$[Os_2Cl_{10}]^{2-}$, rather than Cl_2 oxidation of the octahalide which serves well[14] for the synthesis of $[Re_2Cl_9]^{1-}$.

Corresponding studies on $[Os_2Br_8]^{2-}$, in CH_2Cl_2 at 235 K, reveal successive one-electron oxidations at 1.35 and 2.03 V. The δ/δ^* band for $[Os_2Br_8]^{1-}$ is found at 4630 cm^{-1}, and the associated vibronic progression is 225 cm^{-1}. Efforts are continuing to isolate or further characterize these highly reactive molecules. The present results confirm the value of pursuing periodic relationships in binuclear heavy element chemistry through low-temperature voltammetry and spectroelectrogeneration.

Acknowledgment. We thank the Institute for Advanced Studies, ANU, for financial support of this work.

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Enantioselective Polymerizations of Achiral Isocyanides. Preparation of Optically Active Helical Polymers Using Chiral Nickel Catalysts

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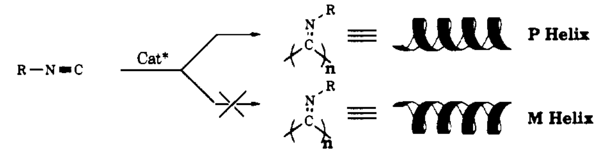
Received May 22, 1992

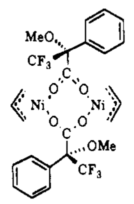
The issue of stereochemistry in macromolecules has received a wide range of treatment, both experimental and theoretical.[2] Pioneering work with vinyl and other addition polymers utilizing chiral catalysts and initiators as well as optically active monomers has led to the development of a new dimension of organic stereochemistry.[3] The helical motif is a fine example of stereochemistry commonly found in polymers yet which is quite rare in small-molecule chemistry.[4] Polymers which maintain stable helical conformations in solution, namely, polyisocyanides,[5] poly(triarylmethacrylates),[6] and chloral oligomers,[7] have received much attention since they can possess optical activity due solely to main chain conformations (atropisomers). Consequently, helix-sense-selective preparations of these polymers have been an important goal in this field.

Scheme I

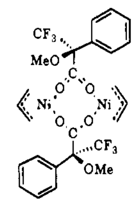


In the polyisocyanides, polymers with sterically bulky substituents have been resolved using chiral chromatography[5b,f] and helix-sense-selective polymerizations have been attempted using optically active end groups.[8] These attached chiral end groups produce diastereomeric polymers (due to the chirality of the helix and the end group) as opposed to purely enantiomeric polymers. We would like to prepare enantiomeric polyisocyanides using a chiral catalyst (Scheme I) in order to study properties of the helix in the absence of any chiral side or end groups. Successful asymmetric induction of this type requires that there be a high helical inversion barrier associated with the polymer, so that racemization of a kinetically controlled helix sense will not be possible.[9] We now report the use of chiral catalysts (*R*)-(−)-$[(\eta^3\text{-}C_3H_5)Ni(O_2CC^*(OCH_3)(C_6H_5)CF_3)]_2$ (**R-I**), (*S*)-(+)-$[(\eta^3\text{-}C_3H_5)Ni(O_2CC^*(OCH_3)(C_6H_5)CF_3)]_2$ (**S-I**), and (*S*)-(−)-$[(\eta^3\text{-}C_3H_5)Ni(O_2CC^*HN(CH_2CH_2CH_2)C(O)CF_3)]_2$ (**SII**) for the enantioselective polymerization of achiral *tert*-butyl isocyanide (**III**) and diphenylmethyl isocyanide (**IV**) to yield optically active, enantiomerically enriched samples of poly(*tert*-butyl isocyanide) (poly(**III**)) and poly(diphenylmethyl isocyanide) (poly(**IV**)).

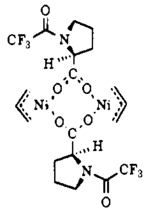
We designed our optically active catalyst around the complex, $[(\eta^3\text{-}C_3H_5)Ni(OC(O)CF_3)]_2$, which promotes the homogeneous, living polymerization of select isocyanides.[10] Subsequent modification of this catalyst with an optically active ligand would lead to our desired chiral catalyst. Addition of chiral donors (e.g., phosphines) was ruled out due to the very high ligand strength of isocyanides and inevitable dissociation of any optically active donor under polymerization conditions.[11] Our approach therefore was the incorporation of optical activity into the anionic carboxylato ligand which, due to high Coulombic attractions, would not be expected to dissociate in organic solvents (e.g., toluene). Consequently, we prepared the optically active compounds **R-I**, **S-I**, and **S-II** from commercially available, optically pure carboxylic acids. Note that, while these compounds are dimeric, they are readily cleaved into monometallic catalytic species by high ligand concentrations present under polymerization conditions.[10]



