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Hydrooligomerization of cycloolefins –a view of the microstructure of polynorbornene

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Abstract

Hydrooligomerizations of norbornene were carried out using C_2, C_s and C_{2v} symmetric zirconocenes with methylaluminoxane as catalysts. The structures of the hydrodimers and -trimers were investigated and correlated to the symmetry of the metallocene. The polymerization of norbornene is shown to proceed by *cis–exo* insertion. The mechanisms of polymerization and stereocontrol are closely related to the ones observed in the polymerization of α-olefins. Thus the C_2 symmetric metallocene features erythrodiisotactic structures, while erythrodisyndiotactic products are observed in case of the C_s symmetric one. This is caused by enantiomorphic site control, while stereospecificity in the hydrooligomerization using Cp_2ZrCl_2/MAO is determined by chain end control mechanism.

1. Introduction

Homogeneous Ziegler–Natta catalysts based on Group IV metallocenes and methylaluminoxanes (MAO) are known to be capable of polymerizing cyclic olefins like cyclobutene, bicyclo [3.2.0.]hept-6-ene, cyclopentene, norbornene and dimethanooctahydronaphthalene [1–13]. The polymers decompose in air at high temperatures before they melt and are insoluble in organic solvents. These features complicate the examination of the polymer microstructure.

To determine the stereochemistry of the polymers it is necessary to produce model compounds in the form of oligomers offering the opportunity to apply high resolution NMR techniques. One way of getting oligomers in Ziegler–Natta polymerization is the addition of hydrogen to the reaction mixture thereby forming hydrooligomers [8,10,11,14–19].

This paper deals with the structure of norbornene hydrooligomers produced by using three different types of zirconocenes. The zirconocenes used were bis(cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2), racemic dimethylsilyl-bis(1,1'-indenyl)zirconium dichloride (rac-[$Me_2Si(Ind)_2$]$ZrCl_2$) and diphenylmethylidene- (cyclopentadienyl) (9-fluorenyl) zirconium dichloride ([$Ph_2C(Flu)(Cp)$]$ZrCl_2$). Cp_2ZrCl_2/MAO affords atactic poly(α-olefins) whereas rac-[$Me_2Si(Ind)_2$]$ZrCl_2$/MAO and [$Ph_2C(Flu)(Cp)$]$ZrCl_2$/MAO produce isotactic and syndiotactic polymers, respectively [20].

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2. Experimental part

2.1. Reagents

Cp_2ZrCl_2 [21] and rac-[$Me_2Si(Ind)_2$]$ZrCl_2$ [22] were prepared according to the literature, [$Ph_2C(Flu)(Cp)$]$ZrCl_2$ was a gift of the Hoechst AG. Toluene was dried over Na/K alloy. A solution of norbornene (Merck) in toluene was dried by distillation from triisobutylaluminium. The concentration of norbornene was determined iodometrically to be 5.88 mol/l. MAO (Schering) and H_2 (Linde) were commercial products.

2.2. Hydrooligomerization

In a glass autoclave 50 ml of the norbornene solution were diluted with 100 ml of toluene and saturated with H_2 at the reaction temperature and 0.3 to 0.5 bar. After that a solution of 3.48 mmol MAO and 210^{-3} mmol metallocene is syringed into the reaction mixture through a septum. The hydrooligomerization was quenched after 48 h, the products were isolated by Spaltrohr distillation.

2.3. NMR analysis

^{13}C-and ^{1}H-NMR measurements were carried out on a Bruker AC 100 spectrometer at 298 K in $CDCl_3$.

3. Results and discussion

^{13}C-NMR measurements on the hydrotrimers of norbornene obtained with all three catalysts indicate 2,3 disubstitution at the configurational base unit.

From a comparison of the chemical shift data (^{13}C-and ^{1}H-NMR) of the hydrotrimers with that of methyl-and dimethylnorbornanes [23–25] an exo-(exo,exo)-exo conformation is deduced [1]. From complexation to transition metals [26] and

insertions into M–C bonds [27–34] the exo positions are known to be more reactive than the endo positions. This is explained in terms of electronic and steric effects [8,35].
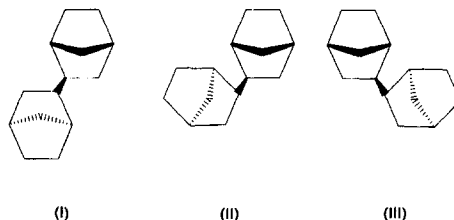
Cis–exo insertion features erythroditactic polymers. A look at the hydrodimers assuming cis–exo insertion should allow conclusions about the stereospecificity of the first insertions. From the hydrotrimers the erythroditacticity may be deduced. While a 2,3-bis(exo) disubstituted norbornane features R,S(S,R) configuration at the configurational base unit if the substituents are identical the erythroditacticities are represented by the configurations in Table 1.

