Palladium Complexes as Catalysts for the Synthesis of Functional Polymers Based on Carbon Monoxide

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Abstract—A review of the history and present state of the use of palladium complexes in the synthesis of alternating CO copolymers with different monomers (mainly ethylene, propylene, and styrene) is presented. The effect of mono- and bidentate phosphine ligands, the nature of reaction medium and acid on the rate of the CO copolymerization with ethylene, and the effect of different bidentate P^P, P^N, and N^N ligands on the structure and properties of chiral CO–propylene and CO-styrene copolymers are considered.

The chemistry of carbon monoxide, one of the most important small C_1 molecules, plays an important role in human life. The history of CO use in organic synthesis dates back to the 1930–1940s, when large-scale industrial processes of hydroformylation, carbonylation, and Fischer–Tropsch synthesis based on catalysis by metal complexes were developed. However, the use of CO in copolymerization reactions resulting in the formation of high-molecular compounds with high yields was unsuccessful until the 1980s. During the last decade, researchers from leading scientific centers and companies involved in new promising polymer syntheses gave attention to the search for and study of catalysts capable of carrying the copolymerization of CO with different monomers (olefins, dienes, and others). In these syntheses, strictly alternating copolymers are usually formed, which are new-generation functional copolymers. Some of them have already found applications and their production is expanding.

Carbon monoxide is a readily available monomer that can be produced in virtually unlimited amounts. Currently, commercial processes are available for producing syngas with a high concentration of CO and its further isolation [1]. The strict alteration of CO and the other monomeric unit in a polymer chain provides several advantages:

– It enhances the photo- and biodegradability of a polymer;

– It expands the capabilities of copolymer modification by carrying reactions in polymer chains and obtaining new oligomeric and polymeric properties with a new set of properties; and

– It makes these polymers and compositions based on them more adhesive.

Alternating copolymers of ethylene and CO with a molecular weight (M) of up to 10000 g/mol were first obtained by Gouch [2], who applied a palladium phosphine at 200 MPa and temperature above 100°C. More recently, Fenton [3] used $Pd(CN)_2$ as a catalyst. Synthesized copolymers had a melting point of ~250°C, but in some cases polymers with higher melting points were obtained. Nonpolar (heptane and toluene) and polar (THF, chloroform, water, halogenated acetic acid, etc.) solvents were used. Nozaki [4] showed that the efficiency of the $Pd(PPh_3)_4$ catalyst decreases in the following series of solvents: $CH_3OCH_2CN > CH_3CN > (CH_3)_2NOCH > C_5H_5N > C_6H_6 > HC(OCH_3)_3 > CH_3OCH_2CH_2OCH_3 = C_6H_{14}$.

In the case of another palladium phosphine derivative $(PR_3)_2PdXY$, the catalyst activity decreases in the following series of phosphines: $P(Aryl)_3 > P(Aryl)_2R > P(Aryl)R_2$ [5]. The corresponding nickel, platinum, rhodium, and cobalt compounds do not catalyze the copolymerization of ethylene and CO. The phosphine complexes of ruthenium show a low catalytic activity. The use of the hydride form of palladium cyanide made it possible to obtain alternating polymers of carbon monoxide and ethylene or propylene at moderate temperatures with a high yield compared to previous yields [6]. Polymers formed in this reaction had a high characteristic viscosity ($[\eta]$ up to 5.5 dl/g in *m*-cresol) and a melting point of up to 260°C. The reaction medium affected substantially the characteristic viscosity of polymers. The yield of the polymer decreased in the following series of solvents: ethyl acetate > methyl ethyl ketone (MEK) > without a solvent > acetic acid > cyclohexane > dimethoxyethane > hexane > chloroform > *m*-cresol > acetonitrile > ethanol > cyclohexene > water. The characteristic viscosity decreased in the following series: cyclohexane > ethyl acetate > chloroform > without a solvent > hexane > cyclohexene > MEK > acetic acid > acetonitrile > ethanol > dimethoxyethane.

The use of $Pd(CN)_2$ in the medium of halogenated acetic or propionic acid made it possible to obtain low-molecular copolymers (the extent of polymerization lower than 10) terminated by a halogen or –COOH [7].

However, patented catalysts for the alternating copolymerization of ethylene and CO required a high temperature (100–200°C) and the yields were relatively low ($\leq$20–70 g (g Pd)$^{-1}$ h^{-1}). The first report on the copolymerization of these monomers at room temperature appeared in 1982 [8]. The reaction was carried out in the presence of the $Pd[(CH_3CN)(PPh_3)_3](BF_4)_2$ complex in the medium of $CHCl_3$ and the pressure of the equimolar monomer mixture of 5 MPa. The average rate of copolymerization was at most 10 g (g Pd)$^{-1}$ h^{-1}.

