



University of Nottingham

18th - 19th July 2022

Welcome to the YRM 2022!

Welcome to the YRM 2022, hosted by the University of Nottingham! We hope you enjoy the conference and the opportunity to discuss your exciting polymers!

Finding your way around:

A map of the University Park campus can be found here at the end of the programme booklet.

Social events:

There will be a BBQ held at Cripps Hall, University Park (building **L** on map) from 17:30 onwards on 18th July. There will also be live music from 'The Ramshackle Men'!

Following the BBQ, we will meet at the Robin Hood Statue in Nottingham where we will have a group photo. We will then separate into groups and enjoy:

- Ye Old Trip to Jerusalem – *England's Oldest Inn*
- Fothergills – *Historic venue with great views of the Castle*
- The Castle Pub – *Classic pub opposite the historic Castle gate house*
- The Navigation Inn– *Traditional canalside pub*
- Canalhouse – *Waterside pub located in former canal museum*
- Via Fossa— *Waterside pub located in former canal museum*

For more information on the location of these venues, see the last page.

Day 1— Monday 18th July, Morning

08:30	Registration and Coffee	
09:15	Welcome from Prof. Steve Howdle Introduction to Macro Group UK (Macro UK Committee)	
	Session 1 Chair: Dr. Vincenzo Taresco	
09:30	Dr. Jennifer Garden <i>"Simple Strategies to Harness Mixed-Metal Cooperativity in Cyclic Ester Ring-Opening Polymerisation"</i>	
10:00	Wouter Lindeboom <i>Oxford University</i>	Effects of Ligand Backbone on Co(III)/K(I) Heterodinuclear Catalysts for Carbon Dioxide and Propylene Oxide Ring Opening Copolymerization.
10:12	James Runge <i>University of Bath</i>	Sugar-based polymers for renewable, degradable, and efficient battery electrolytes
10:24	Lloyd Shaw <i>University of Durham</i>	Advancing the Field of Bio-Derived Polymers Synthesised by Living Anionic Polymerisation
10:36	Joseph Sefton <i>University of Nottingham</i>	ω -vinyl Methacrylate Oligomers from In Situ Catalytic Chain Transfer Polymerisation: Synthesis, Purification and Application
10:48	Sponsor talk: Merck	
11:03	Coffee Break	
	Session 2 Chair: Dr. Umut Can Oz	
11:30	Flash Presentations	
	1. Dominic Gray <i>University of Liverpool</i> 2. Ryan Larder <i>Loughborough University</i> 3. Helen Tunstall-Garcia <i>University of Cambridge</i> 4. Georgia Maitland <i>Aston University</i> 5. Chester Blackburn <i>University of Nottingham</i> 6. Matthew Laurel <i>University of Warwick</i> 7. Mark Sullivan <i>De Montford University</i>	8. Damla Ulker <i>University of Sheffield/Near East University</i> 9. Julia Yu-Jung Rho <i>University of Warwick</i> 10. Haoran Wang <i>University of Liverpool</i> 11. Edyta Niezabitowska <i>University of Liverpool</i> 12. Helena Henke <i>University of Nottingham</i> 13. Yuming An <i>Queen's University Belfast</i> 14. Cordula Hege <i>University of Nottingham</i>
12:30	Lunch and Poster Session	

Day 1— Monday 18th July, Afternoon

	Session 3 Chair: Dr. Valentina Cuzzucoli Crucitti	
	Dr. Antoine Buchard	
14:00	“Polysaccharide mimics towards more sustainable polymers and functional materials”	
14:30	Sarah Woods <i>Loughborough University</i>	Synthesis of renewable diblock copolymers by aqueous RAFT polymerisation induced self-assembly of lactic acid-based monomers
14:42	Aziana Abuhassan <i>University of Nottingham</i>	Engineering of Enzymes for the Degradation of Synthetic Rubbers
14:54	Holly Yeo <i>Oxford University</i>	CO ₂ -derived Poly(carbonate-b-ester) Electrolytes for Lithium-Ion Batteries
15:06	Julian Heuer <i>Max Planck Institute</i>	Controllable photocatalysis by altering the active centre microenvironment of an organic polymer photocatalyst
15:18	Sponsor Talk: Synthomer	
15:33	Coffee Break	
	Session 4 Chair: Dr. Cara Moloney	
	Dr. Sebastian Spain	
16:00	“Polymers: from paint to patches”	
16:30	Sponsor talk: Polymer Chemistry	
16:45	Hannah Burnage <i>University of Warwick</i>	Study of functionalised RAFT polymer nanoparticles and their protein coronas formed in biological media
16:57	Hulya Bayraktutan <i>University of Nottingham</i>	Synthesis and application of PEGylated triblock copolymers on delivery of RNA and DNA for cancer immunotherapy
17:09	Ashfaq Ahmad <i>University of Warwick</i>	The impact of glycoproteins-corona on targeting ability of Glycopolymer-tethered glycosylated gold nanoparticles.
17:21	Elisabeth Trinh <i>Univserisy of Sheffield</i>	Using bridging flocculation for the development of a polymer-based point-of-care diagnostic for targeted detection of DNA
17:33	End of Day 1, BBQ at Cripps Hall	

Day 2— Tuesday 19th July

	Session 5 Chair: Dr. Pratik Gurnani	
09:00	Panagiotis Georgiou <i>University of Warwick</i>	New Nanomaterial Design Principles for Biomacromolecular Antifreezes
09:15	Ellen Quane <i>University of Sheffield</i>	Time-resolved small angle x-ray scattering study of polyurethane film formation from particle dispersions
09:27	Jungyeon Kim <i>University of Warwick</i>	Enabling RAFT Polymerisation for Brush Copolymers with a Poly(2-oxazoline) Backbone
09:39	Caty Marsden <i>University of Loughborough</i>	Towards Macromolecular Dual Imaging Particles
09:51	Sophie Laroque, <i>University of Warwick</i>	Antimicrobial star copolymers induce bacterial cell aggregation compared to linear copolymer counterparts
10:03	Despina Coursari, <i>University of Warwick</i>	Synthesis of Amphiphilic Functional Glycopolymers and their Self-Assembly into Glycosylated Nanoparticles
10:15	Coffee Break	
	Session 6 Chair: Dr. Simeng Wang	
11:00	Prof. Ricky Wildman “Manufacturing a career: a journey from physics to bioprinting”	
11:30	Peiyao Yan <i>University of Liverpool</i>	Mechanical properties and functional applications of high-sulfur polymers prepared by inverse vulcanisation
11:42	Kam Poon	Toughening CO ₂ -Derived Elastomers Through Ionomer Networking
11:54	Emma Salisbury <i>University of Warwick</i>	Novel gelatin-based biomaterials for 3D tissue modelling of the human endometrium
12:06	Simon Fawcett <i>University of Sheffield</i>	Exploring new Thermoplastic Polyurethanes (TPU) via non-covalent interactions
12:18	Abigail Collins	Tuning the solar spectrum using organic-inorganic hybrid polymers
12:30	Lunch	
14:00	Prizes and Closing Remarks	

Poster Presentations

N°	Presenter	Title
1	Alexandros Magiakos <i>University of Warwick</i>	Development of pH responsive platinum-containing polymeric arsenical hydrogels for bio-medical applications
2	Anisha Patel <i>Aston University</i>	New Sustainable Polymers: A Greener Future for Commercial Inkjet Printing
3	Frances Dawson <i>University of Bath</i>	Fully degradable polyacrylate networks from conventional radical polymerization enabled by thionolactone addition
4	Boyu Zhao <i>University of Warwick</i>	Active learning as a tool for optimizing electrochemical atom transfer radical polymerisation
5	Helen Sims <i>University of Durham</i>	Responsive Polymeric Receptors as Diagnostic Tools
6	Bryn Jones <i>University of Warwick</i>	Controlled Electropolymerisation of HEMA using Nanopipettes
7	Jack Fradgley <i>University of Durham</i>	Development of a Universal Polymer Labelling Strategy using a Novel Photo-Affinity Labelling Probe
8	Congkai Ma <i>University of Warwick</i>	Well-defined polyacrylamides with AIE properties via rapid Cu-mediated living radical polymerizations in aqueous solution: thermoresponsive nanoparticles for bioimaging
9	Joe Dale <i>University of Liverpool</i>	Dark sulfur: Quantifying unpolymerized sulfur in inverse vulcanized polymers
10	Siddhi Trivedi <i>University of Nottingham</i>	Developing a library of ionic liquid-based resins for use in printable electrochemical sensors
11	Douglas Soutar <i>University of Warwick</i>	A means to an end-group modified poly(vinyl alcohol)
12	Bethany Husband <i>University of Nottingham</i>	Synthesis of low molecular weight polyimides for additive manufacturing

Poster Presentations

N°	Presenter	Title
13	Phoebe Lowy <i>University of Edinburgh</i>	Is Three a Crowd? Trimetallic Catalysts for Lactide Ring-Opening Polymerisation
14	Euan Kendall <i>University of Warwick</i>	Alternate Non-Silicone Based Lubricants Synthesized via CCTP from Naturally Derived Materials
15	Rafal Kopiasz <i>University of Nottingham</i>	The impact of hydrophobicity, flexibility, and backbone isomerism on biological activity and mechanism of action of ionenes
16	Lena Dalal <i>University of Warwick</i>	Synthesis and evaluation of cationic antimicrobial polymers
17	Cristina Parisi <i>University of Nottingham</i>	Enhancing the anticancer activity of doxorubicin via simultaneous delivery with a peroxyinitrite generator using polyester based polymeric nanoparticles
18	Xander Praet <i>University of Sheffield</i>	Reversible Acrylic Adhesives based on Covalent Adaptable Networks
19	Mahir Mohammed <i>University of Warwick</i>	Aqueous Electrochemical Synthesis of Polymers using ATRP on the Nano/Macro Scale
20	Bawan Hadad <i>Aston University</i>	Tuning the Elasticity of Biodegradable Polymers using Vegetable Oils
21	Mantas Drelingas <i>University of Warwick</i>	Formulation of elastomeric 3D printing resins for vitrimer components in soft robotics
22	James Cresswell <i>University of Durham</i>	Synthesis of well-defined biodegradable polymers and study of their materials properties
23	Romy Dop <i>University of Liverpool</i>	Antibacterial Sulfur Polymers
24	Melissa Ligorio <i>University of Warwick</i>	Glycan-functionalised gold nanoparticles for the detection of cholera toxin
25	Supisara Jearranai-Prepame <i>University of Nottingham</i>	Preliminary study of the modified Poly(β -amino ester)s (PBAEs) for gene delivery in glioblastoma

Poster Presentations

	Presenter	Title
26	Meshari Alqarni <i>University of Warwick</i>	Polymer/ Metal Oxide Hybrid Latexes Prepared via Surfactant-Free RAFT-Mediated Polymerization
27	Emily Brogden <i>University of Warwick</i>	Linerless Pressure Sensitive Adhesives Made by Mixtures of Hard and Soft Polymer Colloids
28	Jonathan Gregg <i>University of Sheffield</i>	Facile & versatile covalently adaptable Diels-Alder networks for adhesive application
29	Min Zeng <i>University of Warwick</i>	Customizing the self-assembly of supramolecular peptide nanotubes via the linker group
30	Jinge You <i>University of Nottingham</i>	Development of nanovectors for targeted delivery of p38 MAPK inhibitors to dendritic cells
31	Rory McBride <i>University of Sheffield</i>	Synthesis of High Molecular Weight Water-Soluble Polymers as Low-Viscosity Latex Particles by RAFT Aqueous Dispersion Polymerisation in Highly Salty Media
32	Mohammed Aljuaid <i>University of Warwick</i>	Exploiting monothiomaleimide [2+2]-photocycloaddition in linear polymers and network formulation
33	Rachel Lee <i>Newcastle University</i>	Materials for Bioelectronic Applications
34	Muzhao Wang <i>University of Warwick</i>	Functional polymers from sustainable electrosynthesis
35	Veronica Hanna <i>University of Liverpool</i>	Incorporation of fillers to modify the mechanical performance of inverse vulcanised polymers
36	Karolina Kasza <i>University of Nottingham</i>	Grafted poly(β -amino esters) as versatile scaffolds for biomedical applications
37	Natasha Reddy <i>University of Warwick</i>	Synthesis of cationic polymers to exert antimicrobial activity
38	Beth Jordan <i>Loughborough University</i>	Microplastic mimics produced using polymerisation induced self-assembly

Poster Presentations

N°	Presenter	Title
39	Qiao Tang <i>University of Warwick</i>	Why are polyampholytes so good at freezing A549 cells?
40	Benjamin Fiedler <i>University of Nottingham</i>	Unlocking the macrophage: Lipid-terminated glyco-polymers as liposomal targeting ligands
41	Lynn Anderson <i>Northumbria University</i>	Recyclable, high performance thermoset polymers from dynamic epoxy-amine-boronic ester hybrid networks
42	Sophie Hill <i>University of Warwick</i>	Cyclic Peptide – Polymer Conjugates for Drug Delivery Applications
43	Josh Ryan <i>University of Warwick</i>	Small Molecule Organic Glasses as Replacements for Polymers in Colloidal Delivery Systems
44	Nazgol Karimi Dastgerdi <i>University of Nottingham</i>	Synthesis and characterization of quaternised poly (amidoamine) qpABOL in a combination of PGA for highly efficient delivery of saRNA
45	William Pointer <i>University of Warwick</i>	Synthesis and Modifications of Polybutadiene Under Continuous Flow With Real-Time NMR Analysis, Online Monitoring and Self Optimisation using AI
46	Oliver Harris <i>Loughborough University</i>	Synthesis of vinyl monomers from commercial olive oil via transesterification with N-hydroxyethyl acrylamide
47	Zhongyuan Wan <i>University of Warwick</i>	Investigation of novel addition fragmentation monomers to improve the properties of 3D-printer resins
48	Joshua Davies <i>University of Warwick</i>	ω -Unsaturated methacrylate macromonomers as reactive polymeric stabilizers in mini-emulsion polymerization
49	Zihe Cheng <i>University of Warwick</i>	Responsive Nanotubes from Asymmetric Cyclic Peptide-Polymer Conjugates
50	Bradley Hopkins <i>University of Nottingham</i>	Microwave-assisted Degradation of Polymers with Supercritical Carbon Dioxide for Plastic Recycling

