Reviews

Cationic Pd^{II}, Ni^{II}, and Ru^{II} complexes in the synthesis of alternating copolymers of CO with vinyl monomers

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The history and state-of-the-art of the synthesis of alternating copolymers of CO with vinyl monomers in the presence of Pd^{II}, Ni^{II}, and Ru^{II} complexes are considered. The influence of P⌒P, P⌒N, and N⌒N mono- and bidentate ligands and the nature of the reaction medium and the acid on the rate of CO copolymerization with ethylene and on the structure and some properties of optically active CO—propylene and CO—styrene copolymers is discussed. A possible mechanism of CO and ethylene copolymerization in the presence of Pd^{II} complexes is proposed.

Key words: palladium(II), nickel(II), and ruthenium(II) cationic complexes, homogeneous catalysis, alternating copolymerization, carbon monoxide, vinyl monomers.

Introduction

The carbon monoxide chemistry is very significant in the mankind´s life. The use of carbon monoxide in organic synthesis started in the 1930s—1940s with the development of large-scale industrial hydroformylation and carbonylation processes and the Fischer—Tropsch synthesis in the presence of metal complex catalysts. However, it was not until the early 1980s that CO could be involved into copolymerization to give high-molecular-weight compounds in good yields. In the last decade, the attention of researchers in the leading scientific centers and companies engaged in the development of new promising polymers has been focused on the search and investigation of catalysts active in copolymerization of CO with various monomers (olefins, dienes, *etc.*). As a rule, this gives strictly alternating copolymers representing a new generation of functional copolymers. Some of them have already found application and their industrial production expands. The ever increasing interest in the alternating copolymerization of CO with various monomers is also indicated by the annually growing number of relevant publications (Fig. 1), ~60% of which are devoted to the synthesis of alternating CO copolymers with olefins, dienes, and styrene and its derivatives (Fig. 2). Only the European patent authority has now granted more than 300 patents for catalyst systems and methods of synthesis of CO-based alternating copolymers and compositions of these copolymers with other polymers.

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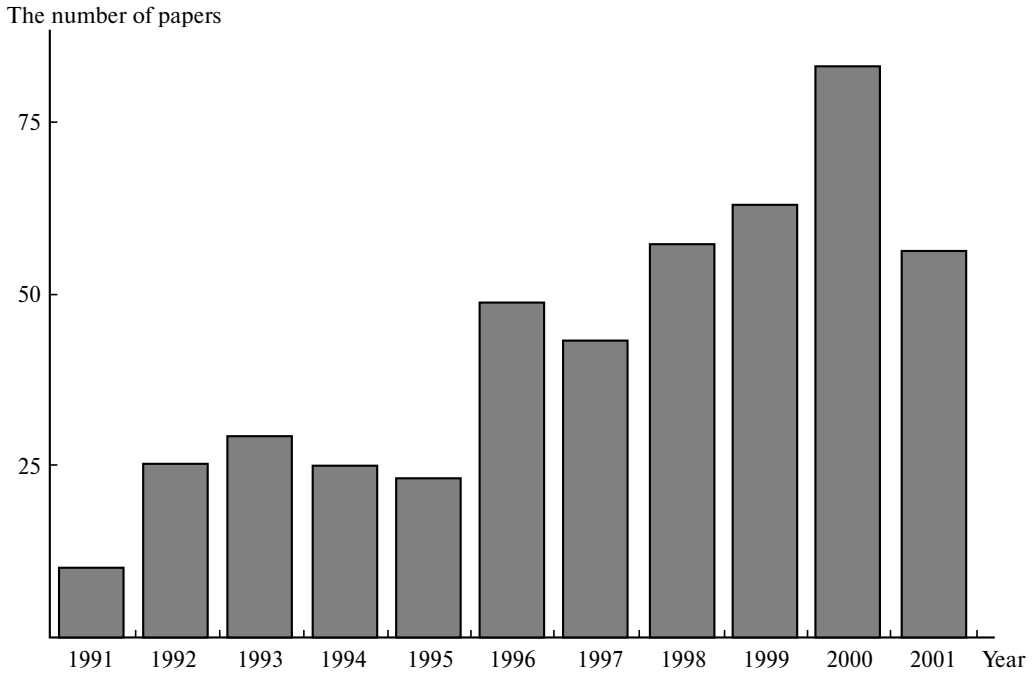


Fig. 1. Chart of publications dealing with copolymerization of CO with various monomers and the properties of copolymers published from 1987 to 2001. The papers published in 1987—1990 are included in the data for 1991. The 2001 value is the number of studies published by August 1, 2001.

It is known that CO is a readily available monomer with a virtually unlimited raw materials source. Modern industrial processes allow the production of synthesis gas with high contents of CO, which can be then concentrated up to a CO content of >99%.[1] The presence of CO strictly alternating with another monomer unit in the copolymer chain increases the polymer susceptibility to photo- and biodestruction,[2,3] extends without limit the scope of copolymer modification by conducting reactions in polymer chains to give new oligomeric and polymeric products with new sets properties,[2] and imparts high adhesive capacity to these polymes and compositions based on them.[4]

