Enantioselective Alternating Terpolymerization of Styrene and Ethene with Carbon Monoxide

Preliminary Communication

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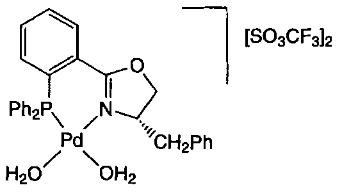
In spite of the higher reactivity of styrene with respect to ethene for the alternating copolymerization with carbon monoxide, catalyzed by chiral (dihydrooxazole)(phosphino)palladium complexes, ethene is preferentially (and randomly) enchained in terpolymerization experiments; enantioface selection for styrene is comparably high in both copolymerization and terpolymerization processes.

The alternating copolymerization of olefins with carbon monoxide (CO) has attracted much attention in the last few years [1–4]. Although the newly developed commercial material is, indeed, a terpolymer containing ethene and propene [5], much less attention has been paid to terpolymerization reactions [6–11]. Using ethene and styrene as the olefin, in addition to the possibility mentioned [12] for obtaining the terpolymer with 2,2′-bipyridine-based catalytic systems, only the synthesis of materials using a catalyst formed *in situ* from $[Pd(MeCN)_4](BF_4)_2$ and 5-methyl-1,10-phenanthroline was reported [7]. The structure of the produced terpolymers was claimed to be random, and no information on initiation and termination reactions was given. The reactivity of the two olefin comonomers in the above terpolymerization experiments [7] seems comparable. In the alternating copolymerization of styrene with CO an effective control of the stereochemistry was reached. The three limiting structures (iso-, syndio-, and atactic) are all accessible for poly(1-oxo-2-phenylpropane-1,3-diyl) [13–15]. The 1,10-phenanthroline-containing catalyst precursors give the syndiotactic copolymer by chain-end control [16][17]. Catalysts containing enantiomerically pure bis[dihydrooxazoles] [13][18][19] or hybrid (dihydrooxazole)phosphino ligands [15] give highly isotactic, optically active poly(1-oxo-2-phenylpropane-1,3-diyl). Even though an enantiomorphic site control is to be expected, a possible role of the growing chain in stereocontrol cannot be excluded. We report here preliminary results of the enantioselective alternating terpolymerization of ethene and styrene with CO which not only suggest which factors may be responsible for the stereocontrol in the aforementioned process, but also reveal interesting features of reactivity relative to the enchainment of the two different comonomers.

The copolymerization of either styrene [15] or ethene using comparable molar amounts of the olefin substrate was carried out at 50° in MeOH as the solvent and with $[Pd(P^{\wedge}N)(H_2O)_2](SO_3CF_3)_2$ (**1**) as the catalyst precursor (see *Exper. Part*). The reaction time was 40 h. Under these conditions, the productivity of the two olefins was 80.9 mmol · g^{-1}(Pd) · h^{-1} and 23.1 mmol · g^{-1}(Pd) · h^{-1}, respectively. From the analysis of the gas phase, we evaluated that only *ca.* 35% of the ethene was dissolved. Despite this, a higher reactivity of styrene with respect to ethene is evident.



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Some results for terpolymerization experiments, which were carried out under similar reaction conditions, are reported in the *Table*.

Table. *Alternating Terpolymerization of Styrene* (435 mmol) *and Ethene with Carbon Monoxide Using* $[(P^{\wedge}N)Pd(H_2O)_2](SO_3CF_3)_2$ (**1**) *as the Catalyst Precursor*

Ethene [mmol]	CO Pressure [bar]	Productivity $[\text{mmol} \cdot g^{-1}(\text{Pd}) \cdot h^{-1}]$	Terpolymer composition C_2H_4CO/C_8H_8CO	$\Delta\varepsilon$[a]) (282 nm) $[l \cdot mol^{-1} \cdot cm^{-1}]$
202	290	27.5	80:20	−11.1
362	290	27.4	87:13	−12.0
458	290	23.0	92:8	−13.2
368	140	12.9	90:10	−12.9

[a]) In $(CF_3)_2CHOH/CHCl_3$ 1:10; $c = 6\ \text{mg} \cdot \text{ml}^{-1}$.

