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Note

Enantioface discriminating carbonylations of styrene with cationic palladium(II) catalyst precursors

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Dedicated to Professor Dr Piero Salvadori, a friend, a colleague and a teacher, on the occasion of his 65th birthday.

Abstract

The enantioface discriminating copolymerization of styrene with carbon monoxide using palladium complexes $[(L\wedge L')Pd(S)_2](X)_2$ of the C_1-symmetric ligands (*S*,*S*)-2-[2-(diphenylphosphino)phenyl]-3-phenyl-4-methoxymethyl-4,5-dihydrooxazole or (*S*,*S*)-2-(2-pyridyl)-3-phenyl-4-methoxymethyl-4,5-dihydrooxazole gives highly isotactic or syndiotactic poly(1-oxo-2-phenyl-1,3-propanediyl), respectively. With the former catalytic system, efficient enantioface discrimination takes place only after the first insertion step and is only slightly influenced by the growing chain, as shown by the chiroptical properties of terpolymers with ethene. Similar terpolymerization experiments with the latter catalyst precursor show that the fairly good enantioface discrimination due to the catalyst is in opposition to the influence of the chirality of the growing chain. The latter effect predominates resulting in the formation of the overwhelmingly syndiotactic copolymer. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Enantioselective catalysis; Carbonylation; Olefins; Palladium complexes; Carbon monoxide copolymers

1. Introduction

Catalytic enantioselective carbonylation reactions (such as hydroformylation and hydro-carbalkoxylation) of olefin substrates have considerable potential for industrial use and have been studied for a long time [1–4]. However, the level of enantioface discrimination reached has seldom been high [5] and was only moderate in the most cases. In contrast, essentially diastereospecific enantioselective carbonylations to highly isotactic poly(olefin-*alt*-CO) have been obtained rather easily [6–13]. When styrene is the substrate, catalyst precursors of the type $[(L\wedge L)Pd(S)_2](X)_2$ [14] or $[(L\wedge L)Pd(CH_3)(S)](X)$ [15] ($L\wedge L$ is 1,10-phenanthroline or 2,2′-bipyridine, S is a solvent molecule and X is a weakly coordinating anion) produce poly(1-oxo-2-phenylpropane-1,3-diyl) with the prevailing (~ 90%) formation of *u*-diads [16], independent of the anionic ligand [17,18]. Optically active, highly isotactic copolymers were obtained with $[(N\wedge N)Pd(CH_3)(S)](X)$ catalyst precursors (where $N\wedge N$ is the C_2-symmetric ligand (*S*,*S*) - 2,2′ - propanediylbis(4,5 - dihydro - 4 - (1 - methylethyl)-2-oxazole) [8,10,19]. Similarly high isotacticity associated with high optical activity of the produced copolymer was obtained using the $[(P\wedge N)Pd(H_2O)_2](OTf)_2$ catalyst precursors [20] (where $P\wedge N$ is, e.g. (*S*,*S*)-2-[2-(diphenylphosphino)phenyl]-3-phenyl-4-methoxymethyl-4,5-dihydrooxazole [21]). Surprisingly, the $[(N\wedge N')Pd(CH_3)(S)](X)$ system modified by the chiral C_1-ligand (*S*,*S*)-2-(2-pyridyl)-3-phenyl-4-methoxymethyl-4,5-dihydrooxazole gave copolymers with a predominantly syndiotactic structure [8,21]. The new results presented here are related to end group analysis and oligomer formation as well as to the alternating terpolymerization of ethene and styrene with carbon monoxide and help clarify the mechanism of enantioface selection during the carbonylation reactions.

