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Journal of Molecular Catalysis A: Chemical 96 (1995) 31–34



Single crystals of isopolyoxometallate(VI) salts as catalysts for the ring-opening polymerization of norbornene

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Received 5 July 1994; accepted 31 October 1994

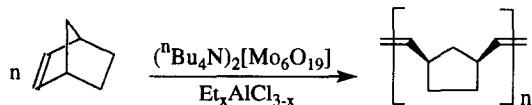
Abstract

A single crystal of each of the isopolyoxometallate(VI) salts $(^n\text{Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$, $(^n\text{Bu}_4\text{N})_2[\text{W}_6\text{O}_{19}]$ and $(^n\text{Bu}_4\text{N})_4[\text{W}_{10}\text{O}_{32}]$, in combination with EtAlCl_2 cocatalyst, heterogeneously catalyses the ring-opening metathesis polymerization of norbornene at room temperature. Polymer yield is found to be dependent upon the reaction solvent, and it is generally found that the inclusion of a chain transfer reagent in the reaction mixture leads to significantly improved yields of chloroform-soluble polynorbornene.

Keywords: Isopolyoxometallate; Metathesis; Molybdenum; Norbornene; Polymerization; Ring opening; Tungsten

1. Introduction

Recently, we reported that a single crystal of the isopolyoxomolybdate(VI) salt $(^n\text{Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$, when treated with an alkylaluminium compound, is a good heterogeneous catalyst for the room temperature ring-opening metathesis polymerization of norbornene [1]. The main features of this reaction were that the polymerization



was essentially instantaneous at room temperature, the catalyst crystal was readily recovered fully intact and, the crystal could be reused to polymerize further batches of norbornene without any marked deterioration in activity. In these batch

reactions the yield of chloroform-soluble polynorbornene was 19–38%.

Herein, we present the results of further studies with $(^n\text{Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$, in which a chain transfer reagent has been employed to give markedly improved yields of soluble polynorbornene. In addition, the range of single crystal isopolyoxometallate heterogeneous catalysts has been extended to include the two isopolyoxotungstate(VI) salts $(^n\text{Bu}_4\text{N})_2[\text{W}_6\text{O}_{19}]$ and $(^n\text{Bu}_4\text{N})_4[\text{W}_{10}\text{O}_{32}]$.

2. Experimental

Literature methods were used to prepare the isopolyoxometallate(VI) salts $(^n\text{Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$ [2,3], $(^n\text{Bu}_4\text{N})_2[\text{W}_6\text{O}_{19}]$ [4] and $(^n\text{Bu}_4\text{N})_4[\text{W}_{10}\text{O}_{32}]$ [5]. Slow recrystallization

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(twice) from the specified solvent (in parentheses) gave large single crystals of yellow $(^n\text{Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$ (acetone), colourless $(^n\text{Bu}_4\text{N})_2[\text{W}_6\text{O}_{19}]$ (DMSO) and cream $(^n\text{Bu}_4\text{N})_4[\text{W}_{10}\text{O}_{32}]$ (DMF). A solution of EtAlCl_2 in toluene (1.8 mol dm^{-3}) was purchased from Aldrich. The polymerization reactions were carried out in conical shaped test tubes (centrifuge tubes) to facilitate easy recovery of the single crystal of catalyst.

2.1. Instrumentation

^{13}C NMR spectra of the chloroform-soluble polymers, as solutions in CDCl_3 , were recorded on a Bruker AC 80 spectrometer. The spectra of the polymers were compared with the data in the literature [6]. Gel permeation chromatographic analyses were carried out using a Waters 150C GPC instrument equipped with a refractive index detector. Polymer samples were dissolved in chlorobenzene ($15 \text{ mg}/10 \text{ cm}^3$) at ambient temperature and filtered through a 0.45 Teflon filter. All molecular weights are relative to polystyrene.

