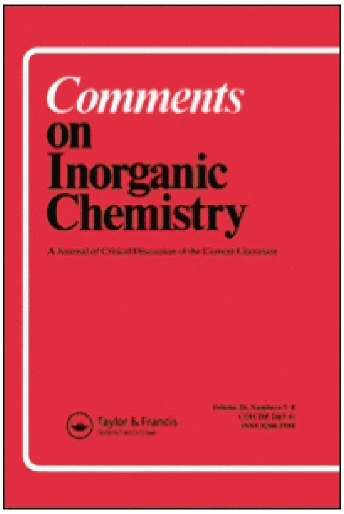

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Pd(II) Complexes with Bidentate Nitrogen-Donor Chelating Ligands: Very Versatile and Active Catalyst Precursors for the CO/Olefin Co- and Terpolymerization Reactions

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The perfect alternating CO/olefin copolymers constitute an important class of new materials. Their synthesis requires a catalyst; in general, the applied catalytic systems are formed by a palladium(II) salt, modified by diphosphine or dinitrogen chelating ligands, in the presence of a Brønsted acid as cocatalyst and, frequently, an oxidant such as 1,4-benzoquinone. Alcoholic medium is generally preferred. This overview will report on the main catalytic systems based on bidentate nitrogen-donor chelating ligands; particular attention will be dedicated to the CO/styrene copolymerization. A detailed analysis of several parameters influencing the yield and the quality of CO/styrene polyketone will be presented, together with the discussion of the control of the stereochemistry of the insertion of styrene in the growing chain.

Keywords: *palladium, copolymerization, nitrogen-donor ligands, polyketones, catalysis, olefins, carbon monoxide*

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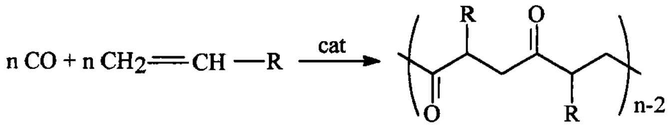
I. INTRODUCTION

The C-C bond-forming reactions catalyzed by transition metal complexes have constituted a very important class of reactions for several years.[1,2] In this wide class of reactions, a very attractive field of research is represented by the copolymerization between carbon monoxide and olefin yielding perfectly alternating polyketones (Eq. (1)).[3]



(1)

R = H, CH_3, Ph

The great academic and industrial interest in this research, witnessed by the increasing number of reports appearing in the current literature,[4] arises from the ready availability of base materials and, above all, from the properties of the product. Indeed, these polyketones have interesting engineering-plastic type properties, and the CO/ethylene/propylene terpolymer, named Carilon®, has been commercially developed by Shell Chemicals.[5] Very recently BP Chemical has also placed on the market another aliphatic polyketone, Ketonex®.[5c] In addition, because of the presence of the carbonyl group, these polyketones can constitute a new class of photodegradable polymers[6] and can be used as excellent starting materials for other new types of functionalized polymers.[7]

The copolymerization reaction is homogeneously catalyzed by Pd(II) compounds, and the first catalytic system applied to it was reported by Sen in 1982.[8] He found that a series of Pd(II) compounds of general formula $[Pd(PPh_3)_n(CH_3CN)_{4-n}][BF_4]_2$ (n = 1–3) catalyzed the CO/ethylene copolymerization in non-coordinating solvents under very mild reaction conditions.[8] The two most important features of this catalytic system are (i) palladium is the metal able to promote the perfect alternation of the two monomeric units along the main chain and (ii) the phosphorus-donor ligand is necessary for the catalytic activity. However, with this catalytic system the yields in polyketones, as well as their molecular weights, were very low.

The essential advance in this research was performed by Drent at Shell Chemicals.[9] His approach was based on replacement of the monophosphine ligand with a bidentate one. He studied an *in situ* catalytic system based on $Pd(CH_3COO)_2$ or $Pd(CF_3COO)_2$, modified with diphosphine (P-P) or dinitrogen (N-N) chelating ligands and with a Brønsted acid as cocatalyst. The yields in polyketones were enhanced by adding an oxidant, such as 1,4-benzoquinone. Methanol was preferentially the solvent of choice.[9,10] Detailed analysis of this catalytic system showed that, for the CO/ethylene copolymerization, $Pd(CH_3COO)_2$ is the best source of palladium, 1,3-bis(diphenylphosphino)propane is the most active among the tested phosphorus-donor ligands, and *p*-toluenesulfonic acid is the best acid co-catalyst. With this *in situ* system, high rates (~6000 g CP/g Pd·h) have been achieved under mild reaction conditions (90 °C, 45 bar).[3] This catalytic system was also found to be efficient for the terpolymerization of CO and ethylene with propylene, yielding the perfect alternating polyketone, Carilon®, in which some ethylenic units are randomly substituted by propylene along the main chain.

As research progressed, several catalytic systems have been reported in the literature; they comprise either *in situ* systems or preformed complexes. In the catalytic systems based on preformed complexes, the palladium compounds always bear at least one molecule of diphosphine or dinitrogen chelating ligand in the coordination sphere. The other two coordination sites can be occupied either by anionic or neutral ligands. For the CO/ethylene copolymerization, some examples of preformed complexes are $[Pd(dppp)(CH_3CN)_2][BF_4]_2$,[11] $[Pd(dppp\text{-}SO_3K)(H_2O)_2][BF_4]_2$,[12] $[Pd(dppp)(H_2O)(TsO)][TsO]$,[41] $[(PCy_3)_2Pd(H)(H_2O)][BF_4]$,[4m] and $[Pd(dppp)(C(O)^tBu)Cl]$.[4p,q] In particular, the derivative $[Pd(dppp\text{-}SO_3K)(H_2O)_2][BF_4]_2$ allowed the CO/ethylene copolymerization to be carried out in pure water,[12] while $[Pd(dppp)(C(O)^tBu)Cl]$ was used for the copolymerization in the presence of alumoxanes as co-catalysts, in analogy with the cationic zirconocene polymerization of ethylene.[4p,q] However, in all cases the productivity was found to be lower than that of comparable *in situ* systems.