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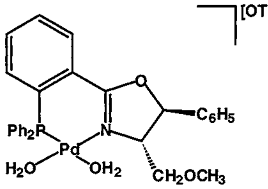
Table 1
Alternating co- and terpolymerization of styrene and ethene with carbon monoxide using **1** and **2** as the catalyst precursors [a]

Entry	Catalyst precursor	Ethene (mmol)	CO pressure (bar)	Productivity (mmol/(g Pd·h))	Polymer composition (styrene/ethene)	$\Delta\varepsilon$ ($\sim$282 nm) (l·mol^{-1}·cm^{-1})
1	**1**	0	320	74.4	100/0	−10.12
2	**1**	485	280	20.2	0/100	0
3	**1**	497	260	68.3	13/87	−12.65
4	**2**	0	5	31	100/0	−1.78
5	**2**	961	10	1015	7/93	−7.56
6	**2**	633	10	170	19/81	−6.18
7	**2**	187	10	191	45/55	−3.61

[a] Styrene concentration 435 mmol in 10 ml CH_3OH, except for entry 2 for which no styrene was used.

2. Results and discussion

The polymerization experiments were carried out using $[(P^\wedge N)Pd(H_2O)_2](OTf)_2$ (**1**) or $[(N^\wedge N')Pd(H_2O)_2](OTf)_2$ (**2**) as the catalyst precursor. The results are shown in Table 1 and the experimental conditions are described in the experimental section. The experiments with the two catalyst precursors were carried out under different conditions of carbon monoxide pressure, due to the inverse kinetic order with respect to CO exhibited by the two types of ligand systems [15,20,22]. As mentioned briefly elsewhere [21], **1** gives isotactic poly(1-oxo-2-phenylpropane-1,3-diyl), whereas **2** gives a prevailingly syndiotactic copolymer. Fig. 1 shows the ^{13}C-NMR spectrum in the region of the *ipso*-carbon atom for both copolymers. The material obtained with **2** shows the four broad bands associated with the possible triads (*ll*, *ul* or *lu*, and *uu* that are centered at about 136.2, 135.8, 135.45 and 134.95 ppm) [16,23]. The other signals at lower fields are most probably associated to end groups. In contrast, the copolymer obtained with **1** shows essentially a single sharp band in that region, consistent with a highly ordered structure; in the spectrum of a mixture of the two copolymers this sharp band is superimposed to the aforementioned one at 136.2 ppm. The isotacticity of the latter material is demonstrated by the very high optical activity and, correspondingly, by the very high intensity of the circular dichroism band ($\Delta\varepsilon$) in the region of the $n \rightarrow \pi^*$ chromophore ($\sim$ 282 nm). The low molar ellipticity ($\Delta\varepsilon$) value observed for the former copolymer is consistent with the low concentration of the *l*-diads (Fig. 1).



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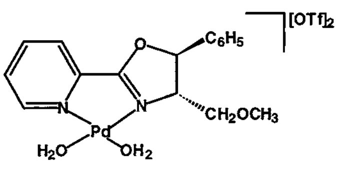
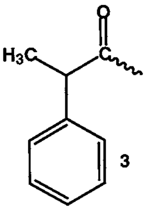


2

End group analysis of the copolymers reveals the presence of terminal 2-phenylpropionyl groups **3** at a concentration close to 50%; alternative end groups are usually the two possible unsaturated terminations **4** and **5**.



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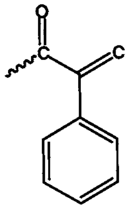

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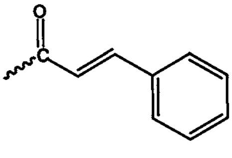
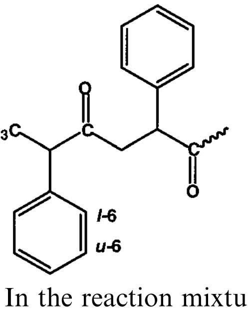
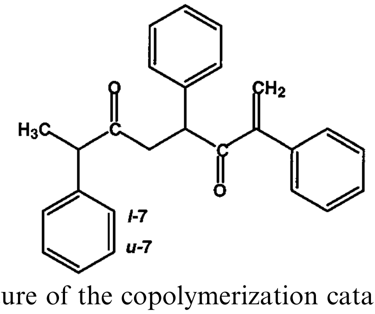


