Institution: University of East Anglia

Unit of Assessment: 8 - Chemistry

Title of case study:

Industrially relevant olefin polymerisation catalysis at UEA

1. Summary of the impact

Research at UEA over a 20 year period in the area of olefin polymerisation catalysis has had significant **economic impact** through:

- industrial uptake of new activator systems crucial for solution phase polymerisation processes
- improvement in catalyst performance by the 'trityl effect' which is now implemented in industrial processes
- patents taken out and maintained by industry.

2. Underpinning research

From 1993 to present, the research group of **Bochmann** has carried out a series of research programmes into the activation chemistry and mechanisms of single-site catalysts for olefin polymerisation, mainly metallocenes. This research has been undertaken alongside 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
Early work (93-96) was on the identification and spectroscopic characterisation of cationic, 14-electron group 4 metallocenes as active species. This 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
From 2000-2007, studies on polymerisation kinetics, the solution dynamics and on aggregation phenomena of metallocenes 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
Research into the role of trimethylaluminium (TMA) in polymerisation catalysis includes the first identification of TMA association equilibria and their influence on catalyst activity in zirconocene and hafnocene polymerisation catalysts.

Cationic Polymerisation and Butyl Rubber Production
In addition, in collaboration with Bayer and Lanxess (95-08), Bochmann developed an alternative to the, then 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 delivers industry-standard polymers at -30 °C.

Total industrial investment in Professor Bochmann's olefin polymerisation catalysis research from BP, Bayer Leverkusen, Bayer Canada, Lanxess, BASF and Exxon has been ca. £1M, supporting 7 postdoctoral researchers and 6 PhD students.

3. References to the research

(UEA authors in bold)

Weakly Coordinating Anions

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 (154 citations)
doi: 10.1021/ja002820h

2. Cationic Group IV Metallocene Complexes and Their Role in Polymerisation Catalysis: The Chemistry of Well-defined Ziegler Catalysts
M. Bochmann
J. Chem. Soc., Dalton Trans. **1996**, 255 - 270 (855 citations)
doi: 10.1039/DT9960000255

Trityl Effect

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 (36 citations)
doi: 10.1016/j.molcata.2004.03.042

Trimethylaluminium and Hafnium Catalysis

4. Monomer-Dimer Equilibria in Homo- and Heterodinuclear Cationic Alkylzirconium Complexes and Their Role in Polymerization Catalysis
M. Bochmann and **S.J. Lancaster**
Angew. Chem. Int. Ed. Engl. **1994**, *33*, 1634 - 1637 (258 citations)
doi: 10.1002/anie.199416341

5. Cationic Group IV Metal Alkyl Complexes and their Role as Olefin Polymerization Catalysts – The Formation of Ethyl-bridged Dinuclear and Heteronuclear Zirconium and Hafnium Complexes
M. Bochmann and **S. J. Lancaster**
J. Organomet. Chem. **1995**, *497*, 55-59 (86 citations)
doi: 10.1016/0022-328X(95)00109-4

Cationic Polymerisation and Butyl Rubber Production

6. Highly Electrophilic Organometallics for Carbocationic Polymerizations: From Anion Engineering to New Polymer Materials
M. Bochmann
Acc. Chem. Res. **2010**, *43*, 1267 – 1278 (9 citations)
doi: 10.1021/ar100044s

Key Grants and Personnel (all with **Bochmann** as PI)**:**

4. Details of the impact

World polyolefin production has risen from 25.6M tonnes in 1983 to an estimated 150M tonnes in 2010, with a total market value of several billion US$. Research at UEA has focussed on single-site polymerisation catalysts 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 has been through industry funded IPR protection. For example, within the butyl rubber polymerisation area, research has resulted in 5 world-wide ‘patent families’ each containing 5-7 filings and naming UEA

academics as the inventors [corroborating source A]. Importantly, these patents were all financed and continue to be maintained by the industrial partner.

The specific uptake of UEA research results within the industrial sector is a matter of commercial secrecy. However, statements from key industrial partners, DSM and Sabic, indicate quite clearly the importance of the UEA research.

DSM is a Dutch-based global life sciences and materials company with a wide range of products including a range of ultra high molecular weight polyethylene (UHMwPE) 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). In 2012 DSM had net sales figures of €9.13B.

Bochmann's research on the **trityl effect** has been instrumental in the development of commercially viable polyolefin products at DSM, as shown by the following statement from [redacted]:

> 'If I was asked to be specific on a particular theme that has had industrial significance and that can be easily linked to $$$ then it would be his [Professor Bochmann's] work on the 'trityl effect' …. 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' [redacted] which resulted in the products becoming economically attractive to produce. . . . The "trityl" effect and the mechanistic review papers also aided the development of commercial heterogeneous catalysts.'

[corroborating source B]

Sabic, one of the World's top 10 petrochemical companies, is based in Riyadh, Saudi Arabia. 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 (940 ktpa), and polypropylene (620 ktpa). Geleen's output is used in the automotive, luggage, and food packaging industries.

A supporting statement from [redacted] shows the importance of Bochmann's research on **weakly coordinating anions** (WCA) to the operation of [redacted]:

> 'To the best of my knowledge, almost all low pressure/high temperature solution phase processes currently operated by industry make use of such WCA's as activators for polyolefins. 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 groundbreaking technology. [redacted] **Without the introduction of these speciality olefins it is hard to envisage that** [redacted] **would still be in operation today**.'

[corroborating source C]

The packaging market accounts for nearly a 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. Bochmann's research on [redacted] has been important within such polymer production, as shown by the statement from [redacted]:

> 'The commercial relevance of [redacted] was not very well recognized because of the generally encountered low productivity. For this, pioneering publications on the performance of [redacted] catalysts by Professor Bochmann's group .... were and still are leading references …Although not able to go into details, the large economic relevance of [redacted] EU's positive list for

substances allowed in Food Contact Applications.'
[corroborating source C]

5. Sources to corroborate the impact

[A] **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)

(copies of all patents held on file at UEA)

[B] Supporting letter from [redacted] DSM

(held on file at UEA)

[C] Supporting letter from [redacted] SABIC-Europe

(held on file at UEA)