An important relationship between the nature of the chelating ligand and the olefinic comonomer was found in the early studies on these systems. Diphosphine ligands are required to achieve high yields in the copolymerization of aliphatic α-olefins.[3] On the contrary, a catalytic system modified by nitrogen-donor chelating ligand is required to prepare the CO/styrene copolymer.[4j,13,14] The catalytic systems based on diphosphine ligands catalyze the selective carbonylation of styrene to (E)-1,5-diphenylpent-1-en-3-one instead of its copolymerization.[13]

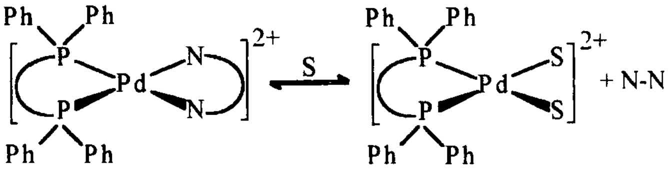
Moreover, problems related to the control of regio- and stereoselectivity of polyketones arise with α-olefins.[15–19] Particular attention has been dedicated to the regio- and stereochemistry of the insertion of propylene in the growing chain of the corresponding copolymer. The highly regio- and stereoregular CO/propylene polyketone has been obtained recently by using either an *in situ* system[4a] or preformed Pd(II) complexes modified by chiral diphosphine ligands.[4c,e] The factors responsible for the enantioface discrimination of the insertion of propylene have been studied in detail by Consiglio in the CO/propene co-oligomerization, as a model of the corresponding copolymerization.[15c] The reported results indicate that a mechanism of double stereodifferentiation is effective; the asymmetric induction is influenced both by the presence of the chiral ligand and by the chiral center of the last inserted olefin.[15c]

Even though, as mentioned above, various ligands have been tested, and several alkenes were used as comonomers, this overview will focus on the copolymerization promoted by Pd(II) compounds with bidentate nitrogen-donor chelating ligands; most of the results presented were obtained in our laboratories.

II. COPOLYMERIZATION PROMOTED BY $[Pd(dppp)(N\text{-}N)][X]_2$

Preliminary results on the carbon monoxide/ethylene copolymerization catalyzed by $[Pd(N\text{-}N)(N'\text{-}N')][PF_6]_2$ complexes, with N-N either equal or different from N′-N′, allowed us to recognize some important features of the catalytic system: (i) the active species is very likely a monochelated one, and therefore the dissociation of one of the two chelating ligands has to occur in solution; (ii) the other nitrogen chelating ligand is important in increasing the stability of the catalyst toward decomposition to palladium metal. On the basis of the strong *trans* effect of the phosphine ligands and the lability of the Pd-N bond,[21] a new class of palladium(II) complexes, $[Pd(dppp)(N\text{-}N)][X]_2$ (N-N = bipy, dmbipy, phen, tmphen; $X = PF_6^-$, BF_4^-), with a diphosphine and a dinitrogen chelating ligand coordinated to the same palladium center, was synthesized, fully characterized, and tested in the CO/ethylene and CO/ethylene/propylene polymerization reactions.[22]

The chemical behavior of this series of complexes in coordinating solvents, such as dimethylsulfoxide, is characterized by the establishment of an equilibrium of dissociation of the nitrogen ligand, yielding a solvated species, (b) (Eq. (2)).



(2)

(a) (b)

Depending on the nature of the nitrogen chelating ligand, the dissociation rate at room temperature can be slow, when N-N is bipy or its substituted derivatives, or relatively fast, when N-N is phen or its substituted derivatives, on the NMR time scale. Morover, the ^{31}P NMR spectra of complexes with bipy or dmbipy present two peaks of different intensities. While the major peak depends on the nature of N-N, the minor resonance has the same chemical shift in both spectra, indicating that the same dissociation product was formed. The dissociation product (b) with the dppp ligand bound to palladium has two other *cis* coordination sites. These are filled by easily displaceable solvent molecules permitting favorable *cis* coordination for the copolymerization catalytic process.

The influence of the nature of the nitrogen-donor chelating ligand on the catalytic activity was studied in the CO/ethylene copolymerization. A remarkable decrease in the yield of the copolymer with increasing coordinating ability of the nitrogen ligand was found (Table I), and the highest activity was obtained with bipy.[22] The complex $[Pd(dppp)(bipy)][PF_6]_2$ is indeed a very active precatalyst in the CO/ethylene copolymerization in methanol without any acid cocatalyst. The nature of the nitrogen ligand also influences the limiting viscosity number (η, a parameter directly related to the molecular weight of polymers) and, therefore, polyketones of the desired molecular weight might be produced on choosing the proper nitrogen ligand. Polyketones obtained with this new series of compounds are white, indicating no apparent decomposition of the active species to palladium metal.

TABLE I CO/ethylene Copolymerization: Effect of Catalyst Precursor

Precatalyst	*kg CP/g Pd*	*η (dL/g)*[a]	*Pd (ppm)*[b]
$[Pd(dppp)(phen)][PF_6]_2$	11.2(w)	2.13	n.d.
$[Pd(dppp)(tmphen)][PF_6]_2$	3.9(w)	1.2	n.d.
$[Pd(dppp)(dmbipy)][PF_6]_2$	18.2(w)	2.88	n.d.
$[Pd(dppp)(bipy)][PF_6]_2$	42.3(w)	1.52	17.7
$[Pd(dppp)_2][PF_6]_2$	3.5(w)	n.d.	221.3
$[Pd(CH_3COO)_2]$+dppp+ CF_3COOH[c]	21.5(w)	1.03	38.7

Reaction conditions: $n_{Pd} = 0.1$ mmol; $n_{BQ} = 8$ mmol; solvent, methanol $V = 1200$ mL; $P_{tot} = 56$ atm; $T = 80$ °C; time = 5h.

[a] Measured in *m*-cresol at 100 °C.

[b] Measured by atomic absorption.

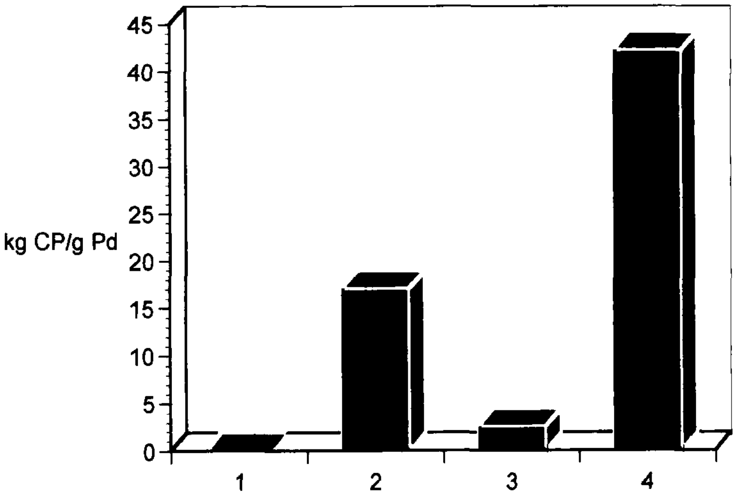
[c] Reaction conditions: $n_{Pd} = 0.1$ mmol; $n_{dppp} = 0.1$ mmol; $n_{CF3COOH} = 2$ mmol; solvent, methanol $V = 1200$ mL; $P_{tot} = 56$ atm; $T = 80$ °C; time = 5h.

w = white copolymer.

