Synthesis of a Stereoblock Polyketone through Ancillary Ligand Exchange

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Because block copolymers provide the most effective method of combining the properties of two or more homopolymers in one material, considerable effort has been directed toward their synthesis. Changes in polymer microstructure can dramatically affect polymer properties; thus, stereoblock polymers with unique physical characteristics can be constructed from the same monomer through variation in the stereochemistry along the main chain in each block. Waymouth[1] has reported a strategy for synthesis of stereoblock polypropylene[1−5] which is hypothesized to operate through conformational *isomerization* of a bis-2-arylindenyl zirconium catalyst between chiral and achiral coordination geometries. The chiral geometry generates polypropylene with an isotactic microstructure while the achiral form produces atactic polypropylene. We report a new strategy for synthesis of stereoblock polymers involving ancillary ligand *exchange*[6] during a living transition-metal-catalyzed polymerization. We have also demonstrated cooperativity between chain-end and site control mechanisms through ligand exchange.

Alternating copolymerization of CO with 4-*tert*-butylstyrene (TBS) using bipyridine-based catalyst **I-1** (see Scheme 1) yields polyketone **4** with a syndiotactic microstructure through a chain-end control mechanism.[7] In contrast, catalysts **I-2** or **I-3** derived from enantiomerically pure C_2-symmetric bis-oxazoline ligands **2** and **3** produce optically active, highly stereoregular polyketone with an isotactic microstructure.[8] In this case stereocontrol by enantiomorphic catalyst sites overrides chain-end control of microstructure. Figure 1 shows the ^{13}C spectrum of these two polymers in the C(2) region (Figure 1a illustrates the corresponding ^{13}C spectrum of the atactic polymer[9]). The copolymerizations described in Scheme 1 are known to be living under certain conditions.[7] Thus, if exchange of bidentate ligands **1** and **2** (or **3**) could be achieved without inducing chain transfer, stereoblock polymers would result.

Prior to attempting synthesis of the stereoblock copolymer, the effect of added bidentate ligand on these polymerizations was examined. Initiation of a copolymerization using bipyridine complex **I-1** in the presence of bis-oxazoline ligand **3** had no effect on either polymerization rate or polymer microstructure. However, a copolymerization initiated with isospecific catalyst, **I-3**, in the presence of 1 equiv of bipyridine **1** gave syndiotactic **4**, implying that bipyridine rapidly and completely displaced the bis-oxazoline ligand, **3**, to form the syndiospecific bipyridine-substituted catalyst *in situ*. As confirmation, we observed by ^1H NMR spectroscopy that displacement of bis-oxazoline ligand from **I-2** by bipyridine to yield **I-1** occurred rapidly in the absence of CO and TBS monomers.

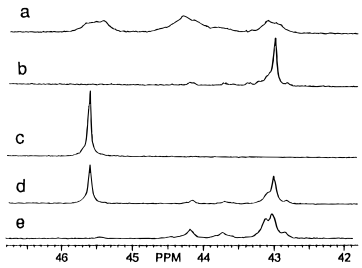


Figure 1. ^{13}C NMR spectra in the region of C(2) resonance of poly(4-*tert*-butylstyrene-*alt*-carbon monoxide) (**4**) for (a) atactic polymer, (b) syndiotactic polymer, (c) isotactic polymer, (d) stereoblock polymer containing isotactic and syndiotactic segments, and (e) polymer produced from **I-2** and **3** which undergoes rapid ligand exchange.

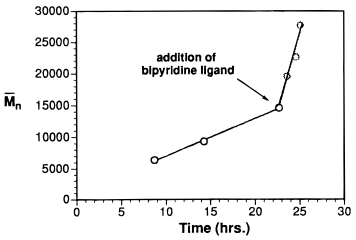
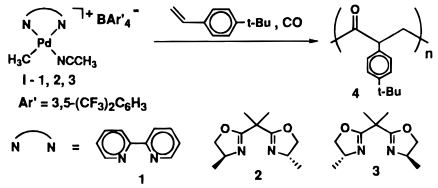
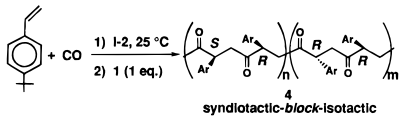


Figure 2.

