

70. Enantioselective Alternating Olefin-Carbon Monoxide Copolymerization: a New Concept for Activity and Stereoselectivity

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Cationic Pd-complexes modified by dicyclohexyl{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]ethyl}phosphine (**1a**) give very active catalytic systems for the regioregular isotactic specific copolymerization of propene with CO. Other alk-1-enes also give stereoregular and regioregular copolymers, even if with lower productivity. The copolymers are isolated as poly(4-alkyl-tetrahydrofuran-2,2,5,5-tetrayl-2-oxy-2-methylenes) **B** in the solid state and give the isomeric poly(2-alkyl-1-oxopropane-1,3-diyls) **A** by dissolution in (CF₃)₂CHOH. Solid polymer **A** (R = Et) is formed back at least partially when the dissolved material is reprecipitated from MeOH. The use of the related (ferrocenyl)diphosphine ligands **1b–e** and **2** as the catalyst modifier shows that the presence of both elements of chirality and of large substituents on the P-atoms of the ligand is necessary to achieve good stereocontrol, and that the large difference in basicity between the two P-atoms is probably the reason for the good catalytic activity.

Diphosphine-containing cationic Pd-catalysts of the type [PdX₂(P–P)] [1] (X = weakly coordinating or non-coordinating anion, P–P = diphosphine) led to the commercial application of the alternating copolymerization of ethene with CO [2], at least on a pilote-plant scale [3]. To extend the scope of the reaction to other aliphatic olefins, problems related to the regioselectivity [4] and to the stereoselectivity [5] of the copolymerization process must be solved. Even though the requirements of the ligands to achieve the above goals seem to be reasonably well identified [4–7], the catalytic activity of the stereoselective systems investigated remains low, thus hampering potential applications. The most active system for the copolymerization of propene reported so far seemingly contains propane-1,3-diylbis(diethylphosphine) [7] as the modifying ligand. The absence of chirality in this ligand, however, causes formation of a material having a low stereoregularity. Surprisingly, the copolymers of propene [7–10] were not of type **A** (Fig. 1), e.g. poly(2-methyl-1-oxopropane-1,3-diyl) (R = Me), but of type **B**, e.g. poly(tetrahydro-4-methylfuran-2,2,5,5-tetrayl-2-oxy-2-methylene (R = Me)).

The stability of the spiro structure **B** for the olefin-carbon monoxide copolymers seems to be influenced by the degree of substitution of the C=C bond of the olefin substrate [11] [12]. These results imply that the copolymerization mechanism is less simple [8] [9] than expected [1] [13]. In spite of different working hypothesis that may be

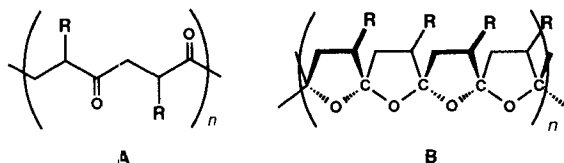


Fig. 1. Possible structures for carbon monoxide-olefin copolymers

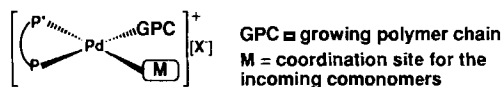


Fig. 2. Model of the catalytically active species for the carbon monoxide-olefin copolymerization

proposed [8] [9] it is generally agreed that the catalytic species contains the chelate ligand and the growing chain (Fig. 2).

In fact, the stereochemical characteristics of the copolymerization reaction correspond to those of an insertion polymerization [3] [14] and, therefore, activation of the two comonomers by the catalyst must be taken into account (Fig. 2, M = CO or olefin). The catalytic systems reported to date contain almost exclusively symmetrical diphosphine ligands ($P = P'$) [15]. However, the use of nonsymmetric ligands ($P \neq P'$) could help achieve better catalytic activities due to proper differences in the *trans*-effect displayed by the two different phosphine moieties. This approach was already applied with success to the Rh-catalyzed asymmetric hydrogenation [16] and led to the successful exploitation of dicyclohexyl{(*R*)-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethyl}phosphine (**1a**) as the chiral ligand in some highly enantioselective catalytic reactions [17]. Moreover, a site-selective π - σ - π isomerisation of $[Pd(\eta^3\text{-allyl})]$ (**1a**)(CF_3SO_3), which seems to be guided by the steric differences between the two halves of **1a**, was recently reported [18].

