NZIC

Chemistry

IN NEW ZEALAND

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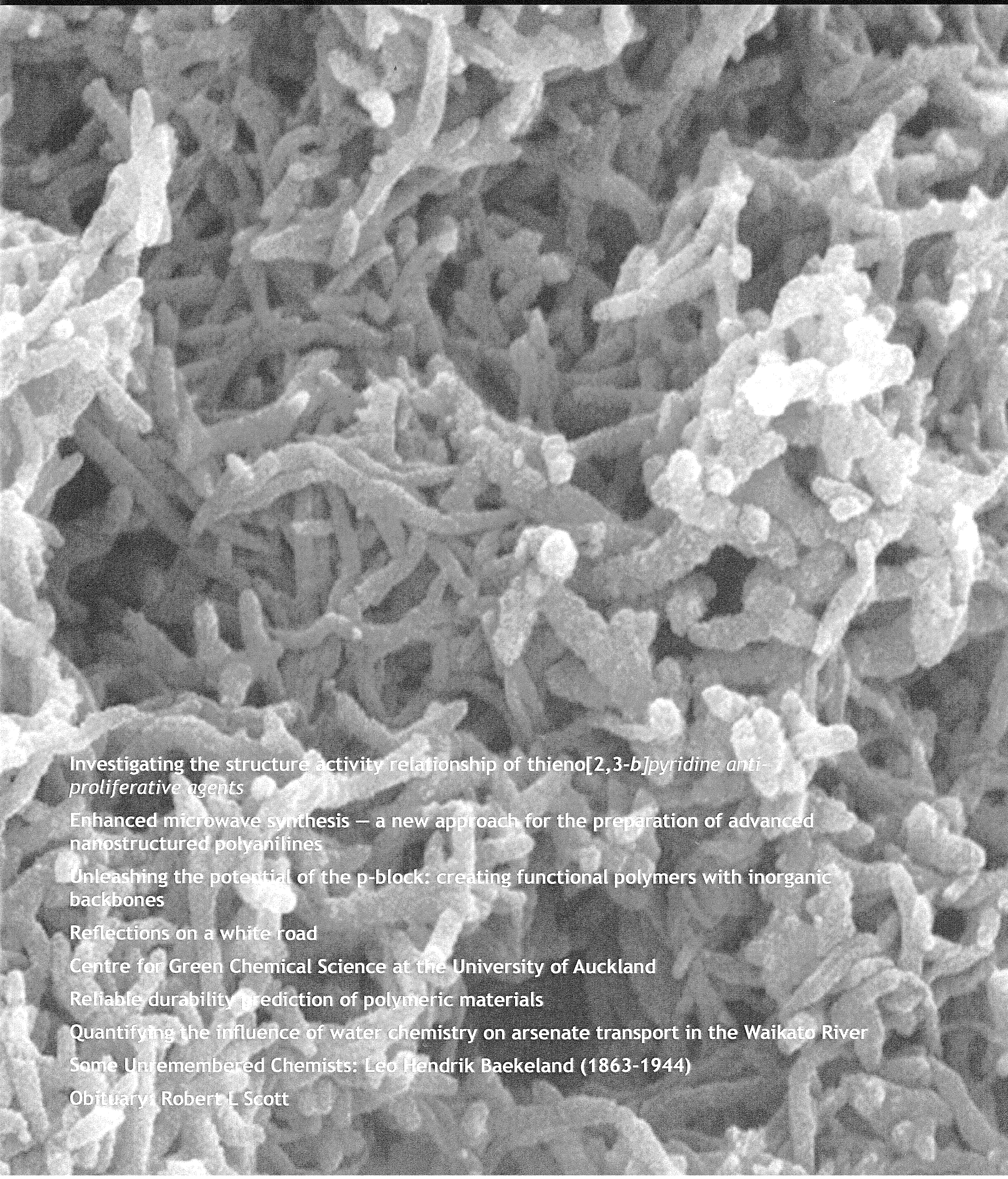

Investigating the structure activity relationship of thieno[2,3-*b*]*pyridine anti-proliferative agents*

Enhanced microwave synthesis — a new approach for the preparation of advanced nanostructured polyanilines

Unleashing the potential of the p-block: creating functional polymers with inorganic backbones

Reflections on a white road

Centre for Green Chemical Science at the University of Auckland

Reliable durability prediction of polymeric materials

Quantifying the influence of water chemistry on arsenate transport in the Waikato River

Some Unremembered Chemists: Leo Hendrik Baekeland (1863-1944)

Obituary: Robert L Scott

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NZIC Chemistry
IN NEW ZEALAND

Volume 80, No.3, July 2016

Articles and Features

Other Columns

Comment from the President

The 2016 budget provided a significant boost to science research spending over the next four years which the chemistry-related fields should hopefully be able to share in. There will be an increase in the Endeavour Fund (formally the Ministry of Business, Innovation and Employment Contestable Science Fund) of $113.8 million, a $66 million increase over four years for the Marsden Fund and a further $63 million increase over four years for the new Strategic Science Investment Fund (formally Core Funding) although in this case, it appears a significant amount of this is pre-allocated to non-chemistry related disciplines. There has been further investment in the development of NZ and international research collaborations as well, with the new Catalyst international fund receiving $15 million over four years. While it may not be as much as people were hoping for, it is certainly a move in the right direction. See: *www.budget.govt.nz/budget/2016/releases/r9a-joyce-fact-sheet-1-innovative-nz-410-5m-boost-for-science-and-innovation.htm* for further details.

In my last President's comment, I made a call to the membership to freely express any opinions they might have about the NZIC as an organisation to either myself or to other members of the sub-committee, Associate Prof Paul Plieger (p.g.plieger@massey.ac.nz) (Chair), Prof. Penny Brothers (p.brothers@auckland.ac.nz), Associate Professor Gordon Miskelly (g.miskelly@auckland.ac.nz), Associate Prof. James Crowley (jcrowley@chemistry.otago.ac.nz) and Dr Suzanne Boniface (suzanne.boniface@vuw.ac.nz). It appears the NZIC is doing a bang up job and the membership is extremely happy as I did not receive any comments at all! And neither, for that matter, did the committee. I do implore you to take the time to express your opinion, good or bad, as it is clear from our declining membership that we are not delivering the required experience / value to members that we should be.

I hope everyone took the opportunity to partake in the salary survey held recently. Results should be ready by the October issue.

Finally, members are reminded that it is not too late to register for the NZIC conference for 2016 in late August. It promises to be a memorable conference with a diverse programme.

Paul Plieger

Comment from the Editor

Thanks to everyone who took the time to respond to the salary survey that ran during March. The response rate was not overwhelming, at around 30%, and as Paul has already mentioned, we do face difficulty in extracting feedback and comment from our membership. I hope that this is simply due to people just having too many demands on their time. During the month-long period that the NZIC survey ran, I had no less than 4 requests to complete various other surveys myself which, to be honest, became tedious. However, if the reason for a poor response is that the Institute is not seen to be particularly relevant to many people then we need to know so that this can be addressed and remedied.

Nevertheless, there is still a lot of information to have come out of the salary survey and I think it will prove to have been a valuable exercise. I am currently in the midst of compiling a summary of the results which will be published in the October issue of *Chemistry in New Zealand*. While the questionnaire was designed to be quick and easy to complete by making it as much a "tick the boxes" exercise as possible, the individual comments are always very interesting to read and provide some illuminating perspectives on various aspects of chemistry employment in NZ.

I am looking forward to attending the NZIC-16 conference in Queenstown in August, catching up with old colleagues and meeting some new members. While it is not the purpose of my attendance (!), I will be on the lookout for interesting presentations which might provide the opportunity to be easily converted to articles that could be published in our journal without too much extra effort. So I may take the opportunity to shoulder-tap a few people for additional contributions that I hope will appear in future issues. See you there.

Cath Nicholson

New Zealand Institute of Chemistry
supporting chemical sciences
July News

AUCKLAND

The University of Auckland School of Chemical Sciences

Autumn graduation 2016

The School of Chemical Sciences held a morning tea on 11 May to celebrate graduation. This included a short prize-giving to award the Briggs Prize for the most distinguished research worker who has submitted a thesis for the degree of PhD in chemistry during the calendar year. We congratulate the winner *Lisa* **Pilkington** and her supervisor (Associate Professor *David* **Barker**) on this high level of achievement. Congratulations also to our 200 graduates (including ten PhD graduates) with eight different degrees between them including: chemistry, medicinal chemistry, food science, wine science and forensic science.

Upper: Associate Professor David Barker holding the Briggs Prize with Professor Kevin Smith (Head of School), Middle and Lower: School of Chemical Sciences, Autumn Graduation Photos

SCS success in Silicon Valley

Associate Professor *Cather* **Simpson**'s *Engender technologies* has made the finals in the AgTech category for the World Cup Tech Challenge 2016. This is the only NZ company to make the finals in any category. Cather will compete on the World Cup Tech stage at Microsoft's Mountain View campus in Silicon Valley. See more at: www.siliconvalleyforum.com/article/world-cup-tech-challenge-2016---finalists-announced#sthash.oJuZ88Wi.dpuf

Congratulations

Congratulations to Cather again for being named a finalist for the KiwiNet Research Commercialisation Awards 2016. See more: www.nzherald.co.nz/science/news/article.cfm?c_id=82&objectid=11637593. Cather also did an interview with Kim Hill on the radio. For more details see: www.radionz.co.nz/national/programmes/saturday/audio/201801569/cather-simpson-photonics-and-sperm

Dr Duncan McGillivray has been awarded the Dean's Award for Excellence in Teaching for 2015. Congratulations Duncan!

Dr Duncan McGillivray winning the Teaching Excellence Award from the Dean of Science, Professor John Hosking

Professor *Christian* **Hartinger** has been named as the recipient of the 2016 Society of Biological Inorganic Chemistry Early Career Award. This is a significant international award and is well deserved. Congratulations to Christian!

Aeroqual, co-founded by Professor *David* **Williams**, won a NZTech Award (the *Endace Innovative Hardware Product Award*). More details here: www.hitech.org.nz/2016-hi-tech-awards-winners-announced.html

Congratulations to Bicheng (Amy) Zhu who received the *Best Poster Award* at the 19th Topical Meeting of the International Society of Electrochemistry held at The University of Auckland. Amy is a PhD candidate in Professor *Jadranka* **Travas-Sejdic**'s group and the research she presented at the conference was on *Label-free electrochemical aptasesnor forfemtomolar detection of 17β-estradiol.*

Recent successful PhD completions from SCS (with supervisor names)

- Eletra Williams – Dr Douglas
- Elisa Lam – Associate Professor Yacine Hemar
- Meet Mistry – Dr David Ware and Penny Brothers
- Lachlan Blair – Dr Jonathan Sperry
- Michelle Van Rensburg – Dr David Barker

The Chemistry Olympiad camp

The Chemistry Olympiad camp was held in the School during the mid-semester break in April. 28 students from high schools around New Zealand participated in morning lecture sessions and afternoon laboratory sessions. This culminated in a practical exam and a theory exam to choose four students to attend the 48th International Chemistry Olympiad in Tibilisi, Georgia. Three of the students selected were from Maclean's College in Howick: Edward Liu, Lucas

Lee and Frank Zhang. The fourth student attends St Andrew's College in Christchurch: Ellena Black. We were particularly impressed with Ellena's progress during the six-month programme. She went from number 92 on our ranking list to make the team. Many thanks to *Katrina* ***Graaf*** and her team who did a great job with the laboratory arrangements.

Auckland Cancer Society Research Centre (ACSRC)

The Auckland Cancer Society Research Centre (ACSRC) celebrated the 60th anniversary of its founding with an Open Day on 9 April at the Medical and Health Sciences Grafton campus of the University of Auckland. The celebrations were opened by introductory comments from the Dean of the Faculty Professor John Fraser, the CEO of Cancer Society Auckland-Northland John Loof and ACSRC Director Professor *Bill* ***Denny***. Activities included posters on the history of the ACSRC, posters presented by attendant staff on their work, a series of 15-minute talks by staff and guided tours of the laboratories. The day was a great success, with over 600 visitors attending.

The ACSRC was set up in 1956 by Cancer Society Auckland, with an initial staff of six and a mission to develop new therapies for cancer. It has a current staff of about 80 and during its 60 years to date it has delivered on that mission, bringing (with various industrial partners) 12 new drugs to clinical trial with a further five currently partnered for development towards trial.

The New Zealand Institute of Advanced Study (NZIAS)

From the Massey University Albany Campus

Professor *Peter* ***Schwerdtfeger*** has accepted the position of Institute Head for the New Zealand Institute for Advanced Study at Massey University Auckland. He is currently invited by the Noble Foundation in Sweden to give a talk on superheavy elements.

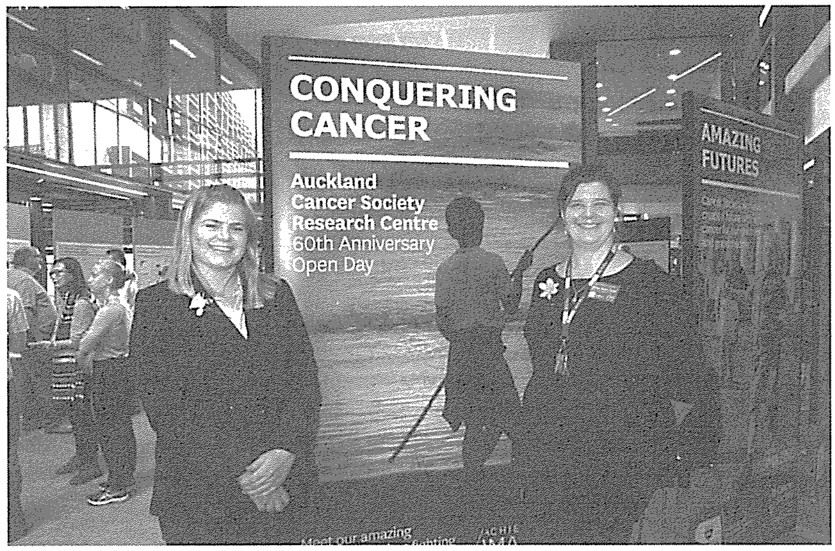
Auckland University of Technology

AUT's new Bruker 400 MHz NMR spectrometer was officially 'launched' by Steven Joyce, Minister of Tertiary Education, on 23 February. This has greatly facilitated synthetic chemistry at AUT and the multinuclear probe means that some less common nuclei are being actively explored.

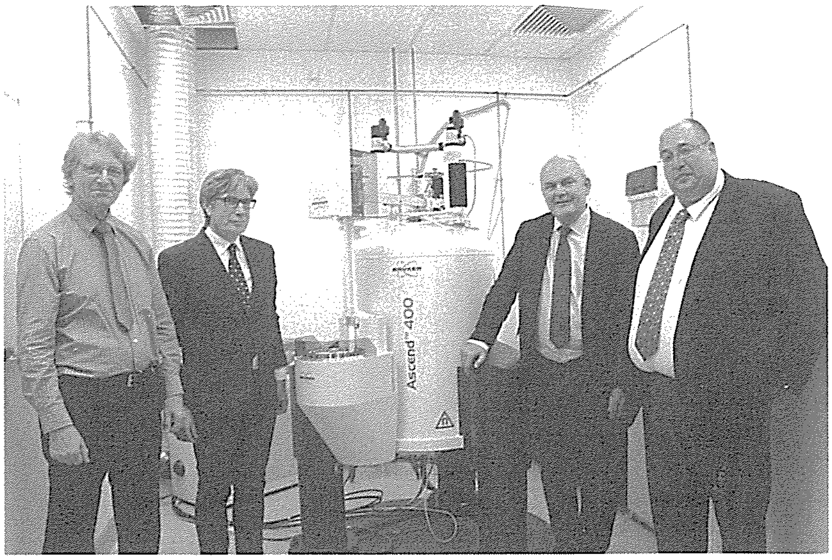
The (newly christened) School of Science has appointed *Jack* ***Chen*** as a lecturer in organic chemistry. Jack hails from the Brimble Group, and for the last few years has been a postdoc at both Bristol and Padova. Jack starts at AUT in early July. The large number, high quality, and international nature of the applicants for this position speak to the allure of academic positions not only in New Zealand but worldwide. Other new faces in the School of Science include Frank Müller, a part time technician employed to look after the NMR, and Franko Schrumpf and Vinay Bharadwaj, PhD students with *Allan* ***Blackman*** and *Nicola* ***Brasch***, respectively.

Allan Blackman's scientific activities were somewhat curtailed when he managed to break both arms in an apparently mundane fall off his bike. While making life in the lab pretty much impossible, he was, to his chagrin, still able to give lectures. The osseo-integrative abilities of element 22 have led to a fairly rapid recovery.

John ***Robertson*** is retiring from AUT after over 22 years of service, to move to Dunedin. He did his PhD in organic chemistry at Auckland under Con Cambie, and after some years spent in Canada, returned to



The ACSRC open day



The new AUT NMR spectrometer, pictured with (from left), Len Gillman (Head of School), Derek McCormack (Vice Chancellor of AUT), Steven Joyce (Minister of Tertiary Education) and Dr Frank Müller (NMR Technician) a lectureship at, what was then, the Auckland Institute of Technology. Over the intervening years he has broadened the scope of his science such that he has managed a course on food industry legislation and flies drones in Australia. His common-sense approach to bureaucracy (ignore it), and his vast practical knowledge, will be sorely missed.

In November 2015 Nicola Brasch went to the US, visiting her PhD students at her former institution and Florida International University, in Miami. In December 2015 Nicola gave an oral presentation at the Australasian and Japanese Joint Meeting of the Societies for Free Radical Research (SFRR A+J) in Christchurch and in April this year she visited colleagues at the Institute of Fundamental Sciences at Massey University. In January and February her and Cather Simpson's US collaborator Paul Sampson and their jointly supervised student Yang Zhou visited AUT, thanks to a Supplemental Funding grant from the US NSF. Nicola's PhD student, Ruth Cink, chaired the inaugural annual AUT School of Applied Sciences Showcase (SASS) of research earlier this year.

We are pleased to report that the newly renovated chemistry lab, officially opened late last year, has taken the recent investment in chemistry by AUT to in excess of $2.5 million.

CANTERBURY

University of Canterbury

Congratulations to *David **Lim*** and *Laura **Lopez Comi*** who both completed their PhD studies in March. David Lim successfully defended his thesis entitled *Synthesis of O-linked glycopeptides using enzymatic catalysis* supervised by *Antony **Fairbanks**.* Laura Lopez Comi successfully defended her thesis entitled *Single-column model analysis of available NIWA observations to determine the self-cleaning capacity of the atmosphere* supervised by *Bryce **Williamson**.* We wish them all the best and many years of success in their brilliant-to-be careers.

Welcome to Professor *Richard F. W. **Jackson**,* Professor of Synthetic Organic Chemistry. Richard obtained his BA in Chemistry from the University of Cambridge in 1981. After his PhD (Cambridge 1984) he became a Postdoctoral Research Fellow at the ETH in Zürich, Switzerland. In 1985 he was appointed to a lectureship at the University of Newcastle, where he was promoted to Reader in 1994 and to Professor in Synthetic Organic Chemistry in 1996. In 2001 he was appointed to a Chair in Synthesis at the University of Sheffield. He served as Head of the Department of Chemistry from 2003-2007 and returned to this role for a further term (2011-2014).

Welcome to Postdoctoral Fellow Dr *Prathik **Roy*** who has joined Professor Alison Downard's group and is co-supervised by Dr *Martin **Allen**.* He earned his MSc at VIT University in India, and his PhD in Material Chemistry from National Taiwan University in Taiwan working with Professor *Huan-Tsung **Chang*** and Professor *Chi-Te **Liang*** in 2013. In his thesis work he pioneered the development of iron chalcogenide and graphene composites which were applied towards bio-sensing and photocatalytic applications. During his postdoctoral work he developed plant leaf-derived graphene quantum dots and graphene nanocomposites that have been used for two-fold applications in both the electronic world as ultra-responsive photodetectors and cancer cell detection systems in the bio world. Prathik has over 25 high quality peer-reviewed publications and also serves as a scientific advisor for Elsevier.

Professor Ian Shaw is doing a regular monthly slot on RNZ National's *This Way Up* with Simon Morton – so far alcohol, cured meats, phthalates and parabens have been featured. To listen to the last features, follow the link: www.radionz.co.nz/national/programmes/thiswayup/library?utf8=%E2%9C%93&q=Ian+Shaw.

MANAWATU

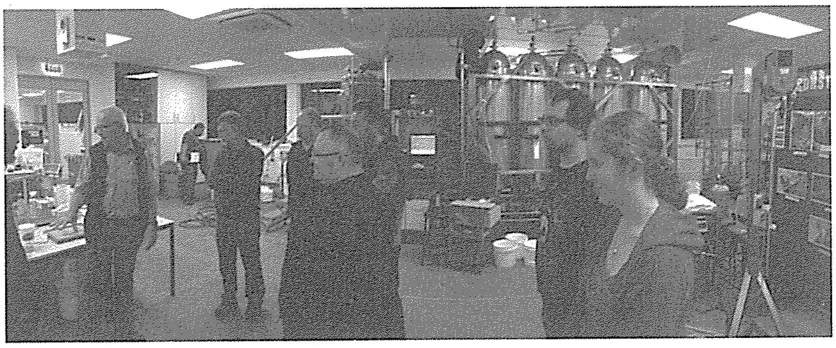
Dr Vyascheslav Filichev along with Dr Elena Harjes, Professor Geoff Jameson and US microbiologist Professor Reuben Harris, have been chosen by the prestigious Worldwide Cancer Organisation to receive a $430,000 grant. They will be investigating the enzyme APOBEC3B, which has been identified as causing tumour cells to mutate during treatment, with the aim of creating a new drug that would inhibit the process.

NZIC Manawatu Student Prizes were awarded to two students in March, in recognition for their high grades in 2015. Stephen Hutton was awarded $300 for the top 300-level student; and $300 to Rebecca Tavendale as the top level-6 student.

In April, a tour of the Massey University Microbrewery facilities was held, hosted by Mr Alan Hardacre of the Massey Institute of Food Science and Technology. This gathering was well attended, and all thoroughly enjoyed both the technical talk on the brewing process, as well as the discussion of the chemistry behind the taste and fragrances of various beers.

Massey University welcomed many guest speakers including:

- Distinguished Professor Margaret Brimble CNZM, FRSNZ from the University of Auckland who came to give the RSC Australasian Lectureship on *Nature's medicine chest: opportunities for synthesis*.
- Dr Siobhan Bradley, postdoc at VUW, who gave a seminar on 9 March about *Graphene and gra-*



Tour of the Massey microbrewery

phene oxide quantum dots: the implications of heterogeneity on the determination of structure-property relationships.

- Dr Kai Chen, postdoc at VUW, who gave a seminar on 13 April about *Using laser spectroscopy to study advanced optoelectronic materials*.
- Professor Donald Craig, Department of Chemistry, Imperial College London, who gave a seminar on 19 April about *Natural product synthesis*.
- Professor Nicola Brasch, Head of Chemistry at AUT, who gave a seminar on 27 April about *Reactions of vitamin B12 and its derivatives with small molecules of biological interest*.
- Professor Amanda Ellis, ARC Future Fellow at Flinders University, who gave a seminar on 11 May about *Structural and dynamic DNA origami: design and applications*.
- Dr Andrew Pratt, Senior Lecturer in Chemistry at Canterbury, who gave a seminar on 18 May about *Proximity and the origin of biochemistry*.
- Professor Stephen J Loeb, Canada Research Chair in Supramolecular Chemistry and Functional Materials, University of Windsor, who gave a seminar on 25 May about *Supramolecular chemistry*.

OTAGO

The Branch co-hosted a poster evening with Chem Club on 22 April. An excellent turnout ensured a great evening. The poster prize was awarded to *Siddharth* ***Matikonda*** from the Department of Pharmacy with his poster entitled *New "stable" and "tunable-release" enabled self-immolative linkers for tumour-targeted prodrug therapy*. The prize was awarded by the Chair of the Branch, *Guy* ***Jameson***.

University of Otago, Department of Chemistry

Professor Stephen Pyne from the University of Wollongong visited the group of *'Bill'* ***Hawkins*** on a William Evans fellowship. Professor Pyne presented a 400-level lecture series as well as a departmental seminar.

James ***Crowley*** was awarded the 2015 Organometallic Chemistry award, jointly awarded by the Inorganic Chemistry and Organic Chemistry Divisions of the RACI.

Jaydee ***Cabral*** was awarded a Lottery Health Equipment Grant for $100,000 to go towards the purchase of a 3D-bioprinter.

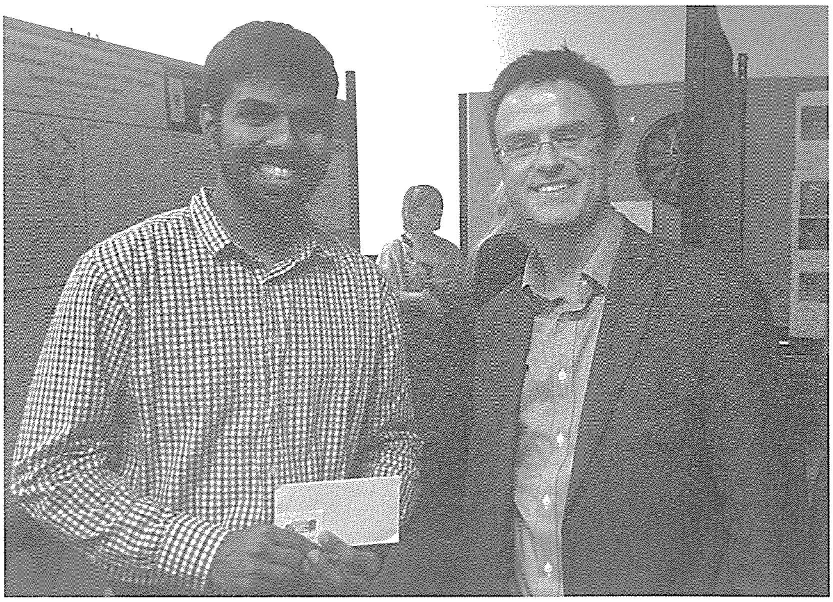
Anna ***Garden*** was a guest lecturer at the Nanocluster Synthesis, Characterization and Applications workshop at the Okinawa Institute of Science and Technology in Okinawa, Japan.

Carla ***Meledandri*** and *Stephen* ***Moratti*** are both finalists in the 2016 KiwiNet awards. Carla has been nominated for the Norman F. Barry Trust Emerging Innovator Award and Steve for the Baldwins Researcher Entrepreneur Award (Newshub: Kiwi ingenuity on show: www.newshub.co.nz/nznews/kiwi-ingenuity-on-show-2016051120#axzz48Ns1q9kI).

It has been a busy period for the group of *Keith* ***Gordon***. The new laser laboratories were commissioned in April. All of the experiments have been moved over and a new Raman microscope (a WITEC Alpha 300 R) has been commissioned. The new facilities provide better climate control and will be PC2 labs.

Jonathan ***Barnsley*** (PhD student Gordon group) presented the poster *Donor-acceptor interactions of 2,1,3-benzothiadiazole push-pull dyes; an experimental and computational study* at the PhysChem 2016 conference in Christchurch. His paper on this was published in J. Phys. Chem. A (2016) 120, 1853 doi: 10.1021/acs.jpca.6b00447. Jono has been awarded a Johan Gadolin Scholarship to lend computational expertise at the Åbo Akademi University in Turku, Finland. Computational investigation of polymer-based chemical sensors will be conducted in collaboration with Professor Johan Bobacka and Dr Grzegorz Lisak.

Georgina ***Shillito*** and *Ruth* ***Sales*** started PhDs and *Sara* ***Miller*** started as a postdoc (all in the Gordon group). Georgina (who is affiliated with the MacDiarmid Institute) is working on spectroscopy and computational chemistry of electronic materials and Ruth (who is a Dodd Walls Centre student) is working on analytical spectroscopy of meat and other biological samples. Sara (Dodd-Walls funded) will develop new spectroscopic methods for medical analysis; she was a recipient of a research grant from the New Zealand Society of Gastroenterology to look at spectroscopy of gastrointestinal disorders. Sara has been working on a variety of projects including studies of seaweed (Journal of the Royal Society Interface (2016) doi: 10.1098/rsif.2015.1083), excipients in drug fomulations (Pharmaceutical Research (2016) doi: 10.1007/s11095-016-1915-3) and snake fangs (Journal of Raman Spectroscopy (2016)



Sid receiving his poster prize from Guy Jameson doi: 10.1002/jrs.4903). Sara also gave a talk to the Dodd-Walls Centre in April about her work.

Geoff ***Smith*** (Gordon group) has submitted his PhD on heterogeneous mixtures (such as cheese) using Raman microscopy. His work with Sally Gaw's group (at the University of Canterbury) on plastics on beaches was recently published (New Zealand Journal of Marine and Freshwater Chemistry (2016) doi: 10.1080/00288330.2015.1132747). He also published a piece on the use of low frequency Raman spectroscopy which he has been working on since submitting his thesis (Spectroscopy, (2016) 31(2), 42-50). Geoff also helped the Otago Museum analyse a whale tooth: http://otagomuseum.nz/blog/tooth-be-or-not-tooth-be/.

Congratulations to *Thomas* ***Hall*** and *Chris* ***Larsen*** who graduated in May. Chris worked with *Nigel* ***Lucas*** and *Keith* ***Gordon*** and is hoping to go to Europe for a postdoc. Tom has started a PhD with Nigel and Keith and is working on graphene-type bowl structures and donor-acceptor compounds.

Keith ***Gordon*** and Justin Hodgkiss (VUW) were awarded an MBIE Catalyst grant to extend their collaborative work with Korean solar cell researchers. This will fund PhD students to work in Korea for extended periods. Keith was also on a successful Massey-led project by Chris Anderson entitled *Phytocat: high-value products from metal-rich biomass* which will, in part, use spectroscopy to examine metal build-up in plant materials. The group met at Massey and Otago in June.

WAIKATO

The composition of the Waikato Branch committee for 2016 as published in the last issue of the journal was ratified at the Branch AGM.

Ryland Fortney-Zirker has recently completed his MSc and is now starting on a PhD with *Bill* ***Henderson***, looking at the chemistry of platinum group metals using ESI MS. Ryan Sutton and Ben O'Shea have also recently started MSc degrees with Bill. Ryan is investigating the chemistry of $Pt_2S_2(PPh_3)_4$, and Ben looking at aspects of forensic chemistry.

Raymond ***Onyekachi*** recently returned from a productive period at St Andrews, working with Professor Michael Buehl on computational chemistry.

Lewis Dean recently completed his BSc(Hons) degree and is starting a PhD with *Michèle* ***Prinsep*** looking at the chemistry of marine macroalgae. Cameron Crombie is also working with Michèle on the chemistry of marine species.

Michèle Prinsep attended the 17th Conference of the International Bryozoology Association (IBA), which was held in Melbourne in April and gave a plenary address on the status and potential of biologically active metabolites of bryozoans.

WELLINGTON

The Wellington Branch has continued to be busy, with activities every month. March saw the Branch meeting link in with the annual Ferrier Lecture at Victoria University, given by Dr Peppi Prasit and entitled *A new model for biotechnology – a journey through drug discovery and development*. Peppi is a highly innovative and successful entrepreneur in the biotech field, having worked in the pharmaceutical industry and founded two companies, Amira Pharmaceuticals and Inception Sciences in California. Dr Prasit was a PhD graduate of Victoria University, where he studied with the late Professor Robin Ferrier. As well as presenting the Ferrier Lecture to a packed audience, Peppi interacted with students and staff at the School of Chemical and Physical Sciences and at the Ferrier Institute, presented a research lecture, and took part in a forum on wealth creation from science.

