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Stereospecific propene polymerization with rac-[1,2-bis(η^5-(9-fluorenyl))-1-phenylethane]zirconium dichloride/methylalumoxane

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Summary

Methylalumoxane (MAO)-activated rac-[1,2-bis(η^5-(9-fluorenyl))-1-phenylethane]zirconium dichloride (1) was used for propene polymerization at 30, 50, and 70°C and constant monomer concentration. The polypropene products are isotactic with stereoregularities depending on the polymerization temperature. The pentad distributions follow "enantiomorphic site statistics", indicating stereocontrol being conducted by the chiral catalyst site.

Introduction

Chiral *ansa*-zirconocene complexes have proven to be excellent catalysts for the polymerization of propene, after activation with methylalumoxane (MAO). Most of the metallocenes investigated up to now bear a C_2-symmetry axis (1) and carry two equivalent but unsymmetric cyclopentadienyl groups, like indenyl- or substituted Cp(R)-fragments. Two well known examples of this kind are rac-[1,2-bis(η^5-(1-tetrahydroindenyl))ethane]zirconium dichloride (2) and rac-[1,1-bis((2-methyl-4-*t*-butyl-cyclopentadienyl)zirconium dichloride (3). The stereoselectivity of these and structurally related systems for α-olefin polymerization is defined by the coordination mode of the indenyl- or Cp(R)-moieties which open a chiral cage tight enough for an efficient enantiofacial discrimination of the prochiral propene monomer during insertion (4).

We report here that isospecific propene polymerization can also be achieved at elevated polymerization temperatures (T_p) with rac-[1,2-bis(η^5-(9-fluorenyl))-1-phenylethane]zirconium dichloride which contains two C_2-symmetric fluorenyl groups.

Experimental
Routine ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 250 spectrometer at ambient temperature; chemical shifts are referenced with respect to TMS. ^{13}C NMR spectra of the polymer products were measured in $C_2D_2Cl_4$ at 120°C and analyzed by known methods (1a,3c). Mass spectra were acquired with Finnigan instruments (MAT-711A, modified by AMD Intectra (FD, FAB); Finnigan TSQ70 (EI, FAB), 70eV). Molecular weights and molecular weight distributions of the polymers were determined by gel-permeation chromatography (GPC, Waters 150 Chromatograph, 140 °C in 1,2,4-trichlorobenzene). Elemental analyses: Microanalytical laboratory of the Institute (Carlo Erba, Model 1106).

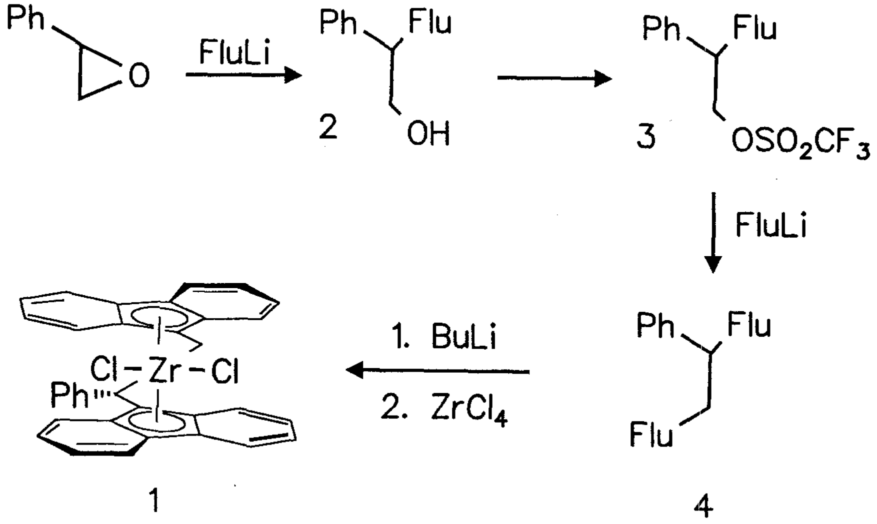
1,2-[Bis(9-fluorenyl)]-1-phenylethane: (4): Trifluoromethanesulfonic acid anhydride (5.73 ml, 34.9 mmol) was added to a solution of alcohol **2** (5) (10 g, 34.9 mmol) and pyridine (2.82 ml, 34.9 mmol) in CH_2Cl_2 (75 ml) at 0°C. The reaction mixture was stirred for 15 min. The organic layer was washed with ice water and dried with Na_2SO_4. Evaporation of the solvent at 0°C gave a slightly yellow oil of the trifluoromethanesulfonate which was dissolved in 75 ml of dioxane at 5°C. Fluorenyllithium (45 mmol) was added to the solution. After stirring overnight at ambient temperature the solvents were evaporated and the solid residue was dissolved in a mixture of H_2O/NH_4Cl and diethyl ether. From the dried ether phase the solvent was destilled off. **4** (5.4 g; 12.4 mmol; 36%) resulted after column chromatography over silica (eluent: toluene/hexane, 2:7) as crystalline solid; mp. 180-181.5 °C. - ^1H NMR ($CDCl_3$): δ = 7.0-7.6 (m, 21H, aromatic H), 4.13 (d, J=4.3Hz, 1H, CH_{Flu2}), 3.89 (ddd, J=11.2, 4.2, 4.3Hz, 1H, CH_{bridge}), 3.69 (dd, J=9.5, 4.2Hz, 1H, CH_{Flu1}); two diastereotopic protons: 2.56 (ddd, J=14.5, 10.8, 4.2Hz, 1H, $CH_{2,bridge}$), 1.81 (ddd, J=14.25, 9.5, 4.2Hz 1H, $CH_{2,bridge}$). - FDMS: 433.9 [M^+]. Anal. Calcd for $C_{34}H_{26}$: C, 93.97; H, 6.03. Found: C, 94.08; H, 6.24.