The productivity of the mixed-ligand complex with bipy was doubled with respect to that of the *in situ* system (Table I); in addition, the polyketone has a higher limiting viscosity number and contains a lower amount of palladium with respect to those of the copolymer obtained with the *in situ* system.

The complex $[Pd(dppp)(bipy)][PF_6]_2$ showed a much higher productivity than that of the corresponding bischelated symmetrical compound $[Pd(dppp)_2][PF_6]_2$ (Table I). This difference could be related to the different nature of the Pd-P and the Pd-N bonds.[21] Dissociation of one of the two molecules of dppp from the symmetrical bischelated species is expected to be rather difficult, with a consequent reduction of the concentration of the monochelated active species.

The monochelated phosphorus ligand derivatives were also less active than the mixed-ligand compound with bipy (Fig. 1). Between the two carboxylato anions, the productivity of the acetato derivative was almost negligible, and there was complete decomposition of the active species to palladium metal. This difference could be related to the ability of acetate and trifluoroacetate to undergo esterification and to their σ-donor power. Since acetate is more esterifiable than trifluoroacetate,[23] a greater amount of water is expected to be formed by the methanol esterification reaction with the acetato derivatives than with the trifluoroacetato ones. The presence of an excess of water might favor reduction of the catalyst to the inactive Pd^0.[17] Therefore, the ideal anion should be non-coordinating and non-esterifiable. Surprisingly, the replacement of PF_6^- with BF_4^- caused a strong decrease in productivity (Fig. 1). This decrease might be related to the incomplete inertness of tetrafluoroborate anion, which can partially react with palladium in the reaction mixture.[24]



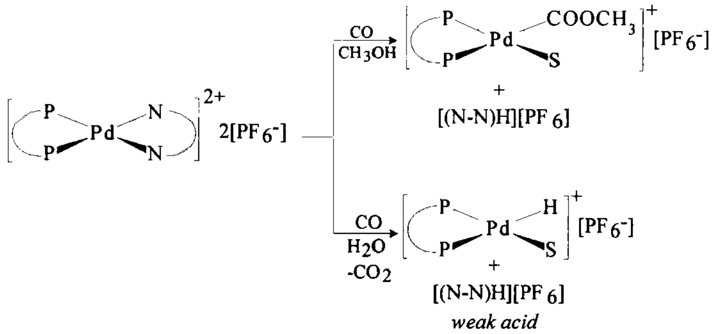
1 $[Pd(dppp)(CH_3COO)_2]$ 2 $[Pd(dppp)(CF_3COO)_2]$

3 $[Pd(dppp)(bipy)][BF_4]_2$ 4 $[Pd(dppp)(bipy)][PF_6]_2$

FIGURE 1 CO/ethylene copolymerization: effect of the anion. Reaction conditions: see Table I

The mixed-ligand compound with bipy was also found to be efficient for the terpolymerization of CO with ethylene and propylene. Productivities up to 37 kg TP/g Pd were obtained in methanol without any acid co-catalyst and any oxidant. Instead, when this compound was used as precatalyst in the CO/styrene copolymerization, no polyketone was obtained, thus indicating that the active species is one with a phosphorus ligand.[13a,b]

On the basis of the above results, we propose that the active species is formed by dissociation of the nitrogen-donor chelating ligand, generating the active monochelated phosphorated species. The latter can then react either with CO and CH_3OH, yielding the carbomethoxy species (Scheme 1a), or with CO and water, yielding the hydrido species (Scheme 1b). In both cases the free molecule of N-N can react with the protons generated in the precedented reactions to give the weak acid $[(N\text{-}N)H][PF_6]$. This hypothesis reveals one of the main differences between these complexes and the catalytic systems reported in the literature, where the formation of the active species led to strong acids.[10]



(1a)

(1b)

S = ROH

SCHEME 1

The information obtained with the mixed-ligand compounds allowed us to consider the catalyst precursor as the result of an assembly of different parts, each one with a well-defined role: (i) the anion has to be non-coordinating and unreactive in the reaction mixture and the hexafluorophosphate represents the best choice to date. It should be noted that some results in this field were obtained with BF_4^-derivatives,[4e,25] the activity of which might be enhanced by appropriate change of the anion; (ii) labile ligands must be present in the coordination sphere of palladium and they can dissociate, leaving two vacant coordination sites; (iii) when the labile ligand is a chelating nitrogen ligand it can bind to protons, buffering their concentration and influencing the molecular weight of polykotones; (iv) non-labile ligands should be present in the coordination sphere of the metal and they should have a high specific catalytic activity in the copolymerization process. Therefore, if an aliphatic α-olefin is the comonomer, phosphorus-donor ligands are better and dppp is the ligand of choice; if an aromatic olefin is used, nitrogen-donor ligands are needed.

III. COPOLYMERIZATION PROMOTED BY $[Pd(N\text{-}N)(R\text{-}COO)_2]$ $(R = CH_3, CF_3)$

The catalytic activity of the monochelated carboxylato complexes, $[Pd(N\text{-}N)(R\text{-}COO)_2]$, was investigated in the CO/styrene copolymerization reaction in methanol without any acid co-catalyst.[18] As observed with the monochelated phosphorated compounds, the effect of the anion evidenced that the acetato derivative was unreactive together with its complete decomposition to metal. Instead the trifluoroacetato compound showed a high productivity, which, at low temperature, was even higher than that of the corresponding symmetrical bischelated compound $[Pd(phen)_2][CF_3COO]_2$ (Table II).