The styrene content was evaluated by ^{1}H-NMR spectroscopy on the basis of the intensity of the signals corresponding to CH ($\delta = 4.15$–4.32 ppm, styrene unit) and CH_2 ($\delta = 2.5$–3.0 ppm, ethene and styrene units). The intensity of the signals in the ^{13}C-NMR spectrum, particularly in C=O region (*Fig.*), suggests that the terpolymer actually contains isolated styrene units. The assignment shown in the *Figure* is based on the relative change in intensity of the various signals for terpolymers having increasing styrene concentration.

In view of the above-mentioned difference in reactivity of the single olefins favoring styrene, the content of ethene is unexpectedly large. The relative content of both olefins in the terpolymers corresponds to an enchainment rate *ca.* 10 times higher for ethene than for styrene.

Both for the styrene copolymerization [15] and for the terpolymerization experiments (*Table*), we observed a comparable decrease in productivity as a consequence of the decrease in the CO pressure.

As chain end groups, the methoxycarbonyl group ($-CH_2CH_2COOCH_3$), the styrene-α-carbonyl group ($CH_2{=}C(Ph)CO-$) [15], and vinyl groups ($CH_2{=}CHCO-$) are clearly identified. The presence of the alternative linear styrene-β-carbonyl group ($PhCH{=}CHCO-$) is less evident. Furthermore, both the 1-phenylethyl (MeCH-

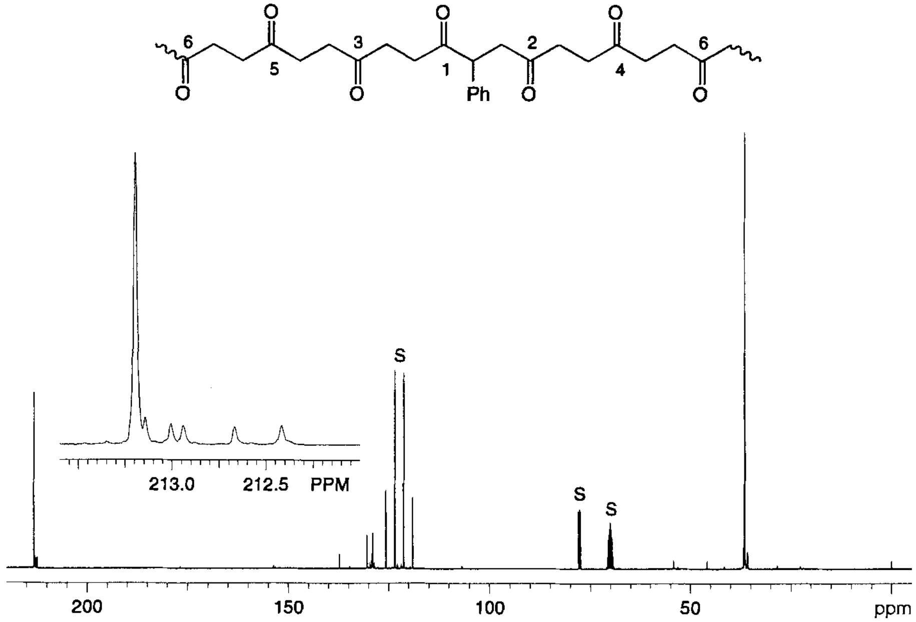


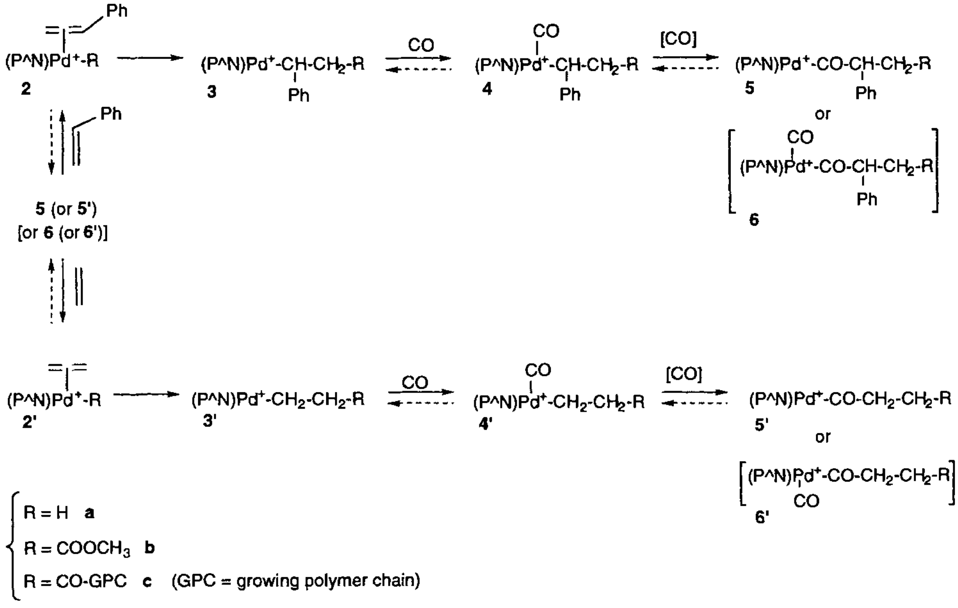
Figure. *^{13}C-NMR* ($(CF_3)_2CDOD/CDCl_3$ 1:1, 125 MHz) *of an ethene-styrene carbon monoxide terpolymer* (S = solvent; assignment for the C=O region according to decreasing chemical shift: 6, [5?], 2, 3, 4, 1).