5

Fig. 2 shows the ^{1}H-NMR spectrum in the region of the methyl group of the 2-phenylpropionyl termination **3** for both copolymers. For the material produced with **1**, the two internal doublets (1.375 and 1.355 ppm) with the highest intensities are assigned to the *l* and *u* terminations **6** (diastereomeric excess $\sim$ 30%), based on NMR data of 2,4,7-triphenyl-oct-1-en-3,6-dione **7** and on ^{1}H-^{13}C-correlation spectra. The prevailing diastereomeric termination is unknown so far, but probably corresponds to the *l* relative absolute configuration. As a matter of fact, this class of $P^\wedge N$ ligands causes enantioselective carbonylation of styrene to homochiral methyl 2-phenylpropanoate and dimethyl 2-phenylbutanedioate [20,24,25]. The doublet at higher field (1.24 ppm) was analogously attributed to one diastereomer of the alternative regioisomeric termination (*l*- or *u*-$CH_3CH(C_6H_5)CO–CH(C_6H_5)CH_2CO–$), whereas the fourth doublet (1.445 ppm) could not be assigned conclusively. Remarkably, the prevailingly syndiotactic copolymer seems to show the signal of only one diastereomeric termination **6**, which is probably broadened by variations in the microstructure of the following monomer units. Furthermore the regioselectivity of the insertion of the first two styrene units in this case appears to be complete.



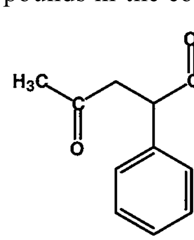
***l*-6**
***u*-6**



***l*-7**
***u*-7**

In the reaction mixture of the copolymerization catalyzed by **1** (*R*)-dimethyl phenylsuccinate (**8**) (54% ee), 2,4-diphenyl-3-oxo-pent-1-en (**9**) (38% ee) and E-1,4-diphenyl-3-oxo-pent-1-en (**10**) (18% ee) were identified.