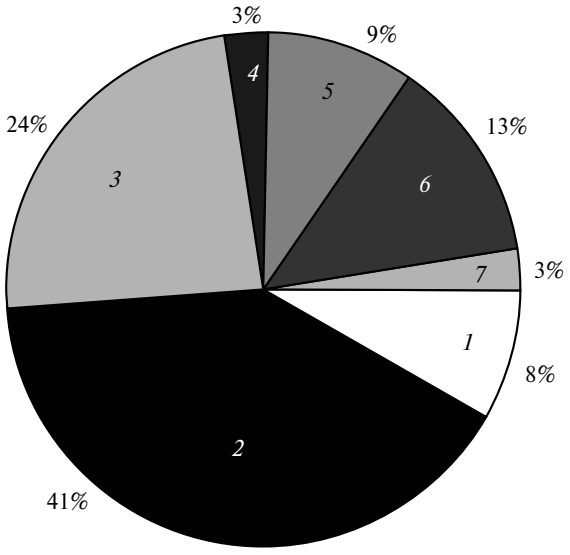


Fig. 2. Percent ratio of the numbers of papers published from 1988 to 2001 dealing with the following topics: copolymerization of diene monomers with CO (*1*), copolymerization of ethylene, propylene, and cyclic olefins with CO (*2*), the properties of alternating copolymers (thermodynamic, physical, chemical, mechanical) (*3*), triple copolymerization of CO (*4*), styrene copolymerization with CO (*5*), palladium-free catalysts (containing other metals) (*6*), copolymerization of CO with various monomers in water (*7*).

The purpose of this review is to analyze the use of Pd^{II}, Ni^{II}, and Ru^{II} cationic complexes in the catalytic synthesis of alternating copolymers of CO with vinyl monomers used most extensively in the polymer synthesis (ethylene, propylene, and styrene) and to consider the possible prospects of this relatively new field of polymer chemistry.

With the use of palladium cationic complexes, it became possible to involve CO into a broad range of reactions with diverse monomers and to synthesize new low- and high-molecular-weight compounds that cannot be prepared by other methods.

The possibility of synthesis of low-molecular-weight CO copolymers with olefins was first reported in 1951.[5] The catalysts used in these processes were $Ni(CN)_2$ and $K_2Ni(CN)_4$. The first synthesis of ethylene—CO alternating copolymers with higher molecular weights, namely, with the number-average molecular weight (M_n) <10000,

Table 1. Data on the catalytic alternating copolymerization of ethylene with CO

Catalyst	Copolymerization conditions			Copolymer yield*	M.p./°C ([η]/dL g^{-1}) or [M_n]	Ref.
	T/°C	Solvent	p/MPa			
$Ni(CN)_2$, $K_2Ni(CN)_4$	100—250	Water	1—10	<1	—**	5
$(Bu_3P)_2PdX_2$ (X = Cl, I)	120—210	MeCN, C_6H_6, EtOH	45—200	≤68	[(7—10)·10^3]	6
$Pd(CN)_2$	90—125	THF, water, toluene	2—4	2—4	—	7
$Pd(PPh_3)_4$	75—125	MeCN, Py	2.5—15	≤14	125—225 (≤9)	8
$(PPh_3)_2PdCl_2$	75—125	MeCN	2.5—15	≤4	210—225	9
$HPd(CN)_3$	75—150	MeCN	2.5—15	≤30	260 (1.4—5.4)	10
$Ni(CN)_2$—*p*-TsOH, BF_3, H_2SO_4, H_3PO_4	100—150	*m*-Cresol, hexafluoroisopropanol (HFIP)	5—10	≤20	[≤20000]	11
$Pd(CN)_2$	50—200	$CH_nX_{3-n}COOH$ (X = Cl, Br, F)	4—7	≤4	[≤500]	12

* The weight (g) of the polymer per g of the catalyst.
** Low-molecular-weight polyketones.

by copolymerization catalyzed by a palladium phosphine complex under a pressure of <200 MPa and at a temperature of >100 °C was described in a patent[6] (Table 1). In subsequent works,[7] $Pd(CN)_2$ was used as the catalyst. The resulting copolymers had melting points of ~250 °C but in some cases, they melted at higher temperatures. The reaction was carried out in both nonpolar (heptane, toluene) and polar (THF, chloroform, water, haloacetic acids, *etc.*) solvents. The use of $Pd(CN)_2$ dissolved in halo-substituted acetic or propionic acids allows the synthesis[12] of low-molecular-weight copolymers (degree of polymerization ≤10) containing halogen and —COOH as the terminal groups. In a patent,[8] the efficiency of the $Pd(PPh_3)_4$ catalyst was found to decrease in the following sequence of solvents: $MeOCH_2CN$ > MeCN > > Me_2NOCH > C_5H_5N > C_6H_6 > $HC(OMe)_3$ > > $MeOCH_2CH_2OMe$ = C_6H_{14}.

The use of the $(PR_3)_2PdXY$ phosphine complexes showed[9] that the catalyst activity decreases in the phosphine sequence PAr_3 > PAr_2R > $PArR_2$. Similar compounds containing nickel, platinum, rhodium, and cobalt are inactive in ethylene—CO copolymerization, while ruthenium phosphine complexes exhibit relatively low catalytic activity.

The use of the hydride form of palladium cyanide[10] allowed the preparation of alternating copolymers of CO with ethylene and propylene at relatively moderate temperatures and pressures, the product yield being higher than that in any of the previous studies. The resulting ethylene and CO copolymers had high molecular weights (MW) (intrinsic viscosity [η] ~5.5 dL g^{-1} in *m*-cresol) and melting points of <260 °C. The yield and the intrinsic viscosity of the copolymers depend substantially on the nature of the reaction medium; the yield increases 50-fold and [η] increases 2-fold over the solvent sequence: water, ethanol, *m*-cresol, acetic acid, methyl ethyl ketone, ethyl acetate.

However, the catalysts for alternating copolymerization of ethylene with CO described in the patent literature required high temperatures (100—200 °C) and provided a relatively low copolymer yields (≤20—70 g per g of Pd). Copolymerization of these monomers at room temperature was accomplished[13] in the presence of the $Pd[MeCN(PPh_3)_3](BF_4)_2$ complex dissolved in $CHCl_3$ under a 5 MPa pressure of an equimolar monomer mixture. The average copolymerization rate did not exceed 10 g (g Pd)$^{-1}$ h^{-1}.

