

Ring opening metathesis polymerization of bisnorbornene derivatives linked by $\text{Cp}_2\text{Ni}_2(\mu\text{-S})_2$ bridge

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Received 10 March 2006; received in revised form 28 March 2006; accepted 30 March 2006

Available online 6 April 2006

Abstract

ROMP of **2** with Grubbs I catalyst in CH_2Cl_2 furnished the corresponding polymer **5** which was characterized by spectroscopic means, particularly, MAS ^{13}NMR . The EXAFS of **5** results were compared with those of the monomeric starting material **2** and the X-ray data of **2**.

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Keywords: Ring opening metathesis polymerization; Bisnorbornene; Ni_2S_2 ; EXAFS; Crystal structure

1. Introduction

Ring opening metathesis polymerization (ROMP) of cyclic alkene derivatives has provided unique protocol for the synthesis of a range of polymers that are not readily accessible by other polymerization methods [1]. Polymers and block copolymers of norbornene derivatives having a variety of substituents are prepared conveniently [1,2]. ROMPs of bisnorbornene derivatives have briefly explored [3,4]. We recently reported the first double stranded helical polymer **1** by ROMP of a bisnorbornene derivative linked by a ferrocene moiety (Scheme 1) [4]. The key to success of this approach relies on the coherent alignment of the endo pending groups in the ROMP of the norbornene derivatives [5]. In addition, the relatively rigid but slightly flexible ferrocene-derived linker may accommodate appropriate

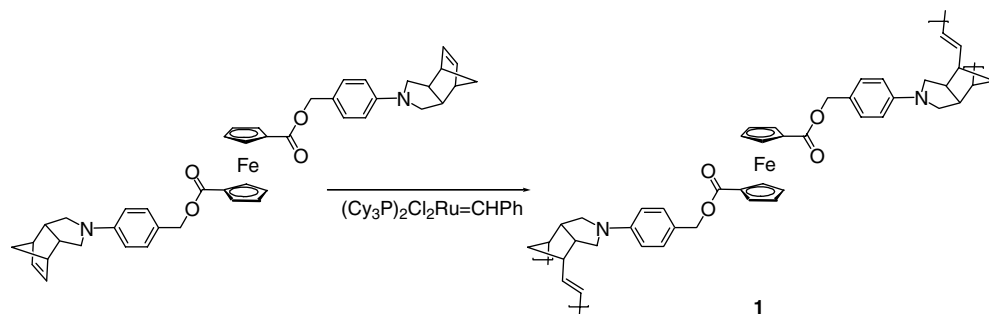
orientation of the second norbornene moiety for polymerization. It is interesting to note that the distance (ca. 5 Å) between two neighboring iron atoms in **1** is comparable with those in single crystals of ferrocene derivatives [6]. Presumably, interactions between the linkers may generate a favorable stereochemical requirement for the formation of the double stranded polymer **1**.

Square planar $\text{Cp}_2\text{Ni}_2(\text{SR})_2$ complexes are well documented and the Ni_2S_2 moiety is arranged as a rigid square [7]. It is envisaged that the alkyl substituent in this complex can be a norbornene moiety (e.g. **2**). In this paper, we wish to report the synthesis and ROMP of organonickel-linked bisnorbornene **2**.

