Asymmetric Polymerization

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Synthesis of Optically Active Polystyrene Catalyzed by Monophosphine Pd Complexes

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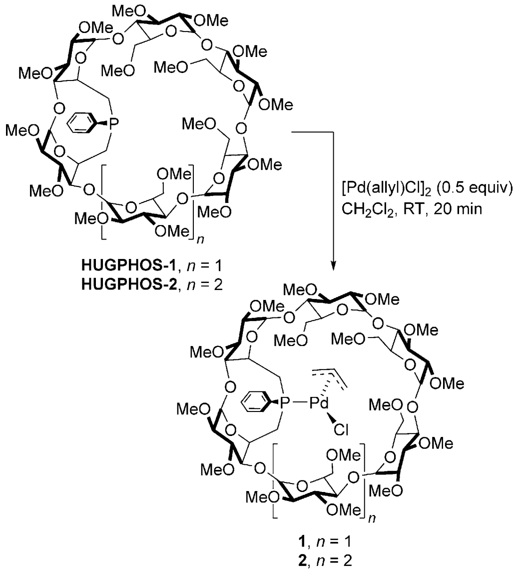
Abstract: *Cationic Pd^{II} monophosphine complexes derived from α- and β-cyclodextrins (CDs) promote the homopolymerization of styrene under carbon monoxide pressure. Although reversible CO coordination takes place under catalytic conditions according to ^{13}C NMR studies with ^{13}C-enriched CO, both complexes catalyze the formation of CO-free styrene polymers. These macromolecules display optical activity as a result of the presence of stereoregular sequences within the overall atactic polymer.*

Optically active polymers are abundant in the natural world, but their chemical synthesis through polymerization of prochiral monomers remains challenging.[1,2] Although monosubstituted olefins have a prochiral sp^2-hybridized group, their stereospecific addition polymerization results in optically inactive polymers. The absence of optical activity arises because a stereoregular isotactic or syndiotactic polymer possesses a mirror plane in its macromolecular chains.[1] An interesting approach for generating an optically active polymer was reported by Wulff and Dhal, who described the radical copolymerization of styrene with a monomer made up of two styryl units joined together by a cleavable chiral spacer.[3] Removal of the tether after copolymerization afforded an atactic polystyrene containing chiral diads, thereby resulting in an optically active material. Another study by Okuda and co-workers established that isotactic polystyrene with an oligohexene segment attached to one of the two polymer ends showed optical activity when $M_n < 5000$.[4] This was attributed to the combined presence of stereoregular alignment of the styrene units and an unsymmetrical polymer structure. However, the polymer with higher molecular weight becomes optically inactive. To the best of our knowledge, there is no reported example of optically active polystyrene produced by direct homopolymerization of styrene, thus reflecting the difficulty in introducing both a stereoregular sequence and an unregulated atactic enchainment in the polymer chain.[1]

Very recently, confining phosphine ligands (HUGPHOS-1[5a] and HUGPHOS-2,[5b] Scheme 1) derived from cyclodextrins (CDs) were shown to selectively give monophosphine complexes in reactions where classical phosphines (L) lead to ML$_2$ complexes. This particular feature was found to have a substantial impact on the catalytic outcome of the rhodium-catalyzed asymmetric hydroformylation of styrene, thereby resulting in a unique multiselective process (> 98% isoselectivity, 95% *ee*).[6] Tertiary phosphines, which are ubiquitous in coupling reactions catalyzed by late transition metals,[7] have scarcely been used as catalyst ligands in olefin polymerization.[8] When coordinated to a palladium center, such phosphines typically produce small oligomeric materials (< 10 repeating units) because of their propensity to increase the rate of β-hydride elimination.[8]



Scheme 1. Synthesis of Pd^{II} allyl monophosphine complexes **1** and **2**, which are derived from HUGPHOS ligands.

We wondered whether the use of confining phosphines would affect the polymerization of styrene as well as the copolymerization of styrene with carbon monoxide.[9] Herein, we describe an unprecedented asymmetric, palladium-catalyzed homopolymerization of styrene under CO when using HUGPHOS Pd^{II} monophosphine complexes.