Copolymerization of ethylene with CO

The use[14] of bidentate organophosphorus ligands, instead of monodentate ligands used previously, and acids with pK_a ≤ 2 represented a new stage in the subsequent search for efficient catalysts of the alternating copolymerization of olefins and other vinyl monomers with CO. It was shown that $Pd(OAc)_2$ in combination with bidentate phosphorus-containing ligands and an acid with pK_a ≤ 2 provides active copolymerization of ethylene with CO in MeOH giving rise to a high-molecular-weight alternating copolymer (M_n ≤ 3.0·10^4). The copolymer yield reaches 6000 g per g of Pd^{-1}. Subsequently,[15—17] alternating copolymers of CO with propylene or but-1-ene and terpolymers containing CO, ethylene, and a higher α-olefin have been prepared under similar conditions. The incorporation of a higher α-olefin into an alternating copolymer structure decreases the material melting point. Patent data concerning the synthesis of ethylene and CO copolymers indicate that

$Pd(OAc)_2$—CF_3COOH—1,3-bis(di-2-methoxydiphenylphosphino)propane (**1**) is the most active catalyst system.[18] The copolymerization rate can reach 33000 g (g Pd)$^{-1}$ h^{-1} for a total pressure of 9 MPa. The reaction at a lower pressure and temperature proceeds more slowly and the copolymer yield decreases.

The use of a monodentate organophosphorus ligand (*e.g.*, PPh_3) combined with *p*-toluenesulfonic acid in glacial AcOH produces[19—21] an alternating copolymer of ethylene and CO at a rate of ≤1000 g (g Pd)$^{-1}$ h^{-1}. With bidentate ligands the rate of copolymerization increases several-fold.[22]

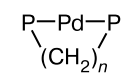
Detailed study[23—27] of the effects of temperature, pressure, and the natures of diphosphine and the acid on the ethylene—CO copolymerization kinetics in the presence of $Pd(OAc)_2$—$PPh_2(CH_2)_nPPh_2$—CF_3COOH (and *p*-$MeC_6H_4SO_3H$ = TsOH) catalyst systems for n = 3 and 4 and on the molecular weights of the resulting copolymers showed that the initial copolymerization rate depends substantially on the nature of the acid (the rate decreases by an order of magnitude as the acid pK_a increases from 0.23 to 1.2) and on the pressure of the equimolar CO—C_2H_4 mixture (the rate increases almost linearly upon a pressure increase in the reaction zone). The nature of the solvent and the acid : Pd and diphosphine : Pd molar ratios exert a more complex influence on the kinetics and the initial rate of copolymerization.

Copolymerization of ethylene and CO catalyzed by $Pd(OAc)_2$ or other Pd complexes is usually carried out in a rather polar medium. Methanol is the solvent of choice. Other solvents such as acetone, THF, methyl ethyl ketone, nitromethane, ethylene glycol or diethylene glycol, diglyme or triglyme, dichloromethane and other chloro-containing solvents can also be used.[28,29] To increase the catalytic activity in any solvent, the presence of methanol or water is required (at least, traces, or perhaps several percent).[29—31] Without these additives, copolymerization has a long induction period and a low rate.[30] Copolymerization can be carried out not only in the liquid phase but also in the gas phase. To this end, $Pd(OAc)_2$ in combination with a diphosphine and HBF_4 is applied on a powder of the ethylene—CO alternating copolymer. When ethylene and CO are copolymerized in the gas phase, the reaction rate is comparable with the rate observed in a methanol solution,[32—35] but the presence of traces of methanol in the reaction zone is obligatory. The use of other polymers (*e.g.*, polypropylene foam)[35] or silica[36] as catalyst supports has also been reported.

Copolymerization in the presence of various palladium-containing complexes, such as $[(Ph_2P(CH_2)_3PPh_2)Pd(MeCN)_2](BF_4)_2$, $[(Ph_2P(CH_2)_3PPh_2)Pd(H_2O)(TsO)](TsO)$, or *trans*-$[P(Cy_3)_2Pd(H)(H_2O)](BF_4)_2$,[29—31,37] proceeds somewhat more slowly; when Pd^{II} acetate is replaced by Ni^{II}, Co^{II}, Cu^{II}, or Ag^{I} acetate, the copolymerization rate decreases by a factor of several tens.[14,38] It has been shown recently[39—42] that the $[Ph_2P(CH_2)_3PPh_2]Pd(OAc)_2$ complex performs copolymerization of ethylene and CO in toluene at a rate of ≤2900 g (g Pd)$^{-1}$ h^{-1} in the presence of *tert*-butylalumoxane in place of an acid.

Instead of the acids used normally (CF_3COOH or *p*-$MeC_6H_4SO_3H$), their copper salts as well as nickel(II), copper(II), iron(II), zirconium(IV), or vanadium(IV) sulfates or perchlorates can be used with equal efficiency.[17,43,44] The copolymerization rate of ethylene and CO decreases[32,43] in the sequence CF_3SO_3H > > $MeC_6H_4SO_3H$ > CF_3COOH > PhCOOH ≈ HBF_4 > > CCl_3COOH > $C_6H_3Cl_2COOH$ > HCl. As the acid strength decreases, the rate of copolymer formation (w) diminishes. However, systematic research is needed to establish a quantitative correlation between w and the acid pK_a. Data on activating effects of perchloric[45] and phosphoric[46] acids have also been published.