Scheme 1



On the basis of these results, stereoblock copolymer synthesis was approached by first growing an isotactic segment with **I-2**, then switching on syndiotactic growth by displacing the bis-oxazoline ligand from the Pd(II) catalyst with bipyridine. The procedure is shown in eq 1. Specifically, exposure of **I-2** (0.1 mmol) in 20 mL of stirring TBS to CO (1 atm) at 25 °C for 23 h was followed by the addition of 1 equiv of **1**. Precipitation in methanol after a total polymerization time of 25 h gave 2.9 g of copolymer with $[\Phi]^{25}_D$ −204° (c = 0.50, CH_2Cl_2).[8a] The ^{13}C spectrum of this polymer clearly shows distinct isotactic and syndiotactic resonances (Figure 1d). In order to confirm that this material was indeed a stereoblock copolymer and not a mixture of two stereoregular homopolymers, the polymerization was followed by GPC. Figure 2 is a plot of M_n versus time for a series of GPC samples taken during the course of the polymerization. A linear increase in molecular weight with time is observed for both the isospecific and syndiospecific portions of the polymerization. This characteristic of living polymerizations supports a stereoblock structure for the copolymer produced.[10] The expected increase in polymerization rate upon addition of the bipyridine ligand is also observed.[11]



(1) (a) Waymouth, R. M.; Coates, G. W. *Science* **1995**, *267*, 217. (b) Waymouth, R. M.; Hauptman, E.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 11586.

(2) Chien, J. C. W.; Mallin, D. T.; Rausch, M. D.; Lin, Y. G.; Dong, S. *J. Am. Chem. Soc.* **1990**, *112*, 2030.

(3) Chien, J. C. W.; *et al. J. Am. Chem. Soc.* **1991**, *113*, 8569.

(4) Collette, J. W.; *et al. Macromolecules* **1989**, *22*, 3851.

(5) Collette, J. W.; Ovenall, D. W.; Buck, W. H.; Ferguson, R. C. *Macromolecules* **1989**, *22*, 3858.

(6) Ligand variation has been used to control *cis* versus *trans* structures in 1,4-polybutadiene: Teyssie, P.; Dawans, F.; Durand, J. P. *J. Polym. Sci., Part A-1* **1970**, *8*, 979.

(7) (a) Brookhart, M.; Rix, F. C.; DeSimone, J. M.; Barborak, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 5894. For earlier reports of Pd(II)-catalyzed CO/styrene copolymerizations, see: (b) Drent, E. Eur. Pat. Appl. 229,408; *Chem. Abstr.* **1988**, *108*, 6617. (c) Corradini, P.; De Rosa, A.; Panunzi, A.; Pino, P. *Chimia* **1990**, *44*, 52.

(8) (a) Polymerization catalyzed by **I-2** gives **4** with $[\Phi]^{25}_D$ −536°: Brookhart, M.; Wagner, M. I.; Balavoine, G. G. A.; Haddou, H. A. *J. Am. Chem. Soc.* **1994**, *116*, 3641. See also: (b) Bartolini, S.; Carfagna, C.; Musco, A. *Macromol. Rapid. Commun.* **1995**, *6*, 9.

(9) Atactic polymer was produced through epimerization of syndiotactic polymer in aqueous base.

(10) $\bar{M}_w/\bar{M}_n$ for the stereoblock polymer is 1.4. The GPC trace is monomodal with a small, low molecular weight tail from slight catalyst decomposition. The GPC traces are contained in the supporting information.

