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Copolymerization of cyclopentene and carbon monoxide with palladium catalysts ☆

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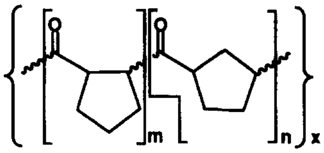
Abstract

The alternating copolymerization of cyclopentene with carbon monoxide using palladium catalyst systems of the type $[PdX_2(L_2)]$ (where (L_2) is a diphosphine or dinitrogen ligand, and X is a weakly coordinating or non-coordinating anion) is reported. High yields of the copolymer can be obtained in spite of the rather low catalytic activity of these systems. With molecular masses up to 8500 g mol^{-1} the chains of these copolymers are short. The enchainment of the olefin comonomer occurs seemingly statistically by 1,2 and 1,3 insertion, the latter insertion type being normally prevailing. Within the copolymers 95/5% regioselectivity towards the 1,3 addition product have been achieved, whereby copolymers with higher contents of 1,3 insertion usually show lower molecular weights. The ^{13}C spectra of these copolymers are in most cases rather simple even in the region of the carbonyl signal. This region of the spectra does not seem to be particularly sensitive to the regiochemistry of the copolymer. Its narrowness is taken as an indication of stereoregularity of the copolymers, most probably of the isotactic type.

Keywords: Palladium; Copolymerization; Cyclopentene; Carbon monoxide

1. Introduction

The exploitation of active soluble Ziegler–Natta catalysts based on the chiral metallocene complexes pioneered by Brintzinger and coworkers [1] has allowed the first production of crystalline polymers of cyclopentene and of copolymers thereof with ethene without any ring opening [2]. On the contrary the development of very active catalytic systems of the type $[PdX_2(L_2)]$ (where (L_2) is a diphosphine or dinitrogen ligand, and X is a weakly or non-coordinating anion) [3] allowed the preparation of alternating copolymers from olefins having different degree of substitution on the double bond. In fact it was reported in the patent literature that the latter catalytic systems modified by basic phosphines such as 1,3-propanediylbis(di-*n*-butylphosphine) but not by 1,3-propanediylbis(diphenylphosphine) [4] in the presence of a quinone as the oxidant are able to catalyze the strictly alternating copolymerization of cyclopentene with carbon monoxide. According to these reports the produced copolymers showed at least 90% 1,3-enchainment and a prevailing stereoregular structure (**1**, $n/m > 9$):



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The more strained olefin norbornene was found to give oligomers not only with the aforementioned cationic catalyst precursors [5,6] but also with palladium triphenylphosphine complexes under basic conditions [7].

With the long-term goal of producing optically active copolymers from optically active substituted cyclopentenes [8] we have investigated in more detail the copolymerization of cyclopentene using different catalyst precursors in order to identify the factors influencing catalytic activity, stereoselectivity and regioselectivity of the copolymerization reaction involving cyclic olefins.

☆ Dedicated to Professor Hans-H. Brintzinger on the occasion of his 60th birthday.

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Table 1
Copolymerization of cyclopentene with carbon monoxide using 1,3-propanediylbis(diphenylphosphine) as the ligand

Run	Solvent (ml)		Reaction time (h)	Yield (g)		Productivity (g (g Pd)$^{-1}$ h^{-1})
				Polymer	Oligomer	
1	–	MeOH (75)	111	1.857	1.524	8.0
2	–	MeOH (37)	71	2.805	1.083	14.3
3	–	MeOH (19)	87	4.650	0.957	16.8
4	CH_2Cl_2 (21)	MeOH (9)	51	9.110	0.87	50.6
5	CH_2Cl_2 (25)	MeOH (5)	91	20.650	–	58.1
6	CH_2Cl_2 (28)	MeOH (2)	88	21.300	–	62.0
7	CH_2Cl_2 (30)	–	113	–	0.736	1.7
8	Acetone (28)	MeOH (2)	47	14.428	2.473	91.3
9	THF (21)	MeOH (9)	71	4.470	0.645	19.0

Reaction conditions: $Pd(OAc)_2$, 0.037 mmol; dppp, 0.045 mmol; 1,4-naphthoquinone, 1.9 mmol; $Ni(ClO_4)_2$, 0.186 mmol.