(Ph)CO– ; *doublet* at 1.47 ppm) and the Et groups (EtCO– ; *triplet* at 1.11 ppm) can be recognized. Their molar ratio, *e.g.*, for the terpolymer containing *ca.* 10% styrene is close to 1, and their concentration is small (*ca.* 10% of all end groups). Due to this low concentration, it is not possible to draw conclusions about the reactivity of the first olefin insertion (formation of **3a** *vs.* **3′a**; *Scheme*) or on the relative rate of CO insertion into the two hydrocarbyl–Pd bonds (formation of **5a** *vs.* **5′a**; *Scheme*), particularly because these groups can also correspond to chain interruption by protonolysis reactions [3][20].

The reported results can be tentatively interpreted on the basis of the *Scheme*. The lower reactivity of ethene for copolymerization and its higher concentration in the terpolymer chains can be understood by assuming that formation of intermediate **2′c** is favored with respect to that of **2c**, but insertion to form **3′c** is inherently slower than insertion to form **3c**. In fact, it appears very likely that the olefin insertion (step **2′** → **3′** or **2** → **3**) is irreversible [21]. In both cases, however, the slowest step in the catalytic cycle should correspond to reactions **3** → **4** and **3′** → **4′**, or to the successive CO insertion, since this insertion could be assisted by carbon monoxide to form (acyl)(carbonyl)-palladium intermediates (**6c** and **6′c**). Species of the latter type have been identified as the catalyst resting state for systems modified by 1,10-phenanthroline [4].

The intensity of the rotatory strength of the transition associated with the C=O chromophore for the terpolymers ($\Delta\varepsilon = -12 \pm 1\ \mathrm{l \cdot mol^{-1} \cdot cm^{-1}}$), when extrapolated to 100% concentration of the styrene units, is almost equal to that determined for highly

Scheme



isotactic poly(1-oxo-2-phenylpropane-1,3-diyl) obtained with the same ligand [15]. Therefore, it seems that similar, very high enantioface selection takes place at the level of the formation of intermediate **3**, independent of the nature of the last inserted olefin unit (either ethene or styrene).

The reported results thus show substantial differences related not only to the relative rate of the different steps in the catalytic cycle, but also to the mechanism of steric control during the copolymerization process with those obtained with achiral and chiral dinitrogen ligands [4][12][19].

Experimental Part

General Procedure for the Copolymerization Reaction of Styrene and CO. A 250-ml stainless steel autoclave under N_2 atmosphere was charged with 1,4-benzoquinone (0.216 g; 2.0 mmol). In a *Schlenk* tube, the palladium complex **1** (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 to the pre-evacuated autoclave. After pressurizing to 290 bar of CO, the autoclave was placed in an oil bath, and the mixture was stirred and heated to 50°. After 40 h, the autoclave was cooled down 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. Prior to NMR analysis, part of the recovered copolymer was extracted with MeOH in a *Kumagawa* extractor.

General Procedure for the Copolymerization Reaction of Ethene and CO. A similar procedure as for the copolymerization of styrene and CO under comparable conditions was used. To 10 ml of MeOH, 50 ml of toluene were added as the solvent. The ethene (489 mmol) was added with a '*Büchi* press-flow gas controller bpc'. During the copolymerization reaction, the pressure was kept constant by adding a gas mixture ethene/CO 1:1.

General Procedure for the Terpolymerization Reaction of Styrene and Ethene with CO. The procedure was similar to that of the copolymerization of ethene and CO except that toluene was replaced by styrene (50 ml, 435 mmol).

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