Institution: University of Bradford		
Unit of Assessment: B8 Chemistry		
Title of case study: Controlling Polymer – Solvent Interactions to Improve British Manufacturing Performance		
Period when the underpinning research was undertaken: September 2015 – March 2020		
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:**
Dr Thomas Swift Prof Stephen Rimmer Dr Richard Telford	Assistant Professor Professor of Chemistry Associate Professor	2016 – Present 2015 – Present 2005 – Present
Period when the claimed impact occurred: September 2017 – July 2020		
Is this case study continued from a case study submitted in 2014? N		

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

We have provided expertise on polymer/solvent interactions to UK companies to enable them to develop manufacturing processes and resolve product performance issues. This has led to the development and soft launch of two new products (Silicone Ostomy Adhesive Dressings and Melt and Pour Soap Base Formulations), with associated capital investment (a combined value of over GBP2,000,0000) in manufacturing activities (Brighouse, W. Yorkshire and Skipton, N. Yorkshire) resulting in job creation and product diversification for the companies. Additionally, characterisation method development on difficult (previously described as impossible) to characterise materials enabled the defence of manufacturing patents and retention of a product line that was challenged by regulatory bodies.

2. Underpinning research (indicative maximum 500 words)

The polymer industry is a major component of UK manufacturing, with the plastics industry having a turnover of approximately GBP23,500,000,000 and currently employing approximately 170,000 people (6.5% manufacturing jobs in the UK), 10% of which are in the Yorkshire & Humberside region rising to almost 50% in the surrounding regions. The University of Bradford (UoB), with its location at the centre of this activity, is ideally suited to assist industry in solving many of the material challenges it faces.

Our research has focussed on providing a better understanding of how polymers respond to their environment, either by changes in their configuration or degradation (R1), and how internal (molecular weight (R2), charge (R3)) and external (temperature, pH, humidity, adsorption (R2-R4)) factors alter their physical properties. This fundamental research into polymer properties has greatly advanced understanding of interpolymer (R3,R5) and polymer-mineral (R4) complexation.

We have studied the complex interactions of stimuli-responsive polymer systems in solvated systems. For example, a system was developed, using methanol as a mobile phase, to investigate molar mass distributions of poly(N-isoproplylacrylamides (PNIPAM) that are often difficult to analyse by size exclusion chromatography (Wellcome Trust, 0998800/B/12/Z) (R6). DOSY NMR generated intrinsic viscosity data that was employed, in conjunction with a viscometric detector, to provide absolute calibration. The system's utility was demonstrated by providing the absolute molar mass distributions of dispersed highly branched PNIPAM with biologically functional end groups. We have also used fluorescence polarised anisotropy to study segmental mobility, and diffusion studies to measure hydrodynamic radii (R6).

By combining fluorescence and NMR methods we provided breakthrough explanations for the behaviour of solvated polymers in complex mixtures (R5), composite gels (R3) and dilute solutions (R2). Fluorescence anisotropy was used to demonstrate complex formation of a range of polymers in dilute solutions of poly(acrylic acid) (PAA), functionalised with acenaphthylene, by monitoring the reductions in segmental motion of the chain as the complexes formed. We also showed that solvation energies and p*K*a play an important role in complex formation. Using FRET studies, we demonstrated that complexes are not ladders composed of extended chains as generally believed, but colloidal 'co-globules' (R5). We also showed how ionic block copolymers of opposite charge segments can form self-healing gels (R3) (MRC MR/N501888/2). Employing fluorescence spectroscopy on aqueous solutions of PAA we established that polymers with low molar mass, (Mn < 16.5 kDa) do not exhibit a pH-responsive conformational change, typical of higher molar mass PAA (R2). This research has established the Polymer Chemistry Group at UoB as a centre of expertise in polymer/solvent interaction.

These techniques can be used to study model systems and can easily be applied to industrially relevant polymers that are vital components in many manufacturing processes (R1,R2,R5). The group has drawn on these studies and offered our expertise to industrial partners during the period. Partners who have benefitted from our research insights and expertise include Trio Healthcare Ltd (understanding the behaviour of additives in silicone materials (TS (2017 - 2019)), White Sea and Baltic (improving analytical capabilities on difficult to characterise polymeric materials (TS, SR, RT (2018 – 2019)) and John Drury (improving our understanding of fundamental processes that underpin thermally responsive materials (TS, SR (2018 – 2020)).