2. Results and discussion

2.1. Copolymerization reactions

The copolymerization experiments were usually carried out at 40 °C and under CO at 40 bar. The catalyst was normally formed in situ, starting with palladium acetate, the ligand, a source of the anion and the oxidant. The reactions were monitored by following the decrease in pressure. The absorption rate normally decreases with increasing conversion. This effect is probably influenced by the increase in the viscosity of the reaction medium. At the end of the reaction the reaction mixture is chromatographed on silica. The low molecular weight compounds are eluted first with dichloromethane (oligomers) whereas the higher molecular weight compounds (polymers) are eluted with acetone.

Since 1,3-propanediylbis(diphenylphosphine) (dppp) can be handled much better than the corresponding basic counterparts 1,3-propanediylbis(diethylphosphine) (depp) or 1,3-propanediylbis(dibutylphosphine) (dbpp) and because of the easy availability of chiral homologues thereof we first attempted to find conditions under which systems modified by dppp could show catalytic activity and give reasonable yields of the polymeric material.

The influence of the solvent using catalyst systems modified with dppp is reported in Table 1. We find in contrast with previous reports [4] that these catalytic systems give copolymerization even in the presence of small amounts of 1,4-naphthoquinone as the oxidant. When only methanol is used as the solvent, formation of solid material is normally observed. Moreover there is a significant increase in both the reaction rate and the ratio of the higher polymers (i.e. of the less soluble polymers) with decreasing methanol content of the reaction mixture. When dichloromethane was used as the co-solvent the reaction could be carried out homogeneously, since the copolymers formed are soluble in this medium. Under these conditions the yields are higher and the rate increases with decreasing concentration of methanol. Nevertheless an experiment without methanol showed that, under these conditions, methanol is necessary for the reaction since only trace amounts of the copolymer were formed even in the presence of traces of dihydrogen. The highest productivity (62 g (g Pd)$^{-1}$ h^{-1}) was found using a methanol : dichloromethane volume ratio of 1 : 14. In tetrahydrofuran and in acetone the yields were lower than in dichloromethane.

In the case of the more basic ligand depp, $[Pd(OAc)_2(depp)]$ was used as the catalyst precursor in order to facilitate the handling due to air sensitiveness of depp. The results reported in Table 2 show that with this ligand the copolymer yields were lower than with the ligand dppp. This is in sharp contrast with the polymerization of propene using the same ligands [9]. However, in the case of propene the improved activity was probably caused by a more rapid insertion of carbon monoxide due to a change to primary regioselectivity of the insertion of the olefin. This change is of course not possible for cyclopentene. As far as the effects of the different solvents are concerned, we observe for depp the same trend as for dppp.

Table 2
Copolymerization of cyclopentene with carbon monoxide using $[Pd(OAc)_2(depp)]$ as the catalyst precursor

Run	Solvent (ml)		Reaction time (h)	Yield (g)		Productivity (g (g Pd)$^{-1}$ h^{-1})
				Polymer	Oligomer	
10	THF (28)	MeOH (2)	95	2.301	1.499	10.2
11	Acetone (28)	MeOH (2)	86	3.472	5.027	25.1
12	CH_2Cl_2 (28)	MeOH (2)	72	8.397	4.647	46.0

Reaction conditions: $[Pd(OAc)_2(depp)]$, 0.037 mmol; $Ni(ClO_4)_2$, 0.186 mmol; 1,4-naphthoquinone, 1.9 mmol.

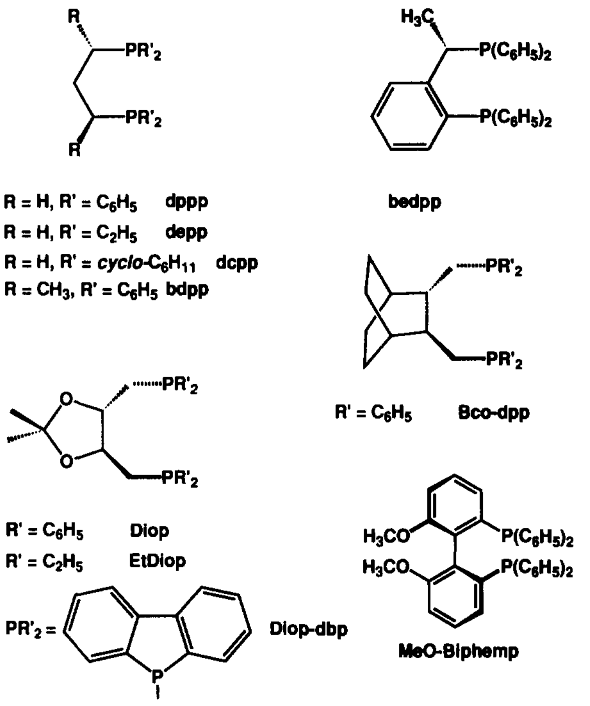
Table 3
Copolymerization of cyclopentene with carbon monoxide using various diphosphine ligands