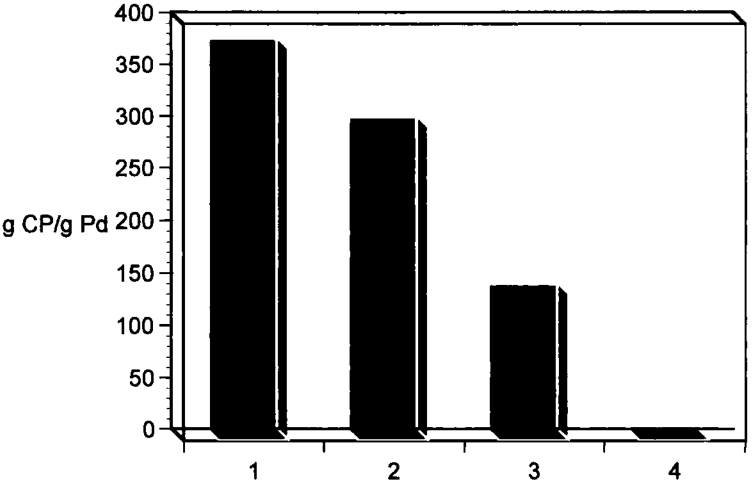
TABLE II CO/Styrene Copolymerization: Effect of Catalyst Precursor and of the Amount of 1,4-Benzoquinone

Precatalyst	*BQ (mmol)*	*g CP/g Pd*	*η (dL/g)*
$[Pd(phen)(CH_3COO)_2]$	40	4	n.d.
$[Pd(phen)(CF_3COO)_2]$	40	300	0.07
$[Pd(phen)_2][CF_3COO]_2$	40	118	n.d.
$[Pd(phen)(CF_3COO)_2]$	10	269	n.d.
$[Pd(phen)(CF_3COO)_2]$	5	188	n.d.
$[Pd(phen)(CF_3COO)_2]$	0	81	0.15

Reaction conditions: $[Pd] = 1 \times 10^{-3}$M; styrene $V = 50$ mL; solvent, methanol $V = 500$ mL; $P_{tot} = 40$ atm; $T = 40$ °C; $t = 10$ h.

In the catalytic systems based on a chelating nitrogen ligand the 1,4-benzoquinone plays an important role both on the activity and the selectivity.[10,13a,b,26] Therefore, the dependence of the catalytic activity on concentration of 1,4-benzoquinone was analyzed.[18] Marginal loss of activity resulted when the quinone amount was reduced from 40 to 10 mmol, but became relevant when the benzoquinone was further decreased (Table II). However, it should be noted that the catalytic system was still active in the absence of the oxidant. In agreement with the literature,[13a] an increase in the intrinsic viscosity number was found on lowering the benzoquinone concentration (Table II).

The specific catalytic activity of each ligand was also examined.[18] As already observed with the mixed-ligand compounds, a decrease of productivity was found on going from bipy, to phen, to tmphen (Fig. 2). Complete loss of activity resulted when the complex with 2,9-dimethyl-1,10-phenanthroline was used as precatalyst (Fig. 2), probably due to the steric hindrance of the methyl groups in the 2 and 9 positions.



1 $[Pd(bipy)(CF_3COO)_2]$ 2 $[Pd(phen)(CF_3COO)_2]$
3 $[Pd(Me_4\text{-phen})(CF_3COO)_2]$ 4 $[Pd(2,9\text{-}Me_2\text{-phen})(CF_3COO)_2]$

FIGURE 2 CO/styrene copolymerization: effect of nitrogen chelating ligand. Reaction conditions: see Table II; $n_{BQ} = 40$ mmol

The catalytic system based on $[Pd(bipy)(CF_3COO)_2]$ was optimized with respect to pressure and temperature.[18b] The productivity at 1 atm, under a stream of CO, was twice that at 40 atm (Table III), suggesting the inhibiting role of carbon monoxide; this inhibition was confirmed by Brookhart.[4n] At $T \geq 40$ °C the copolymer is grey, due to the presence of palladium metal. At 30 °C the catalytic activity was higher than at 50 °C and no decomposition of the active species to palladium metal was observed, a clear white copolymer being obtained (Table III).

TABLE III CO/Styrene Copolymerization: Effect of Carbon Monoxide Pressure and Temperature. Precatalyst: $[Pd(bipy)(CF_3COO)_2]$

P_{CO}*(atm)*	*T(°C)*	*t (h)*	*g CP/g Pd*	*g CP/g Pd·h*
40	50	6	207(g)	34.5
1	50	2	175(g)	87.5
1	40	2	122(g)	61.0
1	30	2	282(w)	141.0

Reaction conditions: $n_{Pd} = 0.05$ mmol; $n_{BQ} = 1$ mmol; solvent methanol, $V = 20$ mL; styrene $V = 10$ mL. g = grey copolymer.

Even though, according to these results, $[Pd(bipy)(CF_3COO)_2]$ was one of the most active catalyst precursors among those operating under such mild conditions, its productivity was still low, and the molecular weight of polyketones was also very low.

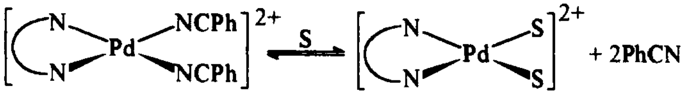
IV. COPOLYMERIZATION PROMOTED BY $[Pd(N\text{-}N)(PhCN)_2][PF_6]_2$

In agreement with the precatalyst subdivision in different parts (see above), we synthesized and tested a series of dicationic monochelated Pd(II) complexes $[Pd(N\text{-}N)(PhCN)_2][PF_6]_2$, with the benzonitrile as the labile ligand, and the hexafluorophosphate as the anion.

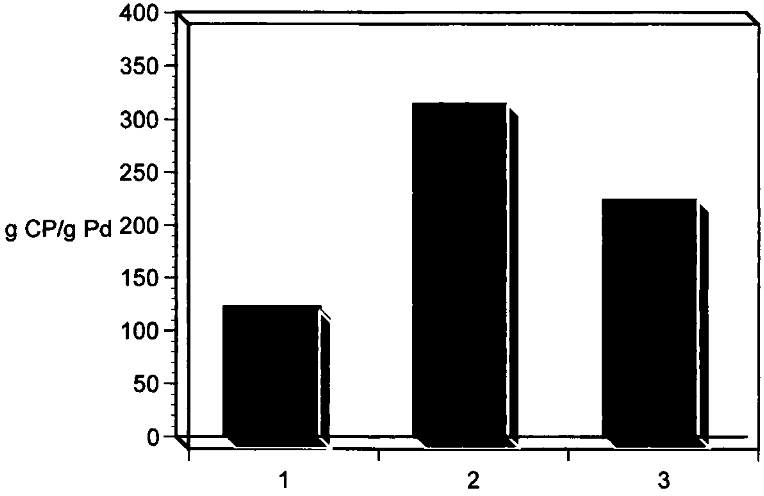
Their synthesis was performed using the dichloro derivatives as starting materials and extracting the chloride as a silver salt (Eq. (3)).[27]

$$Pd(CH_3COO)_2 \xrightarrow[\substack{NaCl\\CH_3OH}]{N\text{-}N} [Pd(N\text{-}N)Cl_2] \xrightarrow[\substack{PhCN\\-AgCl}]{Ag\,PF_6} [Pd(N\text{-}N)(PhCN)_2][PF_6]_2 \qquad (3)$$

In coordinating solvents, such as dimethylsulfoxide, an equilibrium of dissociation of the benzonitrile molecules is established, generating a monochelated nitrogenated species (Eq (4)).



