

# Quantum chemical insights into the initiation mechanism of transition metal catalysed polymerisation of isobutene

Hugh Chaffey-Millar, Fritz E. Kühn\*

Molecular Catalysis, Catalysis Research Center, Technische Universität München, Lichtenbergstrasse 4, D-85747 Garching b. München, Germany

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## ABSTRACT

During the polymerisation of isobutene using highly active Lewis-base initiators such as  $\text{AlCl}_3$ , it has typically been necessary to polymerise isobutene at temperatures between  $-80$  and  $-20$  °C, sometimes in the presence of chlorinated solvents, to minimise the effects of unwanted side reactions. However, a transition metal based catalyst system which enables polymerisation at room temperature and without chlorinated solvents has recently been discovered. In the current manuscript, the first molecular level insights into the previously proposed mechanisms for the polymerisation process are presented based on an ab initio/density functional theory study. Using hexakis-acetonitrile-manganese(II) as a model system, reaction enthalpies and barriers are calculated to determine which mechanisms may or may not be possible. The formation of a hydrogen or alkyl group bonded directly to the manganese may lead to polymerisation, but the proposed mechanisms to generate such a species, as well as other proposed mechanisms, have not been found to be feasible (at least in the exact form originally proposed).

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## 1. Introduction

Polyisobutenes (PIBs) have found application in a range of areas, with the specific application area depending on the molecular weight. High molecular weight polyisobutenes (HM PIBs) with molecular weights above  $3 \times 10^5 \text{ g mol}^{-1}$  have a high viscosity and are used, for example, as additives for chewing gum or as sealants. Medium molecular weight polyisobutenes (MM PIBs) have a molecular weight in the range  $4 \times 10^4$  to  $1.2 \times 10^5 \text{ g mol}^{-1}$  and for instance, due to their cold flow behaviour, find applications as adhesives. Low molecular weight polyisobutenes (LM PIB) are those with molecular weights in the range  $3 \times 10^2$  to  $3 \times 10^3 \text{ g mol}^{-1}$ . Whilst conventional low molecular weight PIBs contain only circa 10% terminal (or “exo”, see Scheme 1(III) vs. Scheme 1(IV)) C=C bond functionalisation, those with high (more than circa 75%) exo functionalisation and which fall into the low molecular weight range are termed highly reactive PIBs. They have particular importance due to their modifiability, finding application in lubricant preparations and as fuel additives [1].

Each year, Badische Anilin- und Soda-Fabrik (BASF) alone produces 100,000 tonnes of PIB [2]. Traditionally, PIB has been prepared via cationic polymerisation using a Lewis Acid (such as  $\text{AlCl}_3$ ,  $\text{BCl}_3$  or  $\text{BF}_3$ ), a trace proton source (such as alcohol or water)

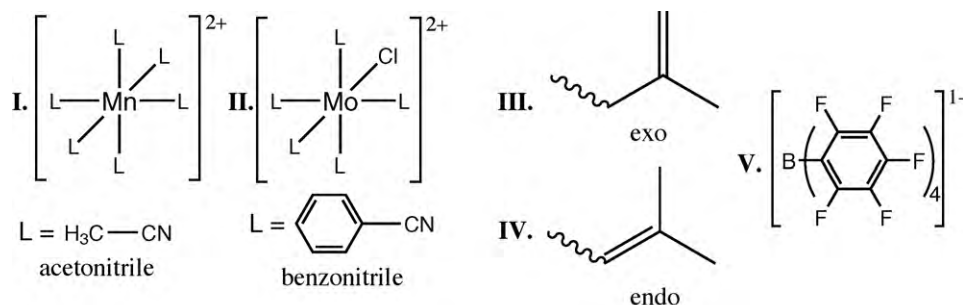
and solvents such as hexane, methyl chloride or dichloromethane. The generated carbocations are extremely reactive and have the potential to undergo chain transfer reactions, which, if it occurs to too great an extent, is undesirable as it inhibits the development of high molecular weights. Consequently, the current industrial production method makes use of temperatures in the range  $-80$  °C to  $-20$  °C as well as chlorinated and non-chlorinated solvents. It is therefore relatively environmentally taxing [2]. In addition to isobutene (IB) homopolymers, there is significant interest in copolymers with isoprene, styrene and derivatives thereof [3–5].

In 2003, a novel class of catalyst comprised of transition metals (originally manganese) complexed with solvent ligands and associated with weakly coordinating counter-anions was shown to be extremely effective for the production of highly reactive PIB at room temperature [2,6–8]. Since the initial proof of concept employing manganese based catalysts (e.g. Scheme 1(I)), subsequent catalysts based on, for example molybdenum [9] (e.g. Scheme 1(II)) and copper [10–12], have achieved operation at room temperature, in non-halogenated solvents (i.e. toluene), up to 90% exo double bond functionalisation of the resulting polymer and nearly 100% conversion after a time of only 15 min.

Despite this considerable and still growing body of experimental work probing the effectiveness of various metals, ligands, solvents, and so on, the mechanism is still poorly understood. A number of possible mechanisms have been proposed [2] but the extent to which these have previously been explored is minimal and has thus far been limited to, for example, inferences from the response of experimentally measurable bulk properties such as end group

\* Corresponding author.