Run	Ligand	Reaction time (h)	Yield (g)		Productivity (g (g Pd)$^{-1}$ h^{-1})
			Polymer	Oligomer	
6	dppp	88	21.300	–	62.0
13	dcpp	137	0.085	0.047	0.3
12	depp	72	8.397	4.647	46.0
14	bdpp	91	2.440	2.070	12.9
15	bedpp	190	12.009	5.202	23.0
16	Diop	113	0.078	0.747	1.9
17	Et-Diop	118	0.014	0.161	0.4
18	Diop-dbp	96	1.147	2.023	3.0
19	BCO-dpp	93	0.298	1.297	4.4
20	MeO-Biphemp	118	1.154	0.166	2.8

Reaction conditions: solvent, dichloromethane (28 ml)–methanol (2 ml) (except for runs 13 and 14 for which a 21 ml–9 ml mixture was used); Pd(OAc)$_2$, 0.037 mmol; ligand, 0.045 mmol (except for run 12, where 0.037 mmol of [Pd(OAc)$_2$(depp)] was used); Ni(ClO$_4$)$_2$, 0.186 mmol; 1,4-naphthoquinone, 1.9 mmol. For the abbreviations of the ligands used see Scheme 1.

Table 3 summarizes the experiments carried out using the following bidentate ligands (Scheme 1) in dichloromethane–methanol, with perchlorate as the anion and 1,4-naphthoquinone as the oxidant:

In fact, systems containing tridentate ligands such as tripod (2-[(diphenylphosphino)methyl]-2-methyl-1,3-propanediyl-bis[diphenylphosphine]) and triphos (bis[2-(diphenylphosphino)-ethyl]phenylphosphine) show only low catalytic activity, although tripod, which is structurally related to dppp is significantly more active (productivity up to 21 g (g Pd)$^{-1}$ h^{-1}) than triphos which forms five-membered rings. Ligands giving six-membered chelation rings show much better catalytic activity than those forming seven-membered rings. The catalytic activity seems to be influenced by both the electronic and the steric properties of the ligand. In fact, 1,3-propanediylbis(dicyclohexylphosphine) shows a very low catalytic activity, while depp has a catalytic activity which is almost comparable with that of dppp. In contrast, bdpp has a lower catalytic activity which in turn is smaller than that of bedpp. Control experiments carried out using the dppp ligand have shown that the concentration of ligand hardly affects the yield at least at molar ratios up to 2.



Scheme 1.

Table 4
Comparison of different anions for the ligands dppp, bipy and depp as the chelate ligand for the copolymerization of cyclopentene

Run	Ligand (mmol)	Source of the anion (mmol)	Reaction time (h)	Yield (g)		Productivity (g (g Pd)$^{-1}$ h^{-1})
				Polymer	Oligomer	
6	dppp (0.045)	Ni(ClO$_4$)$_2$ (0.186)	88	21.300	–	62.0
21	dppp	CF$_3$SO$_3$H	88	15.830	2.500	52.9
22	dppp (0.045)	TsOH (0.186)	89	8.478	1.607	28.8
23	bipy (0.045)	Ni(ClO$_4$)$_2$ (0.186)	96	–	1.072	2.8
24	bipy (0.045)	CF$_3$SO$_3$H (0.186)	65	0.168	–	0.6
25	bipy (0.045)	TsOH (0.186)	117	0.151	–	0.3
12	depp	Ni(ClO$_4$)$_2$ (0.186)	72	8.397	4.647	46.0
26	depp	CF$_3$SO$_3$H (0.186)	70	13.313	7.664	76.1
27	depp	TsOH (0.186)	41	11.025	11.498	139.5

Reaction conditions: CH$_2$Cl$_2$ (28 ml)–MeOH (2 ml); Pd(OAc)$_2$, 0.037 mmol (except for run 21 where 0.037 mmol of [Pd(CF$_3$SO$_3$)$_2$(dppp)] was used and for runs 12, 26 and 27 where 0.037 mmol of [Pd(OAc)$_2$(depp)] was used). 1,4-naphthoquinone, 1.9 mmol.

