Control of Polymer Composition in Pd-Catalyzed CO/Olefin Terpolymerization Reactions

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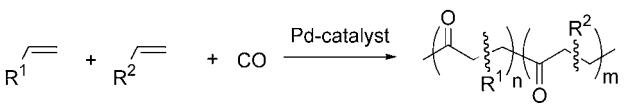
Abstract: The CO/*tert*-butylstyrene/ethylene terpolymerization catalyzed by Pd-(N-N′) complexes was studied. The results evidence that the olefin preferentially inserted in the terpolymer chain is strictly related to the nature of the nitrogen ligand, mainly to its steric constraints, and not to the kind of ligand. Indeed, slight variations in the backbone of the nitrogen ligands coordinated to palladium allow for the synthesis of terpolymers with a controlled composition.

Keywords: carbon monoxide; catalysis; N ligands; palladium; polyketone; polymerization

Introduction

After the discovery that palladium(II) complexes with diphosphine ligands efficiently catalyze the perfectly alternating terpolymerization of CO with ethylene and propene,[1] polyketones became a commercial reality in the form of *Carilon* from Shell[2] and *Ketonex* from BP.[3] Although the presence of two different olefins in the polyketone backbone allows for the synthesis of thermoplastics with variable physical properties, these terpolymers[4–11] have been less studied than the related copolymers (Scheme 1).[12]

Analogous to what was reported for the catalytic CO/olefin copolymerization, also for the terpolymerization reaction a correlation between the olefin co-monomer and the ancillary ligand present in the palladium catalyst can be found. When carbon monoxide is terpolymerized with aliphatic α-olefins, phosphorus-donor ligands are preferentially used.[5c,7a,9,13] Up to now, only one example of the terpolymerization of two vinylarenes with CO has been reported. [17] The catalytic system used is based on palladium complexes containing 1,10-phenanthroline. The terpolymerization of one aromatic and one aliphatic olefin with CO seems somehow more versatile, and different kinds of ligands such as P-P,[14] P-OP,[8] N-N,[4,5b,10,14,15] and hybrid P-N molecules[5a,16] have been successfully tested.



Scheme 1. Terpolymerization of olefins with carbon monoxide.

From a general point of view, the chain propagation of the Pd-catalyzed terpolymerization of carbon monoxide with olefins is based on the alternating migratory insertion of CO into a Pd–alkyl bond and of one of the olefins in the reaction mixture into a Pd–acyl bond. Therefore, depending on the relative characteristics of both the olefins and the catalyst, the obtained terpolymers may have different composition and, as a consequence, different properties.

We have recently reported the applicability of new nitrogen ligands for the Pd-catalyzed CO/*tert*-butylstyrene (TBS) copolymerization.[18–20] Effects on catalytic activity and polymer properties (mainly M_w and stereoregularity) were observed through slight modification of the ligand backbone. Here we study the catalytic activity of palladium complexes containing the chiral C_1-symmetrical pyridine-imidazolines **1**–**4**[19,20] and the planar C_s-symmetrical pyrazole-pyrimidines **5**[18] and **6**[21] on the CO/ *tert*-butylstyrene/ethylene (CO/TBS/E) terpolymerization (Scheme 2).

Despite the structural similarities presented by the chelating nitrogen ligands **1**–**6**, the corresponding palladium complexes behave in an unexpectedly different fashion towards ethylene and styrene. NMR analysis of the terpolymers makes it possible to assign the different compositions of the polymers and, in conjunction

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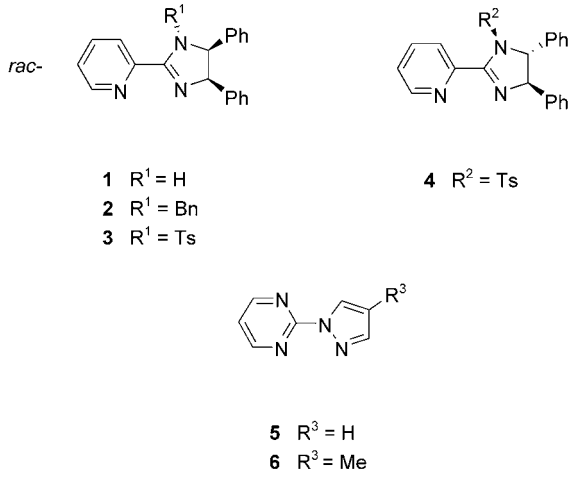


Scheme 2. N ligands used in this work (pyridine-imidazolines **1**–**4** and pyrazole-pyrimidines **5** and **6**).

with circular dichroism (CD) measurements, the effect of the chiral ligand on the stereoregularity of some of the terpolymers can be envisaged.