The Branch meeting in April centred around a seminar by Dr *Rob* ***Keyzers*** (VUW), *Pied piper wanted: better lures for pest mammals*. A range of pheromone and food-related compounds are being investigated as attractants for pests such as possums, rats and stoats. This approach is expected to be particularly advantageous in areas of low population density, including as the final stage complete eradication after traditional poisoning and trapping methods have been employed.

The annual Wellington Space and Science Festival was held at Onslow College on 14 May and attracted nearly 3,000 attendees. The Wellington Branch, in conjunction with the School of Chemical and Physical Sciences (VUW), had a major presence. 18 L of liquid nitrogen ice cream was consumed, and a hands-on chemistry room was open all afternoon, at which 350 pots of slime were made, cornstarch in water was used to illustrate non-Newtonian fluids, alginate worms were formed and laser beams were visualised in jelly. A *Chemistry of matter* demonstration, conducted by members of the Branch committee, was very popular. The chemistry of solid and gaseous forms of carbon dioxide was shown, the effect of liquid nitrogen on foods and flowers was shattering, and balloons were shrunk when cooled in liquid nitrogen. The final flourish was a spectacular demonstration of "elephant's toothpaste". The evening session included a *Chemistry of light* show, with fluorescent minerals, colours of the elements and luminol lighting up the audience, again run by members of the Branch committee.

The Royal Society of Chemistry 2015 Australasian Lecture tour by Distinguished Professor *Margaret* ***Brimble*** (University of Auckland) came to Wellington in May hosted by the local NZIC Branch. The lecture on *Nature's medicine chest: opportunities for synthesis* was presented to a packed audience and covered the delights of natural product and peptide synthesis. Margaret described the discovery and development of the drug trofenitide for Rett's syndrome and recent approaches to combatting antibiotic resistant bacteria.

The student members of Wellington Branch committee, led by *Matt* ***Fisk***, have been running a chemistry study incubator session for VUW students every Thursday evening during university term time, which has been welcomed by undergraduate students at all levels. Participants have been connecting to help each other with their academic challenges, with refreshments provided by the Branch.

The first round of student travel grants have been awarded. Recipients *Justin* ***Butkus***, *Sophie* ***Geyrhofer***, *Shyamal* ***Prasad*** and *Ryan* ***Schwamm*** are attending various international conferences later in the year.

The Branch congratulates *Ralf* ***Schwörer*** (Branch treasurer) and family on the recent arrival of their second child.

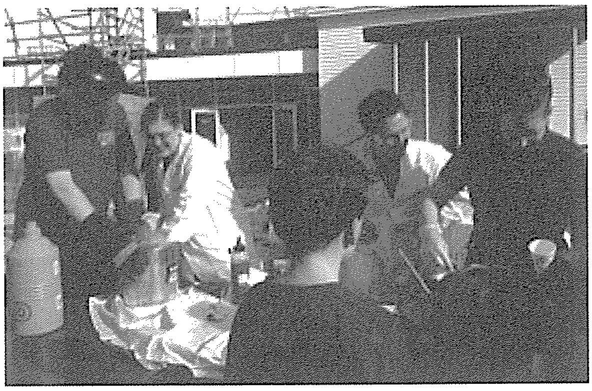
Victoria University (VUW)

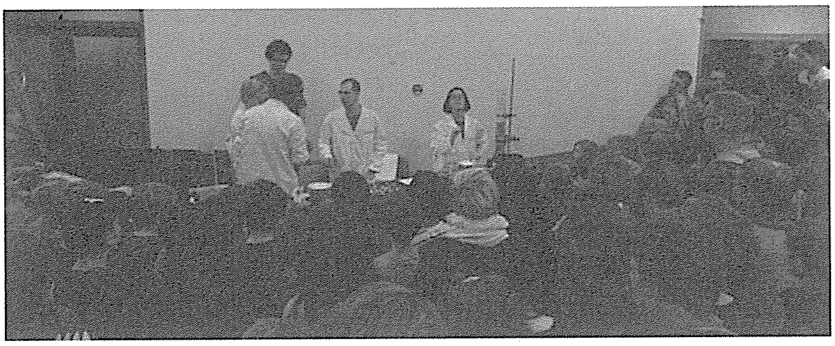
Dr *Anna* ***Henning***, a VUW graduate with a PhD from Professor *Richard* ***Tilley***'s group and now at spin-off company Boutiq, was a finalist for the Norman F. Barry Trust Emerging Innovator Award.

Congratulations to *Thomas* ***Bevan***, who successfully defended his PhD thesis entitled *Azulene-based protecting groups*. Thomas has been working in Dr *Joanne* ***Harvey***'s research group, co-supervised by Associate Professor *Peter* ***Northcote***.

BRANZ

Trish ***Shaw*** gave a presentation on corrosion at the Building Officials Institute of NZ annual conference and expo in Christchurch, 15-18 May. *Katy* ***Stokes*** attended the Wood Innovations 2016 conference in Rotorua, 24-25 May and Changing Perceptions of Engineered Timber for Construction conference, Rotorua, 26 May. *Nick* ***Marston*** presented a training module on durability and materials performance to the NZ Institute of Building Surveyors in Auckland on 25 May.





Wellington Space and Science Festival

Margaret Brimble presenting to the Wellington audience as part of her RSC 2015 Australasian Lecture tour

NZIC Conference 2016 (NZIC-16)

21-24 August 2016, Millennium Hotel, Queenstown

Celebrating chemistry in New Zealand and showcasing research from around the globe. The programme includes plenary lectures from Donna Blackmond, Sam Kean, Peter Schwerdtfeger and Peter Stang, and will include keynote lectures, invited presentations and poster sessions. The broad range of chemistry will be attractive to all chemists from academia, industry and will be particularly informative for student delegates.

NZIC-16 will host the 4th Supramolecular Chemistry in New Zealand and Australia meeting (**SCiNZA-4**). We therefore extend a special invitation to Australasian researchers in this field. Professor Peter Stang will present the supramolecular chemistry plenary talk, and one of the parallel sessions of the conference will be set aside for SCiNZA-4 talks. SCiNZA-4 delegates should register and submit abstracts via the main conference portal.

www.nzic16.org

Investigating the structure activity relationship of thieno[2,3-*b*]pyridine anti-proliferative agents

Michelle van Rensburg,[1] Euphemia Leung,[2] Chatchakorn Eurtivong,[1] Jóhannes Reynisson,[1] David Barker[1]

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Keywords: *cancer, thieno[2,3-b]pyridine, phospholipase C, tyrosyl-DNA phosphodiesterase I*

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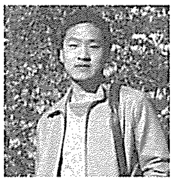
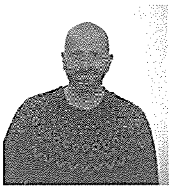
Dr Euphemia Leung received her PhD degree in molecular medicine from the University of Auckland, specialising in novel gene discovery and gene regulation under the supervision of A/Prof Geoff Krissansen and Prof Jim Watson. She is currently a senior research fellow in the Auckland Cancer Society Research Centre and the Department of Molecular Medicine and Pathology. The major focus of her research is the study of heterogeneity and endocrine resistance in breast cancer using cell lines as a model. Her research interests include drug discovery as well as mechanistic study of novel anticancer compounds.



Chatchakorn Eurtivong was born in Bangkok, Thailand, where he spent most of his childhood. In 2002 he came to New Zealand for his secondary studies. He then enrolled for his BSc at the University of Auckland in 2009 and graduated with a BSc Hons, specialising in medicinal chemistry. He is currently enrolled as a PhD candidate at the University of Auckland under the supervision of Dr. Jóhannes Reynisson. His research focuses on chemoinformatics and computer-aided drug discovery and design.



Dr Jóhannes Reynisson began his academic career at the University of Iceland where he read chemistry (BSc/MSc). His PhD was obtained from the University of Copenhagen in 2000; the research work was carried out at the Risø national laboratory. He spent two years in Germany as a post-doc at the Max-Planck-Institut für Strahlenchemie. He worked for five years at the Institute of Cancer Research in London as a molecular modeller/computational chemist developing anticancer drug candidates. Before he left the UK he was a lecturer in chemistry at the Nottingham Trent University. He has visited three institutes for approximately six months each at Worcester Polytechnic Institute (MA, USA), Georgia Institute of Technology (GA, USA) and The University of Leipzig (Germany).

David Barker was born in Altrincham, UK. After moving to Australia, he graduated from the University of Sydney with a BSc degree (1st Class Honours) and then completed his PhD in 2002 at the same university. After post-doctoral research at the School of Medical Sciences at the University of New South Wales working with Prof Larry Wakelin, he joined the University of Auckland as a lecturer in 2004. He is currently Associate Professor in Organic and Medicinal Chemistry and he has a diverse range of synthetic interests including biologically active natural products, drug discovery and development of novel polymeric scaffolds.

Introduction

Thieno[2,3-*b*]pyridines have been shown to be a novel class of compounds which exhibit potent anticancer activity against a variety of tumour cell lines.[1–3] We have previously prepared a range of thieno[2,3-*b*]pyridine analogues which were investigated for their anti-proliferative activity against the National Cancer Institute's human tumour cell lines (NCI-60). Derivative **1** was found to be most active, while the smaller compounds **2** and **3** were found to have decreased bioactivities when compared to their parent compounds (Fig. 1).[3] It has been suggested that their activity is due to their ability to inhibit the phospholipase C (PLC) enzymes and, more recently, due also to interactions with tyrosyl-DNA phosphodiesterase I (TDP1) enzymes – both of which are key enzymes involved in cell proliferation and motility.[4,5]

In 2009, we reported the potent thieno[2,3-*b*]pyridine **4**, which exhibited nanomolar growth inhibition against the human tumour cell lines MDA-MB-435, MDA-MB-468, NCI-H522 and SF-295, which has since been the subject of two intensive studies to further determine its biological activity (Fig. 2).[1,6] In 2014, we tested the cytotoxicity activity of thieno[2,3-*b*]pyridine **4** in relation to its effect on morphology and migration of the human breast cancer cell line MDA-MD-231 (Figs. 3 and 4).[6] Thieno[2,3-*b*]pyridine **4** was found to severely affect the cytoskeletons of the cancer cells, with a clear dose response relationship observed. Similarly, thieno[2,3-*b*]pyridine **4** was also found to suppress the migration of the cancer cells. This observed activity coupled with the nanomolar growth inhibition already noted for thieno[2,3-*b*]pyridine **4,** further stimulated interest in these types of compounds as possible anti-cancer agents.

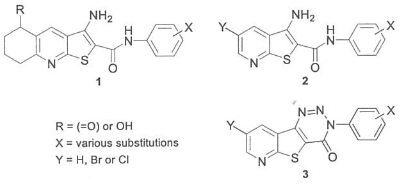


Fig. 1. Thieno[2,3-*b*]pyridine analogues previously prepared[3]

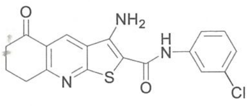


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Fig. 2. Thieno[2,3-*b*]pyridine 4

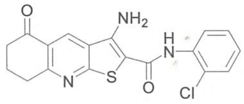

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Fig. 5. Thieno[2,3-*b*]pyridine 5

Also in 2014, we reported the cytotoxic activity of the closely related 2-chlorophenyl derivative **5** (Fig. 5).[2] In the study thieno[2,3-*b*]pyridine **5** was selected by the NCI for dose response testing based on its favourable growth inhibition. Like compound **4,** thieno[2,3-*b*]pyridine **5** showed the best activity against tumour cell lines MDA-MB-435, MDA-MB-468, NCI-H522, SF-295 and K-562.

Due to the promising activity seen for thieno[2,3-*b*]pyridine **5**, our interest was to develop a series of derivatives to further elucidate structure activity relationships (SAR). Previous molecular modelling studies on similar compounds have been performed to predict binding patterns with results suggesting that the 3-amino and 2-aryl carboxamide moieties of the ligand are involved in hydrogen bonding within the PLC enzyme active site.[1] Docking studies of thieno[2,3-*b*]pyridine **5** against the binding site of PLC-δ1 showed that the 2-aryl carboxamide has hydrogen bond interactions with Asn312 and His311 side chains. Side chain interactions with Arg549 and Glu341 were also observed with the amine group of the ligand. The cyclohexanone moiety occupies the right hand side of the binding pocket with hydrogen bond interactions observed with Lys438 and Arg549. Lastly, the phenyl group occupies a lipophilic pocket on the left hand side of the binding site (Fig. 6). These binding interactions are in accordance with previous molecular modelling studies.[1,2,6]

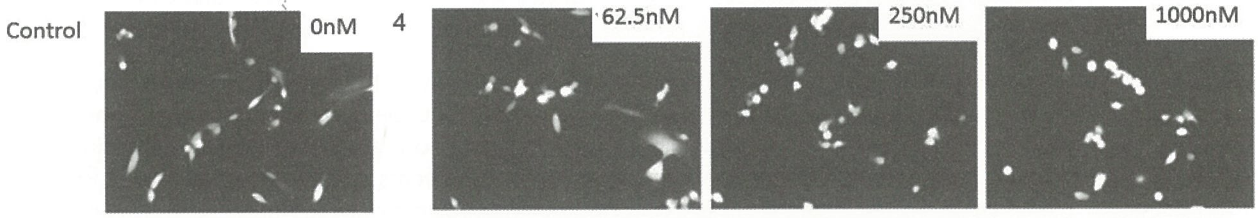


Fig. 3. Effects of thieno[2,3-*b*]pyridine **4** on the morphology of red fluorescent labelled MDA-MB-231 human breast cancer cells. Cells were incubated for 16 h. Photographs were taken by Floid imaging station (460 magnification).

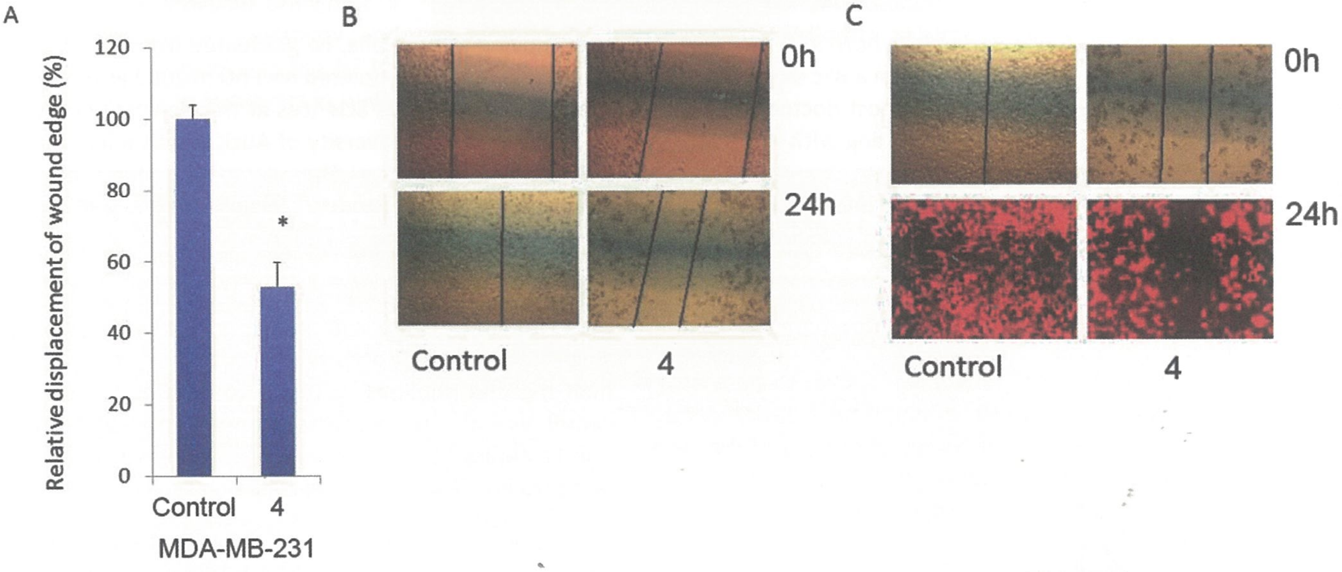


Fig. 4. Effects of thieno[2,3-*b*]pyridine **4** on migration of human breast cancer cells. (A) Relative migration of MDA-MB-231 in 24 h. (B) Images were acquired at 0 and 24 h in in vitro scratch assay. The lines define the areas lacking cells. (C) Red fluorescent MDA-MB-231 mKATE2 cells were used to demonstrate wound healing. 1μM of **4** was used.

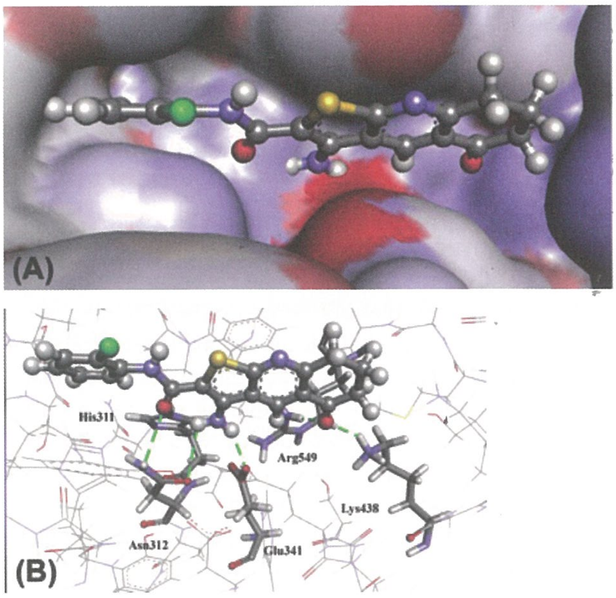


Fig. 6. The docked configuration of compound **5** to the binding site of PLC-δ1 using ChemPLP. (A) The protein surface is rendered. The phenyl group occupies a lipophilic cavity to the left hand side. Red depicts positive partial charge, blue depicts negative partial charge and grey depicts lipophilic/neutral areas. (B) Hydrogen bonds are depicted as green dotted lines. The amino acids bolded in stick display style contribute to hydrogen bonds with compound **5**.

The synthetic objectives were therefore driven by the desire to further investigate the importance of the 3-amino and 2-aryl carboxamide moieties as well as what effect changing the 5-keto moiety has on the activity, thereby expanding the current SAR knowledge of this class of compounds. As such, a group of eight derivatives were targeted for synthesis and subsequent testing (Fig. 7).

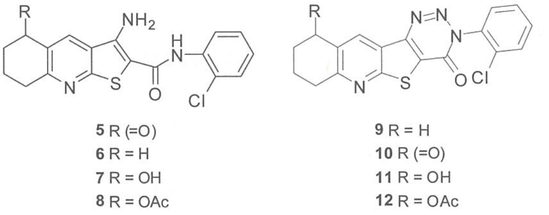


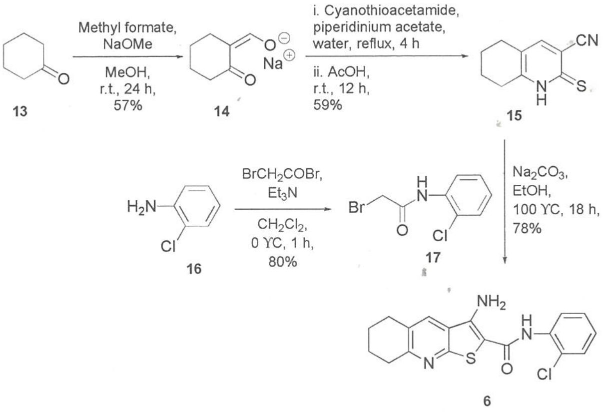
Fig. 7. Target compounds to further investigate SAR of the thieno[2,3-*b*]pyridine family

Results and discussion

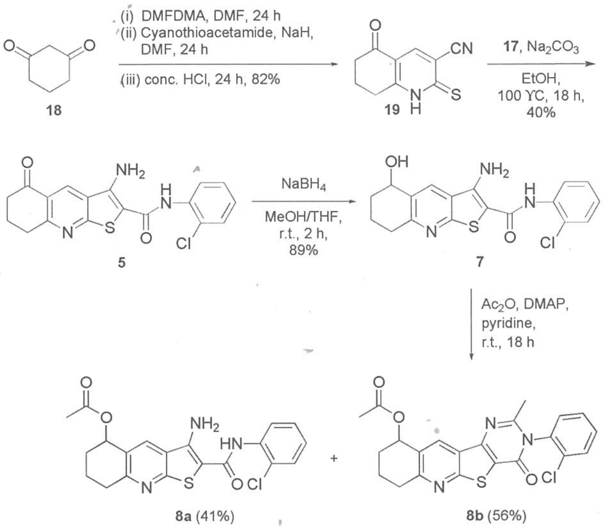
Synthesis of compounds

Thieno[2,3-*b*]quinoline **6** was prepared by reacting cyclohexanone **13** with sodium methoxide and methyl formate to give salt **14** which was reacted immediately with cyanothioacetamide and piperidinium acetate followed by acidification with acetic acid to give the bicyclic carbonitrile **15** (Scheme 1). Carbonitrile **15** was then coupled with 2-chloro bromoaniline **17**, which was obtained by the reaction of 2-chloroaniniline **16** with bromoacetyl bromide and triethylamine, to give thieno[2,3-*b*]quinoline **6** in 78 % yield.

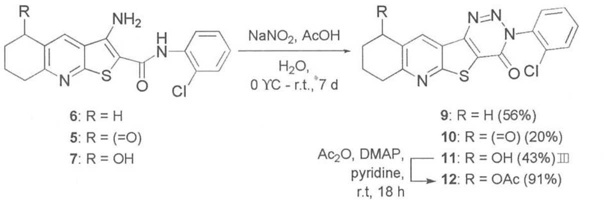
In a similar manner, 5-oxo-thieno[2,3-*b*]pyridine **5** was prepared in 40 % yield by coupling 2-chloro bromoaniline **17** with carbonitrile **19**, which itself was obtained from diketone **18** (Scheme 2). 5-Oxo-thieno[2,3-*b*]pyridine **5** was reduced with sodium borohydride to give 5-hydroxy-thieno[2,3-*b*]pyridine **7**. Acetylation of 5-hydroxythieno[2,3-*b*]pyridine **7** gave the corresponding acetate **8a** as well as the secondary product, acetate **8b**.



Scheme 1. Synthesis of thieno[2,3-*b*]quinoline **6**



Scheme 2. Synthesis of derivatives **5**, **7**, **8a** and **8b**



Scheme 3. Synthesis of derivatives **9-12**

Thieno[2,3-*b*]quinoline **6,** 5-oxo-thieno[2,3-*b*]pyridine **5** and 5-hydroxythieno[2,3-*b*]pyridine **7** underwent diazotisation using sodium nitrite to give the corresponding thienotriazinones **9-11** (Scheme 3). 5-Hydroxy-thienotriazinone **11** was acetylated using acetic anhydride to give acetate **12**.

Thus, a series of nine 2-chlorophenyl analogues **5-12** were succesfully prepared to investigate what effects differing substitution on the cyclohexane ring have on the activity of the compound, as well as what effect ring closure involving the 3-amino and 2-aryl carboxamide moieties have on the activity of the parent compounds.

Anti-proliferative activity

Of the nine analogues synthesised, six (compounds **5-7** and **9-11**) were tested against the National Cancer Institute's human tumour cell lines (NCI-60) (Table 1).

The anti-proliferative activity of the nine synthesised derivatives, **5-12**, were also assessed at the Auckland Cancer Society Research Centre against three tumour cell lines, HCT116, MDA-MB-468 and MDA-MB-231 with all compounds being initially tested at 1 μM concentration (Table 2).

Compounds **7** and **8a** were further evaluated to determine their IC$_{50}$ values, due to their promising activity observed against all three tumour cell lines (Table 3). The results obtained from each source for the activity of compounds **5-12** were consistent with each other, allowing for general trends to be made.

It can be seen that acetate (**8a**) and then alcohol (**7**) substitution on the cyclohexane ring is more favourable over keto (**5**) or non-substitution (**6**) (Table 2), with **8a** and **7** exhibiting IC$_{50}$ values in the nano-molar range (Table 3). In all cases, cyclisation involving the 3-amino and 2-arylcarboxamide moieties (**8b**, **9-12**) resulted in inactive compounds, with direct comparisons able to be made between compound **7** (11-30% relative growth across the three tumour cell lines) and **11** (80-96%) as well as between compounds **8a** (3-10%), **8b** (64-93%) and **12** (93-98%) which confirms that these groups which are modified in **8b**, **9-12** are important for bioactivity. These findings would appear to validate the importance of the hydrogen bonding observed during docking experiments between the ligand and amino acids (Glu341 and Lys438) within the enzyme active site.

Derivative **5** has also been evaluated by NCI using *in vivo* toxicity testing and was found to be non-toxic in non-tumoured animal studies. Proceeding from this result, hollow fibre assays are currently being undertaken by the NCI. Recently, we reported the results from a mouse xenograft study in which a related thienopyridine showed encouraging activity in tumour size/mass reduction.[7]

Conclusions

Nine derivatives were prepared to explore what effect changes at C-5 and C-2/C-3 amine carboxamide have on the activity of the thieno[2,3-*b*]pyridines. The biological activity results show that modifications are tolerated at C-5 but not at C-2/C-3, which resulted in the loss of activity. Interestingly, acetate derivative **8a** was more active than its corresponding 5-keto derivative **5**, a result which is in contradiction with the predicted binding activity from docking studies. It is proposed that acetate **8a** may be acting as a prodrug in order to elicit this observed activity. Current synthetic objectives are exploring this concept further.

Acknowledgements

The authors would like to thank the Auckland Medical Research Foundation and the University of Auckland for funding.

References

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2. Arabshahi, H. J.; Leung, E.; Barker, D.; Reynisson, J. *MedChemComm* **2014**, *5* 2., 186–191.

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Table 1. The NCI mean percentages (%) of growth arrest at 10 μM as compared to untreated cells (100% growth) as well as their percentage (%) of growth arrest against select tumour cell lines.

Compound	NCI Mean	HCT116	MDA-MB-468	MDA-MB-231
5	48	76	25	70
6	99	107	91	100
7	36	30	26	58
9	89	88	88	81
10	96	96	86	94
11	97	102	91	86

Table 2. Anti-proliferative activity of compounds **5-12**. ^{a}Values represent relative growth (%) versus control. All compounds were tested at 1 μM against the specified cell lines.

Compound	HCT116^a	MDA-MB-468^a	MDA-MB-231^a
5	99	94	104
6	94	95	119
7	11	14	30
8a	3	7	10
8b	92	64	82
9	99	81	94
10	97	91	97
11	96	80	91
12	98	93	95

Table 3. IC$_{50}$ values calculated for compounds **7** and **8a**.

Compound	IC$_{50}$ (nM)			
	HCT116	MDA-MB-468	MDA-MB-231	K562
7	616 ± 3	546 ±22	675 ± 21	431 ± 68
8a	184 ± 7	181 ± 4	201 ± 1	192 ± 18

Enhanced microwave synthesis - a new approach for the preparation of advanced nanostructured polyanilines

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Keywords: *enhanced microwave synthesis, polyaniline, nanostructures*

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Introduction

Polyaniline (PANI) is one of the most extensively studied conducting polymers (CPs) because of its simple and low cost synthesis, unique redox properties, high conductivity, excellent environmental stability and ability to form various nanostructures.[1-4] These features have enabled PANI to be used in range of applications such as catalysts, antioxidant and antimicrobial agents, chemical/biological sensors, electronic devices, corrosion protection, actuators and light emitting diodes.[1,4-12] PANI is typically produced through the oxidative polymerisation of aniline, using a strong oxidising agent such as ammonium persulfate (APS) or potassium iodate (KIO_3) in a solution of a strong acid such as hydrochloric or sulfuric acid.[2,12] PANI synthesised in this way using a classic chemical synthesis (CS), exhibits a featureless, granular morphology and possesses high conductivity. However, by changing the synthesis conditions, the solid PANI particles can be produced in many different sizes and shapes such as nanofibres and nanosheets, or as very well defined structures: nanoplates, nanospheres, nanotubes and nanorods.[6,8,9]

Lately, the synthesis and structural investigation of nanostructured PANIs has become one of the most important domains in the field of CPs. It is well known that the physical and chemical properties of nanomaterials are highly dependent on their morphology. Moreover, the nanosized materials very often exhibit new, different and sometimes even unexpected properties compared with their well-studied and known bulk counterparts.[10,11] As the field of nanotechnology becomes more commercially attractive, the extensive adoption of nanomaterials is restricted by a need for the development of a methodology that can provide facile and fast production of large-scale quality products.

Enhanced vs. conventional microwave synthesis method for preparation of polyaniline nanostructures

The microwave irradiation (MW) method is an eco-friendly, rapid and convenient way to get advanced polymer nanomaterials in high yield at desirable temperature. So, in contrast with CS PANI synthesis, for which the reaction duration can be several hours or even days, application of microwaves can greatly reduce the reaction duration so that product can be obtained in just 5 min with ca. 76 % yield in the form of nanostructured polymer.[13-15]

Gizdavic-Nikolaidis *et al.* developed an enhanced microwave synthesis (EMS) method for large-scale preparation of advanced nanostructured PANI materials at ambient temperature for environmental monitoring, water reuse, energy storage, food and biomedical applications.[14-17] By externally cooling the reaction vessel and simultaneously applying irradiating microwaves, a steady amount of energy can be transmitted to the reaction mixture, while preserving a constant temperature. Furthermore, enhanced polymer product purity is achieved by reducing unwanted side reactions compared to conventional heating methods. This is a considerably different approach relative to conventional microwave synthesis (CMWS), where the microwave irradiation increases the bulk temperature to the desired set point very quickly. When the reaction system reaches the desired bulk temperature, the microwave power automatically decreases or shuts off. Therefore, the CMWS approach cannot preserve a constant reaction temperature over an extended period of time while maintaining a continuous flow of microwave energy into the system.

The essence of the EMS approach is removal of the MW heating by cooling the system during irradiation, which allows experiments at high MW power levels and permits microwave assisted enhancement of chemical reactions. These reactions will only take place during application of microwave energy that can directly activate the molecules in a chemical reaction.[14] Moreover, EMS as a leading-edge technology has been established with applications to a variety of fields such as green chemistry, polymer chemistry, biotechnology, pharmaceutical, chemical and agrochemical industries.[14-34]

Yield and morphology

Under MW irradiation, PANI material using 1 M HCl acid as dopant was produced with high yield (ca. 76 %) after only 5 min at room temperature while the CS method took 5 h to achieve the same yield.[13,35] The MW PANI product showed a nanofibrillar morphology. The MW PANI fibres were relatively uniform (60-70 nm) but partial morphological heterogeneity of the PANI product was noticeable (Fig.1a). Although CS PANI product (0.0 W) after 5 min showed some mixed fibrillar morphology, the yield was only ca.12 % (Fig.1b). The CS PANI product obtained after 5 h is shown in Fig. 1c. The CS PANI exhibits a featureless, granular structure with an obvious absence of elongated nanostructures.