R-I



S-I



S-II

To verify whether the chiral pendant groups do indeed affect the stereochemistry at the active catalytic site, we separately polymerized both enantiomers of a chiral monomer (1-phenylethyl isocyanide, **S-V** and **R-V**), using either **S-I**, **R-I**, or **S-II** while monitoring the reaction kinetics. **R-I** polymerizes **S-V** and **R-V** under O_2[10] at 298 K to yield the rate constants (rate = k[catalyst]) $k_R = 6.2\ (2) \times 10^{-3}\ s^{-1}$ and $k_S = 14.6\ (2) \times 10^{-3}\ s^{-1}$ with $k_S/k_R = 2.3\ (5)$. Conversely, **S-I** polymerizes **S-V** and **R-V** under O_2 at 298 K to yield the rate constants $k_R = 15.4\ (2) \times 10^{-3}\ s^{-1}$ and

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Table I. Polymerizations of **IV** Using Cyanide-Modified Versions of **R-I** and **S-I**[a]

catalyst	yield (%)	$\bar{M}_n$	PDI[d]	$[\alpha]^{23}_D$
R-I	80	880	1.10	+10
R-I-(CN)-Bu[b]	88	680	1.23	+13
R-I-$(CN)_2$-Bu	50	550	1.24	+23
S-I	81	820	1.10	−10
S-I-(CN)-Bu[c]	74	680	1.23	−13
S-I-$(CN)_2$-Bu	54	630	1.20	−23

[a] Polymerizations were all run under N_2 atmosphere for 36 h. [b] **R-I**-(CN)-Bu is the monocyanide adduct of **R-I**, $N(Bu)_4^+$ salt. [c] **S-I**-(CN)-Bu is likewise a monocyanide adduct of **S-I**, $N(Bu)_4^+$ salt. [d] PDI = polydispersity index, as determined by GPC = $\bar{M}_w/\bar{M}_n$.

$k_S = 6.2\ (2) \times 10^{-3}\ s^{-1}$ with $k_R/k_S = 2.5\ (5)$. Finally, **S-II** polymerizes **S-V** and **R-V** under O_2 at 298 K to yield the rate constants $k_R = 6.8\ (2) \times 10^{-3}\ s^{-1}$ and $k_S = 6.5\ (2) \times 10^{-3}\ s^{-1}$ with $k_R/k_S = 1.05\ (5)$. These kinetic experiments show that the chiral ligands on **S-I**, **R-I**, and **S-II** do have a significant effect at the active site.

We then polymerized *tert*-butyl isocyanide (**III**), a sterically hindered monomer known to form a kinetically controlled helical polymer as evidenced by its resolution on a chiral column.[9] Neat **III** was reacted with **S-I**, **R-I**, and **S-II** under O_2 at 298 K to prepare polymer samples in moderate yield (25–30%). Cleavage of the optically active catalyst from the polymer chains was evidenced by spectroscopic as well as elemental analysis. **III**/**R-I** gave poly(**III**) which had a specific rotation of $[\alpha]^{20}_D = +12$ ($\bar{M}_n = 880$;[12] M helix). (The helix sense of the poly(**III**) has been assigned previously using circular dichroism.)[13] In contrast, **III**/**S-I** gave poly(**III**) which had a specific rotation of $[\alpha]^{20}_D = -12$ ($\bar{M}_n = 800$; P helix). Finally, **III**/**S-II** gave poly(**III**) which had a specific rotation of $[\alpha]^{20}_D = -18$ ($\bar{M}_n = 1100$; P helix). These polymerizations have shown that chiral catalysts **S-I**, **R-I**, and **S-II** do display diastereotopic interactions between the optically active catalyst and helical polymer chains. Furthermore, the presence of such interactions proves that helical poly(**III**) is formed kinetically at the active catalytic site. In contrast, polymerizations of less hindered monomers, e.g., *p*-methoxyphenyl isocyanide (**VI**), using **S-I**, **R-I**, and **S-II** gave only optically inactive polymers, suggesting that their presumed helical conformations are either readily racemized at room temperature[14] or are nonexistent.[5g,h]