In case of a catalyst producing erythrodiisotactic polynorbornene the meso (R,S) hydrodimer is expected to be generated while a catalyst forming erythrodisyndiotactic polymer should yield the racemic (R,R/S,S) hydrodimer. A catalyst working not stereospecific will form equal amounts of both diastereomeric hydrodimers (Scheme 1).

Investigations on the hydrodimers showed all three catalysts to form both diastereomers. Dis-

Table 1
Configuration of the linkages and pseudoasymmetric centers in ditactic polymers

	Configuration of the centers and linkages
erythrodiisotactic	–(RS)(RS)(RS)(RS)(RS)(RS)(RS)(RS)– m m m m m m m
erythrodisyndiotactic	–(RS)(SR)(RS)(SR)(RS)(SR)(RS)(SR)– r r r r r r r
erythroatactic	–(RS)(RS)(SR)(SR)(SR)(RS)(RS)(SR)– m r m m r m r

Scheme 1. Structures of the norbornene hydrodimers. (I) meso dimer (R,S); (II) (R,R)-enantiomer of the racemic dimer; (III) (S,S)-enantiomer of the racemic dimer.

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[1] The complete NMR analysis is published in [8].

Table 2
Distribution of the hydrodimers of norbornene produced by using different metallocene precursors

T	Cp_2ZrCl_2		$[Ph_2C(Flu)(Cp)]ZrCl_2$		$rac-[Me_2Si(Ind)]ZrCl_2$	
	meso	rac	meso	rac	meso	rac
(°C)	(%)	(%)	(%)	(%)	(%)	(%)
−30	79	21	–	–	78	22
30	65	35	53	47	58	42
60	–	–	79.5	20.5	63	37

crimination of the diastereomers is possible separating the racemate by gas chromatography on a chiral stationary phase, while the meso dimer causes one peak (Table 2).

^{13}C-NMR chemical shift assignment is achieved using one and two dimensional NMR spectroscopy in combination with model compounds (Scheme 2, Table 3).

Dimerization catalyzed by the achiral Cp_2ZrCl_2 favours the formation of the meso dimer indicating 'chain end control' [36–40] by the α-carbon atom of the first inserted monomer unit. The difference of the free energies of activation $\Delta G^{\neq}_{meso} - \Delta G^{\neq}_{rac}$ calculated from the meso/rac rate is 1.5 kJ/mol at 30°C and 2.7 kJ/mol at −30°C. Comparison with values for the polymerization of propene (0.63 kJ/mol at 0°C [41]) shows the stronger influence of an asymmetric carbon atom in α-position compared to one in β-position.

The production of both diastereomeric hydrodimers using C_2 or C_s symmetric metallocenes is explained by a partially aspecific first insertion into the Zr–H bond. This behaviour of metallocene based catalysts was proven by Pino et al. [15,16] performing deuterooligomerizations of 1-pentene using enantiomerically pure catalyst precursors.