Gizdavic-Nikolaidis *et al.* reported that MW PANI products synthesised using either APS or KIO_3 as an oxidant showed mainly fibrillar or rodlike morphologies regardless of the MW power applied during synthesis, though the high aspect ratio and morphological homogeneity were dependent on the applied power and anion type.[14] Jevremovic *et al.*[15] demonstrated that an increase in the aqueous HCl concentration (0.5-3 M) led mostly to porous PANI products which consist of short, rod-like structures. For example, the MW PANI obtained using 0.5 M HCl at 93 W had very obvious slab-like morphology with a lesser amount of fibrils compared to its counterpart synthesised at lower microwave power, 8 W.[15] This suggests that higher microwave power favours cross-linking and the formation of slab-like structures. With decreasing pH of the reaction medium the morphology of MW HCl doped PANI products changed from slab-like with a small amount of fibrils to porous products which consist of short, rod-like structures.

Gizdavic-Nikolaidis *et al.* also prepared MW H_2SO_4 doped PANI products using APS as an oxidising agent in 0.5-2.5 M concentration range of aqueous H_2SO_4 at 93 W applied microwave power of 10 min duration.[17] The authors showed that MW H_2SO_4 doped PANI products obtained using the EMS approach had a mixed nanoporous/fibrous morphology with irregularly shaped particles. The result that the morphology depends on the acid concentration can potentially be used to adjust and optimise conditions for the formation of porous products suitable for sensors or filters.[15,17,35] This is in line with the results obtained by Merian *et al.* who confirmed that nanoporous/fibrous H_2SO_4 doped PANI prepared using microwave irradiation for a duration of 10 min had good sensor performance.[35]

Spectroscopic studies

FTIR spectroscopy

FTIR spectra of PANI products synthesised using either the MW or CS method are presented in Fig. 2. All FTIR spectra showed characteristic peaks for chemically synthesised HCl doped PANI, the emeraldine salt (ES) form of PANI, as previously reported.[13-15] The most intense bands are assigned to the C-C stretching of quinoid rings at 1572-1564 cm^{-1} and to benzene ring stretching at 1490 cm^{-1}. The C-C stretching of quinoid rings for the 5 min CS HCl doped PANI (Fig. 2b) was observed at 1572 cm^{-1} in comparison to lower wavenumbers (1566-1564 cm^{-1}) for PANI products, 5 min MW HCl doped PANI (Fig. 2a) and 5 h CS HCl doped PANI (Fig. 2c). This suggests that for 5 min CS HCl doped PANI the polymerisation did not go to completion in comparison to 5 min MW HCl doped PANI and 5 h CS HCl doped PANI (ca. 76 %) where a large shift of 20-22 cm^{-1} from the position of the C-C stretching band in PANI, emeraldine base (EB), undoped at 1586 cm^{-1} was observed.[36] The band at around 1303 cm^{-1} originates from C-N stretching of the secondary aromatic amine function, while the band at around 1248 cm^{-1} is due to the protonated C-N group. The strong band at 1151-1154 cm^{-1} is referred to as an "electronic band" and is assigned to the doped structure in standard PANI.[14,15,17] A band at 823 cm^{-1} is assigned to the out-of-plane bending of C-H bonds in the 1,4-disubstitued ring (*para*-coupling), indicating the presence of the head-to-tail coupling during the polymerisation.[13-15] All FTIR spectra have similar features, the PANI structure is retained even in the product obtained by MW irradiation after 5 min.

Similar observations were found for the FTIR spectra of MW H_2SO_4 doped PANI products synthesised using different concentrations of aqueous H_2SO_4 (0.5-2.5 M) where the presence of PANI backbone structures with prevalence of benzenoid/quinonoid alternating segments in all products were confirmed.[17]

Raman spectroscopy

In Fig. 3 the Raman spectra of MW HCl doped PANI (5

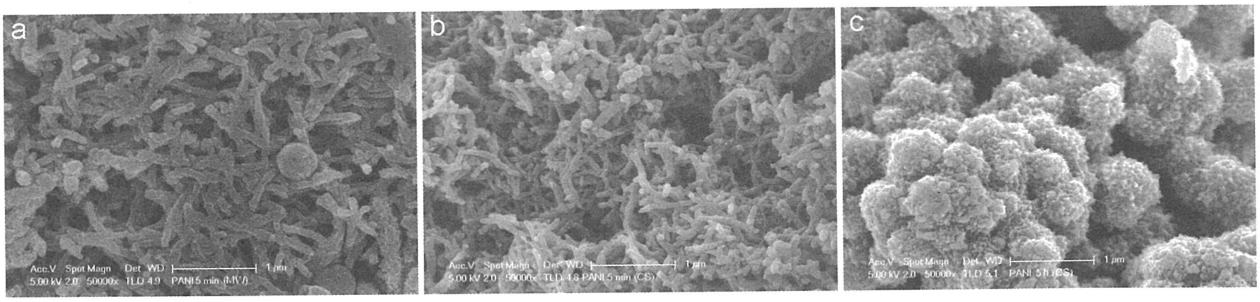

Fig. 1. SEM micrographs: MW HCl doped PANI taken after 5 min at 93 W (a); CS HCl doped PANI taken after 5 min (b) and 5 h (c) at 0 W.

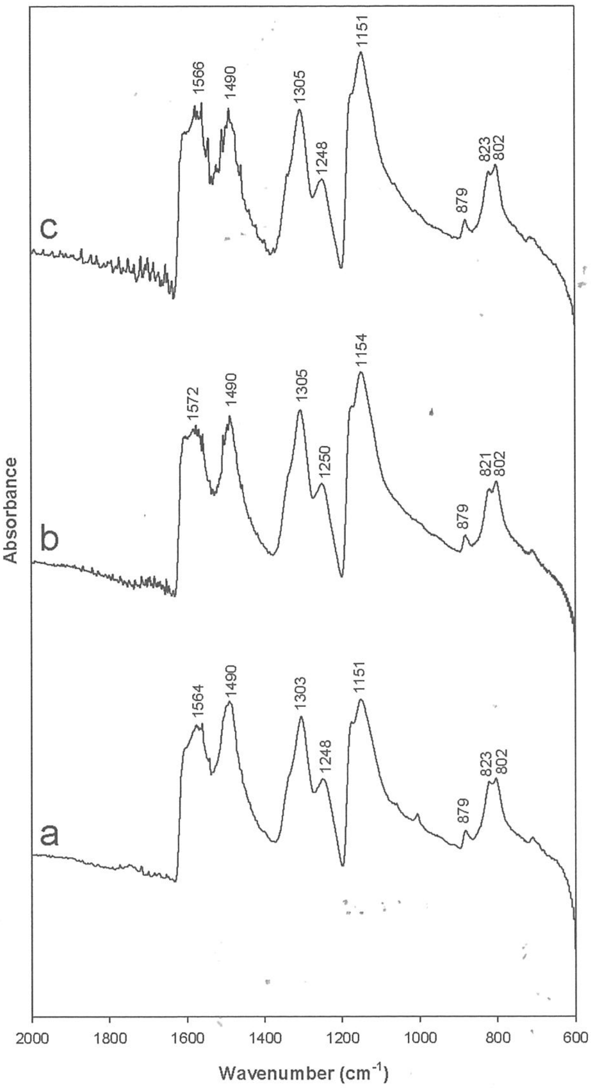

Fig. 2. FTIR spectra: MW HCl doped PANI taken after 5 min at 93 W (a); CS HCl doped PANI taken after 5 min (b) and 5 h (c) at 0 W.

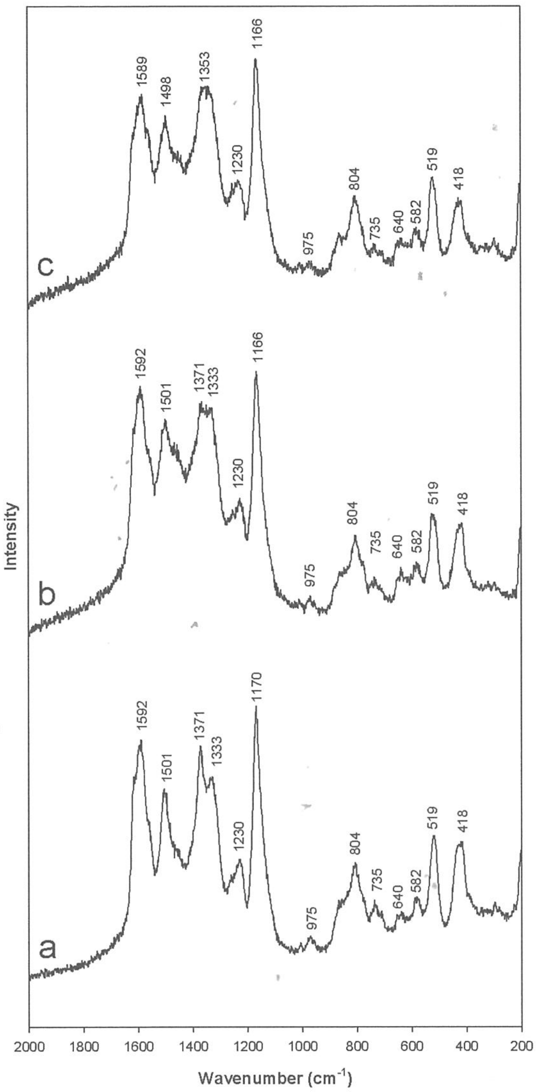

Fig. 3. Raman spectra: MW HCl doped PANI taken after 5 min at 93 W (a); CS HCl doped PANI taken after 5 min (b) and 5 h (c) at 0 W.

min), CS HCl doped PANI (5 min) and CS HCl doped PANI (5 h) are presented.

The band at 1589-1592 cm^{-1} is characteristic for C-C stretching in-plane of the benzenoid ring, while that at 1498-1501 cm^{-1} is the C=N stretching band of the quinoid diimine units. The C-N stretching of the cation radical species is at 1333 cm^{-1}, while the band at 1230 cm^{-1} belongs to C-N of benzenoid units.[13,16,36] The band at 1185 cm^{-1} is attributed to C-H bending of the quinoid rings. The bands at 804 cm^{-1} and 735 cm^{-1} are characteristic of the out-of-plane C-H wag of the *para*-benzenoid ring and C-H wag of the *mono*-benzenoid ring. The band at 640 cm^{-1} is due to an in-plane benzenoid ring deformation of the benzenoid ring whereas the band at 519 cm^{-1} is assigned to an in-plane quinoid deformation of the benzenoid ring. The out-of-plane ring deformation of the benzenoid ring appears at 419 cm^{-1}.[13,16,36] Consistent with FTIR results, the Raman spectra confirmed the PANI structure in all products synthesised by either the CS or MW method.

UV-Vis spectroscopy

The UV-Vis spectra of either MW or CS PANI products in N-methyl-2-pyrrolidone (NMP) solution usually show strong absorption in two areas, with maxima at around 325 nm and 635 nm.[14,17] The band at 325 nm corresponding to π–π* excitation of the *para*-substituted benzenoid segment (B), while the band at 635 nm is associated with the excitation of the quinonoid segment (Q). As an example, the UV-Vis spectra of MW HCl doped PANI products prepared at 93 W microwave power using different concentrations of aqueous HCl (0.5-2.5 M) are presented in Fig. 4. Both characteristic peaks, the B band at 325 nm and the Q band at 635 nm, are observed. The Q/B ratio was in the range 0.63-0.69 which indicates more benzenoid than quinonoid groups in the PANI structures which is in agreement with previously reported results for both MW HCl or H_2SO_4 doped PANI.[14,17] The structural characteristics of MW HCl doped PANI products revealed by UV-Vis implied that the PANI structure was not considerably changed by exposure to the MW irradiation. Similar observations in the UV-Vis spectra were made by Gizdavic-Nikolaidis *et al.* for HCl doped PANI products obtained in MW at different power levels using KIO_3 or APS as an oxidising agent.[14] These authors also reported that the obtained UV-Vis data showed that the PANI structural characteristics were consistent with FTIR spectra.

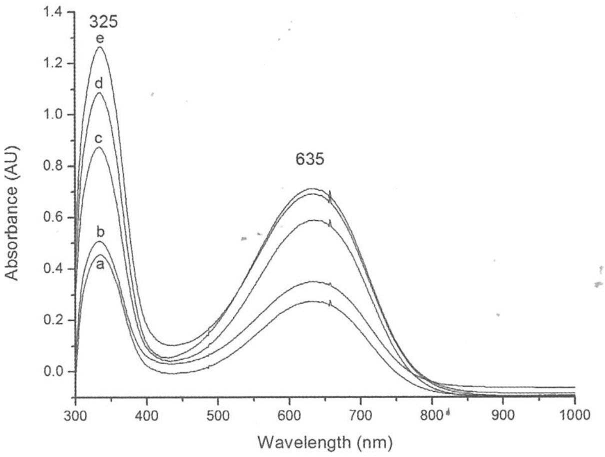

Fig. 4. UV-Vis spectra of the MW synthesised HCl doped PANIs at 93 W power (a) 0.5 M HCl doped PANI; (b) 1 M HCl doped PANI; (c) 1.5 M HCl doped PANI; (d) 2 M HCl doped PANI; (e) 2.5 M HCl doped PANI

EPR spectroscopy

Electron paramagnetic resonance (EPR) spectroscopy was applied to examine the influence of acid dopant on the spin concentration in doped PANI ES products.[15-17,36,37] It was reported that for granular HCl doped PANI products prepared by the CS method, the spin concentration initially increases with increasing dopant concentration, reaches a maximum at 1 M HCl dopant concentration, and then decreases due to formation of bipolarons at higher doping levels.[36,37] The initial increase in the spin concentration was expected because of the increased possibility of reaction between the dopant HCl and imine nitrogens of PANI. It is known that the polarons and the bipolarons are in equilibrium, with pairing of polarons at high doping levels to form bipolarons which are spinless so they cannot be detected by EPR.[36,37]

The spin concentration, N_{sample} (spins g^{-1}) can be calculated using the area calculated from the second integral of the first-derivative EPR signals according to:

$$N_{\text{sample}} = \frac{Area_{\text{sample}}}{Area_{\text{reference}}} \times \frac{\text{mass}_{\text{reference}}}{\text{mass}_{\text{sample}}} N_{\text{reference}} \qquad \text{(Eq. 1)}$$

where the reference substance used is $CuSO_4 \times 5H_2O$, for which $N_{reference} = 2.412 \times 10^{21}$ spins g^{-1}.

The results of using different concentrations of aqueous HCl for the preparation of MW PANI products using 93 W microwave power are presented in Table 1. The spin concentration for MW HCl doped PANIs varies systematically with HCl concentration as previously reported, first showing an increase at low HCl concentrations due to an increase in the number of polarons, but then a decrease at higher concentration due to the formation of spinless bipolarons. Similar observations were also reported previously,[15] where the authors found the doping levels for MW HCl doped PANI products synthesised either at low or high microwave power, 8 W and 93 W respectively, are considerably higher than those for the HCl doped PANIs prepared by the CS method.

Gizdavic-Nikolaidis *et al.* also confirmed a similar trend in the change of spin concentration with acid dopant in MW PANI products prepared using different concentrations of aqueous H_2SO_4.[17] Furthermore, a shift of the maximum of the deprotonated band in H_2SO_4 doped PANI samples in FTIR spectra correlated well with the changes in polaron concentration with the H_2SO_4 dopant concentration observed in the EPR results.[17]

Specific surface area and conductivity

The specific surface area (SA) values for MW HCl doped PANI products using either APS or KIO_3 as an oxidising agent do not appear to depend on MW power.[14] At the same time, the SA values for PANI products obtained using the EMS approach were 30±1 m^2g^{-1} in comparison to 17±1 m^2g^{-1} for those prepared using the CS method. The interesting point is that CS HCl doped PANI products synthesised for the same time duration as MW HCl doped PANI show comparable SA values. This suggests that morphology also has an influence on SA values. CS synthesised PANI products formed after 5 h reaction time showed granular and featureless morphological characteristics and consequently exhibit lesser values for surface area in comparison to nanofibrillar morphology for 5 or 10 min duration synthesised MW or CS PANIs.

Because MW PANI products have larger SA, this material may be suitable as a chemical sensor. Merian *et al.*[35] showed that MW synthesised PANI gives rise to sensors presenting with better metrological performances relative to CS PANIs, and this can be correlated with the physical properties of the products revealed by FTIR and EPR spectroscopies. Moreover, the same authors showed that a composite containing 38 % of doped MW H_2SO_4 doped PANI in a polyurethane (PU) blend gave the best response to 1 ppm of ammonia.[35] Compared to pure MW synthesised H_2SO_4 doped PANI the PU composite with 38 % of doped MW PANI had a better response at very low concentration of ammonia with a quantification limit to 0.3 ppb. This suggests the possibility of optimising the chemical and physical properties of MW PANI to fabricate ultra-sensitive sensors.

Table 1. Spin concentration N_{sample} and conductivity values for the synthesised MW HCl doped PANIs at 93 W

Sample	**Spin concentration N_{sample} (spin g^{-1}) $\times 10^{19}$**	**Conductivity (S cm^{-1})**
0.5 M MW HCl doped PANI	0.6978	2.59
1.0 M MW HCl doped PANI	0.0163	3.61
1.5 MW HCl doped PANI	0.0482	3.84
2.0 M MW HCl doped PANI	0.9515	4.03
2.5 MW HCl doped PANI	0.1133	4.34

Similar to the SA trend for PANI products synthesised using the EMS approach, the electrical conductivity also does not change significantly with the microwave power used in the synthesis.[14] The conductivity values for MW PANI products prepared at 93 W microwave power using different concentrations of aqueous HCl were 2.59-4.34 S cm^{-1} (Table 1). The values are in agreement with the conductivity results found by Gizdavic-Nikolaidis *et al.* for MW PANI products prepared using APS or KIO_3 as an oxidising agent and 1.25 M aqueous HCl acid.[14] The same authors[14] also showed that the molecular weight has no significant influence on the macroscopic electrical conductivity in the series produced at different microwave power levels, though there was a small increasing trend in conductivity values as a function of molecular weight which agrees with the theoretically predicted weak dependence of electronic properties on chain length.[37]

The conductivity results obtained for MW H_2SO_4 doped PANI products are in the range 14.66-15.06 S cm^{-1} which are ~1.5 times higher than the values for PANI products prepared by the CS method after the same reaction time.[17] This is also in good correlation with the higher doping levels (measured by the elemental S/N ratios) observed for MW H_2SO_4 doped PANI products in comparison to CS H_2SO_4 doped PANI products. Furthermore, conductivity values for MW H_2SO_4 doped PANI products were ~4 times higher than those for MW HCl doped PANI, which suggests that the nature of dopant anion also has a strong influence, as sulfate produces higher conductivity values than chloride as a dopant.[17] The reason for this is that sulfate has double the charge relative to chloride, so that for a given concentration of dopant acid in the doping solution, the positive charges in the polymer (polarons/bipolarons) and thus the conductivity will be higher for the sulfate case. Also, significant differences in the conductivities between the MW and CS synthesised PANI products imply that a microwave approach can be used for the rapid synthesis of highly conductive PANIs.[14, 17]

Tentative mechanism of formation of PANI nanofibres prepared using the EMS approach

The suggested mechanism is consistent with the previously suggested approaches by Li and Kaner[38] for PANI polymerisation using additives and mechanical agitation and their effects on nucleation modes. The issue of whether effects can be attributed to thermal or "specific" non-thermal effects related to MW irradiation during EMS synthesis should be taken into account. The existence of non-thermal effects has been the subject of strong debate in recent years.[14,16,33,39]

Broadly, the increasing rate of reaction by MW irradiation results from interactions between the electromagnetic field and polar molecules. In the EMS approach, as proposed by Gizdavic-Nikolaidis *et al.*[14,16,33], hot spots formed at the molecular level[39] and homogeneously distributed throughout the solution can form high level supersaturation sites which can be further promoters for homogeneous nucleation.

In order to explain the formation mechanism of nanostructured PANIs prepared using the EMS approach, Gizdavic-Nikolaidis *et al.*[14,16,33] assumed that two reaction stages exist, both affected by MW irradiation: 1) nucleation and 2) chain growth during the polymerisation process. The primary phase is based on immediate local heating that develops conditions for homogeneous nucleation. Other effects such as molecular agitation or diffusion could also drive the second fast phase. The complex relationship between these factors appears to be an answer for the fast formation of PANI nanofibres under MW irradiation. However, these are not the only factors that can influence the aniline polymerisation. The reaction could be also affected by the type of dopant acid and the oxidising agent, reagent concentration, etc.[14,16,33]

An in-depth knowledge and exact mechanistic theory for nanofibre growth is required, together with a better understanding of MW irradiation effects on chemical reactions. At this stage, the exact influence of the MW on the transition states for nanoparticle formation is still tentative.

Conclusions

The EMS approach for the synthesis of PANI nanofibres was investigated, with microwave power levels varied while the reaction system was kept at a constant ambient temperature of 24±1 °C. This is a novel, green method for fast and facile preparation of nanostructured PANI in high yield at ambient temperature. The SEM images of MW PANI products showed the presence of a mixed morphology with the predominance of nanofibrilar and porous morphology. This observation along with a good conductivity obtained for MW PANI suggested that the MW PANI material could be a good candidate for sensor applications. FTIR, Raman and UV-Vis spectroscopic results confirmed that the MW synthesised material structurally consists of PANI. A formation mechanism of PANI nanofibres under MW conditions is tentatively proposed. The EMS synthesis is also promising in that the formation of PANI nanofibres can be carried out at lower temperatures. This would ultimately lead to materials with improved thermal and mechanical characteristics.

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Unleashing the potential of the *p*-block: creating functional polymers with inorganic backbones

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Keywords: *main-group bond formation, p-block, inorganic polymers, catalysis, polymerisation*

Dr Erin Leitao was born and raised on Vancouver Island in Canada. She obtained her BSc degree in chemistry from the University of Victoria in 2006 and received her PhD degree from the University of Calgary in 2011 under the supervision of Prof Warren Piers. Following her graduate studies, she was a Marie Curie Postdoctoral Research Fellow with Prof Ian Manners at the University of Bristol, UK. In December 2015 Erin was appointed as a lecturer at the University of Auckland where her research involves investigating the mechanisms of main-group bond formations in an effort to create new inorganic materials.

Introduction

Conventional carbon-based polymers – long chain molecules comprised of repeat units termed monomers – feature prominently in our daily lives (Table 1), whether it is in the form of consumer materials (**A**-**C**, **H**), structural materials (**A**, **D**, **E**, **G**), biomaterials (**F**-**I**) or electronic devices (**J**, **K**).[1] This selection of relatively simple materials is the result of over 100 years of research in developing controlled and efficient methods to link carbon atoms together. Simultaneously, advanced methods for testing the material properties of the polymers as well as their fabrication have also been developed. The wide range of properties of these polymers demonstrates the diversity possible from essentially a single element – carbon – linked with itself.

When compared with the development of its carbon-based congeners, the synthesis of inorganic polymers, in this context containing *p*-block elements in the polymer backbone, is in its infancy.[2,3] Although several synthetic techniques have been elegantly exploited to connect main-group elements together to form polymers, there is a need for new developments as many of these techniques are inefficient and uncontrolled. This results in low-molecular weight, insoluble, and poorly-characterised materials of limited scope.

The main commercially available inorganic polymers are polysiloxane, polyphosphazane and polysilane (Fig. 1). These materials offer interesting properties such as excellent thermal and/or oxidative stability, maintained flexibility at lower temperatures, oxygen permeability, water repellence, and semi-conducting abilities. For example, silicone (**L**, polysiloxane) is ubiquitous in everyday uses as oils, greases, rubbers, polishes, coatings, sealants, biomaterials, *e.g.* contact lenses, artificial skin, and insulating materials.[4-7] Polyphosphazane (**M**) has been used in fuel pipes, as metal ion conductors in batteries, in foams, and as water repellent and fire retardant materials.[8,9] Polysilane (**N**) is an attractive material as the silicon-silicon backbone is σ-conjugated making these materials semi-conductors.[5,10] The electron delocalisation gives rise to electrical conductivity when doped with an oxidant. Polysilanes have found uses as ceramic precursors to silicon carbide fibres, explosive detecting materials, and as photoresist materials in microlithography for the electronics industry.[11-14]

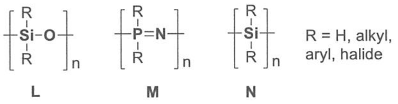


Fig. 1. Commercially available polymers containing an inorganic backbone

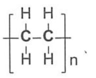
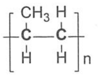
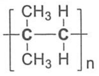
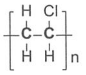
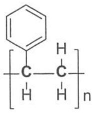
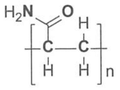
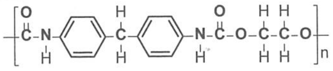
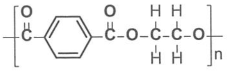
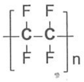
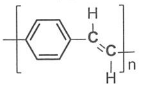
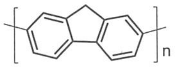
This article summarises the research and challenges in synthesising and characterising inorganic polymers, with an emphasis on recent breakthroughs and future opportunities.

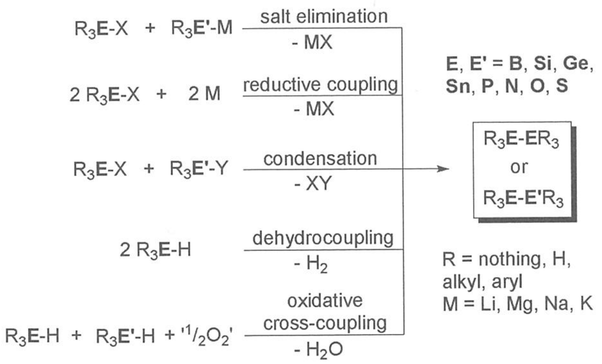
Ways to connect main-group elements together

The lack of sophisticated methods to link main-group elements with one another is responsible for the relative dearth of inorganic polymers compared with carbon-based systems. One breakthrough, the development of inorganic rings, has enabled facile access to inorganic polymers through the use of ring opening polymerisation (ROP).[15] This method has been demonstrated to be crucial for the synthesis of polysiloxanes (**L**) and polyphosphazenes (**M**) and will be discussed in more detail later.

Simply connecting main-group elements together can be accomplished by a variety of methods, many of which suffer from harsh reaction conditions and toxic reagents (Scheme 1). It is important to note, that when creating molecules such as inorganic rings and other monomers to be used in polymerisation reactions, some of the methods described below, *e.g.* salt elimination, are employed, while other methods, *e.g.* dehydrocoupling, can be applied directly as a technique to synthesise polymers (*vide infra*).

Table 1. Structures and applications of common carbon-based polymers

	Polymer	Structure	Applications
A	Polyethylene (PE)		packaging, toys, car parts, playground equipment
B	Polypropylene (PP)		banknotes, thermal clothing
C	Polyisobutylene (PIB)		tyres, chewing gum
D	polyvinylchloride (PVC)		clothing, ropes, pipes, door frames, wood composites
E	polystyrene (PS)		insulation
F	Polyacrylamide (PAA)		contact lenses
G	Polyurethane (PUR)		paint, wheels, insulation, seals
H	polyethylene terephthalate (PET)		clothing
I	Polytetrafluoroethylene (PTFE)		(**G, H, I**) used in heart valve and blood vessel replacements and vaccination/IV needles
J	poly(*p*-phenylene vinylene) (PPV)		(**J, K**) light emitting diodes
K	Polyfluorene (PFN)		



Scheme 1. General routes of linking main-group elements together

Salt elimination

This synthetic strategy reacts main-group halides (E-X) with main-group alkali metals (E-M; *e.g.* M = Na, Li) with the concomitant loss of a salt by-product (*e.g.* NaCl, LiCl).[16] It is an attractive route to connect main-group elements together as a large variety of substrates are available, evidenced by its wide-spread use.[17] Furthermore, using a different *p*-block element in each of the substrates can give facile access to heteronuclear main-group compounds and rings. However, drawbacks to this method include atom efficiency, highly reactive reagents which lead to limited functional group tolerance, and multi-step syntheses as the main-group alkali metals are often generated *in situ*.

Reductive coupling

Similar to the salt-elimination route in the by-products formed, reductive coupling involves the stoichiometric reaction of main-group halides with electropositive metals *e.g.* Na, K, Li, to generate new bonds between *p*-block elements.[17] This method is often used to form homonuclear main-group compounds and rings and is very sensitive to the rate of substrate addition. Under certain conditions, reductive coupling such as Wurtz coupling (typically using Na) has been shown to polymerise inorganic substrates. The shortcomings of this synthetic strategy are similar to the salt elimination route, in addition to being difficult to control, which is problematic for polymerisation reactions.

Condensation

Condensation is another synthetic strategy to form homonuclear and heteronuclear main-group bonds and rings. It operates on the same principles as salt elimination, *i.e.* two different leaving groups on two different substrates or attached to the same element. However, a small molecule *e.g.* H_2, H_2O, HCl, is eliminated instead of a salt by-product.[17] Condensation reactions can occur spontaneously (by design), in the presence of heat, or with the aid of a catalyst. It can be extremely difficult to control the stoichiometry of this reaction and, therefore, substrates of very high purity are required.

Dehydrocoupling

Dehydrocoupling, a specific variant on the condensation strategy, is an attractive method as the elimination by-product - dihydrogen - is non-toxic and potentially useful *e.g.* the hydrogen economy. Dehydrocoupling of main-group substrates is usually achieved catalytically by using a transition metal or main-group catalyst but has also been demonstrated to occur thermally and photochemically.[3,18,19] Unsurprisingly, the substrates amenable to dehydrocoupling have, therefore, recently received a lot of attention as hydrogen storage precursors.[20-22] As a result, synthetic strategies for the preparation of main-group complexes with hydrogen substituents, and the preparation of dehydrocoupling catalysts are both well-developed.

Oxidative cross-coupling

Cross-coupling of two main-group substrates is a second specific example of a condensation strategy. Its application with *p*-block substrates requires a catalyst *e.g.* CuX, CuX_2; X = halide, OAc, and a base under aerobic conditions (or the presence of an oxidant), eliminating water as a by-product. This technique, specifically employed to access a variety of P-E bonds *e.g.* E = S, N, P, O-P, O-R, from hydrogenphosphonates or N-sulfenylimines e.g. S-N bonds, from amines and thiols has been rapidly gaining momentum in the past few years.[23-30] Oxidative cross-coupling is an attractive method as it avoids the need for inefficient nucleophilic substitution reactions which use difficult-to-handle and highly reactive reagents (*e.g.* chlorophosphonates).

Of the above methods, the most environmentally friendly candidates to synthesise main group polymers are the condensation routes which eliminate water or dihydrogen. Catalytic methods, in particular, are advantageous as there is a wide range of possibilities surrounding catalyst and substrate modification which can be exploited to achieve more efficient and selective syntheses.

