

Catalytic properties of novel chiral polyoxomolybdate(VI) salts: The ring-opening metathesis polymerization (ROMP) of norbornene

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Received 25 July 1995; accepted 16 October 1995

Abstract

Each of the chiral polyoxomolybdate(VI) salts $(R_3NH)_4[Mo_8O_{26}(R_3N)_2]$ and $(Na)_2(R_3NH)_2[Mo_8O_{26}]$ ($R_3N = (+)$ -cinchonine, $(+)$ -hydroquinidine or $(-)$ -quinine), in the presence of the cocatalyst $EtAlCl_2$, catalyses the ring-opening metathesis polymerization of norbornene at room temperature. The polynorbornene produced in these reactions was found to be mostly insoluble. Inclusion of a chain transfer agent, 1-hexene, in the reactions leads to greatly improved yields of polynorbornene which is freely soluble in chloroform, and the quantity of polymer formed is highly sensitive to the amount of 1-hexene added.

Keywords: Polyoxomolybdate; Chiral; Metathesis; Ring-opening; Polymerization; Norbornene; Molybdenum

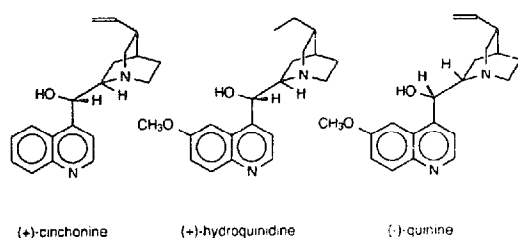
1. Introduction

Recently, the syntheses of some novel polyoxomolybdate(VI) compounds comprising chiral organic bases have been reported by this laboratory [1]. We now report the catalytic properties of these compounds with respect to the ring-opening metathesis polymerization (ROMP) of norbornene (bicyclo[2,2,1]hept-2-ene). The polymerization of norbornene is an active area of research, mainly because study of the microstructure of the polymers produced can provide useful insight into the mechanism of the important alkene metathesis reaction. Previous work by this research group has shown that the

ROMP of norbornene is catalysed efficiently by a single crystal of $(Bu_4N)_2[Mo_6O_{19}]$ which had been activated by the cocatalyst $EtAlCl_2$ [2].

We have now studied the polymerization of norbornene by a series of chiral iso- and heteropolyoxomolybdate(VI) salts of general formula $(R_3NH)_4[Mo_8O_{26}(R_3N)_2]$ and $(Na)_2(R_3NH)_2[Mo_8O_{26}]$ respectively, where $R_3N = (+)$ -cinchonine (cin), $(+)$ -hydroquinidine (hqid) and $(-)$ -quinine (qin) (Scheme 1). In the isopolyoxomolybdates the chiral base is coordinated directly to the $[\beta-Mo_8O_{26}]^{4-}$ unit as well as being present in protonated form as a counter ion. In the heteropolyoxomolybdates the base is present only as a counter ion, which may be hydrogen bonded to the $[\beta-Mo_8O_{26}]^{4-}$ moiety. It is thought that at least one of the sodium

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Scheme 1.

ions is coordinated to the β -octamolybdate core, as has been shown in the crystallographically characterised salt $(\text{Et}_3\text{NH})_3[\text{NaMo}_8\text{O}_{26}]$ [3].

2. Experimental

2.1. Instrumentation

^{13}C NMR spectra were recorded on a Bruker AC 80 spectrometer. Samples were dissolved in CDCl_3 and TMS was used as a standard. The spectra were compared with data in the literature [4] and were used to calculate the proportions and distribution of *cis* and *trans* double bonds in the polymer chains.

Molecular weight determinations were carried out by gel permeation chromatography. Samples were dissolved in chlorobenzene (15 mg in 2 cm^3) and filtered through a $0.45\ \mu\text{m}$ Teflon syringe filter prior to injection. Molecular weights are given relative to polystyrene.