Assuming the same mechanism as in the polymerization of α-olefins, independent of the relative topicity the stereogenic C_s-symmetric metallocenes should feature erythrodisyndiotactic polymers, whereas C_2-symmetric metallocenes are expected to form erythrodiisotactic products[2] (Scheme 3 and Scheme 4).
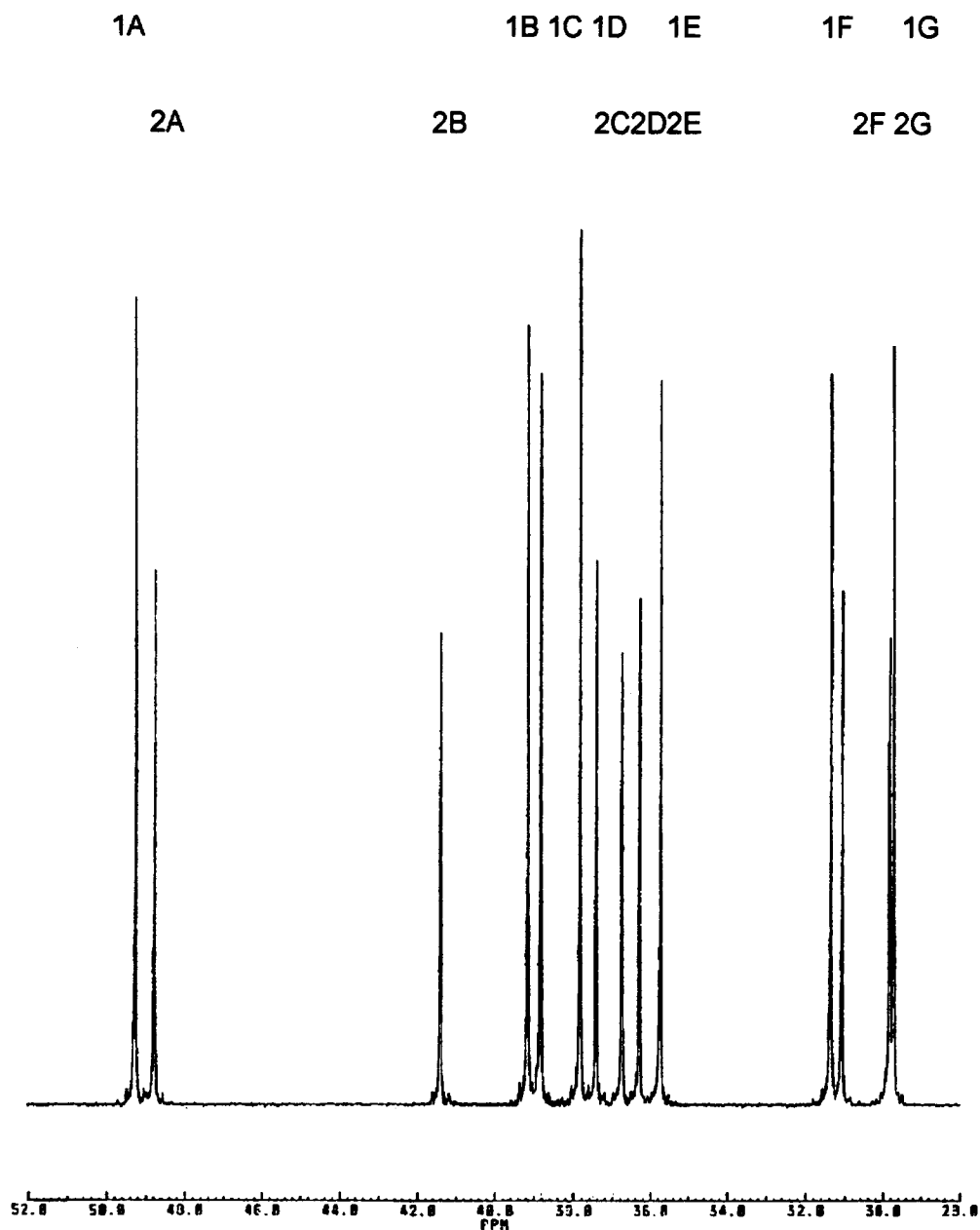
A single inversion of the relative topicity causes a meso (racemic) linkage in the product of the C_s-(C_2-) symmetric catalyst (Scheme 5 and Scheme 6).

Thus the predominant formation of the meso product by the C_s-symmetric metallocene is a consequence of an inversion of the relative topicity from first to second insertion. Based on the results of Pino et al. [15–17] and Corradini et al. [42–46] this may be interpreted in terms of different mechanisms of stereocontrol working for the first and consecutive insertions. While direct control of stereospecificity by the ligand framework determines the orientation of the olefin for the first insertion (direct control) [15–17], the growing chain controls the stereochemistry of further insertion (indirect control) [42–46]. The same effect was proven by Longo et al. to work in the polymerization of propene using this type of catalyst [47] (Scheme 7 and Scheme 8).

