Statistical Approach for the Determination of the Stereoregularity of Optically Active Propylene–CO Copolymers

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Dedicated to Professor *Giambattista Consiglio* on the occasion of his 65th birthday

A two-parameter statistic model was applied to analyze the NMR spectra of a series of stereoregular propylene–CO copolymers synthesized by catalytic polymerization in the presence of various transition-metal complexes containing chiral ligands. The concentration of the different pentads, estimated to be recognizable in the spectra, was determined. A tentative assignment of the nature of the different peaks composing the signal of the C=O group in the ^{13}C-NMR spectra is proposed.

Introduction. – Interest in optically active polymers arose from analogy with macromolecules of biological origin that are derived from the readily available pools of chiral monomers such as amino acids and sugars present in high enantiomeric purity. Attempts to direct the course of the reaction with the aid of chiral reagents were made prior to the discovery of stereospecific polymerizations. It was only after the 1950s, however, that the problem of polymer chirality was tackled in a rational way. Actually, most man-made optically active polymers are derived from chiral monomers [1].

Given the limited availability of enantiomerically pure monomers that can be polymerized, it is far more attractive to design synthetic strategies involving the *enantioselective* polymerization of prochiral monomers. Reports of such procedures, with the polymer chirality arising from an asymmetric backbone configuration rather than from restricted conformational states (*e.g.*, helicity), are exceedingly rare [2a,b].

The alternating copolymers of α-olefins and carbon monoxide (CO) represent an interesting class of synthetic macromolecules. As a matter of fact, they contain true stereogenic centers in the polymer backbone **A** (*Fig. 1*). For these copolymers, the stereoregularity is a consequence of enantioface selection of the olefin during chain growth, similarly to *Ziegler–Natta* catalysis [3]. Interestingly, these copolymers may also be isolated as the corresponding spiroacetals **B** (*Fig. 1*) [4]. In these tetrahydrofuran-based polyspiro compounds, a second element of chirality does exist, namely that of the atropisomeric structure itself.

In this paper, the stereoregularity of propylene–CO copolymers, prepared with catalysts containing the chiral ligands **1**–**20**, will be analyzed with respect to the polyketone structure, *i.e.*, the form in which the polymers are present when dissolved in,

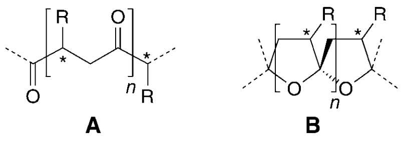


Fig. 1. *Repeating units in alternating Olefin–CO regular-chain* (**A**) vs. *spiro-type* (**B**) *copolymers*

e.g., hexafluoroisopropanol (HFIP). For the configuration of these copolymers, the Me and C=O ^{13}C-NMR signals were found to be diagnostic [5].

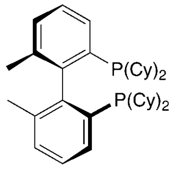
The first stereo- and regioregular propylene copolymer was obtained using a catalytic system modified by the atropisomeric ligand (*R*)-(6,6′-dimethylbiphenyl-2,2′-diyl)bis(dicyclohexylphosphane) ((*R*)-Cy$_4$-Biphemp; **1**) [4][6]. The stereoregularity of this material was first tentatively analyzed with a one-parameter *Bernoulli* statistic model (enantiomorphic site control) due to the chirality of the catalyst. Further investigations using homologous atropisomeric ligands, as well as ligands of type **12**, related to (*S*)-(R_p)-Josiphos, allowed the synthesis of samples of poly[1-oxo-2-methylpropane] having various degrees of stereoregularity [7–10]. The use of two further chiral ligands was also reported in the literature [11][12]. Also, ternary polymerization of ethene, propylene, and CO showed that enantioface discrimination is generally less effective than during propylene–CO polymerization [10].

In this paper, the influence of two different discriminating factors, associated with the relative topicity of the last inserted propylene unit and of the catalyst, on the enantioface selection of the inserting monomer will be considered. The analysis of the structure of the polymers through a two-parameter statistical model will allow us to tentatively identify the stereochemical sequences mirrored in the ^{13}C-NMR spectra.