The polymerization experiments were carried out using HUGPHOS complexes **1** and **2** (Scheme 1), which form quantitatively upon reacting [Pd(allyl)Cl]$_2$ with a stoichiometric amount of the appropriate ligand. Table 1 summarizes the

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Table 1: Palladium-catalyzed polymerization of styrenes under CO pressure.[a]

Run	cat.	P_{CO} [MPa]	Solvent	T [°C]	conv.[b] [%]	M$_n$[c]	M$_w$/M$_n$[c]	Triad [%][d] *mm*	*rm* (*mr*)	*rr*	$[\alpha]_D^{25}$[e]
1	**1**	0	dichloromethane	40	> 99	–	–	–	–	–	–
2	**2**	0	dichloromethane	40	> 99	–	–	–	–	–	–
3	**1**	0.1	dichloromethane	40	> 99	7300	1.98	24.5	46.0	29.5	−4.8°
4	**2**	0.1	dichloromethane	40	> 99	9100	2.08	25.8	48.8	25.4	−5.3°
5	**1**	0.1	toluene	40	92	2350	2.09	29.5	42.5	28.0	−3.9°
6	**1**	0.1	hexane	40	35	2720	1.83	26.0	42.0	32.0	−3.1°
7	**1**	0.1	dichloromethane	RT	trace	–	–	–	–	–	–
8	**1**	1.0	dichloromethane	40	< 5	26400	1.77	–	–	–	–
9	**1**	1.0	toluene	80	70	4200	1.82	24.5	40.0	35.5	+ 0.8°
10	**1**	2.0	toluene	80	92	3800	2.14	26.4	41.7	31.9	+ 0.7°
11	**1**	5.0	toluene	80	77	4300	1.92	26.4	39.6	34.0	+ 1.0°
12[f,g]	**1**	0.1	dichloromethane	40	> 99	43400	2.77	–	–	–	+ 1.0°
13[h]	**1**	0.1	dichloromethane	40	> 99	23600	3.36	–	–	–	+ 1.7°
14[i]	**1**	0.1	dichloromethane	40	> 99	4600	6.01	–	–	–	−1.4°
15[j]	**1**	0.1	dichloromethane	40	70	9300	2.04	–	–	–	−0.6°

[a] Experimental conditions: catalyst (0.014 mmol), styrene/complex = 1000, AgSbF$_6$/complex = 1.00, solvent (2.5 mL), 16 h. [b] Conversion (%) determined by ^{1}H NMR using naphthalene as internal standard (styrene/naphthalene = 10). [c] Molecular weight distribution determined by GPC using polystyrene standards. [d] Tacticity determined by ^{13}C NMR according to the literature.[10] [e] Optical activity measured in dichloromethane with $c = 0.01$ g mL^{-1}. [f] styrene/complex = 100. [g] *p*-Methoxystyrene. [h] *o*-Methoxystyrene. [i] *p*-Methylstyrene. [j] 2-Vinylnapthalene.

reactions in the absence or presence of CO. In the absence of CO, complexes **1** and **2** showed the standard reactivity of phosphine palladium complexes, since only dimers were produced after in situ activation of the corresponding neutral complex with AgSbF$_6$ as halide scavenger (runs 1 and 2). Conversely, under a CO atmosphere, styrene was straightforwardly converted in 16 h under the same reaction conditions to give polystyrene with $M_n = 7300$–9100 in dichloromethane (runs 3 and 4). Surprisingly, no carbonyl groups were detected in the resulting polymer, as inferred from ^{13}C NMR and IR spectroscopy, as well as elemental analysis (see the Supporting Information).

Late transition metal catalyzed alternating copolymerization of CO with ethene or α-olefins such as propene and styrene affords polyketones with either perfectly or non-perfectly alternating ethylene/CO motifs.[11] For example, a non-perfect copolymer forms when CO is reacted with ethene in the presence of palladium complexes with phosphine sulfonate or phosphine carboxylate ligands.[12,13] In stark contrast, complexes **1** and **2** provide carbonyl-free polymer under carbon monoxide pressure. The polymers produced were mostly atactic as shown by ^{13}C NMR, but displayed optical activity ($[\alpha]_D^{25} = -4.8°$ to $-5.3°$).