2.2. Synthesis of chiral polyoxomolybdate(VI) salts

The chiral isopolyoxomolybdate(VI) salts $(\text{cin-H})_4[\text{Mo}_8\text{O}_{26}(\text{cin})_2]$ (**1a**), $(\text{hquid-H})_4[\text{Mo}_8\text{O}_{26}(\text{hquid})_2]$ (**1b**) and $(\text{qin-H})_4[\text{Mo}_8\text{O}_{26}(\text{qin})_2]$ (**1c**) were prepared by literature methods [1]. The chiral heteropolyoxomolybdate(VI) salts $(\text{Na})_2(\text{cin-H})_2[\text{Mo}_8\text{O}_{26}]$ (**2a**), $(\text{Na})_2(\text{hquid-H})_2[\text{Mo}_8\text{O}_{26}]$ (**2b**) and $(\text{Na})_2(\text{qin-H})_2[\text{Mo}_8\text{O}_{26}]$ (**2c**) were prepared as follows [5]: 0.47 g (1.6 mmol) of the appropriate chiral base was dissolved in boiling water (100 cm^3) acidified with concentrated hydro-

chloric acid (2 cm^3). Sodium molybdate (1 g, 4.13 mmol) was added slowly resulting in the formation of a blue precipitate. The resulting suspension was then refluxed for 24 h, after which the reaction mixture was filtered while still hot. The blue product was then washed with water, followed by hot acetone and dried in vacuo (yield 60–65%, based on sodium molybdate).

2.3. Typical procedure for the polymerization of norbornene

15 mg of the powdered polyoxomolybdate(VI) salt was placed in the bottom of a conical shaped test tube. A single drop of a 1.8 mol dm^{-3} solution of EtAlCl_2 in toluene (0.025 cm^3 , 0.045 mmol) was added by syringe, resulting in a colour change of the polyoxomolybdate(VI) salt from blue to dark brown. After approximately 30 s a solution of norbornene (0.5 g) in toluene (0.5 cm^3) was added resulting in an immediate and exothermic polymerization reaction. In some reactions a chain transfer agent (1-hexene) was co-dissolved in the monomer solution prior to addition to the activated catalyst. Ethanol was then added to the reaction and the cone shaped polymer, with the catalyst powder concentrated at the tip, was removed from the tube. The polymer was then easily separated from the catalyst when the mixture was shaken with chloroform (15 cm^3) for 2 h. The chloroform solution of the polymer was separated from any insoluble material (catalyst and insoluble polymer) and the soluble polymer was re-precipitated by addition of the chloroform solution to ethanol (100 cm^3) acidified with concentrated hydrochloric acid (1 cm^3).

3. Results and discussion

All of the isopolyoxomolybdate(VI) salts **1a–c**, and all the heteropolyoxomolybdate(VI) salts **2a–c**, in the presence of added EtAlCl_2 cocata-

lyst, efficiently catalysed the ROMP of norbornene at room temperature. The salts were completely inactive in the absence of the cocatalyst. As in the reactions of single crystals of isopolyoxometallate(VI) compounds [6], addition of the cocatalyst EtAlCl_2 to the polyoxomolybdate(VI) salt caused a colour change, from the original blue colour of the molybdenum compound to dark brown. This is believed to be due to reduction of some of the surface Mo(VI) centres to Mo(V) (or Mo(IV)) and is an important step in the formation of active catalytic species. Addition of the monomer solution to this activated catalyst resulted in an immediate and exothermic polymerization reaction. In reactions where 1-hexene was used as a chain transfer agent an induction period of several seconds was observed after addition of the monomer before polymerization became visually evident (an increase in the viscosity of the solution was observed). After addition of ethanol and removal of the polymer from the catalyst, the catalyst quickly regained its original colour.