Experimental. – *Copolymerization Reactions.* All polymerizations were performed in a 500-ml stainless-steel rocking autoclave (*Hastelloy C*) heated with an electric heater. The temp. was kept constant (±1°) by a thermostat (*Eurotherm*). The pressure was measured with a manometer (*Keller*; 0–250 bar) or a piezo-sensitive element (*Keller E176*; 0–200 bar). Before and after each polymerization, the autoclave was drilled with abrasive brushes, using a detergent in warm H_2O, rinsed with H_2O, CH_2Cl_2, and acetone, and rubbed dry with cotton wool. Sometimes, the use of sandpaper was required. When necessary, the manometer and the valve were removed and cleaned with solvents and pipe-cleaners. The cleaned autoclave was closed and set under vacuum. The soln. of the catalytic precursor contained 70 µmol of ligand, 60 µmol of [Pd(OAc)$_2$], 0.3 mmol of [Ni(ClO$_4$)$_2$], and 3.0 mmol of 1,4-naphthoquinone in a mixture of THF (151.5 ml) and MeOH (8.5 ml) (unless specified otherwise). This soln., kept under N_2, was sucked up inside the autoclave. Then, the gaseous monomers were introduced in the order (after purging the circuit) propylene (39 g) > CO (80 bar). The autoclave was hold at a const. temp. of 42° during the reaction time. At the end of the reaction, the autoclave was cooled down to r.t., and unreacted gases were released. The mixture was added to cold MeOH (500 ml) and left standing at 5° for 24 h. Then, the copolymer was filtered off, washed with MeOH, and dried under high vacuum.

NMR Spectroscopy. The ^{13}C-NMR spectra were recorded on a *Bruker AMX-500* apparatus at 25° in (D_2)hexafluoroisopropanol ((CF_3)$_2$C(D)OD) (δ(C) 71.5, 122.5 ppm). The spectra were analyzed on a PC with the *Bruker* Win-NMR software. The peak areas were analyzed with the same software using the interactive deconvolution package. Initial starting values for the peaks were defined manually, and then fitted automatically with *Lorentzian* lines.

Results. – In previous studies [9][10], we have extensively investigated palladium (Pd) catalysts modified with chelating diphosphine ligands (based on atropisomeric



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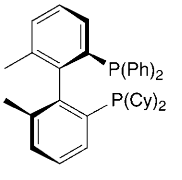

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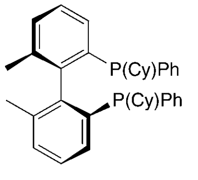

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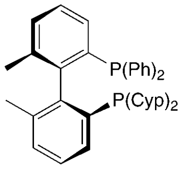

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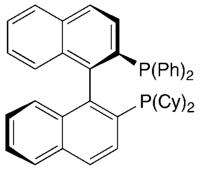

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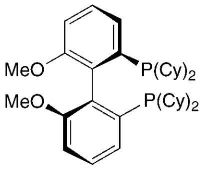

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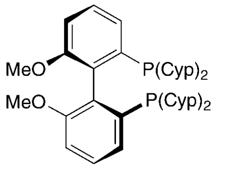

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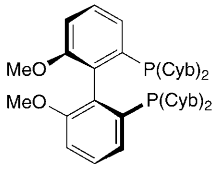

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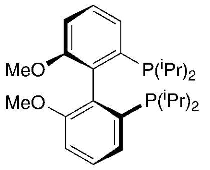

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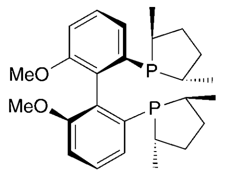

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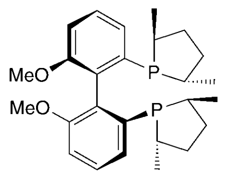

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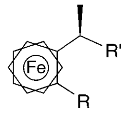
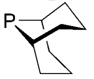
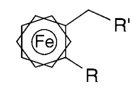
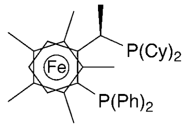


	R	R'
12	P(Ph)2	P(Cy)2
13	P(Cy)2	P(Ph)2
14	P(Cy)2	P(Cy)2
15	P(Ph)2	P(Ph)2
16	P(Ph)2	P(Et)2
17	P(Ph)2	



	R	R'
18	P(Ph)2	P(Cy)2
19	P(Ph)2	P(Et)2



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diphenyl or on ferrocenyl moieties) for the synthesis of alternating propylene–CO copolymers, giving rise to high regio- and stereocontrol. To compare the influence of the nature of the catalytic system on stereocontrol, the percentage of the most-intense ^{13}C-NMR signal in the region of the C=O group was assumed as a discriminating parameter. Stereochemical analyses were carried out according to a simple *Markov* process, as previously discussed by other authors [13] [14], by assuming that stereoselection is determined by both the innate asymmetry of the catalyst site and the configuration of the last monomeric unit; the influence of the penultimate and preceding units was considered negligible. This aspect was confirmed by the analysis of a terpolymer (ethene–propylene–CO polymerization) obtained with the ligand (*R*)-Cy$_4$-Biphemp ((*R*)-**1**), even if the $\Delta\varepsilon$ values in the circular dichroism (CD) spectra extrapolated for 100% incorporated propylene seemed to indicate that the influence of the chain end on the enantioface selection of the inserted olefin is smaller than the control of the enantiomorphous catalyst. Moreover, the relationship between the prevailing absolute configuration of the asymmetric C-atoms and the sign of the CD band corresponding to the n → π^* transition was established based on the octant rule [10].