Since **III**, a tertiary isocyanide, polymerizes very slowly and gives only low yields of polymer, we prepared a secondary, but also sterically hindered, achiral monomer, diphenylmethyl isocyanide (**IV**) and studied its polymerization chemistry with **S-I** and **R-I**. This monomer polymerizes homogeneously in toluene under N_2 or O_2 at 298 K and forms polymer in high yields (73–98%). The **IV**/**R-I** system gave poly(**IV**) which had a specific rotation of $[\alpha]^{20}_D = +10$ ($\bar{M}_n = 880$), and **IV**/**S-I** gave poly(**IV**) which had a specific rotation of $[\alpha]^{20}_D = -10$ ($\bar{M}_n = 820$). In an effort to increase our catalyst's helix-sense selectivity, we sought to block some of the many (up to 3) open coordination positions on **S-I** and **R-I**, which should lower some of the degrees of freedom at the active site. To accomplish this task we used anionic cyanide ligands which should not dissociate under polymerization conditions. Indeed, when 3 equiv of CN^- was added to either **S-I** or **R-I**, the resulting complexes were completely ineffective as polymerization catalysts. Mono- and biscyanide complexes of **S-I** and **R-I** were prepared with $N(Bu)_4^+$ counterions, and the results of polymerizations with **IV** are presented in Table I.

In summary, we have demonstrated that, by modifications in optically active catalyst as well as in monomer, both helix-sense selectivity and yield (30 to >90%) in isocyanide polymerizations were increased. The actual extent of enantiomeric excess in these samples remains unknown due to the dependence of optical rotation on molecular weight as well as helical excess.[5b,f] By comparison of optical rotations of our poly(**III**) samples with that of a resolved polymer of **III** of "low molecular weight"[5f] ($\bar{M}_n < 1800$, $n < 20$, $[\alpha]^{20}_D = +26$), we can, ignoring molecular weight effects, set a minimum on percent ee at 46% for **R-I**, 46% for **S-I**, and 69% for **S-II** for polymerizations of **III**. At present, we are working on developing the necessary calibration curves to determine true enantiomeric excess values.

Acknowledgment. We gratefully acknowledge financial support for this work from the National Science Foundation and industrial PYI donors. T.J.D. acknowledges the NSF for a graduate student fellowship.

Supplementary Material Available: Experimental procedures for the preparation of **R-I**, **S-I**, and **S-II** and for all of the polymerization reactions (9 pages). Ordering information is given on any current masthead page.

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Evidence for Aryne-Ring Rotation in Isomeric 4,5-Dehydro[2.2](1,4)naphthalenoparacyclophanes

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Received April 23, 1992

There are a few reports on the reactions of dehydrocyclophanes generated from [*n.n*]paracyclophane compounds.[1-3] However, it is not known whether the aryne ring in dehydrocyclophanes can rotate through 180° without reaction. We have now obtained evidence for such aryne-ring rotation by examining adducts from isomeric 4,5-dehydro[2.2](1,4)naphthalenoparacyclophanes **2a** and **2s** generated from the corresponding *anti*- and *syn*-4-bromocyclophanes **1a** and **1s**.

The experimental procedure was as follows. To 0.20 g of **1** in 15 mL of *tert*-butylbenzene was added 1.32 g (20 equiv) of potassium *tert*-butoxide. The mixture was refluxed at 175–180 °C for 3.5 h, worked up in the usual manner,[1] and then subjected to preparative TLC on silica gel using hexane–ethyl acetate (10:1) and dichloromethane–hexane (1:2). In this manner, both **1a** and **1s** gave a bridged dibenzobarrelene **3**, as well as *anti*- and *syn*-4-hydroxy[2.2](1,4)naphthalenoparacyclophanes **4a** and **4s** and their *tert*-butyl ethers **5a** and **5s**, as shown in Table I. The products **3**, **4a**, and **4s**, known substances, showed the same melting points and ^1H NMR spectra as those reported.[4] The structures of unknown ethers **5a** and **5s** were determined by ^1H NMR and mass spectroscopy.

Interestingly, **1a** gives anti products **4a** and **5a** in preference to the others, and **1s** gives syn products **4s** and **5s**, similarly. The formation of phenolic products **4a** and **4s** results from butoxide anion addition[3] to *anti*- and *syn*-4,5-dehydrocyclophanes **2a** and **2s**, whose 4,5-dehydro bond is arranged anti and syn, respectively, to the bridge-free benzo ring of the naphthalene moiety. The above results can be explained by an aryne route involving aryne-ring rotation, as shown in Scheme I.

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0002-7863/92/1514-7927$03.00/0