rac-[1,2-Bis(η^5-(9-fluorenyl))-1-phenylethane]zirconium dichloride (1): To a solution of the ligand precursor **4** (22 mmol) in 50 ml diethyl ether *n*-butyllithium (27.6 ml, 1.6 M in hexane) was added at room temperature. The solvent was removed and the dry dilithio salt was mixed with $ZrCl_4$ (5.12 g, 22 mmol) and 100 ml CH_2Cl_2, which was cooled to -80°C. The suspension was warmed up to room temperature and stirred overnight. LiCl was filtered off and the solvent was evaporated, leaving deep red micro crystalline **1** which was recrystallized from toluene solution at -30°C. **1** (4.7 g; 7.9 mmol; 36 %): - ^1H-NMR ($CDCl_3$): δ = 7.4 - 8.2 (m, 21H, arom. H), 6.53 (dd, J=12.4, 13.1 Hz, 1H, CH_{bridge}), 2 diastereotopic protons: 5.1 (dd, J=14.3, 13.1 Hz, 1H, $CH_{2,bridge}$), 4.65 (dd, J=12.4, 14.3 Hz, 1H, $CH_{2,bridge}$). - FABMS: 594.1 [M^+], 558.7 [M^+-Cl].

Polymerizations: 300 ml toluene were mixed with the desired amount of MAO (solution in toluene; 4.7 weight.% Al; M_w = 900 g mol^{-1}) in a 1l-Büchi-glasautoclave, thermostated at 30, 50 or 70°C, respectively. The system was charged with propene up to the desired concentration (6). The polymerization reaction was started by addition of a calibrated metallocene/toluene solution. Monomer pressure (±50 mbar) and temperature (±0.5 °C) were kept constant. Monomer consumption, pressure and inside temperature were controlled by real time monitoring taking one data set every 2 s. After one hour the polymerization was quenched by addition of 10 ml of methanol. The polymer was quantitatively precipitated by pouring the solution to excess acidified methanol. After thorough washing with methanol/HCl and methanol the product was dried overnight at 70°C.

Results and Discussion

Synthesis of the title complex **1** was accomplished according to a route published by us recently (5). Racemic epoxystyrene undergoes ring-opening with fluorenyllithium (FluLi) in diisopropyl ether. The trifluoromethanesulfonate (**3**) of the corresponding primary alcohol (**2**) was treated with a second equivalent of FluLi to give the ethylene-bridged bisfluorenyl ligand precursor **4**, as depicted in Scheme 1. Deprotonation of **4** with *n*-butyllithium and subsequent reaction with $ZrCl_4$ in CH_2Cl_2 at -78°C afforded the *ansa*-zirconocene dichloride **1** in 36% yield.



Scheme 1. Synthesis of **1**.

1 was used together with MAO (Al/Zr = 2000) for the polymerization of propene at 30, 50 and 70°C under constant monomer concentration (6). A comparison of the polymerization data in Table 1 shows that all of the polymers produced with **1**/MAO are isotactic materials with [mmmm]-pentad contents ranking between 31.2 and 64.1%.

Table 1. Polymerization data of 1/MAO at different temperatures and constant monomer concentration[a].

Entry	T_p[b], °C	t_p[c], s	[Zr][d]	Yield, g	Activity[e]	[mmmm] %	M_w[f]	M_w/M_N
1	30	2720	29.1	1.1	70	64.1	21.2	1.7
2	50	3140	31.1	12.6	650	49.6	18.5	1.4
3	70	1430	31.1	25.6	2920	31.2	1.8	1.9

[a] Monomer concentration: [C_3] = 0.71 mol/l (7). [b] T_p: polymerization temperature. [c] t_p: polymerization time. [d] Zr-concentration, 10^{-6} mol/l. [e] Activity in 10^3g pp ([mol C_3]·[mol Zr]·h)$^{-1}$. [f] Molecular weight, 10^3 g/mol.