Poster Presentations

N°	Presenter	Title
51	Daniel MacKinnon <i>University of Warwick</i>	Tuneable N-Substituted Polyamides with High Bio-mass Content via Ugi 4 Component Polymerisation
52	Zivani Varanaraja <i>University of Warwick</i>	Poly(2-Oxazoline) Terpolymers with Tuneable Thermal Properties and Solution Behaviour in Non-aqueous Media
53	Xiao Yuan Wang <i>University of Nottingham</i>	The Synthesis and Continuous Manufacture of Novel, High Performing Polymeric Lubricants for the Next Generation of Electric Transportation
54	Roberto Terracciano <i>University of Warwick</i>	Glycosylated liposomes for cell-targeted delivery of active compounds
55	Toby Watts <i>University of Kent</i>	The application of ion-pairs in the synthesis of sequence-controlled polymers
56	Benedetta Brugnoli <i>University of Nottingham, Sapienza University of Rome</i>	Development of smart polydiacetylene nanosystems for in vitro and in vivo tracking
57	Jonas Becke <i>University of Warwick</i>	Step-growth glycopolymers with a defined tacticity for selective biological recognition
58	Hubert Buksa <i>University of Sheffield</i>	Synthesis and Characterisation of Thermoresponsive Poly(4-hydroxybutyl acrylate) Latexes: Precursors for Reverse Sequence Polymerisation-Induced Self-Assembly in Aqueous Media
59	Abdulrahman Alhathir <i>University of Warwick</i>	Synthesis of Poly(isoxazoles) from Renewable Biomass
60	James Lefley <i>University of Warwick</i>	Direct endcapping of Poly(2-ethyl-2-oxazoline) Homopolymers and their Self-assembly
61	Charles Tkaczyk <i>Durham University</i>	PET/PEG Copolymer Electrolytes for use in All-Solid-State Li-ion Batteries

Poster Presentations

N°	Presenter	Title
62	Yangshuo Jessie Hu <i>Imperial College</i>	Platelet-Inspired Nanoparticles for Targeted Drug Delivery to the Atherosclerotic Plaque
63	Ella Clark <i>University of Bath</i>	Novel polymers from anhydrosugars: synthesis, catalysis and applications of polysaccharide mim-
64	Fatemeh Mehradnia <i>University of Nottingham</i>	Disulfide cross-linked Linear methacrylamide based micelles as Redox-responsive drug nanocarriers for Triple Negative Breast tumour-targeted therapy: Histopathological evaluation
65	Lewis O'Shaughnessy	Tracking Intracellular Transport of Self-Reporting
66	Joshua Hayles <i>University of Sheffield</i>	Acetals for Adaptable, Degradable and Reprocessable Thermosets

Flash and Poster Presentations

N°	Presenter	Title
P1	Dominic Gray	Synthesis of dual-responsive PLGA nanoparticles
P2	Ryan Larder <i>Loughborough University</i>	Antimicrobial 'Inks' for 3D Printing: Block Copolymer-Silver Nanoparticle Composites Synthesised Using Supercritical CO ₂
P3	Helen Tunstall-Garcia	Polymer-POSS Composites As Hosts For Lumines-
P4	Georgia Maitland	Block copolymer nanoparticles for next genera-
P5	Chester Blackburn	Polymer Functionalised topographies for cardiac
P6	Matthew Laurel <i>University of Warwick</i>	Comparative stability of thiomethacrylate and methacrylate crosslinking.
P7	Mark Sullivan <i>De Montfort Univeristy</i>	Magnetic Molecularly Imprinted Nanoparticles for the Extraction and Detection of Molecules of Interest.
P8	Damla Ulker <i>University of Sheffield, Near East University</i>	Synthesis and Aqueous Self-Assembly of Amphiphilic Poly(2-hydroxypropyl methacrylate)-Poly(N,N'-Dimethylacrylamide) Diblock Copolymers
P9	Julia Yu-Jung Rho	Studying well-defined cationic polymers for gene
P10	Haoran Wang <i>University of Liverpool</i>	Oxygen heteroatom enhanced sulfur-rich polymers synthesized by inverse vulcanization for high-performance lithium-sulfur batteries
P11	Edyta Niezabitowska <i>University of Liverpool</i>	Insights into the Internal Structures of Nanogels Using a Versatile Asymmetric-Flow Field-Flow Fractionation Method

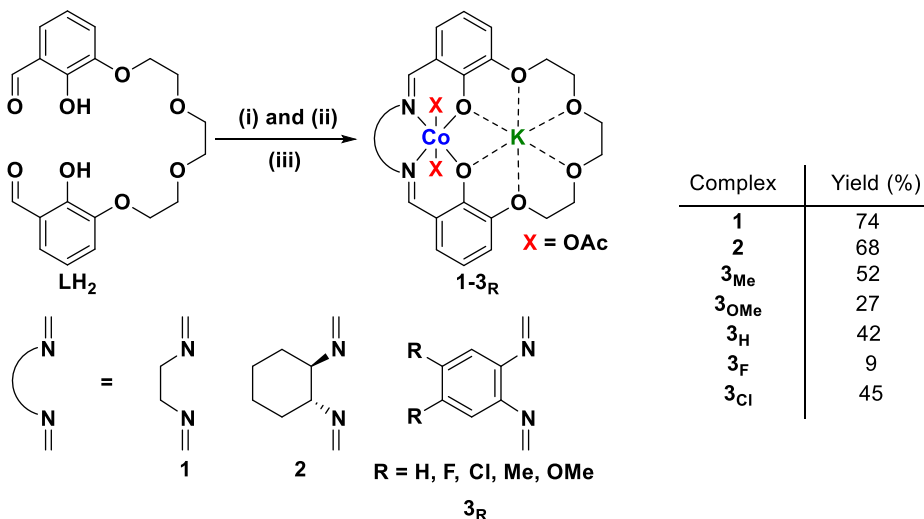
Flash and Poster Presentations

N°	Presenter	Title
P12	Helena Henke <i>University of Nottingham</i>	Oligomerization of Butyl Methacrylate via CCTP: from small lab scale to microwave reactors
P13	Yuming An Queen's University Bel-	Long-acting injectable D and L- α peptide hydrogels for HIV/AIDS treatment and prevention
P14	Cordula Hege	Using iron-catalysts for the catalytic chain-transfer

Oral Abstracts

Effects of Ligand Backbone on Co(III)/K(I) Heterodinuclear Catalysts for Carbon Dioxide and Propylene Oxide Ring Opening Copolymerization.

Wouter Lindeboom



Scheme 1: Synthesis of Complexes 1-3_R.

The efficient utilization of CO₂ to produce useful products is a significant challenge in sustainable chemistry driven by the large production of carbon dioxide as a by-product in a wide range of industries across the globe.¹ One industrially relevant option is the copolymerization of epoxides with CO₂ to make polycarbonates.² At the forefront of these polymers are those derived from carbon dioxide and propylene oxide, which have been shown to be useful as low molar mass polyols for polyurethane synthesis replacing petrochemical polyols in the manufacturing of household goods, home insulation and coatings.³ In this presentation a series of novel heterodinuclear Co(III)/K(I) catalysts are explored showing good activity for the ring-opening copolymerization of propylene oxide (PO) and carbonate dioxide. The complexes are amongst a new family of heterodinuclear catalyst, which are active for this copolymerization without co-catalyst. These catalysts show a wide variety of selectivities and activities for poly(propylene carbonate) (PPC) with cyclic car-

bonate (CC) as the only other by-product. The most active catalyst, **3_H**, shows a turnover frequency (TOF) of 389 h⁻¹ and selectivity of >99% for PPC ($k_p = 10.10 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, 50 °C, 20 bar). The polymerizations are well controlled and produce hydroxyl telechelic PPC with narrow dispersity ($\bar{D} < 1.15$). A close relation was observed between Hammett parameter, activity and selectivity of the different catalysts with different electron withdrawing and donating backbones, with both having an overall negative impact on the catalysis. This was further studied by Eyring analysis of the CC formation from PPC of the most and least selective catalyst, revealing they to have an almost equivalent barrier to backbiting: $\Delta G^\ddagger = +81.4$ and $+83.4 \text{ kJ mol}^{-1}$, respectively. Meaning other factors must be used to explain the differences in activities and selectivities, which are explored here.

References

- 1 Artz, J.; Müller, T. E.; Thenert, K.; Kleinekorte, J.; Meys, R.; Sternberg, A.; Bardow, A.; Leitner, W. *Chem. Rev.*, 2018; Vol. 118, pp 434-504.
- 2 Wang, Y.; Darensbourg, D. J. *Coord. Chem. Rev.*, 2018; Vol. 372, pp 85-100.
- 3 Langanke, J.; Wolf, A.; Hofmann, J.; Böhm, K.; Subhani, M. A.; Müller, T. E.; Leitner, W.; Gürtler, C. *Green Chemistry*, 2014; Vol. 16, pp 1865-1870.

Sugar-Based Polymers for Renewable, Degradable, and Efficient Battery Electrolytes

James Runge

Traditional lithium-ion batteries (LIBs) possess several issues regarding their safety, performance and sustainability owing to their use of liquid electrolytes based upon organic solvents. Consequently, there is growing interest in replacing the liquid electrolyte with a solid-state counterpart as a strategy to combat these flaws. Solid polymer electrolytes (SPEs) have gained considerable attention as alternative electrolyte materials for LIBs due to their low cost of manufacture, greater mechanical strength, and solvent-free nature¹. Poly(ethylene oxide) (PEO) is the current benchmark for SPE applications owing to its high ionic conductivity (*ca.* $10^{-3} \text{ S cm}^{-1}$ at 70 °C). However, PEO-based SPEs possesses several shortcomings which restricts their practical application, including limited ionic conductivity at ambient temperature, poor mechanical strength at elevated temperatures (T_m of PEO = 60-65 °C), high crystallinity and low lithium-ion transference numbers (~ 0.2)². Therefore, it is necessary to design alternative host materials which can replace PEO to advance the field of SPEs for the next generation of rechargeable LIBs³.

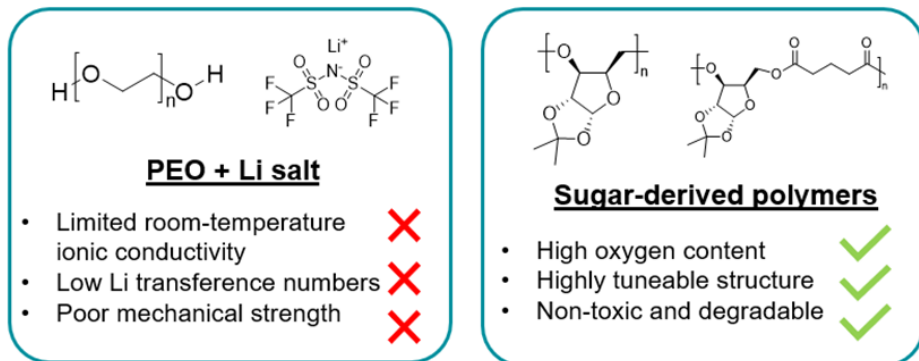


Figure 1: The shortcomings of PEO-based SPEs that hinder their practical application and the advantages of replacing these materials with sugar-based polymers.

The objectives of the work that will be presented is to develop high performance alternative SPE materials derived from renewable feedstocks. A platform of functionalisable sugar-derived polymers has been developed which contain a high oxygen content to promote coordination and dissolution of lithium salts. The structure and properties can be easily varied to explore a wide chemical space (e.g. T_g , crystallinity, pendant functional groups, crosslinked networks). Finally, these sugar-based polymers are non-toxic and can exhibit biodegradability which would facilitate recycling of battery technologies and recovery of precious elements involved in their manufacture thus improving their sustainability.

This work will involve using ring-opening polymerisation (ROP)⁴ and ring-opening co-polymerisation (ROCOP)⁵ strategies of a xylose-derived oxetane to prepare novel bio-derived polyether and polyester based SPE materials. These polymers are amenable to further post-polymerisation functionalisation which can be exploited to improve the electrochemical performance of the SPEs.

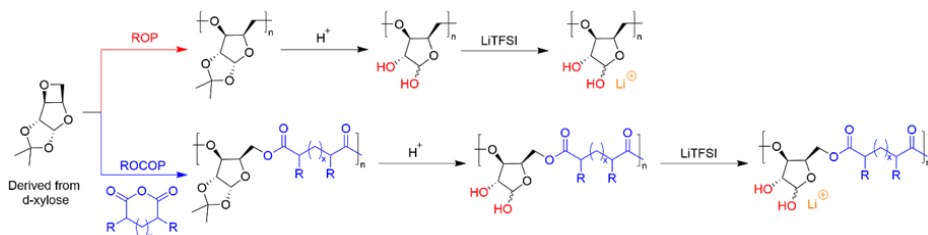


Figure 2: ROP and ROCOP strategies of a xylose-derived oxetane to prepare sugar-based polyether and polyesters for application as novel bio-derived solid polymer electrolyte materials.

References

- 1 V. Bocharova and A. P. Sokolov, *Macromolecules*, 2020, **53**, 4141–4157.
- 2 Z. Xue, D. He and X. Xie, *J. Mater. Chem. A*, 2015, **3**, 19218–19253.
- 3 J. Mindemark, M. J. Lacey, T. Bowden and D. Brandell, *Prog. Polym. Sci.*, 2018, **81**, 114–143.
- 4 T. M. McGuire, J. Bowles, E. Deane, E. H. E. Farrar, M. N. Grayson and A. Buchard, *Angew. Chemie - Int. Ed.*, 2021, **60**, 4524–4528.
- 5 T. M. McGuire, E. F. Clark and A. Buchard, *Macromolecules*, 2021, **54**, 5094–5105.

Advancing the Field of Bio-Derived Polymers Synthesised by Living Anionic Polymerisation

Lloyd Shaw

Despite celebrating its 65th anniversary last year, the field of living anionic polymerisation (LAP) is ever growing and evolving. In recent years this has resulted in an increasing amount of activity in the field of sustainable materials, including extensive research into the use of bio-based monomers with a focus on improving the sustainability and performance of new polymer compositions. This consequently has led to significant interest from both academia and industry into the very promising class of bio-based monomers called terpenes, including myrcene, farnesene and ocimene. [1] These bio-based conjugated dienes, which can be extracted from plants, synthesised through the pyrolysis of another naturally occurring plant oil – β -pinene – and synthesised via fermentation of genetically modified bacteria, represent a compelling alternative to both butadiene and isoprene. [2] In this paper, we will present a summary of our work on the living anionic (co)polymerisation of terpene monomers - much of which is previously unpublished work - including what we believe to be the first example of the anionic polymerisation of β -ocimene. [3] [4] Moreover, we will report selective post-polymerisation functionalisation reactions for terpene-containing copolymers synthesised by LAP, including epoxidation and, for the first-time, bromination reactions.