(4)



1 $[Pd(bipy)(CF_3COO)_2]$ 2 $[Pd(bipy)(PhCN)_2][PF_6]_2$
3 $[Pd(phen)(PhCN)_2][PF_6]_2$

FIGURE 3 CO/styrene copolymerization: effect of catalyst precursor. Reaction conditions: $n_{Pd} = 0.05$ mmol; $n_{BQ} = 1$ mmol; solvent methanol, $V = 20$ ml; styrene $V = 10$ ml; $P_{CO} = 1$ atm; $T = 40$ °C; time = 2h

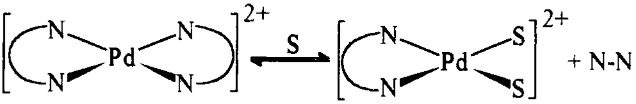
These compounds were tested in the CO/styrene copolymerization under very mild reaction conditions. The compound $[Pd(bipy)(PhCN)_2][PF_6]_2$ was found to be more active than the corresponding trifluoroacetato derivative $[Pd(bipy)(CF_3COO)_2]$ (Fig. 3). This result might be due to the higher lability of benzonitrile with respect to that of trifluoroacetato, and to the presence of hexafluorophosphate. Again the complex with bipy showed a higher productivity than that of the complex with phen (Fig. 3). For the bipy-benzonitrile derivative, a strong dependence of productivity on temperature was found. In the investigated range 40 °C was the temperature at which the highest rate was observed without decomposition to metal.

In agreement with these results, $[Pd(N\text{-}N)(PhCN)_2][PF_6]_2$ are better precatalysts than $[Pd(N\text{-}N)(R\text{-}COO)_2]$, but their productivity is still quite low.

V. COPOLYMERIZATION PROMOTED BY $[Pd(N\text{–}N)_2][X]_2$ $(X = PF_6^-, BF_4^-, CF_3COO^-)$

The dicationic bischelated complexes $[Pd(N\text{-}N)_2][X]_2$ have been known for a long time.[28] Nevertheless, only very recently has a straightforward procedure for their synthesis been optimized in our laboratories.[29]

In coordinating solvents, as found for the mixed-ligand compounds $[Pd(dppp)(N\text{-}N)][X]_2$, these $[Pd(N\text{-}N)_2][X]_2$ complexes very easily equilibrate with a solvated species by dissociation of one of the two molecules of the chelating nitrogen ligand (Eq. (5)). Unlike the mixed-ligand complexes, the rate of this equilibrium is intermediate on the NMR time scale and no difference among the several nitrogen ligands could be detected.



(5)

In the past, these compounds have been succesfully applied to the reductive carbonylation of nitroaromatic compounds to urethanes in methanol.[30] Because of the similarities between reductive carbonylation and copolymerization reactions, we tested their effect as catalysts in the CO/olefin copolymerization. They exhibited good productivity in methanol without any acid co-catalyst.[20a] These promising preliminary results prompted us to undertake a detailed investigation of the CO/olefin copolymerization promoted by these Pd(II)-bischelated compounds.[20b,29,31]

As already observed with $[Pd(dppp)(N\text{-}N)][X]_2$ and with $[Pd(N\text{-}N)(R\text{-}COO)_2]$, a strong influence of the anion on the productivity was also found with $[Pd(N\text{-}N)_2][X]_2$. On going from hexafluorophosphate to trifluoroacetate to acetate, a strong decrease of activity was observed (Table IVa); indeed, in the case of the acetato derivative the activity was almost negligible, due to the complete decomposition of the active species to palladium metal. Again the replacement of hexafluorophosphate with tetrafluoroborate also led to a strong decrease in catalytic activity (Table IVb). Therefore, we finally observe that the anion plays a very important role in this catalytic system and again PF_6^- remains the best choice to date, not only concerning the productivity, but also the quality of the copolymer. Indeed with PF_6^- precatalysts we obtained polyketones with a ten-fold greater η value compared than those produced with the corresponding CF_3COO^- salts.

TABLE IV CO/Ethylene Copolymerization: Effect of the Anion
(a) Precatalyst: $[Pd(phen)_2][X]_2$

X	*g CP/g Pd*	η *(dL/g)*
PF_6^-	2010	1.13
CF_3COO^-	880	0.10
CH_3COO^{-a}	20	n.d.

Reaction conditions: $[Pd] = 1 \times 10^{-3}$ M; $[BQ] = 8 \times 10^{-2}$ M; solvent methanol, $V = 500$ mL; $P_{tot} = 56$ atm; $T = 90$ °C; time = 5h.
[a] $[Pd(phen)(CH_3COO)_2]$ + phen.

(b) Precatalyst: $[Pd(bipy)_2][X]_2$

X	*g CP/g Pd*	η *(dL/g)*
PF_6^-	2292	1.42
BF_4^-	226	n.d

Reaction conditions: $[Pd] = 1.25 \times 10^{-3}$ M; $[BQ] = 0.1$ M; solvent methanol, $V = 200$ mL; $P_{tot} = 56$ atm; $T = 70$ °C; time = 5h.

Some preliminary results on the CO/styrene copolymerization promoted by $[Pd(N\text{-}N)_2][PF_6]_2$ had indicated the 2,2′-bipyridine as the most active among the tested N-N ancillary ligands.[20a] This catalytic system was strongly influenced by the reaction medium. Indeed, a change of the solvent from methanol to 2,2,2-trifluoroethanol resulted in an increase of productivity (from 650 g CP/g Pd in MeOH to 1134 g CP/g Pd in TFE). Moreover, the copolymer obtained in methanol was grey, while that prepared in TFE was white, indicating that a negligible decomposition of the active species to palladium metal occurred. In TFE the productivity was almost unaffected by the catalyst concentration and values as high as 1.1 kg CP/g Pd at a [styr]/[Pd] ratio of 48,000 were obtained. Despite the increase in productivity the η value is still low (0.21 dL/g) and the amount of palladium residue in the copolymer is quite high (154 ppm).[29] To improve this catalytic system the effect of different parameters was analyzed. Temperature plays an important role, both on the activity of the system and on the quality of polyketones produced (Table V). An increase of temperature resulted in a remarkable increase of productivity, and at 80°C the productivity was almost four times higher than that at 60°C (Table V). The copolymer was white and contained a low amount of palladium. However, the temperature had a negative effect on the molecular weight of the polymer: the η value decreased on increasing temperature (Table V). Since high molecular weight polymers are needed for desirable applications,[4s] we decided to work at 60°C and, in order to increase the yield, the reaction time was prolonged. The effect of reaction time was examined at two different catalyst concentrations, which correspond to [styr]/[Pd] ratio of 48,000 and 96,000, respectively. The reactions were carried out for one or two days, and 5 g of copolymer were recovered in both cases at the end. At the [styr]/[Pd] ratio of 96,000 this yield corresponds to a productivity of 17.4 kg CP/g Pd, with minor decomposition of the catalytic species. The copolymer had an η value of 0.36 dL/g and contained only 32 ppm of Pd. This result represents the first example of production of CO/styrene copolymer in high yield, with the highest molecular weight and the lowest amount of palladium to date.