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

R1. Melo, P. et al. (2019) Osteoinduction of 3D printed particulate and short-fibre reinforced composites produced using PLLA and apatite-wollastonite, *Composite Science and Technology*, 84: 107834. https://doi.org/10.1016/j.compscitech.2019.107834

R2. Swift, T. et al. (2016) The pH-responsive behaviour of poly (acrylic acid) in aqueous solution is dependent on molar mass, *Soft Matter*, 12(9): 2542-2549. https://doi.org/10.1039/C5SM02693H

R3. Banerjee, S. et al. (2018) Self-healable Fluorescence Active Hydrogel Based On Ionic Block Copolymer Prepared via Ring Opening Polymerization and Xanthate Mediated RAFT Polymerization *Polymer Chemistry,* 9: 1190-1205. https://doi.org/10.1039/C7PY01883E

R4. El-Taboni, F. et al. (2020) Fluorescence Spectroscopy Analysis of the Bacteria–Mineral Interface: Adsorption of Lipopolysaccharides to Silica and Alumina, *Langmuir*, 36(7): 1623-1632. https://doi.org/10.1021/acs.langmuir.9b02158

R5. Swift, T. et al. (2017) Resonance Energy Transfer across interpolymer complexes of poly (acrylic acid) and poly (acrylamide), *Polymer*, 123: 10-20. https://doi.org/10.1016/j.polymer.2017.06.069

R6. Swift, T. et al (2017) Analysis using size exclusion chromatography of poly(N-isopropyl acrylamide) using methanol as an eluent, *Journal of Chromatography A*, 1508: 16-23. https://doi.org/10.1016/j.chroma.2017.05.050

Grants and other External Funders:
Swift, T. Solution Properties of Poly(oxazoline) materials, Royal Society of Chemistry (RM1602-1695), 2017 – 2019, GBP5,000

Swift, T. Examining Fundamental Issues in Isopropyl Oxazoline Cationic Ring Opening Polymer Synthesis, Royal Society (RSG\R1\180342), 2018 – 2019, GBP14,880.

Translate Medtech Summer Internship, 2018, GBP2,610.

Swift, T. Proof of Feasibility for non-biodegradable, body-temperature-reverting, shape-memory-polymeric implants, Research England Connecting Capabilities Fund: Grow Medtech, (POF000071), January 2019 – March 2021, GBP19,845.

Swift, T. Time-Resolved Fluorescence Investigation of Polymer-Quenched Pyrene Labelled Stimuli Responsive Polymer Solutions with use as a Light Harvesting Accelerator, Royal Society of Chemistry (RF19-5059), January 2019 – March 2021, GBP3,803.

Rimmer. S & Swift. T. SmartSwab: Smart Materials for Detection of Infection, Research England Connecting Capabilities Fund: Grow Medtech (POC000136), Jan 2020 – Jul 2021, GBP GBP79,429

Industrial sponsorship and funding for this research towards TS research group has come from Trio Healthcare (GBP40,080), White Sea and Baltic Ltd (GBP10,042), John Drury Ltd (GBP30,000), Cimpol (GBP2,620), Scott Bader (GBP480) and Lambson Limited (GBP720).

Rimmer S. & Swift, T. Early detection of urinary tract infection–A smart materials technology application., Research England Connecting Capabilities Fund: Grow Medtech (POM000228), Jan 2021 – Jul 2021, GBP4,992

Rimmer, S.; Garg, P. (LV Prasad), MacNeil, S. (Sheffield), Douglas, I. (Sheffield) UK-India Centre for Advanced Technology-Minimising Anti-Microbial Resistance MRC Centre (MR/N501888/2), 2015-2019, approx. GBP1,500,000.

Rimmer, S. Garg, P. (LV Prasad), MacNeil, S. (Sheffield), Douglas, I. (Sheffield) Development of a rapid system for diagnosing corneal infections using pathogen-responsive polymers (0998800/B/12/Z), 2013 – 2017, total value GBP888,000.

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

Impact on Healthcare

Trio Healthcare Ltd manufacture silicone-based flange extenders and other medical products for people who have stomas, estimated to be around 100,000 people in the UK. Trio wanted to improve their products to make them easier to wear and remove without damaging skin around the stoma. They approached the University of Bradford, due to our expertise in polymer-polymer interactions, to develop a new product.

The Bradford Team identified additives which improved product performance (e.g. flexibility, breathability, improved adhesion, will not absorb moisture). A comprehensive report outlining the scientific rationale for the superiority of this product was presented to Trio in August 2018, enabling them to finalise the product formulation.

Trio then developed new manufacturing processes, requiring in excess of GBP1,000,000 investment in capital and job creation at their plant in Skipton, to trademark and launch a new product range based on Sil2™ Breathable Silicone Technology, a unique silicone adhesive blend that breathes and feels just like normal skin. The University of Bradford team analysed, assessed and provided feedback to Trio about inconsistencies in the products due to large scale manufacturing process, to ensure the mass-produced products can be manufactured to a consistently high quality.