As a feature typical of metallocene catalysts the activity (A) increases with raising temperature, whereas the molecular weight (M_w) declines rapidly (7). A plot of A and [mmmm] versus T_p is shown in Figure 1. Since the present polymerization experiments were conducted at constant *monomer concentration* [C_3], both effects can only be caused by the influence of temperature. In previous reports on polymerizationsat constant *monomer pressure* and different temperatures variations of both data could be accounted to changes of monomer concentration and temperature coincidentally.

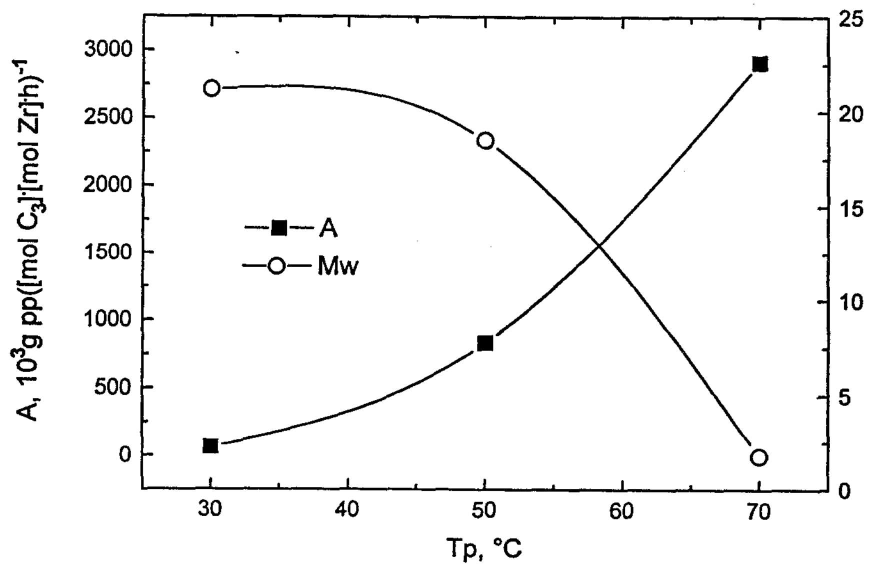


Figure 1. Plot of activity (A) and molecular weight (M_w) versus polymerization temperature (T_p) for 1/MAO.

Interestingly the highly substituted **1**/MAO produces isotactic polypropene with moderate activities. We would like to attribute the catalyst selectivity to the staggered conformation of both fluorenyl groups which is forced by the sterically demanding ethylene bridge, placing the four ß-CH-substituents in a chiral arrangement (Scheme 1). This hypothesis of stereocontrol conducted by the chiral catalyst site is supported by a statistical analysis of the pentad distribution of the total polymers (Table 2). The ratio of mmmr : mmrr : mrrm = 2 : 2 : 1 is indicative for single inversion errors along the chains, as expected for an enantiomorphic site control mechanism (1a).

Table 2. Observed (obs) and calculated (calcd) pentad distributions of polypropene products prepared with **1**/MAO (Al:Zr = 2000) at different temperatures.

Entry	T_p, °C		b[a]	mmmm %	mmmr	rmmr	mmrr	xrmx[b]	mrmr	rrrr	mrrr	mrrm
1	30	obs		64.1	12.0	0	13.0	2.2	1.1	0.7	1.1	5.8
2		calcd	0.92	64.8	12.0	0	12.0	2.3	1.2	0.6	1.2	5.9
3	50	obs		49.7	15.3	1.4	15.2	5.0	1.9	1.1	2.8	7.6
4		calcd	0.87	49.5	15.0	1.3	15.0	5.2	2.6	1.3	2.6	7.5
5	70	obs		32.1	17.7	2.3	16.9	9.5	4.8	2.6	5.5	8.6
6		calcd	0.80	32.0	16.7	2.6	16.7	10.5	5.3	2.6	5.3	8.3

[a] Calculations according to enantiomorphic site statistics with statistical parameter b using the equations of Ewen (1a). [b] xrmm = mrrm + rmrr.

Polymerization experiments with the bisfluorenyl system **1**/MAO demonstrate that stereoregular polyolefins can principally be obtained with complexes bearing four equivalent substituents on each cyclopentadienyl fragment. One basic requirement seems to be a staggered arrangement of both η^5-coordinated ligands in order to provide a chiral cage for coordination and insertion of the incoming monomer unit.

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