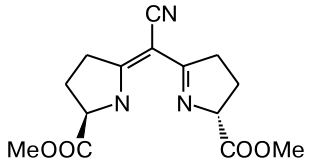
The dependence of the copolymerization rate of ethylene with CO increases[26,43,46—49] in the following sequence of diphosphines: 1,3-bis(diphenylphosphino)methane (**2**) < 1,3-bis(diphenylphosphino)hexane (**3**) < 1,4-bis(methylbutyldiphenylphosphino)butane (**4**) < 1,4-bis(dibutylphenylphosphino)butane (**5**) < < 1,3-bis(diphenylphosphino)ethane (**6**) < 1,3-bis(dibutyldiphenylphosphino)butane (**7**) < 1,3-bis(diphenylphosphino)pentane (**8**) < 1,3-bis(di-*n*-butyldiphosphino)propane (**9**) < 1,3-bis(diphenylphosphino)butane (**10**) < 1,3-bis(diphenylphosphinopropane) (**11**) < **1**. Although no quantitative data on the relationship between w and structural (or other) characteristics of diphosphines are available, it can be suggested that the P—Pd—P angle is one of the significant factors determining the catalytic activity of a Pd diphosphine complex. The angle increases from 74° for n = 1 to 175° for n = 5. All the Pd^{II} diphosphine complexes considered here have a square planar geometry of the coordination unit with *cis*-positions of the P atoms for n = 1—4. As the length of the methylene chain increases ($n \geq 5$), the dimer with *trans*-arrangement of ligands becomes more favorable.



In recent years, various P⌒P derivatives have been used as bidentate ligands; however, the attention of researchers has been focused on the search for novel P⌒N and N⌒N bidentate ligands and the use of some aryl- and fluoro-containing arylboranes or their Na, K, or Li salts instead of acids (CF_3COOH, *p*-$MeC_6H_4SO_3H$, *etc.*).[50—56] Recently, it has been shown[57] that dicationic Pd complexes containing N-heterocyclic carbene ligands and represented generally as {*cis*-$CH_2[N(H)C{=}C(H)N(R)C]_2Pd(NCMe)_2\}(BF_4)_2$

(R = Me, 2,4,6-$Me_3C_6H_2$) carry out copolymerization of ethylene and CO at a rate of ≤810 g (g Pd)$^{-1}$ h^{-1} but are inactive in the copolymerization of CO with propylene or styrene. The rate of CO copolymerization with dienes in the presence of Pd^{II} complexes (*e.g.*, $[Ph_2P(CH_2)_3PPh_2]Pd(OAc)_2$) is comparable with the rate of CO copolymerization with α-olefins.

The ruthenium(II) phosphine complexes, namely, *cis*-{$Ru[\eta^2$-$Ph_2P(CH_2)_2PPh_2]_2(OTs)_2$} and $Ru[\eta^3$-$Ph_2P(CH_2)_3PPh_2]_2(OTs)_2$, exhibit very low activities in the copolymerization of CO with ethylene. However, the addition of trifluoroacetic acid and benzoquinone markedly increases the activity of these catalysts.[58] In this case, apart from the relatively high-molecular-weight product, the process yields a low-molecular weight copolymer soluble in methanol. Formerly, the use of the $Ni[Ph_2PCH{=}C(Ph)(O)(PEt_3)Ph]$ phosphine complex as the catalyst has been studied.[59] More recently,[60,61] Ni^{II} complexes with bidentate N⌒O ligands, NiR(N⌒O)L (N⌒O = 4-nitropyridine-2-carboxylate, 2-pyridinecarboxylate, 4-methoxypyridine-2-carboxylate, L = PPh_3, R = *o*-tolyl), and allylic Pd^{II} complexes with bis-phosphine oxide ligands {(MeCN)(Me)Pd[κ^2P,O—$Ar_2P(CH_2)_nP(O)Ar_2$]}X (*n* = 1—3, X = BF_4, Ar = Ph, *p*-Tol, SbF_6), {(η^3-C_3H_5)Pd[κ^2P,O—$Ph_2P(CH_2)_nP(O)Ph_2$]}X (*n* = 2, X = Ts, OTf) have been synthesized. These complexes also exhibit[14,18] lower catalytic activities than Pd-containing catalyst systems. Nevertheless, the attempts to synthesize Ni complexes capable of conducting efficient copolymerization of CO with olefins deserve attention by themselves, first of all, due to the high cost of palladium. The recently synthesized[62,63] aryl complexes Ni(*o*-Tol)(PPh_3) with bidentate N⌒N-chelating (**A**) and new N⌒O-chelating (**B**) ligands ensure copolymerization of CO with ethylene at a rate of ≤2300 g (g Ni)$^{-1}$ h^{-1}.



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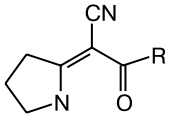


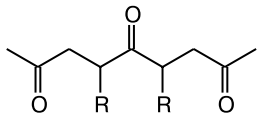
B

R = Me, OMe, Ph, CF_3, C_3F_7, C_7H_{15}

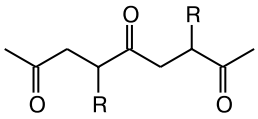
Copolymerization of propylene with CO

The use of propylene, higher α-olefins, styrene, or its derivatives, instead of ethylene, in the copolymerization with CO brings about three factors to influence the structure of the resulting copolymer, namely,

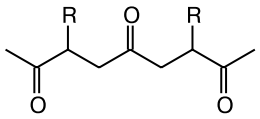
(1) regioselectivity caused by the options of olefin addition according to the head-to-head, head-to-tail, or tail-to-tail pattern;



Head-to-head

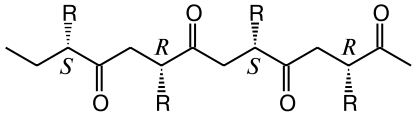


Head-to-tail

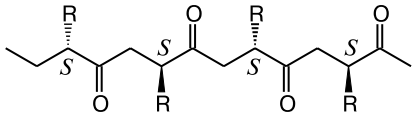


Tail-to-tail

(2) tacticity, *i.e.*, the formation of either iso- or syndiotactic structure;



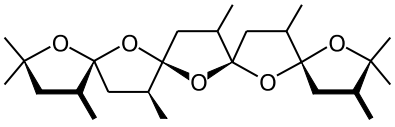
Syndiotactic copolymer



Isotactic copolymer

(3) enantioselectivity; the isotactic copolymer is chiral, therefore, it can exist as two enantiomers, *RRRR* and *SSSS*.

