Synthesis of Cis,syndiotactic ROMP Polymers Containing Alternating Enantiomers

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A polymer that has a single microstructure often is more desirable since its properties are more sharply defined relative to a polymer with a random structure. ROMP polymers prepared from substituted norbornenes and norbornadienes have rich microstructural possibilities. For several decades the structures of ROMP polymers prepared with classical metathesis catalysts have been studied in detail employing NMR techniques (primarily $^{13}$C NMR). However, few polymers with primarily a single structure have been found. A possible reason is that a classical catalyst's structure cannot be varied finely and systematically enough in order to produce a "match" between a catalyst and monomer that allows a single polymerization pathway to dominate and produce a polymer with a given single structure. This conundrum seems inescapable with classical catalysts.

The development of alkylidene complexes of Mo and W with known structures and modes of reaction have allowed an increasing number of ROMP polymers to be prepared that have a single microstructure. We recently reported the $Z$-selective and syndielectroselective polymerization of several ROMP monomers by monooaryloxide monopyrrolide (MAP) imido alkylidene catalysts of Mo to yield cis,syndiotactic polymers. $Z$ selectivity is proposed to arise through an addition of the monomer to syn-Mo(NAd)(CHCMe$_2$Ph)(Pyr)(OH)P (1a) to produce an all cis metallacyclobutane as a consequence of the steric demands of the OH)P ligand. Syndio selectivity is proposed to arise as a consequence of addition of the monomer selectively trans to the pyrrolide and inversion of configuration at the metal center with each metathesis step. It occurred to us that if syndiotacticity is controlled primarily as a consequence of the inherent chirality at the metal, and the monomer in question is chiral and racemic, then enantiomers of that monomer should be selected in a perfectly alternating fashion. In this paper we demonstrate that this approach can lead to polymers that have a cis,syndiotactic structure and an alternating enantiomer sequence in the polymer chain.

We chose first to examine endo,exo-5,6-dicarbomethoxynorborne (DCMNBE), a ROMP monomer that is prepared and resolved readily. Addition of 100 equivalents of rac-DCMNBE to syn-Mo(NAd)(CHCMe$_2$Ph)(Pyr)(OHIMT) (1b) proceeded at an acceptable rate (100 equivalents over a period of 1 hr in toluene). Only two pseudo triplet olefinic proton resonances are present in the proton NMR spectrum of the resulting highly regular polymer (Figure 1), consistent with a structure in which two equivalent protons ($H_1$, $H_6$) and one other proton ($H_2$, $H_5$, equation 1) are on one double bond and coupled to one another with a J$_{HH}$ value typical of cis J$_{HH}$ couplings (~ 11 Hz), as confirmed through a proton/proton COSY spectrum (Figure S3 in Supporting Information). The $^{13}$C NMR spectrum (at 125 mHz) is also sharp and free of any significant fine structure associated with structural irregularities (see Figure S2 in Supporting Information). These results are consistent with a basic cis,syndiotactic structure in which the repeat units in the polymer chain are enantiomers of one another (equation 1). We will call this a cis,syndio,alt structure (alt for alternating). We ascribe the weak resonance at 5.47 ppm in the H NMR spectrum of the polymer displayed in Figure 1 to the presence of a small fraction of trans double bonds. If the 5.47 ppm resonance is ascribed to one proton, then this microstructural error comprises <5% of the cis,syndio,alt structure.

A cis,syndiotactic structure made from a single enantiomer (cis,syndio,alt) could be formed from rac-DCMNBE either through perfect kinetic resolution (with a maximum yield of 50% of the polymer) or through formation of a perfect diblock copolymer that contains cis,syndio,alt blocks constructed from the two enantiomers. In either case, any extended cis,syndio,alt structure would contain uncoupled protons in different $C=C$ bonds as a consequence of a local $C=C$ axis that passes through each $C=C$ bond. Therefore, these possibilities can be discarded. An attempt to prepare cis,syndio,alt-polyDCMNBE through polymerization of enantiomerically pure (+)-DCMNBE with 1b led only to a polymer with no long range structure. This result could have been anticipated since two different types of propagation steps would be required to polymerize (+)-DCMNBE with 1b and it is unlikely that both types of propagation steps would yield the same result that is found in a single type of propagation step in the reaction between 1b and rac-DCMNBE.

Formation of cis,iso tactic ROMP structures are possible through enantionic site control. Addition of enantionicly pure (+)-DCMNBE to Mo(NAr)(CHCMe$_2$Ph)(rac-3,3'-Di-tert-butyl-5,5'-bistrifluoromethyl-6,6'-dimethyl-1,1'-biphenyl-2,2'-diolate) (2; Ar = 2.6-i-Pr,C$_6$H$_4$) produces an all cis polymer with a single structure that contains two inequivalent coupled olefinic protons, but both proton and carbon NMR spectra of this polymer (equation 2) are distinct from those of cis,iso,alt-polyDCMNBE prepared employing 1b (see Figure S4 in Supporting Information). All data are consistent with this polymer being cis,iso,alt-polyDCMNBE (equation 2). As expected, polymerization of rac-DCMNBE with 2 yields a polymer with no long range order since two different types of propagation steps...
again would have to give the same structural result.