The results of the polymerization reactions with the six chiral polyoxomolybdate(VI) salts are summarised in Table 1. In the reactions carried out in the absence of 1-hexene polymerization was instantaneous, and the resulting

polynorbornene consisted of a mixture of mainly chloroform-insoluble polymer with a smaller amount of chloroform-soluble polymer. In reactions where 1-hexene was added to the monomer solution the yield of polynorbornene produced was significantly higher than in the reactions where no chain transfer agent was used. Furthermore, this polymer was also found to consist entirely of chloroform-soluble material. The results shown in Table 1 for the reactions conducted in the presence of chain transfer agent show the amount of added 1-hexene required to give the maximum yield of polynorbornene. The quantity of polymer formed was found to be very sensitive to the amount of 1-hexene added. For example, in the polymerization of a 0.5 g batch of norbornene by 15 mg of $(\text{cin-H})_4[\text{Mo}_8\text{O}_{26}(\text{cin})_2]$ (1a) addition of too little 1-hexene (≤ 0.1 g) resulted in a very low yield ($< 1\%$) of polymer, whilst addition of too much (≥ 0.2 g) suppressed the polymerization reaction completely. It is interesting to note that the optimum amount of 1-hexene required for a given catalyst to produce the best possible yield of chloroform-soluble polynorbornene seems to depend upon which chiral base is present in the polyoxomolybdate(VI) salt.

The chloroform-insoluble polynorbornene

Table 1
Polymerization of norbornene by chiral polyoxomolybdate(VI) salts

Catalyst	1-Hexene added (g)	Yield (%)	
		Soluble polymer	Insoluble polymer
$(\text{cin-H})_4[\text{Mo}_8\text{O}_{26}(\text{cin})_2]$ (1a)	0	12	6
$(\text{cin-H})_4[\text{Mo}_8\text{O}_{26}(\text{cin})_2]$ (1a)	0.15	52	0
$(\text{Na})_2(\text{cin-H})_2[\text{Mo}_8\text{O}_{26}]$ (2a)	0	2	6
$(\text{Na})_2(\text{cin-H})_2[\text{Mo}_8\text{O}_{26}]$ (2a)	0.15	58	0
$(\text{hqid-H})_4[\text{Mo}_8\text{O}_{26}(\text{hqid})_2]$ (1b)	0	10	20
$(\text{hqid-H})_4[\text{Mo}_8\text{O}_{26}(\text{hqid})_2]$ (1b)	0.25	54	0
$(\text{Na})_2(\text{hqid-H})_2[\text{Mo}_8\text{O}_{26}]$ (2b)	0	6	8
$(\text{Na})_2(\text{hqid-H})_2[\text{Mo}_8\text{O}_{26}]$ (2b)	0.25	64	0
$(\text{qin-H})_4[\text{Mo}_8\text{O}_{26}(\text{qin})_2]$ (1c)	0	12	14
$(\text{qin-H})_4[\text{Mo}_8\text{O}_{26}(\text{qin})_2]$ (1c)	0.30	60	0
$(\text{Na})_2(\text{qin-H})_2[\text{Mo}_8\text{O}_{26}]$ (2c)	0	10	30
$(\text{Na})_2(\text{qin-H})_2[\text{Mo}_8\text{O}_{26}]$ (2c)	0.30	56	0

Reaction conditions: polyoxomolybdate (15 mg), EtAlCl_2 (2 drops of 1.8 mol dm^{-3} solution in toluene), norbornene (0.5 g), toluene (0.5 cm^3).

produced in reactions in the absence of 1-hexene was believed to have a high molecular weight and to contain a significant amount of cross-linking of the polymer chains. This cross-linking was so extensive it prevented the dissolution of the polymer in any suitable solvent, thus preventing molecular weight determination. Inclusion of the chain transfer agent 1-hexene in the polymerization reactions promoted the formation of good yields of polynorbornene which was freely soluble in chlorinated solvents. Molecular weight determination of the polynorbornene sample produced by the catalyst $(\text{cin-H})_4[\text{Mo}_8\text{O}_{26}(\text{cin})_2]$ (**1a**) in the presence of 1-hexene gave $M_w = 57100$ and $M_n = 33100$ (polydispersity = 1.73).