Accordingly, it is assumed that the polymer chain starts with secondary styrene insertion into a palladium–hydride species with low enantioface discrimination to give termination **3**. The second insertion of styrene usually takes place with secondary regioselectivity and probably with very high enantioselectivity to give termination **6**. Indeed, the enantiomeric excess of the two oligomers **9** and **10** is similar to the diastereomeric excess determined for chain end **6**. High enantioface discrimination in the following insertion steps leads to the formation of isotactic poly(1-oxo-2-phenylpropane-1,3-diyl). Unfortunately, it was not yet possible to identify similar low molecular weight compounds in the copolymerization mixture catalyzed by **2**.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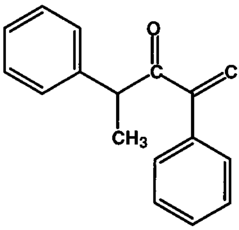
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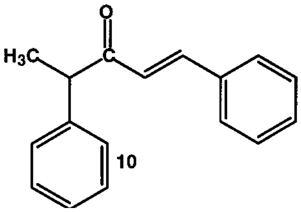
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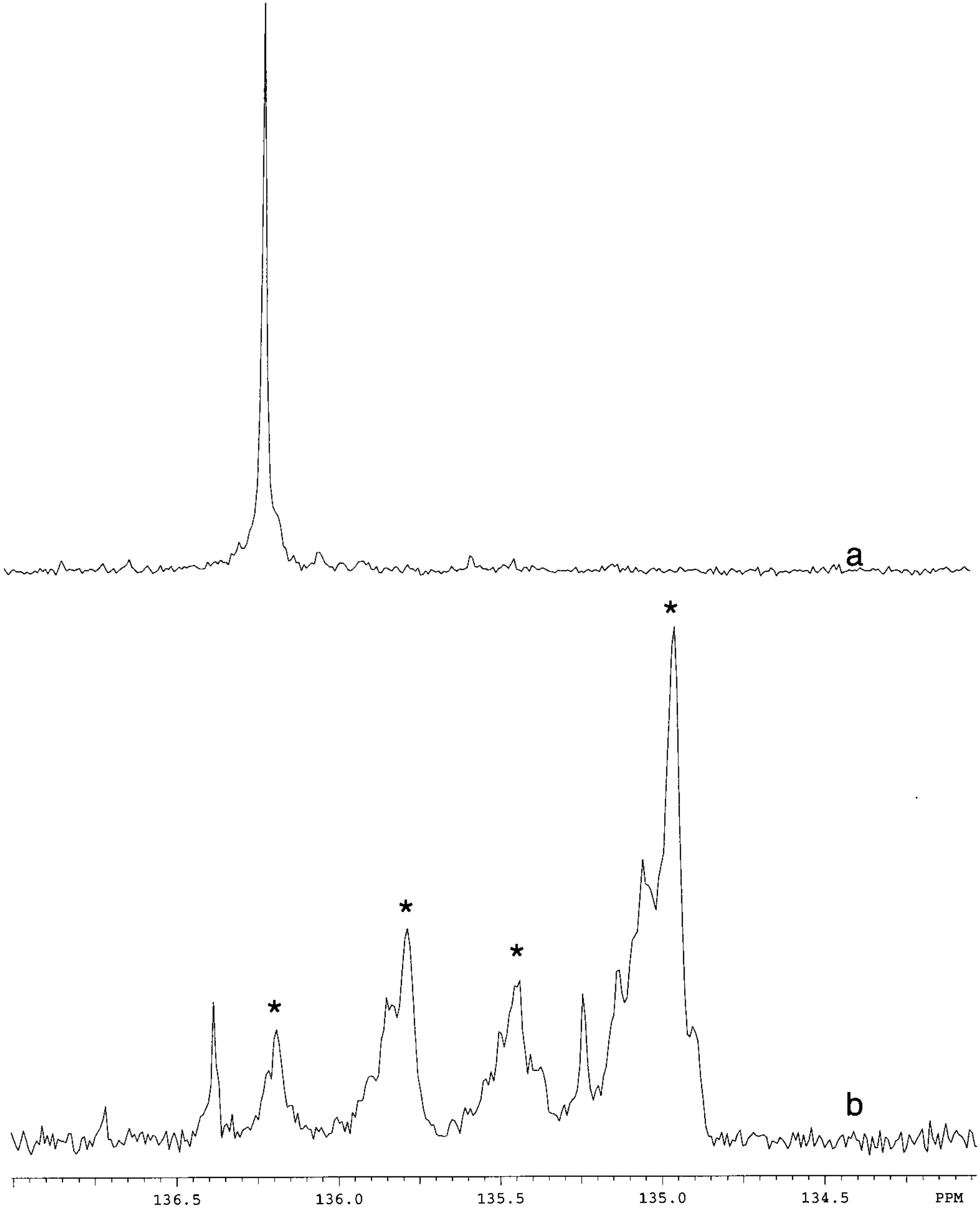

Fig. 1. ^{13}C-NMR-spectrum (1:1 $(CF_3)_2$COD–$CDCl_3$; 125 MHz) (*ipso*-carbon atom region) of poly(styrene-*alt*-CO) prepared with **1** (a) and **2** (b). The most intense signals in the regions of the four triads (*ll*, *ul* or *lu*, *lu* or *ul*, and *uu*) are marked.

