116. Isotactic and Atactic Copolymerization of Styrene and Carbon Monoxide Using Cationic Palladium-Phosphino(dihydrooxazole) Complexes

Preliminary Communication

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Cationic palladium complexes **2** containing coordinated phosphino(dihydrooxazole) ligands **1** give catalytic systems which allow the production of alternating styrene-carbon monoxide copolymers. Depending on the symmetry of the ligand, the copolymers are produced either with a highly isotactic or with an essentially completely atactic microstructure. Termination of the polymeric chain is mainly due to a β-H-elimination reaction. Both linear ((E)-PhCH=CHCO–) and branched (CH$_2$=C(Ph)CO–) unsaturated end groups were identified.

The control of the stereochemistry in the alternating copolymerization of α-olefins with carbon monoxide is a matter of current interest [1–6]. In fact, the use of optically active catalyst allows the enantioselective synthesis of polyketones [7–9]. The first enantioselective copolymerization to regioregular optically active highly isotactic polyketones was realized for propene as the substrate using Pd catalyst systems modified by (S)-2,2'-dimethyl-6,6'-bis(dicyclohexylphosphino)biphenyl [10] [11]. Similar catalytic systems containing dinitrogen ligands (1,1'-bipyridine or 1,10-phenanthroline) are known to promote the syndiotactic copolymerization of styrene or *para*-substituted styrenes by chain-end control [12–16]. Recently, isotactic optically active poly[1-oxo-2-(4-*tert*-butylphenyl)propane-1,3-diyl] has been prepared using Pd catalysts modified by dihydrooxazole ligands [6]. It was reported that the same copolymer albeit with low molecular weight and low stereoregularity has been obtained using a chiral phosphane-phosphite ligand [2]. Moreover, C_2-symmetric bis[dihydrooxazoles] have also been used for the enantioselective synthesis of copolymers of styrene and 4-methylstyrene [5]. However, productivity was low, probably due to the low coordination ability and the consequent sensitivity of the catalyst system to temperature or to high CO partial pressure or to both. Ligands of C_1-symmetry have already been successfully applied to the enantioselective copolymerization of aliphatic olefins [2] [3]. We used P,N-hybrid ligands for the related synthesis of ketones from styrene [17] [18]. We report now on the copolymerization of styrene (PhCH=CH$_2$) and CO using hybrid phosphino(dihydrooxazole) ligands which, due to a better coordination ability, allow us the preparation of large amounts of either isotactic or atactic poly[1-oxo-2-phenylpropane-1,3-diyl].

The preparation of the chiral ligands **1a–c** was previously reported [19]. The achiral one **1d** was similarly prepared. The corresponding Pd complexes were obtained according

Scheme

1a R = Ph   2a R = Ph
 b R = PhCH₂   b R = PhCH₂
 c R = i-Bu   c R = i-Bu
 d R = H   d R = H
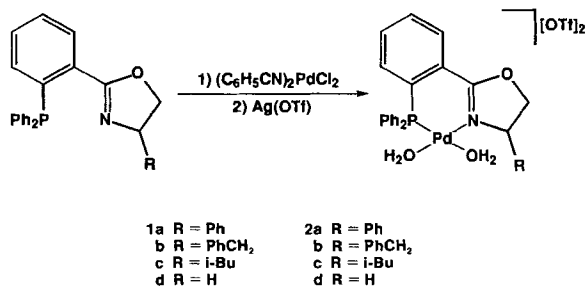
to literature procedures for similar compounds [20]. Traces of H_2O in the reaction medium cause normally the formation of the aquo complexes **2** (*Scheme*) [21].

The copolymerization reactions were carried out at 50° and 320 bar CO due to the fact that high CO partial pressures cause an increase of the productivity. Using **2c** as the catalyst precursor, only trace amounts of the copolymer were isolated under 5 bar of CO. At 320 bar, under otherwise the same reaction conditions, a productivity of $6.4 \text{ g} \cdot \text{g}^{-1}(\text{Pd}) \cdot \text{h}^{-1}$ leads to 19.6 g of isolated copolymer as reported in the *Exper. Part*. The best productivity ($10.7 \text{ g} \cdot \text{g}^{-1}(\text{Pd}) \cdot \text{h}^{-1}$) was observed with the benzyl-substituted catalytic system **2b**. The catalytic systems with the same ligand **1b** but containing the hexafluorophosphate or antimonate anion gave slightly lower productivities. Molecular masses up to 20 000 were evaluated for the copolymers from end groups (*vide infra*) in the ^{1}H-NMR spectra. The materials produced with the catalytic systems **2a–c** show a high stereoregularity as indicated by their ^{13}C- and ^{1}H-NMR as well as their CD spectra. As an example, the ^{13}C-NMR spectrum of the copolymer obtained with **2a** is reported (*Fig. 1*). Further evidence for the isotactic structure of the copolymer derives from the large rotatory strength of the CD spectrum in the region of the carbonyl and phenyl chromophors (*e.g.*, $\Delta\varepsilon = -10.8 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ (284 nm in $(CF_3)_2CHOH/CHCl_3$ 1:10) for the (*S*)-**2a** catalytic system). The optical activity ($[\alpha]_{589}^{25} = -403 \text{ deg} \cdot \text{dm}^{-1} \cdot \text{g}^{-1} \cdot \text{cm}^3$) is comparable to that previously reported [5]. Negative rotation was assigned to prevailing (*R*)-configuration [5].