Results and Discussion

All precatalysts [Pd(Me)(NCMe)(N-N′)][BAr′$_4$] (N-N′ = **1**–**6**) were first tested in the CO/TBS/E terpolymerization reaction under standard conditions, at 10 bar of pressure (CO/ethylene = 1:1). The results are shown in Table 1 which also includes the data of CO/TBS copolymerizations carried out at 1 bar of CO for purposes of comparison.

The productivity of the catalytic systems in the terpolymerization reaction is clearly affected by the nitrogen ligand coordinated to palladium. The catalysts containing the racemic pyridine-imidazolines **1**–**3**, with *cis*-stereochemistry in the imidazoline ring, show modest activities, which are affected by the electronic variations in the imidazoline ring. The most active ligand **3** is the one with the electron-withdrawing substituent. Productivity increases by one order of magnitude with the catalyst containing the pyridine-imidazoline **4**, with *trans* stereochemistry in the imidazoline moiety. Greater amounts of terpolymers are also obtained when the catalysts with planar pyrazole-pyrimidine ligands (**5** and **6**) are used. GPC analysis of the polymers reveals that the most productive systems yield polyketones of higher molecular weight (30000 *vs.* 15000 g/mol). Complete decomposition of the catalysts to Pd(0) is observed for the less active systems (**1**–**3**) after depressurizing the reactors. The solutions obtained at the end of the experiments with ligands **4**–**6**, however, are yellow, indicating the presence of Pd(II) species.[22] This observation, together with the fact that the average TON values found for the systems based on ligands **4**–**6** are higher than those for the systems based on ligands **1**–**3** (Table 1), suggests that the different catalytic behavior might be due to the different stability of the corresponding active

Table 1. CO/TBS/E terpolymerization at 10 bar (CO/E)[a] and CO/TBS copolymerization at 1 bar CO:[b] effect of the nitrogen-donor ligand. Catalyst precursor: [Pd(Me)(NCMe)(**N-N′**)][BAr′$_4$] (N–N′ = **1**–**6**).

Ligand	Prod.[c] [g PK (g Pd^{-1} h^{-1})]	% E [d]	M_n (M_w/Mn)[e]	TON [mol PK·(mol Pd)$^{-1}$]
1	0.3	76	11250 (1.4)	2
2	1.0	92	8600 (1.6)	9
3	1.6	97	14600 (1.4)	9
4	10.6	61	n.d.	n.d.
5	6.9	45	20600 (1.8)	27
6	9.6	50	29800 (1.8)	26
1	2.0[f]	–	42200 (1.1)[g]	6
2	8.9	–	49750 (1.5)[g]	14
3	7.0	–	59300 (1.2)[g]	9
4	27.2	–	54700 (1.4)[h]	40
5	11.8[i]	–	36350 (1.3)[g]	26
6	7.5[i]	–	15400 (1.7)[h]	39

[a] Reaction conditions: [Pd]: 12.5 μmol; [TBS]/[Pd] = 620; p(CO/E) = 10 bar; solvent: 5 mL of CH_2Cl_2; room temperature; 24 hours.
[b] Same conditions, except solvent: 5 mL of chlorobenzene; see refs.[18,20]
[c] Calculated from isolated polymer.
[d] Calculated by relative integration of the ^{1}H NMR signals of the terpolymers.
[e] Determined in $CHCl_3$ *vs.* polystyrene standards.
[f] [Pd] = 8.3 μmol.
[g] Determined by SEC-MALLS in THF.
[h] Determined by GPC in THF, relative to polystyrene standards.
[i] [TBS]/[Pd] = 310.
PK = polyketone; n.d. = not determined.

species under terpolymerization conditions. The trend of productivity in the terpolymerization reaction is analogous to that found in the CO/TBS copolymerization (Table 1): in both reactions the chiral, racemic ligands **1**–**3** with the substituents in *cis*-geometry are the least active and the enantiomerically pure ligand **4** with the *trans*-geometry is the most active. For all the ligands **1**–**6** tested, the activity found in the CO/TBS copolymerization is higher than that reported for the CO/TBS/E terpolymerization, thus indicating that ethylene has a negative effect on these catalytic systems. The comparison of the average TON values for the two reactions suggests that this effect might be related to a decreased stability of the catalyst in the presence of ethylene.

