$[Rh(nbd)_2]SbF_6$ (2.3 mg, 0.0045 mmol) in methanol (3 mL) in a glovebox. After the mixture was stirred for 10 min, the substrate (0.5 mmol) was added. The hydrogenation was performed at room temperature under H_2 (20 psi) for 12–48 h. After carefully releasing the hydrogen, the reaction mixture was passed through a short silica-gel plug to remove the catalyst. The resulting solution was used directly for chiral GC or HPLC to measure the enantiomeric excess. For the hydrogenation of dehydroamino acids, the enantiomeric excesses were measured after conversion into their corresponding methyl esters by treatment with $TMSCHN_2$ (TMS = trimethylsilyl).

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Helical Chiral Polymers without Additional Stereogenic Units: A New Class of Ligands in Asymmetric Catalysis**

Michael Reggelin,* Melanie Schultz, and Michael Holbach

Soluble polymers may be promising ligands in transition metal catalysis for a number of reasons. The reisolation of the chiral catalyst by precipitation or ultrafiltration should be easy, and all the analytical and kinetic advantages of a reaction in homogenous phase should be maintained. If the polymer is chiral and nonracemic, asymmetric induction can be expected, and finally, a number of beneficial effects related to the macromolecular state of the system may allow for the synthesis of novel ligands with properties not achievable with micromolecules. These effects include, for example, cooperativity and chiral amplification as observed in polyisocyanates.[1]

The most obvious way to prepare a polymeric chiral soluble ligand is to attach only one metal binding site per polymer chain. This was rather successful in the asymmetric dihydroxylations described by Bolm et al.[2] and Janda et al.[3] The major disadvantage of this approach is the very low density of reactive centers per unit mass. To improve this situation it is necessary to prepare multiple-site polymeric catalysts with uniform microenvironments. The polybinaphthols prepared by Pu et al. appear to be successful examples of this strategy.[4] The remaining problems with these ligands include the necessity to prepare the enantiomerically pure monomers and the question of contraproductive interactions of the different sources of chirality (planar chirality of the monomers and helical chirality of the polymer). Indeed, we think that for the phosphane-modified helical chiral dodecapeptides developed by Gilbertson et al.[5] the major reason for the failure to achieve good enantioselectivities in asymmetric hydrogenation reactions is such a contraproductive interaction between the centrochirality of the constituting amino acids and the helical secondary structure. Facing this situation we felt it would be best to erase all sources of chirality except the helicity of a stereoregular and configurationally stable polymer containing donor atoms such as nitrogen or phosphorus.

We followed the work of Okamoto et al.[6, 7] and prepared two chiral polymers by helix-sense selective anionic polymerization of sterically congested methacrylates by using a chiral nonracemic base mixture as initiator (Scheme 1, Table 1). The chiral initiator was prepared by mixing either (+)- or (−)-1-(2-pyrrolidinomethyl)pyrrolidine ((*S*)- or (*R*)-**4**) and the diamine **3** with one equivalent of *n*BuLi at room temperature in toluene. This mixture was added to solutions of the monomers **1** and **2** so that the monomer/initiator ratio was

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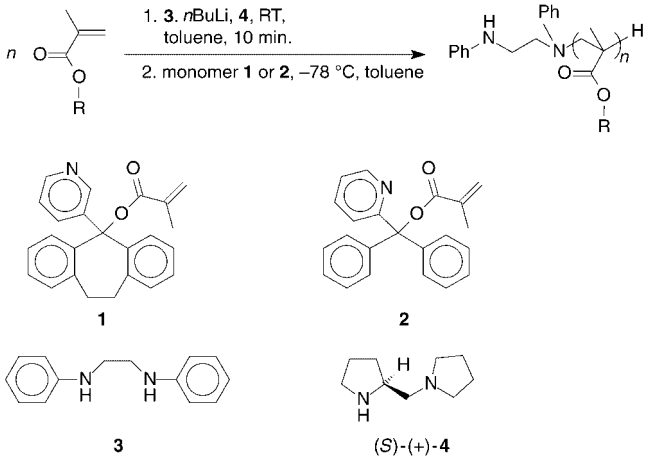
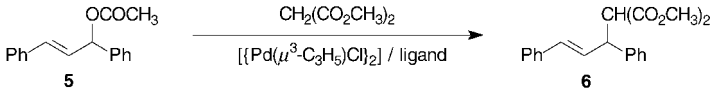


Scheme 1. Helix sense selective polymerization of methacrylates **1** and **2** with the additives **3** and **4**.