Table 5
Influence of the temperature on the copolymerization of cyclopentene with carbon monoxide using dppp as the ligand

Run	Temperature (°C)	Reaction time (h)	Yield (g) Polymer	Yield (g) Oligomer	Productivity (g (g Pd)$^{-1}$ h^{-1})
28	25	141	1.420	–	2.6
29	40	54	9.320	0.760	48.3
30	80	63	–	5.660	22.8

Reaction conditions: solvent, CH_2Cl_2(21 ml)–MeOH (9 ml); $Ni(ClO_4)_2$, 0.186 mmol; 1,4-naphthoquinone, 1.9 mmol.

Table 6
Influence of the pressure on the copolymerization of cyclopentene with carbon monoxide using dppp as the ligand

Run	Pressure (bar)	Yield (g) Polymer	Yield (g) Oligomer	Productivity (g (g Pd)$^{-1}$ h^{-1})
31	20	7.613	6.185	74.6
32	30	16.199	4.369	111.2
33	40	15.768	–	85.2
34	60	7.306	1.806	49.2
35	80	9.980	–	53.9
36	150	4.094	–	22.1

Reaction conditions: solvent, CH_2Cl (28 ml)–MeOH (2 ml); $Ni(ClO_4)_2$, 0.186 mmol; 1,4-naphthoquinone, 1.9 mmol; reaction time, 47 h.

The different anions show the same trend for the catalysis with both dppp and bipyridyl as ligand (Table 4). Perchlorate seems to be the most potent weakly coordinating anion, triflate the worse (not as much for dppp as for bipy), and tosylate the least appropriate anion. For the ligand depp, the preferences are exactly the other way round. Tosylate seems to be the best anion, although it yields many lower polymers, and perchlorate the worst. These results show that the catalytic activity is determined by a balance between ligand and anion.

Copolymerization of cyclopentene with carbon monoxide at lower temperatures usually yields more copolymers than at elevated temperatures (Table 5). It seems that 40 °C is appropriate for this reaction. Experiments with the dppp ligand at room temperature did not yield much polymer. On the contrary, reaction temperatures of 70 or 80 °C are also not favourable, not only because of the smaller productivity but also because the molecular weight of the produced copolymers decreases.

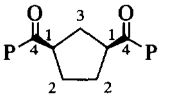
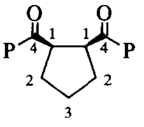
The effect of the carbon monoxide pressure on the copolymerization was analysed using the dppp ligand and is shown in Table 6. The productivity of the system shows a maximum at a carbon monoxide pressure of between 30 and 40 bar. This behaviour has precedents in other carbonylation reactions of olefinic substrates [10]. It is noteworthy that formation of oligomeric materials is more important under conditions of low carbon monoxide partial pressure.

2.2. Characterization of the copolymers

The nature of end groups, the chain lengths and the regioselectivities were determined by ^1H and ^{13}C NMR on the basis of the parameters summarized in the Tables 7 and 8. The corresponding results are shown in Tables 9 and 10. The molecular weights were also determined on the basis of the intensity of the signals corresponding to the end groups in the ^1H NMR spectra. Some of the molecular weights were checked by vapour pressure osmometry. Occasional discrepancies between the values determined by the two different methods might be caused by the difficulty of completely eliminating the solvent from the copolymers.

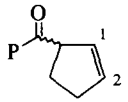
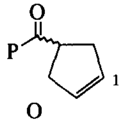
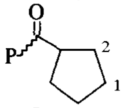
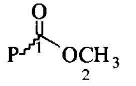
The molecular weights were always calculated or measured for the solid polymer fraction. They are in general rather low, the polymerization degree being seldom larger than 80. The use of dppp as a ligand generally leads to higher molecular weight polymers than the use of other ligands does. Especially interesting is that the basic ligand depp leads to shorter chains, although with propylene the molecular weights are usually higher than with other ligands [9].

Table 7
^{13}C and ^1H chemical shifts for the repeating units in the copolymers

Repeating unit	CH_2	CH	C(1)	C(2)	C(3)	C(4)
	1.50–2.15 (m)	2.95–3.10 (m)	50.3–50.4	28.5–28.6	32.1	212.7–213.1
	1.50–2.15 (m)	3.10–3.30 (m)	53.7–53.8	28.4–28.5	24.1–24.2	212.7–213.1

P, polymer chain; m, multiplet.

Table 8
Diagnostic ^1H and ^{13}C chemical shifts for the various end groups

End group	H(1)	H(2)	C(1)	C(2)
A 	5.71 (m)	5.90 (m)	134.3	128.4
B 	5.63 (m)	–	128.8	–
C 	1.5–1.7	*	*	*
D 	–	3.67 (s)	175.5–175.6	51.7–51.8

P, polymer chain; m, multiplet; s, singlet. * Overlapping with the signals of the repeating units.