The composition of the terpolymers (ethylene/TBS ratio) was evaluated by integrating the signals corresponding to the CH_2 protons in the ^1H NMR spectra (Figure 1). The two methylenic protons of the CO/TBS units are diastereotopic and appear at 3.1 and 2.5 ppm, respectively. On the other hand, the four methylenic protons of the CO/E units are equivalent and appear also at 2.5 ppm.[5a] Table 1 shows how the terpolymer composition depends on the nature of ligands. While catalysts bearing pyridine-imidazolines **1**–**3** lead to terpolymers with high ethylene content (>75%), catalysts containing ligands **4**–**6** yield terpolymers with similar concentration of both olefins (ethylene content: 45–60%).

In order to analyze the different behavior of the catalysts towards pressure, we carried out various terpolymerization experiments varying the CO/E pressure in the range 1–18 bar. The productivities of catalysts containing ligands **1**–**3** generally show an inverse dependency on the pressure of the catalytic experiments (Table 2).[23]

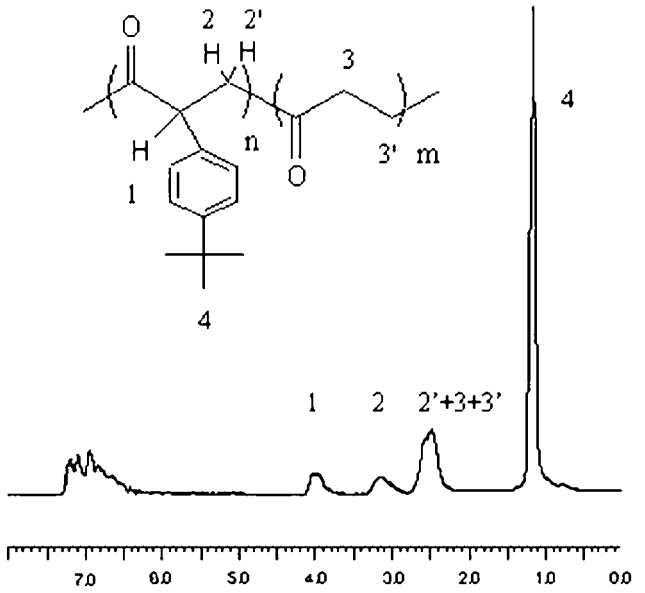


Figure 1. ^1H NMR spectrum of an ethylene/*tert*-butylstyrene/CO terpolymer.

Notably for these systems (**1**–**3**) the variation of the CO/E pressure also affects the composition of the terpolymers (Table 2), thus suggesting that terpolymers of desired composition can be provided by choosing the proper ligand/pressure combination. For instance, terpolymer chains with a content of ethylene of around 80–90% can be prepared with all three catalysts at 10

Table 2. Effect of pressure on the CO/TBS/E terpolymerization with catalysts [Pd(Me)(NCMe)(N–N′)][BAr′$_4$] (N-N′ = **1**–**3**).

Run	Ligand	p(CO/E) [bar]	Prod[a] [g PK (g Pd^{-1} h^{-1})]	% E[b]	M_n (M_w/M_n)[c]
1	**1**	1.0	2.4	49	23600 (1.7)
2		2.5	2.3	55	35250 (1.6)
3		5.0	1.4	82	23100 (1.4)
4		7.5	1.5	85	25550 (1.3)
5		10.0	0.3	76	11250 (1.4)
6	**2**	1.0	3.1	52	8000 (1.5)
7		2.5	2.9	76	20350 (1.4)
8		5.0	1.8	74	9700 (1.4)
9		7.5	1.5	81	10600 (1.3)
10		10.0	1.0	92	8600 (1.6)
11	**3**	1.0	13.7	44	12200 (2.2)
12		2.5	1.5	91	8600 (1.3)
13		5.0	1.7	81	8200 (1.4)
14		7.5	3.2	95	12600 (1.7)
15		10.0	1.6	97	14600 (1.4)