The resolution of the ^{13}C-NMR spectra obtained at 125 MHz in (D$_2$)HFIP allowed us to identify eleven different peaks in the region of the C=O group, thus indicating that this spectral window is sensitive to the pentads. The overlapping ^{13}C-NMR resonances for the C=O bands were quantified by a least-squares-fitting procedure in the frequency domain, followed by integration. As already reported, the resonances were approximated with *Lorentzian* line shapes. The relative area of each peak was calculated with respect to the total area of the band. The downfield signal, which for all copolymers prepared was the most-intense one, was attributed to the isotactic (*llll*)-pentad, and was taken as a reference, since some shifts of the various resonances were observed depending on the sample. One example of deconvolution is reported in *Fig. 2*. Each copolymer was characterized based on a different relative ratio among the signals composing the C=O region. However, the range in chemical shift, where a signal was expected to be in terms of distance with respect to the main peak, was determined. An epimerization experiment carried out on the most-stereoregular material showed that an atactic copolymer displays resonances within *ca.* 1 ppm upfield from the above signal. An amplitude of $\Delta\delta$(C) 0.05 ppm for the same signal in different spectra was assumed.

At the end of the deconvolution, a maximum of twelve different peaks were recognized in the region of the C=O group centered around a medium value of the distance with respect to the main peak, with medium relative distances of 0, 0.26, 0.35, 0.39, 0.47, 0.53, 0.64, 0.69, 0.79, 0.85, 0.87, and 0.92 ppm, respectively. This result is only apparently

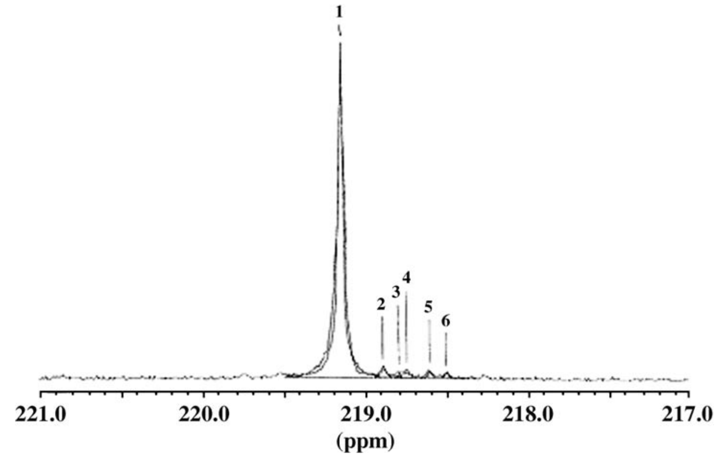

Fig. 2. *Example of the deconvolution of the ^{13}C-NMR C=O signals of a regular olefin–CO copolymer*

in contrast with the well-known distribution of recognizable pentads in the NMR spectra of polypropylene. From the comparison of the monomeric unit in polypropylene and in the polyketones investigated in this work, it is clear that the substituted C-atom in the polyketones is really asymmetric (*Fig. 3*), being directly bound to four different groups.

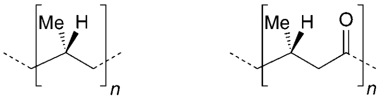

Fig. 3. *Representation of the monomeric units of polypropylene* (left) vs. *propylene–CO copolymers* (right)

Due to the different nature of the terminal groups, as previously indicated [7], there is a greater possibility of stereoisomeric differentiation in the investigated copolymers, which could be responsible of the increased resolution (more pentads identified). In addition to these considerations, it was decided, as a tentative procedure, to couple molecular-mechanics with *ab initio* calculations. The conformational space of the various polymers ((*R*,*R*,*R*), (*R*,*S*,*S*), (*R*,*S*,*R*), and (*R*,*R*,*S*)) was explored using the random-search method available in Sybyl employing the *Merck* Molecular Force Field (MMFF94), which is parametrized for a wide variety of chemical systems. Random torsion searching was performed for each molecule considering all the rotatable bonds. All conformational searches were run without explicit solvent molecules, but applying a dielectric constant of 7.6, corresponding to the solvent (HFIP) employed in the experimental work. Conformations were accepted when their energy gap was within 5 kcal/mol of the lowest-energy conformer, and when the root mean-square deviation (rmsd), obtained by superimposing the heavy atoms of the new conformation with those of the already accepted conformations, was greater than 0.2 Å, to avoid multiple copies. A total of *ca.* 200 structures for each molecule were considered and analyzed. The most-stable twelve structures of each molecule were further optimized *ab initio*, and the obtained conformations were used for chemical-shift calculations. This was done with the B3LYP functional and the 6-311++G** basis set, as implemented in the GAUSSIA03 program. This method makes use of an efficient implementation of the gauge-including atomic-orbital (GIAO) method.