E-mail address: [fritz.kuehn@ch.tum.de](mailto:fritz.kuehn@ch.tum.de) (F.E. Kühn).



**Scheme 1.** (I and II) Two catalysts based on manganese and molybdenum; (III and IV) possible end group structural isomerisms. The former (*exo*) is a requirement for the classification as highly reactive poly(isobutene). (V) An example counter-ion frequently used to form a catalyst.

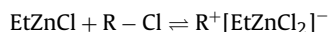
distributions, conversion vs. time, etc. to the various experimental parameters such as reagent concentrations and reaction temperatures.

Thus, the purpose of the current work is to use quantum chemical methods to provide molecular level information about the catalyst system and to gain some insight into which reaction pathways are most likely. This is achieved through a systematic exploration of the proposed mechanisms, with the calculation of reaction enthalpy changes and barrier heights. The manganese catalyst  $[\text{Mn}(\text{NCMe})_6]^{2+}$  appearing in Scheme 1(I) has been chosen for this study since (a) it was the first one to be reported and is therefore subject to a relatively large amount of experimental investigation and (b) it has relatively small ligands, making electronic structure calculations less expensive.

Note that it is not the aim of this study to provide enthalpy changes and barriers that are accurate enough to be compared to experimental data at room temperature. It is also not the aim to consider the role of the counter-ion since it is the previously proposed mechanisms involving interaction of the monomer with the transition metal complex itself that are the focus of this study.

The structure of the manuscript is as follows. Initially, several related systems which have been described in the literature are summarised. Secondly, the computational methods that have been used are detailed. Thirdly, the proposed mechanisms are described in detail, since these set the stage for further discussions. Finally, the computational exploration of the proposed mechanisms and other closely related mechanisms (which are proposed as part of the current manuscript) is discussed.

Bochmann and co-workers have developed a different catalyst system for high temperature (−90 to +35 °C) olefin polymerisations employing on Zinc, and this also yields highly reactive PIBs when isobutene is applied as the monomer [13,14]. These authors proposed a mechanism with an initiation process that depends on the following equilibrium



where R was a cation-stabilising substrate such as *tert*-butyl or cumyl. This makes the mechanism fundamentally different to the one likely to be operative for the catalyst that is the subject of the current manuscript, where no carbocation-stabilising substrate is present.

Two other highly important catalytic systems for olefin polymerisation are those known as Ziegler–Natta and Metallocene polymerisations [15–17], wherein transition metals are also used for the generation of alkyl-backbone polymers from olefins. These differ in the following ways. Firstly, the reagents in Ziegler–Natta and Metallocene polymerisations already contain an alkyl group bonded directly to the metal centre. As can be seen in Scheme 1(I) and (II), the current catalysts do not have this as a feature of their substrate, and various suggestions have previously been made regarding possible pathways to generate this metal–carbon bond.

Secondly, the Ziegler–Natta and Metallocene methods are unable to form homopolymers of the class of monomers known as 1,1-disubstituted  $\alpha$ -olefins, of which IB is a member. (They have, however, been found to form copolymers of isobutylene and ethylene [18].)

## 2. Computational methods

All calculations were carried out using Gaussian 03 revision E.01 [19]. In the literature relating to inorganic complex reactivity, density functional theory (DFT) is frequently used to compute reagent geometries and reaction energetics [20–23]. Whilst these methods frequently generate accurate results for the former task, they can be subject to large errors for energy changes such as enthalpies and barriers [24], particularly when delocalised non-spin-paired electrons are involved [25]. For this reason, after the optimisation of the geometries using DFT methods, the accuracy of the calculated electronic energies have been improved using Møller–Plesset perturbation theory of the second order (MP2) using a large basis set (as detailed below).

The hydrogens of the methyl groups of the acetonitrile (NC–CH<sub>3</sub>) ligands of most of the complexes are subject to very weak interaction with the rest of the molecule [26]. This meant that during optimisation, the forces on these atoms were far below the threshold employed by Gaussian 03 when determining convergence. Even when using tighter convergence criteria and extremely fine integration grids, it was not always possible to fully optimise these methyl groups. Technical considerations aside, the repercussion of the presence of these free-rotor-like groups is that the typical harmonic oscillator approximation of these vibrational modes would be subject to large errors at higher (e.g. room) temperatures. To solve this problem, geometries were considered to have converged if the only remaining (non-reaction coordinate) imaginary frequencies were those of terminal methyl groups. Since low frequency modes contribute very little to the zero-point vibrational energy (ZPVE), this quantity, rather than a full entropy calculation at elevated temperature, was used to calculate a vibrational contribution to the molecular energies. In the cases where imaginary frequencies associated with vibration of these terminal methyl groups existed, they were in the range of −10 to 0 cm<sup>−1</sup> and typically closer to 0 cm<sup>−1</sup>.

Taking the above reasoning into account, the following methodology was employed when calculating the total energy of a species. Geometries and zero-point vibrational energy corrections were calculated using the B3LYP [27–30] functional and a 6-31G(d) [31–34] basis set on all first to third row elements and for manganese a LANL2DZ basis set with an effective core potential (ECP) [35–37]. For geometries with multiple rotational isomers, and pathways involving multiple possible transition states, the lowest energy rotational isomers/transition states were also found by comparing energies calculated at this level. Transition states were located

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