (1997)
11. C. Mehler, W. Risse, *Makromol. Chem. Rapid Commun.* **12**, 255 (1991)
12. W. Heitz, T.F.A. Haselwander, *Macromol. Rapid Commun.* **18**, 689 (1997)
13. K.J. Ivin, *Olefin Metathesis*, Academic Press, New York, **1983**.
14. W. Kaminsky, A. Bark, M. Arndt, *Makromol. Chem. Macromol. Symp.* **47** ,83 (1991)
15. H. Cherdron, M.-J. Brekner, F. Osan, *Angew. Makromol. Chem.* **223**, 121 (1994)
16. W. Kaminsky, M. Arndt-Rosenau, in *Metallocene-based Polyolefins*, J. Scheirs, W. Kaminsky (eds.), Wiley Series in Polymer Science, Chichester, Vol. 2, p. 91, **2000**.
17. W. Kaminsky, A. Noll, *Polym. Bull.* **31**, 175 (1993)
18. W. Kaminsky, R. Spiehl, *Makromol. Chem.* **190**, 515 (1989)
19. S. Collins, W.M. Kelly, *Macromolecules* **25**, 233 (1992)
20. W. Kaminsky, R. Engehausen, J. Kopf, *Angew. Chem.* **107,** 2469 (1995); *Angew. Chem., Int. Ed. Engl.* **34**, 2273 (1995)
21. H.G. Alt, M. Jung, G. Kehr, *J. Organomet. Chem.* **562**, 229 (1998)
22. W. Kaminsky, R. Werner, in: *Metalorganic Catalysts for Synthesis and Polymerization*, W. Kaminsky (ed.), Springer Heidelberg, p. 170, **1999**.
23. W. Kaminsky, A.M. Schauwienold, F. Freidanck, *J. Molecul. Cat. A. Chemical* **112**, 37 (1996)
24. I. Beulich, Thesis, University of Hamburg, **1999**.