

Ring-opening Polymerization of Norbornene using a Single Crystal of $(\text{Bu}^n_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$ as a Heterogeneous Catalyst

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A single monoclinic crystal of the isopolymolybdate(vi) salt $(\text{Bu}^n_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$ when treated with an alkylaluminium compound is an efficient and totally recoverable heterogeneous catalyst for the ring-opening metathesis polymerization of norbornene.

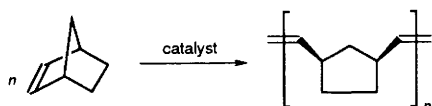
Since the mid-1950s there have been numerous publications in the chemical and patent literature concerning the development of catalyst systems for the ring-opening metathesis polymerization (ROMP) of norbornene-type monomers.¹

The use of high-valent metal oxide complexes as catalysts has been particularly promising. *E.g.*, a solution of OsO_4 in chlorobenzene will slowly (60 °C, 72 h) polymerize norbornene, even in the absence of a cocatalyst.² The versatile Re^{VII} complex MeReO_3 , in combination with an $\text{R}_n\text{AlCl}_{3-n}$ cocatalyst, polymerizes norbornene homogeneously at 25 °C to give the ring-opened polymer in 75–99% yield.³ More recently, Kroenke and his coworkers⁴ have shown that organoammonium isopoly- and heteropoly-metallate salts, such as $[(\text{C}_{13}\text{H}_{27})_3\text{NH}]_4[\text{Mo}_8\text{O}_{26}]$, $[\text{R}_3\text{NH}]_4[\text{PW}_{12}\text{O}_{40}]$ and $[\text{R}_3\text{NH}]_4[\text{PMo}_6\text{W}_6\text{O}_{40}]$ ($\text{R} = \text{C}_{14-18}$ alkyl group), are good homogeneous catalysts for ROMP of dicyclopentadiene and related monomers when used in combination with alkylaluminium-type reducing cocatalysts. These workers claim that their catalyst systems have significant advantages over prior art catalysts in that by using a large alkyl chain (R) the catalysts are soluble in the pure monomer, thus eliminating the need for a reaction solvent. Furthermore, the catalysts are insensitive to air and moisture, have unlimited shelf-life in solution of norbornene-type monomers, and do not function as Lewis acids.

In all of the afore-mentioned polymerization systems complete catalyst recovery and subsequent reuse of the catalyst was not possible. Herein, we outline the novel use of a single crystal of the isopolymolybdate(vi) salt $(\text{Bu}^n_4\text{N})_2$

$[\text{Mo}_6\text{O}_{19}]$ **1** as a totally reusable heterogeneous catalyst for the ROMP of norbornene. The main advantages of using **1** as a catalyst are, (i) the polymerization is essentially instantaneous at room temperature, (ii) the catalyst crystal is readily recovered fully intact and, (iii) the crystal can be reused to polymerize further batches of norbornene without any deterioration in activity. Crystallographic studies on the salts $[\text{NH}_3\text{P}_3(\text{NMe}_2)_6]_2[\text{Mo}_6\text{O}_{19}]$ ⁶ and $[\text{PPh}_3\text{CH}_2\text{R}]_2[\text{Mo}_6\text{O}_{19}]$ ($\text{R} = \text{CO}_2\text{Et}$, Ph)⁷ have shown that the $[\text{Mo}_6\text{O}_{19}]^{2-}$ ion consists of a slightly distorted cage of six molybdenum atoms located octahedrally around a central oxygen atom, with twelve oxygen atoms disposed in $\text{Mo}-\text{O}-\text{Mo}$ units and one terminal oxygen attached to each molybdenum ($\text{Mo}=\text{O}$).

