From atactic to isotactic CO/*p*-methylstyrene copolymer by proper modification of Pd(II) catalysts bearing achiral α-diimines†

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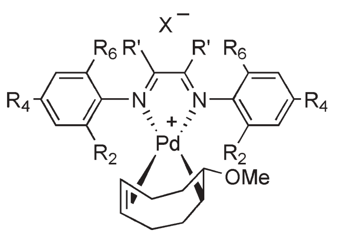
Cationic Pd(II) complexes modified with achiral C_{2v}-symmetric α-diimine ligands allow preparation of atactic or isotactic stereoblock CO/*p*-methylstyrene copolymers; both catalyst activity and polyketone microstructure depend on the choice of α-diimine substituents and counterion.

Palladium(II) catalysed copolymerisations of carbon monoxide with styrene derivatives[1–3] afford syndiotactic polyketones when planar C_{2v}-ligands (2,2′-bipyridine or 1,10-phenanthroline) are employed, due to a regioregular 2,1 insertion mode and a chain-end control mechanism.[4] On the other hand, Pd(II) catalysts bearing enantiomerically pure C_2-symmetric N–N ligands produce highly isotactic, optically active polyketones through an enantiomorphic site control mechanism.[5,6] Isotactic polyketones can also be obtained by means of C_1-symmetric P–N ligands or C_s-symmetric *meso* N–N ligands presumably owing to the site selective coordination of the olefin substrate.[7,8] In addition, while *in situ* ligand exchange (C_2-bis-oxazoline/2,2′-bipyridine) allowed Brookhart and Wagner to synthesise isotactic/syndiotactic stereoblock copolymers,[9] this methodology failed in the preparation of stereoblock polyketones containing isotactic blocks with opposite configuration.

Here we show that CO/*p*-methylstyrene[10] copolymers with atactic or isotactic stereoblock structure can be synthesised using the catalysts illustrated in Scheme 1, by a suitable choice of the α-diimine *ortho*-substituents and counterion.

The results of the polymerisation reactions are presented in Table 1. The activity of the catalysts decreases as the size of the aryl *ortho*-substituents (**1** *vs.* **9**, **12** and **13**), or of the backbone R′ groups (**6** *vs.* **8** and **9**) increases. This is probably due to the difficulty that the monomers have to approach the apical positions of more hindered catalysts.[8,11,12] The productivities increase with more electron donating N–N ligands. The observed trend **3**(F) > **2**(OMe) > **1**(H) > **5**(CF_3) likely reflects the higher stability of catalysts **3** and **2**,[13] due to the stabilizing electron releasing mesomeric effect of the F- and OMe-groups in *para* positions.[14] This is consistent with the better catalytic performances of analogous compounds [Pd(η^1,η^2-5-OMe-C_8H_{12})(2,2′-bipyridine)]X (**16**),[15] bearing the more basic bipy ligand. In agreement with previous results,[15] an increase of the anion coordination power[16] leads to a decrease in the catalyst productivity (compare catalyst **3** and **4**). It is notable that the anion effect is more marked when the anion really has the possibility to access to the metal center. This surely happens for compounds **16**[15] and **3–4**[11] but it does not occur for **6–7** and **9–11** owing to electronic and steric protection of the metal center.[17]†



1-13

14: [Pd(η^1,η^2-5-OMe-C_8H_{12})
(*i*Pr-N=C(H)C(H)=N-*i*Pr)]$^+PF_6^-$
15: [Pd(η^1,η^2-5-OMe-C_8H_{12})((*S*,*S*)-
2,2'-bis(4-*i*Pr-4,5-dihydrooxazole)]$^+PF_6^-$