Observed end groups are unsaturated cyclopentenyl rings (A and B, Table 8), saturated cyclopentyl groups (C) and sometimes carbomethoxy end groups (D). This would have been expected on the basis that end groups of the same nature are observed for copolymers of other olefins [3,9,11]. Most copolymers carry only saturated end groups (C) and unsaturated end groups (A and B). For the materials prepared using only methanol as the solvent in particular, carbomethoxy end groups (D) are also present. Furthermore, the presence of carbomethoxy end groups is mostly found when ligands forming seven-membered chelation rings are used.

The concentration of the asymmetric unsaturated cyclopentyl end group A is normally higher than that of the symmetric end group B (Table 10). This effect might be because the former group can arise from the two different 1,2- and 1,3-disubstituted intermediates (Scheme 2). β-Hydrogen elimination after olefin insertion followed by dissociation of the chain causes direct formation of the former moiety (A). Otherwise, 1,2 addition with the opposite regiochemistry is a premise both for the formation of the alternative unsaturated cyclopentyl group B and for the observed 1,3 regioselectivity in the formation of the copolymers. There does not seem to be any clear correlation between content of 1,3 moiety and percentage of symmetric unsaturated cyclopentyl end group B (Table 10).

Table 9
Chain lengths and end groups for different copolymers

Run	Solvent (ml)		Ligand (mmol)	End group [a]	Molecular weight [b] (g mol^{-1})
8	Acetone (28)	MeOH (2)	dppp (0.045)	A, B, C	3600
33	CH_2Cl_2 (28)	MeOH (2)	dppp (0.045)	A, B, C	8500
2	–	MeOH (37)	dppp (0.045)	A, B, C, D	2180
16	CH_2Cl_2 (28)	MeOH (2)	Diop (0.045)	A, B, C, D	4200
18	CH_2Cl_2 (28)	MeOH (2)	Diop-dbp (0.045)	A, B, C, D	2200
19	CH_2Cl_2 (28)	MeOH (2)	BCO–DPP (0.045)	A, B, C, D	1000
37	CH_2Cl_2 (28)	MeOH (2)	depp (0.045) [c]	A, B, C	2100
38	CH_2Cl_2 (28)	MeOH (2)	depp (0.045)	A, B, C	1360

Reaction conditions: $Pd(OAc)_2$, 0.037 mmol; $Ni(ClO_4)_2$, 0.186 mmol; naphthoquinone, 1.9 mmol.
[a] See Table 8.
[b] Determined by NMR.
[c] In the absence of the oxidant.

Table 10
Regioselectivities obtained with different ligands in the copolymerization of cyclopentene with carbon monoxide

Run	Ligand	Source of the anion (mmol)	Amount of 1,3-moiety	Amount of end group B [a]
33	dppp (0.045)	$Ni(ClO_4)_2$ (0.186)	71	27
22	dppp (0.045)	TsOH (0.186)	48	48
38	depp (0.045)	$Ni(ClO_4)_2$ (0.186)	80	34
27	depp (0.045)	TsOH (0.186)	75	31
13	dcpp (0.045)	$Ni(ClO_4)_2$ (0.186)	69	33
16	Diop (0.045)	$Ni(ClO_4)_2$ (0.186)	87	26
19	BCO–dpp (0.045)	$Ni(ClO_4)_2$ (0.186)	95	32
20 [b]	MeO–Biphemp (0.045)	TsOH (0.074)	85	35

Reaction conditions: $Pd(OAc)_2$, 0.037 mmol (except for runs 38 and 27 where 0.037 mmol of $[Pd(OAc)_2(depp)]$ was used); naphthoquinone, 1.9 mmol; solvent, dichloromethane (28 ml)–methanol (2 ml).
[a] Percentage of B compared with all unsaturated end groups (A and B).
[b] Introduced as the complex $[Pd(TsO)_2(MeO–Biphemp)]$.

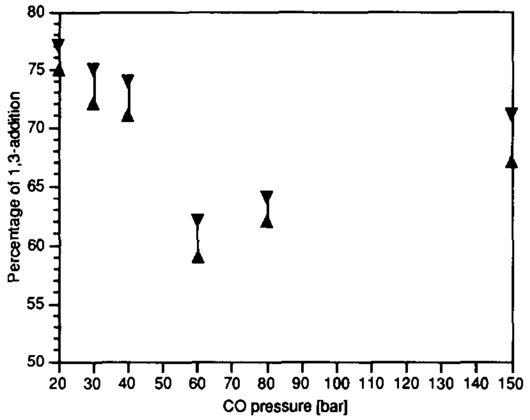


Fig. 1. Comparison of the regioselectivities of different copolymers obtained under various carbon monoxide pressures. The given ranges represent the uncertainty of the integrals in the proton NMR spectrum.

