Institution: University of East Anglia		
Unit of Assessment: 8 - Chemistry		
Title of case study: Industrialisation of olefin polymerisation catalysis		
Period when the underpinning research was undertaken: 2000 – 2016		
Details of staff conducting the underpinning research from the submitting unit:		
Name(s):	**Role(s) (e.g. job title):**	**Period(s) employed by submitting HEI:**
Manfred Bochmann	Professor of Inorganic Chemistry	2000 – to present
Period when the claimed impact occurred: 1st August 2013 to 31st December 2020		
Is this case study continued from a case study submitted in 2014? Yes		

1. Summary of the impact

Professor **Bochmann's** research at UEA has provided an understanding of the mechanism of olefin polymerisation that has had a sustained and significant **economic impact** throughout this impact period. The industrial uptake by, for example, the petrochemical sector of new activator systems and improvement in catalyst performance have underpinned the development of numerous commercially viable polyolefin products (e.g. used in the automotive, luggage, and food packaging industries) with sales equating to USD500,000,000.

2. Underpinning research

Between 2000 and 2016, the research group of **Bochmann** carried out a series of research programmes into the activation chemistry and mechanisms of single-site catalysts for olefin polymerisation, mainly metallocenes. This research was undertaken in collaboration with industrial partners and with industrial funding, thus maximising the opportunity for knowledge transfer to the manufacturing industry throughout the period. The research can be described under the following broad headings:

Weakly Coordinating Anions (WCA) (References 1 & 2): Early work on the identification and spectroscopic characterisation of the active species of molecular olefin polymerisation catalysts was followed by the development of activators that led to ultra-active catalysts of a type that are presently used in industrial solution phase processes. This included the development of "super-weakly coordinating" anions for generating highly active soluble catalysts.

Trityl Effect (Reference 3): From 2000-2007 studies on polymerisation kinetics, the solution dynamics and on aggregation phenomena of metallocene catalysts led to the discovery of the "trityl effect", which can increase the activity of metallocene catalysts by up to an order of magnitude without the need for expensive modification of the metallocene component.

Trimethylaluminium and Hafnium Catalysis (References 4 & 5): Research into the role of trimethylaluminium (TMA) in polymerisation catalysis included the first identification of TMA association equilibria and their influence on catalyst activity in zirconocene and hafnocene polymerisation catalysts. Hafnium-based catalysts are now accepted for polyolefins produced for food packaging.

Cationic Polymerisation and Butyl Rubber Production (Reference 6): In collaboration with Bayer Leverkusen (Germany) and Lanxess Inc. (Canada) (1995-2008), **Bochmann** developed an alternative to the current process for producing butyl rubber, originally developed before WWII, which requires extremely low operating temperatures (-100 °C) and consequently high energy costs. Using his weakly coordinating anion chemistry, **Bochmann** was able to provide a more energy-friendly alternative which yields industry-standard polymers at -30 °C.

3. References to the research

The underpinning research outputs have all been published in competitive, international, peer-

reviewed journals and form part of a larger body of such published work.

(UEA authors in **bold**)

1. Synthesis, Structures and Reactivity of Weakly Coordinating Anions with Delocalized Borate Structure: The Assessment of Anion Effects in Metallocene Polymerization Catalysts
   J. Zhou, **S. J. Lancaster**, **D. A. Walker**, **S. Beck**, M. Thornton-Pett and **M. Bochmann**
   J. Am. Chem. Soc. **2001**, *123*, 223 – 237.
   DOI: 10.1021/ja002820h

2. Zirconocene-Catalyzed Propylene Polymerization: A Quenched-flow Kinetic Study
   F. Song, **R. D. Cannon** and **M. Bochmann**
   J. Am. Chem. Soc. **2003**, *125*, 7641 – 7653.
   DOI: 10.1021/ja029150v

3. Activator Effects in Metallocene-Based Alkene Polymerizations: Unexpectedly Strong Dependence of Catalyst Activity on Trityl Concentration
   F. Song, **R. D. Cannon**, **S. J. Lancaster** and **M. Bochmann**
   J. Mol. Catal. **2004**, *218*, 21-28.
   DOI: 10.1016/j.molcata.2004.03.042