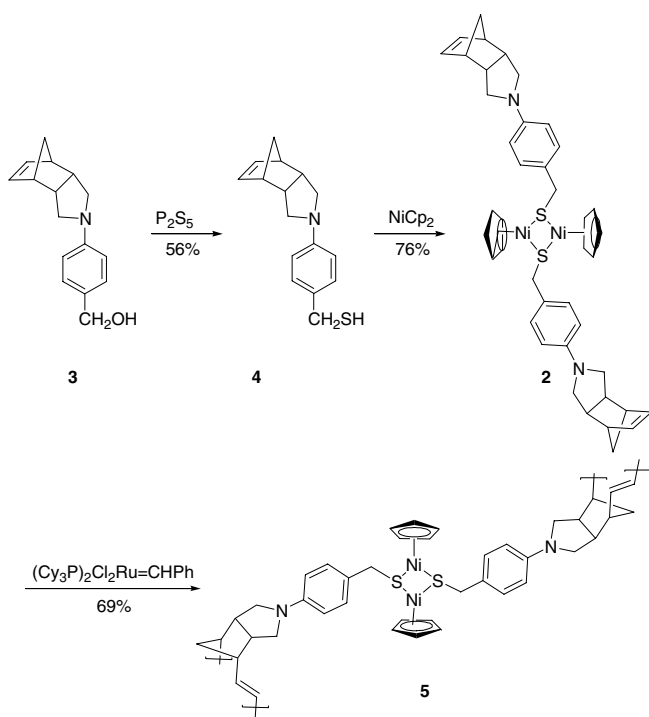
2. Results and discussion

Monomeric bisnorbornene derivative **2** was designed by incorporating a slightly labile benzylic moiety which would allow some flexibility during the course of polymerization step. Thus, the monomeric bisnorbornene derivative **2**

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Scheme 1.



Scheme 2.

was synthesized according to Scheme 2. Treatment of benzylic alcohol **3** with P_2S_5 [8] afforded the corresponding mercaptan **4** in 56% yield. Reaction of **4** with nickelocene [7] gave **2** in 76% yield as a black solid. The X-ray structure of **2** suggested that the molecule has a center of symmetry and the two norbornene moieties are in anti conformation in the crystal (Fig. 1). The packing of **2** in the single crystal is also shown in Fig. 1.

ROMP of **2** with Grubbs I catalyst [9] in CH_2Cl_2 furnished the corresponding polymer **5** in 69% yield. Unlike ferrocene derivatives, polymer **5** was insoluble in any organic solvent. Polymer **5** exhibited an absorption band at 968 cm^{-1} which is characteristic for *trans* carbon–carbon double bond. This band was absent in the starting **2**. ROMPs of norbornene derivatives with Grubbs I catalyst are known to give predominantly, if not exclusively, *trans* double bond [1,4,5]. The infrared data suggested that ROMP might take place with **2**.

As can be seen in Fig. 2, the MAS ^{13}C NMR spectrum of **5** is very similar to that of **2**. The energy dispersive spectrometric (EDS) analysis indicated that the ratio of nickel to sulfur was 56 to 44. The ICPMS also confirmed the presence of nickel in **5**. These results suggested that the $Cp_2Ni_2S_2$ core might remain intact during the course of ROMP process.

The EXAFS spectra of **2** and **5** are shown in Fig. 3. The high intensity peaks at 200 and 300 pm owing to the interactions of heavy atoms in the Ni_2S_2 core were observed for both **2** and **5**. These results again indicated that the Ni_2S_2 core remained intact during the course of polymerization. In addition to these main absorptions at shorter distances, there are also weak long range weak interactions of heavy atoms at 535 and 625 pm for **5**. These results suggested that the two neighboring Ni_2S_2 cores may be in close proximity and these distances happen to fall within the span of each monomeric unit in polynorbornenes, which ranges from 500 to 650 pm [4,5]. Such long range interactions are, in general, difficult to analyze unless there is a closely related model where the interatomic distances are in the same range. As shown in Fig. 1b, the closest intermolecular Ni–Ni distances in the single crystal of **2** were 535 and 610 pm and the intermolecular Ni–S distances were 526 and 615 pm. These distances were reflected as weak peaks in the EXAFS spectrum for **2** (Fig. 3a). Accordingly, the EXAFS results for **2** may support the presence of long range interactions between heavy atoms in **5**. When such interactions are persistent along the polymeric chain, one of the possibilities would be that polymer **5** might also adopt a double stranded structure in a manner similar to that of the analogues with ferrocene linker **1** [4].

3. Conclusions

In summary, we have demonstrated the synthesis and polymerization of a Ni_2S_2 linked bisnorbornene derivative **2**. Although further evidences will be necessary, the preliminary results thus obtained suggested that the polymer **5** might adopt a double stranded structure. Further investigations by designing other linkers as well as other monomeric species having different kinds of cyclic alkenes are in progress.

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