Using the dimers and 2,3-exo,exo-dimethylnorbornane as model compounds in combination with one and two-dimensional NMR spectroscopy

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[2] We are well aware of the fact that we did not use the correct CIP nomenclature at the monomer units (RS) for two reasons: (1) if the polymer chain is still linked to the transition metal the transition metal has the highest priority, (2) the polymers are pseudochiral. Nevertheless we use it to show how the stereochemistry of the insertion is influenced by the symmetry of the metallocene and how the stereochemistry of the insertion determines the microstructure of the polymers. The nomenclature is derived from the hydrooligomers obtained if P = H and the growing chain hydrogenolysed from the transition metal.

1A   1B 1C 1D   1E   1F   1G

2A   2B   2C2D2E   2F 2G

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52.0    50.0    40.0    46.0    44.0    42.0    40.0    39.0    36.0    54.0    32.0    30.0    29.0
                                        PPM
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Scheme 2. ^{13}C-NMR spectrum of a mixture of the diastereomeric hydrodimers (1 = meso, 2 = racemic) of norbornene.

chemical shift assignment for the hydrotrimers is possible (Table 4 and Table 5).

The investigation of the hydrotrimers by ^{13}C NMR spectroscopy showed tactic products to be dominant in case of the bridged metallocene catalysts accompanied by the meso,rac-(rac,meso-) linked hydrotrimer (Scheme 9, Table 6).

From the formation of the meso,meso-(rac, rac-) trimer by the C_2-(C_s-) symmetric metallo-

cene a erythrodiisotactic (erythrodisyndiotactic) microstructure of the polymer is deduced, in agreement with the theory.

While rac-[Me$_2$Si(Ind)$_2$]ZrCl$_2$ produces only the meso,meso-and meso,racemic dimer indicating high stereospecificity on consecutive insertions, small amounts of the meso,meso trimer produced by [Ph$_2$C(Flu)(Cp)]ZrCl$_2$ are the result of double inversions of the relative topicity

Table 3
^{13}C-NMR chemical shift assignment of the norbornene hydrodimers (all chemical shifts in ppm relative to TMS)

| meso-Dimer			rac-Dimer		
Signal	Chem. shift	Assignment	Signal	Chem. shift	Assignment
1a	48.74	C2	2a	48.25	C2
1b	38.53	C1	2b	40.81	C1
1c	38.23	C3	2c	36.77	C4
1d	37.19	C4	2d	36.14	C3
1e	35.07	C7	2e	35.64	C7
1f	30.71	C6	2f	30.41	C6
1g	29.05	C5	2g	29.16	C5
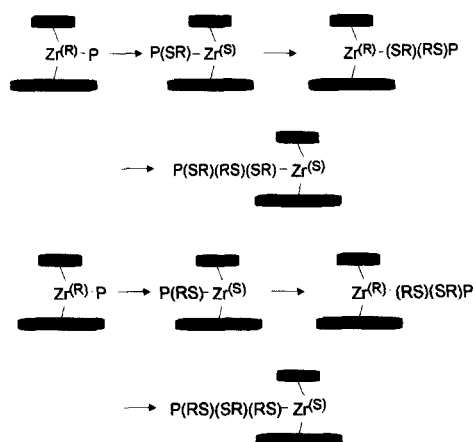
Scheme 3. Stereochemistry during the polymerization of a prochiral cycloolefin using a C_s symmetric metallocene as catalyst.
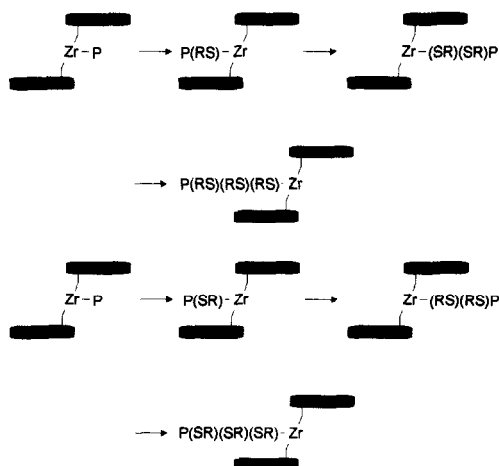

Scheme 4. Stereochemistry during the polymerization of a prochiral cycloolefin using a C_2 symmetric metallocene as catalyst.

of the insertion attributed to stronger impact of the ligand framework on the orientation of the monomer (Scheme 10).