At 60°C the difference between methanol and TFE was investigated in detail. As reported in Fig. 4, although after 5h the yields of copolymer in the two solvents were comparable, for longer reaction times the yield in TFE became increasingly higher than that in methanol. The plot of productivity against the reaction time shows, in methanol, an asymptotic behavior and after 14 h the active species was deactivated and the copolymer was grey (Fig. 4a). In TFE the productivity increased on extending the reaction time and the catalyst was still active after 24 h: a productivity of 8.3 kg CP/g Pd was obtained and negligible decomposition to metal was observed. Moreover, while in methanol the reaction rate decreased with time, in TFE it increased (Fig. 4b). These trends indicate that the difference between the two solvents might be related to the catalyst lifetime. Clearly, the stability of the catalyst is greatly enhanced in trifluoroethanol with respect to methanol.

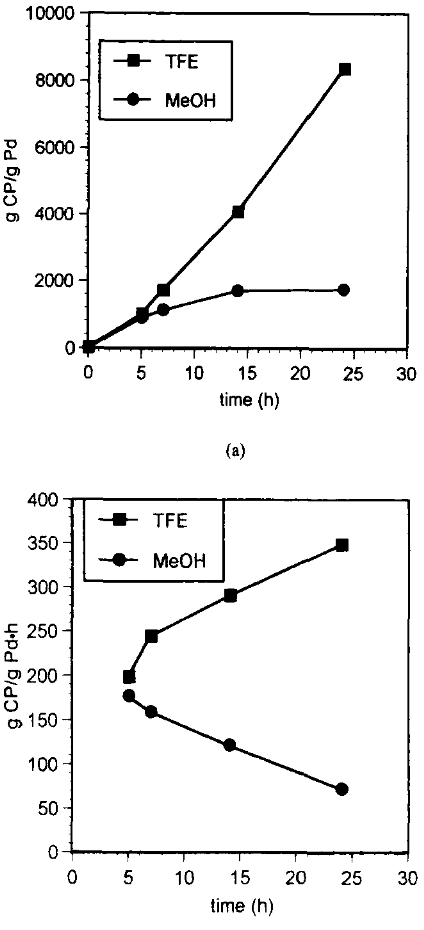
TABLE V CO/Styrene Copolymerization: Effect of Temperature Precatalyst: $[Pd(bipy)_2][PF_6]_2$

T(°C)	*g CP*	*g CP/g Pd*	*g CP/g Pd·h*	*Pd (ppm)*	η *(dL/g)*
60	1.09(w)	1897	271	n.d.	0.27
65	1.60(w)	2784	398	n.d.	n.d.
70	2.36(w)	4107	587	60	0.25
75	3.15(w)	5481	784	49	0.17
80	4.56(w)	7935	1134	44	0.14

Reaction conditions: $n_{Pd} = 0.54 \times 10^{-2}$ mmol; $n_{BQ} = 0.348$ mmol; styrene $V = 30$ mL; solvent TFE $V = 20$ mL; 2,2-dimethoxypropane (DMP) $V = 0.5$ mL; $P_{co} = 40$ atm.

The productivity was also influenced by the pressure of carbon monoxide: it increased on decreasing the CO pressure, confirming the inhibiting role of CO already reported by Brookhart[4n] and observed with the monochelated carboxylato derivatives, too (see above).[18b] At an initial pressure of 10 atm, measured at room temperature, a productivity of at least 15 kg CP/g Pd was achieved.[29]

All these experiments were conducted in the presence of 1,4-benzoquinone, which has been reported to be essential for achieving high productivities in the CO/styrene copolymerization.[3,4s] We found that only a small excess of the oxidant with respect to palladium is required for high yields of polyketones ([BQ]/[Pd] = 5) (Table VI). The most important result concerns the effect of the amount of benzoquinone on the molecular weight of polyketones. We found that this parameter greatly increased by decreasing the BQ concentration. Indeed, the copolymer obatined with a [BQ]/[Pd] ratio of 5 has the remarkably high η value of



(a)

(b)

FIGURE 4 CO/styrene copolymerization: effect of solvent Precatalyst: $[Pd(bipy)_2][PF_6]_2$. Reaction conditions: see Table V; *T*= 60 °C. *(a)* productivity vs reaction time. *(b)* reaction rate vs reaction time

0.64 dL/g, which represents the first case of production of a CO/styrene copolymer with such a high molecular weight. It is realistic to expect that further improvement of the catalytic system might produce copolymers with an η value close to 1 dL/g.

TABLE VI CO/Styrene Copolymerization: Effect of 1,4-Benzoquinone Catalyst Precursor: $[Pd(bipy)_2][PF_6]_2$

BQ (mmol)	*[BQ]/[Pd]*	*g CP*	*g CP/g Pd*	η *(dL/g)*
0.348	64	2.33(w)	4054	0.32
0.108	20	2.15(w)	3741	n.d.
0.054	10	2.18(w)	3793	n.d.
0.027	5	2.58(w)	4490	0.64

Reaction conditions: see Table V, $T = 60$ °C; $t = 14$ h.

VI. COPOLYMERIZATION PROMOTED BY $[Pd(N\text{-}N)(CH_3)(S)][BAr'_4]$ ($BAr'_4 = 3,5\text{-}(CF_3)_2C_6H_3$; $S = CH_3CN$)

As mentioned in the Introduction, when α-olefins are used as comonomers an important goal is the control of regio- and stereochemistry of the insertion of olefin in the growing chain. Since Consiglio already determined in the early studies on the CO/styrene copolymerization that the insertion of styrene takes place with a secondary regiochemistry,[13a,c] the problem of controlling its stereochemistry was more complicated to solve.

