Institution: Cardiff University

Unit of Assessment: Chemistry 8

Title of case study:
Enabling the cost-effective and environmentally friendly production of Perspex

1. Summary of the impact

Cardiff University, through developing and patenting a commercially viable synthetic route to a catalyst, has enabled the application of a new process, the Alpha Process, for the production of methyl methacrylate (MMA), a key commodity precursor to Perspex. The Alpha Process has had economic and environmental impacts.

Lucite International, the world's leading MMA producer, has invested in major Alpha Process production facilities in Singapore and Saudi Arabia, benefitting from a production route which is more efficient, more reliable and cheaper than conventional routes.

The Alpha Process also brings environmental benefits, as it does not rely on the use of corrosive and toxic feedstocks, such as hydrogen cyanide, which are associated with conventional MMA processes.

2. Underpinning research

In 1996 Lucite International (then Ineos Acrylics Ltd., and since incorporated into the Mitsubishi Group) provided a research grant to Professor Peter G. Edwards (Professor of Inorganic Chemistry, Cardiff University) to investigate novel synthetic routes to phosphine ligands for palladium of relevance to the catalysis of the addition of carbon monoxide to ethylene, for the production of MMA and derivative plastics (i.e., PMMA, Perspex or Lucite) [3.1]. This research was carried out in conjunction with Dr Paul Newman (post-doctoral researcher, 1996-99).

Fundamental studies into the reaction and mechanistic chemistry that contributed to the understanding of ligand behaviour and key catalyst design concepts were performed under this grant leading to high-quality outputs in a leading journal [3.2, 3.3]. This work resulted in a much improved synthetic route to the key catalyst ligand component, 1,2-bis(di-*t*-butylphosphinomethyl)benzene. Palladium complexes of this ligand are remarkably active and selective and also show excellent stability (longevity) under reaction conditions; it provides 99.99% efficiency for the addition of carbon monoxide to ethylene in methanol to give the intermediate methyl propanoate.

The new technology this catalyst supports leads to several major advantages:

a) it utilises the efficient conversion of cheap readily available feedstocks (ethylene and methanol),
b) it avoids the requirement for the highly toxic liquid hydrogen cyanide used in the conventional (competitor) process,
c) it is intrinsically more environmentally benign with no toxic waste products,
d) it produces a purer higher quality acrylic resin product for higher value end applications, and
e) it is economically cheaper to operate under milder conditions saving up to 40% on operating costs over the main competitor technologies [3.4].

This methodology was the basis for a patent application, with a priority date of 16th March 1998, naming the Cardiff researchers as inventors [3.5]. Patents have been granted world-wide and are maintained to the present.

In view of its impact, the Alpha process has been recognised by several awards:
The Biennial Kirkpatrick Chemical Engineering Award 2009 - Winner
Chemical Industry Association 2009 Innovation Award - Winner
ICIS Innovations Awards 2009 - Short-listed for Best Product Innovation
The Royal Academy of Engineering MacRobert Award 2010 – Finalist

3. References to the research

[3.1] Research grant: *Catalytic reactions of carbon monoxide with alkenes and alkynes*, ICI Acrylics (name change to Ineos Acrylics), £125,000, 9/12/1996-30/10/1999, PI: Prof. P. G. Edwards.

[3.2] Comments on the Catalytic Alkoxycarbonylation of Alkynes, A. Dervisi, **P. G. Edwards**, **P. D. Newman**, R. P. Tooze, S. J. Coles and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.,* 1999, 1113-1120. Publication date: 01/01/1999. http://dx.doi.org/10.1039/a809624d

[3.3] Synthesis and chemistry of diphenyl-2-pyridylphosphine complexes of palladium(0). X-Ray characterisation of $Pd(Ph_2Ppy)_2$-(η_2-DMAD) and *trans*$Pd(Ph_2Ppy)_2(PhC{=}CH_2)(CF_3CO_2)$ **A. Dervisi**, **P.G. Edwards**, **P.D. Newman** and R.P. Tooze, *J. Chem. Soc., Dalton Trans.*, 2000, 523-528. Publication date: 22/01/2000. http://dx.doi.org/10.1039/a908050c

[3.4] Acrylics for the future, B. Harris, *Ingenia*, issue 45, December 2010, Royal Academy of Engineering, http://www.ingenia.org.uk/ingenia/issues/issue45/harris.pdf

[3.5] Patent: *Process for the preparation of bisphosphines*, **Paul D. Newman**, Richard A. Campbell, Robert P. Tooze, Graham R. Eastham, Jamie M. Thorpe, **Peter G. Edwards**. GB/9805348; PCT/GB/99/00797; WO99/47528; US/6376715. Patent assigned to Ineos then transferred to Lucite and maintained to present. http://www.freepatentsonline.com/6376715.pdf

4. Details of the impact

Advances in bisphosphine ligand synthesis carried out at Cardiff University have enabled industrial scale application of a cost-effective new process, the Alpha Process, for the production of methyl methacrylate monomer for acrylic resins and Perspex production.