1: $R_{2,4,6}$=H; R'=Me; X=PF_6
2: R_4=OMe; R'=Me; X=PF_6
3: R_4=F; R'=Me; X=PF_6
4: R_4=F; R'=Me; X=CF_3SO_3
5: R_4=CF_3; R'=Me; X=PF_6
6: $R_{2,6}$=Me; R'=H; X=PF_6
7: $R_{2,6}$=Me; R'=H; X=CF_3SO_3
8: $R_{2,6}$=Me; R'_2=9-anthryl; X=PF_6
9: $R_{2,6}$=Me; R'=Me; X=PF_6
10: $R_{2,6}$=Me; R'=Me; X=CF_3SO_3
11: $R_{2,6}$=Me; R'=Me; X=BArF
12: $R_{2,6}$=Et; R'=Me; X=PF_6
13: $R_{2,6}$=*i*Pr; R'=Me; X=PF_6
BArF=B(3,5-$(CF_3)_2C_6H_3)_4$

Scheme 1

As far as the microstructure of produced polymers is concerned, catalysts **1–5** afford regioregular polyketones with a "quasi-atactic" microstructure (Table 1 and Fig. 1, B).[18,7,8] This is rather surprising since the analogous complexes **16**[15] and compound **14** (in which *i*Pr groups replace the aryls) afford syndiotactic copolymers with a high stereochemical purity (Table 1). Interestingly, when catalysts **6–11** bearing Me groups in *ortho* positions are used, a remarkable increment of the isotactic component is observed (Fig. 1, A) approaching that obtained with the representative chiral C_2-symmetric bioxazoline ligand[5] (complex **15** in Scheme 1). Triad distribution analysis points out that using compound **15**, as expected, an isospecific site control is active ($ul + lu \approx 2uu$) while with compounds **6–11** the sterochemical control appears to be chain-end ($uu \approx 0$).[19] Therefore, when the latter compounds are used (particularly **9**, **10** and **11**) junctions of the type …*RRRSSS*… (…*SSSRRR*…) must be present along the polymer chains;[19] in other words, *these catalysts bearing an achiral nitrogen ligand are able to produce stereoblock copolymers containing isotactic blocks with opposite configurations*. For instance, the average number of comonomers in each block, calculated for the polymer obtained by catalyst **10**, is *ca.* 20 (10 CO and 10 *p*-methylstyrene units). The molecular weights of the prevalently isotactic copolymers (Table 1) are similar to those reported in the literature for isotactic CO/styrene polyketones obtained with chiral nitrogen ligands, even so the yields result to be lower.[5,6] The counterion significantly affects the stereoregularity of the copolymers: the isotactic content tracks with the coordination ability of the anion. While the use of $BArF^-$ (**11**) and PF_6^- (**9**) resulted in similar percentage of the *ll*-triad (72% and 75%, respectively),

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† Electronic supplementary information (ESI) available: Synthesis and characterisation of complexes **1–15**; copolymerisation details and copolymer characterisation. See http://www.rsc.org/suppdata/cc/b4/b411214h/
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Table 1 CO/*p*-methylstyrene copolymerisation results[a]

Catalyst	Yield[b]/g	CP (%)	gCP/gPd	Stereoregularity (triads %)[c]			$M_w \times 10^{-3}$ (M_w/M_n)
				ll	*ul*/*lu*	*uu*	
1	2.30	>99	154	31	49	20	17.7(1.7)
2	2.90	>99	195	26	52	22	14.0(1.7)
3	3.20	>99	215	29	53	18	16.9(1.6)
4	1.07	>99	72	32	52	16	12.4(1.8)
5	1.36	82	75	36	51	13	17.2(1.5)
6	0.56	93	35	59	35	6	7.7(1.5)
7	0.60	>99	40	60	35	5	9.9(1.6)
8	0.33	69	15	68	29	3	12.6(1.4)
9	0.45	59	18	75	24	1	8.0(1.3)
10	0.15	>99	10	80	20	<1	—
10[d]	0.63	85	36	81	18	1	14.5(1.6)
10[e]	1.33	100	89	80	19	1	20.2(1.4)
11	2.78	10	19	72	26	2	6.2(1.2)
12	0.35	<1	0				
13	0.15	<1	0				
14	1.83	100	123	1	7	92	7.4(1.5)
15	0.32	100	22	90	7	3	5.7(1.1)

[a] Reaction conditions: n_{Pd} = 1.4 × 10^{-4} mol; *p*-methylstyrene V = 5.5 mL (Pd : olefin = 1 : 300); solvent CH_2Cl_2 V = 5 mL; T = 17 °C; P_{CO} = 1 atm; reaction time = 51 h. [b] In some cases a mixture of homo- and copolymer (CP) was obtained. [c] Evaluated from the intensities of the ^{13}C NMR *ipso*-carbon atom resonances. [d] Reaction time = 150 h. [e] Reaction time = 150 h, T = 22 °C.