Table 11
Obtained stereoselectivities with chiral and achiral ligands

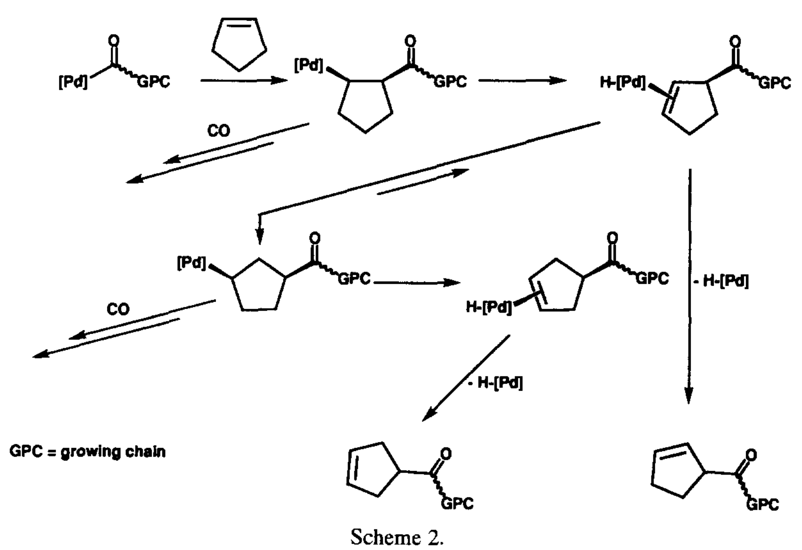
Run	Ligand	Salt or acid (mmol)	Probability for *l*-diade
39	dppp [a]	$Ni(ClO_4)_2$ (0.186)	1.0
16	Diop (0.045)	$Ni(ClO_4)_2$ (0.186)	0.95
13	dcpp (0.045)	$Ni(ClO_4)_2$ (0.186)	0.92
15	bedpp (0.045)	$Ni(ClO_4)_2$ (0.186)	0.91
33	dppp (0.045)	$Ni(ClO_4)_2$ (0.186)	0.91
37	depp	$Ni(ClO_4)_2$ (0.186)	0.90
14	bdpp (0.045)	$Ni(ClO_4)_2$ (0.186)	0.87
27	depp (0.045)	TsOH (0.186)	0.83
26	depp (0.045)	CF_3SO_3H (0.186)	0.64
22	dppp (0.045)	TsOH (0.186)	0.57

Reaction conditions: $Pd(OAc)_2$, 0.037 mmol (except for runs 37, 27 and 26 where 0.037 mmol of $[Pd(OAc)_2(depp)]$ was used); naphthoquinone, 1.9 mmol (except for run 37 where there was no oxidant, but H_2 at 5 bar); solvent, dichloromethane (28 ml)–methanol (2 ml).
[a] Introduced as the complex $[Pd(H_2O)_2(dppp)][ClO_4]_2$.

The effect of the pressure of carbon monoxide on the molecular weight can also be understood on the basis of Scheme 1. The high concentration of carbon monoxide results in a higher rate of insertion of this comonomer. On the contrary owing to facile β elimination reaction, carbon monoxide could compete for coordination with the unsaturated chain in the π complexes, thus causing production of chains with a lower polymerization degree.

The regioselectivity ranges from 50% up to 95% for the 1,3 substitution of the ring. The regioselectivity appears to be influenced by the type of anion. In fact, when using both dppp and depp as the ligand there is a larger amount of 1,2 insertion when tosylate is employed instead of perchlorate. The steric or the electronic properties of the diphosphine ligand appear to be of minor importance in regulating the regioselectivity since we observe only minor changes when dppp, depp or dcpp is used as the ligand. On the contrary there seems to be a correlation between the size of the chelation ring and the regioselectivity. The ligands forming seven-membered chelation rings generally show higher selectivities towards 1,3 insertion. There is a small influence of the carbon monoxide pressure on the regiochemistry of the produced copolymer (Fig. 1). This shows that β-elimination of hydrogen is not much more rapid than carbon monoxide insertion (Scheme 1).