Polymer properties and characterisation methods

Techniques to determine the chemical structure of monomers and polymers are the same and include multinuclear NMR, UV-Vis and IR spectroscopy and X-ray diffraction, as well as mass spectrometry, of which only matrix-assisted laser desorption/ionisation-time-of-flight (MALDI-TOF) and electrospray ionisation (ESI) are useful for polymer characterisation. The determination of properties such as molecular weight, flexibility and thermal stability, relevant for materials applications, require more advanced techniques and are discussed briefly below.[31]

Chain length and polydispersity

Gel permeation chromatography (GPC), a type of size exclusion chromatography, is the main method to measure molecular weight (M_w, based on weight-average of the polymer chains; M_n, based on number-average of polymer chains) and to obtain the molecular weight distribution (polydispersity index [PDI] = M_w/M_n) of polymers.[32,33] Narrow molecular weight distribution (PDI as close to 1.0 as possible) is the target for polymers as it translates nicely into well-defined, defect-free, uniform materials although there are some applications where this is less important. Furthermore, in order for polymers to be useful for fabrication (*e.g.* into films and fibers), a critical molar mass (*ca.* 10,000 Da) needs to be reached to ensure a high degree of interchain entanglement providing the mechanical strength required for materials.[31]

Flexibility

Polymers range from amorphous to semi-crystalline to crystalline. Amorphous materials are comprised of long, flexible chains that pack randomly in the solid state. Increasing the packing regularity of the polymer chains through the introduction of intermolecular forces such as hydrogen bonds produces materials of higher crystallinity. This can have beneficial effects on their physical properties, however, highly crystalline materials may become brittle and insoluble. The state(s) of a given polymer over a temperature range can be measured using differential scanning calorimetry (DSC). Three significant temperatures can be determined using this method: T_m (the melting temperature), an order-disorder transition above which a viscous melt is formed; T_g (the glass transition temperature), the transition above which an amorphous polymer is a viscous gum and below which it is a glassy material, and T_c (the crystallisation transition temperature), the transition above which a crystalline polymer forms from a kinetically stable amorphous one. Polymer morphology can be observed using techniques such as powder X-ray diffraction (XRD), wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS).[31]

Thermal stability

Thermal stability within the typical temperature ranges used on earth (*ca.* -50°C to +150°C) is a desirable property of polymers to prevent degradation during regular use. Nevertheless, there certainly are cases where other temperature ranges are appropriate *e.g.* the use of polysiloxane as a medium to heat reactions during chemical synthesis. In these cases the thermal stability of the polymer must be consistent with the application. Thermogravimetric analysis (TGA) measures weight loss as a function of temperature providing the thermal stability of the polymer.

Polymerisation mechanisms and methods leading to inorganic polymers

Efficient polymerisation methods using monomers containing carbon elements are plentiful. The toolbox of methods contains free radical, anionic, cationic, coordination and condensation polymerisation processes. The polymers formed from these methods grow by one of two mechanisms: step-growth or chain-growth (Fig. 2).[34]

Polymerisation mechanisms

Step-growth polymerisation (Fig. 2I), most commonly observed using condensation polymerisation strategies, requires a substantial amount of monomer conversion before high molecular weight material is observed. This is because the mechanism involves monomers first reacting to form dimers, then trimers, tetramers, etc., until they eventually result in long polymer chains. In the case of condensation polymerisation, where small molecules are eliminated, this method requires fulfilling strict stoichiometric balance and conversion requirements in order to achieve the desired molecular weights. To obtain this balance monomers of very high purity are required, a significant challenge for inorganic monomers as they can be air and moisture sensitive. Therefore, high molecular weight polymers with excellent low polydispersity indices that form *via* a controlled step-growth mechanism are rare.

Chain-growth polymerisation involves i) initiation, ii) propagation, iii) chain transfer, and iv) termination steps. High molecular weight polymer is formed at low conversion as the molecular weight is related to the rate of propagation relative to the rate of individual chain termination steps (transfer and termination) (Fig. 2II). During propagation, the active site(s) (cationic, anionic, radical or catalytic) must be highly reactive as they are the site where the monomer(s) add to the growing polymer chain. A special case, living chain-growth polymerisation (Fig. 2III), can occur when the chain termination is slow. As a result a linear relationship between monomer conversion (%) and polymer molecular weight (M_w) is observed. Under living conditions the synthetic chemist has control over molecular weight by varying the ratio of initiator to monomer, or alternatively, though intentional termination. Therefore, living polymerisation methods are the most controlled routes to high molecular weight polymers with low polydispersities. As a result, living systems have enabled the formation of block and star co-polymers.[35] The availability of co-polymers through living radical and anionic polymerisation strategies has allowed unprecedented access to a variety of advanced architectures in the nanoscale through the self-assembly of co-polymers of mixed morphologies.

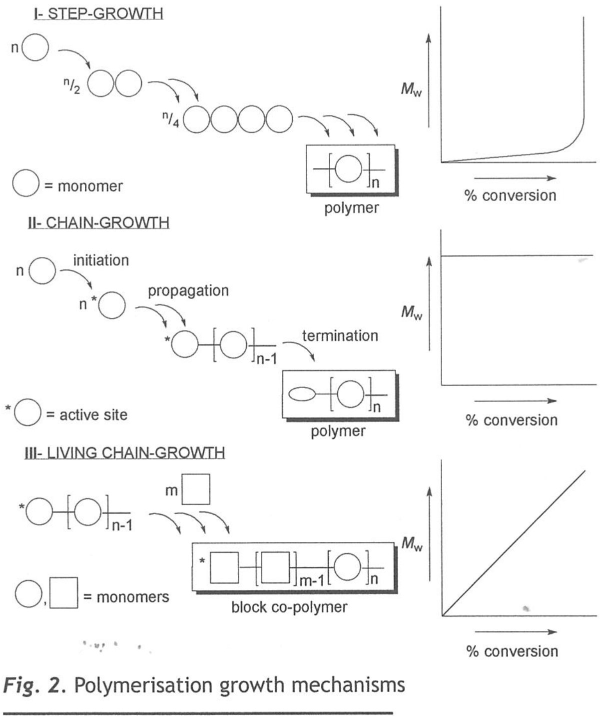
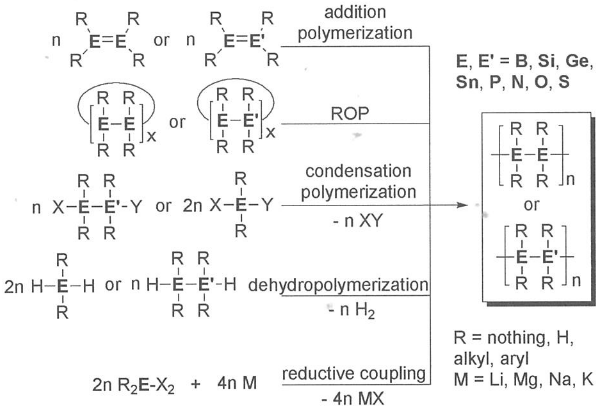


Fig. 2. Polymerisation growth mechanisms

Employing chain-growth approaches to the formation of inorganic polymers is a synthetic challenge. For example, attractive addition polymerisation methods, which use reactive unsaturated monomers such as olefins in carbon-based polymerisations, cannot be applied to inorganic substrates. Bulky stabilising groups are required to isolate unsaturated inorganic monomers as they are *too reactive* and these necessary ancillary groups prevent polymerisation. Condensation methods using inorganic monomers are more limited than with the carbon-based monomers as difunctional inorganic monomers can be highly reactive so their preparation and purification is often difficult.[36] However, there are some methods such as ring-opening polymerisation and dehydrocoupling that are not possible to use with most carbon-based monomers but are key for the polymerisation of inorganic substrates (Scheme 2). Many of the well-known inorganic polymers have been synthesised by more than one of these polymerisation strategies and specific examples of this will follow.



Scheme 2. General polymerisation strategies to be applied to inorganic monomers

Ring opening polymerisation

One successful approach for the formation of inorganic polymers is ring opening polymerisation (ROP). For a standard polymerisation reaction there is a decrease in entropy (order is gained; $\Delta S° < 0$) associated with polymer formation so in order for ROP to be thermodynamically favourable ($\Delta G° < 0$) there must be an enthalpic driving force ($\Delta H° < 0$) to offset the entropic loss.[15] Therefore, researchers have developed creative ways to synthesise strained rings which can be subsequently activated using an initiator (*e.g.* anion, cation, radical, or catalyst) or can be thermally or photochemically induced to undergo ROP. It has been demonstrated that ROP occurs *via* step-growth or chain-growth mechanisms depending on the substrate, initiator and reaction conditions.

Polysiloxanes. ROP to yield high molecular weight polysiloxanes (**L**) generally occurs from readily accessible 6-membered (cyclotrisiloxane) or 8-membered (cyclotetrasiloxane) rings using an anionic or cationic initiator (Scheme 3i).[4] These flexible polymers retain their elasticity even at very low temperatures e.g. T_g = -123°C for polydimethylsiloxane and T_g = -137°C for polymethylhydrosiloxane). Polydimethylsiloxane will crystallise (T_m = -40°C) upon the incorporation of phenyl substituents *via* random co-polymerisation with a phenylsiloxane monomer. Other useful properties of polysiloxanes include hydrophobicity, stability to oxidation and UV radiation, and high gas permeability.[7]

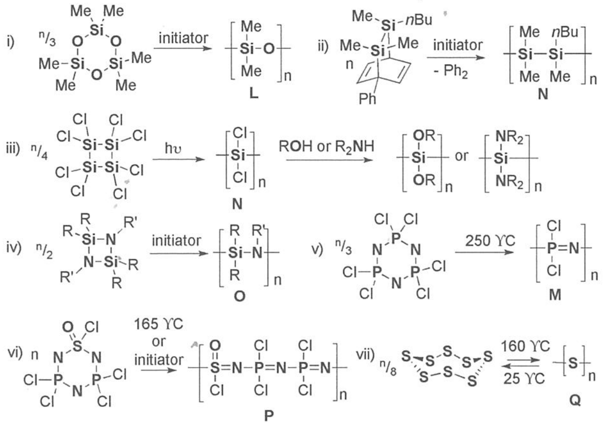
Polysilanes. Strained rings containing an all-silicon backbone suitable for ROP are not easy to find due to their difficult synthesis and isolation. ROP of masked disilenes is a very elegant way to gain control over the synthesis of polysilanes (**N**).[37] The disilene is stabilised through enclosure in a 6-membered phenyl substituted cyclohexadiene ring, which when anionically-initiated (in this case using *n*BuLi) undergoes ROP to yield the desired polysilane and diphenyl as a by-product (Scheme 3ii). Cyclosilane rings comprised of 4 or 5 silicon atoms will undergo ROP if the substituents on silicon are small, *e.g.* Me, Ph, Cl.[38-40] Anionic initiation can be used for alkyl or aryl substituents on silicon whereas octachlorocyclotetrasilane can be initiated photochemically. The resulting polydichlorosilane is highly moisture sensitive but can readily undergo post-polymerisation substitution to afford moisture-stable polysilanes (**N**) upon treatment with alcohols or amines (Scheme 3iii).[41,42]

Polysilazanes. Anionic-initiated ROP of 4-membered rings containing alternating Si and N atoms gives rise to polysilazanes (Scheme 3iv, **O**), an exciting class of materials that are useful as precursors to Si_3N_4 based ceramics.[43-45] Molecular weights of 3,000-4,000 Da can be achieved using this method, much higher than conventional condensation methods by reacting dichlorosilanes with primary amines yielding poorly characterised low molecular weight linear oligomers and cyclic compounds.

Polyphosphazenes. Thermal ROP of cyclo-$N_3P_3Cl_6$ at 250°C is the most established route to inorganic rubber (Scheme 3v, **M**).[8,9] Under these conditions the polymer is highly cross-linked and insoluble in organic solvents. Purification of the monomer along with careful control of the ROP furnishes soluble linear polyphosphazene (**M**). Post-polymerisation substitution of the chloride substituents with various nucleophiles *e.g.* NaOR or HNR_2, is facile, so a large number of polyphosphazanes are available.[46] Unfortunately, this synthetic strategy suffers from a required high reaction temperature, tedious monomer purification, low yield and poor molecular weight control so more recent research has focused on other synthetic routes (see coupling example below). Polyphosphazenes possess a very flexible structure with T_g below -100°C (polybutoxyphosphazene).[8] Thermal and oxidative stability, optical transparency and flame-retardance are other key properties of polyphosphazenes.

Polythionylphosphazenes. The simple replacement of a phosphorus element in cyclotriphosphazane with a four-coordinate sulfur(VI) provides another inorganic ring susceptible to thermal (165°C) or Lewis acid-initiated ($GaCl_3$) ROP (Scheme 3vi).[15,47,48] The polythionylphosphazenes produced (**P**) have molecular weights in the range of 25,000-52,000 Da with a large spread of PDI (1.26-2.18).[15,47,48]

Polysulfur. Elemental sulfur (S_8) exists naturally as an 8-membered ring that can undergo ROP thermally at 160°C to afford a long linear chain of sulfur elements (Scheme 3vii, **Q**) with impressive molecular weights as high as 2 million Da.[49] Sulfur is produced in large amounts as a by-product in the petrochemical industry so commercial-scale conversion to polymeric materials would be an attractive and effective use of it. However, polysulfur is formed in a metastable state and depolymerises back to S_8 under ambient conditions *e.g.* 25 °C.



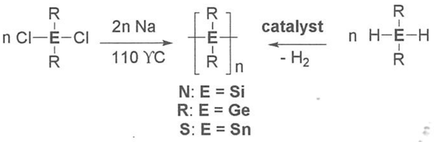
Scheme 3. Selected examples using ROP to synthesise inorganic polymers

Coupling to form homopolymers and heteropolymers

Coupling strategies *e.g.* reductive, dehydro, to access inorganic polymers is an active area of polymer research. Dehydropolymerisation with the aid of a transition metal or main-group based catalyst is the primary catalytic method available to produce high molecular weight inorganic polymers. It is especially effective for the elimination of H_2 from amine-boranes and phosphine-boranes to yield the corresponding heteropolymers. These monomers are polar and as such contain both hydridic hydrogens (on B) and protic hydrogens (on N or P) ready for intramolecular or intermolecular elimination.

Homopolymers

Polytetranes. The most widely applied route to synthesise polytetranes (**N**: E = Si; **R**: E = Ge; **S**: E = Sn)[12,50-54] is by reacting sodium or potassium (or alloys thereof) with dichlorotetrane monomers (Wurtz coupling, Scheme 4) at 110°C. Often these harsh conditions will result in polymodal mixtures of chains varying in size, with short oligomers and cyclotetranes mixed in with the desirable high molecular weight polymer *e.g.* $M_n > 10^5$ Da for polysilanes. Catalytic dehydropolymerisation routes are also attractive for the synthesis of polytetranes *e.g.* using a Ti or Zr catalyst, but in many cases still only result in low molecular weight products ($M_n < 8{,}000$ Da) and have limited scope.



Scheme 4. General coupling methods to access inorganic homopolymers

Heteropolymers

Polyborazylenes. Thermally induced dehydropolymerisation of borazine at 80°C provides facile access to polyborazylenes (Scheme 5i, **T**). These materials are typically low molecular weight oligomers (M_n = 3,400 Da; PDI = 2.2) and/or are highly cross-linked.[55,56] Oligoborazylenes have been successfully employed as precursors to boron-nitride ceramics as pyrolysis at 1200°C furnishes white boron nitride in excellent yield (up to 93%) which can be shaped into fibres and monoliths.

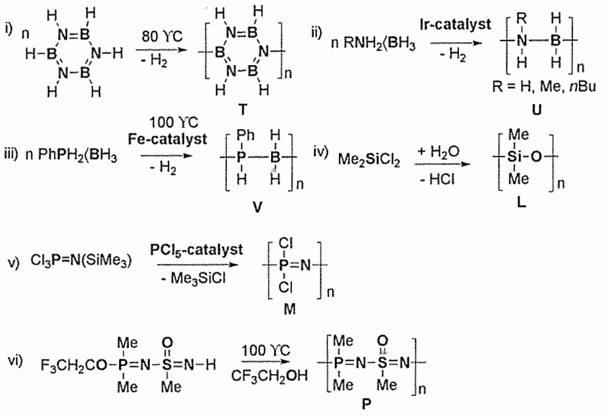
Polyaminoboranes. Soluble polymers with a N-B backbone (Scheme 5ii, **U**) analogous to polyolefins have been prepared by Manners and coworkers by iridium-catalysed dehydropolymerisation of amine-borane monomers ($RNH_2{\bullet}BH_3$) at 20°C (Scheme 5ii).[57] The molecular weights achieved after very short reaction times were substantial (R = Me, M_w = 400,000 Da, PDI = 2.9). The growth mechanism appears to be modified chain-growth as high molecular weight polymer is observed at low conversions but it increases slightly over time as more monomer is consumed.[58] Significant research has been performed in an attempt to expand the scope of polyaminoboranes[59-61] as well as to understand the dehydropolymerisation mechanism using a variety of catalysts.[62-70] Without an accurate picture of how the highly active Ir-catalyst operates, it is difficult to effectively modify the synthesis to improve the processibility of polyaminoboranes. Thermolytic[71] and other metal free routes[62,72] to eliminate H_2 from amine-boranes have been demonstrated, but only low molecular weight polymer is produced under these conditions.

Polyphosphinoboranes. Similar to polyaminoboranes, dehydropolymerisation using transition metal catalysts have allowed access to high molecular weight polymer. The first catalytic examples were using a Rh-catalyst (M_w = 33,300 Da) at 110°C.[73] More recently, polyphosphinoboranes (Scheme 5iii, **V**) have been synthesised (M_n = 59,000 Da; PDI = 1.6) via the Fe-catalysed dehydropolymerisation of phosphine-boranes at 100°C (Scheme 5iii).[74] Control over the molecular weight was achieved through changing the catalyst loading (initiator/monomer ratio), an indication that the catalytic polymerisation operates by a chain-growth mechanism. An exciting[75] metal-free route (using $B(C_6F_5)_3$ as a catalyst) which operates under milder conditions has also been reported and shows modest molecular weights (M_n = 27,800 - 35,000 Da, PDI = 1.6-1.9). Polyphenylphosphinoborane has been used in micro-patterning when fabricated on silicon wafers by soft lithography. Polyphosphinoboranes are attractive because of their flame-retardant behaviour, high thermal and oxidative stability, and for use as precursors to boron-phosphorus-based ceramics.

Polysiloxanes. Industrially, condensation methods involving the addition of excess H_2O to Me_2SiCl_2 with the subsequent elimination of HCl followed by further elimination of H_2O are used to synthesise polysiloxanes (**L**) terminated by OH and H groups of Si and O respectively (Scheme 5iv).[4,5]

Polyphosphazenes. The most recent advance in the development of polyphosphazane (**M**) polymers is the discovery of a low temperature (25°C) living cationic polymerisation route (Scheme 5v).[76] The monomer, $Cl_3P{=}N(SiMe_3)$ is initiated by PCl_5 which results in the elimination of $SiMe_3Cl$ and affords high molecular weight polymer *e.g.* M_n = 5,800 - 66,400 Da, PDI = 1.04 -1.32 for the CH_2CF_3 substituted polymer.[76]

Polythionylphosphazenes. Thermal condensation polymerisation of a cleverly designed monomer with a P=N-S=N backbone structure, forms polythinoylphosphazane (M_n = 8,000 Da) (Scheme 5vi, **P**) upon elimination of CF_3CH_2OH.[77] This monomer is advantageous over the cyclic one used in ROP as there are no halide substituents.



Scheme 5. Selected examples using coupling methods to access inorganic heteropolymers

Interesting materials heavily featuring *p*-block elements

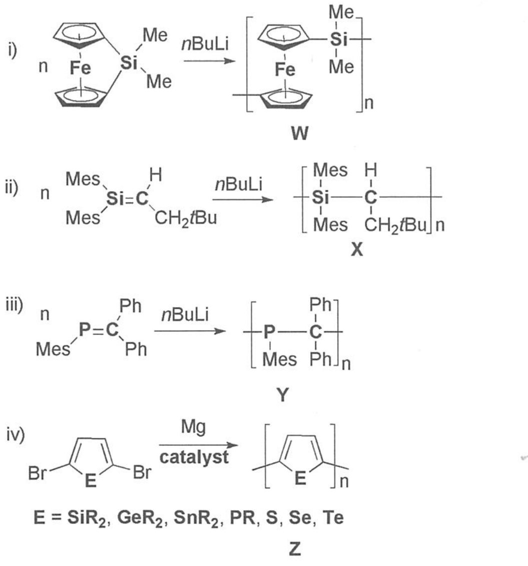
Although there is only a small selection of accessible inorganic polymers containing *p*-block elements in the backbone, there is a substantial body of research in organic-inorganic hybrid polymers as well as polymers containing transition metal elements interdispersed in the polymer backbone. Below are a few exciting examples along with the synthetic details, knowledge acquired on their growth mechanisms, and selected polymer properties and applications.

Polyferrocenylsilanes. Iron and silicon containing polymers (Scheme 6i, **W**), pioneered in the Manners group in the early 1990s, synthesised most commonly by anionically-induced ROP using *n*BuLi, were found to form by a living chain-growth polymerisation mechanism. These polymers have high molecular weights (> 10^5 Da) and excellent PDIs (as low as 1.02).[78] Polyferrocenylsilanes have attracted wide-spread attention as magnetic and catalytic ceramic precursors, etch-resistant, redox-active materials, components of photonic crystal displays, and in self-assembly to obtain a variety of architectures on the nanoscale.[79]

Polycarbosilanes. These polymers are excellent precursors to ceramic silicon carbide featuring high thermo-oxidative stability. Polycarbosilanes (Scheme 6ii, **X**) have traditionally been synthesised by metal-catalyzed ROP using a variety of different 3-membered and 4-membered strained monomers. More recently, these polymers have been prepared by addition polymerisation of kinetically stabilised silenes (Scheme 6ii).[80] The well-characterised products (M_n = 280,000 Da; PDI = 1.2; T_g = 153°C; thermal stability: weight loss at 325-525°C, ceramic yield = 12% at 800°C) are air and moisture stable.

Polymethylenephosphines. The addition polymerisation of phosphaalkenes *e.g.* $MesP{=}CPh_2$, to furnish high molecular weight (M_n = 8,900-29,000 Da, PDI 1.04-1.15) polymethylenephosphines (Scheme 6iii, **Y**) was achieved in 2003 by Gates and coworkers.[81,82] The polymerisation is observed to proceed *via* a living chain-growth mechanism when anionically-induced with *n*BuLi.[82] To this end, the group has been successful in preparing a series of novel derivatives of polymethylenephosphines as well as a co-polymer with styrene, which demonstrates interesting film-forming properties.

Polyheteroles. There has been an explosion in research for the preparation of polyheteroles (Scheme 6iv, **Z**; conjugated, semi-conducting materials), due to the use of polythiophenes in organic electronic devices (OED: light emitting diodes, field effect transistors), photovoltaic cells, and chemical sensors.[83,84] These polymers are available for a wide range of *p*-block elements *e.g.* E = S, Se, Te, P-R, $Sn\text{-}R_2$, $Si\text{-}R_2$, $Ge\text{-}R_2$.[85-88] Polymerisation of the heterole monomers is generally achieved using Kumada coupling which involves the Ni or Pd-catalysed cross-coupling of a Grignard reagent (Scheme 6iv),[89] but Stille coupling is also commonly used. The most widely studied is polythiophene and can undergo living chain-growth polymerisation.[83,84] Interestingly, polyselenophenes[88,89] have low solubility whereas polytellurophene forms soluble oligomers with molecular weights ranging from 5,400 to 11,300 Da.[90]



Scheme 6. Selected examples of the synthesis of polymers designed with *p*-block elements

Conclusions and perspectives

In the past century, the widespread use of synthetic carbon-based polymers has grown from plastic bags and tyres to include electronic, structural and biomedical materials. Controlled polymerisation methods and a detailed understanding of how the elements link together to form long chains have enabled this area of research to advance to a level of profound impact on society. Inserting main group elements into the backbone of polymers has already led to some very interesting materials with wide applications and continued research in this area will lead to the next generation of fascinating materials with potentially useful properties as each new element is introduced. However, controlled methods to synthesise inorganic polymers are required before this is possible. Research into exploring the ways in which main group bonds are linked into long chains is, therefore, paramount to revealing the potential of the *p*-block and uncovering new polymers, along with new molecules and functional materials. Inorganic polymers with interesting properties leading to applications which we cannot even fathom are waiting to be discovered.

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Reflections on a white road

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Edmund de Waal's recent book – *The White Road: a pilgrimage of sorts* – chronicles a field trip by the author to the most significant locales of the discoveries of the two raw materials for the making of porcelain – petunse (or porcelain stone) and kaolin (or porcelain clay) – and the development of porcelain-based crafts and industry.[1] De Waal's itinerary takes him from Jingdezhen in China, to western Europe, and thence to Britain, mirroring the temporal sequence of trading and industrialisation which may have started in China in the early 1400s,[2] and which culminated in the Enlightenment in Europe and the Industrial Revolution in Britain.[3] These milestones in the history of porcelain, as traversed by de Waal, are summarised in Table 1.

Discursive and replete with anecdotal side-bars, de Waal's own journey, reflections on his life and career, the historical events relating to the history of porcelain and his own 'take' on these events are intertwined in the 390 pages of narrative. Indeed, sometimes it is difficult to disentangle the present from the past. He traverses topics as diverse as the field occurrence of petunse and kaolin; experiments in porcelain-making, including firing and glazing; success and failure in the business of porcelain manufacture; and politics. Chemists are unlikely to have been envisaged as part of the potential audience for this book, but connections between the topics covered and chemistry are not hard to find, as the examples below reveal.

Of England's Josiah Wedgwood, de Waal writes, "Wedgwood's pace is tremendous. He has a peg leg, and his passage through life has a fast and rhythmic stamp to it. He casts an appraising eye over the landscape as speculator, property developer, geologist, mineralogist, potter, sorting information for use... He is noting and collecting as he goes, carrying away 'specimens of every kind'." (p. 301) Wedgewood was not the first to cast such an 'appraising eye' over the landscape; indeed the various discoveries of porcelain clay and stone in close proximity and their closeness to sources of fuel and labour for manufacture of porcelain are a recurring theme of the book. Wedgewood is, of course, well known to many: the story of the lesser known William Cookworthy, whose employment as what we would today describe as a commercial traveler enabled him to peruse the countryside for promising outcrops of the raw materials for porcelain manufacture and who then battled to establish manufactories, eventually losing out to Wedgewood, has at least as strong an appeal.

In de Waal's examples the raw materials for porcelain manufacture – petunse (powdered rocks containing feldspar, kaolin or quartz)[4] and kaolin (principally the clay mineral kaolinite) are found close together, but this contiguity is not a common occurrence, echoing the comment in respect of New Zealand's ceramics industry: "... one would expect natural geological processes to provide the required properties consistently, and at the right levels, in only a small number of materials".[5] In fact, "New Zealand had no commercial deposits of well-crystallised kaolinite clays. In some cases sedimentary deposits of poorly crystallised kaolinites mixed with quartz and feldspars were used [in pottery and ceramics manufacturing], but these tended to be of extremely variable composition", [5] as at the Benhar pottery works near Balclutha (Fig. 1) at which, in 1895: "The shelves are loaded with teapots in different designs, from the modest article for afternoon use to the more pretentious family article, all glazed in approved shades; jam jars are piled up by the gross in several sizes and shapes, likewise pie-dishes, baking dishes, butter crocks and jars, demijohns, spitoons, and several sets of bedroom ware, etc. With the exception of the latter all the ware is equal in appearance to the imported article. The toilet-ware, however, while the finish workmanship is unassailable, is rather dark in colour accounted for by the fact that a fine enough quality of clay is not obtainable, and this is what prevents the manufacture of cups and saucers, and ordinary table crockery. It cannot be made white enough to take the eye though just as strong and serviceable as the ordinary article."[6]

On that basis, the prospects for ingredients that would lead to manufacture of porcelain in New Zealand would appear bleak. Clays from Northland that were originally thought to be kaolinite were later found on the basis of differential thermal analysis[7] and X-ray diffraction studies to be rich in halloysite[7] (either chemically identical to kaolinite, *viz.*, $Al_2O_3.SiO_2.2H_2O$, but with a more disordered structure, or a hydrated form of kaolinite, *viz.*, $Al_2O_3.SiO_2.4H_2O$). Although considered less suitable than kaolinite for the ceramics industry,[8] these clays were found in the 1970s to be an effective substitute for a Korean clay long used in Japanese manufacture of highly translucent porcelain figurines.[5]

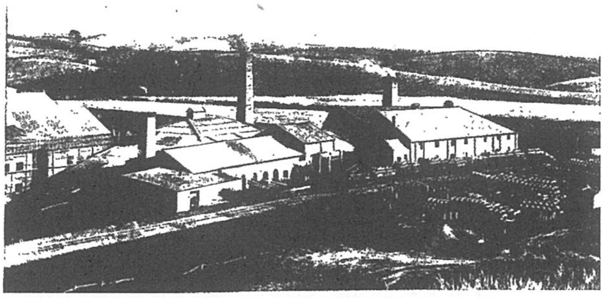

Fig. 1. Benhar Pottery Works (*Otago Witness*, 3 August 1904). Alexander Turnbull Library, Wellington, New Zealand. http://natlib.govt.nz/records/14202188. Prominent in the centre of the image is "that enormous chimney" cited in reference 6.

De Waal reminds us that England was more favored geologically in this regard: a patent was granted to William Cookworthy on 11 July 1768 for the discovery of "Materials of the same Nature with those of which the Asiatik porcelain is made, are found in immense Quantities in Our Island of Great Britain" (p. 283).

Of course it's the firing as well as the feedstock materials that define porcelain. The chemical equations that summarise the high-temperature process of making pottery from clay:[9]

Step 1: $6Al_2Si_2O_5(OH)_4 \rightarrow 6Al_2Si_2O_7 + 12H_2O$ 500°C (1)
kaolinite → metakaolinite

Step 2: $6Al_2Si_2O_7 \rightarrow 3SiO_2 + 3Al_4Si_3O_{12}$ 925°C (2)
metakaolinite → silica glass + silicon spinel

Step 3: $3Al_4Si_3O_{12} \rightarrow 5SiO_2 + 2Al_6Si_2O_{13}$ 1100°C (3)
silicon spinel → silica glass + mullite

... do not come close to the romance of de Waal's portrayal of the process, especially when he includes extracts from historic accounts, as in his describing attempts by Tschirnhaus and his alchemist protégé Böttger to make porcelain in Dresden in the early 1700s: "The accounts [in the archive] are cinematic. 'Every half an hour they looked into the kiln, like cattle, and the glow made everyone jump back, it was so hot that big stones were pulled out of the vaults and the hair on their heads was singed away and the tiles got so hot that big blisters developed on their feet.' There was real danger that the heat of the kilns could ignite the wooden structures above them on the ramparts..."

... of Albrectsburg castle, in which "the manufactory grew out of the laboratory from one cellar to another, across into rooms in the adjoining buildings, up and through the castle until great runs of medieval halls were being used" (p. 190). The result of one of these experiments is described by de Waal in this way:

"He [Böttger] opens the spyhole and the king [Augustus] and skeptical courtier [Prince Fürstenberg] see the saggars appearing darkly among the flames. The men draw a saggar out, and inside is a white teapot. This glowing pot is taken with metal tongs and thrown into a bucket of cold water. There is a loud bang, Böttger then takes the teapot out of the water and it's still intact. And according to the records, though 'the glaze hadn't completely melted', it was otherwise 'completely successful'. Something has gone right." (p. 189)

'Something has gone right' epitomises much of this book: it is a catalogue of efforts of the historical figures de Waal profiles and, to some extent, of his own career in the craft of pottery and its exhibition. In his view, the rewards can be great for the successful alchemist or the potter: "Turn lead into gold. Turn light into a rainbow. Turn clay into porcelain. Change the world in one grand catalytic moment." (p. 161).

While stark white porcelain is highly regarded, pigment, especially that derived from cobalt, "an exalted material", which "was the source of fortunes made and lost" (p. 59) was also a subject of considerable interest and experimentation. De Waal notes of its use:

"It was first used as a pigment at the start of the fourteenth century, imported [to China] from the mines near Kashan in Persia [the unrefined ore was probably asbolite[10]], down the Persian Gulf, across the Indian Ocean, to the port of Aceh on Sumatra and then on to the port of Quanzhou. It arrived either as pure cobalt oxide – difficult to transport – or as smalt, a compound of cobalt with glass that can be ground down, a process that diminishes the chance of the colour running under the glaze." (p. 59).