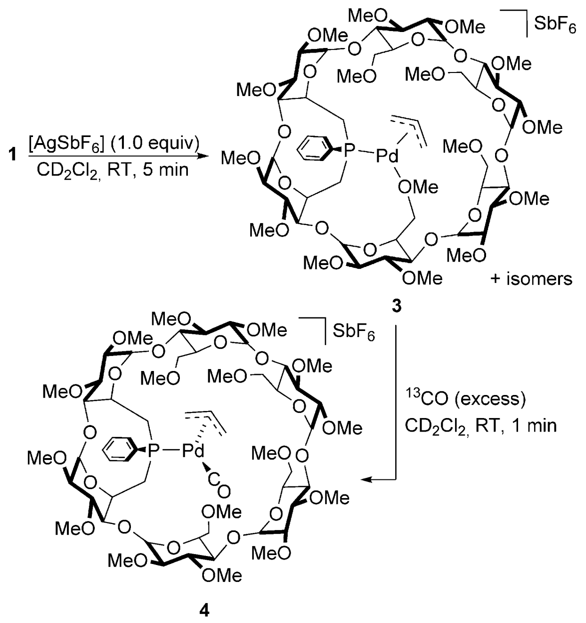
Using toluene or hexane as the solvent instead of dichloromethane decreased the polymerization rate and the molecular weight of the resulting polystyrenes (runs 5 and 6), but again afforded optically active atactic polymers ($[\alpha]_D^{25} = -3.1°$ to $-3.9°$). Interestingly, the polymerization reaction required temperatures above 40 °C (run 7). Furthermore, increasing the CO pressure did not result in the insertion of carbon monoxide into the polymer chains even under 5.0 MPa CO (runs 8–11). The polymers obtained at $P_{CO} = 1.0$–5.0 MPa were atactic, and the amount of *rm* triads decreased compared to those obtained under 0.1 MPa CO. The optical activity also decreased, together with an inversion of optical rotation. These observations suggest that the relative amounts of catalytically active species are not the same under low and high CO pressures. Note that no significantly different results were observed when using **2** instead of **1**.

Introduction of substituents on the styrene aromatic ring did not result in the insertion of CO either (runs 12–15). The presence of an electron-donating methoxy group led to an increase in the polymer molecular weight (runs 12 and 13), whereas the polymerization of *p*-chlorostyrene did not proceed (conv. < 5 %). The optical activity of the polymers obtained from such styrene derivatives was smaller than that observed for polystyrene, and their optical rotation was dependent on the type of substituent.

The unique reactivity of **1** toward CO during polymerization prompted us to investigate the coordination of CO to the palladium center under polymerization conditions.

Cationic complex **3**, synthesized by chloride abstraction from **1** with AgSbF$_6$ (Scheme 2), is air stable and displays a broad singlet in its ^{31}P{^{1}H} NMR spectrum, which is consistent with dynamic behavior of the complex.[14] Addition of ^{13}C-labeled CO to **3** led to the quantitative formation of a new complex formulated as **4**. This result is reminiscent of studies by Keim and Mecking on related cationic [Pd(allyl)L$_{P,O}$(CO)]$^+$ (L$_{P,O}$ = bidentate P^{III},O ligand) complexes.[15,16] Proof that a carbonyl ligand is coordinated to the Pd^{II} center in **4** came from careful examination of its ^{13}C{^{1}H} NMR spectrum at different temperatures. At room temperature, the coordinated CO ligand resonates as a broad signal in the carbonyl region. On lowering the temperature to −30 °C (Figure 1), the CO signal splits into two sharp doublets of unequal intensity (ratio 1:2), both with a $^2J_{PC}$ coupling constant of 19 Hz.

These observations are consistent with the presence of two equilibrating diastereomeric π-allyl complexes (**4a** and **4b**) arising from the two possible orientations of the allyl moiety with respect to the unsymmetrical coordination plane. Note that upon addition of CO or N$_2$, complexes **3** and **4** readily interconvert, thus reflecting weak binding of the



Scheme 2. Synthesis of cationic complexes **3** and **4**.