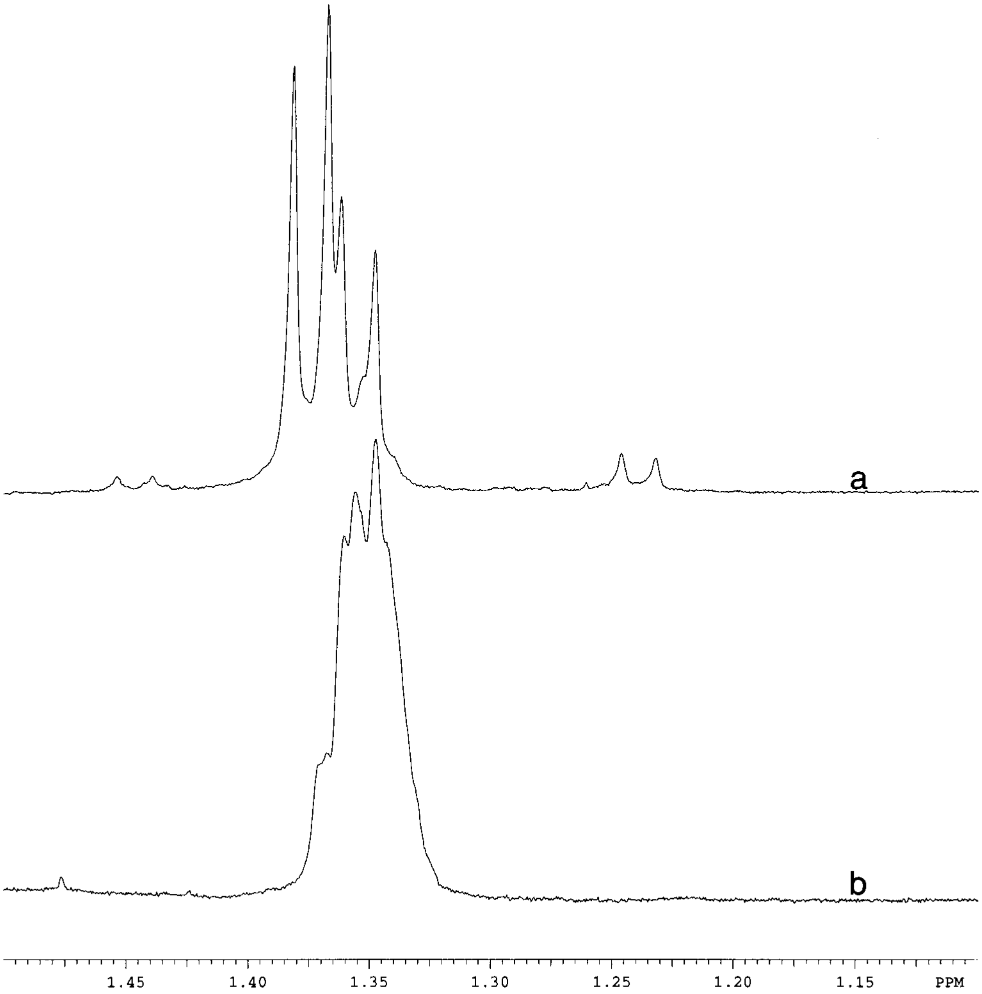

Fig. 2. ^{1}H-NMR-spectrum (1:1 $(CF_3)_2CDOD$–$CDCl_3$; 500 MHz) of poly(styrene-*alt*-CO) prepared with **1** (a) and **2** (b).

Terpolymerization reactions of ethene and styrene, using **1** as the catalyst precursor and an ca. 1:1 molar ratio of the two olefin co-monomers, show the inhibitory effect of ethene that was observed previously with similar phosphino–oxazoline ligands [26,27]. Despite the higher reactivity of the styrene co-monomer with respect to ethene for copolymerization (Table 1, entry 1 vs. entry 2), the latter olefin is preferentially inserted in the terpolymerization reaction (Table 1, entry 3). Therefore only terpolymers with rather low styrene concentrations were obtained. The molar ellipticity, normalized to the styrene content, is somewhat higher in the case of the terpolymer than in that of the copolymer obtained with the same catalyst precursor. It seems reasonable [9] to assume that the chiroptical properties of the carbonyl chromophore of these compounds is not substantially influenced by the macromolecular environment [10,28]. Thus, the result shows that enantioface discrimination by the catalytic system **1** is due essentially to the catalyst enantiomorphic site, with a very low participation of the growing polymer chain.

With catalyst precursor **2**, terpolymers with a high styrene content are also accessible (Table 1), as reported for other N ^ N ligands [29]. For these materials, the molar ellipticity increases strongly with increasing ethene content. Considering that the highest $\Delta\varepsilon$ value ever observed for the styrene copolymers is that reported in Table 1 (-12.65), enantioface selection for styrene insertion in the absence of induction of chirality by the growing chain seems to be rather high.