On the basis of the above approach, the triads *lu* and *ul* resulted to be different, and, in particular, calculated shielding values σ of -44.81987, and -45.04091, respectively, were obtained. Thereby, shielding and chemical shift are related by $\sigma = 186.4 - \delta$, where 186.4 represents the shielding of Me_4Si [13]. This gave δ(C) values of 228.499 and 228.720 for the triads *lu* and *ul*, respectively. The deviation between the calculated and the observed δ(C) values for the C=O groups can be related to the selected hybrid function, which provides the corresponding rmsd error [14].

According to the simple *Markov* process [15][16], the percentage of isotactic pentads (*l*-ads) was calculated starting from the definition of *Bovey*'s tacticity [17][18]. Correspondingly, as independent parameters for the evaluation of the various *n*-ads, the two probabilities $p_{(Re)lk}$ and $p_{(Si)ul}$ were taken (or, for the enantiomeric ligand, $p_{(Si)lk}$ and $p_{(Re)ul}$). For a catalyst associated with a preference for the *Re*-enantioface, $p_{(Re)lk}$ represents the probability to maintain (*Re*)-enantioface selection to give an isotactic sequence, whereas $p_{(Si)ul}$ represents the probability to return to the preferred enantioface after a non-regular (*Si*)-insertion. According to this, the following equations were developed:

$$I_{(llll)} = \frac{p_{(Si)ul}}{p_{(Si)ul} + p_{(Re)ul}} p^{4}_{(Re)lk} + \frac{p_{(Re)ul}}{p_{(Si)ul} + p_{(Re)ul}} p^{4}_{(Si)lk} \tag{1}$$

$$S_{(uuuu)} = p^{2}_{(Re)ul} p^{2}_{(Si)ul} \tag{2}$$

$$H_{(lllu)} = \frac{p_{(Si)ul} p_{(Re)ul}}{p_{(Si)ul} + p_{(Re)ul}} \left(p^{3}_{(Re)lk} + p^{3}_{(Si)lk} \right) \tag{3}$$

$$H_{(lluu)} = \frac{p_{(si)ul} p_{(Re)ul}}{p_{(Si)ul} + p_{(Re)ul}} \left(p_{(si)ul} p^{2}_{(Re)lk} + p_{(Re)ul} p^{2}_{(Si)lk} \right) \tag{4}$$

$$H_{(luul)} = \frac{p_{(Si)ul} p_{(Re)ul}}{p_{(Si)ul} + p_{(Re)ul}} \left(p_{(Si)ul} p^{2}_{(Re)lk} + p_{(Re)ul} p^{2}_{(Si)lk} \right) \tag{5}$$

$$H_{(uull)} = \frac{p_{(Si)ul} p_{(Re)ul}}{p_{(Si)ul} + p_{(Re)ul}} \left(p_{(Si)ul} p^{2}_{(Re)lk} + p_{(Re)ul} p^{2}_{(Si)lk} \right) \tag{6}$$

$$H_{(ulll)} = \frac{p_{(Si)ul} p_{(Re)ul}}{p_{(Si)ul} + p_{(Re)ul}} \left(p^{3}_{(Si)lk} + p^{2}_{(Re)lk} \right) \tag{7}$$

$$H_{(llul)} = \frac{p_{(Si)ul} p_{(Re)ul}}{p_{(Si)ul} + p_{(Re)ul}} \left(p_{(Si)lk} p^{2}_{(Re)lk} + p_{(Re)lk} p^{2}_{(Re)lk} \right) \tag{8}$$

$$H_{(lulu)} = p_{(Re)lk} p_{(Re)lk} p_{(Si)ul} p_{(Re)ul} \tag{9}$$

$$H_{(ulul)} = p_{(Re)lk} p_{(Re)lk} p_{(Si)ul} p_{(Re)ul} \tag{10}$$

$$H_{(lull)} = \frac{p_{(Si)ul} p_{(Re)ul}}{p_{(Si)ul} + p_{(Re)ul}} \left(p_{(Re)lk} p^{2}_{(Si)lk} + p_{(Si)lk} p^{2}_{(Re)lk} \right) \tag{11}$$

$$H_{(luuu)} = \frac{p^{2}_{(Re)ul} p^{2}_{(Si)ul}}{p_{(Si)ul} + p_{(Re)ul}} \left(p_{(Re)lk} + p_{(Si)lk} \right) \tag{12}$$