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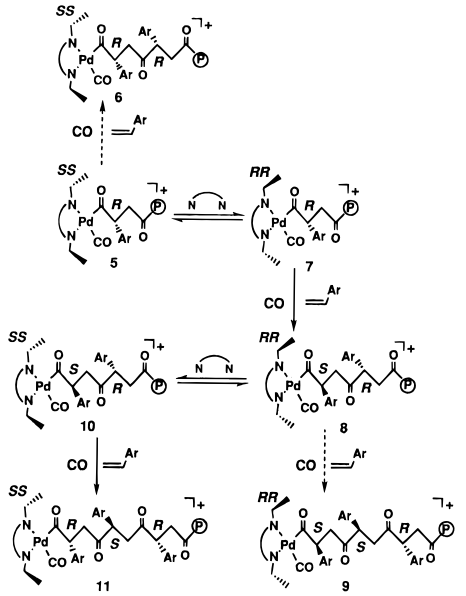
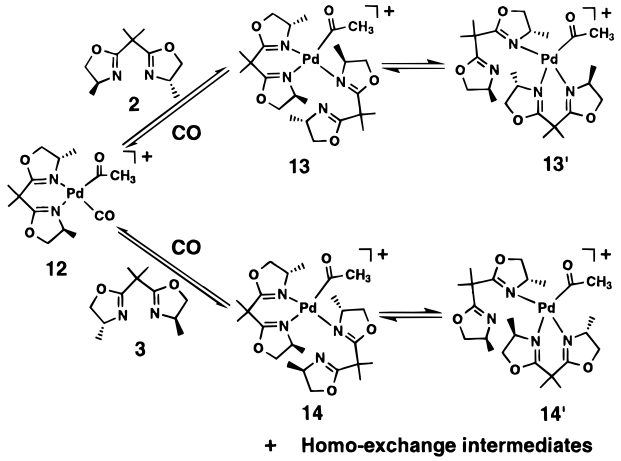
Scheme 2



Scheme 3



Having synthesized a stereoblock copolymer through ligand exchange between chiral and achiral ligands, the polymer produced from ligand exchange between enantiomeric bis-oxazoline ligands **2** and **3** was of interest. If ligand exchange were slow relative to chain growth, then a polymer containing alternating isotactic blocks with *R* and *S* configuration would be produced. To examine this possibility, (*S*,*S*)-bis-oxazoline catalyst (**I-2**) together with 1 equiv of (*R*,*R*)-bis-oxazoline ligand **3** was stirred in 20 mL of TBS under CO (1 atm) for 20 h and the resulting polymer was isolated by precipitation in methanol. Surprisingly, the ^{13}C spectrum of this polymer showed it to be substantially syndiotactic[12] (see Figure 1e); no signal at 45.6 ppm characteristic of isotactic microstructure was observed. In addition, the turnover frequency as monitored by CO uptake was ca. 2.5 times that observed during polymerizations in the absence of added ligand. As a control experiment a similar polymerization was carried out using **I-2** together with 1 equiv of the free *SS* ligand **2**. Highly isotactic copolymer was produced; no rate enhancement was observed.

To explain these results we assume ligand exchange is *rapid* relative to chain growth. This feature allows chain-end control to work in concert with enantiomorphic site control.[13] Consider chain propagation from diastereomers **5** ⇌ **7**[14] (Scheme 2) which are in rapid equilibrium though ligand exchange. Insertion of a TBS/CO unit into **5** would yield species **6** with an *RR* dyad because the *SS* ligand in **5** dictates insertion to give a *R* configuration.[8] In this case enantiomorphic site control overrides the chain-end control mechanism which calls for insertion to yield an *S* configuration. In contrast, in diastereomer **7**, enantiomorphic site and chain-end control mechanisms are *complementary*, both dictating an *S* configuration for the next inserted monomer. The activation energy for insertion of monomer into **7** will therefore be lower than that for insertion into **5**, and thus insertion of monomer into rapidly equilibrating **5** ⇌ **7** will occur predominantly through **7** to produce **8** possessing an *SR* dyad. Similarly, diastereomer **8** will equilibrate with **10** through ligand exchange. Complex **10** is the diastereomer in which chain-end and site control are complementary, and thus **8** ⇌ **10** will yield primarily **11** with *RSR* stereochemistry rather than **9**. In this manner, it is clear how ligand exchange results in primarily *alternating* configurations along the chain and thus a polymer with largely syndiotactic microstructure. This scheme also explains the rate increase observed for the heteroexchange polymerizations in which the more reactive diastereomers (e.g. **7** and **10**) are accessible.[15]