The small signals in *Fig. 1* are either due to end groups or to irregularities during the chain growth. The nature of the irregularities is not clearly identified at the present. However, based on the evaluation of the NMR parameters, they might arise from errors in enantioface selection and not in regioselectivity [22].

The nature of the end groups is dependent on the catalytic system used (different substituent R, different anion) and on the reaction conditions (absence or presence of an oxidant), respectively. Without substantial differences in productivity, the copolymer chain can grow either starting with a Pd–H or a Pd–COOR species. Exclusively secondary insertions of styrene into a Pd–H bond is observed leading to a 1-phenylethyl end group. Termination is mostly caused by β-H-elimination reactions. In contrast to the previously reported copolymers obtained with catalytic systems modified by achiral dinitrogen ligands, in addition to the linear unsaturated end group ((*E*)-PhCH=CHCO–) [14] [23], also the branched unsaturated one (CH_2=C(Ph)CO–) is formed. Signals observed at 205.72 (*C*O), 149.49 (CH_2=*C*(Ph)CO–), 137.81 (C_{ipso}), and
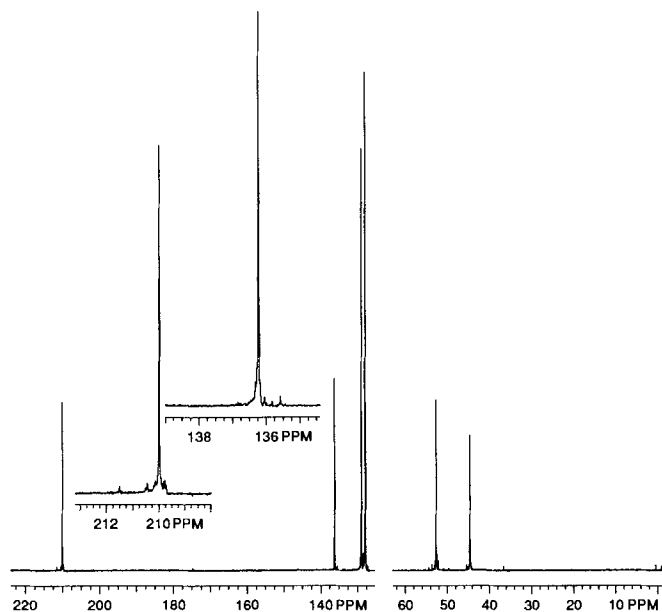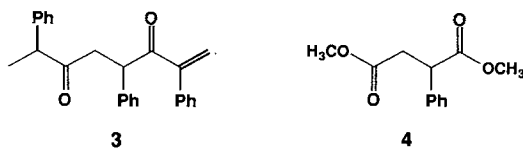
Fig. 1. ^{13}C-NMR Spectrum ((CF$_3$)$_2$CDOD/CDCl$_3$ 1:1, 125.8 MHz) of isotactic poly[1-oxo-2-phenylpropane-1,3-diyl] obtained with **2a**

127.91 ppm (CH$_2$=C(Ph)CO–) in the ^{13}C-NMR and at 6.17 and 5.92 ppm (J < 1 Hz) in the ^{1}H-NMR spectra are assigned to the latter group on the basis of 2D-NMR experiments. This shows that primary insertion of styrene in a Pd–acyl species can take place.

For the Me signal of the 1-phenylethyl end group, two d's at 1.31 and 1.33 ppm (^3J = 7.1 Hz) are observed in the ^{1}H-NMR spectra. A diastereoisomeric relationship is suggested by the analysis of the model compound 2,4,7-triphenyloct-1-ene-3,6-dione (**3**). The molar ratio of these d's is low for all catalytic systems used (e.g., ca.: 40:60 for **2a**). This suggests that the first styrene unit is inserted in a Pd–H bond with a low enantioface selection. Consistent with this observation, trace amounts of (R)-methyl 2-phenyl-propanoate with an enantiomeric ratio of 36:64 were identified in the solution obtained with the same catalyst system and recovered after filtration of the polymeric material.