2.2. Typical procedure for the polymerization of norbornene

All manipulations were carried out in air. A large single crystal (ca. 20 mg) of one of the isopolyoxometalate salts was placed in the bottom of a conical shaped test tube, and then one drop of a 1.8 mol dm^{-3} solution of EtAlCl_2 in toluene (0.025 cm^3 , 0.045 mmol) was added directly onto the crystal surface using a syringe. For each of the separate isopolyoxometalate salts the following colour change immediately occurred on the crystal surface: $(^n\text{Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$ (yellow to dark-brown), $(^n\text{Bu}_4\text{N})_2[\text{W}_6\text{O}_{19}]$ (colourless to black), $(^n\text{Bu}_4\text{N})_4[\text{W}_{10}\text{O}_{32}]$ (cream to blue-black). After ca. 30 s a solution of norbornene in a chosen solvent (toluene, benzene or hexane) was injected into the tube, and polymerization (gelation) was both immediate and exothermic. In reactions where a chain transfer reagent was co-dissolved with the norbornene a period of ca.

5 s elapsed between injection and gelation. Ethanol (1 cm^3) was added, and the polymer with the catalyst crystal attached was then removed from the tube. In most cases the dark catalyst crystal remained attached to the bottom of the polymer gel and could simply be detached from it using forceps. However, in some instances the crystal was embedded within the gel and had to be removed by lancing the gel and lifting the crystal out with forceps. Upon exposure to the atmosphere the dark surface of the crystal quickly returned to its original colour.

3. Results and discussion

A single crystal of each of the isopolyoxometalate(VI) salts $(^n\text{Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$, $(^n\text{Bu}_4\text{N})_2[\text{W}_6\text{O}_{19}]$ and $(^n\text{Bu}_4\text{N})_4[\text{W}_{10}\text{O}_{32}]$, in combination with EtAlCl_2 cocatalyst, heterogeneously catalyses the ring-opening metathesis polymerization of norbornene at room temperature. In all cases, the addition of the EtAlCl_2 cocatalyst to the isopolyoxometalate causes an immediate darkening of the crystal surface as some of the metal atoms there are reduced from M(VI) to a lower oxidation state {M(V) or M(IV)}. It is at this stage that the catalytically active species is formed (possibly an in situ generated metal alkyl or metallacarbene). Subsequent injection of monomer solution causes instantaneous polymer formation. Following the addition of ethanol the crystal is removed from the gel-like polymer where, upon exposure to the atmosphere, it quickly reverts back to its original colour as the surface metal atoms are reoxidised back to the M(VI) state. The recovered single crystal displayed no apparent change in weight or shape, and it could be reused immediately with fresh EtAlCl_2 to polymerize another 0.5 g batch of norbornene.

The polymerization results obtained using the three isopolyoxometalate crystals are summarized in Table 1. In each case the yield of polymer was dependent upon the reaction solvent and also on whether or not a chain transfer reagent (1-hexene or 1-decene) was present. In the absence

Table 1
Norbornene polymerization using single crystals of isopolyoxometallate (VI) salts ^a