The economic impact is demonstrated by investment of US$230 million by Lucite International, part of the Mitsubishi Group, in a new plant in Singapore which has been producing 120 kilotonnes of MMA per annum since 2008.

This process brings major environmental benefits, as it produces only environmentally benign waste products and does not rely on the use of toxic feedstocks, such as hydrogen cyanide and sulphuric acid, commonly used in alternative processes.

Enabling increased end-user applications and industrial production

The success of the Alpha Process was enabled by a patented process developed by Cardiff University [3.5] to scale-up Lucite International's production of the bisphosphine ligand for production of Perspex. Dr. Graham Eastham (Senior Research Scientist for ALPHA Technology, Lucite International) recognised the significance of the Cardiff contribution in developing "a commercially viable synthetic route to produce the phosphine ligand...without this early innovation the Alpha process may well not have become the unqualified success that it is" [5.1].

The key to the process is the remarkable efficiency of the catalyst for the addition of carbon monoxide to ethylene, which is fast (producing 13 kg of methyl propanoate for 1 g of palladium metal per hour of operation) and cost efficient with regard to the amount of expensive and rare palladium metal consumed (10 tonnes of product produced for 1 g of metal consumed). The remarkable selectivity and efficiency of the catalyst allows reliable production under milder reaction conditions, which has a significant beneficial impact on operating costs, safety and energy efficiency. Lucite International estimates that the Alpha process reduces costs by 30-40% compared to the established acetone-cyanohydrin (ACH) process, the mainstay of US and European MMA production, which has remained largely unchanged since the 1930s.

The Alpha process has removed constraints on plant size allowing significantly improved operating economies. As a result of the industrial viability of the process, Lucite invested US$230 Million in 2008 in a manufacturing plant in Singapore to produce 120 kilotonnes of MMA per annum [5.2]. The plant has been running at 100% capacity to date, and accounts for around 3% of global MMA production. Based on the success of the Singapore plant, Mitsubishi Group signed a Letter of Intent with Saudi Basic Industries Corporation, with the tender to issue in 2013, to build the largest MMA plant in the world, costing US$500 million and producing 250 kilotonnes annually (around 6% of global production) [5.3].

The Alpha Process also produces purer MMA, which increases end-user applications. Lucite Perspex is in demand for high margin applications such as screens for mobile phones, televisions and computer monitors, since Alpha process Perspex offers maximum light transmission without disturbing surface hot spots. Growing demand in this area complements conventional uses, including glazing, signage and lighting, moulding and extrusion compounds for automotive, medical and optical industries, surface coatings, emulsion polymers, adhesives, and enamels. Lucite International is the world leader in MMA and PMMA production, with around 25-30% of the global market share, which is valued in excess of US$7 Billion annually and projected to show annual growth of 6.5% up to 2017 [5.4].

Environmental benefits

The Alpha process brings environmental benefits compared to conventional manufacturing technologies, such as the ACH process, which rely on the use of feedstocks that are highly toxic (hydrogen cyanide) and highly corrosive (sulfuric acid). For example, Alpha Process production at the Lucite Singapore plant produces annual savings of 19 kilotonnes of hydrogen cyanide and annual savings of 360 kilotonnes of spent acid, including sulfuric acid and ammonium sulphate, compared to the conventional ACH route.

A further supply chain benefit of the Alpha Process is that it uses cheap, relatively non-hazardous and readily available feedstocks (carbon monoxide, ethylene, formaldehyde and methanol). The atom-efficiency of the process also brings waste management benefits, as it means that there are no toxic wastes or by-products [5.2].

These environmental benefits also have an impact on manufacturing efficiencies through, for example, the reduced use of solvents and reduced storage and waste management facilities required at the Singapore and Saudi facilities. A purer MMA product also has knock-on benefits for downstream users and applications industries in minimising requirements for further purification as well as providing assurance of a dependable supply of higher quality plastics from readily available feedstocks.

5. Sources to corroborate the impact

[5.1] Personal Confirmation of Cardiff's contribution, including through developing patented technology, to the commercial viability of the Alpha process from the Senior Research Scientist

for ALPHA Technology, Lucite International. (Letter on file at UoA)

[5.2] Confirmation of Lucite investment in Alpha process, together with environmental and other benefits, as part of a feature on the Alpha process as a finalist in the Royal Academy of Engineering MacRobert Award 2010,
Acrylics for the future, B. Harris, *Ingenia*, issue 45, December 2010, Royal Academy of Engineering, http://www.ingenia.org.uk/ingenia/issues/issue45/harris.pdf

[5.3] Confirmation of agreement between Sabic and Mitsubishi Rayon to build the largest MMA plant in the world in Saudi Arabia (capital expenditure of $500 million), using the Alpha process. http://www.2b1stconsulting.com/sabic-and-mitsubishi-to-tender-jubail-mma-pmma-epc-contract/.

[5.4] Confirmation of global value of MMA production
http://www.marketsandmarkets.com/PressReleases/polymethyl-methacrylate.asp