A new stage in all further searches for efficient catalysts for the alternating copolymerization of olefins (and other vinyl monomers) with carbon monoxide was marked by the use of bidentate organophosphorus ligands instead of usual monodentate ligands, as well as the use of acids (p$K_a \leq 2$) [9]. It was shown that $Pd(CH_3COO)_2$ together with phosphorous-containing bidentate ligands and an acid with p$K_a \leq 2$ actively catalyzes the copolymerization of ethylene and CO to form a high-molecular alternating copolymer with molecular weights of up to 3.0×10^4 g/mol). The yield of the copolymer reached 6000 g (g Pd)$^{-1}$ h^{-1}. More recently, it was found that alternating copolymers of CO and propylene or butene-1, as well as triple copolymers containing CO, ethylene, and higher α-olefin can be obtained under analogous conditions [10–12]. The inclusion of higher α-olefin in the structure of the alternating copolymer results in a decrease in the melting point. Patent data on the synthesis of ethylene–CO copolymers indicate that the most active catalytic system is $Pd(CH_3COO)_2$–CF_3COOH–1,3-bis(di-2-methoxydiphenylphosphino)propane (**I**) (henceforth, Roman numerals denote phosphine ligands) [13]. In this case the rate of copolymerization may reach 33000 g (g Pd)$^{-1}$ h^{-1} at a total pressure of 9 MPa. Copolymerization at a lower temperature and a lower pressure results in a decrease in the rate of copolymerization and the copolymer yield.

The use of monodentate organophosphorus ligand (e.g., PPh_3) together with p-toluylsulfo acid in the medium of glacial acetic acid makes it possible to obtain an alternating copolymer of ethylene and CO at a rate of 1000 g (g Pd)$^{-1}$ h^{-1} [14–16]. However, the use of bidentate ligands in this case increases the copolymerization rate several times.

A detailed study of the effects of temperature, pressure, the nature of diphosphine and acid on the kinetics of ethylene and CO copolymerization, as well as the molecular weight of copolymers was reported in [17–20] using the catalytic systems $Pd(CH_3COO)_2$–$PPh_2(CH_2)_nPPh_2$–CF_3COOH (and p-$CH_3C_6H_4SO_3H$), where $n = 3$ and 4.

The process of ethylene and CO copolymerization under the action of $Pd(CH_3COO)_2$ and different palladium complexes is usually carried out in a polar medium. Methanol or other solvents such as acetone, THF, MEK, nitromethane, ethylene glycol, diethylene glycol, diglyme, and triglyme are preferable [21, 22]. For a better catalytic activity in these solvents, the presence of at least traces or several percent of methanol or water is necessary [22–24]. In their absence, a long induction period and a low copolymerization rate are observed [23]. Vavasori and Tonilio [25] were first to study a promoting effect of water microscopic amounts on the yield of copolymer in the presence of the catalytic system $Pd(CH_3COO)_2$–p-$CH_3C_6H_4SO_3H$–$PPh_2(CH_2)_3PPh_2$ (**II**). The reaction of copolymerization can be carried out not only in the liquid phase, but also in the gas phase. When $Pd(CH_3COO)_2$ together with diphosphine and HBF_4 are supported on the powder of the alternating CO–ethylene copolymer and the reaction of ethylene copolymerization with CO in the gas phase, the rate is comparable with the rate of reaction in methanol [26–29]. The presence of methanol traces is necessary in this case. It was reported that other organic polymers [29] or silicon oxide [30] can also be used as catalyst support. Copolymerization in the presence of different individual palladium complexes [22–24, 31] is characterized by a somewhat lower reaction rate, and the replacement of palladium acetate by nickel, cobalt, copper, or silver acetate leads to a lower rate of copolymerization by several tens of times [9, 32]. Recently, it was shown that, in the case of palladium diphosphine complexes, the copolymerization of ethylene and CO can be carried out in the medium of toluene at a rate of 2900 g (g Pd)$^{-1}$ h^{-1} when $tert$-butylalumoxane is used instead of acid [33–36].

Instead of the acids that are usually used (CF_3COOH or p-$CH_3C_6H_4SO_3H$), copper salts or nickel, copper, iron, zirconium, or vanadium sulfates or perchlorates can be applied with the same efficiency [12, 37, 38]. It was shown that the rate of ethylene–CO copolymerization decreases in the series $CF_3SO_3H > CH_3C_6H_4SO_3H > CF_3COOH > C_6H_5COOH \approx HBF_4 > CCl_3COOH > C_6H_3Cl_2COOH > HCl$ [26, 37]. The activating effect of perchloric [39] and phosphoric [40] acids was reported.