15:1. After the reaction times compiled in Table 1, the resulting polymers were isolated following published procedures.

To explore the suitability of these polymers as chiral ligands in asymmetric C–C bond forming processes we chose the palladium catalyzed allylic subsitution reaction with 1,3-diphenylprop-2-enyl acetate as substrate and dimethyl malonate (DMM) as nucleophile (Scheme 2, Table 2).[8–11] First, we



Scheme 2. Allylic substitution of 1,3-diphenylprop-2-enyl acetate (**5**) catalyzed by palladium complexes generated in situ.

looked for potential catalytic activity of the nitrogen-containing compounds **3** and **4** used in the anionic polymerization. Especially the former was of interest, because it is incorporated into the polymer as the end group. Entries 1 and 2 show that **3** does not catalyze the reaction at all. On the contrary, (+)-**4** is active and produces (*R*)-**6** with a slight enantiomeric excess of about 10%. For that reason we meticulously purified the polymers to avoid any contamination with this chiral diamine (checked by ^{1}H NMR spectroscopy and gel permeation chromatography (GPC)). Next, we looked for the catalytic activity of the monomers and found that only **1** is active and furnishes **6** with 57% yield (entries 4–7).

After this preparatory work we tried to prepare Pd complexes from the polymers. In a typical experiment we

Table 2. Allylic alkylations of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate.[a]

Entry	Ligand[a]	[Pd] [mol%][b]	Solvent	*T* [°C]	*t* [h]	Yield [%][c]	*ee* [%][d]	Config.[e]
1	**3**	10	CH_2Cl_2	25	48	0	–	–
2	**3**	10	CH_2Cl_2	40	14	0	–	–
3	(+)-**4**	10	CH_2Cl_2	25	14	65[f]	9.9	*R*
4	**2**	10	CH_2Cl_2	40	90	0	–	–
5	**2**	25	CH_2Cl_2	40	40	0	–	–
6	**1**	10	CH_2Cl_2	40	90	48	0	–
7	**1**	25	CH_2Cl_2	40	40	57	0	–
8	(+)-poly-**2**	10	CH_2Cl_2	25	72	0	–	–
9	(+)-poly-**2**	10	CH_2Cl_2	40	72	0	–	–
10	(+)-poly-**2**	10	THF	60	14	0	–	–
11	(+)-poly-**2**	10	C_6H_6	80	14	0	–	–
12	(+)-poly-**1**	10	CH_2Cl_2	25	72	12	29	*R*
13	(+)-poly-**1**	25	CH_2Cl_2	25	72	66[f]	33	*R*
14	(+)-poly-**1**	10	CH_2Cl_2	40	48	74	27	*R*
15	(+)-poly-**1**	25	CH_2Cl_2	40	14	79[f]	32	*R*
16	(−)-poly-**1**	10	CH_2Cl_2	40	70	88[f]	28	*S*
17	(−)-poly-**1**	25	CH_2Cl_2	40	40	81[f]	33	*S*
18	*rac*-poly-**1**	10	CH_2Cl_2	40	70	92[f]	0	–
19	*rac*-poly-**1**	25	CH_2Cl_2	40	40	78[f]	0	–

[a] 24 mol% repeating unit (based on substrate 1,3-diphenylprop-2-enyl acetate) or 60 mol% in experiments with 10 or 25 mol% Pd, respectively. [b] Based on substrate. [c] Yields of isolated product. [d] Determined by ^{1}H NMR in the presence of 20 mol% of the chiral shift reagent [Eu(hfc)$_3$], hfc = 3-(heptafluoropropyl-hydroxymethylene)-D-camphorate. [e] By comparison with reference [12]. [f] Quantitative conversion according to TLC.

mixed 27.2 mg (84 μmol monomeric units) of poly-**2** and and 6.4 mg (17.5 μmol) of dimeric [{Pd(μ^3-C_3H_5)Cl}$_2$] in CH_2Cl_2 at room temperature. After one hour 88 mg (350 μmol) of the substrate and 139 mg (1.05 mmol) of DMM were added. This corresponded to 10 mol% Pd and a [N]:[Pd] ratio of 2.4:1 which reflects our initial assumption that a bidentate complex involving two consecutive turns of the helix might be formed. Not unexpectedly after our experience with the monomer **2**, no reaction with the substrate (Table 2, entries 8–11) could be observed. Although a negative result at first sight, these experiments confirm the complete absence of any residual **4** and any interference of the nitrogen-containing end group (see above).