The White Road does not claim to be a scholarly book; nevertheless, de Waal acknowledges the help of numerous researchers, scholars and archivists. Rather than including a list of references, the reader is referred to the author's website, which includes "a guide to those I have found most useful, with signposts towards books and articles that may prove illuminating".[11] The list is principally a compilation of relatively modern works, but each section includes a selection of earlier books and manuscripts as well (Fig. 2). De Waal tells us in the Acknowledgements "that this book has been many years in the making": the comprehensiveness of the literature cited alone is some proof of that. The book also contains 45 illustrations, well chosen to support the text. The printing process has not been kind to these images, but they are all available on the book's website.[12]

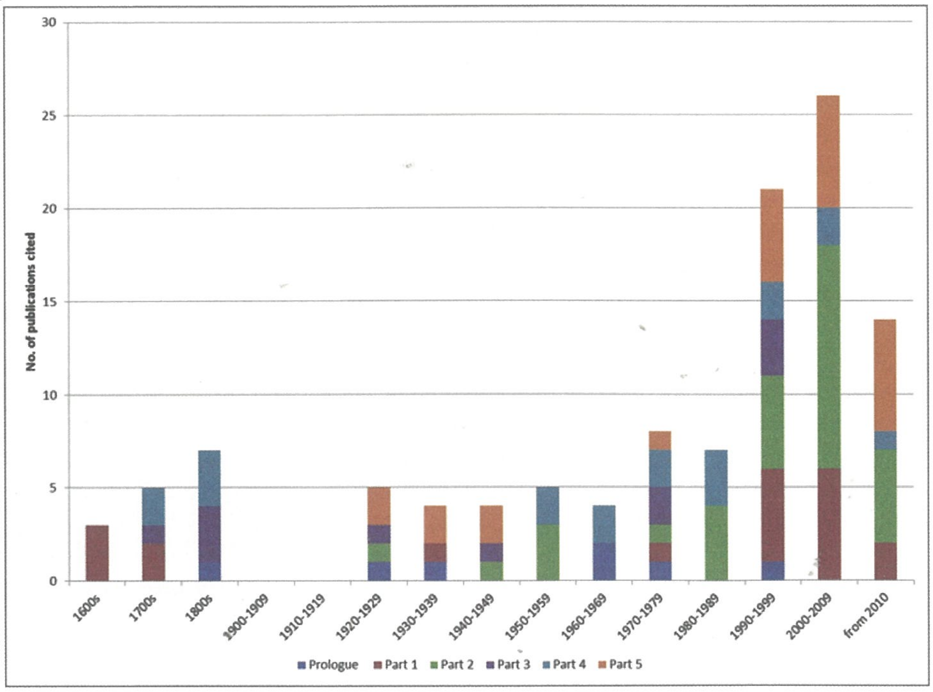

Fig. 2. Distribution of dates of literature cited in reference 11 as supporting *The White Road*.

Table 1. Four stages of the dispersal of knowledge and manufacture of porcelain, deduced from _The White Road_*

Locale		Year	Protagonists	**Activity**
Country	***City***			
PART 1: Jingdezhen (p. 21)				
China†	Jingdezhen	Sung Dynasty, 960-1279 AD		Identification of raw materials for porcelain: petunse and kaolin (from Mount Kao Ling) (pp. 30-35)
		Late 15th century	Chu Yuan-cho	Porcelain manufacture, reflecting on early works and modern-day practices (pp. 36-58)
		Early 14th century		Cobalt as glaze (pp. 59-64)
		Ming Dynasty 1500s		Porcelain manufacture (p. 72)
		After 1369	Zhu De	Yongle emperor, obsessed with white porcelain; he built Bao-ensi Temple of Repaid Gratitude – a 9-storey pagoda faced in white porcelain (pp. 78-84)
PART 2: Versailles – Dresden (p. 111)				
France	Paris	1691	Fr Joachim Bouvet and King Louis XIV	Letters from Jesuit missionaries arrive in Paris from China, stimulating intellectual exchange and trade between France and China (culminating in shipment of chines porcelain to Versailles and the building of a 'porcelain pavilion' – the Trianon de Porcelaine (pp. 113-120)
	Rouen	1680s	Jean-Baptiste Colbert	As Louis' minister of finance, Colbert advocates manufacturing of commodities that "bleed the king's coffers dry", one of which is "achieving porcelain of a kind" in a Rouen factory, trialling various materials. (pp. 126-129)
Saxony [Germany]‡	Dresden	1680s	Ehrenfried Walther von Tschirnhaus	Tschirnhaus was appointed by Colbert as tutor to his son (p. 129); he is a "philosopher and mathematician and observer of how the world changes", for whom "porcelain is an idea to be scrutinized" (p. 141.)
				Augustus, King of Saxony, "thinks that the establishment of glass factories is a good idea and is intrigued by porcelain"; leads to Tschirnhaus starting work in Dresden's Goldhaus, "the experimental laboratory for the king" (pp. 155-156).
	Dresden and Berlin	Autumn 1701	Friedrich Böttger (alchemist turned chemist)	Goldhaus – "a place of alchemy" (p. 159), as well as hosting Tschirnhaus research on porcelain. Meanwhile "there are rumours of a nineteen-year-old boy in Berlin, an apothecary's apprentice who has found the philosopher's stone, transmuted gold in front of reliable witnesses. And then has disappeared." (p. 165)
	Albrechtsburg Castle, Meissen	November 1701 to 1708		Böttger captured and assured protection by king; his alchemy is unsuccessful, but works with Tschirnhaus, not to make gold but porcelain (pp. 171-190). Ultimately "it is announced that there is to be a new factory at Meissen to create this white porcelain invented by the Arcanist, Johann Friedrich Böttger." (p. 193)
PART 3: Plymouth (p. 213)				
England	Plymouth	1719	William Cookworthy (chemist)	From a pharmacy that de Waal recognises as analogous to Botteger's origins (p. 216), Cookworthy initially heads for London , and thence to Plymouth to work as a "retailer and wholesaler to doctors and apothecaries" for a chemical laboratory (p. 225-227); his walking identifies local countryside as "an alchemist's land and a mineralogist's dream" (p.231).
		1736		Cookworthy includes divining (motivated by Emanuel Swedenborgii) in his field work (p. 237), aiming to find materials that will better the "soft-paste porcelains that are springing up across England", eventually finding local sources of both kaolin and petunse (pp. 240-245).
	Tregonnin Hill	1755		Investigations that lead to 'Cornish white' porcelain (pp. 251-255)
PART 4: Ayoree Mountain – Etruria – Cornwall (p. 263)				
England and North America	Bristol	1765	Richard Champion (merchant)	Receives 'a box of Porcelain Earth' from the "internal parts of the Cherokee Nations … on mountains scarcely accessible" (p. 265)

Locale		Year	Protagonists	**Activity**
Country	***City***			
England England	Plymouth		Champion & Cookworthy	New porcelain business to be established in Plymouth, using material to be extracted from land belonging to politician Thomas Pitt: prospect of "shimmering possibility of Chinese porcelains made from minerals under Cornish hills" (p. 266).
	Stoke-on-Trent		Josiah Wedgwood and Thomas Griffiths	Wedgwood develops highly popular 'creamware'; learns of the American pottery clays (p. 269); receives shipment of "white earth, the *unaker* of the Cherokee" in South Carolina from "the seasoned" Thomas Griffiths (pp. 269-277).
	Plymouth	1768	Cookworthy	Success: "The white earth has become this white vessel [a cider tankard]. It is the first piece of true porcelain ever made in England
		1768 - 1772	Cookworthy & Champion	Cookworthy granted patent not only for the materials for porcelain manufacture, but also the use of those materials (pp. 283-284); after manufacturing difficulties, he assigns patent to champion in 1772
	Etruria	1775	Josiah Wedgwood	Challenges Champion's (i.e., Cookworthy's) patent and eventually succeeds (pp. 294-300), and is able to secure materials for manufacture in Cornwall (p. 304)
	Bristol and Etruria	1778	Champion and Wedgwood	Champion's manufactory in Bristol fails, as had Cookworthy's in Plymouth; Wedgwood triumphant (pp. 305-311)

*The Prologue, Part 5 and the Coda are excluded from this compilation
†Supplemented by a section in Part 5 on porcelain in China from the 1920s, including under Mao (pp. 339-342)
‡Supplemented by a section in Part 5 on the Allach porcelain factory at the Dachau camp during World War II (pp. 343-346)

In summary, through its combining elements of field-work, laboratory investigations, the transformation of experiments to manufacturing, and patronage and financial support, *The White Road* is as relevant to our time as to history, and potentially as interesting to chemists as to craftspeople.

Notes and references

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11. See: http://www.thewhiteroadbook.com/resources-list/further-reading (accessed 2/02/2016).
12. See: http://www.thewhiteroadbook.com/resources-list/gallery (accessed 2/02/2016).

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Keywords: *green chemistry, research themes, teaching, water and environment, waste to value, sustainability*

Ivanhoe Leung attained his undergraduate degree and DPhil in chemistry at the University of Oxford, as a member of St Peter's College. After his DPhil he spent a further two years in the same department as a postdoctoral research assistant. Since September 2014, Ivan has worked at the University of Auckland. He is currently a lecturer in chemical biology. As a member of the Centre for Green Chemical Science, he is interested in the development and application of biocatalysts to catalyse reactions that are otherwise difficult and/or wasteful to do by traditional methods.

Viji Sarojini obtained her PhD from the Indian Institute of Science, Bangalore, specialising in peptide chemistry (Prof Padmanabhan Balaram). She then undertook a postdoctoral position with Prof Lars Baltzer in Sweden, which was followed by research positions at the University of Leeds, UK and Texas A & M University, USA. She then joined Plant and Food Research, NZ where she applied her expertise in peptide chemistry to bacterial diseases of plants. She joined the University of Auckland in 2006 where she is currently a senior lecturer in the School of Chemical Sciences. Her current research interests lie in the fundamental and applied aspects of peptide chemistry in agriculture, food technology, medicine, water and the environment.

Jonathan Sperry obtained his BSc (Hons) in 2002 and PhD in 2006 (Professor Chris Moody) from the University of Exeter, UK. He spent three and a half years as a postdoctoral researcher with Distinguished Professor Margaret Brimble at the University of Auckland before taking up a lectureship at the same institution in 2009, where he is currently a senior lecturer and a Rutherford Discovery Fellow.

James Wright completed his PhD at the University of Auckland and after working at the Department of Scientific and Industrial Research (DSIR) in Wellington for two years, he joined the research group of Prof J. P. Collman at Stanford University as a postdoctoral research fellow. He then took up a lectureship at the University of Auckland where he is now a Professor in the School of Chemical Sciences. His current research interests include green oxidation catalysts, water purification, organometallic chemistry including metallabenzenes, CO releasing molecules (CORMs) and the design of new ligands for homogeneous catalysts. He is Deputy Head of the School of Chemical Sciences and Director of the newly formed Centre for Green Chemical Science at the University of Auckland.

Introduction

In a new initiative at the University of Auckland, a group of academics have established a Centre for Green Chemical Science (CGCS).[1] Support for setting up the Centre was provided by the Vice-Chancellor's Strategic Development Fund. The Centre, which is located within the School of Chemical Sciences, aims to facilitate and promote research, teaching and public awareness in the broad area of green chemical science. This article provides an overview of the activities of the Centre and the principles behind its establishment.

To us, the term "green chemical science" means the use of chemical principles, science and technology to advance society in ways that are sustainable and benign to the environment. It involves studies of catalysis, synthesis, toxicology, analytical methodology, materials science, and biochemistry to tackle global issues and problems that impact on sustainability.

The CGCS was launched in September last year and currently has more than 25 scientists as members spanning across the Faculties of Science, Engineering, and Medical and Health Sciences. The mission of the CGCS is to provide the foundations for a sustainable future by promoting and facilitating interdisciplinary research, education and public engagement in green chemical science.

The main goals of the CGCS can be summarised as follows:

- To provide leadership in research, education and outreach in Green Chemical Science
- To inspire world-class research that tackles pressing global issues and problems that impact on sustainability
- To inspire exchange of ideas and establishment of interdisciplinary research collaborations
- To facilitate engagement with industry and to work with them to provide green chemical science solutions
- To provide an excellent education, training platform and experience for students engaged in a green chemical science programme
- To play a prominent role in developing public awareness and communicating information on issues related to green chemical science and Sustainability

The Centre's mission and goals align well with many of the recently released United Nations Sustainable Development Goals,[2] especially those that relate to clean water and sanitation, affordable and clean energy, climate action, good health and well-being, and responsible consumption and production.

Research activities at the CGCS

The current research activities at CGCS fall under the following general themes:

Sustainable Synthesis (Co-ordinator – Jon Sperry)

- Developing biorenewable routes to products currently sourced from fossil-fuels
- Green solvents and reagents

Catalysis (Co-ordinator – Ivan Leung)

- Applications of new catalysts and/or sensors

Waste to Value (Co-ordinator – Bruno Fedrizzi)

- Repurposing of waste materials into high value products

Energy (Co-ordinator – Tilo Soehnel)

- Solar energy conversion
- Sustainable bio-fuel and hydrogen generation

Water and the Environment (Co-ordinator – Viji Sarojini)

- Invention of new methods for the degradation of pollutants
- New efficient methods to remove low levels of problematic materials from drinking water
- Carbon sequestration and greenhouse gas mitigation

Each theme has an associated co-ordinator. The co-ordinators are members of the working committee of the CGCS and the Director of the Centre is Professor James Wright. Since its inception in September last year CGCS members have already obtained $1,200,000 of external funding through four separate grants for green chemical science research. In addition, since that time Centre members have obtained one patent and published four papers[3-6] in the green chemical science area.

The research of two Centre members, Professor Paul Kilmartin and Dr Marija Gizdavic-Nikolaidis was recently highlighted by PureAdvantage, a conglomerate of business leaders who promote the importance of sustainability in New Zealand's future.[7]

Professor Paul Kilmartin's research involves development of a sustainable method to reduce food spoilage. Food spoilage is currently reduced by adding artificial antioxidant and antimicrobial agents to food packaging. However, these chemicals can leach into the food and wider environment. An alternative idea is to incorporate natural polymeric additives to the packaging which, due to their increased size, will not leach into the food product. Antioxidant tannin polymers are excellent candidates for this role. Tannins are natural compounds found in large quantities in grape skins and seeds and provide wines with important mouth-feel properties. A research group led by Paul has developed a water-based extraction procedure to obtain grape tannins from residual grape waste (also known as grape marc) remaining after the juice has been removed by pressing during the wine making process. Grape marc is available in very large quantities as a waste product from the wine industry. The tannin powder obtained by this extraction procedure is rich in polymeric antioxidants, which have also been shown to possess antimicrobial properties. These tannins have been successfully blended into biodegradable polymers such as ethyl cellulose and with a number of the more common plastics such as polyethylene and polypropylene. The resulting films retain the desirable properties of the original plastics but now in addition possess effective surface antioxidant properties. Initial results indicate the new films may provide a sustainable, non-toxic solution to the prevention of food spoilage. This research is currently being further investigated as part of a larger MBIE supported research programme (Biocide Toolbox).

Dr Marija Gizdavic-Nikolaidis' research involves the development of a non-toxic polymer-based antimicrobial that can be used in soaps, detergents and other products as a replacement for currently used problematic and toxic compounds such as trichlosan and triclocarban. As part of a research team at the University of Auckland, Marija has played a leading role in generating a new antimicrobial polymer (AMP) technology, which has potential applications in a range of areas that include personal care, health care, wound dressings, water and air filtration, antimicrobial plastic additives, antimicrobial paints and coatings, wood and paper, the marine industry and consumer products. The AMP technology has exceptional antimicrobial efficacy against a broad range of microorganisms including bacteria, fungi and viruses at a low concentration load (<1 wt %). Current studies show that the material is low-cost, has high temperature stability, is non-leachable, and non-toxic to mammalian cells. The AMP technology has been successfully licensed to the US-based company TiFiber Inc.[8]

Launch of the Centre

The CGCS officially opened with a symposium on the 8th September 2015 that was attended by more than 150 guests from both academia and industry. The event was noted as an Auckland branch news item in the January 2016 issue of *Chemistry in New Zealand* and a fuller description is given here.

In the morning session, the CGCS was officially launched by the Vice-Chancellor, Professor Stuart McCutcheon. This was followed by an excellent lecture by Professor Milton Hearn (Director of the Australian Research Council Special Research Centre for Green Chemistry at Monash University) entitled, *What benefits can be gained from a Green Chemistry Centre for academic researchers?* A cluster of three minute talks from members of CGCS showcased the diverse range of green chemistry research being conducted by members of the CGCS, including smart catalytic surfaces for water purification, biodegradable polymers from renewable resources, biofuels, reduction of toxic waste including biomaterials derived from protein waste, sustainable chemical synthesis, (bio)catalysis, solar cells and combinatorial chemistry.

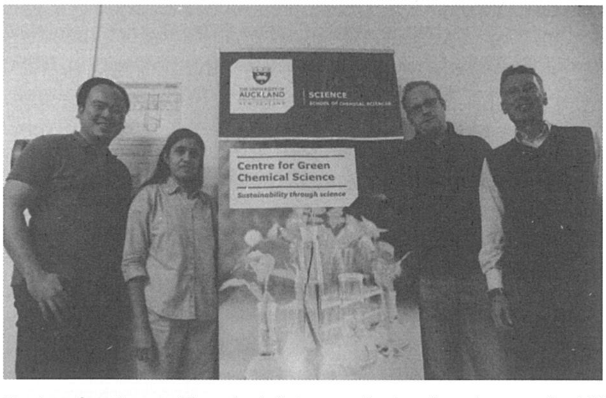
The afternoon session started with the Director of CGCS, Professor James Wright, delivering an overview of the Centre and the Centre's mission and goals, including our aspirations for the future. Professor Paul Kilmartin then delivered an excellent talk on his research entitled *Turning winery waste into active packaging*.

Professor Milton Hearn then delivered his second lecture of the day entitled, *How can a Green Chemistry Centre assist industry achieve its business goals in ever more challenging environments*? which was well received by our industry guests. Professor Hearn described the numerous benefits that arise from the free flow of expertise between industry and academia.

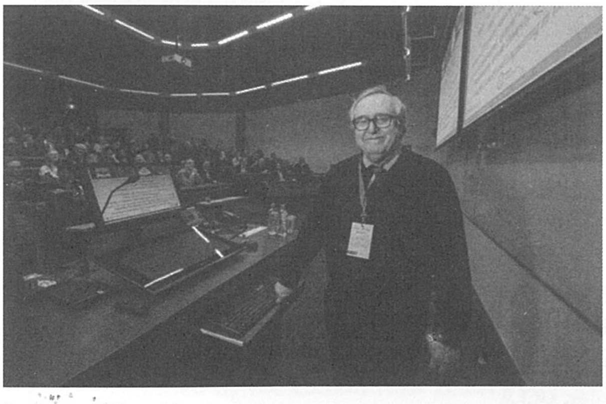
Malcolm Rands, the CEO and founder of Ecostore delivered the talk, *The Adventures of Ecoman*, outlining a fantastic New Zealand success story that charted the rise of Ecostore from humble beginnings to the internationally renowned company it is today. The day's lectures concluded with a talk by Chris Mulcare of Pure Advantage entitled, *How smart science aligned to our advantages will create a smart economy*. The final talk by Chris really emphasised the importance of sustainability in New Zealand's future, and the huge role that science has to play to make this happen.

New teaching programme

Making significant advances in green chemical science characteristically requires creativity, inventiveness and a deep understanding of the fundamental aspects of science. A comprehensive education in these areas is therefore essential for beginning practitioners and a proposed BSc programme with a green chemical science specialisation at the University of Auckland will provide the foundations for this. The present target for the launch of this programme is the 2017 academic year.



Centre for Green Chemical Science: Dr Ivanhoe Leung, Dr Viji Sarojini, Dr Jon Sperry and Professor James Wright (Director)



Professor Milton Hearn delivering his second lecture during the CGCS symposium

As a prelude to establishing this programme, two undergraduate green chemistry courses will be offered for the first time in semester two this year. The first of these is a second year course, CHEM 260, entitled, *Introduction to Green Chemistry*. The course will cover a range of topics including an introduction to the concepts and principles of green chemical science and selected real world applications of green chemistry to illustrate how these important guiding principles can be applied. The course will include an integral laboratory component that will provide valuable practical experience in relevant areas of the green chemical sciences. The second course is a third year course, CHEM 360, entitled, *Contemporary Green Chemistry*. Topics covered in this course will include sustainable syntheses, energy production, catalysis, pollution control and basic toxicology. There will also be an integral laboratory course associated with this course.

Summary and outlook

The CGCS is growing rapidly and many of its members will be housed in the new Science Centre building that has been constructed next to the current building that houses the School of Chemical Sciences on Symonds Street. The move to the new building is scheduled to occur in July this year.

The second annual symposium hosted by the CGCS will be held in September 2016, details of which will be announced shortly. In this symposium we will bring together green chemists from Australasia and across the world both from academia and industry to promote the advancement of green chemical sciences in New Zealand.

The CGCS already has a number of members who are in other Schools or Departments within the Faculty of Science or in other Faculties at the University of Auckland. This reflects the interdisciplinary nature of much of the green chemical science research being carried out, and places us in a good position to achieve one of the important immediate goals we have for the Centre, the first of which is to expand into a Faculty Centre and then to a University Centre. Another important goal for the CGCS is to develop strong interactions and collaborations with industry. To this end we are arranging a series of workshops that will be held with appropriate industries. Our overall aim is that as the next year unfolds these initiatives, in addition to others we have planned, will help the CGCS grow into a large, vibrant and cross-disciplinary centre that supports and promotes research, teaching and outreach in green chemical science.

Acknowledgements

We gratefully acknowledge funding from the Vice-Chancellor's Strategic Development Fund.

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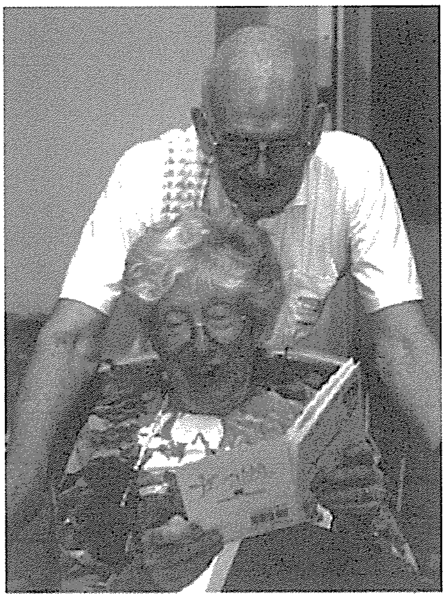
Obituary: Robert L Scott, Emeritus Professor, UCLA



Bob and his wife Libby in 2003, on the occasion of her birthday.

We are sad to report that Emeritus Professor Robert L. Scott passed away on May 1 2016 at age 94.

A distinguished physical chemist, Bob joined the UCLA Department of Chemistry and Biochemistry in 1948. A native Californian, Bob made the trek to the east coast to attend Harvard, where he majored in Chemistry. He then began graduate study at Princeton in 1942, working on polymer physical chemistry with Michel Magat and, after receiving his doctorate in 1945, continued to work there and at Los Alamos on the Manhattan Project. He returned to California in 1946 to carry out postdoctoral research with Joel Hildebrand as a Frank B. Jewett fellow at UC Berkeley.

Early in 1948, in a letter to William G. Young, Joel Hildebrand wrote "I have a remarkably able young man working with me, Dr. Robert L. Scott, who should be snapped up by one of the first class departments....He is good enough to join this Department, but with Zimm and Jura, we are pretty well supplied with good men familiar with this general field. I am writing, therefore to suggest that you might like to use him." In May 1948 Young recommended to the provost that Bob should be appointed as Assistant Professor (at an annual salary of $4200) and enclosed letters of recommendation from Hildebrand, Hugh Taylor of Princeton and Henry Eyring. He noted that he had also spoken with John G. Kirkwood at Yale, who "enthusiastically stated that he considered him one of the most promising younger physical chemists in the country."

Bob lived up to this praise. Over the years he developed an experimental and theoretical research program in thermodynamics and statistical mechanics that established himself as a leading expert in the physical chemistry of liquids, polymer and nonelectrolyte solutions. The book "Solubility of Nonelectrolytes", which he co-authored with Joel Hildebrand is a classic. His theoretical work on the phase behavior of sulfur and the behavior of the heat capacity in the vicinity of a critical point anticipated the intense interest in critical phenomena that blossomed in the early 1960's. In a remarkable series of papers he showed how simple equations of state, such as the van der Waals equation, could account for the panoply of phase behavior seen in fluids at high pressure, work that was cited when he received the 1984 ACS Hildebrand ("Liquids") Award. He was also the recipient of Guggenheim and NSF Senior Postdoctoral Fellowhips and was a Fulbright Lecturer in New Zealand. His first publication, on the thermodynamics of high polymer solutions, appeared in the Journal of Chemical Physics in 1945; his last publication, on an insightful way to understand the statistical mechanical calculation of the heat capacity of gases, appeared in the Journal of Chemical Education 61 years later.

Bob's career at UCLA was notable for his service. Early on, he was chair of the building committee for the design of the labs, classrooms and offices in Charles E. Young Hall. (The Department was housed in Haines Hall when Bob joined the faculty and construction of the new building began in 1963.) He served a five-year term as department chair, and was a member of several important Academic Committees: Academic Personnel; Campus Planning; Academic Innovation; Faculty Welfare; Graduate Council. In 1948 neither quantum mechanics nor statistical mechanics was taught in the Chemistry curriculum. They were introduced by Bob, who taught the first Stat Mech course, and Bill McMillan, who taught the first quantum course. For nearly twenty years after his retirement in 1993, Bob continued to remain active in the department, refereeing papers, attending seminars and serving as the "go-to-guy" when there were knotty questions about statistical mechanics or thermodynamics, and lending his wisdom to discussions in faculty meetings.

Many former students and postdocs have remarked about the hospitality they received from Bob and his wife Libby who welcomed them into their home and introduced them to the joys of hiking in the local mountains and backpacking in the Sierra. Bob was a strong advocate for social justice, an unapologetic liberal who was known to slam his fist on the breakfast room table as he read something upsetting in the morning paper. He had an encyclopedic knowledge of history and a remarkable memory. For example, he was able to recount in precise detail the day-to-day itineraries of his many trips throughout the world.

In the words of David Fenby one of Bob's students, "Bob: an outstanding scholar; a man of wide culture; a family man; a great friend and an immense influence in my life" – a sentiment to which Bob's friends, students and colleagues would heartily agree.

Submitted by Arthur Williamson FNZIC, FIPENZ, Emeritus Professor, University of Canterbury

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Reliable durability prediction of polymeric materials

Patricia Shaw,* Nick Marston

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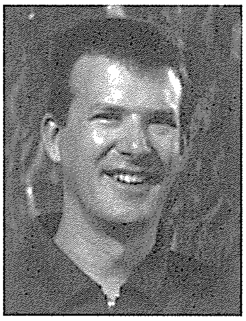
Keywords: *durability, test methods, accelerated weathering*

Trish Shaw is the Better Buildings Research Team Leader at BRANZ, leading a team of material scientists, fire engineers and structural engineers. The team are currently working on over 20 research projects into improved techniques and materials for use in the building industry. Trish obtained a PhD in chemistry from the University of Auckland and has over 20 years' experience as a materials scientist. She previously worked for the NZ Defence Force, specialising in protective coatings and managing their corrosion programme. Since joining BRANZ her research focus has been on the resilience and durability of building materials, with a particular interest in the degradation of polymeric materials.



Nick Marston is the Materials Team Leader at BRANZ where he has worked for nine years. His research has included examining the resilience of buildings and materials as well as researching the effects of environmental exposure on plastics and metals.

Abstract

Most polymeric materials used outdoors undergo degradation due to environmental exposure, particularly solar UV radiation, affecting their durability. New Zealand's climatic variables significantly affect the durability of polymeric materials and reliable durability assessments can be difficult. The New Zealand Building Code is primarily performance-based. This requires the durability performance of materials to be demonstrated through laboratory testing, a documented history of use, or by analogy with the behaviour of similar building components. However, little practical guidance is provided concerning how these criteria might be satisfied. This paper describes the development of a durability verification test method for polymeric materials using FTIR spectroscopy. FTIR, with chemometric analysis, was used to correlate outdoor exposure with accelerated aging tests, looking at both degradation mechanism and exposure time. Once completed, the FTIR method will mean that accelerated aging tests can be used to reliably predict the durability performance of polymeric materials naturally exposed during service. This may include assessment of 'new' products, serving to alleviate the suspicion often associated with new building products. It may also provide a method for predicting the remaining serviceable life of outdoor exposed polymeric materials used in New Zealand.

Introduction

New Zealand Building Code

Ensuring that buildings have an appropriate durability has always been an important aspect of building regulations. This is emphasised by the current New Zealand Building Code (NZBC), which includes the functional requirement that: "*Building materials, components and construction methods shall be sufficiently durable to ensure that the building, without reconstruction or major renovation, satisfies the other functional requirements of this code throughout the life of the building*".[1]

The NZBC is a performance-based, rather than prescriptive code. It is intended to permit innovative solutions and minimise the constraints placed on building design or choice of materials and techniques, providing the mandated minimum performance levels are achieved. The Code's B2 Durability clause is the single exception to this philosophy, setting default lifetimes for building elements depending on their criticality of function and ease of replacement (Table 1). These durability provisions apply to any part of the building which is fulfilling another Code requirement (e.g. structural stability or fire performance).

The reason for retaining this prescriptive aspect in an otherwise performance-based code is essentially one of consumer protection. It was considered inappropriate to allow the service life of buildings to be effectively set by market forces. This was particularly so given that a significant proportion of owners would have little expertise in evaluating the relative benefit of construction styles and materials.[2] Note that despite this prescription, the choice of materials for producing building elements of the required durability is left unregulated.

Durability test methodologies

In practice, there is no shortage of test methods for a vast variety of materials and potential applications. However, a considerable amount of skill is necessary to collate and synthesise this information in a reliable and appropriate

Table 1. A summary of the performance requirements for building elements specified by the NZBC B2 Durability clause. Note that the mandated service life allows for routine maintenance, but not reconstruction or major renovation.

Nature of Building Element	Required Service Life	Typical Examples
(i) Provides structural stability, *or*	50 years	• Load-bearing walls
(ii) Difficult to replace, *or*		• Buried electrical wiring
(iii) Failure undetectable thorough normal maintenance regimes		• Building wraps behind masonry veneer walls
(i) Moderately difficult to replace, *or*	15 years	• Building envelope cladding
(ii) Failure undetectable during everyday occupancy of building		• Sealants and flashings
(i) Easily replaced, *and*	5 years	• Architectural coatings
(ii) Failure readily apparent		• External gutters

test that allows the assessment of a material's durability. Expert judgement is needed for a variety of reasons. This includes considering whether the degradation methods in accelerated tests (heat, moisture cycling, freeze-thaw, UV exposure, etc.) are appropriately matched to real-world causes of deterioration. Expertise is also necessary when assigning quantitative service life predictions on the basis of qualitative rankings of observed durability. Likewise, assessing likely variation in performance due the different macro- and micro-climates, materials interactions, intensity of use and maintenance requires judgement based on experience.