The rate of ethylene copolymerization with CO increases in the following series of diphosphines:

1,3-bis(diphenylphosphino)methane (**III**)

< 1,3-bis(diphenylphosphino)hexane (**IV**)

< 1,4-bis(methylbutyldiphenylphosphino)hexane (**V**)

< 1,4-bis(dibutylphenylphosphino)butane (**VI**)

< 1,3-bis(diphenylphosphino)ethane (**VII**)

< 1,3-bis(dibutyldiphenylphosphhino)butane (**VIII**)

< 1,3-bis(diphenylphosphino)pentane (**IX**)

< 1,3-bis(di-n-butyldiphosphino)propane (**X**)

< 1,3-bis(diphenylphosphino)butane (**XI**)

< $PPh_2(CH_2)_3PPh_2$ (**II**)

< 1,3-bis(di-2-methoxydiphenylphosphino)propane (**I**) [20, 37, 40–43].

The rate of copolymerization usually decreases with time and the molecular weight increases. The catalyst retains its activity for a long time and copolymerization can be continued on the filtrate after separating the copolymer [44]. It is noted that the addition of some oxidants (e.g., quinones) to the catalytic system leads to an increase in the copolymer yield [20, 25, 45].

It has been reported recently that, along with the use of different P^P bidentate ligands, researchers give attention to the search for new P^N and N^N bidentate ligands and the use of some aryl and fluorine-containing arylborane and their sodium, potassium, and lithium salts instead of acids (CF$_3$COOH, p-CH$_3$C$_6$H$_4$SO$_3$H, etc.) [46–51]. It was shown that dicationic palladium complexes containing N-heterocyclic carbenium ligands with a general formula [cis-CH$_2$\{N(H)C=C(H)N(R)C\}$_2$ · Pd(NCCH$_3$)$_2$](BF$_4$)$_2$, where R = CH$_3$, 2,4,6-(CH$_3$)$_3$–C$_6$H$_2$, catalyze ethylene–CO copolymerization at a rate of 810 g (g Pd)$^{-1}$ h^{-1} [52], but these compounds are inactive in CO–propylene copolymerization with propylene or styrene.

When ethylene is replaced by propylene or higher α-olefins (as well as styrene or its derivatives) in copolymerization with CO, one should take into account that three factors may appear that affect the structure of the copolymer formed:

– regioselectivity stipulated by the possibility of olefin addition according to the head-to-head, head-to-tail, and tail-to-tail types:


Head-to-tail   Tail-to-tail

Head-to-head
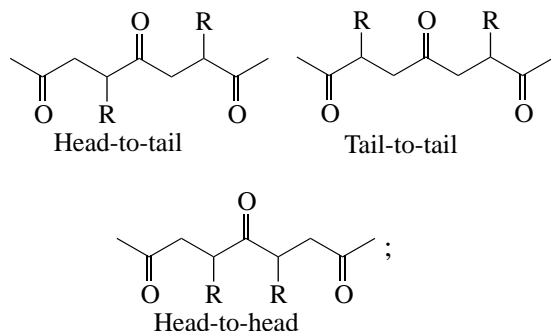
– isotacticity and syndiotacticity:

Syndiotactic structure

Isotactic structure
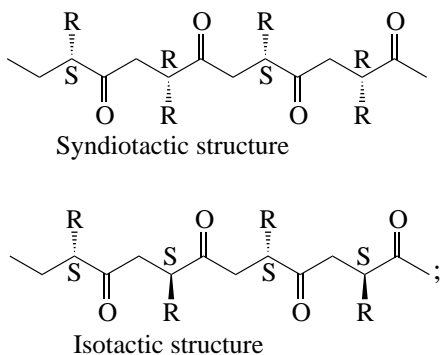
– enantioselectivity; isotactic polymers are chiral and can exist in the form of two enantiomers: RRRR- and SSSS- enantiomers.

The formation of copolymers with a spiroketal structure is unusual in the copolymerization of α-olefins (styrene, its derivatives, and some diene monomers) and CO [53, 54]:
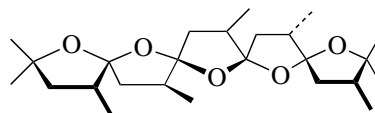
This occurs most frequently when the reaction is carried out at a low temperature (in the case of propylene), but in the copolymerization of higher α-olefins (e.g., hetene-1) and CO, spiroketal and usual 1,4-ketone structures are observed even if copolymerization is carried out at 50°C [55].

The alternating copolymerization of α-olefins (styrene, its derivatives, dienes, and some other monomers) and CO catalyzed by chiral palladium complexes is a promising method for obtaining chiral copolymers for two reasons: (1) chirality of the main chain can be ensured by the use of prochiral monomers and (2) the presence of ketone group simplifies further functionalization of these polymers.