3. Conclusions

In the copolymerization of styrene with carbon monoxide to poly(1-oxo-2-phenylpropane-1,3-diyl) catalyzed by palladium complexes modified with 1,10-phenanthroline or 2,2′-bipyridine, the growing chain induces enantioface selection towards the preferential formation of *u*-diads [16]. For chiral C_2-symmetric catalytic systems such as those containing (*S*,*S*)-2,2′-propanediyl-bis(4,5-dihydro-4-(1-methylethyl)-2-oxazole), the mechanism of selection is modified to cause the preferential formation of *l*-diads (enantiomorphic site control) [19]. Similar highly efficient enantioselectivity by the enantiomorphic catalyst is displayed by systems containing the chiral phosphino-oxazoline chelate ligands, despite their C_1-symmetry. However, in this case high enantioface discrimination does not take place in the first insertion step to give the 1-phenylethyl-palladium intermediate; high enantioselectivity is displayed probably already for the second olefin insertion but surely for the third and successive insertions. The importance of the growing chain for efficient enantioface selection has been similarly proven for the Ziegler–Natta olefin polymerization with metallocene [30,31]. For the pyridine–oxazoline modified catalytic system, the chirality of the catalyst site is not sufficient to overcome the effect of the chirality of the growing chain. A prevailingly syndiotactic copolymer, as for the 2,2′-bipyridine ligand, is thus produced. Site selective coordination of the olefin at the metal center is probably involved in the stereocontrol of both catalysts **1** and **2**.

4. Experimental

4.1. General

Complexes **1** and **2** were prepared as described previously by reaction of the ligands with $PdCl_2(NCPh)_2$ to $PdCl_2(L^\wedge L')$, followed by treatment with silver trifluoromethanesulfonate, which led to the corresponding $[Pd(H_2O)_2(L^\wedge L')](OTf)_2$ [21,32].

The low molecular weight products were characterised by NMR and GC-MS. The enantiomeric excess was determined by gas chromatography using heptakis(6-*O*-TBDMS-2,3-*O*-methyl)-β-cyclodextrin as the stationary phase. The NMR spectra were measured on a Bruker AMX 400 and on AMX 500 with tetramethylsilane as the internal standard. The solvent normally used for co- and terpolymers was a $(CF_3)_2CDOD$–$CDCl_3$ 1:1 mixture. 2D spectra (COSY, INADEQUATE as well as HC- and HCC-correlation) were employed to obtain correct assignment.

The characterization of dimethyl 2-phenylbutanedioate (**8**) [33] and of (*E*)-1,4-diphenylpent-1-en-3-one (**10**) [34] was already reported. 2,4,7-Triphenyloct-1-en-3,6-dione (**7**) and 2,4-diphenylpent-1-en-3-one (**9**) were isolated through chromatography on silica from carbonylation mixtures of styrene obtained as previously described [35].

2,4,7-Triphenyl-oct-1-en-3,6-dion (**7**) was obtained as a mixture of the two diastereomers (D1 and D2). ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.39 (d, 3H, CH_3 (D1 or D2), ^3J(H,H) = 7.0 Hz), 1.41 (d, 3H, CH_3 (D1 or D2), ^3J(H,H) = 7.1 Hz), 2.54 (dd, 1H, CH_2 (D1), ^2J(H,H) = 17.8 Hz, ^3J(H,H) = 3.8 Hz), 2.62 (dd, 1H, CH_2 (D2), ^2J(H,H) = 18.1 Hz, ^3J(H,H) = 4.0 Hz), 3.41 (dd, 1H, CH_2 (D1), ^2J(H,H) = 17.8 Hz, ^3J(H,H) = 10.6 Hz), 3.47 (dd, 1H, CH_2 (D2), ^2J(H,H) = 18.1 Hz, ^3J(H,H) = 10.0 Hz), 3.68 (q, 1H, C*H*(CH_3) (D1 or D2), ^3J(H,H) = 7.1 Hz), 3.88 (q, 1H, C*H*(CH_3) (D1 or D2), ^3J(H,H) = 7.1 Hz), 4.75 (dd, 1H, CH (D2), ^3J(H,H) = 4.0 Hz, ^3J(H,H) = 10.0 Hz), 4.77 (dd, 1H, CH (D1), ^3J(H,H) = 3.8 Hz, ^3J(H,H) = 10.6 Hz), 5.78 (d, 1H, $H_2C{=}C$ (D1 or D2), ^2J(H,H) = 0.7 Hz), 5.80 (d, 1H, $H_2C{=}C$ (D1 or D2), ^2J(H,H) = 0.7 Hz), 6.15 (d, 1H, $H_2C{=}C$ (D1 or D2), ^2J(H,H) = 0.7 Hz), 6.16 (d, 1H, $H_2C{=}C$ (D1 or D2), ^2J(H,H) = 0.7 Hz).

