Institution: Cardiff University		
Unit of Assessment: Chemistry (8)		
Title of case study: Scaling-up the environmentally friendly production of Perspex®		
Period when the underpinning research was undertaken: 2000 – 2010		
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:**
Peter Edwards Paul Newman	Professor Senior Lecturer	01/02/1984 – 31/12/2013 01/03/2002 – 31/12/2020
Period when the claimed impact occurred: 01/08/2013 – 31/12/2020		
Is this case study continued from a case study submitted in 2014? Yes		

1. Summary of the impact (indicative maximum 100 words)

Poly(methyl methacrylate), or Perspex®, is a commercial material employed in almost all industries, but supply constraints have hampered production in recent years. Cardiff research, through close collaboration with industry partner Lucite International, synthesised the key ligand of the ALPHA process, which enabled industrial-scale manufacture of methyl methacrylate (MMA), the precursor to Perspex®. The ALPHA process achieved greater efficiency than competing MMA production methods, reducing costs by 40%, while removing environmentally harmful process chemicals and subsequently reducing waste. This led to a US$1.1 billion investment to construct a new production plant, and the process now underpins 10% of the world's total MMA production, approximately 370 thousand tonnes per annum.

2. Underpinning research (indicative maximum 500 words)

Since the invention of Perspex® (poly(methyl methacrylate), PMMA) in the 1930s by Imperial Chemical Industries (ICI), its precursor material, methyl methacrylate (MMA), has become a globally traded commodity. Historically MMA was created using toxic and corrosive chemicals, such as hydrogen cyanide and sulphuric acid, which raised production costs and limited the scale of industrial manufacture. Lucite International (formally ICI Acrylics, and now part of the Mitsubishi Group) sought the expertise of Edwards and Newman at Cardiff University, who have over 20 years' experience working on the underpinning chemistry of MMA production. The company wished to establish a new economically and environmentally viable catalytic route for the future manufacture of MMA.

2.1 Refining the ALPHA process

Edwards and Newman's research in the late 1990s led to the development of the ALPHA process: a highly efficient synthetic route to the key catalyst ligand component, 1,2-bis(di-t-butylphosphinomethyl) benzene. Once the process had been identified in principle, continuing research at Cardiff then explored the applied chemistry to enable an efficient and cost-effective application of the ALPHA process at industrial scale. Research explored the feedstock of two competing materials, namely ethylene or acetylene. Although both were viable, only one could be taken forward to pilot scale and eventually to MMA production.

In 2004, Cardiff's research demonstrated that the acetylene pathway is, in principle, more efficient since the phosphine used was cheaper and air stable, and its production of MMA was a single-step process, as opposed to two when using ethylene. The catalyst longevity, however, was lower than that used in the ethylene process, as it was poisoned by allene, an impurity present in acetylene feedstocks. This poisoning was irreversible and removal of allene from the acetylene feedstock was not viable. As such, the ethylene route was ultimately selected for development of MMA **[3.1]**.

2.2 Synthesising the Alpha Ligand

The ALPHA process was an entirely new approach to MMA production, but reliant on the synthesis of a phosphine ligand known as the 'ALPHA Ligand' for which the existing synthesis was prohibitively expensive. Lucite International continued to fund the research of the

Edwards/Newman group between 2000 and 2010 to further refine the patented ligand synthesis developed during their earlier work, in the hopes of translating the Alpha process into industrial production.

In 2004, the Cardiff team developed a cost-effective synthesis of the Alpha Ligand that could support the industrial application of the ALPHA process **[**see **5.3]**. As highly sensitive commercial work, this research could not be made publicly available at the time; it was partly published after 2010 **[3.2]**. The key to the process is the remarkable efficiency of the catalyst for the addition of carbon monoxide to ethylene, which is fast (producing 13kg of methyl propanoate from 0.001kg of palladium metal per hour of operation) and cost efficient with regard to the amount of palladium metal consumed (10,000kg of product produced for 0.001kg of metal consumed).

The Alpha Ligand system was extremely efficient, with Cardiff research concluding that its performance could not be matched by any other palladium/phosphine combination **[3.3]**, and that continuing to investigate alternate catalyst structures would likely be fruitless. As such, the optimised synthetic procedure for Alpha Ligand production became the commercial route implemented in 2008.

3. References to the research (indicative maximum of six references)

[3.1] M.J. Green, K.J. Cavell, **P.G. Edwards**, R.P. Tooze, B.W. Skelton, A.H. White, 'Palladium(II) complexes of new OPN phosphine ligands and their application in homogeneously catalysed reactions of CO with alkenes or alkynes'. Dalton Trans*.,* 2004, 3251-3260. https://doi.org/10.1039/b405586c

[3.2] P.G. Edwards, J.C. Knight, P.D. Newman, 'Synthesis of (1R,4S,6R)-5,5,6-trimethyl-2-phosphabicyclo[2.2.2]octane and derivatives'. Dalton Trans*.,* 2010, 39, 3851-3860. https://doi.org/10.1039/b924983d

[3.3] D. Coleman, **P.G. Edwards**, B.M. Kariuki, **P.D. Newman**, 'Coordination chemistry of *cis,cis* and *trans,trans* 1,1'-[1,2-phenylenebis(methylene)]*bis*(2,2,3,4,4-pentamethylphosphetane)'. Dalton Trans., 2010, 39, 3842-3850. https://doi.org/10.1039/b924982f

4. Details of the impact (indicative maximum 750 words)

A more efficient method of producing methyl methacrylate monomer (MMA), the precursor material for Perspex® and acrylic resins, required a crucial phosphine ligand. Cardiff's research determined a cost-effective method to synthesise the required ligand, which enabled the industrial scale production of MMA. Since the inception of the ligand in 2008, Cardiff's research continues to produce a cheaper, less environmentally damaging and higher quality MMA product, and in 2014 led to a US$1.1 billion investment to create the world's largest MMA plant. The new method now accounts for 10% of the world's annual production of MMA, a market share that continues to grow.