By using Cp_2ZrCl_2 as a consequence of chain end control no rac,rac dimer is produced. Calculation of the difference of the free energies of activation between a meso linkage following a meso sequence and a racemic linkage following a
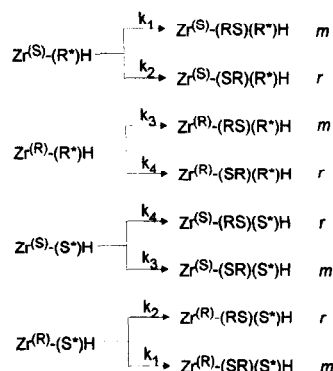

Scheme 5. Kinetic scheme of the insertion of a prochiral cycloolefin into the Zr–cycloalkanyl bond of a C_2-symmetric metallocenium ion derived from a C_2-symmetric metallocene. Changes of the topicity of insertion cause the formation of racemic dimer (k_2,k_4), while conservation of the topicity results in the formation of the meso dimer (k_1,k_3).
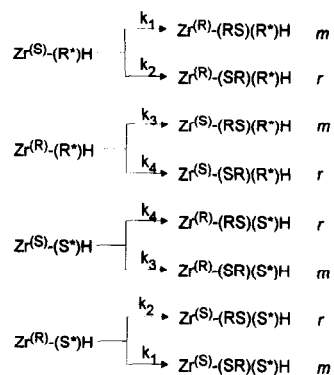
Scheme 6. Kinetic scheme of the insertion of a prochiral cycloolefin into the Zr–cycloalkanyl bond of a C_1-symmetric metallocenium ion derived from a C_s-symmetric metallocene. Changes of the topicity of insertion cause the formation of meso dimer (k_1,k_3) while conservation of the topicity results in the formation of the racemic dimer (k_2,k_4).
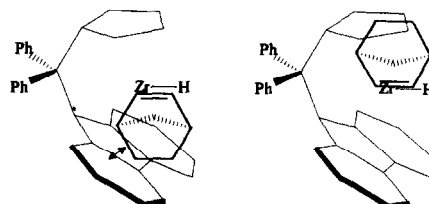
Scheme 7. Insertion into a Zr–H bond; nonbonding interactions between the monomer an the ligand framework determine the topicity of the reaction (direct control of stereospecificity).
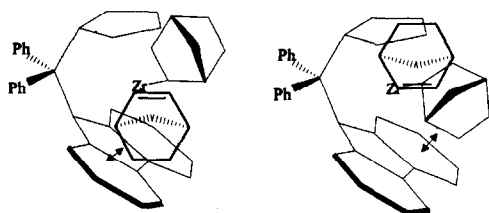
Scheme 8. Insertion into a Zr–(exo-2S-norbornyl) bond; nonbonding interactions between growing polymer chain and monomer determine the topicity of the reaction (indirect control of stereospecificity).

Table 4
Chemical shift assignment of the tactic hydrotrimers of norbornene (all chemical shifts in ppm relative to TMS). The indices a and b correspond to the exo-2-norbornyl groups
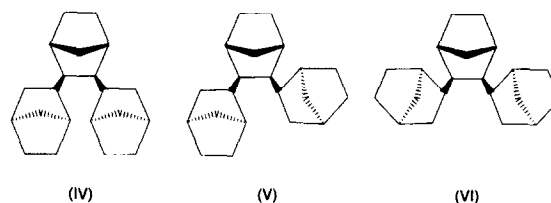
meso,meso-Trimer			rac,rac-Trimer		
Chem. shift	APT	Assignment	Chem. shift	APT	Assignment
53.37	CH	C2,C3	54.71	CH	C2,C3
43.53	CH	C2a,C2b	42.59	CH	C2a,C2b
41.67	CH	C1a,C1b	41.64	CH$_2$	C3a,C3b
39.03	CH	C1,C4	40.29	CH	C1,C4
37.84	CH$_2$	C3a,C3b	40.09	CH	C1a,C1b
36.75	CH	C4a,C4b	36.86	CH	C4a,C4b
36.00	CH$_2$	C7a,C7b	36.00	CH$_2$	C7a,C7b
33.82	CH$_2$	C7	34.30	CH$_2$	C7
30.91	CH$_2$	C6a,C6b	31.13	CH$_2$	C6a,C6b
30.68	CH$_2$	C5a,C5b	30.86	CH$_2$	C5a,C5b
28.50	CH$_2$	C5,C6	29.46	CH$_2$	C5,C6