Propylene and CO copolymerization catalyzed by Pd(CH)$_2$ without mentioning the properties of copolymer was patented in [3]. Therefore, probably the first report on the synthesis of the alternating copolymer of propylene and CO should be considered a patent [10]. The activity of propylene in this reaction was an order of magnitude lower than in the reaction of CO with ethylene. Table 1 shows some typical examples to illustrate catalysts and ligands, conditions of synthesis, and the properties of CO copolymers with α-olefins. For the Pd(CH$_3$COO)$_2$–CF$_3$COOH–**II** catalytic system in the copolymerization of CO and ethylene, propylene, and 1-butene, the reaction under comparable conditions decreases from 6000 to 400 and 250 g (g Pd)$^{-1}$ h^{-1}, respectively [10]. An analogous dependence was observed in the catalytic copolymerization of ethylene and α-olefins in the presence of Ziegler–Natta catalysts in the series ethylene–propylene–heptene-1 when the [**II** · Pd(CH$_3$CN)$_2$](BF$_4$)$_2$ complex was used as a catalyst in the medium of nitromethane and methanol. For the same complex in the medium of 1,2-dichloroethane, the replacement of propylene by 1-butene and 1-hexene virtually does not affect the rate of copolymerization and the molecular weight of copolymers [58]. In the series of diphenylphosphinoalkanes Ph$_2$P(CH$_2$)$_n$PPh$_2$, the highest copolymerization rate was observed when phosphines with $n = 3$ and 4 were used (as in the case of ethylene–CO copolymerization.

Table 1. Binary copolymerization of propylene or higher α-olefins and carbon monoxide

Metal compounds	Acid or salt	Phos-phine (L)	Other compounds	T, °C	Solvent	w, g (g Pd)$^{-1}$ h^{-1}	Copolymer properties	Ref.
					Propylene–CO			
LPd(CH$_3$CN)$_2$	–	TPP	–	50	1,2-DCE	4.7	Oligomer	–
[LPd(CH$_3$CN)$_2$](BF$_4$)$_2$	–	II	–	50	1,2-DCE	490	$T_{gt} = -8$°C	[56]
[LPd(CH$_3$CN)$_2$](BF$_4$)$_2$	–	XII	–	50	1,2-DCE	127	$T_{gt} = 8.9$°C	[56]
[LPd(CH$_3$CN)$_2$](BF$_4$)$_2$	–	XII	–	45	CH$_3$CN–CH$_3$OH	10	$M_n = 5200$	[57]
[LPd(CH$_3$)(CH$_3$CN)](BAr$_4$)	–	XIII	–	20	CH$_2$Cl$_2$	–	$M_w = 104000$	[54]
[LPd(CH$_3$CN)$_2$](BF$_4$)$_2$	–	II	–	20	CH$_2$Cl$_2$ + 0.5%CH$_3$OH;	55.5	$M_w = 230000$	[60]
					CH$_2$Cl$_2$ + 0.5%H$_2$O	51.9	$M_w = 200000$	–
Pd(CH$_3$COO)$_2$	Ni(ClO$_4$)$_2$·6H$_2$O	II	BQ	40	C$_4$H$_9$OH–C$_7$H$_8$–CH$_3$OH	125	$M_w = 66000$	[61]
Pd(CH$_3$COO)$_2$	Ni(ClO$_4$)$_2$·6H$_2$O	II	BQ	50	THF–CH$_3$OH–HC(OCH$_3$)$_3$	39.3	$M_w = 37000$ $M_w/M_n = 1.2$	[61]
Pd(CH$_3$COO)$_2$	Ni(ClO$_4$)$_2$·6H$_2$O	II	PTSA	42	THF–CH$_3$OH (1 : 6)	350	[η] = 0.57 dl/g	[54]
Pd(CH$_3$COO)$_2$	Ni(ClO$_4$)$_2$·6H$_2$O	II	PTSA	42	THF–CH$_3$OH (16 : 1)	150	[η] = 0.80 dl/g	[54]
Pd(CH$_3$COO)$_2$	PTSA	V	–	70	CH$_3$OH	1190	–	[42]
					Butene-1–CO			
[LPd(CH$_3$CN)$_2$](BF$_4$)$_2$	–	II	–	30	CH$_3$OH	170	$M_n = 20000$	[56]
Pd(CH$_3$COO)$_2$	CF$_3$COOH	II	–	90	CH$_3$OH	250	–	[10]
[LPd(CH$_3$CN)$_2$](BF$_4$)$_2$	–	XIV	–	30	CH$_3$OH–CH$_3$NO$_2$	70	$M_w = 38000$	[55]
					Hexene-1–CO			
[LPd(CH$_3$CN)$_2$](BF$_4$)$_2$	–	II	–	30	CH$_3$OH	160	$M_n = 25000$	[56]
					Heptene-1–CO			
[LPd(CH$_3$CN)$_2$](BF$_4$)$_2$	–	XII	–	50	CH$_3$NO$_2$–CH$_3$OH	10	$M_n = 1000$	[23]
					Octene-1–CO			
Pd(CH$_3$COO)$_2$	Ni(ClO$_4$)$_2$·6H$_2$O	XIII	Naphthaquinone	40	THF–CH$_3$OH	167	–	[42]
					Tetradecene-1–CO			
Pd(CH$_3$COO)$_2$	Ni(ClO$_4$)$_2$·6H$_2$O	XIII	Naphthaquinone	35	THF–CH$_3$OH	18.5	$M_w = 103000$	[63]
					Hexadecene-1–CO			
Pd(CH$_3$COO)$_2$	Ni(ClO$_4$)$_2$·6H$_2$O	XIII	Naphthaquinone	50	THF–CH$_3$OH	28.2	$M_w = 35100$	[63]
					Octadecene-1–CO			
Pd(CH$_3$COO)$_2$	Ni(ClO$_4$)$_2$·6H$_2$O	XIII	Naphthaquinone	50	THF–CH$_3$OH	12.7	$M_w = 20300$	[63]
					(Tetradecene-1 + octadecene-1)–CO			
Pd(CH$_3$COO)$_2$	–	XIII	Naphthaquinone	35	THF–CH$_3$OH	19.0	$M_w = 78000$	[63]