2,4-Diphenyl-pent-1en-3-one (**9**): ^{1}H-NMR ($CDCl_3$, 500 MHz): 1.46 (d, 3H, CH_3, ^3J(H,H) = 6.9 Hz), 4.35 (q, 1H, C*H*(CH_3), ^3J(H,H) = 6.9 Hz), 5.75 (d, 1H, $H_2C{=}C$, ^2J(H,H) = 0.7 Hz), 6.01 (d, 1H, $H_2C{=}C$, ^2J(H,H) = 0.7 Hz).

4.2. Copolymerization experiments

4.2.1. Copolymerization reaction of styrene and CO

The copolymerization using the catalytic system **1** is described in detail as an example (entry 1 in Table 1). A 250 ml stainless steel autoclave under an atmosphere of N_2 was charged with 1,4-benzoquinone (0.216 g; 2.0 mmol). The palladium complex (**1**, 0.11 mmol) was dissolved in methanol (10 ml) in a Schlenk tube, and stirred for 15 min. After adding styrene (50 ml; 435 mmol), the solution was transferred to the pre-evacuated autoclave. After pressurising to 320 bar of CO, the autoclave was placed in an oil bath and the mixture stirred and heated to 50°C. After 46 h, the autoclave was cooled down to room temperature (r.t.) and the residual gas released. The mixture was poured into MeOH, and the unsoluble copolymer filtered off, washed again with methanol and dried. Yield 5.5 g (productivity 74.4 mmol g^{-1}(Pd) h). Prior to NMR analysis, some of the recovered copolymer was extracted with MeOH in a Kumagawa extractor.

4.2.2. Copolymerization reaction of ethene and CO

A similar procedure under comparable conditions was used for the copolymerization reaction of ethene and CO (entry 2 in Table 1). 50 ml of toluene, the solvent, were added to 10 ml methanol. Ethene (485 mmol) was added with a 'Büchi press-flow gas controller bpc'. During the copolymerization reaction (41 h), the pressure was kept constant by adding a gas mixture of 1:1 ethene–CO. Yield 0.56 g (productivity 20.2 mmol g^{-1}(Pd) h).

4.2.3. Terpolymerization reaction of styrene, ethene and CO

For the terpolymerisation of ethene, styrene and CO a similar procedure to that of the copolymerization of ethene and CO was used except that toluene was replaced by styrene (50 ml, 435 mmol). The terpolymerization using the catalytic system **1** is reported as an example (entry 3 in Table 1). 497 mmol ethene were added with a 'Büchi press-flow gas controller bpc' to the reaction mixture and during the terpolymerization reaction (46 h) the pressure was also kept constant by adding a gas mixture of 1:1 ethene–CO. Yield 2.1 g (productivity 68.3 mmol g^{-1}(Pd) h).

The co- and terpolymerization reactions using catalyst precursor **2** were similarly carried out using the same quantities of solvents and catalyst and the pressures given in Table 1. Reaction times for entries 4 to 7 were 18.5, 22, 41 and 41 h, respectively.

In all cases, immediate quantitative gas chromatographic analysis for the reaction mixture after filtration was carried out on a Hewlett Packard HP1 (50 m) column using acetophenone as the internal standard. Response factors were obtained from three point calibration with the pure isolated compounds. Correlation factors of 0.998–1.0 were generally obtained for the calibration curves.

Acknowledgements

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