Synthesis of Cis,Syndiotactic ROMP Polymers Containing Alternating Enantiomers

Margaret M. Flook, Victor W. L. Ng, and Richard R. Schrock*

Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

RECEIVED DATE (automatically inserted by publisher); rrs@mit.edu

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\textsuperscript{1} 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 \textsuperscript{13}C NMR).\textsuperscript{2,3} 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\textsuperscript{3} with known structures and modes of reaction have allowed an increasing number of ROMP polymers to be prepared that have a single microstructure.\textsuperscript{4} We recently reported the Z-selective and syndioslective polymerization of several ROMP monomers by monoaryloxide monopyrrolide (MAP) imido alkylidene catalysts of Mo to yield cis,syndiotactic polymers.\textsuperscript{5a-d} Z selectivity is proposed to arise through an addition of the monomer to syn-Mo(NAd)(CHCMe\textsubscript{2}Ph)(Pyr)(OHPT) (1a) to produce an all cis metallacylclobutane as a consequence of the steric demands of the OHPT ligand. Syndio selectivity is proposed to arise as a consequence of addition of the monomer selectively trans to the pyrrole and inversion of configuration at the metal center with each metathesis step.\textsuperscript{5} 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-dicarbomethoxynorbornene (DCMNBE), a ROMP monomer that is prepared and resolved readily.\textsuperscript{5} Addition of 100 equivalents of rac-DCMNBE to syn-Mo(NAd)(CHCMe\textsubscript{2}Ph)(Pyr)(OHMT) (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 inequivalent protons (H\textsubscript{a} and H\textsubscript{b}, equation 1) are on one double bond and coupled to one another with a J\textsubscript{HH} value typical of cis isomers (\textasciitilde 11 Hz), as confirmed through a proton/proton COSY spectrum (Figure S3 in Supporting Information). The \textsuperscript{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 \textless 5% of the cis,syndio,alt structure.
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 CDCl₃, CD₂Cl₂, or toluene-d₈, and has limited solubility in acetone-d₆. However, a 1H spectrum of sufficient quality could be obtained in acetone-d₆ 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,syn,endo,alt structure. The limited solubility of this polymer precluded obtaining its 13C NMR spectrum. However, on the basis of the 1H NMR data alone, it is apparent that the cis,syn,endo,alt selectivity also is realized for DCNNBE polymerized by 1b.

Figure 2. 1H NMR Spectrum of cis,syn,endo,alt-polyDCNNBE formed with 1b (acetone-d₆, 500 MHz, 50 °C)

Polymerization of DCMBNE with 1a in toluene is exceedingly slow; only ~50% of the expected poly-DCMBNE was formed in 72 hours at room temperature. NMR studies show that this poly-DCMBNE 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 with 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-methylnorbornene, and endo,exo-5,6-dimethoxydichloromethylnorbornene 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 sterics of the catalyst (and/or monomer) finely gives us hope that suitable catalysts can be found among the many molybenediun and tungsten MAP possibilities that are now available for polymerization of a variety of monomers.

We conclude that cis,syn,endo,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 ReCl₃. 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]=CHP moiety seems to be too low to withstand in general the adverse factor of steric compression, unlike the analogous [Os]=CHP 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.

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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.