4. Formation and Structures of Hafnocene Complexes in MAO and $AlBu^{i}_{3}$/$[CPh_3][B(C_6F_5)_4]$ Activated Systems
   K. P. Bryliakov, E. P. Talsi, A. Z. Voskoboynikov, **S. J. Lancaster** and **M. Bochmann**
   Organometallics **2008**, *27*, 6333 – 6342.
   DOI: 10.1021/om800664p

5. Ligand Mobility and Solution Structures of the Metallocenium Ion Pairs $[Me_2C(Cp)(fluorenyl)MCH_2SiMe_3^{+}\cdots X^{-}]$ [M = Zr, Hf; X = $MeB(C_6F_5)_3$, $B(C_6F_5)_4$]
   C. Alonso-Moreno, **S. J. Lancaster**, **J. A. Wright, D. L. Hughes**, C. Zuccaccia, A. Correa, A. Macchioni, L. Cavallo, **M. Bochmann**
   Organometallics **2008**, *27*, 5474 – 5487.
   DOI: 10.1021/om800486p

6. Highly Electrophilic Organometallics for Carbocationic Polymerizations: From Anion Engineering to New Polymer Materials
   M. Bochmann
   Acc. Chem. Res. **2010**, *43*, 1267 – 1278.
   DOI: 10.1021/ar100044s

KEY GRANTS:

[redacted]

4. Details of the impact

Despite a general move away from single-use plastics, the need for polymers continues, with global polyolefin production having risen from 25,600,000 tonnes in 1983 to over 180,000,000 tonnes forecast for 2022. The global polyolefin market is expected to gross USD300,000,000,000 at the end of the 2022 and to grow at approximately 7% p.a. from 2016 to 2022 [**corroborating source A**]. Since polyolefins are thermoplastics, they are in principle easily recyclable. Research at UEA focussed on so-called "single-site" polymerisation catalysts (i.e., catalysts based on well-defined molecules) and this market sector shows an annual growth rate of more than 10% p.a.

A key route to economic impact for the UEA research on olefin polymerisation catalysis continues to be through industry funded IPR protection. Within the butyl rubber polymerisation area, UEA research has resulted in 5 world-wide 'patent families' each containing 5-7 filings and naming UEA academics as the inventors [**corroborating source B**]. These patents were all financed and continue to be maintained by the industrial partner.

The specific uptake of UEA discoveries within the industrial sector remains a matter of commercial secrecy. Statements from key industrial partners, DSM and Sabic, first obtained for REF 2014 and updated for REF2021 [**corroborating sources C and D**], underline the continued importance of the UEA research.

DSM is a Dutch-based global life sciences and materials company with a wide range of products including ultra-high molecular weight polyethylene (UHMwPE). DSM's production of this material is reliant upon the **trityl effect** discovered by UEA. This material has applications such as knee implants and high-tensile strength fibres (Dyneema® used for nets and ropes for the commercial fishing / shipping industry, and personal ballistic protection). Thus, UEA discoveries are underpinning secondary impact for society in areas of health, productivity and defence. In 2017 DSM had net sales figures of EUR8,600,000,000.

UEA research on the **trityl effect** was instrumental in the development of commercially viable polyolefin products at DSM, as shown by the following statement from the Principal Scientist (Polymer and Catalysis) at DSM:

> '*If I was asked to be specific on a particular theme that has had industrial significance and that can be easily linked to $$$ then his [Professor Bochmann's] work on the 'trityl effect' would stand out. This work has long been regarded as a step change in our knowledge and has led to the commercial success of a family of polyolefin products that only became commercially viable by the addition of an extra equivalent of 'co-catalyst' that led to a 3-4 fold increase in activity and a 2.5 fold decrease in catalyst cost per ton of polymer. Through this atom efficiency, products became economically attractive to produce. ….their sales equate to a 500M USD business.*'
>
> '*The 'trityl effect', insight into MAO, C-H activation work and the mechanistic review papers have aided the development of commercial homogenous and heterogeneous catalysts.*'
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> [**corroborating source C**]

Sabic, a Global Top 10 petrochemical companies based in Riyadh, Saudi Arabia, reported 2017 total sales of GBP31,000,000,000. In Europe, Sabic is a major producer of plastics and chemicals with approximately 6,300 employees. Sabic-Europe operates 13 petrochemical production sites, including a site at Geleen in The Netherlands which produces large volumes of polyethylene (940kt per annum), and polypropylene (620kt per annum). These materials, used in the automotive, luggage, and food packaging industries, are produced by Sabic using weakly coordinating anion discoveries made by UEA.