$$H_{(uulu)} = \frac{p^2_{(Si)ul} p^2_{(Re)ul}}{p_{(Si)ul} + p_{(Re)ul}} \left(p_{(Re)lk} + p_{(Si)lk} \right) \tag{13}$$

$$H_{(ullu)} = \frac{p_{(Si)ul} p_{(Re)ul}}{p_{(Si)ul} + p_{(Re)ul}} \left(p_{(Si)ul} p^2_{(Re)lk} + p_{(Re)ul} p^2_{(Si)lk} \right) \tag{14}$$

$$H_{(uuul)} = \frac{p^2_{(Si)ul} p^2_{(Re)ul}}{p_{(Si)ul} + p_{(Re)ul}} \left(p_{(Re)lk} + p_{(Si)lk} \right) \tag{15}$$

$$H_{(uluu)} = \frac{p^2_{(Si)ul} p^2_{(Re)ul}}{p_{(Si)ul} + p_{(Re)ul}} \left(p_{(Re)lk} + p_{(Si)lk} \right) \tag{16}$$

The two independent probabilities were arbitrarily changed to calculate a value for the isotactic pentad close to the experimental concentration evaluated from the spectrum. Among the various possibilities, the conclusive set of probabilities describing the polymerization process was chosen such to obtain a concentration of the other pentads as close as possible to the experimental distribution. Sometimes, the combination of two or more pentads was necessary. Because of this, the number of peaks recognizable in the spectra was, in any case, lower than the possible calculated number of 16 pentads. In *Tables 1* and *2*, two typical tentative assignments of the recognized bands for the copolymer obtained with the catalytic system containing (*S*)-Cy$_4$-Biphemp ((*S*)-**1**) and the ferrocenyl (*R*)-(S_p)-Josiphos ligand **12**, respectively, are proposed. The value for each pentad was calculated according to the set of probabilities reported in *Table 3* for the above ligands.

Table 1. *Tentative Assignment of the Deconvoluted ^{13}C-NMR Signals for a Propylene–CO Copolymer Obtained in the Presence of an Atropisomeric Ligand*

Peak	Δδ(C)	Rel. intensity [%]		Assignment
		obs.	calc.	
1	0.0	0.691	0.916	$I_{(llll)}$
2	0.2567	0.111	0.025	$[H_{(lllu)}$ or $H_{(ulll)}] + [H_{(lluu)}$ or $H_{(uull)}$ or $H_{(luul)}$ or $H_{(ullu)}]$ $+ [H_{(llul)}$ or $H_{(lull)}]$
3	–	–	–	
4	0.3913	0.065	0.066	$[H_{(lllu)}$ or $H_{(ulll)}] + [H_{(lulu)}$ or $H_{(ulul)}]$
5	0.4657	0.023	0.023	$H_{(llul)}$ or $H_{(lull)}$
6	0.5259	0.010	0.014	$H_{(lulu)}$ or $H_{(ulul)}$
7	0.6447	0.069	0.060	$[H_{(lluu)}$ or $H_{(uull)}$ or $H_{(luul)}$ or $H_{(ullu)}] + [H_{(llul)}$ or $H_{(lull)}]$
8	–	–	–	
9	–	–	–	
10	0.8486	0.016	0.015	$H_{(luuu)} + H_{(uuul)} + H_{(uulu)} + H_{(uluu)} + S_{(uuuu)}$
11	–	–	–	
12	0.9340	0.015	0.015	$H_{(luuu)} + H_{(uuul)} + H_{(uulu)} + H_{(uluu)} + S_{(uuuu)}$

Table 2. *Tentative Assignment of the Deconvoluted* ^{13}*C-NMR Signals for a Propylene–CO Copolymer Obtained in the Presence of a Ferrocenyl Ligand*

Peak	$\Delta\delta$(C)	Rel. intensity [%]		Assignment
		obs.	calc.	
1	0.0	0.916	0.916	$I_{(lll)}$
2	0.2675	0.025	0.025	$[H_{(lllu)}$ or $H_{(ulll)}] + [H_{(lluu)}$ or $H_{(uull)}$ or $H_{(luul)}$ or $H_{(ullu)}]$
3	0.3620	0.007	0.007	$\mathrm{H}_{(llul)}$ or $H_{(lull)}$
4	0.4091	0.022	0.022	$[H_{(lllu)}$ or $H_{(ulll)}] + [H_{(llul)}$ or $H_{(lull)}]$
5	–	–	–	
6	0.5547	0.013	0.014	$[H_{(lluu)}$ or $H_{(uull)}$ or $H_{(luul)}$ or $H_{(ullu)}] + [H_{(lulu)}$ or $H_{(ulul)}]$
7	0.6589	0.012	0.011	$[H_{(lulu)}$ or $H_{(ulul)}] + [H_{(llul)}$ or $H_{(lull)}]$
8	–	–	–	
9	–	–	–	
10	–	–	–	
11	0.8906	0.005	< 0.001	$H_{(luuu)} + H_{(uuul)} + H_{(uulu)} + H_{(uluu)} + S_{(uuuu)}$
12	–	–	–	