Note: **XII** is 4-trans-(2,2-dimethyl-1,3-dioxalane-4,5-diyl)-bis(diphenylphosphine); **XIII** is (*R*)2-diphenylphosphino)-1,1-binaphthalene-2-yl-(*S*)-1,1-binaphthalene-2,2-diylphosphine; **XIV** is 1,2-bis(2,5-dimethylpholano)benzene; TPP is triphenylphosphine; PTSK is *p*- toluylsulfo acid; BQ is benzoquinone; DCE is dichloroethane; T_{gt} is glass-transition temperature; M_n and M_w are median and mean molecular weights, g/mol.
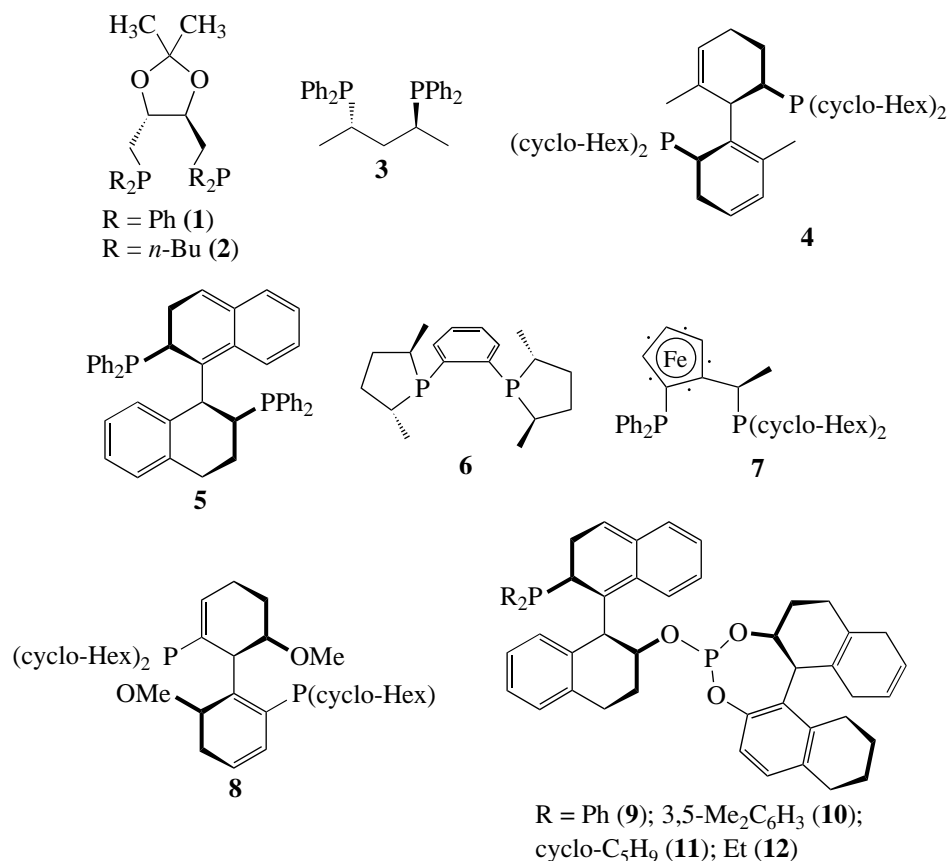
Scheme 1. Ligands of enantioselective isotactic copolymerization of CO and propylene.