A supporting statement from the Chief Scientist at Sabic shows the continued importance of UEA research on **WCA** to the operation of the petrochemical plant at Geleen:

> '*To the best of my knowledge, almost all low pressure/high temperature solution processes make use of such WCA's as discrete activators. It is especially in this important area where Professor Bochmann and his co-workers have played a*

major role in the discovery, fundamental understanding and subsequent further development of boron containing WCA's as activators for polyolefins that allowed commercialization of this ground breaking technology.'

[redacted]

'In 2015, …we started a one-year bilateral collaboration with him …, enabling our company to commercialize new polyolefinic materials using the catalyst system studied in this collaboration.'

[**corroborating source D**]

The packaging market accounts for nearly one third of all Sabic-Europe's polymer sales within Europe. For the production of food packaging materials, it is crucial that all polymers comply with EU Plastics Regulations, including the catalysts. The economic relevance of **hafnium-based polyolefin catalysts** is illustrated by the admission of hafnium containing polyolefins to the EU's positive list for substances allowed in Food Contact Applications for polyolefins.

UEA research on **hafnium catalysis** has been important within such polymer production, as corroborated by the statement from the Chief Scientist at Sabic:

'*The commercial relevance of hafnium was not very well recognized because of the generally encountered low productivity. For this, pioneering publications on the performance of hafnium-based polyolefin catalysts by Professor Bochmann's group were and still are leading references and inspiration sources for the research efforts on hafnium.'*

'Leading companies like Dow Exxonmobil, NOVA Chemicals and Mitsui have commercialized similar high temperature solution technologies, including plants in Europe, the US and South East Asia.'

[**corroborating source D**]

5. Sources to corroborate the impact

[A] Global Polyolefin Market Information by Type (Polypropylene (PP), Polyethylene (PE) and Polymethylpentene (PMP)) by Application (Films & Sheet, Blow Molding, Injection Molding and Tapes & Fibers) and by Region – Forecast to 2022, from marketresearchfuture.com (downloaded March 2021)

[B] Patent details:

I. **Polymerization process using zinc halide initiators**
M. Bochmann, A. Guerrero, K. Kulbaba
Canadian CA 2578679 (15.2.2007); EP1834964 (19/9/2007); US2007238843 (22.2.2007); JP2007246902 (27.2.2007) (Lanxess Inc., Canada)

II. **Process for the Production of Butyl Rubber**
M. Bochmann and S. Garratt
Canadian Pat. Applic. 2,441,079 (16.3.2005); China CN 1654487 (17.8.2005); EP 1516883 (23.3.2005); JP 2005089756 (7.4.2005); US 7,041,760 (31.3.2005) (Bayer Inc., Canada)

III. **Process for Preparing Isobutylene-based Polymers**
M. Bochmann, M. Schormann and S. Garratt
Canadian Pat. Applic. 2,368,724 (filing date 21.1.02); Eur. Pat. Appl. 1470167 A2 (27.10.2004); JP 2005515276 (26.5.2005); RU2004125857 (27.5.2005); US2005165182 (28.7.2005); WO03/062284 (31.7.2003) (Bayer Inc., Canada)

IV. **Process for the Preparation of Polyisoolefins via New Initiator Systems of the Metallocene Type**
G. Langstein, M. Bochmann, D. Dawson, A.G. Carr and R. Commander

German DE 19836663.9 (13.8.98). (Bayer Inc. Canada)

V. **Process for the Preparation of Polyisoolefins via New Initiator Systems of the Metallocene-Type**
G. Langstein, M. Bochmann and D. Dawson
German Pat. Appl. DE 1961003331 (30.1.96); Eur. Pat. Appl. 0787748; US 5703182 (Bayer AG, Germany)

[C] Letter of support from Principal Scientist, DSM materials Science Center BV (obtained February 2019)

[D] Letter of support from Chief Scientist, CRD-Advanced Polymer Science, Sabic (obtained February 2019)