We suspected the nitrogen atom in poly-**2** is not accessible enough to be complexed by palladium and therefore hoped that the situation would be improved when the nitrogen atom is in the 3-position in the pyridine ring. This was indeed the case. As already stated the monomer **1** is an active catalyst (Table 2, entries 6 and 7), and to our delight this was also true for the polymer (+)-poly-**1** (entries 12–15). Moreover, we found a significant enantiomeric enrichment in the resulting

Table 1. Helix sense selective polymerization of methacrylates **1** and **2**.[a]

Entry	Monomer[b]	Polymer[c]	Initiator[c]	*t* [h]	Yield [%][d]	DP[e]	M_w/M_n[f]	Tacticity[f]	$[\alpha]_{365}^{25}$[g]
1	**2**	(+)-poly-**2**	(+)-**4**	4	89	40	1.15	> 99	+ 1452
2	**1**	(+)-poly-**1**	(+)-**4**	43	34	27	1.19	> 99	+ 1385
3	**1**	(−)-poly-**1**	(−)-**4**	48	59	34	1.12	> 99	− 1475
4	**1**	*rac*-poly-**1**	*rac*-**4**	48	50	37	1.21	> 99	0

[a] All polymerizations were carried out with 1.0 g of monomer in toluene at −78 °C. The monomer:initiator ratio was 15:1. [b] The monomer structure corresponds to R in Scheme 1. [c] For abbreviations see Figure 1. [d] Fraction insoluble in methanol and benzene/hexane. [e] DP = degree of polymerization. Determined by GPC (poly(methyl methacrylate) (PMMA) standard) after acidic hydrolysis and conversion to PMMA. [f] Determined by ^{1}H NMR analysis of the derived PMMA. [g] c = 1.0, $CHCl_3$:2,2,2-trifluoroethanol (9:1 by volume).

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substitution product **6** (27–33% *ee*). With 10 mol% Pd at 40 °C the reaction was virtually quantitative as judged by TLC. The yields of isolated products were somewhat lower and variable because of the very small amounts handled in these initial experiments. The major enantiomer formed in the experiments with the polymer derived from the (+)-**4**-containing initiator mixture was *R*-configured. To verify our expectation that the product configuration would be inverted when the configuration of the catalyst is inverted, we repeated the experiment with the polymer having the opposite helical sense (entries 16 and 17). As expected we now obtained (*S*)-**6** in very high yield and with the same *ee*.

Finally, we used *rac*-poly-**1** obtained by polymerization with *rac*-**4**/**3**-*n*BuLi as initiator. This time *rac*-**6** was isolated which shows that the observed selectivities are indeed a direct consequence of the helical chiral nature of the polymer. At this point it is important to note that the investment of chiral nonracemic material (here **4**) is extremely low. In the ideal case a polymerization reaction, in which one mole of chiral initiator is employed, produces *n* moles of homochiral coordination sites in the resulting polymer. The whole process can be interpreted as an autoinductive multiplication of chiral units. Furthermore, different helical ligands exhibiting different chiral environments can be synthesized by using the same cheap auxiliary.

To learn more about the complexed polymers we studied their chiroptical properties and their NMR spectra. From the CD spectra it is obvious that complexation took place without disrupting the helical chiral structure of the polymers (Figure 1). When we calculated the molar masses of the repeating units with a [N]:[Pd] ratio of 1:1, the chiroptical properties of the palladium complexes became close to those of the uncomplexed polymers. This appears to be reasonable if one assumes that the carbonyl chromophore, which gives rise to the absorption at 237 nm, is largely unaffected by the palladium complexation involving the nitrogen atom of the remote pyridine ring. This interpretation is corroborated by our NMR results (Figure 2).