The following polymerization reaction was carried out in air. Typically, a single yellow monoclinic crystal of **1** (7.3 mg, 5.3 μmol) was placed in a test tube and to this was added a 1.8 mol dm^{-3} solution of EtAlCl_2 in toluene (0.025 cm^3 , 0.045 mmol). The surface of the crystal immediately went dark-brown in colour, and after *ca.* 30 s a solution of norbornene (0.5 g, 5.3 mmol) in toluene (1 cm^3) was added, giving a catalyst:monomer ratio of 1:1000. The polymerization of the norbornene was both immediate and exothermic, and the brown crystal was clearly visible embedded in the gel-like polymer. The polymer mixture was then washed with ethanol (2 cm^3). When the crystal was carefully released from within the polymer and then exposed to the air, it rapidly reverted back to its original yellow form without any apparent change in mass or shape. The same crystal could immediately be reused with fresh EtAlCl_2 to polymerize another 0.5 g batch of norbornene, and this process could be repeated many times. It is sometimes found that when very large crystals of **1** are used for repeated polymerizations, the crystal will fragment across fault lines into two or more smaller parts. However, these smaller fragments are equally effective



in promoting the heterogeneous polymerization of norbornene.

In the course of six separate polymerizations (6×0.5 g batches of norbornene) using the same single crystal of **1**, the yield of polynorbornene varied between 19–38%. Similar results were also obtained using Me_3Al as a cocatalyst. Approximately 3% of the polynorbornene produced from the room temperature polymerization reactions was found to be insoluble in CHCl_3 . However, by reducing the amount of added EtAlCl_2 cocatalyst by half, the formation of insoluble polymer was effectively eliminated. The microstructure of the chloroform-soluble polynorbornene, as determined by ^{13}C NMR spectroscopy, remains constant from run to run (*cis* content $\sigma_c = 0.33$). Using gel permeation chromatography (relative to polystyrene; trichlorobenzene as solvent) M_w and M_n of the polymer were found to be 249 000 and 160 000, respectively (polydispersity = 1.56).

The yellow to brown colour change at the crystal surface of **1** observed upon addition of EtAlCl_2 is probably attributable to the reduction of surface Mo^{VI} sites to Mo^{V} by the alkyl-aluminium halide. This reasoning is substantiated by the fact that brown crystals of the mixed valence salt $(\text{Bu}^n_4\text{N})_3\text{[Mo}_6\text{O}_{19}]$ (containing Mo^{VI} and Mo^{V} in a 5:1 ratio) have previously been obtained by the controlled potential electrolysis (one-electron reduction) of a solution of the yellow Mo^{VI} salt **1**.[†] Furthermore, the reversal of the crystal colour (from

brown back to yellow) when it is free from the polymer and exposed to air is consistent with the polarographic and voltammetric reversibility found for **1**. As **1** is inactive towards norbornene in the absence of EtAlCl_2 this means that it is the surface Mo^{V} sites, and not surface Mo^{VI} sites, that are linked to the catalytic activity of **1** in the presence of added EtAlCl_2 .

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[†] M. Che, M. Fournier and J. P. Launay, *J. Chem. Phys.*, 1979, **71**, 1954. These workers initially carried out the polarography of **1** in dimethylformamide (DMF)-tetrabutylammonium tetrafluoroborate at a mercury electrode and found two waves with half-wave potentials of 0.85 and -1.70 V, measured against a reference electrode comprising Ag/AgNO_3 (0.1 mol dm^{-3} in MeCN). $(\text{Bu}^n_4\text{N})_3\text{[Mo}_6\text{O}_{19}]$ was obtained by the electrolysis of **1** using an imposed potential of 1.1 V vs. the above-mentioned reference electrode. We have carried out cyclic voltammetry studies on **1** in DMF-tetrabutylammonium perchlorate at a Pt disk working electrode (scan rate = 20 mVs^{-1}). Over a single cycle between $+1.25$ V and the solvent decomposition potential of -1.70 V, only one quasi-reversible wave corresponding to the $[\text{Mo}_6\text{O}_{19}]^{2-}/[\text{Mo}_6\text{O}_{19}]^{3-}$ couple was observed at $E_1 = -0.29$ V {potentials are with respect to a Ag/AgCl [3.5 mol dm^{-3} KCl (aq.)] reference electrode}.