Considerable research has been carried out into the durability and service life of buildings, materials and components by both BRANZ [3,4] and overseas research organisations, including the National Institute of Standards and Technology (NIST), USA and the Building Research Establishment (BRE), UK. However, there is still a substantial absence of knowledge and information available. This means that New Zealand Standards and Building Code documents cannot provide reliable and quantified methods to determine the likely service life of materials.

Past testing of natural exposed polymeric materials across New Zealand indicated that there was a clear and reliable correlation between the tensile strength loss of clear unstabilised polypropylene (PP) and polyethylene (PE) and solar exposure.[5] Samples were exposed across the length of the country at sites in Kaitaia, Paraparaumu, at the BRANZ site in Judgeford and in Invercargill for up to 6 years. The exposure time to produce a 50% loss of tensile strength varied across the different sites, roughly proportional to the UV index at each site. A predictable relationship between the harmful radiation dose and loss of tensile strength was determined.

Trends for mechanical property change for more UV stable polymers during natural exposures, such as white polyvinylchloride (PVC) and black PE, were less clear cut. It is believed that eventually UV damage will cause the samples to lose strength, but this effect had not occurred by the end of the seven year exposure used in the study. This is not surprising as correctly formulated white PVC would be expected to perform acceptably for ~15 years outdoors in New Zealand.

The dose of harmful radiation required to result in a 50% loss of tensile strength for both PE and PP was determined to be 75 MJ/m^2. The PP and PE materials used in the natural weathering study were then exposed for periods of time in the Q-Panel Q-Sun xenon arc weatherometer. The set-point conditions for the weatherometer were those used by BRANZ for the last decade. Preliminary results showed that accelerated weathering worked well for natural weathering lifetime prediction. For New Zealand, 750 light hours in the Q-Sun weatherometer correlated to one year outdoors.[6]

The tensile strength trends for the PVC samples that underwent accelerated weathering generally replicated the natural weathering results. However, the exposure times for the accelerated samples, up to 3000 hours exposure in the weatherometers, were not long enough to initiate PVC tensile property losses. This is consistent with the European standard for PVC windows, EN12608, which indicates that about 6000 hours of light exposure in a xenon arc accelerated weathering apparatus mimics 5 years in southern European climates such as Spain or Italy.[7] Clearly, extended accelerated exposures will be necessary to begin to replicate the effects of natural weathering on the mechanical properties of more UV durable plastic materials.

Use of FTIR spectroscopy for durability testing of polymers

FTIR is a well-established technique which has been widely used for the analysis of polymeric materials. A recent study demonstrated the use of FTIR to assess the extent of degradation of coatings.[8] FTIR provides a number of advantages as it:

- directly measures any chemical changes in the sample due to aging

- can confirm that the artificial aging reflects the degradation caused by natural weathering
- is non-destructive
- is quick
- can be used in the field

In this paper we describe how FTIR combined with chemometrics has been used to assess the chemical changes that take place in plastics as a result of degradation due to environmental exposure. This has provided a chemical basis for correlating natural weathering and accelerated weathering, rather than the mechanical property measurements previously used.

Experimental

Materials

The polymeric materials selected for the outdoor exposure study were all commonly used within the building and construction industry, usually for internal applications.[5] The PE and PP were clear, unpigmented sheets that contained no UV stabilisers. They are not representative of materials that would typically be specified for outdoor exposure. However, they were chosen as they were expected to degrade quickly enough to yield results in the project timeframe of five years.

Outdoor exposure

The original experimental work was undertaken as part of an earlier project which focused on examining the performance of organic polymers when exposed in the New Zealand environment.[5] In 2001, four exposure sites were established at Kaitaia, Paraparaumu, Judgeford (Wellington) and Invercargill. These exposure sites ranged from latitude 35° South to 47° South and were located within 15 km of the coast, close to sea level. They represent different zones of temperature, moisture/rainfall and UV radiation that exist throughout the country. For example, Kaitaia has a typical annual solar irradiance of over 5.30 GJ/m^2 per year.[9] Judgeford and Paraparaumu have a typical annual solar irradiance closer to 5.10 GJ/m^2 while Invercargill receives an average annual solar irradiance amounting to roughly 4.4 GJ/m^2 per year.

Samples of the plastics were exposed as non-stressed sheets, with exposure racks constructed to allow exposure of the samples at 45° to the horizontal facing the equator, as prescribed in ASTM G7 Clause 4.2.2 (Fig. 1).[10] The exposure racks were aligned with magnetic north, i.e. facing the equator, to maximise solar radiation exposure.[10] Samples were collected from each of the exposure sites on an annual basis, towards the end of summer. Control samples were retained and stored in a climate controlled environment at 23°C and 50% RH for the duration of the outdoor tests.

Accelerated aging

The same PP and PE materials as used in the natural weathering study were exposed in the Q-Panel Q-Sun xenon arc weatherometer (Q-Lab Corporation, Ohio, USA), shown in Fig. 2. The exposure times were 500, 1070, 1500 and 2000 hours. The longest exposures were targeted at a 50% loss of sheet tensile strength. The exposure conditions were cycles of 9 hours light (0.55 W/m^2 irradiance at 340 nm with a black panel temperature of 60°C) and 3 hours dark and spray (black panel temperature of 40°C).

FTIR and chemometric analysis

FTIR analysis was carried out using an Agilent 4300 handheld FTIR. Spectra were measured using a diamond attenuated total reflectance (ATR) sampling head. The spectral range was 4000-650cm^{-1}. A background of 16 scans was recorded before each spectra of 64 scans at 8cm^{-1} resolution. No ATR correction was applied to the spectra as only ATR spectra were analysed.

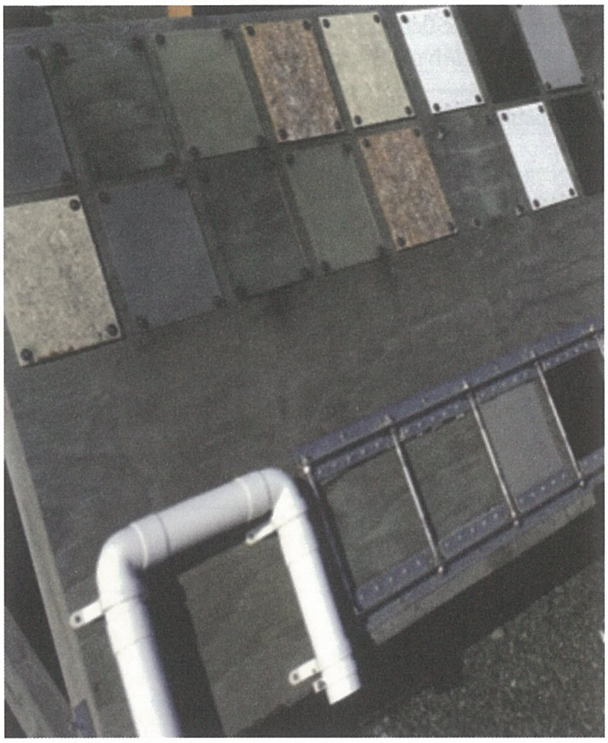


Fig. 1. Typical outdoor exposure rack

Fig. 2. Polymer specimens in the Q-Sun weatherometer

Preliminary predictive models were developed using Grams IQ (Version 9.1) software using PLS-1 calibration and cross validation as a measure of the model quality. At least 5 spectra for each material at the different exposure times were included in the preliminary model. Grams Predict was used to 'predict' the equivalent Q-Sun exposure time represented by the spectra of the samples exposed in the outdoor locations. No assessment of outliers was made in the development of the preliminary models used in this study.

Results

The changes due to aging, for both PE and PP, were seen in the FTIR ATR spectra in the fingerprint region, between 2000cm^{-1} and 650cm^{-1}. Fig. 3 shows FTIR ATR spectra of PE and PP after both outdoor exposure and accelerated aging in the Q-Sun weatherometer. The spectra resulting from both exposure methods are the same, indicating that the accelerated aging method and outdoor exposure cause the same degradation mechanism in the polymer.

Fig. 4 shows the FTIR ATR spectra of PE before and after outdoor exposure at Paraparaumu for 4 years while Fig. 5 shows the FTIR ATR spectra of PP before and after outdoor exposure at Paraparaumu for 1 year.

Once the predictive model was developed, the quality of the model was tested using cross validation. Each spectra used to create the model was then predicted by the model, producing the plots shown in Figs. 6 and 7 (PE and PP respectively). A better model has a correlation coefficient (R^2) closer to 1.00. It can also be a useful method for identi-

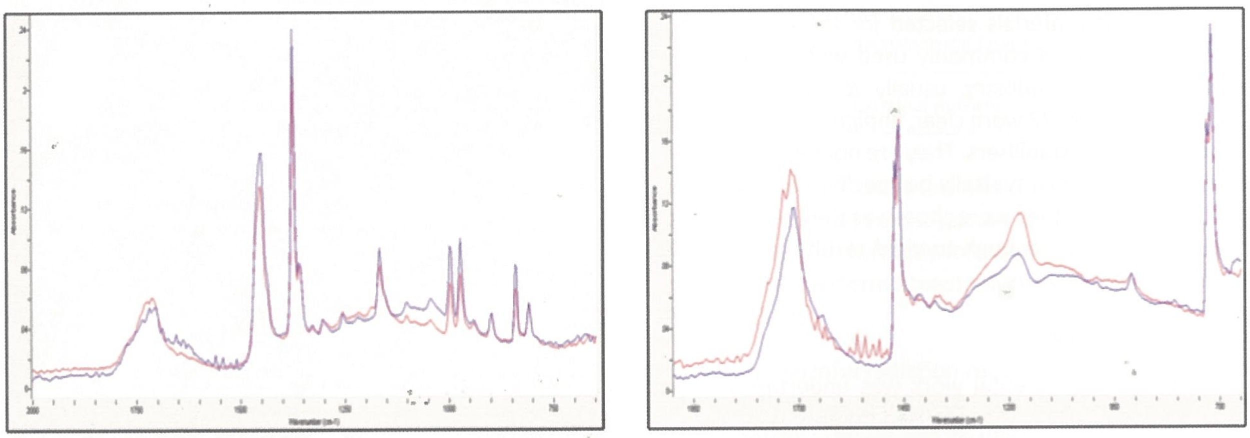


Fig. 3. FTIR ATR spectra of polymers after outdoor exposure (blue) and exposure in the Q-Sun weatherometer (red). Left: polyethylene and right polypropylene.

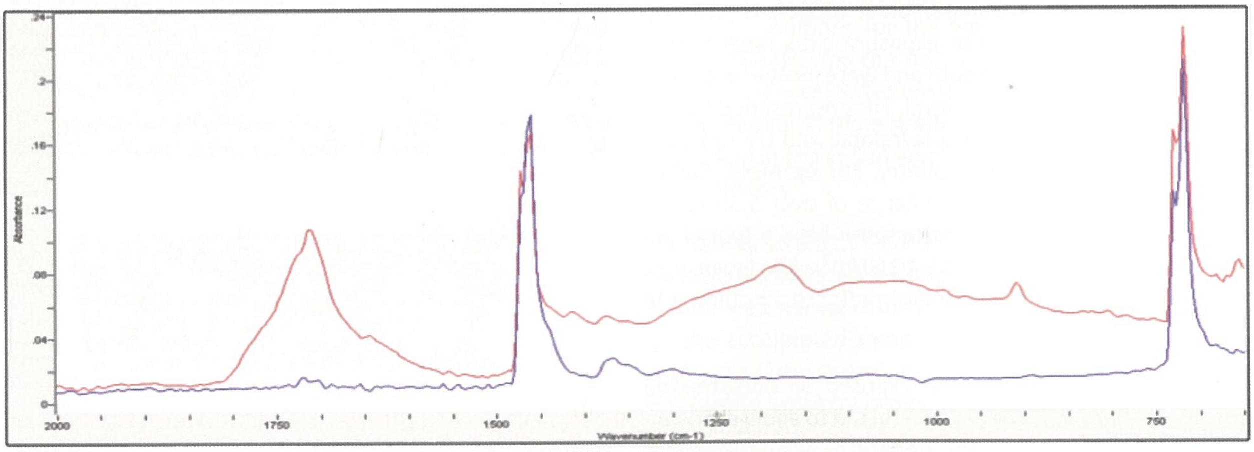


Fig. 4. FTIR ATR spectra of polyethylene before (blue) and after (red) outdoor exposure for four years

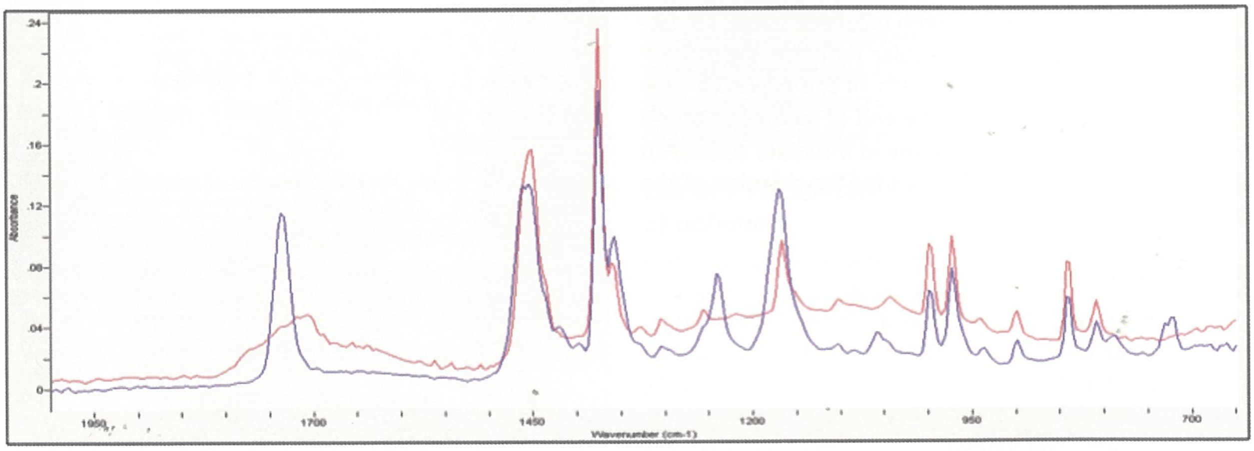


Fig. 5. FTIR spectra of polypropylene before (blue) and after (red) outdoor exposure for one year

fying outliers in the data, where a data point lies a long distance from the line, such as the data point circled in Fig. 6.

Tables 2 & 3 show the Q-Sun exposure time predicted by the model for polymer samples that have been exposed outdoors for 1 and 4 years at four locations for PE and PP respectively. The spectra for the samples exposed outdoors were input into the predictive model. The value reported is the average of results from five spectra. Spectra of the control samples were also input into the predictive model and the average of five results reported.

Discussion

Theoretically, it would be expected that the predicted Q-Sun exposure times for the unaged control samples would be zero hours. However, for PE and PP, the control samples predicted values are 20 and 38 hours respectively. The control samples used in this study were the controls from the original study into plastics weathering[5] and are now 14 years old. Although they were kept in a controlled environment it is likely that they have undergone some degradation during that time.

The potential for a polymer to degrade due to incident radiation is controlled by two factors. One is the ability of the

Table 2. Predicted Q-Sun exposure time for polyethylene samples exposed outdoors for 1 year and 4 years

Location	**Predicted Q-Sun Exposure time (hours)**		
	Control	**One year outdoor**	**Four year outdoor**
Control	20		
Kaitaia		1075	2269
Paraparaumu		366	2129
Judgeford		93	2253
Invercargill		617	2220

Table 3. Predicted Q-Sun exposure time for polypropylene samples exposed outdoors for 1 year and 4 years

Location	**Predicted Q-Sun Exposure time (hours)**		
	Control	**One year outdoor**	**Four year outdoor**
Control	38		
Kaitaia		952	
Paraparaumu		620	1434
Judgeford		792	
Invercargill		720	1176

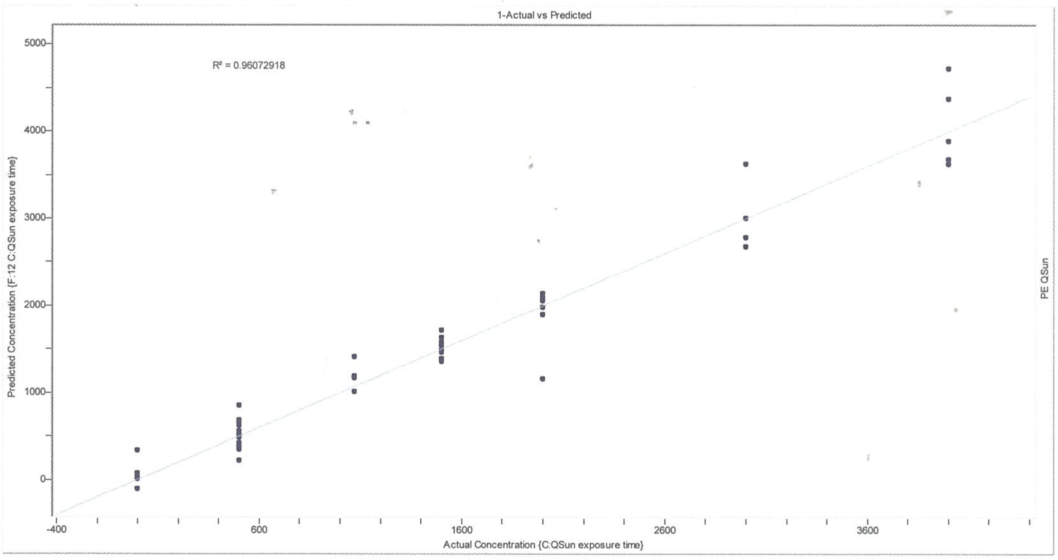


Fig. 6. Cross validation plot for polyethylene predictive model ($R^2 = 0.96$)

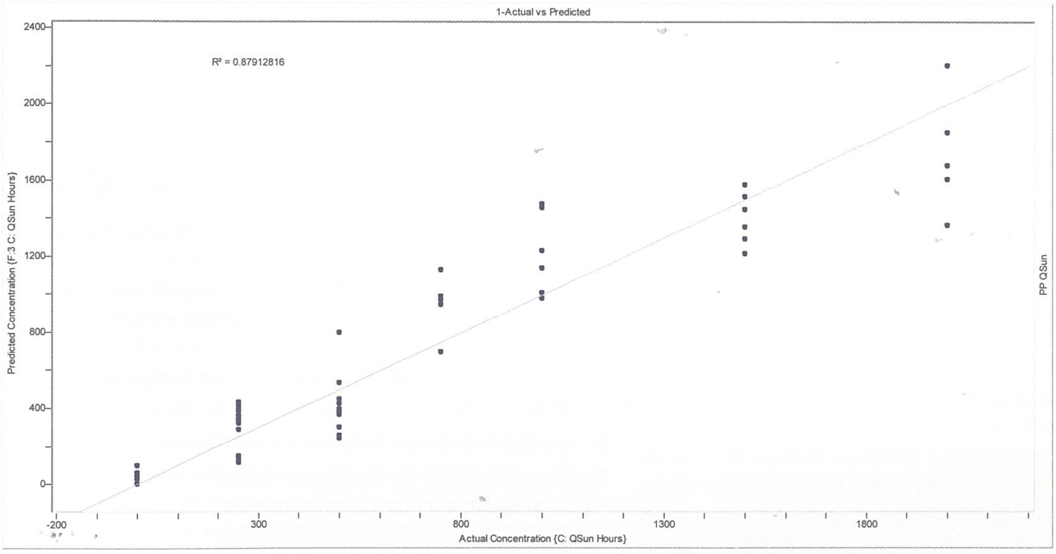


Fig. 7. Cross validation plot for polypropylene predictive model ($R^2 = 0.88$)

material to absorb photons of suitable energy. The other is the availability of photochemical pathways to allow chemical reactions using the absorbed energy.[11] Only radiation absorbed by a system is effective in producing chemical changes. Polymers exhibit marked different wavelength sensitivity in their photo-degradation behaviour since different polymer types consist of different chemical structures. The practical effects of this were reported by Marston and Jones:[5] PE lost 50% of its mechanical strength after approximately four years of exposure outdoors. In contrast, PP took only one year of outdoor exposure to undergo a 50% loss of mechanical strength.

In this study, the results for PE samples exposed outdoors for four years are more consistent than those for the one year outdoor exposure samples. Four years of outdoor exposure correlates to around 2200 hours of exposure in the Q-Sun and is reasonably consistent across the different locations in New Zealand. Assuming a linear relationship, this is equivalent to 550 hours Q-Sun light hours per year of outdoor exposure. The predicted Q-Sun exposure times generally decrease from the northern to southern exposure sites, as is expected from the typical solar irradiance at each location. The one year outdoor exposure results are much less consistent across the locations. On the other hand, the predicted results for PP are more consistent for the one year outdoor exposure. Again, there is a rough correlation between the predicted Q-Sun light hours exposure (620-950 hours) and the typical solar irradiance at the various locations.

One year outdoor exposure may be considered as exposure to a low dose of solar irradiance for PE. In contrast, for PP a four year outdoor exposure corresponds to a very high dose of solar irradiance. It is possible that the inconsistent results seen in this study may be due to the low or high doses of solar irradiance the particular polymer (PE or PP respectively) was exposed to.

Correlating natural weathering and artificial weathering in a reliable and predictable way has always been the challenge in studies of this kind. It has typically been done by comparing mechanical properties, such as strength or flexibility, of natural and artificially aged samples. It was previously reported that 750 hours Q-Sun exposure equated to 1 year out door exposure in New Zealand, as assessed using mechanical properties.[6] This is roughly consistent with the preliminary findings in the current study.

Further work is planned to refine the predictive models, by completing the PP 4 year outdoor exposure data set and analysing the data for outliers. Once more robust models have been developed, tests will be conducted to examine the reliability of further accelerating the exposures by increasing both the set point UV irradiance and cabinet temperature. This has the potential to reduce the time samples will need to be in the Q-Sun chamber. Suitably accelerated exposures may make reliable testing for 50 year durability possible.

The correlation between outdoor exposure time and accelerated aging based on solar irradiance dose, rather than exposure hours, will be investigated. This relationship was explored earlier by assessing the effects on mechanical properties of the polymers.[5] The irradiance dose varies for different polymers as they are primarily degraded by different wavelengths of solar radiation.[11] Future testing will include other more durable polymeric materials such as black PE and polyvinyl chloride in addition to other polymeric materials used in construction such as sealants and adhesives.

Conclusions

While based on sound scientific and engineering precepts, durability assessment remains as much art as science. Past BRANZ research has been successful in developing material test methods that have been integrated into the NZBC for the benefit of the industry. This work builds upon existing research understanding to improve the reliability of accelerated test methods for weathering of polymers.

These preliminary results indicate that FTIR, with chemometrics, has the potential to provide a defined test methodology for reliably predicting the durability of polymeric materials used in the building industry. Once a test method has been quantified and validated it will available for adoption by the regulator, Standards NZ, specifiers, product distributors and product manufacturers.

Acknowledgements

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Quantifying the influence of water chemistry on arsenate transport in the Waikato River

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Peter Swedlund completed a PhD in environmental chemistry at the University of Auckland in 2006 studying the chemistry of iron oxides in acid mine drainage systems. He has an abiding obsession with iron oxides in aquatic systems and using spectroscopic methods and geochemical models to understand the chemistry of H_4SiO_4 at the iron oxide-water interface and its influence on the transport and toxicity of trace elements.

Hannah Christenson was born in Taupo. At a young age the media coverage of nutrient inputs to Lake Taupo sparked an interest in environmental chemistry. She completed a BSc(Hons) at the University of Auckland, majoring in chemistry. Her dissertation was supervised by Peter Swedlund and produced some of the results included in this article. She has since completed her PhD on phosphorus geochemistry in Antarctic meltwater systems and now works for CRL Energy Ltd studying environmental geochemistry associated with mining.

Some history

The Wairakei geothermal power station was commissioned in 1958 and was the first in the world to utilise geothermal fluids. In these stations steam is flashed off the hot geothermal fluid and drives the turbines whilst the remaining liquid phase, with all non-volatile solutes, is a very large waste stream in need of disposal. This is complicated by the fact that geothermal fluids in this region contain elevated levels of several trace elements including As, Hg, B and Sb as well as large amounts of silicic acid (H_4SiO_4). The Wairakei power station was designed to discharge into the Waikato River and it was around this time, in the early 1960s, that John Aggett was appointed as a lecturer in Chemistry at the University of Auckland. In the 1980s there was a proposal to expand geothermal power generation in the region and several questions needed answers in relation to the sources and chemical transformations of arsenic in the Waikato River. One important question related to the transport and fate of the arsenic. In particular the mechanism by which many tonnes of arsenic were retained on the sediment that settled to the floor of the lakes behind the numerous hydroelectric dams on the river was unknown. Aggett used an elegant experimental approach to determine the phase association of the arsenic which accumulated on lake sediments. The experiment used EDTA to slowly dissolve the various metal oxide phases in the sediment over 48 hours. Comparing the dissolution rates of As and the cations of the major solid phase oxides (Fe, Al, and Mn) demonstrated a clear phase association of the solid phase As with the iron oxides in the sediment.[1] This was one of the early definitive indicators of the importance of iron oxide solid phases in arsenic mobility in aquatic systems. The chemistry involved in As retention by iron oxides is similar to some of the chemistry responsible for phosphate immobilisation by soils.

At this time, in the early 1980s, the lead author was a student in an Aggett lecture that included slides of John launching a dinghy on the banks of the Waikato River in order to assess the chemistry of arsenic in this system. At the time the lead author was unaware that in another two decades he would be doing the same thing. The WHO decreased the recommended maximum acceptable value for arsenic in drinking water from 50 to 10 ppb in the 1990s in response to a better understanding of arsenic toxicity.[2] One consequence of this was that the Waikato River water, which just squeaked in below the old standard, was no longer compliant.[3] For this reason the owners of the Wairakei power station were keen to explore water treatment options to remove As from their geothermal brine before it was discharged into the Waikato River and the author was embarking on an MSc and looking for a research project. The most promising water treatment option involved addition of ferric chloride and sodium hypochlorite. This resulted in iron oxide precipitation, arsenite oxidation and then adsorption of arsenate onto the iron oxide surface. The process was, however, confounded by the presence of large amounts of H_4SiO_4, which competes with arsenate for sorption sites. Ultimately the treatment process was viable in terms of the chemistry and engineering but not in terms of the economics and the As discharge to the river continued. On a scientific front it was invaluable to study a system with very high H_4SiO_4 concentrations as it provided insights into important processes occurring in almost any aquatic system where metal oxides are involved.[4]

This century

In the 21st century the aquatic chemistry of arsenic is particularly pertinent. Arsenic contamination of drinking water by natural sources has been described as the "largest mass poisoning in history".[5] In typical surface waters approximately 50% of the As is associated with suspended particulate matter (SPM) via adsorption to surface sites on the iron oxides phases[6] and this provides an important control on As solubility, transport and bioavailability. In many aquatic systems with elevated solution concentrations of As (As_{sol}) the cause is either reductive dissolution of iron oxides or competition for sorption sites from other species in solution. Iron oxides result from oxidation of silicates or sulfides and give sediments their characteristic red-brown-yellow spectrum of colours. Silicic acid also results from silicate mineral dissolution and H_4SiO_4 is ubiquitous in aquatic systems and can displace arsenic from iron oxide surfaces.[7] River systems with anomalously high concentrations of H_4SiO_4 have been reported to have anomalously high proportions of the As present in the solution phase and this implies that H_4SiO_4 displaces As from the surfaces of the iron oxides. New Zealand's Waikato River is a classic example and contains approximately double the world average H_4SiO_4 concentration and only ≈ 25% of the As is bound to suspended sediments compared to world averages of ≈ 50%.[8] More importantly, competitive sorption by H_4SiO_4 is proposed to contribute to high As concentrations in As contaminated aquifers in Bangladesh and West Bengal.[9]

It is reasonably easy to determine and model the effect of competing ligands on As sorption by iron oxides in laboratory systems. However, it is substantially more challenging to do this for natural systems. A particular problem in natural systems is determining the amount of solid phase Si and P associated with the iron oxides because the iron oxides are typically present on the surfaces of the silicate minerals and phosphate can also be associated with calcium phosphate minerals. While there are standard sequential extraction methods which provide "operationally defined" insights into element phase association in sediments, definitive correlations between elements and phases can be elusive even for trace metals for which the methods have typically been optimised.[10] The objective of the current study was to use the extraction method of Aggett and Roberts[1] coupled with ICPMS analysis of the solutions to determine the phase association of Si, P and As in sediment from the lower reaches of the Waikato River. The aim was to provide definitive insights into the impact of H_4SO_4 and P on As distribution in a natural aquatic system. The Waikato River provides a useful system for this study because of high Si, P and As loadings due to geothermal and agricultural inputs. At the sampling site the river is shallow, fast moving and well oxygenated and sampling was undertaken at a time of year when the As is almost exclusively As(V).[11] The bed sediment is coarse with very little associated organic matter and no redox zonation in the sample. All these factors mean the site provides a nice bridge between simple laboratory systems in test tubes to the complex world that exists outside the laboratory window.

Methods

Samples were collected in May 2011 from the lower Waikato River (using a dinghy!). Surface waters were collected and filtered on site through a 0.45 μm cellulose acetate filter. Sediment (≈ 1 kg) was collected from the river bed using an Eckman grab sampler, wet sieved and the <63 μm fraction retained by centrifugation. Sediment was characterised by XRD, SEM and EDX (polished cross sections). EDTA extractions were performed in 10 mM EDTA at pH 7 and 30°C whilst solution samples were taken at time intervals between 15 min and 48 h. In addition a sequential extraction of sediment used ammonium oxalate followed by sodium dithionite and then HCl as previously described.[12] Samples were analysed for As, P and Si by ICP-MS using certified methods at Hill Laboratories Ltd (Hamilton) with matrix matched standards. The speciation of As in the river and in the EDTA extract was analysed for arsenate, arsenite, methylarsenate and dimethylarsenate by HPLC-ICP-MS at the EcoChemistry Laboratory (University of Canberra) as described in Ellwood and Maher.[13] Major cations and anions were determined by atomic absorption spectroscopy and ion chromatography while bicarbonate was analysed by titration.[12]

Geochemical modelling used Visual MINTEQ[14] and sorption to the iron oxide ferrihydrite was modelled using the diffuse layer model (DLM) and the parameters in the "HFO (Dzombak and Morel)" model[15] in Visual MINTEQ. This involves entering a solid concentration for ferrihydrite in g l^{-1}. From this value the model uses the M_w (89 g mol^{-1}), surface area (600 m^2 g^{-1}) and ligand sorbing site concentration ([≡FeOH] = 0.2 mol per mol Fe) from Dzombak and Morel[15] to determine the surface area and site concentration. The Visual MINTEQ feodlm_2008.vdb database of sorption constants was used for all sorbing species except As(V), H_4SiO_4 and P(V) where modelling was performed using the values detailed in the Results section.