Table 3. *Set of Probabilities* (*p*) *and Analysis of the Stereochemistry of Propylene–CO Copolymers Prepared in the Presence of Chiral Atropisomeric Ligands.* For conditions, see *Experimental.*

Ligand[a])	$p_{(Re)lk}$	$p_{(Re)ul}$	$p_{(Si)lk}$	$p_{(Si)ul}$	PMP[b])	*l*-Diads [%]
(*S*)-Cy$_4$-Biphemp (**1**)	0.320	0.680	0.933	0.067	69.0	87.8
(*R*)-Cy$_2$-Biphemp (**2**)	0.900	0.100	0.310	0.690	57.4	82.5
(*R*,*R*,*S*)-Cy$_2$-Biphemp (**3**)	0.250	0.750	0.880	0.120	51.8	79.3
(*S*)-Cyp$_2$-Biphemp (**4**)	0.200	0.800	0.925	0.075	66.9	86.3
(*R*)-Cy$_4$-Binap (**5**)	0.953	0.047	0.200	0.800	77.9	91.1
(*R*)-MeO-Bichep (**6**)	0.978	0.022	0.300	0.700	88.7	95.7
(*S*)-Cyp$_4$-MeO-Biphep (**7**)	0.260	0.740	0.957	0.043	79.3	91.9
(*S*)-Cyb$_4$-MeO-Biphep (**8**)	0.150	0.850	0.978	0.022	89.3	95.7
(*S*)-(i-Pr$_4$)$_4$-MeO-Biphep (**9**)	0.400	0.600	0.978	0.022	89.2	95.7
(all-*S*)-Mephos-(*R*$_a$)-MeO-Biphep (**10**)	0.780	0.220	0.335	0.665	27.2	66.9
(all-*S*)-Mephos-(*S*$_a$)-MeO-Biphep (**11**)	0.320	0.680	0.963	0.037	81.6	93.0

[a]) Cy = cyclohexyl, Cyp = cyclopentyl, Cyb = cyclobutyl. [b]) Percentage of main C=O ^{13}C-NMR peak.

Table 3 lists the set of probability parameters for all copolymers obtained with the atropisomeric ligands **1**–**12**, and the percentage area of the main ^{13}C-NMR peak of the C=O group, determined for each copolymer. Moreover, the concentration of the isotactic diad (*l*-diad), calculated as previously reported, is given to allow an immediate comparison of the stereoregularity of the various copolymers. The same analysis was also carried out for the copolymers obtained with the ferrocenyl ligands **12**–**20**, and the results are summarized in *Table 4*.

In spite of the fact that some ligands were used in their racemic forms, we performed all calculations by assuming that the optically active ligand would prefer the (*Re*)-enantioface. We, indeed, found that, for the Josiphos ligand, both the optically active and racemic ligands gave copolymers giving rise to identical NMR spectra. Therefore, copolymers with the same steric features were assumed. The results of

Table 4. *Set of Probabilities* (*p*) *and Analysis of the Stereochemistry of Propylene–CO Copolymers Prepared in the Presence of Chiral Ferrocenyl Ligands.* For conditions, see *Experimental.*

Ligand	$p_{(Re)lk}$	$p_{(Re)ul}$	$p_{(Si)lk}$	$p_{(Si)ul}$	PMP[a])	*l*-Diads [%]
(*R*)-(S_p)-Josiphos (**12**)	0.984	0.016	0.340	0.660	91.6	96.9
(*R*)-(S_p)-InvJosiphos (**13**)	0.953	0.047	0.340	0.660	77.1	91.2
(*R*)-(S_p)-JosiphosCy$_2$ (**14**)	0.992	0.008	0.250	0.750	95.6	98.4
(*R*)-(S_p)-JosiphosPh$_2$ (**15**)	0.942	0.058	0.280	0.720	72.9	89.3
(*R*)-(S_p)-JosiphosEt$_2$ (**16**)[b])	0.947	0.053	0.440	0.560	73.8	90.5
(*S*)-(R_p)-JosiphosCg (**17**)	0.310	0.690	0.910	0.090	60.8	84.1
NorJosiphos (**18**)[b])	0.940	0.060	0.340	0.660	71.7	89.0
NorJosiphosEt$_2$ (**19**)[b])	0.930	0.070	0.300	0.700	68.1	87.3
rac-Me$_5$Josiphos (**20**)	0.958	0.042	0.280	0.720	79.6	92.1

[a]) Percentage of main C=O ^{13}C-NMR peak. [b]) In THF/MeOH/TMM 151.5 : 8.5 : 2.0 solution (TMM = trimethoxymethane), $T = 50°$.