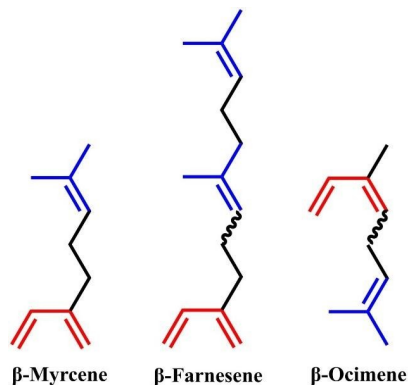


Figure 1: Three common terpene monomers, where the carbons in red represent the polymerisable diene and the carbons in blue represent a functionalisable side chain double bond.

References

- 1 M. Steube, T. Johann, R. D. Barent, A. H. E. Muller and H. Frey, "Rational Design of Tapered Multiblock Copolymers for Thermoplastic Elastomers," *Progress in Polymer Science*, vol. 124, p. 101488, 2022.
- 2 E.-M. Kim, J.-H. Eom, Y. Um, Y. Kim and H. M. Woo, "Microbial Synthesis of Myrcene by Metabolically Engineered *Escherichia coli*," *Journal of Agricultural and Food Chemistry*, vol. 63, pp. 4606-4612, 2015.
- 3 E. Grune, J. Bareuther, J. Blankenburg, M. Appold, L. Shaw, A. H. E. Muller, G. Floudas, L. R. Hutchings, M. Gallei and H. Frey, "Towards bio-based tapered block copolymers: the behaviour of myrcene in the statistical anionic copolymerisation," *Polymer Chemistry*, vol. 10, pp. 1213-1220, 2019.
- 4 L. Shaw and L. R. Hutchings, "Tales of the unexpected. The non-random statistical copolymerisation of myrcene and styrene in the presence of a polar modifier," *Polymer Chemistry*, vol. 11, pp. 7020-7025, 2020.

ω -vinyl Methacrylate Oligomers from *In Situ* Catalytic Chain Transfer Polymerisation: Synthesis, Purification and Application

Joseph Sefton

Catalytic chain transfer polymerisation (CCTP) is a cobalt-mediated form of free radical polymerisation which can be used to control the molecular weight (Mwt) of methacrylate polymers as low as dimerization, i.e. it's primary use is the production of oligomers. In addition to controlling Mwt, CCTP results in formation of an ω -vinyl end-group, yielding oligomers capable of undergoing post-functionalisation or secondary polymerisation. We have investigated the efficiency of two *in situ* catalysts, based on complexation of either dimethylglyoxime (DMG) or diphenylglyoxime (DPG) with cobalt(II) bromide. Chain transfer constants (C_s) for both catalysts have been determined for bulk and solvated reactions taken to high (typically >80%) conversion, highlighting reaction conditions which are suitable for production of different Mwt oligomers. Use of cobalt complexes results in highly coloured crude products, often containing residual monomer, which is undesirable for secondary applications. Thus, we are developing methodologies to purify oligomers. Using an approach akin to recrystallisation, methyl and butyl methacrylate oligomers have been purified and isolated, ultimately resulting in fractionation of the oligomers. The isolated fractions show a narrower dispersity and near-zero residual monomer compared to the crude oligomer, though workup of lower T_g or more hydrophilic materials remains an ongoing challenge. Finally, copolymerisation of CCTP-derived oligomers with a variety of acrylate monomers has been studied, with initial results indicating that the oligomers act as control agents themselves, reducing Mwt and dispersity, in addition to being incorporated well in the final copolymer. These observations have allowed us to begin using methacrylic material in processes where polymerisation of methacrylates would generally be too slow, such as photopolymer additive manufacturing.

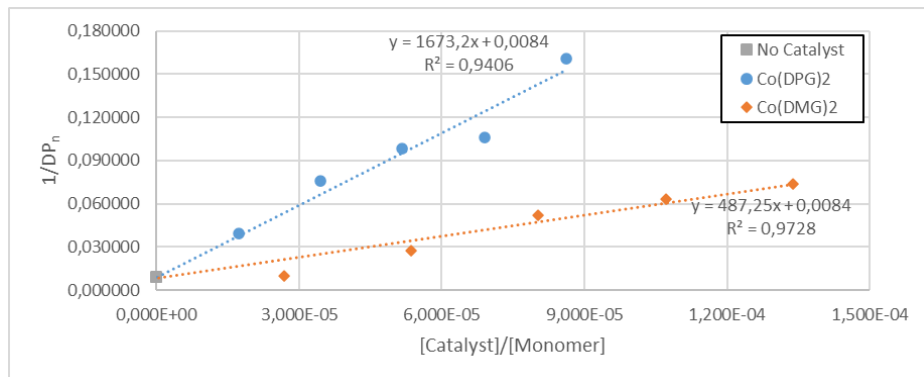


Figure 1: Mayo plot of varied concentrations of in situ catalysts, Co(DPG)₂ and Co(DMG)₂, for polymerisation of bulk MMA at 80 °C for 3 h with 1 mol% AIBN. C_s values of Co(DPG)₂ and Co(DMG)₂ are 1673 and 487, respectively.

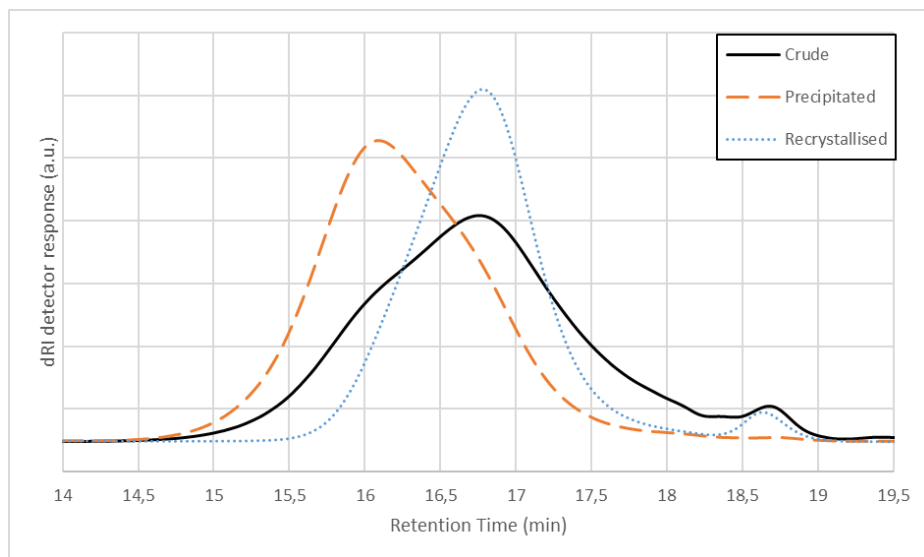


Figure 2: GPC chromatograms of a crude butyl methacrylate oligomer, and corresponding fractions separated from the crude mixture by precipitation and recrystallisation.

Synthesis of Renewable Diblock Copolymers by Aqueous RAFT Polymerisation Induced Self-Assembly of Lactic Acid-Based Monomers

Sarah Woods

In 2016, 90% of all plastics were made from fossil fuels and it's estimated that at the current rate of consumption crude oil and natural gas will have run out by 2070.^[1,2] With 350 million tonnes of plastic produced worldwide in 2017 alone, it is clear that the sustainability of this area requires attention.^[3] Renewable feedstocks, or biomass, are generally plant or biologically-based materials that replenish as they are used.^[4] The monomers *N,N*-dimethyl lactamide acrylate (DMLA) and ethyl lactate acrylate (ELA) are sourced from lactic acid, which is made through the fermentation of carbohydrates.

Reversible addition-fragmentation chain-transfer (RAFT) polymerisation was used to prepare the hydrophilic poly(DMLA). This was then used as a macroRAFT agent and chain extended with ELA in a RAFT-mediated polymerisation induced self-assembly (PISA) reaction in water to form PDMLA-*b*-PELA diblock copolymers. PISA allows for simultaneous synthesis and self-assembly as the PELA grows, reducing the number of steps required and potentially improving the reactions 'green' credentials.^[4] PDMLA_x was synthesised at numerous degrees of polymerisation ($DP_x = 25$ to 400), with narrow molecular weight dispersities ($M_w/M_n = 1.14$ to 1.28) and glass transition temperatures (T_g) between 73 and 78 °C, as determined by DSC. PDMLA₆₄-*b*-PELA_x ($DP_x = 10$ to 400), also achieved narrow molecular weight dispersities ($M_w/M_n = 1.18$ to 1.54). Two distinct T_g s were identified, $T_{g(1)}$ between 5 and 10 °C and $T_{g(2)}$ between 57 and 67 °C, representative of PELA and PDMLA, respectively.^[5] Dynamic light scattering (DLS) analysis showed particle Z-average diameters between 14 and 74 nm ($\sigma = 0.04$ to 0.17). All reactions reached high monomer conversions with short reaction times (<6 hours). Atomic force microscopy (AFM) topographical images showed evidence of spherical particles when prepared at ~5 °C and film formation when prepared at room temperature. It was also found that some of the PDMLA and PDMLA-*b*-PELA polymers exhibited a reversible temperature response when at a critical temperature above 60 °C where a cloud point was observed, with a concomitant increase in z-average diameter for selected PDMLA-*b*-PELA diblock copolymers.

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Engineering of Enzymes for the Degradation of Synthetic Rubbers

Aziana Abu Hassan

Synthetic rubber degradation is a key focus of research in the rubber industry, with the goal to manage rubber waste and to improve rubber processability and characteristics through structure modification. A biotechnology-based solution for rubber degradation is a sustainable approach for managing these polymers at the end of their life. Latex clearing protein (Lcp) is a heme-dependent dioxygenase that can degrade natural latex *via* C=C double bond cleavage. Lcp's are mainly produced by rubber degrading bacteria and the best studied are the Lcp's from *Streptomyces* sp. strain K30 (LcpK30) and *Gordonia polyisoprenivorans* strain VH2 (Lcp1VH2). They are generally specific for natural rubber (NR), which is the *cis*-1,4-polyisoprene polymer and occurs in a latex emulsion form. Only one example has been shown to degrade both *cis*- and *trans*-1,4-polyisoprene (LcpSH22a). Several Lcp's have also shown some potential to degrade synthetic *cis*-1,4-polyisoprene rubber (*cis*-IR), which is the non-emulsified hydrophobic material, however the efficiencies remained low. Furthermore, these enzymes' abilities to degrade the synthetic *trans*-isomer (*trans*-IR) and other synthetic diene rubbers remains underexplored. In this research, we investigate the ability of LcpK30 to degrade synthetic *cis*-IR in different forms and its potential to be engineered towards *trans*-IR degradation. We used computational modelling to study potential modifications to the LcpK30 structure through protein engineering, with the purpose of broadening the substrate range of LcpK30 towards *trans*-IR. The Caver-Pymol plugin was used to calculate putative tunnels that could accommodate substrate and/or product, to predict their access pathway into the active site. Autodock Vina was employed to dock ligands to Lcp protein and identify potential binding sites of the product to the protein. The crystal structure of the *cis*-selective LcpK30 (PDB ID: 5O1L) was compared with the homol-

ogy model of the *trans*-selective LcpSH22a to identify differences in amino acids forming the active site in both structures. Protein-ligand interactions identified from the molecular docking of both polyisoprene isomers showed similar interactions, with slightly different binding energy profiles between both isomers. Based on this, three LcpK30 mutants were designed at position 171, to increase and/or reduce steric bulk and thus change substrate specificity towards the *trans* isomer. The ability of these mutants to degrade the *trans*- isomer and other synthetic rub-

CO₂-derived Poly(carbonate-*b*-ester) Electrolytes for Lithium-Ion Batteries

Holly Yeo

For widespread adoption of electric vehicles, battery development is critical: next generation lithium-ion batteries must have high energy density whilst complying to stringent safety standards. New electrolytes are required with high ionic conductivity ($> 10^{-4}$ S cm⁻¹), electrochemical stability (> 4 V), and cycling capacity. This presentation explores lithium-ion conducting polymer electrolytes and binders for use in batteries and composite cathodes.¹ Other researchers have demonstrated the potential for aliphatic polyesters and polycarbonates as electrolytes.² Balsara and co-workers pioneered poly(styrene-*b*-ethylene oxide), showing promise as mechanically robust electrolytes.³ This work targets phase-separated block polymers, with ABA structures, which show high ionic conductivity and deliver mechanically robust materials which may accommodate cathode volume changes.

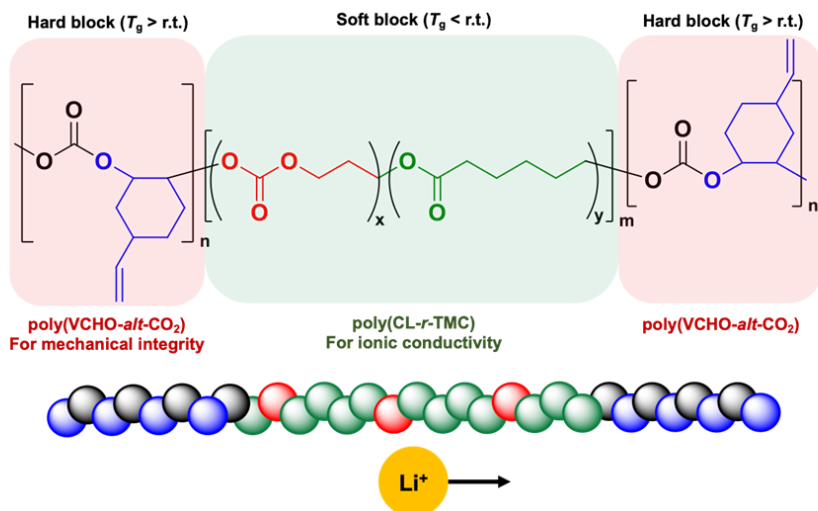


Figure 1: The structure of poly[(VCHO-*alt*-CO₂)-*b*-(CL-*r*-TMC)-*b*-(VCHO-*alt*-CO₂)].