Reaction conditions: [Pd]: 12.5 μmol; [TBS]/[Pd]: 620; solvent: 5 mL CH_2Cl_2; room temperature; 24 hours.
[a] Calculated from the isolated terpolymer.
[b] Calculated from ^1H NMR.
[c] Determined by GPC measurements in $CHCl_3$ *versus* polystyrene standards.

bar of total pressure. On the other hand, the amount of ethylene can be conveniently lowered when the pressure is decreased.[24] The preferential enchainment of ethylene versus *tert*-butylstyrene during the terpolymerization, at similar concentrations of the two olefins, has been previously reported for catalysts containing N-N′ (pyridine-oxazoline) and P-N (phosphino-oxazoline) ligands.[5a, b,16] The molecular weight of the terpolymers obtained using ligands **1**–**3** gave values in the range 8000–35000 (Table 2).

Table 3 shows selected results of experiments performed with the more active systems, that is those bearing ligands **4**–**6**. In the case of pyridine-imidazoline **4** an increase in the CO/E pressure results in an increase in productivity, while no effect on the ethylene content of the terpolymers is observed. In the case of catalyst with ligand **5**, the effect of CO/E pressure on the productivity is very pronounced. In particular, when the reaction is carried out at a total pressure of 1 bar, no incorporation of ethylene into the polymeric chain is observed. This contrasts with the data obtained from catalysts containing ligands **1**–**3** (Table 2). The ethylene content increases to a maximum of 64% only when a total pressure of 18 bar is used (Table 3, entries 3–5). The analysis of the effect of pressure on productivity and terpolymer composition reveals the key role played by the nitrogen ligand in this reaction.

The terpolymers were further analyzed by means of ^{13}C NMR spectroscopy. The spectra of the ethylene/*tert*-butylstyrene/carbon monoxide terpolymers show the signals of the alternating CO/TBS copolymers, with two additional signals at 36.3 and 35.5 ppm corresponding to the presence of CO/E units.[5a] The intensity of these two signals varies with the content of ethylene in the terpolymers (Figure 2). In particular, the intensity of the peak at 36.3 ppm increases when the amount of ethylene in the terpolymers increases. On this basis it is possible to assign this signal to CO/E units in CO/E blocks, while the peak at 35.5 ppm is attributed to a CO/E unit followed by a CO/TBS unit.

The analysis of the signals related to the methylenic carbon of *tert*-butylstyrene (46.5–43.0 ppm range) is