Ligand exchange was verified by variable temperature ^1H NMR spectroscopy using the acyl carbonyl complex (*S*,*S*)-**12**,[16] a good model for the catalyst resting state (Scheme 3).[14] Treatment of (*S*,*S*)-**12** under CO with ca. 1 equiv of (*S*,*S*)-**2** at −80 °C leads through displacement of CO to a new complex **13**, assigned as the η^2, η^1 complex in Scheme 3. As the sample is warmed, the concentration of **13** increases so that at +40 °C it is present at 23%, along with unreacted **12** (49%) and free ligand **2** (28%). Complex **13** is dynamic and undergoes a rapid intramolecular degenerate isomerization in which the η^1 bis-oxazoline becomes η^2 and the η^2 bis-oxazoline becomes η^1.[17] For example, four methyl singlets are observed for the gem-dimethyl group of **13** at −80 °C; these broaden and merge to a singlet at +40 °C.[18] Treatment of **12** with (*R*,*R*)-**3** leads to formation of diastereomers **13** and **14** in approximately equal ratios as evidenced by a doubling of resonances at 40 °C. Rapid reversible exchange of a bis-oxazoline ligand with CO coupled with $\eta^1 \rightleftharpoons \eta^2$ ligand interchange clearly provides a facile pathway for the ligand exchange process proposed in Scheme 2.

Experiments described herein demonstrate a new, potentially general method for preparing stereoblock polymers through ancillary ligand exchange during polymer chain growth. In addition, rapid exchange of enantiomeric ligands in these systems has illustrated how cooperativity between chain-end and site control mechanisms can operate to control polymer microstructure.

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Supporting Information Available: Syntheses and analyses of stereoblock polyketones (8 pages). See any current masthead page for ordering and Internet access instructions.

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(11) Polymerization rates from the achiral, syndiospecific catalysts are approximately 10 times faster than those of isospecific polymerizations.

(12) A racemic mixture of chiral catalysts **I-2** and **I-3** produces isotactic copolymer with no optical activity.

(13) Consiglio has reported that enantioselectivity in similar systems is determined by both the chiral ligand and the last inserted monomer unit: Consiglio, G.; Sperrle, M. *J. Am. Chem. Soc.* **1995**, *117*, 12130.

(14) The catalyst resting state for these polymerizations is the acyl carbonyl species (N^N)Pd(CO)COR$^+$. See ref 7a.

(15) The pairs of diastereomers **7**,**10** and **5**,**8** are comparable to matched and mismatched pairs, respectively, in double asymmetric synthesis: Masamune, S.; Choy, W.; Peterson, J. S.; Sita, L. R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1.

(16) Exposure of **I-2** to CO purge at 0 °C in CH_2Cl_2 solution produces **12** in situ. The synthesis, isolation, and purification of **12** are contained in the supporting information.

(17) Similar behavior has been observed in Rh systems with bidentate and terdentate nitrogen ligands: (a) Nishiyama, H.; Kondo, M.; Nakamura, T.; Itoh, K. *Organometallics* **1990**, *10*, 500. (b) Brunner, H.; Brandl, P. *Tetrahedron: Asymmetry* **1991**, *2*, 919.

(18) The switching of the ligands leads to topomerization of pairs of geminal methyl groups. Rotation around the N−Pd bond in the η^1 bound ligand leads to topomerization of gem dimethyls on the same ligand.