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Asymmetric deuteration and deuteriooligomerization of 1-pentene

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Abstract

1-Pentene has been polymerized in the presence of deuterium using as catalyst precursors $[Al(CH_3)–O]_n$ and (–)-ethylenebis(4,5,6,7-tetrahydro)-(*R*)-1-indenylzirconium derivatives ((–)-(*R*)-EBTHI–ZrX_2, X = CH_3 (I); X = (*R*)-1′,1″-bi-2-naphtholate (II)). The investigation of 1,2-dideuteriopentane and of the deuteriooligomers thus obtained shows that the (*Re*) enantioface of the olefin is predominantly involved in the deuteration but its (*Si*) enantioface in the dimerization and oligomerization. These results, which show the participation of the growing chain in the enantioface discrimination in the stereospecific polymerization of 1-pentene are discussed on the basis of a simple stereochemical model for the transition state of the olefin insertion step.

The polymerization of α-olefins with Ziegler–Natta catalysts is characterized by a very sharp discrimination between the monomer enantiofaces [1]. For propylene polymerization the chirality of the catalyst has recently been shown experimentally [2] to be essential for stereoregulation, as foreseen by Natta [3]; the steric relationships between the catalyst precursor chirality and the enantioface of the monomer predominantly undergoing reaction is of the "*k*" type [4].

To obtain further information on the geometry of the transition state and on the enantioface discriminating ability of the chiral catalytic centers when the growing chain is not present [2], the simultaneous deuteration and deuteriooligomerization of 1-pentene has been investigated (Scheme 1).

A very high degree of conversion (ca. 100%) of 1-pentene into deuterated products was obtained with both catalytic systems (I + III and II + III) at temperatures between 25 and 40 °C. The extent of conversion of 1-pentene into deuterated pentanes $C_5H_{12-x}D_x$, isolated by fractional distillation, was 6.3 and 9.9%, respectively with respect to the consumed 1-pentene, when I and II were used as catalyst precursors. The $C_5H_{12-x}D_x$ fraction was investigated by mass spectrometry and ^{13}C, ^{2}H and ^{1}H NMR spectroscopy. As shown in Table 1, according to the mass spectra, non-deuterated, mono- and di-deuterated products are present in this fraction.

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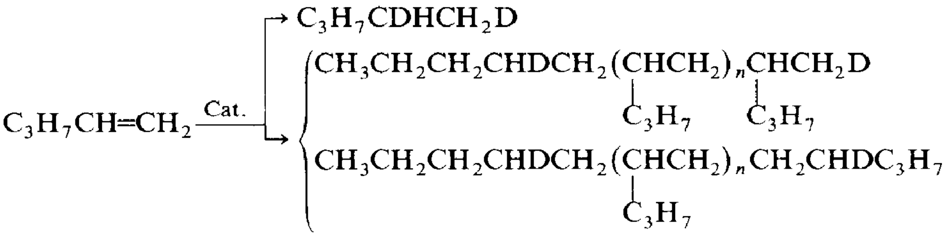

$$C_3H_7CH{=}CH_2 \xrightarrow{\text{Cat.}} \begin{cases} C_3H_7CDHCH_2D \\ \left\{\begin{array}{l} CH_3CH_2CH_2CHDCH_2(\underset{C_3H_7}{CH}CH_2)_n\underset{C_3H_7}{C}HCH_2D \\ CH_3CH_2CH_2CHDCH_2(\underset{C_3H_7}{CH}CH_2)_nCH_2CHDC_3H_7 \end{array}\right. \end{cases}$$

Cat. = (−)-(*R*)-(EBTHI)$ZrX_2/[-Al(CH_3)-O]_n$ (III)
X = CH_3 (I)
X = BIN (II)
EBTHI = Ethylenebis-4,5,6,7-tetrahydroindenyl
BIN = (*R*)-1′,1″-bi-2-naphtholate

Scheme 1.

The ^{13}C NMR spectra indicate that substantially no deuterium is present in position 3, and that no CD_2 and CHD_2 groups are present in the deuterated products.

In the ^1H NMR spectra the intensities of the signals corresponding to the deuterated methyl and methylene groups are about the same. Therefore, the presence of CD_2 groups and deuterium in position 3 being excluded, in both mono- and di-deuterated products deuterium is equally distributed between position 1 and 2.