Catalyst	Monomer solvent (0.5 cm ³)	Chain transfer reagent (g)	Polymer yield (%)	
			soluble ^b	insoluble ^b
(ⁿ Bu ₄ N) ₂ [Mo ₆ O ₁₉]	toluene	none	38	0
(ⁿ Bu ₄ N) ₂ [Mo ₆ O ₁₉]	toluene	1-hexene (0.2)	35	0
(ⁿ Bu ₄ N) ₂ [Mo ₆ O ₁₉]	benzene	none	8	38
(ⁿ Bu ₄ N) ₂ [Mo ₆ O ₁₉]	benzene	1-hexene (0.1)	63	0
(ⁿ Bu ₄ N) ₂ [Mo ₆ O ₁₉]	hexane	none	4	2
(ⁿ Bu ₄ N) ₂ [Mo ₆ O ₁₉]	hexane	1-hexene (0.1)	5	0
(ⁿ Bu ₄ N) ₂ [W ₆ O ₁₉]	toluene	none	1	8
(ⁿ Bu ₄ N) ₂ [W ₆ O ₁₉]	toluene	1-hexene (0.2)	32	0
(ⁿ Bu ₄ N) ₂ [W ₆ O ₁₉]	benzene	none	2	50
(ⁿ Bu ₄ N) ₂ [W ₆ O ₁₉]	benzene	1-hexene (0.2)	20	0
(ⁿ Bu ₄ N) ₂ [W ₆ O ₁₉]	hexane	none	0	56
(ⁿ Bu ₄ N) ₂ [W ₆ O ₁₉]	hexane	1-hexene (0.2)	60	0
(ⁿ Bu ₄ N) ₄ [W ₁₀ O ₃₂]	toluene	none	2	28
(ⁿ Bu ₄ N) ₄ [W ₁₀ O ₃₂]	toluene	1-hexene (0.2)	14	0
(ⁿ Bu ₄ N) ₄ [W ₁₀ O ₃₂]	benzene	none	0	70
(ⁿ Bu ₄ N) ₄ [W ₁₀ O ₃₂]	benzene	1-hexene (0.2)	60	0
(ⁿ Bu ₄ N) ₄ [W ₁₀ O ₃₂]	hexane	none	3	16
(ⁿ Bu ₄ N) ₄ [W ₁₀ O ₃₂]	hexane	1-hexene (0.2)	14	0

^a Room temperature, 0.5 g norbornene, 1.8 mol dm⁻³ solution of EtAlCl₂ in toluene (one drop, 0.025 cm⁻³, 0.045 mmol).

^b In chloroform.

of a chain transfer reagent polymer formation was instantaneous, and usually the polynorbornene obtained from these reactions tended to be a mixture comprising a small amount of chloroform-soluble polymer with a larger quantity of chloroform-insoluble polymer. In general, it was found that when a chain transfer reagent was included in the reaction mixture polymer formation was visibly slower (ca. 5 sec for gelation), and also the yield of chloroform-soluble polynorbornene increased significantly in comparison to reactions where no chain transfer reagent was present. The results displayed in Table 1 for polymerizations conducted in the presence of a chain transfer reagent were obtained under optimum conditions with respect to the amount of added chain transfer reagent required to produce the maximum yield of chloroform-soluble polymer (and without the formation of any appreciable amount of chloroform-insoluble polymer). It was found that the ratio of chain transfer reagent:norbornene used in the reactions was quite critical. For example, in reactions where a single

crystal of (ⁿBu₄N)₂[Mo₆O₁₉] was used to polymerize a 0.5 g batch of norbornene the following trends were observed. If the mass of 1-hexene used was <0.08 g then insoluble polymer formed along with the soluble polymer, whilst at levels of 1-hexene of >0.3 g all polymer formation was essentially inhibited.

The chloroform-insoluble polymer obtained in the absence of chain transfer reagent is believed to have a very high molecular weight. As expected, the introduction of a chain transfer reagent into the reaction mixture induces formation of a polymer which has a lower molecular weight and is thus chloroform-soluble. For instance, when (ⁿBu₄N)₂[Mo₆O₁₉] was used to polymerize norbornene in toluene, without added chain transfer reagent, a chloroform-soluble polymer was recovered with $M_w = 249000$ and $M_n = 160000$ (polydispersity = 1.56). Under the same reaction conditions, but this time using 1-decene as a chain transfer reagent, the resulting soluble polymer had $M_w = 183000$ and $M_n = 68400$ (polydispersity = 2.68). These results substantiate the belief

that the chloroform-insolubility of the majority of polymers prepared in the absence of chain transfer reagent is indeed attributable to their high molecular weight.

Finally, there was little variation in the *cis* content (σ_c ca. 0.36) of the polymers obtained using the three different isopolyoxometallate catalysts in the presence of added chain transfer reagent. Furthermore, the value of $\sigma_c = 0.33$ found for the soluble polymer formed using the (ⁿBu₄N)₂[Mo₆O₁₉]/toluene system was the

same as that for the polymer produced in the (ⁿBu₄N)₂[Mo₆O₁₉]/toluene/1-hexene reaction.

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