The *cis* content of the small quantities of chloroform-soluble polymers produced in reactions with no added 1-hexene was found to vary little between the different catalysts (σ_c ca. 0.40). However, the polymers produced in reactions with added 1-hexene showed lower and rather more variable values for the *cis* content ($0.24 \leq \sigma_c \leq 0.30$). All of the polymers showed a random distribution of *cis* and *trans* double bonds ($r_1 r_c = 1.25-1.40$).

In all of the reactions the recovered catalysts quickly regained their original colour and appeared unchanged by the reaction. However, when these recovered catalysts were reused to polymerize further batches of norbornene they exhibited a dramatic decrease in activity (Table 2). For example, in the polymerization of the first batch of norbornene by **1a** in the presence

of 1-hexene a yield of 52% of polynorbornene was obtained. When the recovered catalyst was used to polymerize a second batch of norbornene a polymer yield of 42% was obtained. Subsequent reuse of this catalyst in a third reaction gave only 5% polymer yield. This behaviour contrasts somewhat with that found for large single crystals of isopolyoxomolybdate(VI) salts, which can be used repeatedly in the polymerization of norbornene without any apparent loss in activity [6]. Unfortunately, the chiral polyoxomolybdate(VI) salts described here could not be crystallised to produce crystals of sufficient size to use singly in reactions. Therefore, in order to approximate the reaction conditions used for polymerization of norbornene by a single crystal of an isopolyoxomolybdate(VI) salt the following procedure was carried out. $(\text{cin-H})_4[\text{Mo}_8\text{O}_{26}(\text{cin})_2]$ (**1a**) (0.06 g) was mixed with KBr (0.1 g) and the mixture was ground with a mortar and pestle. This powder was then formed into a pellet using a pelleting press of the sort used to make KBr discs for infrared spectroscopy. The pellet was then broken roughly into quarters and one of these was used to polymerize norbornene, in the presence of 1-hexene, as described for the powdered catalysts, to give a yield of polynorbornene of 58%. The pellet was then recovered whole and apparently unchanged. In this way each $(\text{cin-H})_4[\text{Mo}_8\text{O}_{26}(\text{cin})_2]/\text{KBr}$ pellet could be used in four successive reactions before a significant loss of activity was observed (Table 2). The fall-off in activity here may, in part, be due to

Table 2

Catalyst reuse for the polymerization of successive batches of norbornene

Catalyst system	Polymer yield (%)				
	Reaction 1	Reaction 2	Reaction 3	Reaction 4	Reaction 5
$(\text{cin-H})_4[\text{Mo}_8\text{O}_{26}(\text{cin})_2]$ (powder)	52	42	10	0	0
$(\text{cin-H})_4[\text{Mo}_8\text{O}_{26}(\text{cin})_2]$ (in KBr Pellet)	58	46	38	30	6

Reaction conditions: polyoxomolybdate (15 mg), EtAlCl_2 (2 drops of a 1.8 mol dm^{-3} solution in toluene), norbornene (0.5 g) and 1-hexene (0.15 g) in toluene (0.5 cm^3).

the presence of the hygroscopic KBr, where after four reactions it could be that the KBr had absorbed sufficient water to affect the catalytic activity. The polymers produced in the above reactions showed similar *cis* content and distribution to those produced from the powdered catalyst.

The results reported here clearly demonstrate the high activity of chiral polyoxomolybdate(VI) salts towards ROMP of norbornene in the presence of the cocatalyst EtAlCl₂. Work is currently under way on the polymerization of the substituted monomers 7-methylnorbornene and 5,6-*endo,exo*-dimethylnorbornene and structural analysis of the polymers produced. The purpose of this is to determine the tacticity of the polymers, and to study the influence of chirality in the catalyst on the stereochemical outcome of the metathesis reaction.

Acknowledgements

This work was funded under the EU Human Capital and Mobility Programme (contract No. ERBCHRXCT930158).

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