An unusual feature in copolymerization of α-olefins (styrene and its derivatives or some diene monomers) with CO is the formation of copolymers having a spiroketal structure[64,65] (**C**). Most often, this is the case when the reaction is carried out at a low temperature (for propylene), while in the copolymerization of CO with higher α-olefins (for example, hept-1-ene), the spiroketal structure is formed, in addition to the usual 1,4-ketone structure,[66] even when copolymerization is carried out at 50 °C.



C

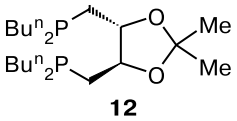
The activity of propylene in the copolymerization with CO is approximately an order of magnitude lower than the ethylene activity. With the $Pd(OAc)_2$—CF_3COOH—**11** catalyst system, the rates of CO copolymerization with ethylene, propylene, and but-1-ene under comparable conditions equal[15] 6000, 400, and 250 g (g Pd)$^{-1}$ h^{-1}, respectively. A similar dependence has been found for the catalytic copolymerization of ethylene with α-olefins involving heterogeneous and most of homogeneous Ziegler—Natta catalysts and for copolymerization of CO with ethylene, propylene, and hept-1-ene in the pres-

ence of the $\{[Ph_2P(CH_2)_3PPh_2]Pd(MeCN)_2\}(BF_4)_2$ complex in a nitromethane—methanol solution. Over the series of diphenylphosphinealkanes $Ph_2P(CH_2)_nPPh_2$, the highest rate of copolymerization of olefins with CO is observed for phosphines with $n = 3$ and 4, which is also true for ethylene copolymerization with CO. The activity of the $Pd(OAc)_2$—*p*-$MeC_6H_4SO_3H$ catalyst in the copolymerization of propylene with CO increases[48] in the following sequence of phosphines: **11** < **9** < **4**.

Olefins with internal double bonds can also be involved in the copolymerization with CO. Thus using $[Pd(Me\text{-}DUPHOS)(MeCN)_2](BF_4)_2$ catalyst (DUPHOS is 1,2-bis-2,5-dimethylphosphanobenzene), it was shown[66] that the activity of *cis*-but-2-ene is approximately an order of magnitude lower than that of but-1-ene. The process yields an isotactic optically active oligomer with $M_n = 600$, whereas copolymerization of CO with but-1-ene affords a copolymer with $M_n = 4.0 \cdot 10^4$, which contained both 1,4-ketone and spiroketal structures. It is assumed that during copolymerization, *cis*-but-2-ene is isomerized into but-1-ene. It is also noted that *trans*-but-2-ene is inactive in copolymerization with CO.

The alternating copolymerization of CO with α-olefins, styrene and its derivatives, dienes, and some other monomers, catalyzed by chiral palladium complexes, is a promising method for the preparation of optically active copolymers. This is favored by two factors: (1) the backbone chirality can be ensured by using prochiral monomers and (2) the presence of ketone groups in the chain facilitates further functionalization of these polymers.

Copolymers of propylene and CO prepared using bidentate arylphosphine ligands have a low regioregularity. The use of enantiopure symmetrical (C_2) alkyl-substituted and other diphosphines **1** and **12—19** allows one to increase the regioregularity of the synthesized copolymers, which possess high optical activity dependent on the ligand nature (Table 2). Both dextro- and levorotatory stereoisomers can be prepared. Other co-monomers that can be involved in copolymerization with CO to give optically active copolymers include higher α-olefins (but-1-ene, hex-1-ene, 4-methylpent-1-ene, cyclopentene, *cis*-but-2-ene),[68,69] vinyl alcohols and carboxylic acids,[70] allylbenzenes,[71] and hexa-1,5-diene.[72,73]



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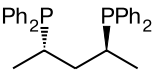

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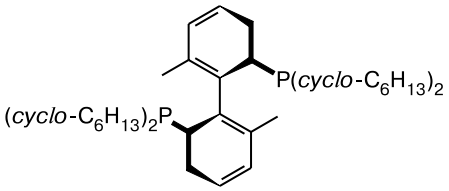

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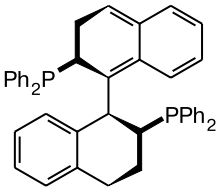

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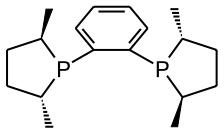

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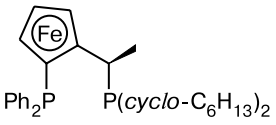

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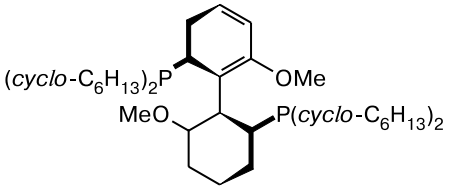