The activity of the Pd(CH$_3$COO)$_2$–p-CH$_3$C$_6$H$_4$SO$_3$H catalyst for propylene and CO copolymerization increases in the following series of phosphines: **II** < **X** < **V** [42].

Palladium phosphine catalysts for the alternating copolymerization of olefins and CO usually retain their activity during storage in toluene [19], methanol, acetone, or methyl acetate [62, 64, 65]. However, a decrease in the characteristic viscosity of copolymers is observed. The longer the storage time, the lower the viscosity. Based on indirect data, we assume that the concentration of active centers is only a small part of the overall concentration of palladium compounds in the reaction solution. These compounds may have different structures and compositions. Thus, it was shown for the Pd(CH$_3$COO)$_2$–CF$_3$COOH–**I** system that, when the overall concentration of components is halved, the copolymer yield does not decrease, but the characteristic viscosity increases from 1.88 to 2.28 dl/g [65]. Copolymerization can be carried out on the filtrate after polymer separation from the liquid phase. It was found that, for copolymerization on the filtrate containing 66 wt % of the initial palladium concentration, the rate of copolymerization decreases from 14000 to 12000 g (g Pd)$^{-1}$ h^{-1}, but the characteristic viscosity and copolymer melting point increase [39].

Copolymers of propylene and CO obtained using bidentate arylphosphine ligands have a poorly regio-regular structure. The use of enantio-pure C$_2$-symmetric alkyl-substituted and other diphosphines (Scheme 1) made it possible to make copolymers more regio-regular. The copolymers had a higher chirality depending on the nature of a ligand (Table 2). Both L- and D-stereomers can be obtained. Higher α-olefins (1-butene, 1-hexene, 4-methylpentene-1, cyclopentene, and *cis*-2-butene) [63, 70], vinyl alcohols and carboxylic acids [75], allylbenzenes [76], and 1,5-hexadiene can also be involved in copolymerization with CO [77, 78].

Olefins with a nonterminal double bond can also be involved in copolymerization with CO. Thus, Jiang and Sen showed that the activity *cis*-2-butene is about an order of magnitude lower than the activity of 1-butene [55]. An oligomer is formed from *cis*-2-butene, whereas 1-butene and CO yield a copolymer with a molecular weight of 40000 g/mol. It was assumed that, during copolymerization, *cis*-2-butene isomerizes into 1-butene. In copolymerization with CO, *trans*-2-butene is inactive.
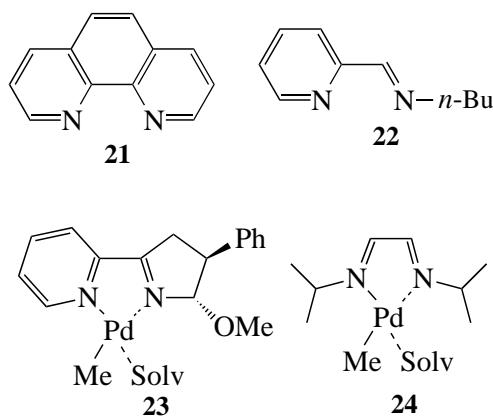
The enantioselective copolymerization of CO and styrene or its derivatives was given considerable attention. For that, P^N and N^N ligands were used (Schemes 2 and 3, Table 3) [69, 72, 73, 79, 80]. In the

Scheme 2. Ligands for enantioselective isotactic copolymerization of CO with styrene.
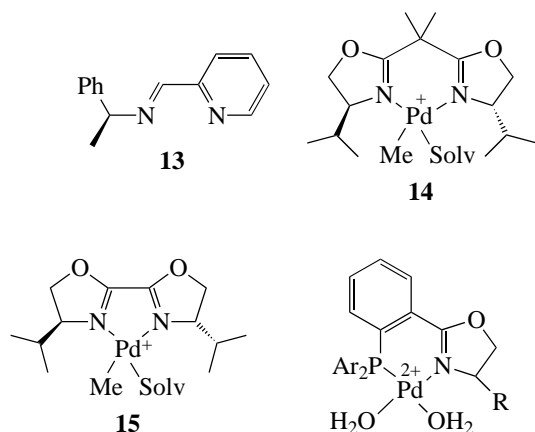
Ar = Ph, R = Ph (**16**); Ar = Ph,
R = CH$_2$Ph (**17**);
Ar = 4-MeOC$_6$H$_4$, R = CH$_2$Ph (**18**);
Ar = 2-MeOC$_6$H$_4$, R = CH$_2$Ph (**19**);
Ar = 2-MeC$_6$H$_4$, R = CH$_2$Ph (**20**)