The University of Bradford has been engaged in further product development through evaluation of product performance and volunteer feedback from wearers who have reported increased quality of life due to its increased comfort for extended wear and reduced pain on removal (E1, E2). Without the expertise of the team at the University of Bradford the products would not contain the final additive mixture that leads to its high levels of performance, including increased comfort for extended wear, reduced pain on product removal and thus improved quality of life (E2). Although the formal product launch, was delayed due to the COVID-19 pandemic (E2), Trio nevertheless pressed forward with a soft launch in summer 2020, allowing customers to request samples of the product ahead of the formal launch. Trio anticipate a global market of USD3,5,000,000,000, with GBP300,000,000 anticipated for the UK market alone. The Sil2™ technology has already been employed in a range of flange extenders, with end-users enthusiastically expressing how the improved formulation has improved their quality of life, exemplified by the following quote from a user: "*The extenders have literally **changed my life**. I was extremely allergic to every other extender product and they would peel off at the edges. The Trio extender not only agrees with my skin, I can also manipulate it to work with my belly button. They do not peel at the edges and I can re-stick them if I need to*" (E1).

Impact on Product Development for International Markets

White Sea and Baltic (WSB) hold two long-standing patents on their product Glo-Quench™ PAS, a cationic water-soluble polymer used for the neutralization of the optical brightening effect of fluorescent whitening agents which is added to paper and packaging products to ensure reader comfort for long periods of reading and that light colours are not "washed out" (for example enhancing eye comfort for people reading printed papers). This is a product that WSB have manufactured and sold since 1999 and whose sales in 2019 were worth in excess of GBP100,000 (E3) to the company. The use of Glo-Quench™ PAS was challenged in 2017 by the US Food and Drug Administration (FDA) on the grounds that the FDA did not believe the chemical manufactured by WSB was the same as that listed in the patents. This halted WSB in its attempts to introduce Glo Quench™ PAS into new markets which require regulatory approval from the FDA.

Previous testing by conventional methods, carried out by multiple analytical suppliers, had yielded inadequate data. In 2018 the material was analysed by the Polymer Chemistry group at the University of Bradford. The team used techniques described in section 2 to fully characterise the material. Specifically, methanol size exclusion chromatography to reduce column adsorption, diffusion NMR to determine product hydrodynamic radii and viscosity profiles, and in-depth fluorescence spectroscopy were employed to produce a full characterisation of the material across five repeat batches, and produce a final report. This report was submitted by WSB to the FDA as supporting evidence for the validity of the original patents.

This allowed WSB to successfully defend the patents by demonstrating the properties of the specified polymers systems. As of 2019 the FDA has accepted the validity of the original patents, based on the analytical evidence provided by the team at the University of Bradford. This has provided the company the opportunity to advance to the next stage of approval process for their products to enter new markets (E3).

Impact on Personal/Home Care Product Development

In 2018 John Drury Ltd (JD) approached the University of Bradford to lead the redevelopment of their soap product towards the melt and pour market. This is a completely different commercial sector that required ground up reformulation of their soap product in an area of formulation science in which JD had limited expertise. JD was particularly interested in the thermal responsiveness of their product materials, to ensure both stability and functionality of the melt and pour aspects.

As a result of the successful completion of early proof-of-concept research led by the University of Bradford, in 2019, JD procured and replaced 2 plastic tanks with 2 new 4 Tonne heated, jacketed tanks to facilitate full-scale production. This represented a significant manufacturing investment (GBP35,000 per tank). JD then went on to purchase ancillary equipment such as a filling line, in total representing a six-figure investment which the company would have not made without the findings from our work. JD is now confident that the melt and pour product will become a key product offering for the business and this has provided increased flexibility to their manufacturing operations enabling them to respond to a volatile international marketplace. The new tanks and filling lines have opened up new product range opportunities in lotions and creams, previously not available.

The new understanding of ingredient interactions with moisture has allowed the provision of specific guidance on the storage conditions, use and shelf life of materials based around sound formulation and polymer science not previously understood by the business before their interactions with the University of Bradford (E4).

Given the demand for core antibacterial products and hand sanitisers throughout 2020, the increased production capacity purchased as part of this collaborative effort has been used to generate over a thousand tonnes of antibiotic (disinfectant) cleaning materials for use throughout the UK to assist with the pandemic. The availability of the new manufacturing capacity was directly responsible for their ability to respond to the changing market focus (E4).

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

E1. Osteomates: User Reviews https://trioostomycare.com/ostomates/reviews/

E2. Testimonial letter from Global Marketing Director, Trio Healthcare

E3. Testimonial letter from Technical Manager, White Sea and Baltic

E4. Testimonial letter from General Manager, John Drury