To study the influence of the polymerization process as well as the one evoked by complexation we recorded a series of

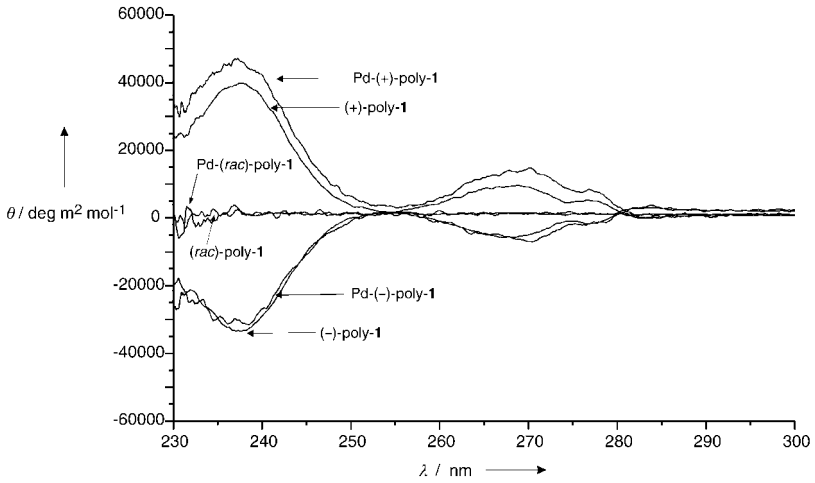

Figure 1. CD spectra of poly-**1** and the corresponding palladium complexes. The CD spectra were recorded in CH_2Cl_2 solutions at 25 °C with polymer concentrations of 37.2 to 78.8 nmol monomer units mL^{-1}.

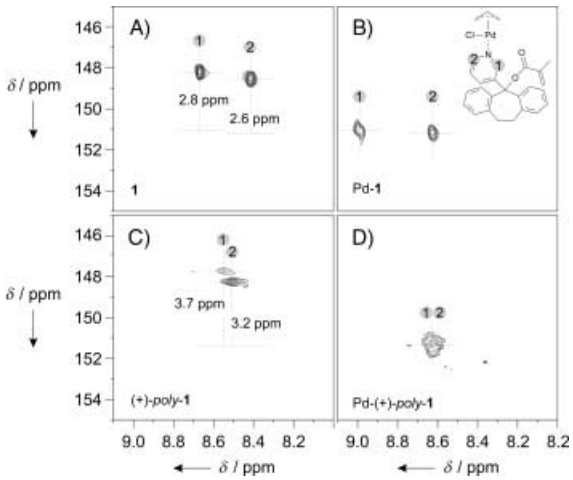

Figure 2. Downfield portion of 500 MHz sensitivity-enhanced gradient-HSQC spectra showing CH correlations of the carbon atoms flanking the nitrogen atom. A) Monomeric **1**. B) Monomeric Pd complex. C) Polymeric **1**. D) Polymeric Pd complex.

HSQC spectra. From these it is obvious that the polymerization of **1** entails a strong reduction of the ^1H chemical shift difference of the protons flanking the nitrogen atom (Figure 2, cf. A and C as well as B and D; $\Delta\delta = 0.22$ ppm and 0.37 ppm, respectively). On the other hand the corresponding carbon shifts are only marginally affected. In contradiction to this behavior, complexation by palladium ([N]:[Pd] = 1:1) is accompanied by a significant downfield shift of carbon atoms 1 and 2. This is true for both the monomeric and the polymeric complex (Figure 2A, 2B, and 2C, 2D, respectively). We interpret these chemical shift alterations as evidence of successful complexation of the polymer by palladium. When we increased the [N]:[Pd] ratio to 2:1 (not shown) the complexation was incomplete as indicated by the persistence of signals from the uncomplexed polymer. This finding is in accordance with a monodentate complex which corroborates our interpretation of the results from the CD data.

From these results it can be concluded that poly-**1** forms monodentate complexes with palladium and that the resulting complex is able to catalyze the allylic substitution reaction. Furthermore the enantiomeric excesses of the products are a direct and sole consequence of the uniform helicity of the polymeric ligand employed. Thus, it is the first example of an asymmetric induction in a catalytic C–C bond forming reaction that involves a uniformly configured polymeric helical chiral ligand lacking any other elements of chirality. Although this is an encouraging first step we are aware that the system must be improved considerably with respect to both reactivity and enantioselectivity. At present, we are working on ligands with alternative coordination sites and the exploitation of the already mentioned cooperative effects in polyisocyanates.

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