The $C_5H_{12-x}D_x$ fraction is optically active ($[\alpha]_D^{25} = +0.18$ and $[\alpha]_D^{25} = +0.12$, respectively, when I and II were used as catalyst precursor). As the presence of a deuterium atom in a position vicinal to a (RR′CHD) chirogenic center does not substantially influence the optical rotation [5], the sign of the rotation shows beyond doubt that the predominant chirality of the main optically active component of the $C_5H_{12-x}D_x$ fraction, that is mainly 1,2-dideuteriopentane, is (*R*) [6]. Therefore the 1-pentene enantioface predominantly undergoing reaction in the deuteration is the (*Re*) one.

If the influence of the presence of a deuterium atom in position 1 [5] is neglected, the enantiomeric excess, on the basis of the literature data [6], can be estimated to be about [7*] 35% and 23% for precursor I and II, respectively. Although a small amount of pentane was present in the substrate (< 1%) and 0.2% of H_2 in the D_2, this only partly accounts for the amount of pentane present in the fraction. Its origin during the reaction is still under investigation [8*].

Table 1

Composition of the $C_5H_{12-x}D_x$ fraction obtained using the catalyst precursor I or II [a]

Catalyst precursor	*T* (°C)	C_5H_{12} (%)	$CH_2DCH_2C_3H_7$ (%)	$CH_3CHDC_3H_7$ (%)	$CH_2DCHDC_3H_7$ (%)
I	40	23 (1.5)	15.5 (1.0)	15.5 (1.0)	46 (2.9)
II	25	9 (0.9)	15 (1.5)	15 (1.5)	61 (6)

[a] Values in parentheses indicate the percentage of each fraction with respect to the total deuteriooligomerization products.

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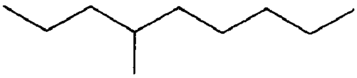
[*] Reference number with asterisk indicates a note in the list of references.

Concerning the deuteriooligomerization products (see Table 2) the most interesting indications arise from the deuterated dimers. As expected from the hydro-oligomerization of propylene [2,9] from 1-pentene two isomeric dimers $C_{10}H_{22-x}D_x$, with the carbon skeletons IV and V, respectively, are formed.


(IV)


(V)

Isomer IV consists of a mixture of 4-methylnonane and deuterated 4-methylnonanes containing 1 to 4 deuterium atoms which, according to the ^{13}C NMR data, are mainly located in positions 4,4′, and 6. The position of the fourth deuterium atom in the tetradeuterated compound could not be identified. For IV obtained with the catalyst precursor I, 8% D_0, 18% D_1, 46% D_2, 17% D_3 and 10% D_4 were found by mass spectrometry. For IV obtained with the catalyst precursor II, the ^{13}C NMR data indicate that deuteration decreases on going from position 4′ (~ 80%), through position 6 (~ 60%), to position 4 (~ 30%). As a consequence at least two asymmetric carbon atoms are present in IV. The contributions to the optical rotation expected from the (R_1,R_2CHD) chirogenic centers are much lower than that from the (R_1,R_2,R_3CH) chirogenic centers which are very near [10] to that of the (R_1,R_2,R_3CD)) chirogenic centers. Therefore at least the sign of the rotation of IV must be significant. It indicates that the chirogenic center in position 4 of IV is dominantly of absolute configuration (*S*) [11]. This means that when the insertion of the monomer is into a M–C_5H_{11} bond the enantioface (*Si*) reacts predominantly.

Taking into account the presence of deuterium-containing chirogenic centers, the contributions of which have not been investigated, the enantiomeric excess can be only roughly estimated. On the basis of the literature data [11] it is about 38% and 49% for the dimer IV obtained with the catalyst precursors I and II, respectively.

The structures of the two isomeric dimers IV and V indicate that, as in the case of propylene [2], both 1–2 and 2–1 insertions are possible. The predominance of the 1–2 insertion as indicated by the IV/V ratio is larger than in the case of propylene.

The number of deuterium atoms present in the dimers and their distribution do not provide a basis for further speculation on the insertion mechanism. No investigation of the optical activity of $C_{10}H_{22-x}D_x$ (V) was carried out because of the small amount available and of the low optical rotation expected from the contribution of the two (R_1,R_2,CHD) chirogenic centers.