Scheme 3. Ligands for syndiotactic copolymerization of CO with styrene.

copolymerization of CO and styrene, both isotactic and Syndiotactic copolymers can be formed. In the latter case, ligands based on the derivatives of phenanthroline **21** [47, 71, 81, 82], dipyridyl [71, 80, 82], pyridinimine

22 [58], pyridinoxazoline **23** [72], and diimine **24** [83] (Scheme 3). Brookhart [80] showed that the replacement of the bisoxazoline ligand in cationic complex **14** (Scheme 2) for the achiral dipyridine ligand makes it possible to obtain a chiral iso-syndiotactic stereoblock-polymer.

Water-soluble palladium complexes are of great scientific and practical interest. These are complexes active in alternating CO copolymerization with different monomers (Scheme 4). The possibility of copoly-

Table 2. Isotactic copolymerization of propylene and CO [66]

Ligand/catalyst	Copolymer yield, g polymer/g Pd	Copolymer properties	Ref.
1/A	93	$[\alpha]_D^{25} = +6.6°$ (HFIP)	[67]
2/A	703	$[\alpha]_D^{25} = +10.4°$ (HFIP)	[67]
4/A	No data	$[\alpha]_D^{25} = +26°$, $\Delta_\varepsilon = -1.56$ l mol^{-1} cm^{-1}, $T_{melt} = 245°$C, highly regioregular polymer	[68, 69]
1/B	500	$[\alpha]_D^{20} = -7°$ (CH$_2$Cl$_2$), 78% head-to-tail	[58]
3/B	630	$[\alpha]_D^{20} = -29°$ (CH$_2$Cl$_2$), 78% head-to-tail	[58]
5/B	300	$[\alpha]_D^{20} = +36°$ (CH$_2$Cl$_2$), 66% head-to-tail	[58]
6/B	1462	$[\alpha]_D^{25} = +70°$ (CHCl$_3$), $[\alpha]_D^{25} = -30°$ (HFIP), $M_n = 36000$	[63]
7/A	2975	$\Delta_\varepsilon = 1.84$ l mol^{-1} cm^{-1}, 99% head-to-tail, $M_n = 63000$	[70]
8/A	391	$[\alpha]_D^{25} = -29.1°$ (HFIP), $\Delta_\varepsilon = 1.73$ l mol^{-1} cm^{-1}, $T_{melt} = 237°$C, 100% head-to-tail, $M_n = 69000$	[71]
9/C	284	$[\alpha]_D^{24} = +57.2°$ (HFIP), 100% head-to-tail, $T_{melt} = 164°$C, $M_n = 65000$	[59]

Note: **A** = Pd(CH$_3$COO)$_2$, Ni(ClO$_4$)$_2$, and naphthaquinone; **B** = [Pd(CH$_3$CN)$_2$](BF$_4$)$_2$; **C** = Pd(1,5-cyclooctadiene)(Cl)(CH$_3$), Na[B(3,5-CF$_3$)$_2$C$_6$H$_3$)$_4$]; HFIP—hexafluoroisopropanol; $[\alpha]_D$ is optical rotation of chiral copolymer; Δ_ε is a change in the extinction coefficient; T_{melt} is the melting point.
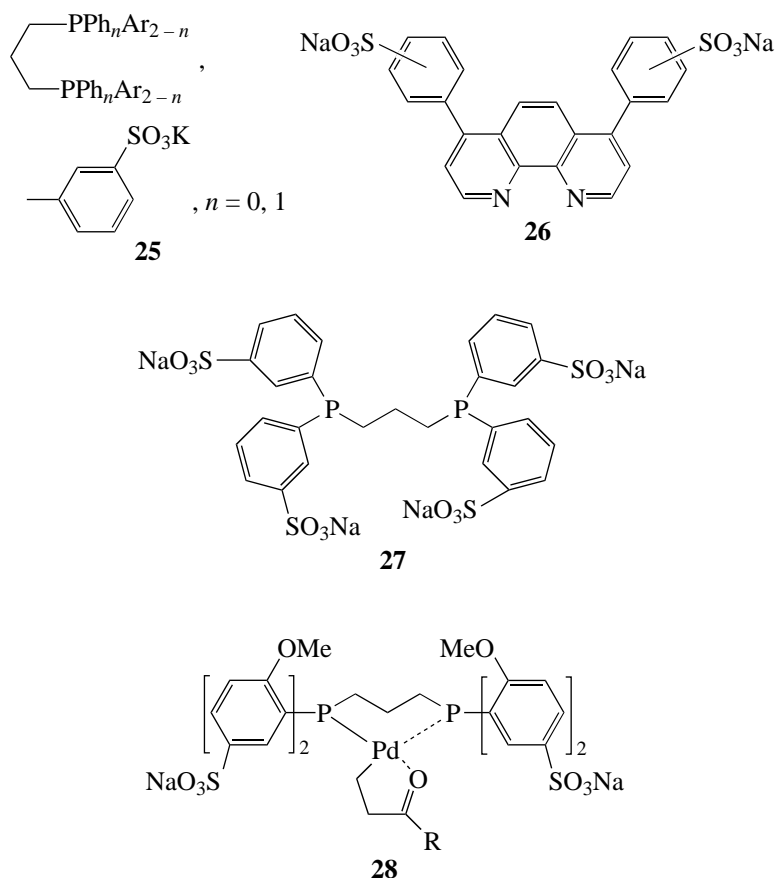
Scheme 4. Water-soluble ligands for CO copolymerization with olefins.