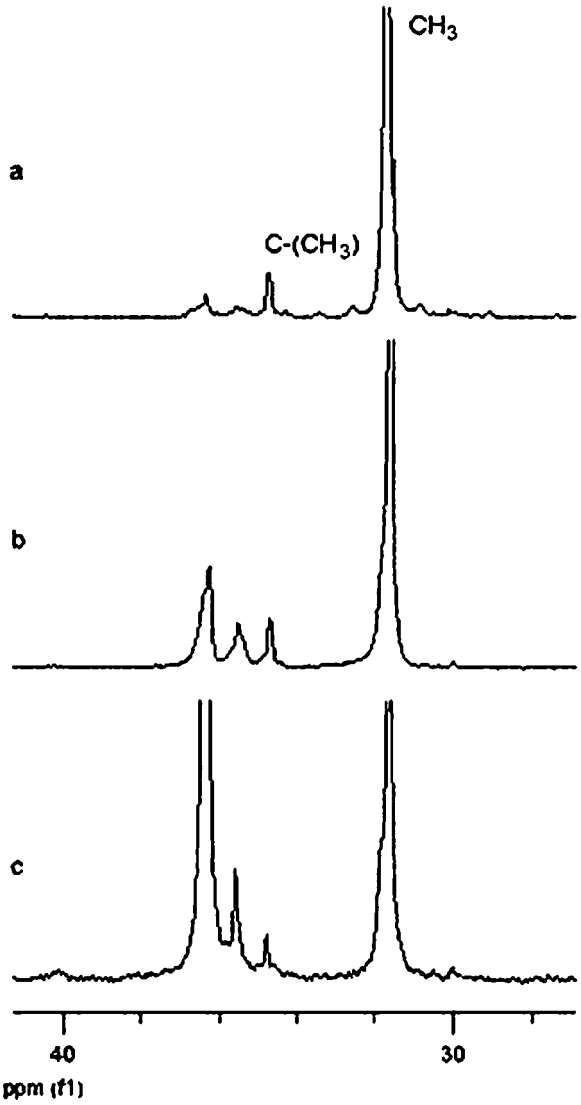


Figure 2. Comparative ^{13}C NMR spectra of the -CH_2-CH_2-C(O)- region from CO/TBS/E terpolymers with increasing ethylene content (**a**: 12.3%; **b**: 52.3%; **c**: 92.0%, respectively), obtained with catalyst [Pd(Me)(NCMe)(**2**)][BAr′$_4$].

Table 3. Effect of pressure on the CO/TBS/E terpolymerization with catalysts [Pd(Me)(NCMe)(N-N′)][BAr′$_4$] (N-N′ = **4**–**6**).

Run	Ligand	nPd [μmol]	p(CO/E) [bar]	Prod. [g PK(g Pd^{-1} h^{-1})]	% E[a]	M_n (M_w/M_n)[b]
1	**4**	12.5	7.5	6.7	58	29100 (1.3)
2		12.5	10	10.6	61	n.d.
3	**5**	12.5	1	21.6	0	n.d.
4		12.5	10	6.9	45	20600 (1.8)
5		12.5	18	6.6	64	24100 (1.6)
6	**6**	12.5	10	9.6	50	29800 (1.8)
7		6.25	10	5.9	59	25600 (1.8)

Reaction conditions: [TBS]/[Pd] = 620; solvent: 5 ml CH_2Cl_2; 24 hours; room temperature.
[a] Calculated from ^1H NMR.
[b] Determined by GPC measurements in $CHCl_3$ *vs.* polystyrene standards.

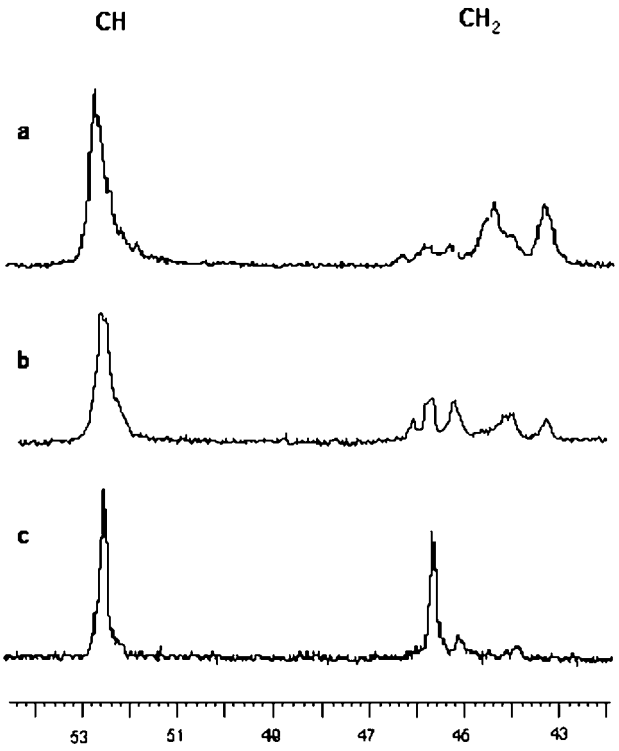


Figure 3. Comparative ^{13}C NMR spectra of CO/TBS/E terpolymers with increasing ethylene contents (**a**: 12.3%; **b**: 52.3%; **c**: 92%, respectively), obtained with catalyst [Pd(Me)(NCMe)(**2**)][BAr′$_4$].