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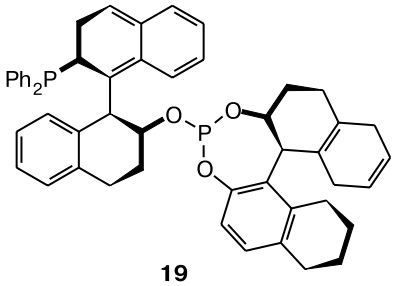


19

Copolymerization of styrene with CO

Primary attention was devoted to enantioselective copolymerization of CO with styrene and its alkylated derivatives. This was done using bidentate P⌒N and N⌒N ligands (**20—27**).[74—78] By copolymerization of CO with styrene, not only an isotactic (Table 3) but also a syndiotactic copolymer can be prepared. The latter type of polymer is synthesized using ligands **24—27** based on phenanthroline **24**,[51,79—81] dipyridine,[78,79,81] pyridineimine **25**,[82] pyridyloxazoline **26**,[75] and diimine **27** [83] derivatives. Previously,[78] it was shown that replacement of bis-oxazoline ligand in the cationic Pd complex **14** by the achiral dipyridine ligand provides the possibility of preparing optically active iso- and syndiotactic stereoblock copolymer.

Despite the existence of many experimental data (see Figs. 1 and 2) on the alternating copolymerization of CO with various monomers on Pd catalysts, it is impossible yet to formulate the general conditions for controlling the regio- and stereoselectivity of the copolymerization of CO with olefins or styrene. One can only note that

Table 2. Isotactic copolymerization of propylene with CO [67]

Ligand/ catalyst[a]	Copolymer yield[b]	Copolymer properties		
		$[\alpha]_D^{25}$ (solvent)	M.p./°C ($\Delta\varepsilon$/L mol^{-1} cm^{-1}) or [M_n]	Structure[c]
1/I	93	+6.6 (HFIP)	—	—
1/II	500	−7[d] (CH_2Cl_2)	—	H—T (78%)
12/I	703	+10.4 (HFIP)	—	—
13/II	630	−29[d] (CH_2Cl_2)	—	H—T (78%)
14/I	—[e]	+26	245 (−1.56)	Regioregular polymer
15/II	300	+36[d] (CH_2Cl_2)	—	H—T (66%)
16/II	1462	+70 ($CHCl_3$), −30 (HFIP)	[36000]	—
17/I	2975	—	(1.84) [63000]	H—T (99%)
18/I	391	−29.1 (HFIP)	237 (1.73) [69000]	H—T (100%)
19/III	284	+57.2[f] (HFIP)	164 [65000]	H—T (100%)

[a] The following catalysts have been used: $Pd(OAc)_2$, $Ni(ClO_4)_2$, naphthaquinone (I); $[Pd(MeCN)_2](BF_4)_2$ (II) and Pd(1,5-*cyclo*-C_8H_{12})(Cl)(Me), Na{B[3,5-$(CF_3)_2C_6H_3]_4$} (III).
[b] The weight (g) of the polymer per g of Pd.
[c] H stands for head and T stands for tail.
[d] The $[\alpha]_D^{20}$ value is given.
[e] Unknown.
[f] The $[\alpha]_D^{24}$ value is given

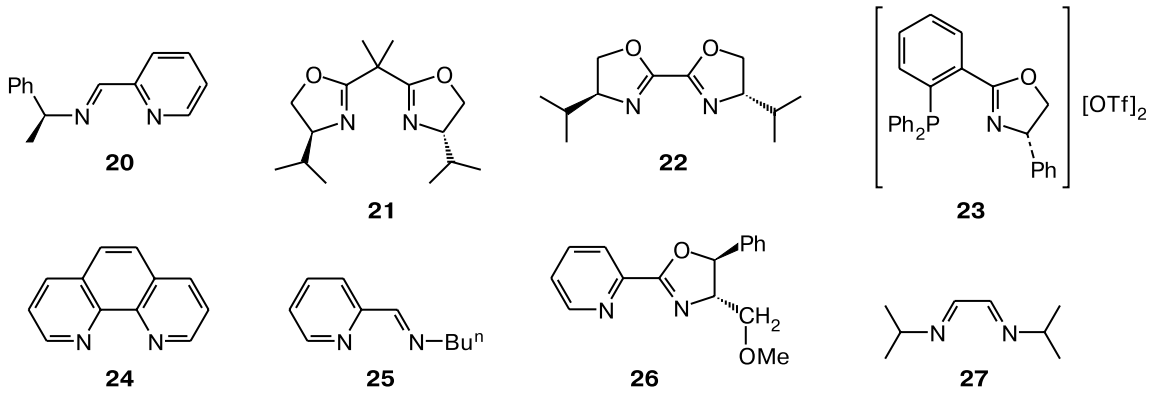
Table 3. Isotactic copolymerization of styrene and its alkylated derivatives and CO [67]