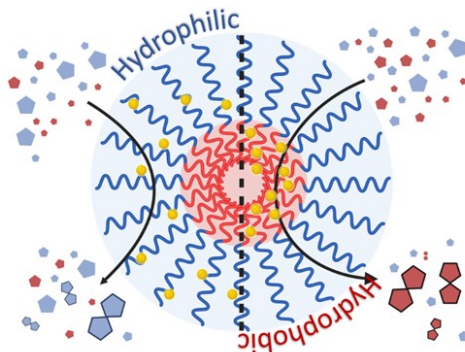
Here, the synthesis, characterization, and electrochemical properties of a series of ABA block polymers are presented. These polymers have structures; poly[(VCHO-*alt*-CO₂)-*b*-(CL-*r*-TMC)-*b*-(VCHO-*alt*-CO₂)], where VCHO = vinylcyclohexene oxide, CL = ϵ -caprolactone, and TMC = trimethylene carbonate. The polymers are produced by a one-pot, switchable catalytic process using CO₂ in the second stage to enchain the polycarbonate blocks.⁴ The polyester blocks are amorphous with low T_g values (-52 – -19 °C); polycarbonate blocks are amorphous with higher T_g values (82 – 102 °C). By mixing with a lithium salt (LiTFSI, 17 wt%), a series of polymer electrolytes were produced and structure-property relationships are presented. The optimum molar mass, PCHC wt. fraction, and other parameters controlling ionic conductivity are reported. Block polymer characterization data is presented including morphology investigations by small-angle X-ray scattering; mechanical properties (rheology and tensile testing); and thermal properties. The best block polymers show lithium-ion conductivity of 2.2×10^{-4} S cm⁻¹ at 60 °C, measured by electrochemical impedance spectroscopy. Further key performance parameters will be presented, including the polymer's oxidative stability, Li-ion transference number, and cycling ability.

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Controllable Photocatalysis by Altering the Active Centre Microenvironment of an Organic Polymer Photocatalyst

Julian Heuer



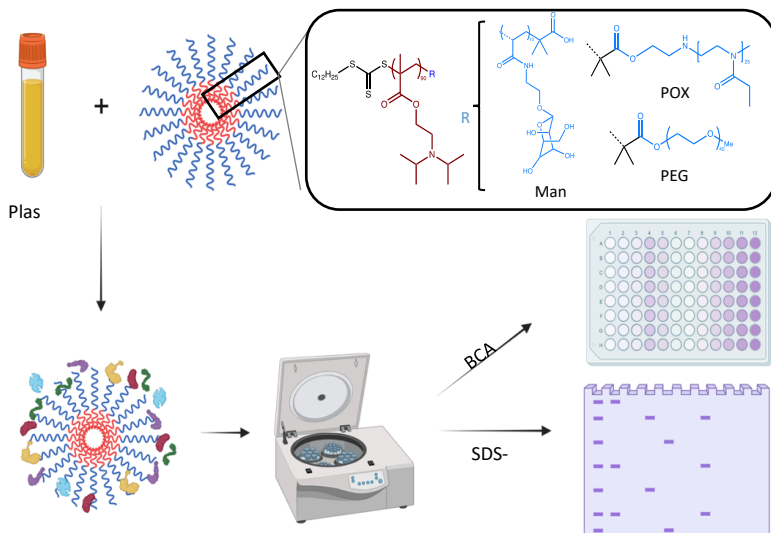
The favoured production of one product over another is a major challenge in synthetic chemistry, reducing the need for purification and enhancing atom efficacy. The formation of catalytic species that have differing reactivities based on the substrate being converted has been targeted to selectively control reactions over the last decades. We present the production of photocatalytic self-assembled amphiphilic polymers using PISA-RAFT techniques, with either hydrophilic or hydrophobic microenvironments at the reactive centre. Controlling the microenvironment of the photocatalytic centre allows for careful investigation regarding solvation effects, reactivity influences by the polymer microenvironment and possible assembly promoted reactivity processes. The difference in reactivity of the microenvironments was controlled by the physical properties of a variety of substrates within different reactions. Stark differences in reactivity were observed for polar substrates, where a hydrophilic microenvironment was favoured. Conversely, both microenvironments performed similarly for very hydrophobic substrates, showing that reagent partitioning is not the only factor that drives photocatalytic conversion, pointing towards possible diffusion limited processes. Moreover, by further alteration of the catalytic species with a secondary swelling solvent, the performance was further modified and could be optimized with a maximal 5.4 fold increase in conversion rate compared to the non-swollen particle.

Study of Functionalised RAFT Polymer Nanoparticles and Their Protein Coronas Formed in Biological Media

Hannah Burnage

Polymeric nanoparticles are being increasingly used as drug delivery systems to treat diseases such as cancer. Current anti-cancer drugs suffer from many issues, including side effects such as hair and muscle loss, damage to the stomach lining etc. In addition, since the drugs are not specific to cancer cells, they sometimes require the use of higher doses to ensure their activity, thus increasing side effects. Drug delivery vehicles enable drugs to be delivered specifically to the tumour, thus limiting these side effects. We are currently developing a new family of nanoparticles that can be used as drug delivery vectors. An important parameter in our design is the engineering of a surface which targets specific cells, thus reducing the dose required and therefore limiting the side effects. However, independently of the surface functionality, it has been shown that proteins in the blood interact with the particles, and alter the surface functionality of the particles, forming a protein corona.

The protein corona is a phenomena observed when nanoparticles enter the bloodstream. Proteins that are present in the bloodstream bind to the surface of the nanoparticle in two layers; the 'hard corona', containing strongly bound proteins, and the 'soft corona', containing more loosely bound proteins that undergo frequent exchange. This protein corona then becomes the surface visible to the cells which uptake these particles and therefore the formation of the corona, and how this varies between nanoparticles, is an important factor in the cell penetration properties of particles. Here we show the synthesis of polymeric nanoparticles functionalised with PEG, polyoxazolines, or mannose and we demonstrate how this functionalisation affects the protein corona formation.



Synthesis and Application of PEGylated Triblock Copolymers on Delivery of RNA and DNA for Cancer Immunotherapy

Hulya Bayraktutan

Throughout the last decades, immunotherapy-based treatments have attracted attention as a novel therapeutic method for challenging illnesses, particularly cancer. Nanotechnology-mediated targeted vaccine delivery has proven to increase safety and efficacy. For example, polyelectrolyte complexes formed by positively charged lipids or polymers and nucleic acids have been demonstrated to be successful vaccine delivery vehicles. These complexes protect the gene from enzymatic degradation in transit in the body and can facilitate membrane translocation at the target cell site. However, clinical application of these materials requires low cytotoxicity of the vectors along with the efficient nucleic acid protection and condensation. To address the issues an efficient poly(beta-amino ester) (PBAE) was used as polymer core and then modified with low molecular weight poly(ethylene glycol) (PEG) for further formulation optimisation. The molecular weight and structure of the PEGylated and non-PEGylated polymers were evaluated using GPC and ^1H -NMR spectroscopy, respectively. Then, the engineered PEG-PBAE-PEG triblock copolymer was evaluated in vitro for efficient RNA and DNA delivery using HEK293T and DC2.4 cell lines. It has been shown that, compared to positive control Lipofectamine, both PEGylated and non-PEGylated polymers have ability to transfect HEK293T cells with low toxicity. However, it has been shown that only PEGylated polymers can transfect to dendritic cells with

low toxicity profile. In addition, it has been demonstrated that this PEGylated polymer can successfully delivery RNA and DNA to the cells. Overall, the synthesised PEG-PBAE polymer can significantly improve the safety and transfection efficacy of PBAEs to dendritic cells, which has a main role in immune treatment, thus highlighting the great promise for the successful application in immunotherapy.

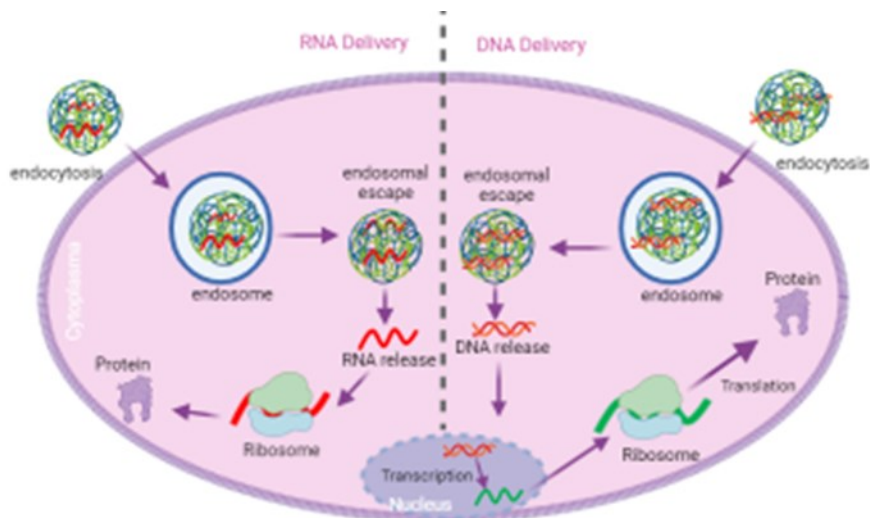


Figure 1: Delivery of RNA and DNA using positively charged polymers.

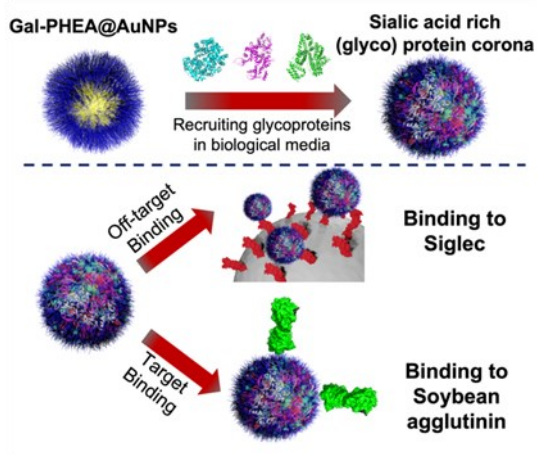
The Impact of Glycoproteins-Corona on Targeting Ability of Glycopolymer-Tethered Glycosylated Gold Nanoparticles

Ashfaq Ahmad

Glycopolymer-tethered glycosylated gold nanoparticles have shown promise for use in biosensing/diagnostics and targeting. However, the translation of such glycosylated nanoparticles from bench to clinic has been limited by poor understanding of the Bio-Nano interface. It is known that when a nanomaterial (NM), with a synthetic identity, comes in contact with biological fluids (blood, plasma, or serum), the biomolecules (proteins, sugars, lipids, and nucleic acids) are adsorbed onto the surface of the NM. This gives the NM a new biological identity (also known as biomolecular corona) which shields the original synthetic identity. Past studies have mainly focused on the protein component of the corona, and it has been found to negatively impact the targeting ability of NM. However, more than 50% of the plasma protein in humans are glycosylated, and there is increasing interest in studying the impact of such glycans (as glycoproteins) on the targeting ability of NM.

Here, we investigate if glycopolymer-tethered glycosylated gold nanoparticles retain their binding towards targeted glycan binding proteins (lectins) post-corona formation or lead to unwanted off-target binding. We found that the glycopolymer-tethered glycosylated gold nanoparticles retained their binding towards the target lectin even after formation of protein corona. Indicating the availability of the originally installed glycan on the surface for binding to the target. This is important in assays where nanoparticles encounter blood/plasma, and where target binding is crucial. However, we also found that glycoproteins corona introduces significant amounts of additional glycans such as sialic acids (confirmed by western blotting assays) on the nanoparticles surface, and which leads to off-target binding to important immune receptor such as SIGLEC-2. In an in vivo scenario, this would lead to an unwanted immune response. In order to avoid or reduce the off-target binding post-corona formation, the nanoparticles were pre-incubated with a known blocking agent, deglycosylated bovine serum albumin. This led to little impact on the total protein corona, but significantly reduced the amount of the sialic acids, however, strong off- target binding was still observed.

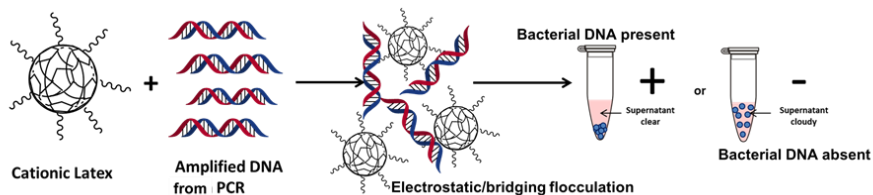
This study highlights the importance of the non-protein components of the biomolecular corona, and the need for better blocking agents and designing better nanoparticles to avoid or reduce the off-target effects.



Using Bridging Flocculation for the Development of a Polymer-Based Point-of-Care Diagnostic for Targeted Detection of DNA

Elisabeth Trinh

The current gold standard diagnostic for bacterial infections is the use of culture, which can be time consuming and can take up to five days for results to be reported. There is therefore an unmet clinical need for a rapid and cost-effective alternative. This paper demonstrates a method of detecting the presence of amplified DNA from bacterial samples using polymer latexes and widely available equipment, providing an accessible alternative to more expensive DNA detection techniques. If DNA is present in a sample, it's successful amplification results in flocculation of the polymer latex followed by rapid sedimentation, thus giving a clear visual result. The sensitivity and speed of the test has been investigated using a combination of disc centrifuge photosedimentometry, UV-Visible spectrophotometry and aqueous electrophoresis. To-date, label-free detection of DNA has been achieved at amplified DNA concentrations as low as 0.57 ng/ μ l within 2 hours from the start of amplification to detection.



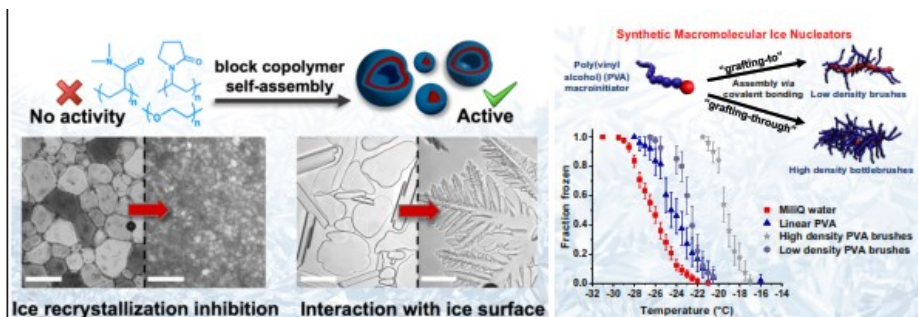
New Nanomaterial Design Principles for Biomacromolecular Antifreezes

Panagiotis Georgiou

Ice growth is a major problem in cell storage, infrastructure maintenance and in food industry. Chemical tools to modulate ice formation/growth have great (bio) technological value. Existing solutions to control ice growth have focussed on using antifreeze/ice-binding proteins from extremophile organisms, while recently polymeric inhibitors have emerged. There are only few synthetic materials that reproduce their function, and rational design is challenging due to the outstanding questions about the mechanisms of ice binding. Previous reports of nanomaterial architectures containing ice recrystallization-active macromolecules did not show enhancements in activity. In contrast, native antifreeze proteins show size and aggregation state-dependent activity, which we have successfully mimicked here. This work explores the design of different nanomaterial architectures

that are capable of inhibiting ice growth. We primarily introduce polymer nano-materials that are potent inhibitors of ice recrystallization using polymerization-induced self-assembly (PISA) strategy, employing steric stabilizing polymers known to inhibit ice growth such as poly(vinyl alcohol) and others, with not any known activity such as PEG, and poly(vinyl pyrrolidone) (PVP). In the first case, a PVA graft macromolecular chain transfer agent was developed to perform PISA and the most active particles inhibited ice growth as low as 0.5 mg.mL⁻¹, and were more active than the PVA stabilizer block alone, showing that the dense packing of this nanoparticle format enhanced activity. PEG and PVP coronas were also active when assembled into nanoparticle formulations, whereas the core-block composition had no impact. This challenges the hypothesis that specific ice-binding domains are essential for activity. Larger nanoparticles demonstrated higher activity than smaller ones, but ice-nucleation activity was not observed in this case.