When achiral chelating nitrogen ligands, such as bipy or phen, are used, the resulting CO/styrene polyketone (as well as the CO/4-*tert*-butylstyrene copolymer) has an essentially syndiotactic structure (80% of stereoregularity), as assigned on the basis of measured and calculated X-ray patterns and of ^{13}C NMR spectra.[13,18a] This stereoregularity was enhanced to 90% by using $[Pd(N\text{-}N)(CH_3)(NCCH_3)][BAr'_4]$, where N-N is the 2,2′-bipyrimidine, in CH_2Cl_2 exposed to 1 atm of CO at 25°C.[14b] The main peculiarity of this last catalytic system consists in the living nature of the polymerization. Indeed, it represents a rare example of living alternating copolymerization.[14]

In this last catalytic system when N-N is an enantiomerically pure C_2-symmetric bis-oxazoline, the copolymer has a highly isotactic microstructure, with a stereoregularity greater than 98%, and a high optical activity.[4j,14b] Therefore, by using the enantiomerically pure C_2-symmetric ligand, the enantioface discrimination was shifted from the chain-end control mechanism, which is responsible for the syndiotactic microstructure,[13a–c] to an enantiomorphic site control.[14b]

On the basis of these considerations, the synthesis of a stereoblock CO/4-*tert*-butylstyrene polyketone was realized through the ancillary ligand exchange during the living copolymerization.[19] Indeed, when the copolymerization was performed with the compound [Pd(N-N)(CH_3)($NCCH_3$)][BAr′], where N-N is the enantiomerically pure bis-oxazoline, and after 23 hours of reaction bipy was added in the catalytic mixture, a stereoblock copolymer was obtained. Its ^{13}C NMR spectrum showed isotactic and syndiotactic resonances, indicating that ligand exchange between the chiral bis-oxazoline and the achiral bipyridine occurred.[19] Moreover, when for the copolymerization the catalyst with (S,S)-bis-oxazoline was used together with the free (R,R)-bis-oxazoline, a substantially syndiotactic polyketone was the product. This result was explained assuming that the ligand exchange was rapid with respect to chain growth, allowing chain-end control to work in concert with the enantiomorphic site control.[19]

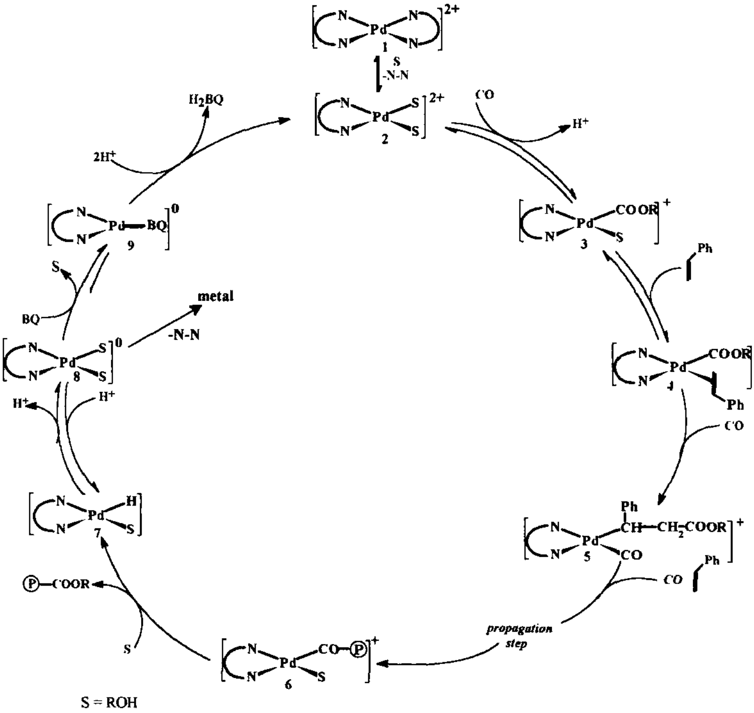
VII. THE MECHANISM

The reaction mechanism has been extensively discussed by Drent,[3,10] Consiglio,[4r,13,15C] Brookhart,[4i,n,14,19] Vrieze,[32] and Sen.[33] It is generally accepted that the catalytic cycle comprises three parts: initiation, propagation, and termination steps. The propagation steps are recognized to be the same in all the copolymerization processes and consist of subsequent alternated migratory insertions of alkyl group to CO and of acyl group to olefin, which have been studied by NMR spectroscopy by Brookhart[4i,n] and Vrieze.[32] Instead the initiation and termination steps are different, depending on the nature of the olefinic comonomer.

For our system we propose the catalytic cycle reported in Scheme 2. The initiation steps comprise the formation of the active species **3** through the dissociation of one of the two molecules of nitrogen ligand and the subsequent reaction with CO and alcohol. This is followed by coordination of the olefin and the first insertion of olefin in the Pd-acyl, bond, with the formation of the species **5** containing the Pd-alkyl group.

Then there are the propagation steps, where the copolymeric chain grows bonded to palladium. After these there are the termination steps, where the polymeric chain leaves the palladium, yielding a palladium-hydride species **7**, which can either decompose to palladium metal or regenerate the catalyst through the action of benzoquinone.

In particular, for our system we propose the initiation steps as formed by three different equilibria. First (Eq. (5); S = ROH) the dissociation of

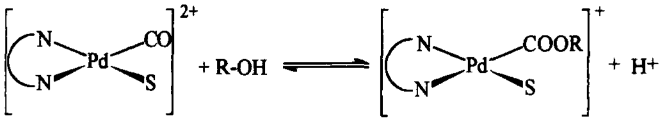


SCHEME 2

one molecule of nitrogen ligand from palladium generates a monochelated species with two very easily available coordination sites in *cis* configuration. The affinity of palladium for CO is known[3]; therefore the coordination of carbon monoxide is likely to occur on this species (Eq.(6)), followed by the interaction with alcohol and the subsequent formation of the monocationic carboalkoxy derivative and one proton (Eq. (7)). This carboalkoxy intermediate may be considered as the real active species. The proton can react with the free N-N molecule according to the equilibrium (8), yielding the monoprotonated ligand. This equlibrium is important for the control of the proton concentration during the copolymerization process, and it might contribute to increasing the concentration of the carboalkoxy intermediate.