Ligand	R	R'	R''
1a	Me	cyclo-C ₆ H ₁₁	Ph
b	Me	Et	Ph
c	Me	Ph	cyclo-C ₆ H ₁₁
d	Me	cyclo-C ₆ H ₁₁	cyclo-C ₆ H ₁₁
e	Me	Ph	Ph
2	H	cyclo-C ₆ H ₁₁	Ph

We found now that **1a**, when used as the ligand for the Pd-catalyzed copolymerization of alk-1-enes with CO, gives catalytic systems that are in any respect superior to those previously reported [14]. Productivities in propene copolymer at 50° of up to 600 g · g[Pd]⁻¹ · h⁻¹ are obtained without optimization (see *Exper. Part*). The regioselectivity in the copolymerization process is very high, as expected [6]. The intensity of signals due to head-to-tail (h-t) enchainments in the ¹³C-NMR spectrum amounts to more than 99%. Furthermore, the isotacticity of the produced poly(2-methyl-1-oxopropane-1,3-diyl) is substantially higher than that previously observed using atropisomeric diphosphine ligands [7] [12]. The evaluation is based on the comparison of the intensity of the ¹³C-NMR signals in the region of the C=O and of the Me group as well as on the intensity of the absorption band in the CD spectrum in the region of the n - π^* transition

($\Delta\epsilon = -1.66$ vs. $-1.56 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ at 275 nm in $(\text{CF}_3)_2\text{CHOH}$). As a measure of the isotacticity, we take the content (percentage) of the most intense signal in the region of the C=O group [5] [7].

The same catalytic system is also able to copolymerize but-1-ene and CO, though with lower productivity (*ca.* $40 \text{ g} \cdot \text{g}[\text{Pd}]^{-1} \cdot \text{h}^{-1}$). The copolymer is formed exclusively as poly-(4-ethyltetrahydrofuran-2,2,5,5-tetrayl-2-oxy-2-methylene) (**A**, R = Et). When dissolved in $(\text{CF}_3)_2\text{CHOH}$, this material completely rearranges to poly(2-ethyl-1-oxopropane-1,3-diyl) (**B**, R = Et) and shows essentially complete regioregularity and isotacticity. Treatment of the $(\text{CF}_3)_2\text{CHOH}$ solution of this copolymer with MeOH causes precipitation of **A** (R = Et) contaminated by some **B** (R = Et).

Similarly, poly[tetrahydro-4-(2-methylpropyl)furan-2,2,5,5-tetrayl-2-oxy-2-methylene] (**B**, R = Me_2CHCH_2) is produced from 4-methylpent-1-ene. The productivity is even lower (*ca.* $6 \text{ g} \cdot \text{g}[\text{Pd}]^{-1} \cdot \text{h}^{-1}$) than for but-1-ene. Due to solubility problems, this copolymer is only incompletely characterized as yet; however, it appears to be quite stereoregular. Good productivity (*ca.* $80 \text{ g} \cdot \text{g}[\text{Pd}]^{-1} \cdot \text{h}^{-1}$), combined with good stereocontrol, is also observed in the case of allylbenzene. To get some information on the factors determining the very good performance of ligand **1a** on the copolymerization process, the copolymerization of propene and CO using the related ferrocenyl ligands **1b–e** and **2** was studied. Preliminary results (*Table*) indicate the importance of the following factors: *i*) The presence of a stereogenic center in addition to the planar chirality is essential to achieve a good stereochemical control (ligand **2** vs. **1a**). *ii*) The presence of a bulky dialkylphosphino group at the stereogenic center is also important for the stereoselection process (ligand **1a** vs. **1b**). *iii*) The best results as far as catalytic activity and stereoselectivity are concerned are obtained with the ligand having the larger differences between the electronic characteristics of the two P-atoms (ligand **1a** vs. **1c**). However, ligand **1d** shows a good performance in stereo- and regioregularity, even if the catalytic activity is somewhat lower. *iv*) In contrast to other bis(diphenylphosphino)-substituted ligands [4] [19–21], **1e** exhibits a quite good regioregularity. The stereoregularity remains, however, rather low.