To further examine how grafting density affects overall activity, PVA based bottle-brushes were developed. A combination of ROMP and RAFT polymerization, using “grafting-to” and “grafting-through” approaches were employed to develop bottle-brush copolymers with different densities. The facile preparation of the PVA bottle-brushes was performed *via* selective hydrolysis of the acetate esters of the poly(vinyl acetate) (PVAc) side chains of the PVAc bottlebrush precursors. We demonstrate that

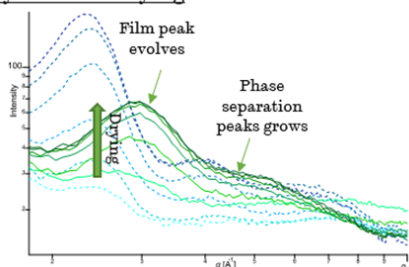
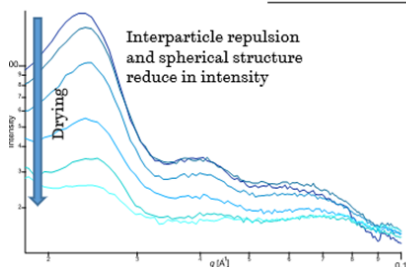


Time-Resolved Small Angle X-Ray Scattering Study of Polyurethane Film Formation from Particle Dispersions

Ellen Quane

Interest in aqueous dispersions is growing as industry strives to produce environmentally friendly products. In particular, incorporation of hydrophilic monomers into polyurethane (PU) gives aqueous dispersions that provide low VOC, high performance coatings. Controlling the phase separation within the PU film is fundamental for targeting specific coating properties. It is, therefore, essential to understand the morphology of PU particles in dispersion and morphological transformations taking place during the drying process that forms the final PU film. Small angle x-ray scattering (SAXS) is exploited in this study as a non-intrusive method for probing the morphology of polyether-based PU, colloiddally stabilised by inclusion of acidic monomers. Effects of chemical composition on the particle morphology are studied systematically. Structural models developed in this work for SAXS analysis of PU dispersions enable a relationship between particle size, composition and water content to be established. SAXS analysis of PU films shows that some particle interfaces remain during drying forming a periodic structure dictated by the size of the original particles, in addition to phase separation. *In situ* studies of the drying process by time-resolved grazing incidence SAXS reveals morphological rearrangement that is triggered in the bulk after particle coalescence. Results are confirmed using atomic force microscopy by trapping the particle morphology using spin-coating from dilute solution and comparing with air-dried films. This suggests that the confinement imposed by the size of the PU nanoparticles in dispersion causes frustration of phase separation that is released during drying, allowing chain rearrangement to more thermodynamically favourable length scales. A relationship between polyether Mn, polyether content and phase separation is established.

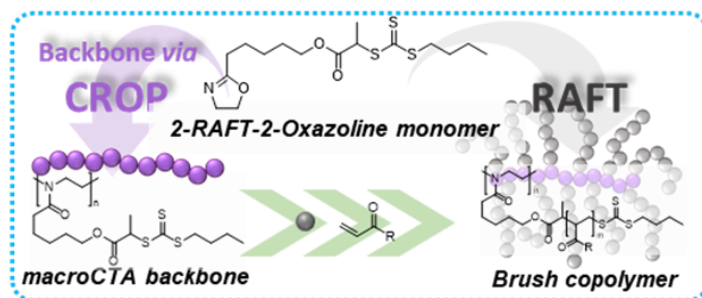
SAXS *in-situ* during polyurethane drying



Enabling RAFT Polymerisation for Brush Copolymers with a Poly(2-oxazoline) Backbone

Jungyeon Kim

The combination of different monomer classes has been sought after to access a wider range of brush copolymers, owing to their unique properties derived from their dense macromolecular structures. Herein, we report the synthesis of a 2-oxazoline monomer (RAFTox) containing a chain transfer agent at the 2 position, and its subsequent utilisation in RAFT polymerisation. With the aim of tuning the brush density in these polymers, homopolymers, block copolymers and gradient copolymers of various ratios with 2-ethyl-2-oxazoline and RAFTox have been prepared. Selected brush macroCTAs were then used for the RAFT polymerisation of *N,N*-dimethylacrylamide and 2-ethylhexyl acrylate to prepare brush copolymers of different architectures.

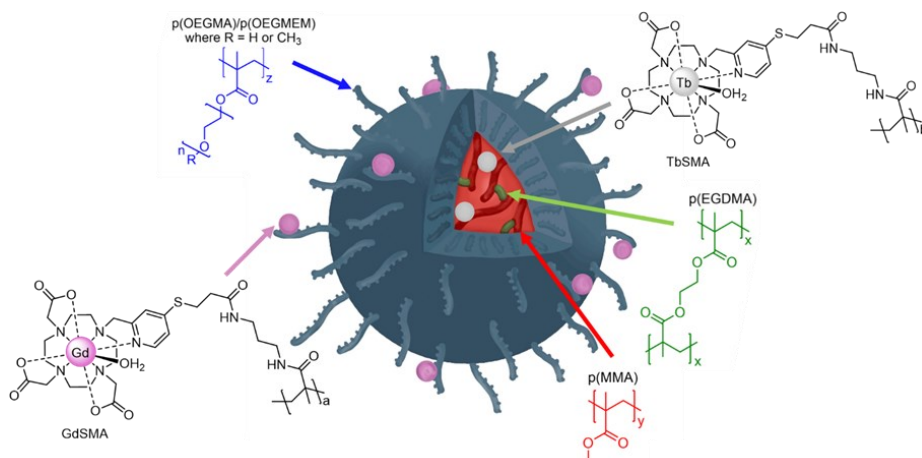


Towards Macromolecular Dual Imaging Particles

Caty Marsden

Magnetic resonance imaging (MRI) is an invaluable tool for imaging tumours and diagnosing disease. Despite the widespread use of MRI in the clinic, the largest downfall of the technique is its lack of sensitivity. For this reason, contrast agents have been developed to lower the relaxation time of surrounding water molecules, increasing 'relaxivity' and brightening the image.¹ Gadolinium-based contrast agents are regularly used, consisting of a gadolinium(III) ion surrounded by a strongly chelating ligand. However, commercial contrast agents are far from optimal, and the relaxivity is nowhere near the theoretical maximum value.²

Previous work in the group demonstrated that incorporating Gd(III)-based monomers into polymeric structures decreases the tumbling speed and significantly increases relaxivity of MRI contrast agents, potentially decreasing the dose required.³ Use of amphiphilic block copolymers can allow access to an array of supramolecular architectures, including particles, worms, and vesicles.⁴ Recently, we demonstrated control over particle size and stability by varying ratios of the particle hydrophilic shell and hydrophobic core.⁵ In this work we present the incorporation of readily polymerizable Gd(III) complexes into block copolymer particles, allowing production of macromolecular MRI imaging agents, with improved relaxivity due to the slowed tumbling of the macromolecular system. Further work will focus on incorporating Tb(III) complexes, to provide a complementary imaging technique with higher sensitivity: optical imaging.



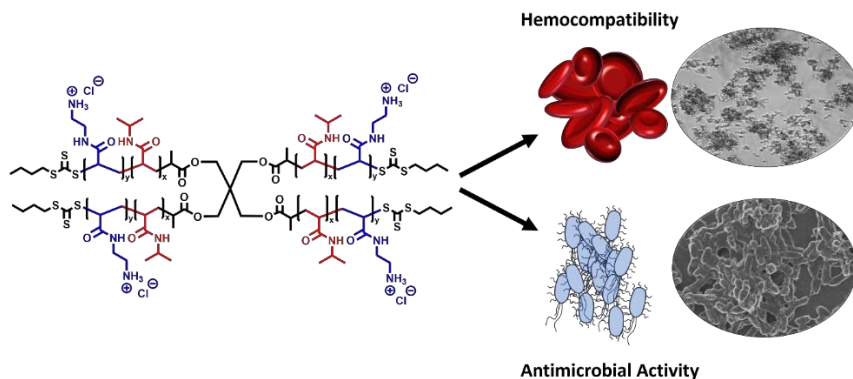
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Antimicrobial Star Copolymers Induce Bacterial Cell Aggregation Compared to Linear Copolymer counterparts

Sophie Charlotte Laroque

Antimicrobial Resistance has become a worldwide issue with an alarming rate of multi- resistant bacteria strains emerging.[1] Multivalent antimicrobial polymer architectures such as bottle brush or star polymers have shown great potential, as they could lead to enhanced binding and interaction with the bacterial cell membrane.[2-3]. In this study, a library of amphiphilic star copolymers and linear copolymer equivalents based on acrylamides were synthesized by RAFT polymerisation. Subsequently their antimicrobial activity towards a gram-negative strain (*P. aeruginosa*), positive bacteria strain (*S. aureus*) and their hemocompatibility were investigated. The star architecture was found to induce a four-fold increase in antimicrobial activity for the statistical star copolymer compared to its linear equivalent towards *P. aeruginosa*. Furthermore, the diblock copolymers were found to be active towards both strains but show little difference between linear and star architecture. Finally, the star copolymers did not show any hemolytic activity but were found to induce aggregation of red blood cells, and in addition also appear to cause aggregation in *P. aeruginosa*.



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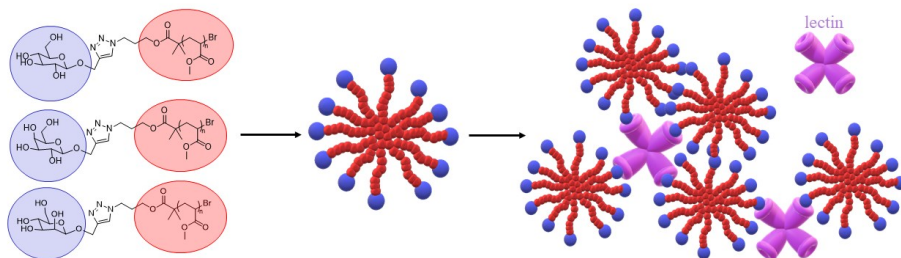
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Synthesis of Amphiphilic Functional Glycopolymers and their Self-Assembly into Glycosylated Nanoparticles

Despina Coursari

Saccharide-containing polymers have been extensively studied in the past years with the sugar moiety often being introduced as a monomer in the backbone, as a linear block or as a branch. This big interest stems from their biological and bio-medical applicability as they can mimic multivalent natural oligosaccharides. Such systems can be used to characterise cell receptor functions, for drug delivery, as biosensors and imaging agents.¹⁻³

Herein, we demonstrate the synthesis of new amphiphilic glycopolymers *via* post-polymerisation functionalisation using azide-alkyne cycloaddition click reaction with alkyne glycosides of preformed well-defined acrylate-based polymers prepared by Cu(0)-mediated RDRP. The obtained glycosylated polymers are fully characterised by GPC, ¹H- and ¹³C-NMR and ATR-FTIR spectroscopies. The capability of the prepared amphiphilic glycopolymers to self-assemble in aqueous solution into nano-structures is demonstrated by dynamic light scattering (DLS) and transmission electron microscopy (TEM). The binding interactions of glycopolymers with lectins (cell surface receptor proteins) are studied using turbidimetry assays and DLS. Applications of these glycopolymers vesicles are foreseen in nano-medicine as delivery systems.



Scheme 1. Graphical illustration of the synthetic plan of the project.

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Mechanical Properties and Functional Applications of High-Sulfur Polymers Prepared by Inverse Vulcanisation

Peiyao Yan

The invention of inverse vulcanization provides great opportunities for generating functional polymers directly from elemental sulfur, an industrial by-product. However, unsatisfactory mechanical properties have limited the scope for wider applications of these exciting materials. In this project, we have proposed an effective synthesis method that significantly improves mechanical properties of sulfur-polymers and allows control of performance. Rather than using traditional one-step synthesis method of inverse vulcanization, a linear pre-polymer containing functional group was produced first in this work, and this pre-polymer was then further crosslinked by difunctional secondary crosslinker.

In first case, urethane linkages were introduced into polymer networks. By adjusting the molar ratio of crosslinking functional groups, the tensile strength was controlled, ranging from 0.14 ± 0.01 MPa to 20.17 ± 2.18 MPa, and strain was varied from $11.85 \pm 0.88\%$ to $51.20 \pm 5.75\%$ (As shown in Figure 1). Control of hardness, flexibility, solubility and function of the material were also demonstrated. We were able to produce materials with suitable combination of flexibility and strength, with excellent shape memory function. Combined with the unique dynamic property of S-S bonds, these polymer networks have an attractive, vitrimer-like ability for being reshaped and recycled, despite their crosslinked structures. We have realized enhancing the strength of sulfur-polymers (e.g. >20 MPa tensile strength, an increase of ≈ 135 times), but combining such high strength

with high flexibility for sulfur polymers is still challenging.

Furthermore, considering the polymer structure design, the synthesis of a series of flexible inverse vulcanized polymers with the combination of high strength, high elongation, and high toughness was carried out. In this case, ester linkages were introduced into polymer networks, and a range of cross-linked sulfur polymers with high tensile elongation and toughness and without losing high strength were successfully synthesized (As shown in Figure 2). Additionally, the obtained cross-linked sulfur polymers show high solvent tolerance in most organic solvents but are demonstrated to be chemically de-cross-linked in polar solvents dimethylformamide, dimethylacetamide, and N-methyl-2-pyrrolidone and can be re-cross-linked after removing the solvent due to the high sulfur ranks present in the polymer network. Despite the significantly improved mechanical properties, highly efficient thermal recycling performance typical of inverse vulcanized polymers was retained. Flexibility and durability, combined with chemical and thermal recycling, could open a new door for wider applications of inverse vulcanized polymers.

