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(PPh₃)₄ catalyst decreases in the following series of solvents: CH₃OCH₂CN > CH₃CN > (CH₃)₂NOCH > C₂H₅N > C₆H₆ > HC(OCH₃)₃ > CH₃OCH₂CH₂OCH₃ = C₆H₁₄.

In the case of another palladium phosphine derivative (PR₃)₂PdXY, the catalyst activity decreases in the following series of phosphines: P(Aryl)₃ > P(Aryl)₂R > P(Aryl)R₂ [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 ([η] 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 > dimethylxethane > 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.

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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$_3$CN)(PPh$_3$)$_2$)(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 ($pK_a \leq 2$) [9]. It was shown that Pd(CH$_3$COO)$_2$ together with phosphorus-containing bidentate ligands and an acid with $pK_a \leq 2$ actively catalyzes the copolymerization of ethylene and CO to form a high-molecular alternating copolymer with molecular weights of up to $3.0 \times 10^5$ 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 $\alpha$-olefin can be obtained under analogous conditions [10–12]. The inclusion of higher $\alpha$-olefin in the structure of the alternating copolymer results in a decrease in the melting point. Patent data on the synthesis of ethylene–CO alternating copolymer results in a decrease in the melt viscosity under the action of Pd(CH$_3$COO)$_2$ and different palladium complexes is usually carried out in a polar medium. Methanol or other solvents such as acetone, THF, MEK, 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$_3$COO)$_2$–p-CH$_2$C$_6$H$_5$SO$_3$H–PPh$_3$(CH$_3$)$_2$PPh$_2$ (II).

The reaction of copolymerization can be carried out not only in the liquid phase, but also in the gas phase. When Pd(CH$_3$COO)$_2$ together with diphenylphosphine 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$_3$COOH or $p$-CH$_2$C$_6$H$_5$SO$_3$H), 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$_3$SO$_3$H > CH$_2$C$_6$H$_5$SO$_3$H > CF$_3$COOH > $C_6$H$_5$COOH ≈ HBF$_4$ > CCl$_3$COOH > $C_6$H$_5$ClCOOH > 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:

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\begin{align*}
1,3\text{-bis(diphenylphosphino)}\text{methane (III)} & < 1,3\text{-bis(diphenylphosphino)}\text{hexane (IV)} \\
< 1,4\text{-bis(methylbutyldiphenylphosphino)hexane (V)} & < 1,4\text{-bis(dIBUTYLPHENYLPHOSPHINO)butane (VI)} \\
< 1,3\text{-bis(diphenylphosphino)ethane (VII)} & < 1,3\text{-bis(dibutyldiphenylphosphino)butane (VIII)} \\
< 1,3\text{-bis(diphenylphosphino)pentane (IX)} & < 1,3\text{-bis(di-n-butylphosphino)propane (X)} \\
< 1,3\text{-bis(diphenylphosphino)butane (XI)} & < \text{PPh}_3(\text{CH}_3)_2\text{PPh}_2 (\text{II}) \\
< 1,3\text{-bis(di-2-methoxydiphenylphosphino)propane (I)} & [20, 37, 40–43].
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