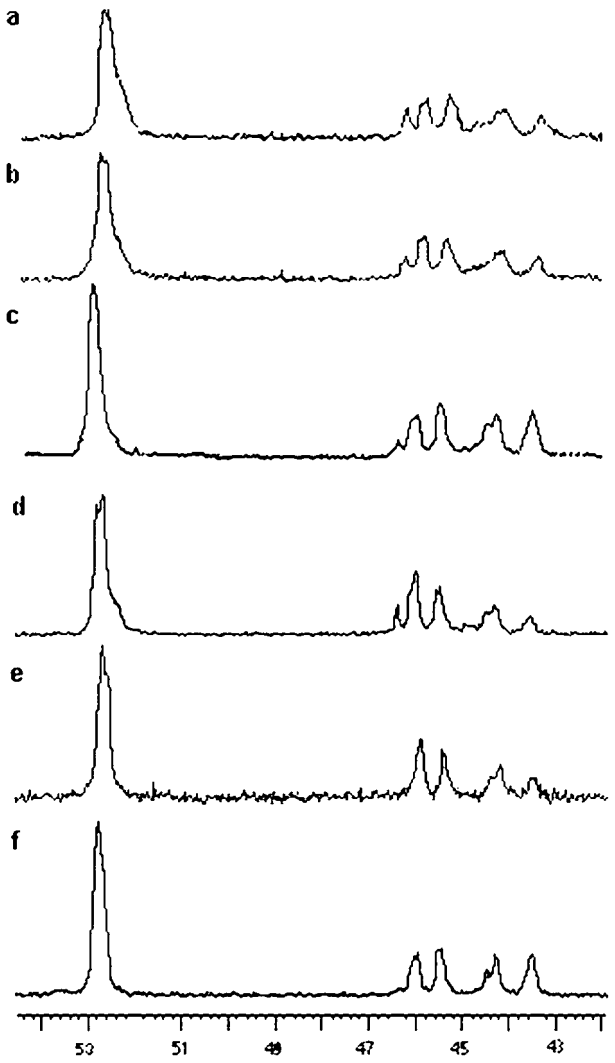


Figure 4. Comparative ^{13}C NMR of terpolymers with *ca.* 50% ethylene content obtained with ligands **1**–**6** (**a**–**f**, respectively).

somewhat more complicated, since not only composition but also tacticity may be seen in this region (Figure 3). The terpolymers with a high content of ethylene (*ca.* 90%) show only a major signal at 45.9 ppm, irrespective of the ligand used. In agreement with the literature, this signal is attributed to isolated CO/TBS units.[5a] Figure 3 compares the spectra of the terpolymers synthesized with the same catalytic system, but with different amounts of ethylene. The spectra of terpolymers with an ethylene content lower than 25% are similar to those of CO/TBS copolymers although three small signals appear in place of the isotactic triad signal (45.9 ppm)[20] (Figure 3a). These three new signals become more evident when the ethylene content in the terpolymers is increased (Figure 3b) and at higher contents, as stated above, only one of these signals remains (Figure 3c).

In order to tentatively understand the origin of these new signals, we compared the spectra of terpolymers, with an ethylene content of about 50%, obtained with all the series of ligands studied here (**1**–**6**) (Figure 4). It is worth noting that the number of signals and their intensity clearly depends on the ligand used. In the spectra of the polyketones synthesized with ligands **5** and **6** (Figure 4e and 4f) only two peaks are present in the region between 45.0 and 47.0 ppm, while in the spectra of the polyketones prepared with the pyridine-imidazolines ligands **1**–**4** an additional resonance at 46.3 ppm is evident (Figure 4a–4d).

Considering that the two olefins are randomly distributed and that all the polymers have the same composition (*ca.* 50% ethylene), it could be speculated whether this signal is related to tacticity. If we consider that planar nitrogen ligands lead to syndiotactic terpolymers (as previously stated for CO/styrene copolymers),[13] it seems that the chiral pyridine-imidazoline ligands **1**–**4** lead to variations in the degree of stereoregularity of the terpolymers. The CD spectrum of the CO/TBS/E polyketone obtained with the catalytic system based on the enantiomeric pure ligand **4** shows a clear absorption band at 284.8 nm (Figure 5) and a specific rotation $[\alpha]_D$ of +4.94. On the other hand, a syndiotactic polyketone is obtained when the same catalyst is used in the CO/TBS copolymerization. Thus, these results indicate