(The presentation will be prepared basing on the published papers: Angew. Chem. Int. Ed., 59(32), 13371-13378; Chem. Mater. 2022, 34, 3, 1167–1178)

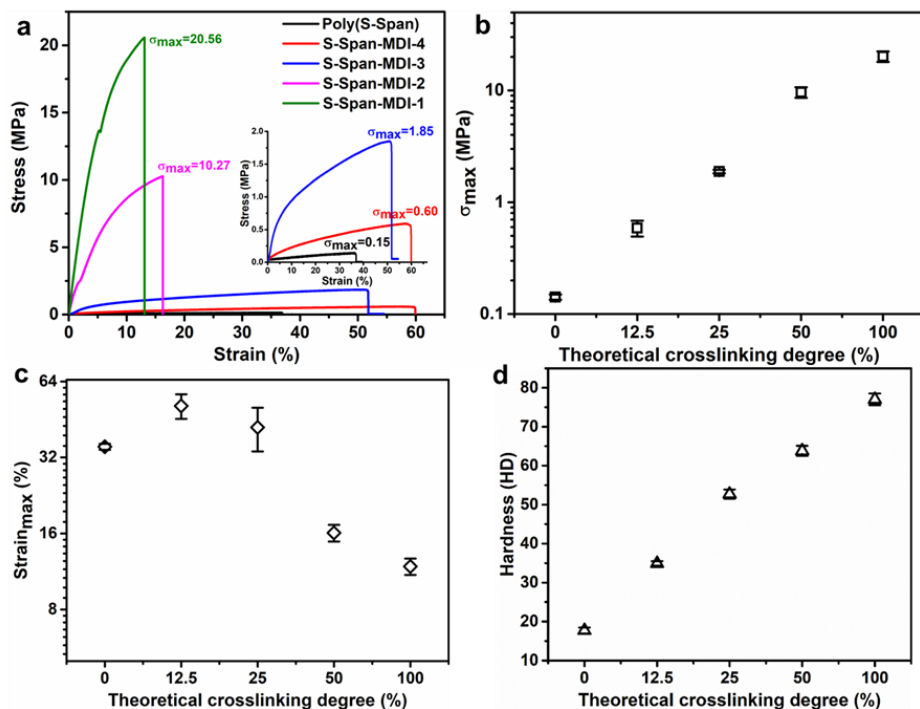


Figure 1 a) The typical strain-stress curves of sulfur-polymers. b) The stress at break, c) the strain at break and d) hardness of crosslinked polymers plotted against theoretical crosslinking degree.

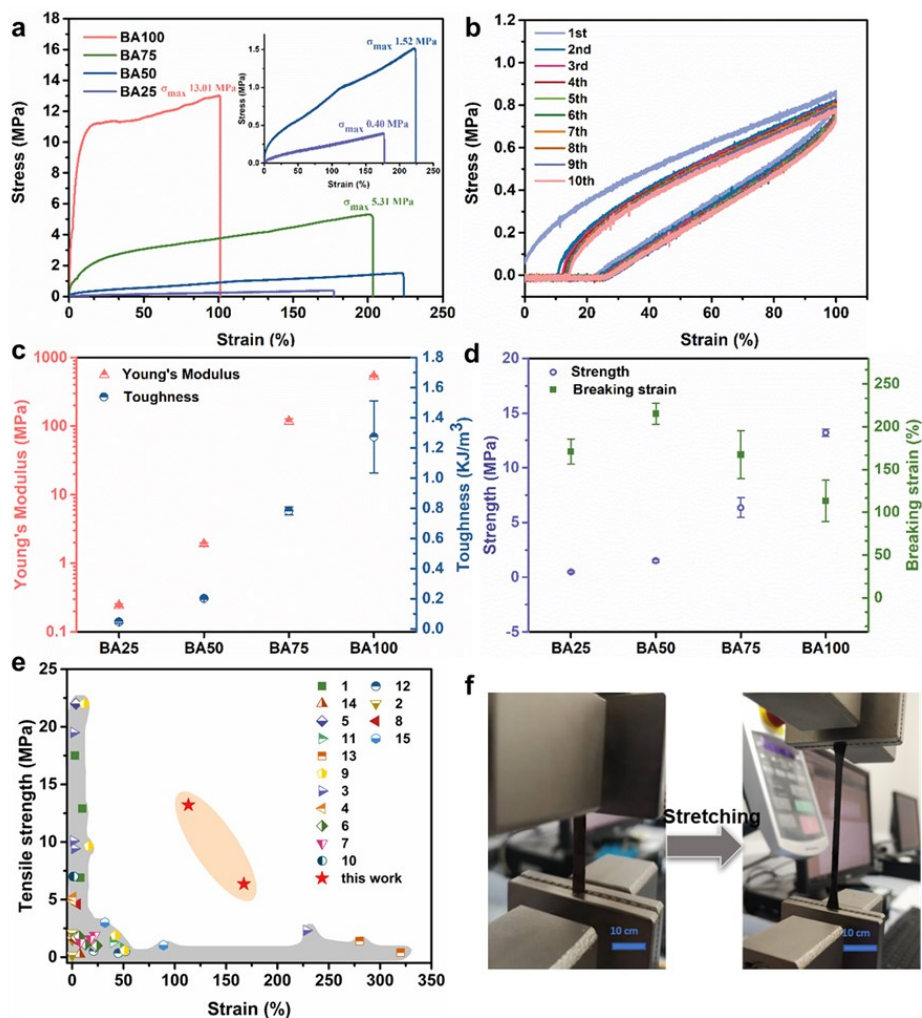


Figure 2 a) The typical stress-strain curves of obtained polymers under strain rate 10 mm/min. b) Stress-strain curves in cyclic tensile tests of polymer BA50 under strain rate 5 mm/min. c), d) Average young's modulus, toughness, maximum strength and breaking strain of obtained polymers. e) Comparison of tensile strength and strain of our polymers with other sulfur-sulfur bond based inverse vulcanized polymers. f) photo record of polymer BA75 in stretching process.

Toughening CO₂-Derived Elastomers Through Ionomer Networking

Kam Charles Poon

The formation of block copolymers can be a successful strategy to improve the thermal and mechanical properties of CO₂-derived polymers, for example by toughening brittle plastics or producing thermoplastic elastomers.¹ Modification of only the polymer backbone is unlikely to afford the broadest range of thermal-mechanical properties. This lecture discusses an alternative strategy where ion coordinating ligands are attached to the polymer backbone and used to prepare ionomers. The ionomers form reversible crosslinks that can significantly toughen elastomers.² This presentation will focus on the synthesis of a series of CO₂-derived block polymers and ionomers, with a focus on application of s-block and other abundant metal ions. In particular, it focusses on the installation of carboxylic acid ligands onto a poly(carbonate-*b*-ester-*b*-carbonate) and the subsequent formation of ionomers through metal carboxylate coordination chemistry. The resulting ionomer networks display greater strength, toughness, stiffness, and elasticity compared to the unfunctionalized materials. The reversible nature of the polymer-metal bonds allows for material reprocessing and recycling.

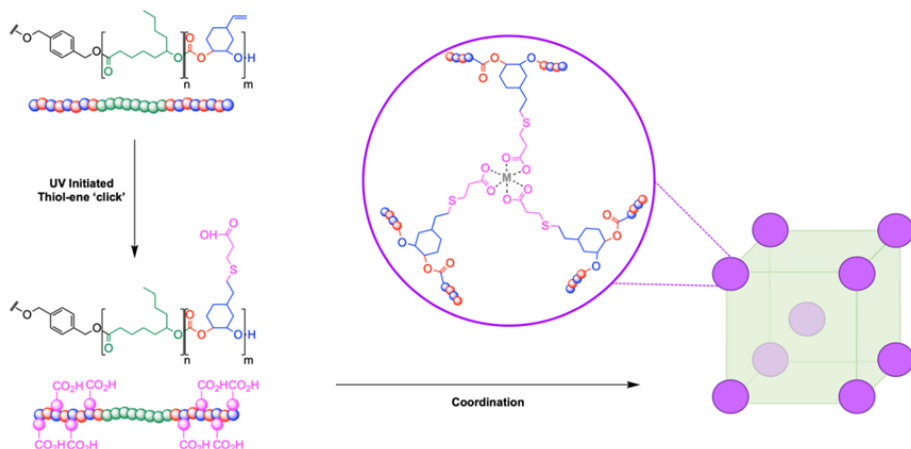


Figure 1: Schematic showing the structures for block polymers and ionomer networks formed by metal coordination.

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Novel Gelatin-Based Biomaterials for 3D Tissue Modelling of the Human Endometrium

Emma Salisbury

Introduction

The endometrium is a complex, multicellular tissue, and the site of embryo implantation. Dysregulations between embryo-endometrial interactions during implantation are known to result in recurrent pregnancy loss and implantation failure, affecting 250,000 women every year. Due to a lack of appropriate study models the mechanisms surrounding human embryo implantation are still largely unknown. Novel biomaterials capable of supporting the structure and function of multiple endometrial cell types are needed. Our long-term goal is to create an *in vitro* model of the human endometrium and use this to assess the processes that control implantation and address unanswered questions around reproductive failure.

Here, we describe 2 novel gelatin-based materials: photo-crosslinked gelatin methacryloyl (GelMA) hydrogels and porous GelMA scaffolds. We investigate and compare their ability to support the viability and function of multiple human endometrial cell types.

Methods

A simple protocol was developed whereby primary human endometrial cells were encapsulated in photocrosslinked GelMA hydrogels, employing a cytocompatible photoinitiator (LAP) and 3 minutes UV exposure (365 nm).

A highly porous GelMA scaffold was fabricated from an oil-in-water emulsion. The high internal phase emulsion (HIPE) was then polymerised using a Fusion UV systems Inc. Light Hammer 6 variable power UV curing system. The resulting polymerised HIPEs (polyHIPEs) were thoroughly washed and dried.

Results

Hydrogels

Rheological analysis demonstrates GelMA hydrogels can be produced with a range of stiffness degrees by altering the degree of substitution (DS) of the GelMA and the concentration of GelMA used in hydrogel fabrication. Endometrial stromal cells retain high levels of viability after a 7-day culture period. A clear differentiation response monitored over 4-days of hormone treatment was seen in GelMA hydrogels. Stiff DS100 GelMA hydrogels enable endometrial epithelial cells to form organoids. The efficiency of organoid formation can be enhanced through addition of the basement membrane protein, laminin to GelMA hydrogels.

PolyHIPE scaffolds

GelMA polyHIPE morphology was examined using SEM, a highly porous, interconnected structure with an average pore size of $13.3 \pm 4.8 \mu\text{m}$ (Fig. 1) was seen. Preliminary results demonstrate polyHIPE biocompatibility while further experiments to investigate cell function are underway.

Exploring New Thermoplastic Polyurethanes (TPU) via Non-Covalent Interactions

Simon Fawcett

Thermoplastic polyurethanes are typically phase separated hard/ soft block copolymers. The synergy of the distinct blocks gives strength and flexibility to afford materials with high mechanical properties. Strong intermolecular interactions between chains within the hard segment accounts for its rigidity, however these physical forces prevent low melt viscosity, limiting processing flexibility. The aim of this research is to investigate and understand methods of creating disparity between the solid and melt states of thermoplastic polyurethanes.

Low molecular weight polyurethanes ($M_n < 15\,000 \text{ g mol}^{-1}$) with differing hydrogen bonding potentials were synthesised by altering the chain extender structures within semi-crystalline polycaprolactone-MDI copolymers. Analytical techniques such as NMR and FTIR spectroscopy, GPC, DSC, DMA, rheology, adhesion and tensile testing were used to characterise the products. A correlation between structure and morphology and performance was made. Chain extender asymmetry had a negative impact on the mechanical properties by increasing phase mixing and hindering a hard segment from associating. Urea groups (*Figure 1*) enhanced hydrogen bonding, phase separation and mechanical properties by forming a much finer morphology with the semi-crystalline polycaprolactone.

This work demonstrates how segment compatibility determines thermal and mechanical properties of low molecular weight thermoplastic polyurethanes and the potential for tailored design for desired material behaviour.

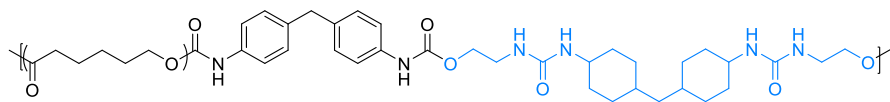


Figure 1. Thermoplastic polyurethane containing urea groups displays a finer morphology and higher mechanical properties.

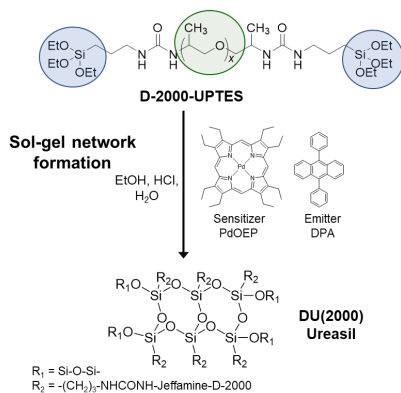
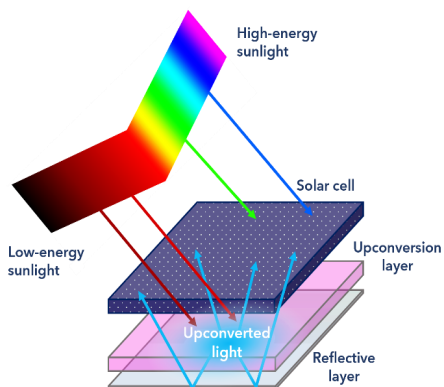
Tuning the Solar Spectrum Using Organic-Inorganic Hybrid Polymers

Abigail Collins

In a changing world, harnessing the sun's energy will be crucial in providing renewable, clean, and low-cost electricity. Solar cells are only able to harvest wavelengths of light that match the 'band-gap' energy, meaning energies above and below the band-gap are not fully utilised leading to a 'bottleneck' of efficiency. Upconverting layers can be applied to finished solar cells to boost performance. Photons at the low energy boundaries (near-IR) of the solar spectrum, which are not absorbed by the solar cell, are transformed into wavelengths matching the bandgap via a process called *triplet-triplet annihilation upconversion* (TTA-UC) between organic *chromophore* molecules in the UC layer.¹ This means a wider portion of the solar spectrum can be used and can increase overall efficiency of solar cells by up to 10%.²

Since the process is diffusion-controlled, UC efficiency is much lower in solid-state than solutions. To maximise the efficiency of UC, chromophores should be encapsulated in a host system which enables intermolecular collisions in the solid-state and facilitates the energy transfer process, whilst protecting the system structurally and chemically.³ In this work, we use organic-inorganic hybrid polymers called *ureasils* as a solid-state host for the TTA-UC process. Ureasils contain an organic polymer backbone covalently grafted to an inorganic silica network, combining the benefits of optical transparency, mechanical strength, and oxygen protection from the silica with the processability, flexibility and functionalisation ability from the polymer.⁴ Since the TTA-UC process is completely halted by the presence of oxygen from the air, protection is an important consideration.