merization in an aqueous medium was first reported in [84]. The potassium salt of bis(diphenylphosphino)propane sulfo-acid and the sodium salt of phenanthroline sulfo-acid were used as ligands. However, the rates of CO copolymerization with ethylene and propylene were much lower than in methanol. Recently, Sheldon [85–87], reported on the synthesis of palladium complexes with new water-soluble ligands, which enabled the copolymerization of CO with ethylene at a rate of 32000 g (g Pd)$^{-1}$ h^{-1}.

Table 3. Isotactic copolymerization of styrene and CO [66]

Ligand	R	Copolymer yield, g polymer/g Pd	Copolymer properties	Ref.
13	H	**	$[\alpha]_D^{20} = -16°$ (CH$_2$Cl$_2$), $M_n = 5600$	[58]
13	CH$_3$	**	$[\alpha]_D^{20} = -14°$ (CH$_2$Cl$_2$), $M_n = 14000$	[58]
14	*tert*-Bu	179	$[\alpha]_D^{25} = -284°$ (CH$_2$Cl$_2$), $M_n = 26000$	[73]
15	H	13	$[\alpha]_D^{25} = -348°$ (Cl$_2$HCCHCl$_2$)	[73]
15	CH$_3$	66	$[\alpha]_D^{25} = -350°$ (CH$_2$Cl$_2$)	[73]
16	H	**	$[\alpha]_D^{25} = -403°$ (HFIP/CHCl$_3$)	[74]
12/A*	*tert*-Bu	192	$[\alpha]_D^{23} = -261°$ (CH$_2$Cl$_2$), $M_n = 4300$	[59]

* **A** = Pd(1,5-cyclooctadiene)(Cl)(CH$_3$), Na[B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$].

** No data.

CONCLUSION

This review does not pretend to cover all scientifically and practically interesting aspects of the use of palladium complexes in the catalytic syntheses of alternating CO copolymers with different monomers. The goal of this review is to give some general idea of the present state of the art, at the beginning of 2000, of the studies of this relatively new area of polymer chemistry and the avenues it opens.

I hope that this review will promote greater interest from academic and applied researchers in Russia in the syntheses and applications of palladium complexes with new ligands and in the study of the properties of a new, promising generation of functional polymers based on carbon monoxide.

The studies toward the search for new catalysts, more specifically new and modified ligands, that can carry CO copolymerization with olefins and other vinyl monomers in an aqueous and gas phases are of certain interest. There is some progress along these lines [86, 87]. From the practical standpoint (in connection with the high palladium cost), the search for new catalysts based on nickel and cobalt is also of interest, although there is no noticeable progress in this area.

It is also worth mentioning that palladium complexes used in alternating CO copolymerization with different monomers have many common features with the Ziegler–Natta catalysts (including metallocenes) despite apparent differences [65]:

– An electrophilic metal cation and poorly coordinating anion are present in the reaction zone.

– Both metal cations have a coordination number of four. The Ziegler–Natta catalyst is mostly tetravalent and requires four anionic ligands, two of which are strongly coordinated to the anion (e.g., Cp) and the two others are weakly coordinated. Palladium catalysts are bivalent compounds containing two neutral and two poorly coordinated anionic ligands.

– For the existence of the active centers of a growing chain and a vacant site for monomer coordination in the catalysts of both types, the presence of the *cis*-structure is necessary. In the d^0-metallocene complex, the *cis*-structure is organized automatically by the pseudotetragonal coordination envelope of the metal. In the square–planar d^8 palladium complex, the *cis*-structure is maintained by the presence of neutral ligands.

ACKNOWLEDGMENTS

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