The stereoselectivity of these copolymerizations varies with different reaction conditions [12] (Table 11). However, no definite conclusion could be drawn on the correlations between the different parameters and stereoselectivity. In most cases the ^{13}C NMR spectra of the copolymers are quite simple (see Fig. 2 as an example) and therefore the materials should have a good stereoregularity [9]. In particular, in most cases, one peak in the region of the ^{13}C NMR spectrum corresponding to the carbonyl groups is present in larger concentrations



Scheme 2.

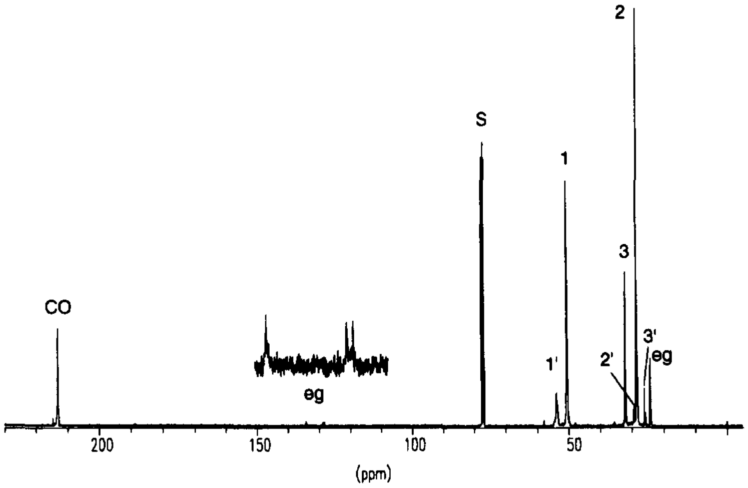


Fig. 2. Example of a ^{13}C NMR spectrum ($CDCl_3$; 125 MHz) of a copolymer obtained with the ligand dppp (run 40): signals 1, 2 and 3 correspond to the 1,3 moiety, and signals 1′, 2′ and 3′ to the 1,2 moiety; S, solvent signal; eg, end group signals.

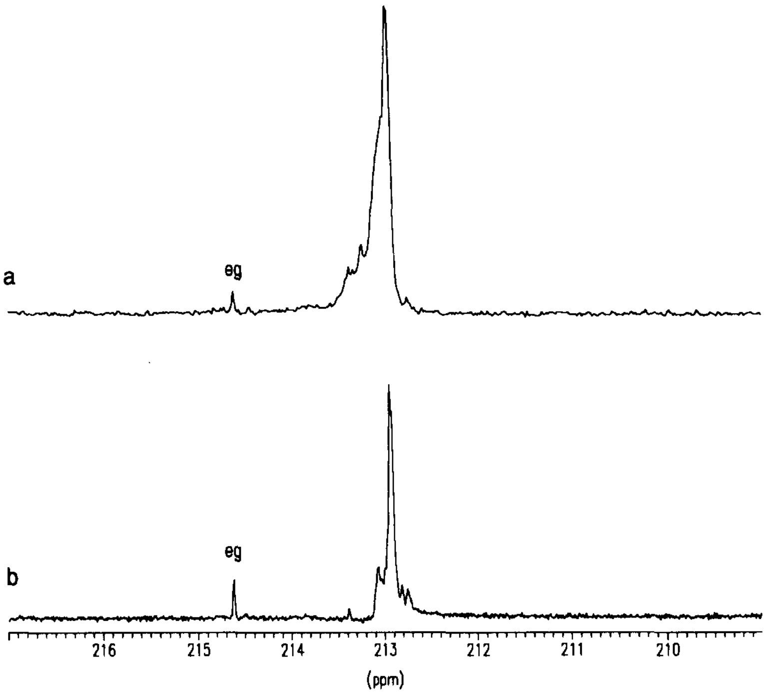


Fig. 3. Comparison of the carbonyl signals of copolymers obtained with an achiral chelating ligand dppp (run 40) (curve a) and a chiral chelating ligand bdpp (run 14) (curve b): eg, assigned to end group carbonyl signal.

(Fig. 3). This region of the spectrum was found to be quite sensitive to the stereochemistry of the copolymers of other olefins [9,13]. Whether the polymers are prevailingly diisotactic or disyndiotactic could not be determined so far. In most cases we observe one sharp peak at 212.9 ppm for the carbonyl groups. On the basis of the similarity of the spectra of copolymers obtained with chiral and achiral ligands we assume that the copolymers have a prevailingly diisotactic microstructure [14]. The stereochemical control in the case of the achiral ligands should therefore occur via chain end control [15].