Our results demonstrate high UC efficiencies of up to 18% (capped at 50% by the process) which is significantly high for solid-state when compared with organic polymers commonly used, especially in the presence of air. This is the first report of organic-inorganic hybrid TTA-UC hosts and highlights their potential. The structure of ureasils is tuned by changing the branching and molecular weight, which affects the mechanical and photophysical properties. Another generation of ureasil hybrids has been developed to allow the chemical functionalisation of the polymer backbone to covalently graft chromophores to the structure, surpassing the diffusion-control via intramolecular energy transfer. UC layers have exciting potential to maximise solar light harvesting and future work would focus on enhancing the long-term stability, working towards commercialisation. Further investment in these research areas will provide the planet with the tools it needs to deal with the looming climate crisis.



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Flash Presentation

Synthesis of dual-responsive PLGA nanoparticles

Dominic Gray, Poster No: P1

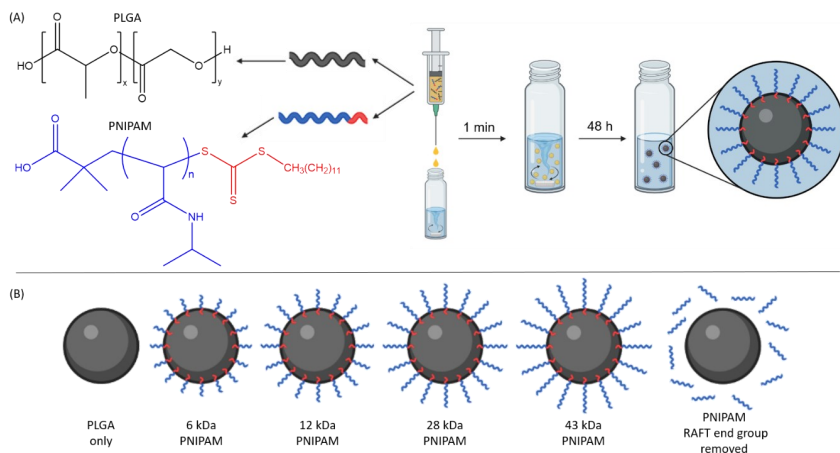


Figure 1. Schematic representation of the project. Nanoprecipitation synthesis of PLGA particles is conducted by the addition of an acetone solution containing PLGA and PNIPAM stabiliser into water (structures shown). This is then stirred for 48 h to remove the acetone, leaving behind particles dispersed in water (A). The particles generated are; in the absence of stabiliser, stabilisers of increasing molecular weight, and particles generated in the presence of PNIPAM with no hydrophobic end group (B).

Nanoparticle aggregation is often viewed as an undesirable particle behaviour. However, aggregating particle systems have many applications from pore-blocking to catalysis.¹ The aggregation of particles in nanomedicine can be used for long-acting drug delivery applications forming a solid drug depot. It is hoped future work will allow similar particles to those synthesised in this work to be used for this application.

In this research we synthesise poly(lactic-co-glycolic acid) (PLGA) nanoparticles that are responsive to increases in ionic strength and temperature. This is due to incorporated poly(*N*-isopropylacrylamide) (PNIPAM) stabilisers of varying molecular

weights synthesised by reversible addition-fragmentation chain-transfer (RAFT) polymerisation. These are added at the time of PLGA particle synthesis via the nanoprecipitation method.

PNIPAM polymers have a lower critical solution temperature (LCST) of 32 °C, above which the polymer transitions from being hydrophilic to hydrophobic. Steric stabilisation of the PLGA particles provided by these polymers can be removed by heating these particles above this temperature. Electrostatic stabilisation is provided by the charged initiator fragment and RAFT agent leaving group. This electrostatic stabilisation can be removed by the addition of salt to screen the charge.

While the varying molecular weight does not affect the response temperature of the polymers, the increasing molecular weight causes aggregation of the particles to occur under different conditions. With smaller molecular weight PNIPAM chains unable to stabilise the particle without the additional electrostatic stabilisation. The concentration of the polymer stabiliser also has an effect.

This work also shows the importance of the hydrophobic RAFT end group, which provides a small amount of amphiphilicity to the PNIPAM stabiliser. This is proven to be necessary for the PNIPAM to effectively stabilise the particle.

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Antimicrobial 'Inks' for 3D Printing: Block Copolymer-Silver Nanoparticle Composites Synthesised Using Supercritical CO₂

Ryan Larder, Poster No: P2

Silver nanoparticles (AgNPs) are widely exploited for their effective antimicrobial activity against a range of pathogens. Their high efficacy in this regard has seen the global demand for AgNPs in consumer products steadily increase in recent years, necessitating research into novel low environmental impact synthesis approaches. Here we present a new synthetic methodology to produce polymer-AgNPs composite microparticles using supercritical carbon dioxide (scCO₂) and avoiding use of any petrochemically derived solvents. Poly(methyl methacrylate)-poly(4-vinylpyridine) block copolymers (PMMA-b-P4VP) were synthesised via RAFT-mediated dispersion polymerisation in scCO₂, with in-situ thermal degradation of various amounts of a CO₂-soluble silver complex. Selective interaction of the silver with the pyridinyl moieties of the block copolymer allowed the formation of AgNPs, dispersed within the block copolymer microparticles, leading to homogeneous composites. The by-products of the reaction were also removed by extracting with a flow of CO₂ to yield a clean dry product in a single process (Figure 1).

The composites were found to be non-cytotoxic and proved to have good antimicrobial activity against two bacterial strains. Though no significant activity was seen for at least the first 24 hours, inhibition of bacterial growth afterwards proved to be extremely persistent, with inhibition observed even after 15 days. Finally, the microparticulate nature of the synthesised composites was exploited and tested for compatibility in the Laser Sintering (LS) 3D printing process. Composite microparticles were fused to produce solid objects, without aggregation of the AgNPs. With further optimisation, these composites could prove to be an incredibly versatile 'ink' that may be used within additive manufacturing and 3D printing to rapidly produce bespoke medical devices with inherent antimicrobial activity.

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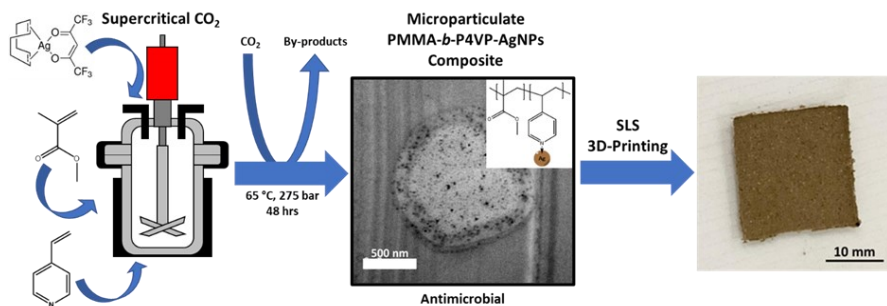


Figure 1: Process scheme for the synthesis of AgNP loaded PMMA-*b*-P4VP microparticles and the resulting 3D-printed object.

Polymer-POSS Composites As Hosts For Luminescent Solar Downconverters

Helen Tunstall-Garcia, Poster No: P3

Solar power has great promise as a renewable energy source. However, current photovoltaic (PV) technologies suffer from losses such as thermalisation and recombination, limiting their efficiencies.¹ Spectral converters can overcome these problems by converting incident sunlight into wavelengths that better match the spectral response of an attached PV cell, for example by converting UV to visible light through luminescence downshifting (LDS) (Figure 1).² These layers are deposited on top of the solar cell and thus must withstand significant weathering. While previous work has investigated nano-reinforced protective coatings with potential for solar cells;³ these materials are yet to be adapted LDS host materials.

In this work, we investigate the effect of polyhedral oligomeric silsesquioxanes (POSS) as additives in a polyethylene-co-glycidyl methacrylate (PEcGMA) host, both in the presence and absence of a fluorescent dye (Coumarin 1). POSS has shown great potential as a thermal and mechanical reinforcement in polymeric materials,⁴ and the blended material is easily processable and tunable. Furthermore, the properties of light-emitting materials can be improved by the introduction of POSS, which reduces aggregation-caused quenching and increases photostability.⁵ The compatibility and polymer properties of a series of POSS-PEcGMA blended films are investigated, as well as the effect of the additive in the mechanical and thermal properties. In order to examine the performance as LDS layers, the optical properties of the composite films are investigated through microscopy, transmittance, steady-state and time-resolved photoluminescence. The knowledge gleaned through these studies will enable us to identify the optimum POSS reinforcement loading to obtain highly robust and efficient luminescent downconverters.

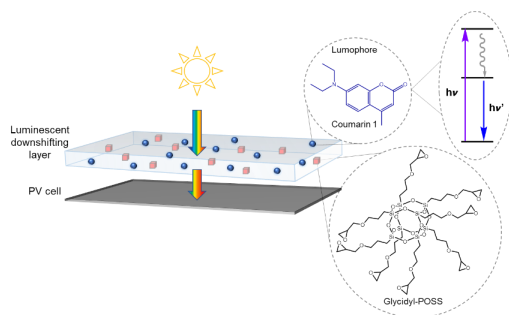


Figure 1. Schematic representation of an LDS layer which adjusts the solar spectrum incident on the PV cell through photoluminescence comprising a polymer host, glycidyl-POSS nanocages and Coumarin 1 lumophore.

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Block copolymer nanoparticles for next generation electrolytes

Georgia Lucy Maitland, Poster No: P4

Energy storage is vital in this day and age, particularly for storing clean energy produced from renewable resources. As a result of their high energy densities, lithium ion batteries have attracted and continue to attract considerable interest in contrast to other energy storage formulations. [1] [2] In order to meet this ever growing demand and enhance sustainability in this field, more efficient and cleaner materials must be generated. So-called ionogels (gel materials comprising an ionic liquid immobilised in a cross-linked polymer matrix) are a class of materials that offer much promise in the way of improving energy storage for future generations. Ionic liquids (ILs) are defined as liquid electrolytes solely comprising ions with a melting point below 100 °C. [3] [4] Compared to many standard organic solvents, ILs exhibit advantageous properties such as high ionic conductivity, thermal stability, nonflammability and low vapour pressure, [5] which are highly preferable properties that can potentially yield functional ionogels. Additionally, as a result of having an al-

most inexhaustible combination of cations and anions, ILs provide great flexibility in terms of tuning desirable properties i.e., hydrophobicity/hydrophilicity, hydrogen bonding and solubility etc. [3] [6] and therefore can be tailored for specific applications. ILs have been utilised for a diverse number of applications in electrochemistry, catalysis and analysis as well as being used as performance additives such as anti-static agents and dispersing agents. [6] In this project, hydrophilic ILs provided by BASF are being utilised to maximise commercial relevance of the synthesised ionogels. In order to do this, block copolymers will be synthesised and self-assembled directly in these ILs via reversible addition-fragmentation chain transfer-mediated polymerisation-induced self-assembly (RAFT-PISA, Fig. 1) to generate worm gels. In summary, the first block in the block copolymer is synthesised via RAFT solution polymerisation, followed by chain extension of the second block to form the block copolymer which self-assembles in the IL and gives rise to a range of morphologies as a result of varying chain lengths of each block (volume block fractions).

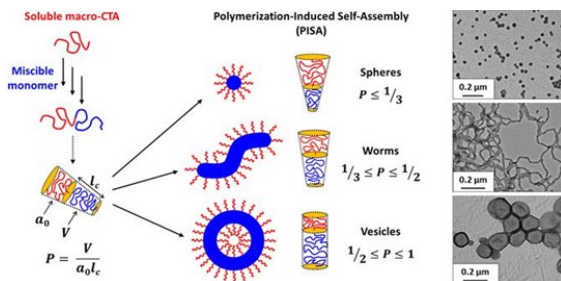


Figure 1: Summary scheme of RAFT-PISA to generate an array of morphologies [7]

Both the block copolymer and the IL have desirable properties that contribute towards producing a functionally ideal ionogel: the polymer provides mechanical integrity whereas the IL provides thermal stability and high ionic conductivity. Traditional polymer ionogel electrolytes are developed through the polymerisation of ILs or doping pre-synthesised polymers with ILs. [8] [9] In this project, considerable focus has been placed on a new class of materials whereby physically crosslinked worm ionogels that offer increased ionic conductivity with considerably less polymer content can be generated in-situ (Fig. 2).

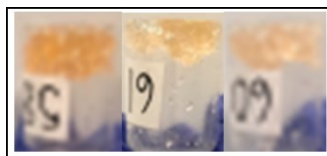


Figure 2: Preliminary syntheses of block copolymers in ionic liquids that have yielded free-standing gels

Polymer Functionalised topographies for cardiac modelling

Chester Blackburn, Poster No: P5

Cell instructive polymers which modulate stem cell expansion through their relatively simple surface chemistries have been identified using high throughput screening [1]. Micro and nano topographies have also been found to control stem cell differentiation[2]. Furthermore, polymer microparticles with a combination of defined surface chemistry “chemo” and topography have been found to mediate formation of stem cell aggregates and cardiomyocyte function[3]. In this presentation we will explore the methods behind the fabrication of chemo-topographical substrates for heart disease modelling using cardiomyocytes derived from human pluripotent stem cells. Exploring the printing of a master mould with a SU8 photoresist and the subsequent intermediate lithographic process required before the embossing of a topographically enhanced sheet (Figure 1). Furthermore, the synthetic methodology and characterisation techniques employed to assess both fidelity and resolution of topographies (Optical Profilometry) and surface chemistry modifications (Water contact angle and TOF-SIMS) are presented, showcasing a platform and pipeline that demonstrates the potential of surfaces as non-invasive tools for biological instruction.

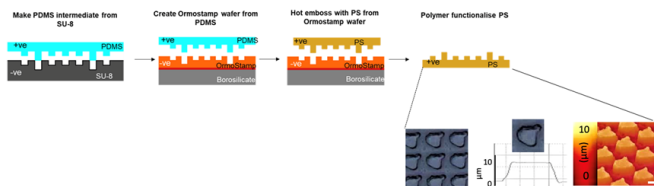


Figure 1 : Lithographic production pipeline towards topographically enhanced polystyrene sheets.