$C_{10}H_{20-x}D_x$ olefins are present only in a very small amount in the C_{10} fractions. Therefore the presence of M–H groups together with predominant M–D groups cannot be excluded, and deuterated monomers can be formed by an addition-elimination sequence involving M–D. This possible path would also account for the presence of deuterium in position 4, and the formation of a relatively large amount of pentane.

The positive sign of the optical rotation of the deuteriooligomers fractions, some of which have been shown by X-ray diffraction to be crystalline, can be taken as an indication, by comparison with the sign of the optical activity calculated as described by Brewster [14], that the first asymmetric carbon atom following the n-pentyl terminal group is predominantly in the (*S*) configuration.

Table 2

Composition and characterization of 1-pentene deuteriooligomers obtained using catalyst precursor I or II

Compound or fraction	% [a]		$\overline{M}_n$ [b]		$\alpha_{meas.}$ [h]		$[\phi]^D_{25}$		e.e. (%)		abs. conf.
	I	II	I	II	I [f]	II [f]	I	II	I	II	
IV	10.9	7.3	n.d.	n.d.	+0.013 [i]	+0.013 [l]	+0.99 [c]	+1.18 [c]	38 [d]	45 [d]	4 S
V	0.5	0.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Deteriooligomers [e]											
A	70.3	5.4	497	309	+0.105 [m]	+0.116 [n]	+17.7 [f]	+19.07 [f]	n.d.		
B	12.0	32.8	558	513	+0.080 [o]	+0.060 [p]	+20.6 [f]	+27.50 [f]	n.d.		S [g]
C	–	41.7	–	1230	–	+0.028 [q]	–	+48.46 [f]	n.d.		
D	–	2.1	–	2560	–	n.d.	–	n.d.	n.d.		

[a] 100 weight of product / weight of 1-pentene reacted. [b] Determined by vapour pressure osmometry in $CHCl_3$ at 25 ° C. [c] Value extrapolated from measurements in toluene according to ref. 13 and 14. [d] Assuming for optically pure (+)-(*S*)-4-methylnonane $[\phi]^{25}_D = +2.4$. [e] The extractions were made at 25 ° C. A, methanol-soluble; B, methanol-insoluble, acetone-soluble; C, acetone-insoluble, ethyl acetate-soluble; D, ethyl acetate-insoluble. [f] In methylcyclohexane at 25 ° C. [g] Of the asymmetric carbon adjacent to the n-pentyl group. [h] Measured at 589 nm. [i] in toluene, $d = 1.90$ g/100 cm^3. [l] In toluene, $c = 1.50$ g/100 cm^3. [m] $c = 2.95$ g/100 cm^3; [n] $c = 1.88$ g/100 cm^3; [o] $c = 2.17$ g/100 cm^3. [p] $c = 1.12$ g/100 cm^3. [q] $c = 0.71$ g/100 cm^3.

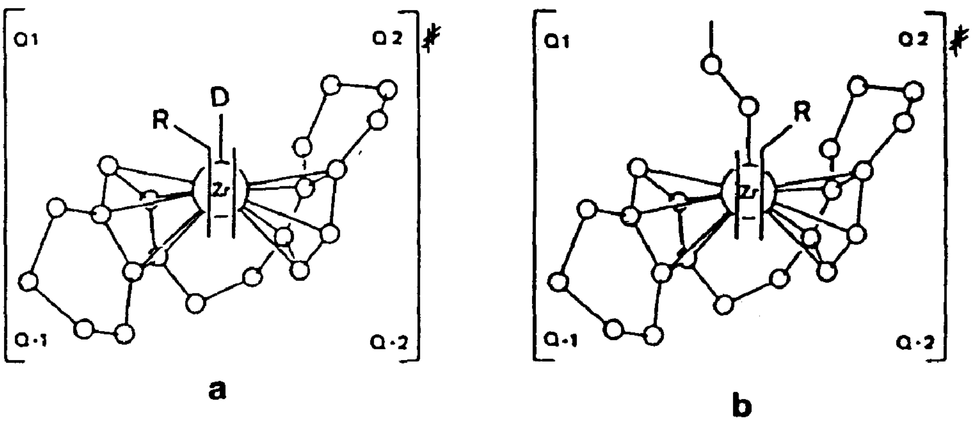


Fig. 1. Simplified stereochemical model of a transition state for 1-pentene insertion (a) in the Zr–D bond, (b) in the Zr–CH_2 bond ($R = C_3H_7$).