3. Conclusion

Low molecular weight copolymers between cyclopentene and carbon monoxide can be synthesized with good yields using palladium-based cationic complexes modified with diphosphine ligands. A good control of the regiochemistry towards 1,3 insertion (up to 95%) has been reached at the expense of the polymerization degree.

4. Experimental details

4.1. General comments

All reactions were carried out with exclusion of air under nitrogen atmosphere using Schlenk or glove-box techniques. The solvents used were dried according to normal procedures and distilled under nitrogen. Cyclopentene was obtained from Fluka in purum quality and was refluxed over $LiAlH_4$ and distilled under nitrogen.

$Ni(ClO_4)_2$–$6H_2O$, dppp and 1,4-naphthoquinone were purchased from Fluka. $Pd(O_2CCH_3)_2$ was purchased from Aldrich. 1,3-Bis(diethylphosphino)propane (depp) was prepared according to the literature. The NMR spectra were measured on a Bruker AMX 400 WB and Bruker AMX 500 spectrometer with tetramethylsilane and phosphoric acid as the internal standard in $CDCl_3$ as the solvent. IR spectra were recorded on a Mattson Instruments 6020 Galaxy series Fourier transform IR spectrometer in chloroform. Vapour pressure osmometry was carried out on a Corona Wescan C32A osmometer in chloroform.

4.2. Palladium diacetate(1,3-bis(diethylphosphino)propane)

The dark reddish brown solution of 0.486 g (2.16 mmol) $Pd(OAc)_2$ in 26 ml or toluene was filtered into a Schlenk tube. To this a solution of 0.788 g of depp with 40% toluene (2.15 mmol) in 17 ml of toluene was added. The solution first turned yellow, and a precipitate formed. Soon it began to darken and after 1 h it was filtered, and a light-yellow solid was collected (yield, 559 mg, 1.26 mmol (59%)).

^{31}P-NMR (acetone-d_6, 200 MHz): δ 22.8 ppm.

4.3. Palladium complexes [$PdX_2(L_2)$]

The complexes [$Pd(CF_3SO_3)_2$(dppp)], [$Pd(TsO)_2$-(MeO-Biphemp)] and [$Pd(ClO_4)_2$(dppp)] were synthesized according to the literature [16]; from palladium dibenzonitrile dichloride the complexes [$PdX_2(L_2)$] were formed via the dichloro complexes [$PdCl_2(L_2)$] with the appropriate silver salt. Special caution was paid during the synthesis of the perchlorate complex. Since perchlorates are very explosive, it was only synthesized in very small amounts and was never dried, warmed or handled under reduced pressure.

4.4. General procedure for polymerizations

All reactions under high pressure were carried out in an autoclave from Hastelloy of a capacity of 500 ml. All reagents according to the tables were dissolved in the appropriate solvent and 30 ml of cyclopentene under nitrogen in a 100 ml Schlenk tube. The autoclave was evacuated for at least $\frac{1}{2}$ h. Both the Schlenk tube and the autoclave were connected via a three-way tap to the vacuum–nitrogen line. The poly(vinyl chloride) tubes were evacuated; then the tap to the line was closed and the solution sucked from the Schlenk tube into the autoclave. Afterwards it was filled with CO at 40 bar (except where otherwise mentioned) and heated to the appropriate temperature. During the whole reaction the autoclave was shaken or stirred.

At the end of the reaction the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and chromatographed on silica (CH_2Cl_2; later acetone with some CH_2Cl_2). In the tables the first fraction, which usually was an oily liquid and soluble in methanol, is referred to as "oligomers", and the second fraction, which formed a stiff foam when dried under reduced pressure, is called "polymers". The first fraction usually contained the oxidant. Some polymers can be cleaned by dissolving them in a little dichloromethane and dropping this solution into cold stirred methanol. An off-white precipitate forms, which can be filtered off.

4.5. Determination of influence of the CO pressure on the regioselectivity

Under the following reaction conditions a series of polymerization reactions under various CO pressures has been carried out (Fig. 1): 0.037 mmol of $Pd(OAc)_2$, 0.186 mmol of $Ni(ClO_4)_2$, 0.045 mmol of dppp, 1.9 mmol of NQ in CH_2Cl_2(28 ml)–MeOH (2 ml); temperature, 40 °C; reaction time, 47 h. Applied pressures were 20, 30, 40, 60, 80 and 150 bar.

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