Table 5. *Analysis of the Stereoregularity of the Copolymers Obtained in the Presence of the Josiphos Ligand under Different Reaction Conditions*

Conditions	$p_{(Re)lk}$	$p_{(Re)ul}$	$p_{(Si)lk}$	$p_{(Si)ul}$	PMP[a])	*l*-Diads [%]
[Ni(ClO$_4$)$_2$], 1,4-NQ[b]), THF, MeOH, 42°	0.984	0.016	0.340	0.660	91.6	96.9
[Ni(ClO$_4$)$_2$], THF, MeOH, TMM[c]), 50°	0.986	0.014	0.100	0.900	92.9	97.2
[Ni(ClO$_4$)$_2$], 1,4-NQ, THF, MeOH, TMM, 50°	0.985	0.015	0.280	0.720	92.2	97.1
[Ni(ClO$_4$)$_2$], 1,4-NQ, ^{t}BuOH/PhMe/MeOH, 42°	0.970	0.030	0.290	0.710	85.0	94.2
BF$_3$·Et$_2$O, 1,4-NQ, THF, MeOH, 42°	0.977	0.023	0.150	0.850	88.7	95.5
CH$_2$Cl$_2$, MeOH, BF$_3$·Et$_2$O, 1,4-NQ, 42°	0.973	0.027	0.35	0.65	86.1	94.8
CH$_2$Cl$_2$, H$_2$ (g), BF$_3$·Et$_2$O, 1,4-NQ, 42°	0.965	0.035	0.340	0.660	82.4	93.3

[a]) Percentage of main C=O ^{13}C-NMR peak. [b]) 1,4-NQ = 1,4-Naphthoquinone. [c]) TMM = trimethoxymethane.

some experiments carried out in the presence of the ligand (*R*)-(S_p)-Josiphos under different reaction conditions are summarized in *Table 5.*

Discussion. – In the copolymerization reaction, similar to propylene polymerization with chiral metallocene catalyst precursors [19], the enantiomorphic site of the catalyst is able to control the enantioface selection of the olefin. In the former case, however, when optically active ligands are used, the stereochemical relationship between the geometry of the catalyst and the enantioface of the olefin prevailingly inserted is easily recognized from the chiroptical properties of the copolymer [10]. In our previous studies [10], a model for the catalytic site was proposed, as shown in *Fig. 4*, to account for enantioface selection during copolymerization.

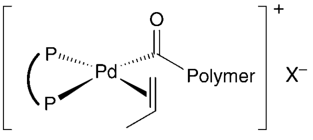

Fig. 4. *Structural representation of the catalytic intermediate*

The essentially complete regioselectivity shows that only one direction of insertion of the olefin must be taken into account, and the high regiocontrol observed with these ligands is usually associated with a high enantioface selection. We had observed before [10], that the presence of an additional discriminating factor such as the atropisomeric conformation, in addition to electronic factors, modifies the relative energies of the transition states and produces an improvement in both regio- and stereocontrol during copolymerization. In addition, evaluation of the chiroptical properties of the terpolymers made of CO, ethene, and propylene showed that the enantiomorphic site of the catalyst, coupled with the chirality of the last inserted unit of the copolymer, has an effect on the selection of the enantioface of the olefin. The percentage of isotactic pentads was calculated for each copolymer obtained in the presence of chiral ligands by using a simple *Markov* process [15][16].

With the remarkable exception of ligands **3** and **10**, a common feature of the catalytic systems used is that enantioface discrimination is always quite effective ($p_{(Re)lk}$ or $p_{(Si)lk} > 0.90$) when the macromolecular chain is growing isotactically. The occasional inversion of the prevailingly inserted enantioface tends to be corrected ($p_{(Re)ul}$ or $p_{(\mathrm{Si})ul} > 0.50$), even though the discrimination of the preferred enantioface takes place in a less-efficient way compared to the previous case. Copolymers with the same concentration of *l*-diads in the chain showed a different distribution of the stereo-irregular sequences, as evaluated from the shape of the NMR signals of the C=O groups.