4.1 Enabling the efficient production of MMA

Lucite International is a global leader in the design, development, and manufacture of acrylic products, with 22 plants across 14 locations worldwide and annual revenues of US$1.7 billion. Lucite is the owner of the ALPHA process: a process technology for MMA production that offers significant advantages over existing production methods. Until 2004, however, the potential of the ALPHA process was restricted by the limited availability of an essential phosphine ligand. Dr Jonathan Runnacles, Business Research Director at Lucite International, stated that "*methods of producing this phosphine ligand were at the time prohibitively expensive*" **[5.1]**.

As noted in Section 2, Cardiff's research resulted in a cost-effective synthesis of the phosphine ligand, as well as carbonylation and ligand optimisation needed to support the ALPHA process. Lucite stated: "*Without the development research undertaken at Cardiff by the Edwards-Newman group rendering the Alpha process ligand synthesis commercially feasible,* *the very substantial economic and environmental benefits of the Alpha process would not have been realized as effectively as they have been*" **[5.1]**.

4.2 Improved product quality and reduced waste

The ALPHA process has several significant advantages over the competing acetone-cyanohydrin (ACH/C3) MMA process used in the USA and Europe **[5.2]**, or the isobutylene-based (C4) process used in Asia **[5.2]**. Lucite estimate that the cost of running the ALPHA process is 40% cheaper to operate than their previous ACH-based plants **[5.3]**. Crucially, the feedstock for the ALPHA process (ethylene, methanol and carbon monoxide) are cheaper and more widely available than feedstock for other processes, allowing greater operational flexibility for supply chains and plant locations **[5.1]**.

The ALPHA process has additional environmental benefits as the required feedstock are much less toxic and corrosive than those required for the ACH/C3 process, which are reliant upon hydrogen cyanide and concentrated sulphuric acid **[5.1]**. The atom-efficiency of the ALPHA process also means that there are no toxic wastes or by-products **[5.1]**, in contrast with the stoichiometric ammonium sulphate by-product produced by ACH methods **[5.2]**.

Perspex® with high optical clarity is in demand for applications such as mobile phones, televisions, and computer monitors, and offers maximum light transmission without surface hot spots. Perspex® production has traditionally required an additional step to achieve this clarity, however. Lucite stated that: "*MMA derived through the ALPHA process produces the required quality as an end product, removing the significant manufacturing costs involved for this extra step*" **[5.1]**.

4.3 Investment and launch of the world's largest MMA plant

The first ALPHA-based MMA Production Plant (named Alpha 1) went online in 2008. Following the success of Alpha 1, a joint venture was formed between Lucite, Mitsubishi Chemical Company, and Saudi Basic Industries Corporation to establish the world's largest MMA production plant. As a result, in 2014 the joint venture invested US$1.1 billion to begin construction of the Alpha 2 plant in Saudi Arabia **[5.1]**. The Alpha 2 plant began full production in 2018 and produces 250,000 tonnes of MMA annually **[5.1]**. Alongside the continuing production from Alpha 1 (120,000 tonnes per annum), Lucite confirmed that since Alpha 2 came online, the combined current output has "*contributed approximately 10% of the world's MMA demand*" **[5.1]**, approximately 370,000 tonnes per annum, significantly helping to relieve global supply constraints **[5.3, 5.4]**.

A key advantage of the ALPHA process is that it removes scale limitations, "*enabling large single stream scale plants*" such as Alpha 1 and 2 **[5.1]**. The ALPHA process removed constraints on plant size experienced by other MMA production processes (e.g. maximum 80,000 tonnes per annum for the C4 Process), allowing significantly improved economies of scale **[5.2]**. Lucite have since confirmed their intention to construct an even larger plant on the Gulf of Mexico, USA **[5.5]**; the Alpha 3 plant has a planned capacity of 350,000 tonnes per annum and is due to begin operations in 2025 **[5.1]**.

In summary, Cardiff research changed the landscape of global Perspex® production via enabling the industrial scale application of the ALPHA process. This provided the global Perspex® industry with a cost-effective approach at scale, delivering significant economic and environmental benefits.

5. Sources to corroborate the impact (indicative maximum of 10 references)

[5.1] Testimonial: Dr Jonathan Runnacles, Business Research Director, Lucite International

[5.2] A Winning Process. Chemistry & Industry: 20 (2009). Society of Chemistry and Industry website

[5.3] Methyl Methacrylate (MMA) Production and Manufacturing Process (2010). Independent Commodity Intelligence Services website

[5.4] Katherine Sale. EPCA ’17: Global MMA supply constraints may put Europe at its tightest year to date (2017). Independent Commodity Intelligence Services website

[5.5] New ALPHA MMA plant to be constructed on the US Gulf Coast (2020). Company News. Lucite International website