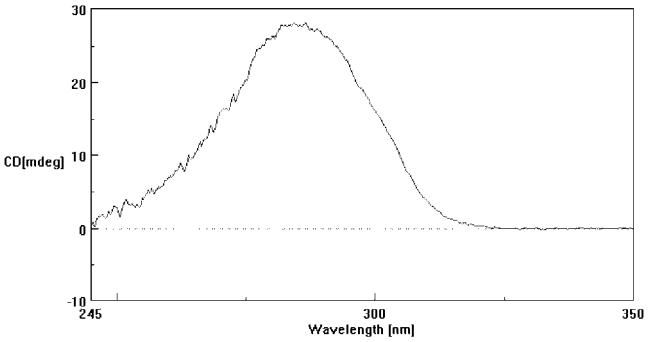


Figure 5. CD spectrum of the CO/TBS/E polyketone synthesized with [Pd(Me)(NCMe)(**4**)][BAr′$_4$]. Ordinate is expressed in millidegrees as measured in the CD spectrum ($T = 25\,^{\circ}C$; 0.091 mg of terpolymer dissolved in 10 mL of $CHCl_3$).

that in the terpolymerization reaction the enantioface selection is, at least partially, under enantiomorphic site control, while during the copolymerization it is dictated by the chain-end control. An analogous shift of the enantioface control from the growing chain to the enantiomorphic site has been recently reported for the co- and terpolymerization promoted by the pyridine-oxazoline Pd-complexes.[5b]

Conclusions

The analysis of the reported catalytic systems applied to CO/aromatic olefin/aliphatic olefin terpolymerization reveals that with N–N ligands, such as bisoxazoline[10] or pyridine-oxazoline,[5c] the aromatic olefin is preferentially inserted in the growing polymeric chain with respect to the aliphatic one, whereas with P donating ligands the aliphatic olefin is preferred.[5a, b,8,16] The present investigation evidences that the choice of the olefin preferentially inserted in the terpolymer is strictly related to the nature of the nitrogen ligand present in the catalyst, not only to the kind of ligand, as has been reported in the literature. Indeed, a slight modification in the chelating N ligands coordinated to palladium terpolymerization catalysts leads to unexpected results in the composition of the terpolymers. The catalysts containing pyridine-imidazolines **1**–**3** readily insert ethylene, even at low pressures and if the ethylene/styrene ratio is varied, terpolymers with a perfectly controlled composition are obtained. On the other hand, complexes with ligands **4**–**6** show less versatility towards ethylene pressure and give terpolymers with similar amounts of both olefins (in the pressure range investigated).

Differences are also encountered in activity: while catalysts with ligands **4**–**6** are highly active, those with ligands **1**–**3** decompose quickly. Comparing the planar ligands **5** and **6** with the bulkier chiral ones **1**–**4**, it seems that the chiral pyridine-imidazolines interfere more with the coordination/insertion of the olefin, which is the rate-determining step of the reaction. Apparently this would explain why the systems containing planar ligands **5** and **6**, are more active than the system containing **4**. The similarity between ligands **3** and **4**, which only differ in the configuration of one asymmetric carbon atom, and their disparate productivities show that it is more probable that a steric not an electronic effect is responsible for the results. In fact, X-ray analysis of the complex [Pd(Cl)$_2$(**4**)] shows that ligand **4** present a unique distortion in the imidazoline plane, which may account for the high reactivity observed with this ligand both in co- and terpolymerization reactions.[20]

Comparison with the CO/TBS results shows how the size of the polymer chain is lower when the chain contains ethylene, because of the favored β-H elimination.

Finally, CD analysis of the terpolymer obtained with the enantiomerically pure ligand **4** shows that it has main chain chirality. Since this ligand was not able to induce chirality in the CO/TBS copolymerization (syndiotactic copolymers were obtained), it is clear that the presence of ethylene in the growing polymer chain decreases the probability of chain-end control exerted by the last inserted styrene unit and makes enantiomorphic site control possible.