Considering the atropisomeric ligands, the presence of various stereogenic elements in the ligand itself causes a less-efficient control of the stereochemistry in terms of isotactic stereoselection. The degree of stereoregularity decreases considerably for the copolymers produced with the ligand (*R*,*R*,*S*)-Cy$_2$-Biphemp (**3**), which has two chiral P-atoms, in addition to atropisomerism. In this case, the probability value associated with the discrimination capability of the enantiomorphic site of the catalyst is not particularly effective ($p_{(Si)ul} > 0.1$) and, apparently, a considerable chain-end control takes place. This result could be associated with the presence of the two chiral P-atoms, in addition to the chirality axis. Particularly impressive is the difference in behavior between the catalytic systems containing (all-*S*)-Mephos-(R_a)-MeO-Biphep (**10**) and (all-*S*)-Mephos-(S_a)-MeO-Biphep (**11**). The calculated concentrations of *l*-diads in the copolymers produced with the two systems are 66.9 and 93.0%, respectively. The former copolymer is the most-atactic, completely regioregular material reported in the literature [10]. Considering that both ligands should have very similar characteristics of basicity, we think that the difference cannot be caused by a change in the regioselectivity of the insertion, but rather by steric factors. A small difference between the relative energies of the four intermediates give a poor sterecontrol, and, thus, an essentially atactic copolymer. The probability values set to describe the peak distribution for each copolymer confirm this hypothesis, with $p_{(Re)ul} > 0.2$ and $p_{(Si)ul} < 0.05$, respectively. The higher stereocontrol observed upon introducing MeO substituents on the biphenyl moiety (ligand **6** *vs.* **1**) indicates that electronic effects are not negligible.

The study of the copolymers produced with catalysts modified by ferrocenyl ligands (**12**–**20**) confirms the results obtained with atropisomeric diphosphines. However, the most-interesting results related to this ligand class was the remarkable increase in stereoselectivity. A trend similar to that observed with the atropisomeric ligands was found, when two cyclohexyl (Cy) groups are attached to each P-atom ($p_{(Re)lk} = 0.992$).

The steric hindrance of the alkyl substituents on the P-atoms seems to play a role also in terms of stereoselection. In the presence of larger alkyl groups (Cy in Josiphos instead of Et groups in JosiphosEt$_2$), a better stereocontrol was observed ($p_{(Re)lk}=0.984$ *vs.* 0.947, resp.). Interestingly, Ph substituents on the stereogenic P-atoms also seem to improve the stereocontrol by the enantiomorphic site ($p_{(Re)lk}=0.984$ *vs.* 0.953, resp.).

When the cyclopentadienyl ring not involved in coordination was fully substituted with Me groups, a decrease in asymmetric induction was observed. The probability value changed from $p_{(Re)lk}=0.984$ (Josiphos) to 0.958 ((*rac*)-Me$_5$Josiphos). To achieve good stereocontrol, the presence of a stereogenic center as well as the planar chirality of the ferrocenyl system appear to be necessary ($p_{(Re)lk}=0.940$ *vs.* 0.984 for **18** and **12**, resp.; $p_{(Re)lk}=0.947$ *vs.* 0.930 for **16** and **19**, resp.).

Changes in reaction conditions seemed to have only a small influence on the stereocontrol of the process. A decrease in the stereoregularity was observed in runs where a different solvent mixture (*t*-BuOH/PhMe/MeOH) and a different counter-ion (use of $BF_3 \cdot Et_2O$) were used. The stereoregularity further decreases when *a*) CH_2Cl_2 was used instead of THF, *b*) in the absence of MeOH, or *c*) when small amounts of H_2 were added (*Table 5*).

No significant differences were found when comparing the ^{1}H- and ^{13}C-NMR spectra of the copolymers obtained with Pd catalysts modified by the optically acitve Josiphos ligand **12** or the racemic variant under otherwise identical reaction conditions. Noteworthyly, there was an increase in stereocontrol by the last inserted unit when TMM (=trimethoxymethane) was absent in the solvent mixture ($p_{(Si)lk}=0.340$ *vs.* 0.100).

Conclusions. – Comparison of the chiroptical properties of propylene–CO copolymers and of propylene–ethene–CO terpolymers, in addition to the NMR characteristics of the former materials, indicates that stereocontrol during propylene insertion into the Pd−CO bond is influenced by both the enantiomorphic site of the catalyst and the enantioface of the last inserted propylene unit. The application of a two-parameter statistic model for the analysis of the deconvoluted ^{13}C-NMR C=O bands for the propylene–CO copolymers allowed us to determine a set of parameters describing stereoselection. In this way, it is possible to correlate the nature of the catalytic system, which is influenced by the molecular characteristics (elements of chirality, electronic and steric features) of the diphosphine ligand, with the prevalence of one of the other factors. The set of probabilities describing the stereoselection of the enantioface of the olefin allows one to calculate the value of all possible *n*-ads.

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