Table 5
Chemical shift assignment of the atactic hydrotrimer of norbornene (all chemical shifts in ppm relative to TMS). The indices a (meso) and b (rac) correspond to the exo-2-norbornyl groups

Chem. shift	APT	Assignment	Chem. shift	APT	Assignment
55.01	CH	C3	36.66	CH	C4a
53.28	CH	C2	36.43	CH$_2$	C7b
42.81	CH	C2a	35.74	CH$_2$	C7a
42.10	CH$_2$	C3b	34.12	CH2	C7
41.91	CH	C2b	31.34	CH$_2$	C6b
41.87	CH	C1a	31.08	CH$_2$	C6a
39.62	CH	C4	30.91	CH$_2$	C5b
39.54	CH	C1	30.38	CH$_2$	C5a
38.79	CH	C1b	29.26	CH$_2$	C5
38.37	CH$_2$	C3a	28.42	CH$_2$	C6
36.78	CH	C4b			

meso sequence or a meso linkage following a racemic sequence respectively $\Delta G^{\neq}_{\text{meso,meso}} - \Delta G^{\neq}_{\text{meso,rac}}$ shows that alternating sequences are favoured over diisotactic ones
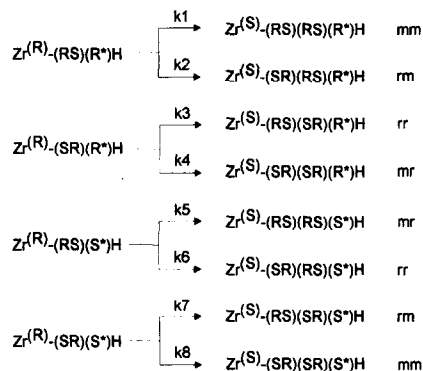

Scheme 9. Structures of the hydrotrimers of norbornene. (IV) meso,meso-trimer; (V) meso,rac-trimer; (VI) rac,rac-trimer.

Table 6
Distribution of the hydrotrimers of norbornene produced by using different metallocene precursors

T	rac-[Me$_2$Si (Ind)$_2$]ZrCl$_2$			[Ph$_2$C(Flu) (Cp)]ZrCl$_2$			Cp$_2$ZrCl$_2$		
(°C)	mm (%)	mr (%)	rr (%)	mm (%)	mr (%)	rr (%)	mm (%)	mr (%)	rr (%)
−30	66	34	0	–	–	–	28	72	0
30	38	62	0	7.5	15	77.5	23	77	0
60	71	29	0	9	36.5	54.5	–	–	–

Scheme 10. Kinetic scheme of the third insertion of a prochiral cycloolefin into the Zr–cycloalkanyl bond of a C_1-symmetric metallocenium ion derived from a C_s-symmetric metallocene.

(30°C: −1.96 kJ/mol; −30°C: −1.43 kJ/mol). This behaviour results from the influence of the penultimate monomer unit on the insertion reaction. The chiral center in β-position dominates the influence of the chiral center in the α-position.

4. Conclusions

The hydrooligomerization of cyclic olefins is a powerful tool in the investigation of the polymerization mechanism and features insights into the microstructure of the polymers.

Recently cyclopentene was shown to homopolymerize via cis-and trans-1,3 insertion [8,10,11], while cis-1,2 insertion is observed in copolymers with ethene [1,8]. No blocks of cyclic units are observed up to molar ratios of cyclopentene/ethene = 150 [8,48]. These features indicate the extreme steric effects in the homopolymerization of cyclic monomers.

In contrast 1,3 insertion is unlikely in the polymerization of norbornene since a zirconium–(2-norbornyl) complex is not capable of β-hydrogen elimination towards the bridgehead atom forming an anti-Bredt olefin [49]. Thus in homo- and copolymerizations a cis–exo insertion is observed. The copolymers of norbornene and ethene show blocks of cyclic units expressing the higher reactivity of norbornene.

In case of the norbornene hydrooligomerization and polymerization the mechanisms of polymerization and control of the microstructure are closely related to the ones observed for α-olefins. Enantiomorphic site control is assumed to be responsible for the erythrodiisotactic structure if C_2 symmetric metallocene is used as well as for the erythrodisyndiotactic structure featured by the C_s symmetric metallocene. Chain end control by the rigid monomer units of the growing polymer chain controls the orientation of the incoming monomer in case of the achiral C_{2v} symmetric metallocene.

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