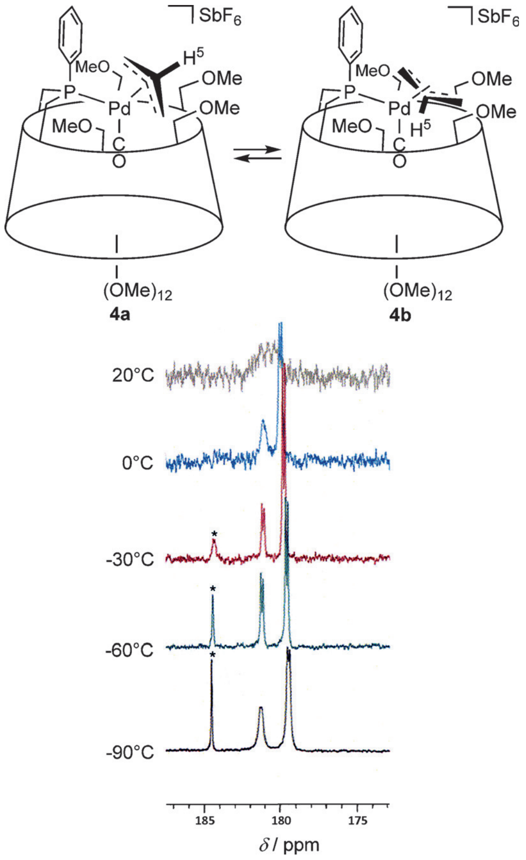
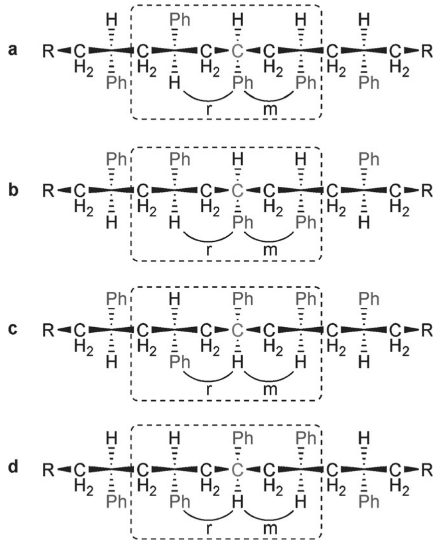


Figure 1. Variable-temperature $^{13}C\{^{1}H\}$ NMR study of palladium complex **4** recorded in CD_2Cl_2, revealing the two diastereomeric complexes **4a** and **4b**. The asterisk denotes free ^{13}CO in solution.

carbonyl ligand. In the presence of styrene, **4** gave three unidentified products as observed by $^{31}P\{^{1}H\}$ NMR (see the Supporting Information). Mass spectroscopic measurements carried out on the crude reaction mixture showed a major species at $m/z = 1521.65$ (100%), which corresponds to the $[\mathbf{3} + \text{styrene} - SbF_6]^+$ cation.

To sum up, styrene polymerization using Pd complexes **1** and **2** afforded polymers with optical activity but with unregulated tacticity. Selective coordination of the metal center to an enantioface of prochiral α-olefins may explain the formation of a polymer with high isotacticity, but not the selectivity of the present polymerization. Wulff and Dhal synthesized optically active polystyrenes displaying optical activity ($[\alpha]_{365}^{30} = -0.5$ to $-3.5°$) through radical copolymerization of styrene and a distyryl monomer (styrene/distyryl monomer = 85:15 to 65:35), in which the two styryl units are linked together by a D-mannitol spacer that was removed after polymerization.[3] The polymers obtained under 1 atmosphere of CO in the present study also showed negative optical rotation (run 3–6 in Table 1). Such polymers should at least contain *rm* or *mr* triads, which constitute the smallest chiral enchainments for them to be chiral. Scheme 3 lists four possible chiral pentads containing an *rm* triad in its middle.[17] Structures **a** and **b** have the same absolute configuration as those present in the Wulff polymer,[3] whereas **c** and **d** have the opposite absolute configurations. Therefore, in the CD/Pd-based polymerization reaction described in this study, structures **a** and **b** are obviously formed more readily than the corresponding enantiomeric structures **c** and **d**. Furthermore, the CO pressure influences the sign and the optical rotation magnitude, thus showing that CO has a substantial impact on the polymer growth.[18]



Scheme 3. Four possible chiral pentads containing an *rm* triad in the middle.

In summary, the polymerization of styrene and styrene derivatives using cationic monophosphine Pd complexes derived from HUGPHOS ligands **1** and **2** afforded atactic polystyrene displaying optical activity. Remarkably, the formation of this optically active polymer did not require the use of a chiral comonomer. When operating under carbon monoxide, CO was not inserted into the growing macromolecule, but likely acted as a ligand that suppresses β-hydrogen elimination. Overall, the above results provide an unprecedented illustration of the strong effect metal confinement exerts on metal-catalyzed polymerization.

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[16] Note that, as observed by Keim and Mecking, CO coordination could not be detected by IR spectroscopy.
[17] The central carbon atom of the other four possible pentads are chirotopic but not stereogenic. See Ref. [3].
[18] So far we have no rationale for the observed chiral induction. This is possibly related to the reversible coordination of CO (see supporting information).

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