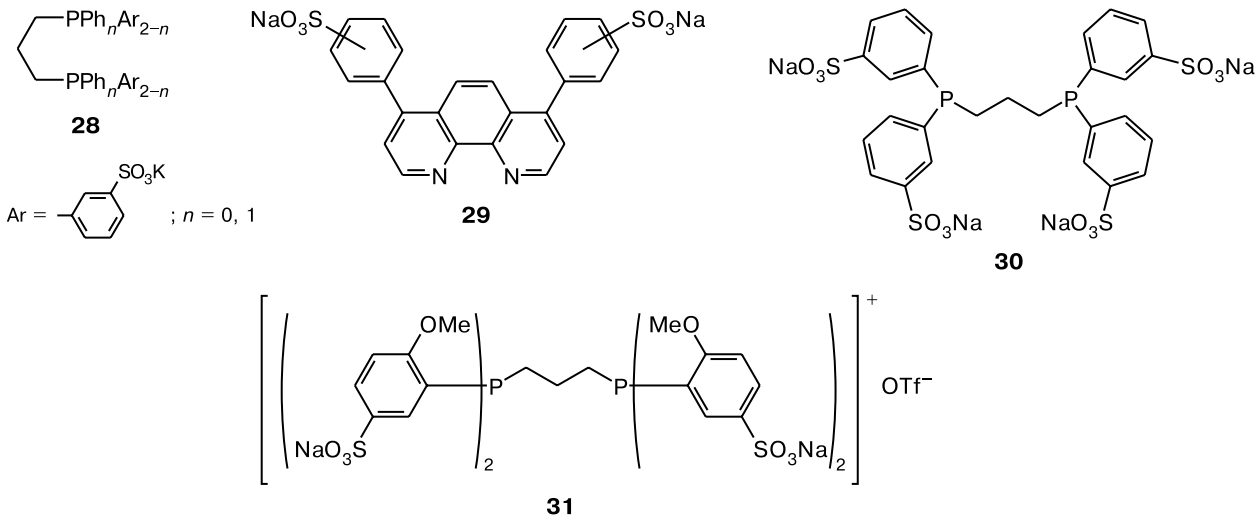
Ligand	Alk	Copolymer yield[a]	Copolymer properties	
			$[\alpha]_D^{25}$ (solvent)	M_n
20	H	—[b]	−16[c] (CH_2Cl_2)	5600
	Me	—[b]	−14[c] (CH_2Cl_2)	14000
21	Bu^t	179	−284 (CH_2Cl_2)	26000
22	H	13	−348 ($Cl_2HCCHCl_2$)	—
	Me	66	−350 (CH_2Cl_2)	—
23	H	—[b]	−403 (HFIP/$CHCl_3$)	—

[a] The weight (g) of the polymer per g of Pd.
[b] Unknown.
[c] The $[\alpha]_D^{20}$ value is given.

catalysts containing 1,10-phenanthroline form copolymers with a syndiotactic structure. The use of enantiopure bis(dihydrooxazoles) or hydrid(dihydrooxazole)phosphine ligands with C_2 symmetry makes it possible to prepare highly isotactic optically active CO—styrene copolymers, whereas analogous ligands with C_1 symmetry provide copolymers with essentially syndiotactic structures.

Of high practical interest are bidentate P⌒P, P⌒N, or N⌒N ligands (**28—31**), which form water-soluble Pd^{II} complexes active in the alternating copolymerization of CO with various monomers. The possibility of such copolymerization in an aqueous medium has been reported in a publication[84] where the potassium and sodium sulfonates **28** and **29** were used as ligands. However, the rate of CO copolymerization with ethylene and propylene in water is ~10 times lower than in methanol. Recent publications[85—87] describe the synthesis of Pd^{II} complexes with new water-soluble ligands (**30**, **31**), which ensure a rate of CO copolymerization with ethylene equal to ≤32000 g (g Pd)$^{-1}$ h^{-1}. The resulting copolymers had





a rather high MW (M_n = 69200) and a narrow molecular-weight distribution (M_w/M_n = 1.9—2.0, where M_w is the weight-average molecular weight).

The mechanism of alternating copolymerization of CO with ethylene

It can be assumed on the basis of indirect data that the concentration of catalytically active sites is much lower than the total concentration of palladium compounds in the reaction system. Let us consider in more detail the possible steps of CO copolymerization with ethylene in relation to the catalyst system studied most comprehensively, $Pd(OAc)_2$—diphosphine—acid (Scheme 1).

When the catalyst is formed *in situ* in a homogeneous phase, reactions (1)—(7) can proceed between the catalyst components, depending on the nature of the solvent (alcohol, water, or a less polar hydrocarbon). At this stage, in the case of an alcohol medium, the catalytically active species will be represented by the methoxyl palladium complex (reaction (2)), existing in a dynamic equilibrium with the inactive Pd complex at a diphosphine : Pd molar ratio of > 1 .[88] In an aqueous medium and in other moisture-containing solvents, the formation of Pd hydride complexes is possible (reaction (4)). The formation of palladium hydride species can also occur by reactions (3), (5), and (6).

The initiation of the polymer chain in the solution, *i.e.*, the primary insertion of the CO or C_2H_4 molecule into the Pd-alkyl or Pd-acyl complex, respectively, has been studied rather comprehensively.[89—95] Recently, this process, along with the chain propagation reaction with the $[Ph_2P(CH_2)_3PPh_2]Pd(Me)(OSO_2CF_3)$ heterogeneous mononuclear complex has been studied using the polarization-modulated absorption IR spectroscopy;[96] this allowed visual representation of the changes in the IR spectra induced by successive insertion of CO and ethylene molecules. The L_2PdH^+ hydride species arising during the catalyst formation and especially during the subsequent steps (chain termination and transfer) can be converted again into catalytically active species by reactions (10), (11), and (13).

Depending on the nature of the initiating complex, L_2PdOMe^+ or L_2PdH^+, the growing polymer chain will have either a methoxyl or an ethyl group at one end (reactions (14)—(16)). When the polymer chain is transferred to an alcohol molecule (*via* either protonolysis or alcoholysis reaction), the other end can contain either a methoxyl or an ethyl group. In these cases, diester (reaction (17)), keto ester (reaction (18)), or diketone (reaction (19)) type copolymers can be formed. Recently,[97] it was found that in the homogeneous phase, when the length of the growing polymer chain does not exceed 500, chain transfer and termination proceed mainly by protolysis of the active site, whereas at higher molecular weights (when the system becomes heterogeneous due to precipitation of the resulting polymer), both protonolysis and alcoholosis take place. Determining the rates of these reactions depending on the type of the catalyst and copolymerization conditions requires further systematic research. Copolymerization carried out in aprotic solvents is subject to spontaneous chain termination (reactions (20) and (21)); in this case, one end of the polymer chain contains a vinyl group.