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Interestingly, the catalytic system **2d** containing the unsubstituted achiral ligand gives a copolymer which is substantially atactic (Fig. 2) [24]. A similar copolymer is obtained using a catalytic system modified with 2-[2-(diphenylphosphino)ethyl]pyridine. Such atactic materials have been previously prepared using thioether ligands; however, the polymerization degree was much lower (M_n up to 3300 from VPO) [25] [26].
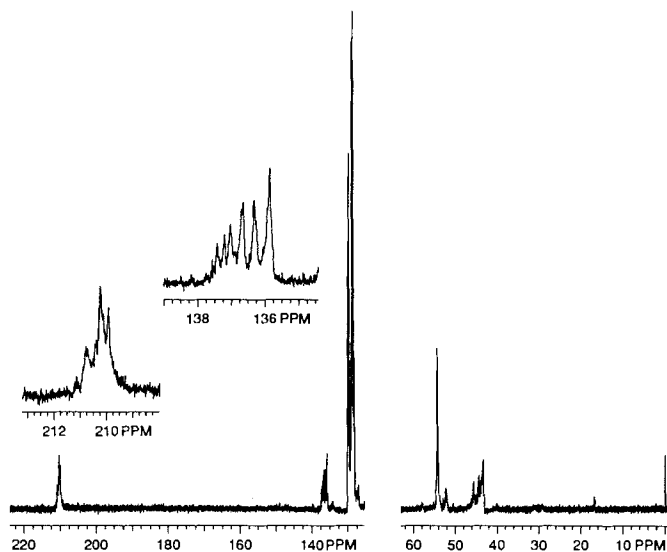
Fig. 2. ^{13}C-NMR Spectrum ((CF$_3$)$_2$CDOD/CDCl$_3$ 1:1, 125.8 MHz) of atactic
poly[1-oxo-2-phenylpropane-1,3-diyl] obtained with **2d**

It is worthwhile to note that catalytic systems modified by the achiral ligands 2,2′-bipyridine or 1,10-phenanthroline give a syndiotactic copolymer by chain-end control [13] [14]. The interesting question now arises as to how the atactic copolymer obtained with the achiral catalytic system **2d** is formed. We propose as a working hypothesis that the enantioface discrimination for the catalytic systems investigated is determined within a complex like that reported in *Fig. 3* for which we assume a site-selective coordination of the olefin [27] [28] and a secondary insertion [14] for the incoming styrene units. Steric repulsion between the substituent R of the ligand (when present) and the Ph group of the substrate determines enantioface selection during chain growth. According to the model the (*S*)-phosphino(dihydrooxazole) ligands should cause preferential selection of the *re*-enantioface of the styrene leading to the (*R*)-copolymer as inferred by the sign of the optical rotation [5] [29]. Moreover, the trace amounts of dimethyl 2-phenylbutanedioate (**4**) [30] formed as a by-product during the copolymerization shows the same relative
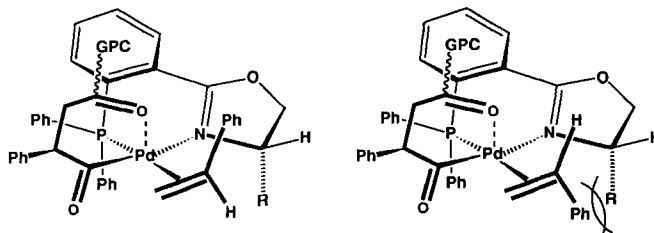

Fig. 3

topicity as the copolymer with respect to the ligands used. However, like in the case of insertion into a Pd—H bond, the first insertion of styrene into a Pd—COOR bond occurred with low selection (maximum ee of 28% for (R)-4 obtained with (S)-2c as catalyst precursor). This strongly suggests that the conformation of the growing chain improves the discrimination ability of the ligand used towards enantioface selection (double stereodifferentiation [31]) leading to isotactic copolymers as already inferred for the analogous copolymerization of aliphatic olefins [20].

The most important aspect of the reported results is concerned with the possibility to synthesize both isotactic and atactic styrene-carbon monoxide copolymers. Furthermore, the ligands used allowed us to observe for the first time a primary insertion of styrene into a Pd—acyl bond. For related Pd catalytic systems containing bipyridine or phenantroline, a living syndiotactic copolymerization was realized [29]. We are pursuing our investigation with the synthesis of other catalyst precursors in order to achieve living copolymerization to polyketones with different configuration.

Experimental Part

General Procedure for the Copolymerization Reaction. As an example, the copolymerization using the catalytic system **2c** is described in detail. A 250-ml stainless steel autoclave under N_2 was charged with 1,4-benzoquinone (0.216 g, 2.0 mmol; if used). In a *Schlenk* tube, the Pd complex (0.11 mmol) was dissolved in MeOH (10 ml) and stirred for 15 min. After the addition of styrene (50 ml, 435 mmol), the soln. was transferred into the pre-evacuated autoclave. After pressurizing to 320 bar of CO, the autoclave was placed in an oil bath and the mixture stirred and heated to 50°. After 260 h, the autoclave was cooled to r.t. and the residual gas released. The mixture was poured into MeOH and the unsoluble copolymer filtered off, washed again with MeOH and dried: 19.6 g (productivity 6.4 $g \cdot g^{-1}(Pd) \cdot h^{-1}$). Prior to NMR analysis, part of the recovered copolymer was extracted with MeOH in a *Kumagawa* extractor.

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