The presence of the growing chain seems to increase the stereoselectivity of the process, as shown by the higher optical purity of the dimer IV than of the deuteriopentanes. The formation of optically active deuteriopentanes also indicates that with the catalytic system used asymmetric hydrogenation of olefinic hydrocarbons can also be readily obtained with moderate optical yields above room temperature with either I or II as catalyst precursor.

Our data indicate that different enantiofaces of 1-pentene are predominantly involved in deuteration and deuteriooligomerization; the presence of the growing chain must be responsible for the opposite topicity of the two reactions. This fact is well accounted for in terms of the previously fomulated hypothesis that the stereoselectivity in α-olefins polymerization at temperatures above 0 °C is connected both to the chirality of the catalytic center and to the position of the last monomeric unit of the growing chain with respect to the metal atom in the catalytic center. This situation can be easily visualized in terms of the previously proposed stereochemical model for the transition state of the olefin insertion step [2].

This model shows that the monomer enantioface which predominantly reacts in the deuteriooligomerization is the one in which the substituent at the ethylene double bond is situated in a rather crowded quadrant (Q_2) (Fig. 1b), the least crowded quadrant being occupied by the growing chain, as foreseen by Corradini and coworkers [16]. In contrast, in the deuteration, no growing chain being present, the last crowded quadrant Q_1 is occupied, as expected, by the substituent on the ethylene double bond. (Fig. 1a).

Experimental

General

The preparations of the catalysts and the polymerizations were carried out under N_2. All the solvents were distilled before use, as previously described [2]. The NMR spectra were recorded on a Bruker AM 300 wp (300 MHz) and Bruker AC 200 (200 MHz). The mass–spectra were recorded on an Hitachi MRU 6L connected to a gas chromatograph Perkin–Elmer Model 990. The X-ray analysis was performed with a Seifert Röntgendiffractometer MZ 111 (Cu-K_α).

Preparation of the catalytic systems

The preparation and the characterization of the catalyst precursors I and II and of the methylalumoxane were carried out as previously described [2,15]. The chemical purity of I, determined by ^{1}H NMR spectroscopy with anthracene as internal standard, was about 60%. The optical purity was about 100%.

The chemical purity of II was 81%, the main impurities being diethyl ether (11%) and racemic ethylene-bis-tetrahydroindenylzirconium dichloride (8%). The methylaluminoxane contained 3% of methoxy groups, and about 12% of $[Al(CH_3)_3]$, as indicated by ^{1}H NMR spectroscopy.

Polymerizations of 1-pentene with catalyst precursors I and III

A solution in 75 ml of toluene of 30 ml of 1-pentene and 366.5 mg of methylalumoxane was introduced in a water-jacketed glass autoclave (volume 400 ml) and thermostated at 40 ° C. A solution of 68.5 mg of I in 35 ml of toluene was added, and then D_2 was introduced into the autoclave up to a pressure of 9 bar. The light yellow solution was stirred for 2 h, and the autoclave then cooled at 0 ° C, and the liquid layer was transferred (under D_2 pressure) into a glass-vessel cooled at 0 ° C.

Polymerization of 1-pentene with catalyst precursors II and III

The reaction was carried out as described above with 90 ml of toluene, 30 ml of 1-pentene, 366.5 mg of methylaluminoxane, 12.8 mg of II in 20 ml of toluene, and 9 bar of deuterium. The temperature was 40 ° C.

Isolation of the products

The deuteropentanes were isolated by careful fractional distillation of the product mixture. The residual solution of oligomers was distilled under vacuum and the products present in the distillate were separated by fractional distillation with a Perkin-Elmer 251 Auto Annular Still. The solid residue was separated into fractions at 25 ° C by successive extractions with methanol, acetone, and diethyl ether [2].

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7 This value is calculated by assuming that the relationship between sign and value of optical rotation and absolute configuration and optical purity, respectively, are the same in the 2-deuteriopentane and 1,2 dideuteriopentane [5].
8 Hydrogen transfer from the catalytic system to the products is in principle possible. However not only the hydrogen present in the zirconium complex hut also part of that present in methylaluminoxane must be involved in order to produce the amount of non-deuterated pentane found experimen-

tally. Another more likely origin of the hydrogen is the monomer, via a series of addition–β-elimination reactions as discussed later in this paper.

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