The very efficient enantioface discrimination during the copolymerization process using **1a** as the ligand appears to be determined both by the intrinsic ability of the chiral

Table. Influence of Some Ferrocenyl Ligands on the Copolymerization of Propene with Carbon Monoxide^{a)}

Ligand	Characterization of the copolymer						
	Productivity [g · g[Pd] ⁻¹ · h ⁻¹]	$M_n \cdot 10^{-3}$	Regioregularity [%]			Stereoregularity [%]	$\Delta\epsilon$ [l · mol ⁻¹ · cm ⁻¹]
			h-h	h-t	t-t		
(<i>R</i>)-(S)- 1a ^{b)}	165	6.3	0.5	99	0.5	91	+1.84
(<i>R</i>)-(S)- 1b ^{b)}	88	8.7	1.0	98	1.0	74	+0.86
(<i>R</i>)-(S)- 1c ^{c)}	28	5.6	1.0	98	1.0	78	+0.72
(<i>R</i>)-(S)- 1d ^{c)}	35	3.6	0.0	100	0.0	91	+1.80
(<i>R</i>)-(S)- 1e ^{c)}	38	13.0	1.0	98	1.0	63	+0.11
<i>rac</i> - 2 ^{b)}	40	6.7	1.0	98	1.0	72	–

^{a)} Reaction conditions: propene (0.93 mol), CO (*p* = 80 bar), ligand (0.07 mmol), [Pd(OAc)₂] (0.06 mmol), Ni(ClO₄)₂ · 6H₂O (0.3 mmol), and naphtho-1,4-quinone (3.0 mmol).

^{b)} In THF/MeOH/CH(OMe)₃ (151.5, 8.5, and 2.0 ml, resp.) at 50°.

^{c)} In THF/MeOH (151.5 and 8.5 ml) at 42°.

ligand and by the asymmetric bias of the growing chain. In fact, the intensity of the band in the circular-dichroism (CD) spectrum in the region of the $n\text{-}\pi^*$ transition is smaller for the terpolymers containing ethene (after extrapolation to 100% content in the alk-1-ene) than for the corresponding copolymers of propene and but-1-ene.

Due to the easy manipulation of the ligand under examination with respect to changes in the nature of the substituents on the P-atoms [22] [23], the reported results open new possibilities for effective tailoring of efficient catalysts for the synthesis of copolymers of alk-1-enes with CO.

Experimental Part

General. THF (*Fluka*) was freshly distilled from Na/benzophenone under N_2 . MeOH (*Fluka*) was freshly distilled from Mg under N_2 . ^1H and ^{13}C -NMR Spectra (in soln.): *Bruker AMX 500* (500 and 125.8 MHz, resp.); δ in ppm rel. to SiMe_4 as the internal standard. ^{13}C -NMR Spectra (solid state): *Bruker AMX 400* (400 MHz). CD Spectra ($(\text{CF}_3)_2\text{CHOH}$): *Jasco 600* at 25°; ($\Delta\epsilon$) in $\text{l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$.

Typical Copolymerisation. A mixture of $[\text{Pd}(\text{OAc})_2]$ (0.06 mmol), dicyclohexyl[(*R*)-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethyl]phosphine (**2a**; 0.07 mmol), $\text{Ni}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ (0.3 mmol), and naphtho-1,4-quinone (3.0 mmol) in 151.5 ml of THF, 8.5 ml of MeOH, and 2.0 ml of $\text{CH}(\text{OMe})_3$ was introduced under N_2 in a 500-ml stainless-steel rocking autoclave. Then 39 g of propene was introduced under cooling at -60° . After heating at 50° , CO was pressurized up to 80 bar. The autoclave was kept at 50° for 5 h under stirring. After cooling to r.t. and releasing the unreacted gases, the suspension was added to 500 ml of cold MeOH and left at 4° for 24 h. The copolymer was filtered, washed with MeOH, and dried: 19 g of copolymer. Productivity: $595\text{ g}\cdot\text{g}[\text{Pd}]^{-1}\cdot\text{h}^{-1}$. M_n 5900 (^1H -NMR).

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