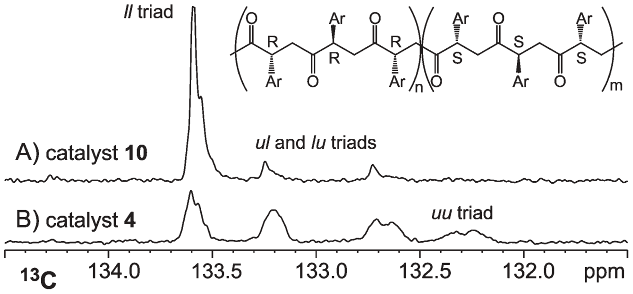
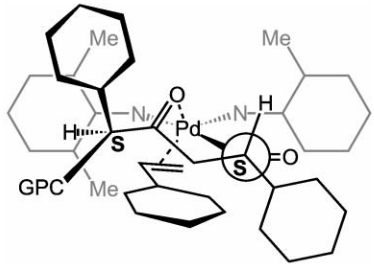


Fig. 1 Sections of the $^{13}C\{^1H\}$ NMR spectra (308 K, $(CF_3)_2CHOH/CDCl_3$ 1/1 (*v*/*v*)) relative to the *ipso* carbon resonances of polyketones produced by catalysts **10** (A) and **4** (B).



Scheme 2

catalyst **10**, having the more coordinating $CF_3SO_3^-$ anion, affords a polyketone containing 80% *ll*-triad. The effect of the anion on the microstructure is instead negligible when comparison is made between catalysts **3** and **4**, or **6** and **7**. Therefore, to achieve a good stereoselectivity, a peculiar steric/electronic interplay between R, R′ and the anion is necessary.[11,12,17]

The result that mainly isotactic CO/*p*-methylstyrene polyketones are obtained seems to be a special feature of the C_{2v}-symmetric α-diimine ligands used,[20] which is related to the presence of *ortho*-substituted phenyl rings. In particular, the isotacticity increases as (1) the steric hindrance of *ortho*-substituents, (2) "out-of-plane" bulkiness of the backbone R′ group, and (3) coordinating ability of the counterion increase. All three factors go in the direction of orienting the aryl moieties more perpendicularly with respect to the square-planar coordination plane, limiting, at the same time, aryl oscillation around the N–C_{ipso} bond. In the case of compounds **1**–**5**, bearing more flexible diimine ligands, such an oscillation can take place with a consequent statistical insertion of the styrene enantiotopic faces.

As stated above, due to the achiral nature of the N–N ligands a chain-end control mechanism must be invoked to explain the copolymerisation stereochemical control. On the other hand, unlike the case of planar 2,2′-bipyridine or 1,10-phenanthroline ligands, the same olefin enantioface has to be selected in each stereoblock. This may occur according to the working model represented in Scheme 2 based on previously reported studies.[2,8,21] The steric hindrance provided by aryl diimine ligands prevents the coordinated styrene from orienting the phenyl moiety toward the N–N ligand in the putative trigonal-bipyramidal six-member palladacycle intermediate.[2,21] Moreover, the correct olefin enantioface (*Si* in Scheme 2) is selected to minimize the steric interaction between the styrene and the phenyl ring of the last inserted unit.

In conclusion, the results reported here show for the first time that isotactic CO/*p*-methylstyrene polyketones can be produced using Pd(II) catalysts with achiral C_{2v}-symmetric α-diimine ligands. Work is currently in progress to enhance the performances of such systems and to gain further mechanistic information either by modification of the ligands and catalyst structure[6] or by optimizing the reaction conditions (*i.e* solvent,[22] temperature and CO pressure).

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