Despite the apparent difference between the palladium(II) complexes used in alternating copolymerization of CO with various monomers and the well-known Ziegler—Natta catalysts including metallocenes, the following common features can be noted (Table 4).[98]

1. An electrophilic metal cation and a weakly coordinating anion are present in the reaction zone.

2. The coordination number of metal cations is four. The Ziegler—Natta catalyst contains, most often, a tetravalent metal and four anionic ligands including two

Scheme 1

Formation of active sites

$$Pd^{2+} + L_2 \longrightarrow L_2Pd^{2+} \quad (1)$$

$$L_2Pd^{2+} + MeOH \longrightarrow L_2PdOMe^+ + H^+ \quad (2)$$

$$L_2PdOMe^+ \longrightarrow L_2PdH^+ + CH_2O \quad (3)$$

$$L_2Pd^{2+} + CO + H_2O \longrightarrow L_2PdH^+ + CO_2 + H^+ \quad (4)$$

$$L_2Pd^{2+} + C_2H_4 + MeOH \longrightarrow L_2PdH^+ + CH_2{=}CHOMe + H^+ \quad (5)$$

$$L_2Pd^{2+} + H_2 \longrightarrow L_2PdH^+ + H^+ \quad (6)$$

$$L_2Pd^{2+} + CO \longrightarrow L_2PdCO^{2+} \quad (7)$$

Initiation

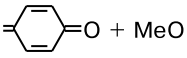
$$L_2PdOMe^+ + CO \longrightarrow L_2PdCOOMe \quad (8)$$

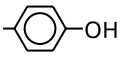
$$L_2PdOMe^+ + C_2H_4 \longrightarrow L_2PdCH_2CH_2OMe^+ \quad (9)$$

$$L_2PdH^+ + C_2H_4 \longrightarrow L_2PdEt^+ \quad (10)$$

$$L_2PdH^+ + CO + MeOH \longrightarrow L_2PdCOOMe^+ + H_2 \quad (11)$$

$$L_2PdCO^{2+} + MeOH \longrightarrow L_2PdCOOMe^+ + H^+ \quad (12)$$

L_2PdH^+ +  + MeOH $\longrightarrow$

$\longrightarrow L_2PdOMe^+$ +  (13)

Chain propagation

$$L_2PdCOOMe^+ + C_2H_4 \longrightarrow L_2PdCH_2CH_2COOMe^+ \quad (14)$$

$$L_2PdCH_2CH_2OMe^+ + CO \longrightarrow L_2PdCOCH_2CH_2OMe^+ \quad (15)$$

$$L_2PdEt^+ + CO \longrightarrow L_2PdCOEt^+ \quad (16)$$

Chain transfer

$$L_2Pd(COCH_2CH_2)_nOMe^+ + MeOH \longrightarrow L_2PdH^+ + MeO(COCH_2CH_2)_nOMe \quad (17)$$

Diester

$$L_2Pd(COCH_2CH_2)_nOMe^+ + MeOH \longrightarrow L_2PdOMe^+ + H(CH_2CH_2CO)_nOMe \quad (18)$$

Keto ester

$$L_2Pd(COCH_2CH_2)_nEt^+ + MeOH \longrightarrow L_2PdOMe^+ + H(CH_2CH_2CO)_nEt \quad (19)$$

Diketone

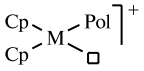
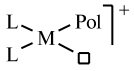
Chain termination

$$L_2Pd(COCH_2CH_2)_nOMe^+ \longrightarrow L_2PdH^+ + CH_2{=}CHCO(CH_2CH_2CO)_nOMe \quad (20)$$

$$L_2Pd(COCH_2CH_2)_nEt^+ \longrightarrow L_2PdH^+ + CH_2{=}CHCO(CH_2CH_2CO)_nEt \quad (21)$$

L_2 is a bidentate ligand.

Table 4. Comparison of catalysts for the synthesis of polyolefins (*A*) and CO—olefin alternating copolymers (*B*)[98]

Parameter	*A*	*B*
Metal ion	Ti^{IV}, Zr^{IV}, Hf^{IV}	Pd^{II}
Ligands	2 Cp^-, 2 X^-	2 L, 2 X^-
Anions	Noncoordinating	Weakly coordinating or noncoordinating
Geometry	Tetrahedral	Square planar
Structure of the active site*		

* Pol is the polymer chain.

strongly coordinated anions (*e.g.*, Cp ligands) and two weakly coordinated anions. The Pd catalyst is a divalent compound containing two neutral and two weakly coordinated anionic ligands.

3. The active sites of both types of catalyst require the *cis*-structure of the catalytically active complex during chain propagation and monomer coordination to the vacancy. In a d^0-metallocene complex, the *cis*-configuration is stipulated by the pseudo-tetragonal coordination environment of the metal. In the square-planar Pd^{II} d^8-complex, the *cis*-structure is ensured by the presence of neutral ligands.

* * *

Although efficient catalysts for the alternating copolymerization of CO and ethylene were discovered[14] at

the Shell company quite recently, CO- and ethylene-based copolymers, so-called aliphatic polyketones, are already produced on an industrial scale.[4] They represent a new class of engineering plastics having high melting points (220—260 °C), good adhesion to organic and inorganic materials, high structural strength and chemical stability.

Of indubitable interest is the search for catalysts able to carry out copolymerization of CO with olefins and other vinyl monomers in the aqueous and gas phases. From the practical standpoint, studies aimed at the development of catalysts based on nickel and cobalt compounds are equally promising.

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