Experimental Section

General Procedure

All reactions were carried out using standard Schlenk techniques, under a nitrogen atmosphere, at room temperature. Solvents were distilled and deoxygenated prior to use unless otherwise stated. The salt NaBAr′$_4$ [Ar′ = 3,5-(CF$_3$)$_2$-C$_6$H$_3$] was prepared according to reported methods.[25] The ligands **1**–**6** and the palladium precursors [Pd(Me)(NCMe)(**1**–**6**)][BAr′$_4$] were prepared as previously described.[18–20]

^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury VX spectrometer with a ^{1}H resonance frequency of 400 MHz. Chemical shifts are reported relative to $CDCl_3$ (7.26 ppm for ^{1}H and 77.23 for ^{13}C). Some assignments in NMR spectra were determined by DEPT and NOE experiments. The molecular weights of the terpolymers and molecular weight distributions were determined by gel permeation chromatography (GPC) in $CHCl_3$ on a Waters 515-GPC device using a linear Waters Ultrastyragel column with a Waters 2410 refractive index detector and polystyrene standards. CD spectra were recorded on a Jasco J-700A spectropolarimeter (0.1 cm cell). Optical rotations were determined on a Perkin Elmer model 241 polarimeter.

Terpolymerization of *tert*-Butylstyrene/Ethylene/Carbon Monoxide

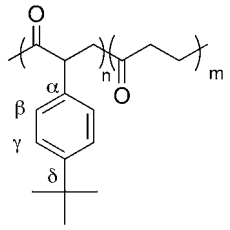
The *tert*-butylstyrene was passed through a small column of Al_2O_3 prior to use. Dichloromethane was distilled over P_2O_5 under N_2 atmosphere and stored over molecular sieves. Ethyl-

ene/carbon monoxide (1/1 mixture) was purchased from Air Liquid with a purity grade of 98%.

In a typical procedure the cationic precursor [Pd(Me)(NCMe)(N-N′)][BAr′$_4$] (N-N′ = **1–6**) (0.0125 mmol) was dissolved in 5 mL of dichloromethane using standard Schlenk techniques. *tert*-Butylstyrene (1.4 mL, 7.75 mmol) was then added and the reaction mixture was introduced into the 100-mL stainless steel Berghoff autoclave applying vacuum. The autoclave had been previously purged with the CO/E mixture. The reaction mixture was then pressurized to the desired level and left to react at room temperature for 24 hours. At the end of the reaction time, the unreacted gases were released. Work-up included filtration of the reaction mixture through Kieselghur and precipitation of the polymeric material by adding the reaction solution into 100 mL of methanol. The terpolymers were collected by filtration, washed with methanol and dried under vacuum.

Characterization of Terpolymers

The spectroscopic data of the terpolymer obtained in Table 1, entry 2 are given as an example. ^{1}H NMR ($CDCl_3$, RT): δ = 7.41–7.15 (aromatic), 4.25 [bs, -C*H*(Ar)-CH_2-C(O)-], 3.43



[bs, -CH(Ar)CH*H*-C(O)-], 2.79 [m, -CH(Ar)CH*H*-C(O)-, -C*HH*-C*HH*-C(O)-], 1.38 [bs, C(CH_3)$_3$]; ^{13}C NMR ($CDCl_3$, RT): δ = 208.3–207.6 [m, -*C*(O)-], 150.6 ($C_δ$), 134.7 ($C_α$), 128.0 ($C_γ$), 126.2 ($C_β$), 52.7 [-*C*H(Ar)-CH_2-C(O)-], 45.9 [-CH(Ar)-*C*H_2-C(O)-], 36.2 [-*C*H_2-*C*H_2-C(O)-E], 35.4 [-*C*H_2-*C*H_2-C(O)-TBS], 34.6 [-*C*(CH$_3$)], 31.5 [-C(*C*H$_3$)].

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$\delta = 8.70$ (dd, $^3J = 5.2$ Hz, $^4J = 2.5$ Hz, 1H, H^4 or H^6), 8.33 (s, 1H, H^{5pz}), 8.29 (dd, $^3J = 5.2$ Hz, $^4J = 2.5$ Hz, 1H, H^6 or H^4), 7.69 (s, 8H, H^{BARF}), 7.67 (s, 1H, H^{3pz}), 7.51 (s, 4H, H^{BARF}), 7.09 (t, $^3J = 5.2$ Hz, 1H, H^5), 2.31 (s, 3H, CH_3CN), 2.24 [s, 3H, $(CH_3)^{4pz}$], 1.27 (s, 3H, Pd-CH_3).

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