We then turned to polymerization of endo,exo-5,6-dicyanonorbornene (DCNNBE). When 100 equivalents of rac-DCNNBE were added to 1b in dichloromethane, the reaction mixture immediately became thick and cloudy. $^1H$ NMR showed that the monomer was completely consumed within one hour. The resulting white solid polymer is essentially insoluble in CDCl$_3$, CD$_2$Cl$_2$, or toluene-$d_8$, and has limited solubility in aceton-$d_6$. However, a $^1H$ spectrum of sufficient quality could be obtained in aceton-$d_6$ at 50 °C. The olefinic region of the $^1H$ NMR spectrum of polyDCNNBE (Figure 2) displays two pseudo triplet resonances, suggesting that this polymer exhibits a highly regular cis,syndio,alt structure. The limited solubility of this polymer precluded obtaining its $^{13}C$ NMR spectrum. However, on the basis of the $^1H$ NMR data alone, it is apparent that the cis,syndio,alt selectivity also is realized for DCNNBE polymerized by 1b.

![Figure 2. $^1H$ NMR Spectrum of cis,syndio,alt-polyDCNNBE formed with 1b (aceton-$d_6$, 500 MHz, 50 °C)](image)

Racemic 1-methyl-5,6-dicarbomethoxy-7-oxanorbornadiene is polymerized by 1b to give a polymer (equation 3) whose proton and carbon NMR spectra are consistent with a cis,syndio,alt structure. In the proton NMR spectrum the resonances for H$_2$ (d), H$_4$ (e), and H$_5$ (d) are all clearly visible with $J_{AB} = 11.5$ Hz and $J_{EC} = 9.5$ Hz. We estimate that the polymer has >95% the cis,syndio,alt structure. The assignments have been proven through proton/carbon HSQC 2D-NMR (Figure S7 in Supporting Information). Polymerization of 1-methyl-5,6-dicarbomethoxy-7-oxanorbornadiene with 1b confirms that cis,syndio,alt polymers can be formed from monomers that are dramatically different than endo,exo-5,6-disubstituted monomers described above.

![image 3](image)

Polymerization of DCMNBE with 1a in toluene is exceedingly slow; only ~50% of the expected poly-DCMNBE was formed in 72 hours at room temperature. NMR studies show that this poly-DCMNBE has no long range regular structure. We propose that the rate and selectivity of this polymerization suffer from steric overcrowding. Similarly, attempted polymerization of 1-methyl-5,6-dicarbomethoxy-7-oxanorbornadiene by 1a also led to a polymer with no regular structure. At the same time attempted polymerization of rac-endo,exo-5,6-dimethylnorbornene, rac-1-methylbornylnorbornene, and endo,exo-5,6-diethoxymethylbornylnorbornene with 1b did not yield polymers with a highly regular structure. It is proposed that these three catalyst/monomer combinations do not provide enough steric crowding to result in formation of a polymer with a single structure. Clearly a suitable "match" between the catalyst and the monomer is required. The ability to adjust the steric of the catalyst (and or monomer) finely gives hope that suitable catalysts can be found among the many molybdenum and tungsten MAP possibilities that are now available for polymerization of a variety of monomers.

We conclude that cis,syndio,alt structures are formed through a combination of Z selective and stereogenic metal control when the metal's configuration inverts with each insertion of monomer. To the best of our knowledge there is only one example of a polymer containing alternating enantiomers in the literature; it is a polymer prepared through ROMP of rac-1-methylnorbornene with ReCl$_3$.

precisely how the structure arises is not known. However, in a prescient statement the authors proposed that "the inherent chirality of the metal centre seems to be of paramount importance in controlling tacticity... with little or no influence by chirality in the permanent ligands or in the polymer chain ends." It should be noted that virtually no polymers with any single microstructure have been prepared with Ru catalysts. One possibility is that enough variations have been explored. However, the problem may be of a more fundamental nature; the carbene simply rotates too readily about the Ru=C bond when the steric hindrance that is required in order to form a specific structure is significant. This problem was noted by Rooney and coworkers in studies involving classical Ru and Os catalysts: "The intrinsic activity of the [Ru]=CH$_2$ moiety seems to be too low to withstand in general the adverse factor of steric compression, unlike the analogous [Os]=CH$_2$ propagating species."

The barrier to rotation of the carbene in a generic NHC dichloride Ru catalyst has now been calculated to be only a few kcal/mol at best. The presence of syn and anti isomers of Mo or W catalysts, and their high reactivity in general, make possible the results reported here. It seems increasingly unlikely that an equivalent circumstance will be found in Ru catalyst systems.

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Supporting Information Available. Experimental details for all reactions and supporting NMR data for polymers. Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

References

(c) Buchmeiser, M. R. Chem. Rev. 2000, 100, 1565.
Abstract

ROMP polymerization of rac-endo,exo-5,6-dicarbomethoxynorbornene (inter alia) yields a cis,syndio,alt polymer, one in which the sequential units in the cis,syndiotactic polymer consist of alternating enantiomers. Cis selectivity arises through addition of the monomer to produce an all cis metallacyclobutane intermediate, while syndioselectivity and alternating enantiomer structures arise as a consequence of inversion of configuration at the metal center with each metathesis step.