Results

The water chemistry was typical for the Waikato River, the main cation being Ca^{2+} (0.25 mM) with Li^+, Na^+, K^+ and Mg^{2+} ions present at 0.011, 0.18, 0.14 and 0.12 mM respectively. The main ligand was HCO_3^- (0.84 mM) followed by H_4SiO_4 at 0.40 mM and this [H_4SiO_4] falls within the typical range for the river (0.35 to 0.9 mM) and is about double the world river most common natural concentration (MCNC) of 0.18 mM.[16] The calculated aquatic speciation based on these measured components and pH had an ionic strength of 1.4 mM and an anion excess charge of 1.6%. The water was supersaturated with respect to hydroxyapatite (SI = 0.706) and a carbonate-fluorapatite (SI = 6.733). The As_{sol} was 0.272 ± 0.005 μM for the river water and 98.7 ± 0.1% of this was present as As(V) with the remainder present as As(III) and no methylated species detected. There was 5.1 mg L^{-1} of suspended particulate matter in the river water that contained 0.48 g kg^{-1} of As, which equates to 0.033 µM of sorbed As. Therefore 89% of the As in the river was dissolved, with 11% adsorbed onto SPM.

The bed sediment at all sites had a coarse, sandy texture and was a rich tan colour. The XRD pattern of the <63 µm fraction showed predominantly quartz, albite and minor components. Under SEM with EDX the majority of the <63 µm grains were aluminosilicate-based with Si as the major cation followed by Al and <5% Ca and Na. Some of the silicate grains were associated with a prominent iron-rich phase with 40 atom % of Fe in addition to some Ti (5%), Al (2%), Mn (1%) and Si (0.6%). The As was present at 80 mg kg^{-1} in the oxalate extract but no further As was detected in the subsequent dithionite or HCl extractions. The total extractable P was 1.47 g kg^{-1} of which 46% was released by oxalate and a further 19% by the dithionite. The remaining 34% of the total extracted P was removed in the HCl step. The marked difference in the As and P extraction profiles indicates that the phosphate is present in more than one phase and could indicate the presence of a calcium phosphate phase, as these have shown some solubility in dithionite.[17] The chemical speciation of the river water indicated that the system was supersaturated with respect to hydroxyapatite and carbonate-fluorapatite and some grains with high Ca and P content were observed in the SEM-EDX of the polished sections. This will be considered when modelling the system but for this study we are predominantly interested in the oxalate extracted P because this is the only phase in which As was extracted.

The dissolution rates of the elements of interest as the Waikato bed sediment reacts with EDTA are shown in Fig. 1 for the 48 hours of the experiment. The dissolution rates are shown in terms of the percentage of the oxalate soluble fraction (termed here OSF). Calcium dissolved rapidly, with 90% of the OSF dissolving in the first 30 minutes of the EDTA extraction. There was a slight decrease in the % Ca^{2+} OSF in the EDTA extract between 30 and 180 min but after 180 min the % Ca^{2+} OSF increases to be 100% at 48 h. Aggett and Roberts[1] also observed almost complete dissolution of Ca^{2+} in the first 30 minutes in EDTA but then a decrease in Ca^{2+} after 30 minutes but they, like us, could offer no explanation for this phenomenon. The Mn profile showed ≈ 70% of the Mn OSF dissolved in the first 30 min and then a linear increase over log time until 100% was extracted after 48 h. Aluminium dissolved very slowly, with only 30% OSF dissolved after 48 hours. The % OSF for Fe, Si, P and As all had similar rates of dissolution which were intermediate between the high rates of extraction for Ca and Mn and the low rates for Al. The % OSF for these 4 elements increased approximately linearly as a function of log(t) with similar slopes. After 48 hours there was 77 and 78% of the OSF extracted for Fe and P respectively, while for As and Si the values were a little lower at 74 and 71% OSF extracted respectively. The Fe dissolution was particularly linear over log(t) with an R^2 value of 1.00. The similar rates of dissolution indicate that the As, Si and P being extracted are associated with the poorly ordered iron oxide phase and the initial assumption is that these are sorbed ligands. Furthermore, the similar profiles over time indicate that there are no major redistribution processes occurring for the As, Si and P during the iron oxide dissolution.

The ferrihydrite particles in siliceous systems are considered to range from 2-4 nm in overall size but each particle consists of up to ≈ 60 domains that are between 0.8 to 1 nm and that contain ≈ 12 Fe atoms.[18] In natural systems the sorbing ligands are present during the precipitation and domain aggregation of ferrihydrite so that sorbing species are present on domain surfaces throughout the interior of the particles. Therefore, in the EDTA extraction there is a steady release of Si, P and As during the ferrihydrite dissolution indicative of a large degree of homogeneity in the system. This result is entirely consistent with the As(V) co-precipitation and sorption experiments of Fuller *et al.*[19] and the structural model of siliceous ferrihydrite from Parfitt *et al.*[18] where the sorbing ligands are distributed throughout the aggregated domains and particles of the ferrihydrite material. The kinetic extraction results also suggest that there is not a significant pool of outer-sphere sorbed As(V) [also known as electrostatically sorbed or electrolyte exchangeable As(V)] associated with the sediment oxides. On exposing the sediment to EDTA solutions the outer-sphere As(V) would have been released into solution rapidly and independently of the Fe dissolution – however, this was not observed.

In general, the data are in good agreement with the trends observed by Aggett and Roberts[1] and support the proposition that the oxalate extraction is targeting no more and no less than the As, Si and P associated with the ferrihydrite phase. This extraction is therefore a useful tool to probe the role that these anions have in displacing As from the iron oxide surfaces which evidently occurs both during ferrihydrite formation and during ferrihydrite equilibration with the aqueous phase. In this context it is useful to note that the As:Fe ratio in the ferrihydrite was ≈ 0.004 whilst the Si:Fe and P:Fe were ≈ 0.30 and 0.08 respectively.

Modelling the system

Modelling the distribution of As between the solid and aqueous phase requires analysis of the SPM. The main distinguishable features of the SPM under the electron microscope were diatoms, small (~ 1 µm) inorganic grains and substantial amorphous material with a high (≈ 50 atom %) organic carbon. A 15 minute oxalate extraction of the SPM released 43.1 g kg^{-1} of Fe and the As, Si and P in the extract yielded mole ratios to Fe of 0.0084, 0.38 and 0.107, respectively. Compared to the bed sediment, the SPM has a higher iron OSF consistent with the smaller particle size and more weathered content. Despite the marked differences in the overall solid phase composition of the bed sediment and SPM the As:Fe, Si:Fe and P:Fe ratios in the OSF were comparable although the SPM had greater loadings of each ligand presumably reflecting the substantially higher ratio of water to solids for the SPM. Because of the comparable ligand:Fe ratios between the bed and suspended sediment the conclusions from the kinetic EDTA extraction of the bed sediment were considered to be applicable to the suspended sediment.

In this work the DLM approach as developed by Dzombak and Morel[15] was used to describe surface complexation and to provide insights into the competitive sorption system. This scheme includes a database of equilibrium constants for the adsorption of many cations, anions and neutral species which has been maintained and updated by Gustafsson[14] as a part of the Visual Minteq geochemical modelling package. In laboratory studies the DLM has been proved capable of predicting anion and cation adsorption under varying conditions, including effects of changing concentrations, pH and ionic strength.[15] The DLM is also capable of predicting competitive adsorption of ligands.

The components used in the model included As(V), P(V), Cl^-, F^-, SO_4^{2-}, NO_3^-, HCO_3^-, H_4SiO_4, Na^+, K^+, Mg^{2+} and Ca^{2+}. The concentration of surface hydroxyl groups on the iron oxide surface is taken as 0.2 times the oxalate Fe concentration as per Dzombak and Morel.[15] The pH and iron oxide concentration will have a large effect on As sorption. However, in comparing the Waikato River and MCNC systems, the pH and iron oxide concentration were fixed because the study's purpose was to explore how the Waikato River solution composition impacted As sorption. Preliminary modelling demonstrated that the HCO_3^-, SO_4^{2-}, Ca^{2+} and Mg^{2+} had a negligible effect on modelled As(V) sorption. In the current study modelling was carried out using As(V) sorption constants for the 150 hour time frame from Swedlund *et al.*[20] This time frame was chosen as it is most compatible with those used for the H_4SiO_4 and P(V) sorption data. The Waikato River is also supersaturated with respect to apatite phases and some coprecipitation process may be occurring in the river. This process is not considered in the model and its possible significance is discussed. The default DLM H_4SiO_4 sorption constants in the Visual MINTEQ feodlm_2008.vdb database were taken from Swedlund and Webster[4] who used a 10 day reaction time in their experiments. These model reactions describe H_4SiO_4 sorption in terms of a ligand exchange reaction analogous to those of As(V). More recent work [21,22] has shown that interfacial H_4SiO_4 polymerisation can be important. For the DLM to accurately describe laboratory measured H_4SiO_4 sorption at Si/Fe mole ratios greater than 0.1, a trimeric silicate species is required with stoichiometry $Fe_2H_{(6-n)}Si_3O_{10}^{-n}$. However, to further complicate matters, in natural systems ferrihydrite precipitates in the presence of H_4SiO_4 and H_4SiO_4 strongly bridges ferrihydrite domain boundaries, i.e. on internal surfaces within a ferrihydrite particle.[18] In this case substantially more Si can be associated with the ferrihydrite than expected from sorption to preformed ferrihydrite. The measured oxalate SPM Si:Fe (0.38) is at the high end for ferrihydrites which are reported to "typically contain up to 9% Si" corresponding to an Si:Fe of 0.38.[23] This is due to the role of the internal surfaces of the ferrihydrite particles as discussed by Parfitt *et al.*[18] Similarly XPS measurements indicate that the Si associated with natural ferrihydrites is predominantly monomeric which implies that most of the Si is on internal domain boundary surfaces where it is not able to form polymeric silicates.[24] The results from the EDTA extraction over time also suggest that H_4SiO_4 is more prevalent on the internal ferrihydrite surfaces. In Fig. 1 between 60 and 480 min the extracted Si:Fe is particularly low but then increases after 480 min suggesting a greater proportion of the Si may be located in the particle interior. The reason why this affects Si more than As and P presumably reflects the influence of ligand concentration on diffusion during the short period of time the internal surfaces are available. The maximum possible model Si:Fe value is 0.2 with the sorption parameters in Gustafsson[14] or 0.3 with the Swedlund *et al.*[22] sorption parameters which include interfacial H_4SiO_4 polymerisation. Therefore the model cannot predict the measured sorption of H_4SiO_4 but to consider the effect of H_4SiO_4 on As(V) sorption in the system it is acceptable to use the default H_4SiO_4 parameters as previously discussed.[22]

The modelled percentage of As(V) sorbed in the absence of P(V) and H_4SiO_4 were 99.6% for the MCNC and 69% for the Waikato River (Fig. 2). These model results suggest that one important factor responsible for the lower % As sorption in the Waikato River is simply the higher As concentration in that river. Typically anion sorption to ferrihydrite is considered to be Langmuirian where the slope of the log-log isotherm is 1 at "low" sorption density and the slope plateaus to 0 at "high" sorption density. This means that the % As sorbed would be independent of the solution As concentration provided the surface coverage is "low". For a system with 0.35 mg L^{-1} ferrihydrite the model concentration of surface sites is 0.79 µM and from modelling it is evident that any increase in As_{TOT} above 0.05 µM will result in an appreciable decrease in the % As sorbed and this impacts the Waikato River with an As_{TOT} of 0.30 µM.

In the MCNC water the presence of 0.30 µM P(V) and 180 µM H_4SiO_4 markedly decreased the modelled % As sorbed. The modelled degree of ligand competition will be strongly influenced by the relative values of the ligands' sorption constants so the As(V) sorption constants for 150 hours reaction time provides a more realistic description of the system. Using these values, 0.30 µM P(V) decreased As sorption from 99.6 to 54% and 180 µM H_4SiO_4 decreased As sorption from 99.6 to 69% whilst the combined effect of P(V) and H_4SiO_4 decreased As sorption to 37%. In summary for the MCNC system the P(V) has a similar but slightly greater inhibitory effect on As sorption than the H_4SiO_4 whilst overall the model makes a reasonably sound prediction of the general observed phenomenon of ≈50% As sorption in these systems.

In the modelled Waikato River system the presence of either 1.0 µM P(V) or 400 µM H_4SiO_4 decreased the modelled % As sorbed by a similar extent; from 69% with neither P nor Si to 25% with P(V) or 26% with H_4SiO_4 (Fig. 2). The combined effect of P(V) and H_4SiO_4 decreased As sorption to 14% compared to the value measured in this study of 11%. As for the MCNC waters the model makes a reasonably sound prediction of the generally observed extent of As sorption in the Waikato River. While the measured As:Fe ratio in the SPM (0.0084) was close to the

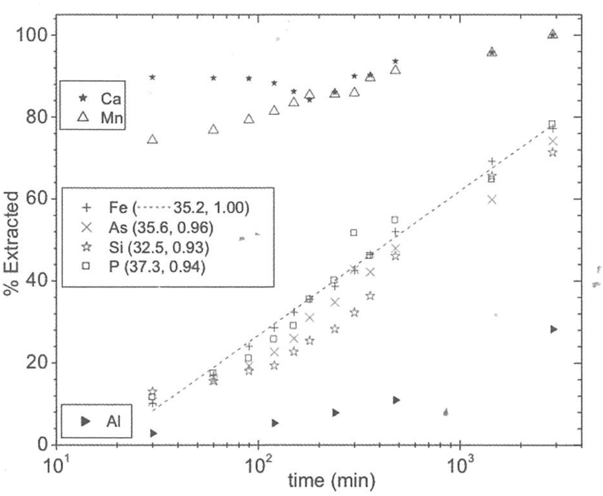

Fig. 1. The rate of element extraction from sediment in 10 mM EDTA at pH 7 and 30°C. The percentage extracted is given in relation to the amount extracted over 15 minutes by 0.3 M oxalate at pH 3 in the dark. The slope and the R^2 for the linear regression of % extracted vs log time are given in brackets for Fe, As, Si and P.

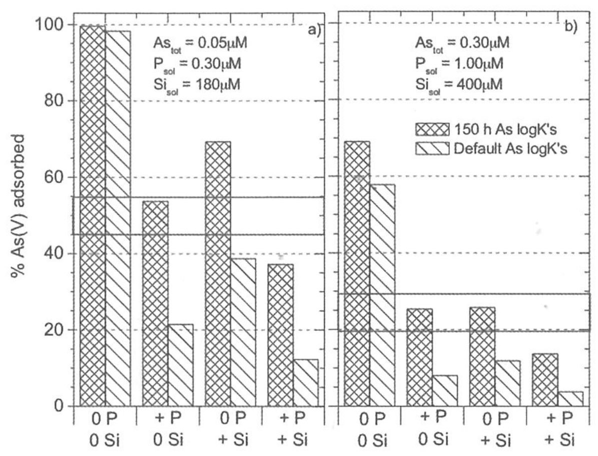

Fig. 2. The modelled effect of P and/or Si on the % As(V) sorbed for (a) the MCNC and (b) the Waikato River. The horizontal boxes indicate the typical % As sorbed in each system.

modelled value of 0.011 the measured P:Fe (0.107) and Si:Fe (0.38) were substantially larger than the modelled values of 0.021 and 0.10, respectively. The reason for the high measured Si:Fe is clear from the various observations indicating the high affinity of the H_4SiO_4 to bridge domains within the particle. This does not appear to be directly applicable to the high P:Fe because the release of P and As over time in the EDTA extraction had similar profiles. Calcium is the dominant cation in the Waikato River and the main difference between the P and As in the system is the supersaturation of a calcium phosphate phase and also the presence in the sequential extraction of P (but no As) in the dithionite and HCl steps. This indicates the presence of a P containing phase (such as an apatite) in addition to that sorbed on ferrihydrite. The timed EDTA extraction indicates that a discreet apatite phase is unlikely to have contributed to the oxalate P. Therefore adding a precipitation of an apatite phase to the model will not resolve the question of the higher measured P:Fe. Some extent of co-precipitation involving the ferrihydrite and Ca-P(V) phases would be a reasonable explanation for the observed results and the model discrepancy for P:Fe but not for As:Fe.

In summary, the DLM and the feodlm_2008.vdb database with the As(V) sorption constants for 150 hours from Swedlund *et al.*[20] made a reasonable description of the system but slightly overestimated As(V) sorption whilst considerably underestimating the oxalate fraction of P(V) and H_4SiO_4. Comparing the modelled sorption for the measured Waikato River solution chemistry with the world MCNC values allows for an estimate of the effect of Waikato River solution composition on As(V) sorption. From this analysis it is clear that the elevated levels of As, P(V) and H_4SiO_4 are all factors that contribute to the % As sorption being lower in the Waikato River than the global average.

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Some Unremembered Chemists

A series of articles that explores the lives and work of selected chemists who have made a significant contribution to the advancement of the discipline, the profession and well-being of mankind, yet who are little remembered.

Leo Hendrik Baekeland (1863-1944)

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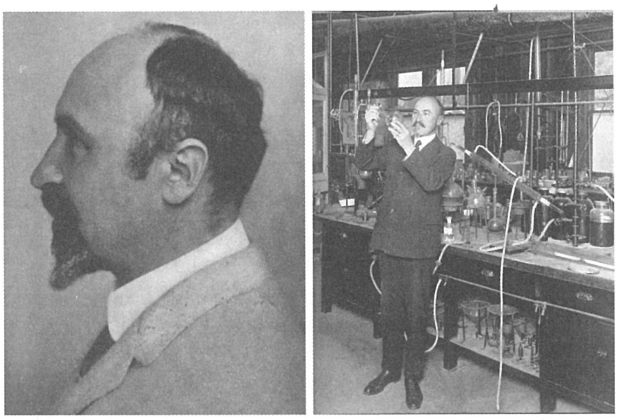


Left: Baekeland in 1916; right: Leo Baekeland in his laboratory (courtesy Mr R. Groot, Amsterdam Bakelite Collection, www.amsterdambakelitecollection.com).

Leo Hendricus (Hendrik) Baekeland was born in St. Martens-Latem near the Flemish city of Ghent in Belgium on November 14, 1863. He was the son of Charles and Rosalie (née Merchie), an illiterate cobbler and a domestic servant. At the age of five he entered the primary school and then, at age 13, his father apprenticed him to another shoemaker. However, his mother, whose work took her to the well-to-do households of Ghent, insisted that her son also be allowed to attend a secondary school so as to gain a better education with improved prospects; Leo entered the Atheneum. When old enough, he enrolled at the Municipal Technical School, where he took evening classes in chemistry, physics, mechanics and economics, winning a medal in each of the four subjects. It was there that his lifelong commitment to chemistry started. In fact, his promise was such that the City of Ghent awarded him a scholarship to attend university. He accepted and entered the University of Ghent in 1880 at age 17, taking natural sciences and specialising in chemistry under Professor Theodore Swarts, who had succeeded Kekulé in 1867. Although the youngest member of his class, Leo was the most gifted graduating with a BSc after two years, and then with a PhD involving electrochemical studies *maxima cum laude* only two years later, ahead of his 21st birthday. During this time Leo supported himself with the scholarship, by serving as a lecture assistant and by teaching so as to reduce the contribution from his parents.[1-3]

Young Baekeland had a boyhood interest in photography, which led him to dissolve the silver chain of his pocket watch in nitric acid because he needed silver nitrate but could not afford to buy it. The resulting solution also contained copper nitrate and, as one of his first chemistry projects, he worked out a separation of the copper from the silver salts.[2] Following his doctoral graduation, Leo taught chemistry and physics at the Government Higher Normal School of Science in Bruges. There, he continued his interest in photography having been encouraged while a student by photographer-chemist Désiré van Monkhoven. During this period he developed a technology with economic potential – the dry bromide photographic plate. His plates carried both a light-sensitive material and a coating of developer in dry form as well as a protective layer to prevent oxidation. The plates were developed in water immediately after exposure and negated the hassles with plates that had to be coated wet just before exposure.[4] He returned to Ghent in 1887 as Assistant Professor where he combined a promising academic career with his industrial activities; he gained a patent for the dry plate. Together with his colleague Jules (and his wife Valérie) Gleesener, he established *Dr. Baekeland et Compagnie* to manufacture the dry plates. Even at the age of 24 it was clear that Baekeland brought the right technology to the company, while the infrastructure and capital were made available by Mde. Gleesener. Sadly for Baekeland, the company failed due to the difficulty of combining academic work with industrial activity and the fact that the era of plate technology, wet or dry, was coming to its end. Baekeland and Swarts quarrelled frequently because the senior wanted his former brilliant student and now a junior colleague to become a famed academic.

The main reason Baekeland returned to Ghent in 1887 was to be closer and better able to court Celine Swarts, the professor's daughter who he had met while a student. That year the four universities of Belgium (Ghent, Louvain, Liege and Université libre de Bruxelles) held a competition among its graduates of the previous three years and awarded Baekeland the first prize. This provided him with a title, a gold medal and a travelling scholarship. So, following his promotion to Associate Professor, he visited Berlin, London, Oxford, and Edinburgh Universities before returning to Ghent where he married Celine on August 8, 1889. Two days later the newlyweds travelled to New York and honeymooned. There he met Richard Anthony of the photographic supply house E. and H.T. Anthony & Co., makers of dry plates and bromide paper. Richard introduced Leo to Columbia University's Chemistry Professor, Charles F. Chandler, a chemical consultant to the company, an enthusiastic amateur photographer, and a force in late 19th century American chemistry. Chandler saw in Baekeland a considerable talent and persuaded him to remain in the US to solve industrial problems. Given this advice, Leo resigned from his position in Ghent, and joined the Anthony Company as their chemist. There, he worked on film emulsions and printing papers. However, he stayed with them for only two years choosing to become an independent consultant and research chemist in 1891.[4] This was after the birth of his first daughter Jennifer in 1890. She died of pneumonia in 1895 and little is written about her.

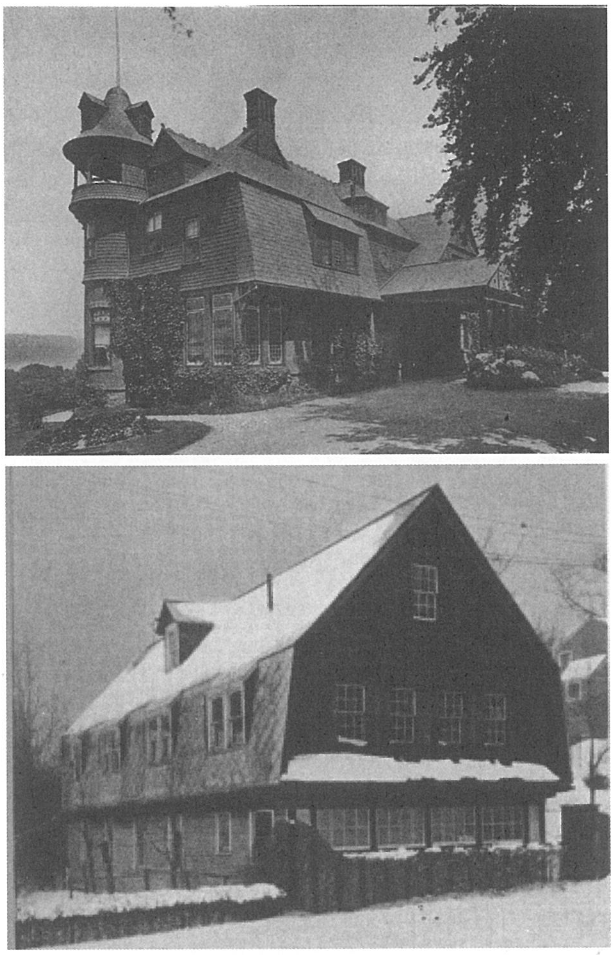
The move to consulting was, perhaps, Baekeland's biggest failing as he tried to develop too many processes too quickly and he became ill; his finances dropped to their lowest. During his recovery he decided to concentrate on one single well-chosen project to give him the best chance for the quickest possible results rather than having many irons in the fire.[2] With his exceptional grasp of the principles of basic science, he then proceeded to produce results that revolutionised several major branches of science and had an impact on the day-to-day lives of millions. They made him a wealthy celebrity.[5] The first success involved a return to his photographic interests with the development of the Velox photographic paper.[4]

Baekeland's objective was to produce a better photographic paper than then available and capable of being developed in artificial light. His *modus operandi* was to think of a problem and then devise an experiment to prove it wrong. If that experiment did not negate his idea he would then experiment meticulously and accurately to gain a new and meaningful solution – a 'look for a problem, get a better solution and commercialise it' approach. After two years of intensive experimentation that included many failures, he perfected a process to his satisfaction and produced a paper using chloride rather than bromide; he named it Velox. He had generated more than 50 variants of his chloride paper each of which was carefully assessed for coatability, sensitivity, tonal quality, shelf life, and image lifetime. Velox gave better light sensitivity with a variability in tonal quality that gave softer prints. However, at that time the US was suffering a recession and there were no investors or buyers for his new superior product despite the growing popularity of the reloadable camera and the increased need for print developing.

Leo Baekeland then found a commercial sponsor for his paper, one Leonardi Jacobi, a scrap metal dealer from San Francisco, and they established the Nepera Chemical Company in Nepera Park, Yonkers, New York. However, when set to produce quantities of photographic paper for market, his factory was beset with summertime humidity problems that caused the emulsions to become sticky, preventing application for weeks at a time. The solution (air conditioning for the plant) was devised by Baekeland. He had the external air passed over ice to condense the moisture sufficiently to allow plant operation. The company began producing paper in 1893. Within a few years Velox had taken a large part of the market; the prints were durable and had excellent tone with rich blue-black colours. Furthermore, Baekeland offered Velox in a range of grades for photo finishers to make the best prints from thin or heavy negatives. Most important was that Velox was easy to use and gave reliable results as it was designed for use in artificial light – it gave rise to the *Back-of-the-Pharmacy* processing and was the first commercially successful photographic paper. Rather than expand the plant and hope to retain his market share, Leo decided to sell and in 1899 he, Jacobi, and Albert Hahn (a further associate) sold Nepera to George Eastman of the Eastman Kodak Co. for $750,000. Baekeland earned *ca*. $215,000 from the transaction and with a portion of the money Leo purchased *Snug Rock*, a handsome estate in the then Harmony Park section of Yonkers overlooking the Hudson River. He also bought a car to satisfy his motoring hobby much to the chagrin of his horse-owning neighbours who thought him a gasoline devil.

Velox photographic papers (courtesy of Early Photography Co. UK)

Although Baekeland was financially set for life with little need to work, he set up his own well-equipped laboratory in what had been a barn on the property and continued his researches there. However, part of his contract with Eastman was not to perform photographic studies for at least 20 years; he had to find a new area of research. He returned to electrochemistry as it had begun to revolutionise chemical industry with, for example, the separation of aluminium from bauxite. He spent the winter of 1900 at the Technical Institute at Charlottenburg (now The Technical University of Berlin) improving his knowledge of the subject. On returning to the US and Yonkers, he equipped his laboratory for electrochemical study. Shortly, Elon Huntington Hooker, who had set up the Hooker Chemical Company in 1903 as a *Development and Funding Company*, asked Leo to assess the recently invented Townsend electrolytic cell. This was with a view to possible industrial electrolysis of brine for chlorine and caustic soda production.[2] The cell, invented by Clinton Townsend and Elmer Sperry (subsequent founder of Sperry Electric) comprised of a tank in which electrolysis generated sodium hydroxide (caustic soda), chlorine, and hydrogen. Townsend had placed a diaphragm between the anode and cathode, had a perforated kerosene-filled

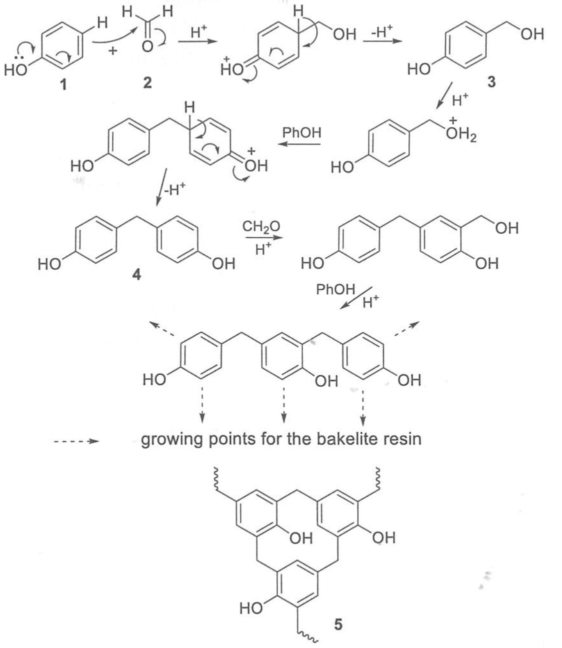


Top: *Snug Rock* (*ca.* 1900), Baekeland's home in Yonkers, New York in the early 1900s (from Bob Piwinski's *Victorian Source*, see ref. 3); bottom: Baekeland's Laboratory at Snug Rock, Yonkers, New York (Chemical Heritage Foundation-Wikipedia)

jacket around the cell, and devised a means of keeping the chlorine, hydrogen and caustic soda separate; its operation needed a plentiful supply of power. Baekeland's work resulted in improvements to the diaphragm, a reduction in corrosion, and higher overall electrical efficiency. Together with Hooker a pilot plant was built in Brooklyn at a cost of $300,000. The electrolytic process was honed and made ready for commercialisation subsequently saving them far more than the pilot plant cost. Full production began at Niagara Falls in 1905 and utilised the low cost electricity from the Niagara Falls power project, water from the Niagara River and, importantly, the abundance of salt from the nearby mines. It was one of the world's largest electrochemical plants. The Hooker Chemical Co. subsequently manufactured a range of chemicals from the electrolytic products. Undoubtedly, Leo Baekeland added to his wealth and it provided for one of his more famous quotations: *Commit your blunders on a small scale and make your profits on a large scale*.

Following the electrolysis of brine, Leo Baekeland turned his attention to organic chemistry and the condensation of formaldehyde with phenols. This came from recognition that phenol-formaldehyde resins, already known but non-commercial, had potential. The initial impetus came from the idea of replacing natural shellac (a resin secreted by the female lac bug on trees in the forests of India and Thailand and used as *e.g.* a natural primer, stain, and a high-gloss varnish also used in electrical applications) with a man-made alternative. The work led to Baekeland's greatest success – the discovery of Bakelite. Von Bayer had described experiments with phenol and formaldehyde some 30 years earlier and a number of other recognised chemists had tried to find useful products from the reactions. Amongst others, Austrian chemist Adolf Luft gained a patent (1902) for a process to produce plastic materials from phenol-formaldehyde resins especially suitable as a celluloid substitute. However, the amber-like material that he obtained from adding camphor was too brittle for technical use. Despite these studies, no one had produced a viable product.[6] The scene was set for the systematic examination that Baekeland provided.