(6)

S = ROH

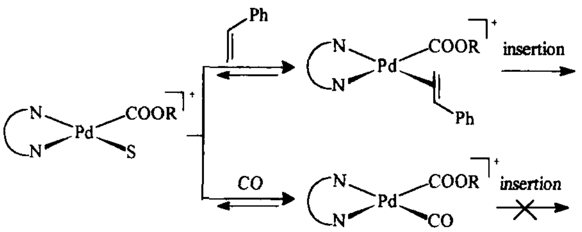


(7)

S = ROH

$$\text{N-N} + \text{H}^+ \rightleftharpoons [(\text{N-N})\text{H}]^+ \qquad (8)$$

Coordination of styrene to the monocationic active species, followed by its insertion, will lead to the propagation of the polymeric chain (Eq. (9a)). On the contrary, coordination of carbon monoxide leads to a carbonyl carbomethoxy intermediate, which, due to the unfavorable thermodynamics of the double carbonylation reaction,[34] can not proceed further (Eq. (9b)). This monocarbonyl carbomethoxy species has been isolated and structurally characterized by Brookhart, who demonstrated that this is the resting state of the catalytic cycle.[4i]



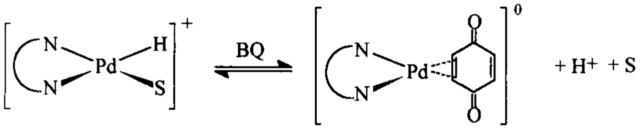
(9a)

(9b)

S = ROH

Drent reported that in the CO/styrene copolymerization the termination steps always produce a hydrido species, which can be either reoxidized to palladium(II) by the oxidant or can decompose to palladium metal.[3] The termination steps can be a β-hydrogen elimination or an alcoholysis, which requires the nucleophilic attack of the alcohol to the metal center. The higher productivity in TFE with respect to methanol might be due in part to the lower nucleophilicity of TFE compared to MeOH.

The hydrido species can dissociate the hydrogen as a proton, and the resulting Pd(0) species can bind the oxidant (Eq. (10)).



(10)

S = ROH

The intermediate with the benzoquinone bound to palladium has been always postulated,[3] but neither detected nor trapped. To tentatively understand its role, the chemical behavior in solution of the Pd(0) compound, [Pd(bipy)(BQ)], was investigated by ^{1}H NMR spectroscopy in DMSO.[29] The color of this solution immediately turned from the initial red to yellow upon addition of CF_3COOH. As shown by the ^{1}H NMR spectrum, benzoquinone completely transformed into free hydroquinone, while the bipy resonances corresponded to those of $[Pd(bipy)(CF_3COO)_2]$.[18a]

The red solution of [Pd(bipy)(BQ)] also turned to yellow upon addition of two equivalents of $[(bipy)H][PF_6]$. Again the ^{1}H NMR spectrum showed the resonances of free hydroquinone and no signal due to benzoquinone. The bipy resonances were the same as in the spectrum of a solution equimolar in $[Pd(bipy)_2][PF_6]_2$ and bipy.

Therefore the benzoquinone Pd(0) complex, which might be considered as a putative intermediate of the catalytic cycle, is readily oxidized to Pd(II) at room temperature in the presence of protons with the contemporary reduction of benzoquinone to hydroquinone. Moreover, the resulting Pd(II) species correspond exactly to the catalyst precursors and can immediately re-enter the catalytic cycle.

VIII. CONCLUSION

Analysis of the catalytic systems reported in this overview showed that both in the mixed-ligand complexes, $[Pd(dppp)(N\text{-}N)][PF_6]_2$, and in the bischelated symmetrical compounds, $[Pd(bipy)_2][PF_6]_2$, the second molecule of nitrogen chelating ligand plays an important role, both on the activity of the system and on the quality of the polyketones. In particular, it is important to control the proton concentration during the copolymerization reaction, through the establishment of the equilibrium (8).

Moreover, $[Pd(bipy)_2][PF_6]_2$ is the most efficient precatalyst for the CO/styrene copolymerization found to date. High productivities of CO/styrene polyketone were achieved in TFE; the polymer has a good molecular weight and contains a low amount of palladium residue.

The copolymers obtained from carbon monoxide and ethylene or from carbon monoxide and styrene have a melting point which is too close to their decomposition temperature[10] and, therefore, they cannot be processed like thermoplastic materials. Drent found that the addition in the reaction mixture of a low percentage of a second olefin, like propylene, caused the formation of the terpolymer named Carilon®, whose melting point is lower than that of the CO/ethylene copolymer, while its decomposition temperature is almost unchanged, allowing this material to be melt processable.[10] The same effect has been reported very recently by BP Chemical upon addition of a second aliphatic α-olefin, like 1-butene and 1-hexene, yielding the terpolymer named Ketonex®.[5c]

We found that the CO/ethylene and CO/styrene polyketones can be transformed into stable objects with good mechanical properties just by pressing the white or colored polyketone powder at room temperature (Fig. 5).[35]

Abbreviations Used: *bipy = 2,2′-bipyridine; phen = 1,10-phenanthroline; tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline; dmphen = 2,9-dimethyl-1,10-phenanthroline; dmbipy = 4,4′-dimethyl-2,2′-bipyridine; dppp = 1,3-bis(diphenylphosphino)propane; PhCN = benzonitrile; BQ = 1,4-benzoquinone; HBQ = hydroquinone; TFE = 2,2,2-trifluoroethanol; CP = copolymer; TP = terpolymer; g CP/g Pd = grams of copolymer per gram of palladium; g CP/g Pd·h = grams of copolymer per gram of palladium per hour; DMSO = dimethylsulfoxide; styr = styrene; S = coordinating solvents, usually DMSO, unless otherwise stated*

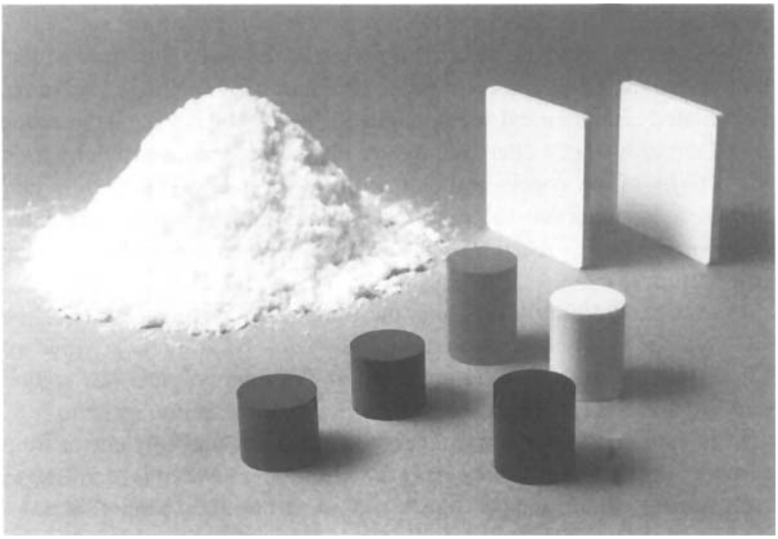


FIGURE 5 The white powder of the copolymer and some objects made of copolymer

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