As was his norm, Leo began his studies by repeating all the early work.[1,2,4] Together with his assistant Nathaniel Thurlow (he rarely had more than two) the same useless resinous masses were obtained. Then began systematic variation of each individual component of the reaction between phenol and formaldehyde. Thus, the aldehyde, the substitution on the phenol, the stoichiometry, the temperature, and the pressure were varied. The acid was replaced by alkali, ammonia and other bases, and the effect of each individual change on the reaction noted. Only after some five years of intensive effort did success come. Baekeland had found that pressure, in particular, impacted on the process and he was able to control the reaction at its various stages, separate it into different steps, and slow it down by adding ammonia. Ultimately, he was able to stop the reaction at almost any stage.[2] We now know that phenol (**1**) and formaldehyde (**2**) react in acid to give condensation product 4-hydroxymethylphenol (**3**) as shown in Scheme 1. This, on protonation and further reaction with phenol gives 4,4'-methylenebisphenol (**4**), in analogy to the ubiquitous bisphenol A. As phenol is an *ortho/para* directing group reaction at the less

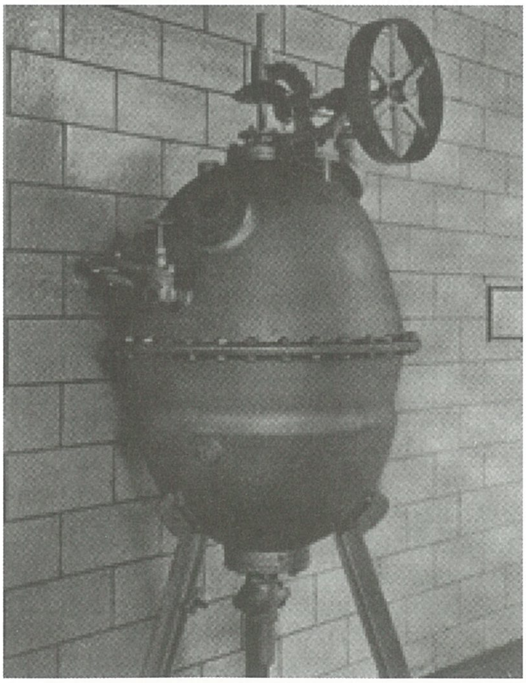


Bakelite core, a cross-linked phenol formaldehyde resin

Scheme 1. The phenol-formaldehyde reaction showing only *para-para* coupling; *ortho-para* and *ortho-ortho* are also possible.

reactive *ortho*-position is also possible. As the reaction sequence proceeds this *ortho*-coupling comes into play generating a cross-linked polymer product. Baekeland's product was just this with the essential core, **5**, illustrated in Scheme 1. It was the world's first completely synthetic plastic and named Bakelite (polyoxybenzyl-methyleneglycol) by its inventor. The first patent was filed on July 13, 1907 and has become known as the '699 patent,[7] the first of some 400.

Despite the laboratory success, Baekeland spent a further two years having the product tested by various potential users so that the processes could be refined for commercial production. At this time the sealed autoclave used in the Snug Rock lab became known as *Old Faithful*; it was rehoused in the Smithsonian Museum in 1983. Only after these trials was commercialisation set with his results publically disclosed at the February 8, 1909 meeting of the New York section of the American Chemical Society. In his presentation Leo said: *Previous reactions had resulted in slow processes and brittle products.... But by use of small amounts of bases I have succeeded in preparing a solid initial condensation product, the properties of which simplify enormously all molding operations.* Because users had difficulty in completing the final steps of production, Leo started semi-commercial production in his laboratory and, in 1910, when daily output had reached 180 litres (mainly for electrical insulators) he formed *General Bakelite* (1911) and began operations in Perth Amboy, New Jersey, to manufacture and market his new industrial material. By 1930, this was *The Bakelite Corporation* with a 128-acre plant at Bound Brook, New Jersey. At 73 years of age and prompted to retire by his son, Baekeland sold the company in 1939 to Union Carbide.



Old Faithful Dr Baekeland's first semi-commercial Bakelizer (Chemical Heritage Foundation-Wikipedia)

Bakelite was not the first plastic, as celluloid - ultimately derived from cotton and other vegetable matter – had been around for some time. What was so special about Baekeland's phenol-formaldehyde resin was that it softened on heating allowing molding and it was capable of dissolution. However, on reheating to higher temperature it set into a permanently hard and insoluble heat-resistant material unaffected by many chemicals. It was tough, stable and fire resistant, and was less expensive and markedly more versatile than any cellulosic material of the day. Most importantly, it was the first completely synthetic plastic and it revolutionised the manufacturing of everything from buttons to car parts. What made **Bakelite** so popular was its multifaceted and extremely useful properties. It was a **thermosetting resin** moldable and high temperature resistant, and it retained its shape. Its resistance to electricity and chemical action made it a great material for electrical insulation and in appliances. *Time* magazine put Leo Baekeland on its May 22, 1924 cover[8] with the article stating: *From the time that a man brushes his teeth in the morning with a Bakelite-handled brush until the moment when he . . . falls back upon a Bakelite bed, all that he touches, sees, uses will be made of this material of a thousand purposes*. This is not far from the truth as Bakelite encompassed the world for years with its products considered synonymous with high quality and durability – essentially becoming the 1920s and 1930s equivalent of today's *Intel Inside*. Some of the more notable uses of Bakelite with their date of introduction are:

- 1912 – Hyat Burroughs replaced celluloid by Bakelite in billiard balls.
- 1914 – The Bakelite telephone receiver case was made by Western Electric.
- 1915 – The US Eastman Kodak camera was encased in Bakelite.
- 1923 – The Philips radio company started its own Bakelite production (*Philite* in The Netherlands) with the first radio speaker in production in 1927.
- 1926 – The first Bakelite chair appeared.

Bakelite was manufactured in several forms to suit varying requirements but the Bakelite resin was fundamental to all. Until the patent expired in 1927, Bakelite was used mostly in industrial applications, such as automobile and electrical insulators. However, once the patent lapsed, it

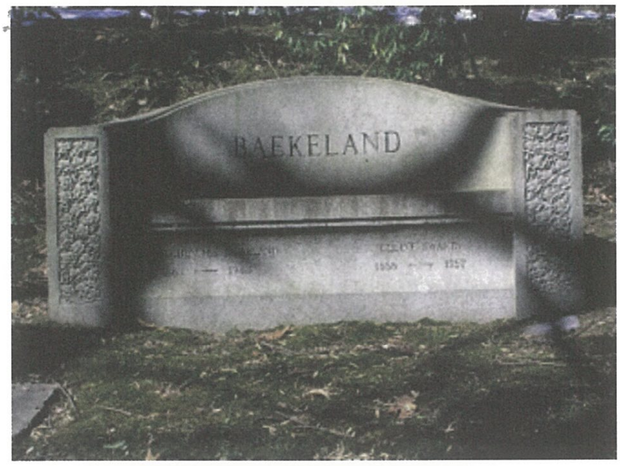
Upper left: Bakelite billiard balls; lower left: a 1931 Ericsson Bakelite telephone; right: a 1928 Philips 2511 radio from the late Jorge Llacer's Home Page (http://www.jllacer.com) broke into more widespread use. In October 1925, the first issue of *Plastics* magazine gave the colour range available with the variety including Clear Material, for jewellery, smokers' articles, *etc*.; cement, used in sealing electric light bulbs in metal bases; varnishes, for impregnating electric coils, *etc*.; lacquers, for protecting the surface of hardware; enamels, for giving resistive coating to industrial equipment; Laminated Bakelite, used for silent gears and insulation; and molding material, from which are formed innumerable articles of utility and beauty. The year 1927 was the turning point in the use of Bakelite because the ‘699 patent expired and real competition with the Bakelite material was then possible.

The 1924 Bakelite colour chart

Bakelite should not be confused with *Catalin*, another thermosetting phenol-formaldehyde resin popular from the 1930s. It was developed and trademarked in 1927 by the American Catalin Corporation after the Bakelite patents had expired. It is produced in a different two-stage manufacturing process than other types of phenolic resins, contains no fillers and is near colorless, rather than opaque. Unlike other phenolics, it can be produced in bright colours or even marbled. This made Catalin more popular than other types of Bakelite for consumer products. Most Bakelite jewellery for sale is actually Catalin.

Phenol-formaldehyde resins are still in use. With an appropriate catalyst the condensation reactions of Scheme 1 can be maximized for *ortho-ortho* or *ortho-para* coupling [the latter using base and dihydroxymethane, $CH_2(OH)_2$]. Such use has given rise to the Novolac and Resol resins of *e.g*. the plastics engineering companies Plenco,[9] and the Sumitomo Bakelite Co. Ltd. based in Japan.[10] Even as late as 1995 one of Baekeland's inventions made the news as the heat shield on the 1995 Jupiter probe was phenol-formaldehyde resin-based.

Leo Baekeland was made a professor by special appointment at Columbia University in 1916, held numerous honorary degrees and awards, and was a member of all the relevant professional societies. He was the 1924 President of the American Chemical Society. After the success of Bakelite, Leo spent much time in his laboratory on various academic projects maintaning his active interest in research. In retirement he spent the winters at his estate in Coconut Grove, Florida but as he aged his mind began to fail. He died of a cerebral hemorrhage in a sanatorium in Beacon, New York on February 23, 1944. He is buried in the cemetery at Sleepy Hollow in New York.



The Baekeland gravesite

Leo and Celine Baekeland had three children, daughter Jennifer referred to above and who appears in only some of the genealogical files, Nina (b.1896, d.1975) and George Washington (b.1895, d.1966), who never lived up to the high expectations of his father. Much of the Baekeland inherited wealth was subsequently squandered by his descendants. Indeed the history of the Baekeland family after Leo’s death has been equated to something of a crime novel as the socialite wife Barbara Daly Baekel of his grandson (George Middleton "Brooks" Baekeland, son of George W.), was murdered by her 26 year old homosexual son Anthony in 1972.[11] Barbara’s high society life was the subject of the 2007 film *Savage Grace* that was based on the book by Robins and Aronson.[12]

Postscript

In the view of this writer, Baekeland has to be given first place among those for emulation by the modern researcher whose support comes from the *funding-for-profit* regime that now applies in New Zealand. Indeed, Baekeland’s portrait would sit well in many a politician’s office. Progressively, governments have set in place a funding system that is now just about capable of an academic field of study of its own. The Hon. Steven Joyce, our current Minister of almost everything, surely deserves a framed Baekeland portrait for espousing the dictum of research for commercialisation. Today’s researcher now has to have a computer whose memory can accommodate the multitudinous and voluminous reports, as well as the hectares of spreadsheets that accompany them .... and a desk drawer is needed for the ever increasing tide of business cards. It needs to be remembered that Baekeland’s successes could not have happened were it not for earlier fundamental non-profit-generating academic research. There are few who could focus so closely and be so gifted as to emulate Leo Baekeland. As long ago as 1890, W.H. Maskell (a then expert in Coccidae, one of the ten families of plant sucking scale insects present in New Zealand) addressing the Wellington Philosophical Society said "a man in New Zealand who attempted any scientific work without showing some immediate money returns for it is generally considered to be a fool". While we may no longer be fools, the philosophy for research in NZ is the same.

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Exclusivity as an IP right

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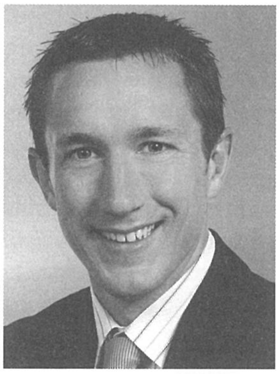

Tim Stirrup of Baldwins Intellectual Property in Auckland specialises in chemistry and biotechnology patents. Tim obtained his PhD in molecular biology from the University of Southhampton in the UK in 2007. He qualified as a registered New Zealand and Australian patent attorney in 2011.

Patents receive the lion's share of publicity when discussing exclusive commercial rights conferred by the State. There are, however, other exclusivities afforded to innovators in fields where regulatory approval is required. We discuss here the non-patent exclusivities conferred by regulatory agencies that cover chemical compounds in New Zealand and overseas.

Basis for the exclusivity rights

The Agreement on Trade-Related Aspects of Intellectual Property Rights (TRIPS)[1] states that members of the World Trade Organisation (WTO) must provide protection for data used to obtain marketing approval for new pharmaceuticals or agricultural chemical products, where that data required considerable effort to obtain. This requirement is the basis for the non-patent exclusivity rights given to drug and agricultural chemical innovators throughout the world.

Patents versus data exclusivity

Patents are granted by the Patent Office in a particular country. As they have their own timeline they can be granted at any time during the lifetime of a product. In contrast, data exclusivity is a protection conferred by a regulatory agency and runs from the date of a particular event in the product lifecycle (usually marketing approval of a new drug).

Regulatory agencies allow follow-on manufacturers (e.g. generics companies) to rely on the data submitted by the product innovator to obtain subsequent approval to sell their own identical products. To compensate the product innovator for its investment in generating that data, the innovator is granted a limited data exclusivity period. This means that whether or not patent protection exists, a competitor cannot rely on the product innovator's data to obtain registration of their own product.

Data exclusivity

The recently signed Trans-Pacific Partnership Agreement (TPPA) discussed one of the key exclusivities used by compound innovators to protect their investment in the product. As discussed in the January 2016 issue of *Chemistry in New Zealand*, "data exclusivity" or "data protection" was one of the battles where New Zealand stood its ground and got its way.

In the pharmaceutical realm, trial data is generated for the purposes of demonstrating the drug's safety, quality and efficacy. The data exclusivity period is the period that such data is kept confidential by the pharmaceutical regulatory agencies, and therefore cannot be relied upon by other parties e.g. generic manufacturers, looking to obtain marketing approval.

After the data exclusivity period has expired other parties can rely on the original trial data and seek government approval to market the same compound without having to conduct their own trials. Although the new product must be shown to have the same qualitative and quantitative composition as the reference product, the time and cost of trials and development is avoided.

Data exclusivity periods do not give a product innovator a true market monopoly because other players are free to carry out their own clinical trials (provided no patent is in force). However, the cost and time of carrying out trials invariably discourages follow-on manufacturers from doing so.

Data exclusivity for drugs with a new active ingredient

For drugs with a new active ingredient, the New Zealand regulatory authority Medsafe currently provides data exclusivity for five years from the date of marketing approval.[2] "New active ingredients" are defined as ingredients that have not been referred to in any previous application to Medsafe. During this time, the innovator's data is treated as a trade secret and competitors that wish to apply for regulatory approval must submit their own safety and trial data.

The US Food and Drug Administration (FDA) refer to new active ingredients as New Chemical Entities (NCEs) and provide the same five year exclusivity period. In this period, competitors cannot even file an application for regulatory approval which relies on the product innovator's data. It is generally recognised that the time for processing an NCE application is about two years and during this time the competitor cannot market/sell their product. Therefore the effective term of protection against new market entrants is about seven years.

The European Medicines Agency (EMA) provides a much longer exclusivity period of eight years from granting of the drug innovator's marketing approval. After the eight years have expired, a competitor can rely on the trial data of the product innovator in their regulatory application, but still cannot market their product. A further two year term of "market exclusivity" is provided to give a total of 10 years exclusivity after which approval can be granted and competitors can market/sell their product.

Data exclusivity for biologics

The variability of biologic medicines and the sensitivity of production processes increase the cost and difficulty of producing commercially viable products. The US FDA provides four years data exclusivity and eight years market exclusivity for biologics to give a total of 12 years. This length of time was justified by reports on the increased investment and the long time-frame required for biologic development and trials.

During negotiations on the recent TPPA, there was considerable debate around introducing an increased data exclusivity period in New Zealand for biologics of 12 years. Despite this, the final agreement required no change and new biologics are afforded the same protection as new chemical compounds – five years. The EMA has no special provisions for biologics and provides the standard 8+2 years.

Changed medicine notifications

Marketing approval is also required for a change in the original approval relating to route of administration, dosage form, dosage schedule, strength, patient group, labelling and/or intended use. For these "Changed Medicine Notifications" (in New Zealand) or "New Clinical Investigations" (in the USA), human trial data is required to substantiate the new use. Although no further data protection is provided in New Zealand, the USA provides a further three years. In Europe, if a "new therapeutic indication" is approved which demonstrates "significant clinical benefit" over existing therapies then the EMA provides an additional one year of marketing exclusivity (to make a total of 11 years).

Orphan drug exclusivity

The US FDA provides an extended exclusivity period for drugs that are used to treat diseases or conditions that affect less than 200,000 individuals in the USA – referred to as "orphan drugs". Two years are added to the standard term to give a seven year exclusivity period. This extension provides an economic incentive for development of medicines that would be less viable otherwise.

In the EU "orphan drug" status is granted to medicines for the treatment, prevention or diagnosis of a rare but life-threatening medical condition that afflicts not more than 5 in 10,000 people in the EU.[3] A 10-year market exclusivity period is provided. This 10 year period provides slightly broader protection than the standard 8+2 years because it also prevents approval of "similar medicinal products". These similar medicinal products differ only in respect of molecular features that are not "principal molecular structural features", thus providing exclusivity over isomers and isoforms of a compound provided they act via the same mechanism.

Exclusivity for agricultural compounds

New Zealand law currently provides data exclusivity of five years for safety and efficacy data relating to new agricultural compounds.[4] Despite a 2012 Ministry of Primary Industries (MPI) report advising against the outright extension of data exclusivity,[5] the TPPA recently committed New Zealand to increasing this exclusivity period to 10 years. The law will be changed in due course to comply with the TPPA.

Interestingly, the MPI's preferred option was to leave the basic term of exclusivity for innovative agricultural compounds at five years, but provide for a one year extension of the exclusivity period for each additional use added to the original approved compound. The extensions would be limited to a maximum of three years additional protection.

The time to develop and obtain approval of an agricultural compound is typically much less than for pharmaceuticals. Accordingly, a 20 year patent term is likely to still be in force once the 10 year exclusivity period ends. This means that the imminent increase in the data exclusivity period for agricultural compounds may have limited effect on the availability or cost of patented agricultural compounds. For non-patented products, however, the longer period of exclusivity could mean a longer time before generic products could enter the market, thus reducing competition and keeping prices higher. This would potentially have negative effects for users and NZ-based agrichem manufacturers. On the other hand, NZ-based agrichem innovators will have the opportunity to make use of the extended exclusivity protection in New Zealand and other TPPA countries.

In summary, the availability and extent of exclusivity rights is an important consideration for product innovators as well as follow-on compound manufacturers. Data and market exclusivity are forms of intellectual property protection that can impact greatly on the competition faced in a market. As such, they should be considered as a key part of IP and business strategy for companies involved in the manufacture, import or export of products subject to regulatory approval.

If you have any queries regarding data exclusivity or other intellectual property related matters (including patents, trademarks, copyright or licensing), please contact:

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References

1. TRIPS text and information at https://www.wto.org/english/tratop_e/trips_e/t_agm0_e.htm (accessed 24/04/2016).
2. Medicines Act 1981, Section 23B.
3. Orphan Drug Regulation Article 3(1).
4. Agricultural Compounds and Veterinary Medicines Act 1997, Section 72/73.
5. Regulatory Impact Statement - Data Protection for Agricultural Compounds ISBN No: 978-0-908334-96-4 https://www.mpi.govt.nz/document-vault/9238 (accessed 24/04/2016).

Dates of Note

July

23 ***Vladimir Prelog***, the Yugoslavian-born Swiss chemist who shared the 1975 Nobel Prize for Chemistry (with Cornforth) for his work on the stereochemistry of organic molecules and reactions, was born his day in 1906.

Sir ***William Ramsay***, the Scottish chemist who discovered the inert gases, neon, krypton and xenon, and co-discovered argon, radon, calcium and barium, died 100 years ago today.

It is the day in 1986 that the US FDA licensed production of the Merck & Co. RecombivaxHB, a new Hepatitis B vaccine and the first recombinant DNA vaccine. It superseded the making of Hepatitis B vaccines from blood taken from human chronic hepatitis B virus carriers.

24 ***Fritz Albert Lipmann***, the German-American biochemist who shared (with Krebs) the 1953 Nobel Prize for Physiology or Medicine for the discovery of coenzyme A, died in 1986.

25 ***Andreas Libavius***, a German alchemist who staunchly believed in the ability to transmute a base metal into gold but also discovered several new chemical processes, died this day 400 years ago.

27 ***Hans Fischer***, the German biochemist who was awarded the Nobel Prize for Chemistry in 1930 for his work into the constitution of haemin [the red blood pigment and a a ferric iron ion (heme B) with a chloride ligand)] and chlorophyll, and especially for his 1929 synthesis of haemin, the non-protein part of haemoglobin that gives blood its red colour, was born this day in 1881.

It is the day in 1921 that insulin was isolated at Toronto University by Canadians Sir ***Frederick Banting*** and ***Charles Best***, and that in 1586 when Sir ***Thomas Harriot*** (and not Raleigh) brought the first tobacco and potato to England from Virginia.

August

1 ***Tadeus Reichstein***, the Swiss chemist who, with Hench and Kendall, received the Nobel Prize for Physiology or Medicine in 1950 for his discoveries concerning hormones of the adrenal cortex, their structure and biological effects, died this day in 1996.

6 ***William Hyde Wollaston***, the English scientist who discovered palladium and rhodium during his investigation of platinum ore and was the first to produce malleable and ductile platinum on a commercial scale, was born this day 250 years ago.

Sir Alexander Fleming, the Scottish bacteriologist who discovered penicillin in 1928 while working on the influenza virus and shared the 1945 Nobel Prize for Physiology or Medicine, was born in 1881.

9 Count ***Amedeo Avogadro***, the Italian chemist and physicist who found that at the same temperature and pressure equal volumes of all perfect gases contain the same number of particles - *Avogadro's Law (1811)* - led to the Avogadro constant of 6.022×10^{23} units per mole of a substance, was born in 1776.

10 The *Smithsonian Institution* was established as a trust to administer the generous bequest of over $500,000 by James Smithson. In 1826, Smithson, a British scientist, drew up his last will and testament, naming his nephew as beneficiary. Smithson stipulated that, should the nephew die without heirs (as he did in 1835), the estate should go to the United States of America, to found at Washington, under the name of the Smithsonian Institution, an establishment for the increase and diffusion of knowledge among men. The motives behind Smithson's bequest remain mysterious as he had never travelled to the US and appears to have had no correspondence with anyone there.

11 ***Aaron Klug***, the British biochemist who received the 1982 Nobel Prize for Chemistry for his development of crystallographic electron microscopy and his structural elucidation of biologically important nucleic acid-protein complexes, was born in 1926.

Cato Maximilian Guldberg, the Norwegian chemist who, with his brother-in-law Peter Waage, formulated the law of mass action in 1864, was born 180 years ago.

12 ***Alfred Stock***, the German chemist whose 1919 system is used for inorganic chemical names, with roman numerals, *e.g.* Fe(III) bromide, died in 1946.

It is the day 20 years ago that NZ's DNA data bank was established and that in 1981 when IBM introduced its first personal computer.

13 ***Francesco Selmi***, the Italian chemist and toxicologist considered a founders of colloid chemistry, died in 1881.

14 ***Paul Sabatier***, the French chemist who shared the 1912 Nobel Prize for Chemistry (with Grignard) and discovered the use of finely divided nickel as a catalyst in hydrogenation, died 75 years ago in 1941.

15 The Procter & Gamble Co. introduced Crisco on this day in 1911. It was the first solidified hydrogenated shortening product made entirely of vegetable oil.

17 ***Hazel Bishop***, the American chemist and cosmetic executive who invented non-smear lipstick, was born in 1906.

Aleksandr Butlerov, the Russian chemist whose theory of organic chemical structure was important in our modern understanding of the area, died in 1886.

18 This day 30 years ago, 72 Nobel science laureates filed a legal brief with the US Supreme Court challenging as unconstitutional a Louisiana law requiring schools that teach evolution to also teach *creation-science*. A news release described the scientists as: *the largest group of Nobel laureates ever to support a single statement on any subject*.

19 ***Josiah Dwight Whitney***, the American geologist and chemist, chemist for the state of Iowa and California State Geologist (1860-1874) who was appointed professor of mineralogy at the University of Iowa in 1874, died 120 years ago. It is he after whom Mount Whitney in east-central California is named.

23 ***Auguste Bravais***, the French physicist and mineralogist best remembered for his work on the lattice theory of crystals and after whom Bravais lattices are named, was born in 1811.

Charles-Augustin Coulomb, the French physicist best known for the formulation of Coulomb's law, died in 1806.

24 ***Pierre Berthier***, the French mineralogist and mining engineer who discovered bauxite (aluminium ore) near the village Les Baux de Provence in southern France, died in 1861.

25 ***Morris William Travers***, the English chemist who, while working with Sir William Ramsay in London, discovered the element krypton in 1898, died in 1961.

26 On this day in 1856, ***William Henry Perkin***, applied for his British patent entitled *Dyeing Fabrics* for his invention of aniline dye *producing a new colouring matter for dyeing*.

30 The famed New Zealander Sir ***Ernest Rutherford*** was born this day in 1871.

31 ***Michel-Eugène Chevreul***, the French chemist who began the study of fats, discovered fatty acids and gave a great improvement in the quality of stearin, was born in 1786.

Hermann von Helmholtz, the German physiologist and physicist known for his work in optics, electrodynamics, mathematics, and meteorology, including the law of the conservation of energy, was born in 1821.

September

1 ***Karl August Folkers***, the US chemist whose research on vitamins resulted in the isolation of vitamin B12, was born in 1906.

2 ***William Henry***, the English physician and chemist who proposed in 1803 what is now called Henry's law, died in 1836 (see *this Journal*, **2014**, *78*, 128-131).

5 ***Ludwig Eduard Boltzmann***, the Austrian physicist and philosopher whose greatest achievement was in the development of statistical mechanics independently of Willard Gibbs, died in 1906.

6 ***John Dalton***, the English teacher who, from investigating the physical and chemical properties of matter, deduced an Atomic Theory (1803) whereby atoms of the same element are the same, but different from the atoms of any other element, was born 250 years ago today in 1766.

Albert ***Sabin*** developed the oral Polio vaccine as advised this day in 1956; it came into use in 1961.

Luis Federico Leloir, the Argentine biochemist who won the Nobel Prize for Chemistry in 1970 for his discovery of sugar nucleotides and their role in the biosynthesis of carbohydrates, was born in 1906.

7 ***Edwin McMillan***, the American nuclear physicist who shared the Nobel Prize for Chemistry in 1951 (with Seaborg) for his discovery of element 93 (neptunium), died in 1991.

11 ***Carl Zeiss***, the German industrialist who gained a worldwide reputation as a manufacturer of fine optical instruments, was born 200 years ago today.

13 Sir ***Robert Robinson***, the British chemist who received the 1947 Nobel Prize for Chemistry for his research on a wide range of organic compounds and especially the alkaloids, was born in 1886.

14 ***Ferid Murad***, the American co-winner of the 1998

Nobel Prize for Physiology or Medicine for demonstrating that nitroglycerin and related drugs worked by releasing nitric oxide into the body, thus acting as a signalling molecule in the cardiovascular system, celebrates his 80th birthday today.

15 ***John Desmond Bernal***, the Irish physicist and X-ray crystallographer who studied the atomic structures of solids, died in 1971.

16 ***Gabriel Fahrenheit***, the German physicist who invented the Fahrenheit scale mercury thermometer and lived most of his life in Holland, died in 1736.

The heaviest man-made element, ***Ununoctium (Uuo 118)***, was announced on this day 10 years ago.

17 ***John Kidd***, the English chemist and physician who named *naphthaline* (naphthalene) in 1821 after describing many of its properties and the means of its production, died in 1851.

Henry-Louis Le Chatelier, the French chemist best known for the principle given his name, died in 1936.

18 ***Armand-Hippolyte-Louis Fizeau***, the French physicist and first to measure the speed of light successfully without using astronomical calculations, died 120 years ago.

19 ***William Lever***, the British manufacturer and philanthropist who formed the Lever Brothers soap manufacturing company with his brother James in 1886, was born this day in 1851.

20 ***Juan José D'Elhuyar***, the Spanish chemist and mineralogist who was the first to separate tungsten metal from its *wolframite* ore, died in 1796.

22 ***Michael Faraday***, the English physicist and chemist whose many experiments contributed greatly to the understanding of electromagnetism, was born in 1791.

Frederick Soddy, the English chemist and physicist who received the Nobel Prize for Chemistry in 1921 for his investigations radioactive substances, died in 1956.

24 ***Philippus Aureolus Paracelsus***, the German-Swiss physician and alchemist who condemned medical teaching that was not based on observation and experience, died in 1541.

It is the day 10 years ago that NASA recorded the largest ozone hole to date in the atmosphere.

25 ***Nikolay Nikolayevich Semyonov***, the Russian physical chemist who shared the 1956 Nobel Prize for Chemistry (with Hinshelwood) for researches into the mechanism of chemical reactions, died 30 years ago.

26 ***Leopold Stephen Ruzicka***, the Croatian-Swiss scientist and co-winner of the 1939 Nobel Prize in Chemistry for his work on *polymethylenes and higher terpenes* working most of his life in Switzerland, died in 1976. He investigated the ingredients of the Dalmatian insect powder pyrethrum (Tanacetum cinerariifolium), a recognised insecticide found in pyrethrins. In this way, he came into contact with the terpenes and the perfume industry, and proved the structure and existence of the compounds of muscone and civet.

Sir ***Geoffrey Wilkinson***, the British chemist and joint recipient (with Fischer) of the 1973 Nobel Prize for Chemistry for pioneering work on sandwich compounds, died 20 years ago today.

27 The first annual meeting of the British Association for the Advancement of Science was held in York in 1831, the year of its foundation.

October

3 ***Peter Jacob Hjelm*** was the Swedish chemist born this day in 1746 who isolated the element molybdenum in 1781, four years after its discovery.

Charles Darwin returned from his voyage on the *HMS Beagle* to the Pacific 180 years ago today.

4 ***Mahlon Bush Hoagland***, the American biochemist who discovered transfer RNA (tRNA), was born in 1921.

5 ***Lars Onsager***, the Norwegian-born American whose development of a general theory of irreversible chemical processes gained him the 1968 Nobel Prize for Chemistry, died in 1976.

6 ***Otto Meyerhof***, the German biochemist and co-recipient (with Hill), of the 1922 Nobel Prize for Physiology or Medicine for work studying the chemical reactions of metabolism in muscle, died in 1951.

8 Sir ***Marcus Laurence Elwin Oliphant***, the Australian physicist who played an important role in the first experimental demonstration of nuclear fusion, was born in Adelaide in 1901.

Harry G. Day, the American nutritional biochemist who helped develop the fluoride additive used in toothpaste to combat tooth decay, was born in 1906.

10 ***Henry Cavendish***, the English physicist and chemist who was born in Nice and conducted experiments in diverse fields, discovering such phenomena as the composition of air, the nature and properties of hydrogen, the composition of water, and various properties of electricity, was born in 1731.

According to an unfounded legend, the metric system was born in 1796. The 10/10 date seems to signify the base 10 system of using measurements.

12 The success in making of X-ray moving pictures of internal organs of the human body was reported at the 37th annual meeting of the American Röntgen Ray Society by Drs Stewart, Hoffman and Ghiselin 80 years ago.

16 In 1846, American dentist, Dr ***William Thomas Green Morton*** gave the first public demonstration of ether as an anaesthetic.

18 ***Friedrich Konrad Beilstein***, the Russian chemist whose lasting legacy was his systematic description of organic compounds, which he compiled in the publication of his *Handbuch der organischen Chemie*, died

in 1906.

20 Sir ***James Chadwick***, the English physicist who received the Nobel Prize for Physics (1935) for his discovery of the neutron, was born 125 years ago today (1891).

The first use of chemical symbols in a British textbook was explained on this day in 1832. ***Edward Turner***'s Preface to the 4th edition of his 1833 textbook, *Elements of Chemistry*, carried an explanation of his use of symbols to represent reactants and products in a chemical reaction of cyanogen. This because he found they solved the difficulty of giving a *clear and concise description of the phenomena in ordinary language*.

21 ***Hermann Hellriegel*** was born this day in 1831. He was the German chemist who determined optimum conditions for growing sugar beets, the primary source of sugar, and discovered that the fixation of nitrogen by certain legumes took nitrogen from the air into a form in the soil accessible for organic assimilation by plants. He showed that it was due to the symbiotic action of soil bacteria in nodules on the roots of the legumes.

William A. Mitchell, the American food scientist and chemist who worked for the General Foods Corp. and held more than 70 patents, was born this day in 1911.

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