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Comparative stability of thiomethacrylate and methacrylate crosslinking

Matthew Laurel, Poster No: P6

The importance of degradable and sustainable polymers has vastly increased in recent years as potential solutions to the plastic waste problem are investigated. While many different chemistries have been explored to increase the recyclability of covalently crosslinked thermosets, the degradability of thioester-containing polymers has not readily been explored. In this work, an aromatic dithiomethacrylate crosslinker is synthesised for investigation as a degradable crosslinker. To test the degradability of polymers containing the crosslinker, star polymers containing both dimethacrylate and dithiomethacrylate crosslinkers are successfully synthesised, via an arm-first RAFT approach, and characterised by advanced GPC. Finally, extensive optimisation reactions have been undertaken to selectively degrade the thioester crosslinks while the methyl esters remain intact.

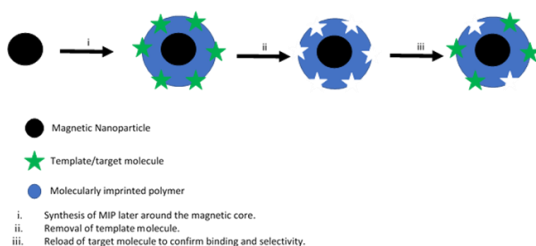
Magnetic Molecularly Imprinted Nanoparticles for the Extraction and Detection of Molecules of Interest

Mark Sullivan, Poster No: P7

Molecularly imprinted polymers (MIPs) are a class of synthetic biorecognition materials, whereby cavities are left within a polymer matrix have affinity for a chosen template molecule (the molecule of interest). The process involves initiating the polymerisation of functional monomers, self-assembled around the template molecule in the form of a monomer-template complex. Subsequent extraction of the template molecule, leaves behind cavities in the polymer matrix that are complementary to the template molecule. With the potential to match the performance of biological recognition molecules MIPs can be advantageous over their biological counterparts (antibodies, enzymes, aptamers etc.) as they offer good recognition, are cheap to produce and have excellent robustness, especially to the extremes of pH and temperature. The development of MIP nanoparticles (nanoMIPs), significantly increased performance of MIPs by reducing binding site heterogeneity, while increasing the potential scope within biological systems. The small particulate size of nanoMIPs allows for more regular structures with a high surface to volume ratio, and a greater yield of useable product. There are three main approaches to the synthesis of nanoMIPs, a solid-phase approach, suspension polymerisation and a core-shell approach. The core-shell approach involves the synthesis of a

MIP shell layer around a solid core nanoparticulate, which can be advantageous as the method allows for heterogeneous nanoparticles with controllable size. Furthermore, a variety of materials are available for use as the core, which opens the opportunity of incorporating additional properties, such as magnetism, plasmonic or antimicrobial properties into the MIPs.

Using a unique solvothermal microwave method, Superparamagnetic Iron Oxide Nanoparticles (SPIONs) of approximately 8 nm, were synthesised and used as a core for the production of magnetic MIP nanoparticles. A MIP shell layer, consisting of 4-vinylpyridine (4-VP) as a functional monomer and trimethylolpropane trimethacrylate (TRIM) as the crosslinker, was synthesised around the magnetic core for a range of small molecular weight targets. The magnetic MIPs of approximately 50 nm in size, showed excellent recognition for their target molecules (<90% binding of target with excellent selectivity in both model and real samples). The incorporation of the magnetic nanoparticulate core property allowed for ease of removal of the nanoparticles from solution in simple batch binding studies suggesting that these materials could find application in both trace analysis and sample clean-up. This was demonstrated with estrogenic/androgenic steroids and Selective Androgen Receptor Modulators (SARMs - a family of compounds that mimic steroidal activity).



Synthesis and Aqueous Self-Assembly of Amphiphilic Poly(2-hydroxypropyl methacrylate)-Poly(N,N'-Dimethylacrylamide) Diblock Copolymers

Damla Ulker, Poster No: P8

It is well-known that amphiphilic block copolymers can form various nano-objects when dispersed in water, such as spheres, worms or vesicles either by traditional post-polymerization processing or by polymerization-induced self-assembly (PISA). In both cases, self-assembly is driven by unfavourable interactions between water

and the hydrophobic block, which drives aggregation of the diblock copolymer chains to form well-defined nano-objects. However, PISA process has some limitations to certain diblock copolymers depending on the comonomer reactivity: for example, an acrylic-methacrylic diblock copolymer in which the acrylic block acts as the steric stabiliser is not achievable via PISA. This synthetic problem has left such copolymers relatively understudied.

Herein, we conduct the reversible addition-fragmentation chain transfer (RAFT) solution polymerization to product a series of amphiphilic PHPMA-PDMAC diblock copolymers. In this process, a series of 2-hydroxypropyl methacrylate (HPMA) purified precursor was obtained, and followed by chain extension of this precursor using N,N'-dimethyl acrylamide (DMAC). The mean degree of polymerisation of the PHPMA precursor was varied from 105 to 147 as judged by ^1H NMR spectroscopy. The DMAC conversion achieved during chain extension experiments was determined by ^1H NMR spectroscopy and gel permeation chromatography (DMF eluent) was used to assess the molecular weight distributions of the final diblock copolymers ($M_w/M_n = 1.14$ to 1.19). Then these PHPMA-PDMAC diblock copolymers were molecularly dissolved in ice-cold water (or PBS) and allowed to warm up to ambient temperature to induce in situ self-assembly. In some cases, relatively soft, free-standing worm gels were obtained. Rheology studies were performed at various copolymer concentrations to determine the critical gelation concentration (CGC) at both 20 °C and 37 °C. In addition, rheology was used to examine their reversible thermo-responsive behaviour from 40 °C to 4 °C. TEM studies confirmed that this induced a worm-to-sphere transition, which leads to concomitant degelation. Such worm gels are expected to be useful for biomedical applications in the context of cell storage. This possibility will be evaluated in the near future [1, 2].

Acknowledgments: This study has been financially supported by The Scientific and Technological Research Council of Turkey (TUBITAK-2219, GN: 1059B192001125)

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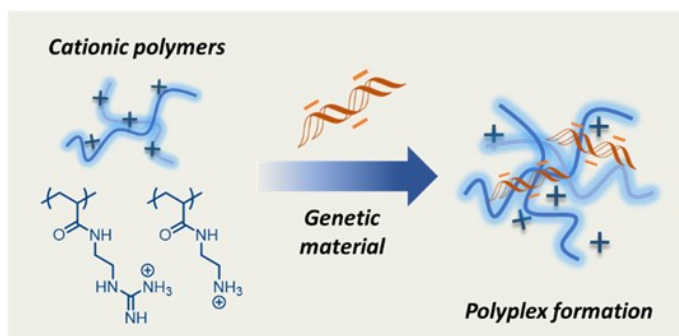
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Studying well-defined cationic polymers for gene delivery

Julia Yu-Jung Rho, Poster No: P9

For the past three decades, medical research has focused on repairing or reconstructing the defective genetic material in patients with hereditary genetic anomalies. Genetic materials have been delivered using non-pathogenic modified viruses like adenovirus or herpes simplex virus to alter or manipulate the biochemical cascade in the diseased cells or tissues. However, the adverse effects of viral gene delivery have not yet been overcome.

The amalgamation of synthetic chemistry and molecular biology has long been used in the development of potential gene therapies. Developing and producing innovative synthetic materials for effectively delivering nucleic acids to the cells have been the primary focus of many pharmaceutical companies. In recent times, researchers have been focusing on developing synthetic materials such as polymers, lipids, or inorganic particles which mimic the functions of proteins involved in stabilising and transporting genetic materials. This talk will focus on utilising the versatility of RAFT polymerisation to synthesise a range of different polymers (compositions and architectures) in the hopes to find scale-able, stable, and efficient gene delivery vectors.



Oxygen heteroatom enhanced sulfur-rich polymers synthesized by inverse vulcanization for high-performance lithium-sulfur batteries

Haoran Wang, Poster No: P10

The “shuttle effect” is one of the key issues to overcome for the practical application of Lithium-sulfur (Li-S) cells.¹ A “chemical confinement” strategy has been recognized as one of the most efficient way to alleviate the dissolution of long-chain lithium polysulfides.² Here, Sulfur-rich polymers, synthesized through inverse vulcanization^{3,4} with heteroatom containing crosslinkers were investigated as the active S containing cathode material within Li-S cells. The polymers possess up to 73% active sulfur while, importantly, not containing any unreacted, crystalline sulfur. Li-S cells based on the polymers achieve specific capacities of 1206 mAh gs⁻¹ for an active material polymer containing 80 wt% sulfur, with 10 wt% of a structural crosslinker (dicyclopentadiene, DCPD), and 10 wt% of an oxygen containing crosslinker (ethylene glycol dimethacrylate, EGDMA). The high capacity achieved within this composition is associated with of this sample, in a higher average sulfur rank within the polymer structure. Furthermore S-polymers with heteroatomic crosslinkers exhibited lower capacity fade (0.093% per cycle) compared with polymers without functionalized heteroatomic crosslinkers (0.165% per cycle) and elemental sulfur (0.312% per cycle). X-ray photoelectron spectroscopy highlights the inherent binding between the ester group carbonyl oxygen within the crosslinker to the long-chain lithium polysulfides, which may inhibit dissolution of these intermediates.

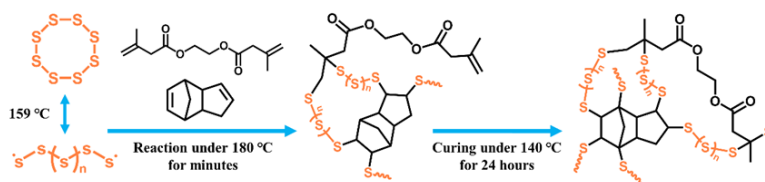


Figure 1. Synthetic scheme for sulfur-EGDMA-DCPD polymer via inverse vulcanization.

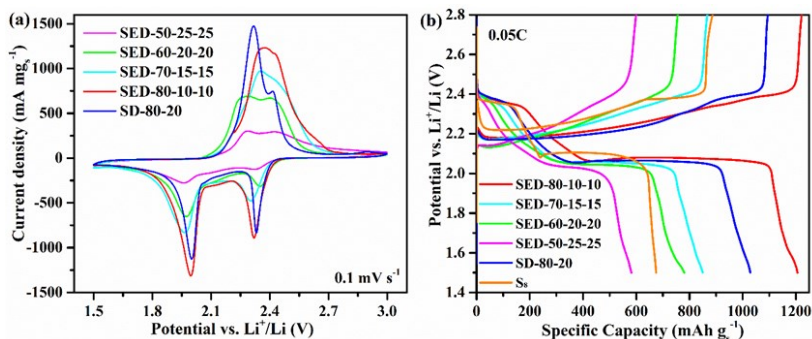


Figure 2. (a) The comparison of the cyclic voltammetry curves of the Li-S cells based on inverse vulcanized polymers. (b) The 1st discharge-charge curves of the Li-S cells based on elemental sulfur and the synthesized polymers under 0.05C.

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Insights into the Internal Structures of Nanogels Using a Versatile Asymmetric-Flow Field-Flow Fractionation Method

Edyta Niezabitowska, Poster No: P11

Poly(N-isopropylacrylamide) (pNIPAM) nanogels are a highly researched type of colloidal material. In this work, we establish a versatile asymmetric-flow field-flow fractionation (AF4) method that can provide high resolution particle sizing and also structural information on nanogel samples from 65-310 nm in hydrodynamic diameter and so different chemical compositions. To achieve this online multi-angle light

scattering and dynamic light scattering detectors were used to provide measurement of the radius of gyration (R_g) and hydrodynamic radius (R_h) respectively. (see Fig 1) Two different eluents and a range of cross-flows were evaluated in order to provide effective fractionation and high recovery for the different nanogel samples. We found that using 0.1 M NaNO_3 as the eluent and an initial cross-flow of 1 mL/min provided optimal separation conditions for all samples tested. Using this method, we analysed two types of samples, pNIPAM nanogels prepared by free radical dispersion polymerisation with increasing diameters and analysed poly(acrylic acid)-b-pNIPAM crosslinked nanogels prepared by reversible addition-fragmentation chain transfer dispersion polymerisation. We could determine that the differently sized free radical nanogels possessed differing internal structures; shape factors (R_g/R_h) ranged from 0.58-0.73 and revealed that the smallest nanogel had a homogeneous internal crosslinking density, while the larger nanogels had a more densely crosslinked core compared to the shell. The poly(acrylic acid)-b-pNIPAM crosslinked nanogels displayed clear core-shell structures due to all the crosslinking being contained in the core of the nanogel.

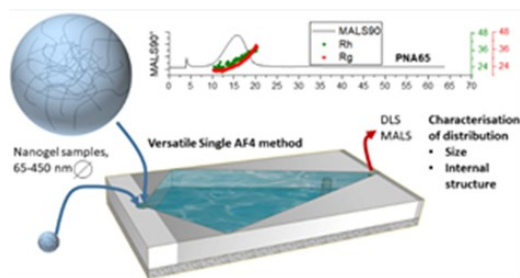


Fig 1. Graphical representation of separation nanogels by AF4.1

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Oligomerization of Butyl Methacrylate via CCTP: from small lab scale to microwave reactors

Helena Henke, Poster No: P12

Catalytic chain transfer polymerization (CCTP) with a cobalt containing catalyst can be effectively used to synthesize oligomers, which, due to their size and viscosity are of interest for medical applications as well as printing. Polymers made from methacrylates are widely applied in biology and medicine, with their application in healthcare ranging from heart valves and catheters to incubation chambers and pumps. An advantage of using polymethacrylates is scalability, with the scaling of methacrylate materials readily being used in industry.

In this contribution the successful scale up of butyl methacrylate via CCTP with azobisisobutyronitrile (AIBN) as initiator and PhCoBF as catalyst in a bulk reaction will be presented. Initial reactions were carried out on a 15 ml scale with various amounts of catalyst, ranging from 16 to 1200 ppm, using conventional heating, and were characterized using NMR and SEC measurements. After finding optimum catalyst conditions resulting in a molecular weight (M_n) range of 500-3000 g/mol, reactions were scaled up to 250 ml using standard laboratory equipment. These reactions showed that the rate of consumption of the initiator, which lead to exotherms, needed to be factored in during the scale up process, and the reaction conditions were altered accordingly. Following the observations and results from the 250 ml laboratory scale, we were able to move onto a 5 L microwave reactor, where initial reactions showed an increase in viscosity and molecular weight, as can be expected with microwave reactions compared to conventional methods.

Long-acting injectable D and L- α peptide hydrogels for HIV/AIDS treatment and prevention

Yuming An, Poster No: P13

Introduction: The majority of licensed HIV/AIDS treatments suffer from low patient compliance due to complicated drug dosage regimens. Developing a convenient long-acting formulation, to deliver drugs over a sustained period e.g. weeks/months, could be an effective strategy to improve treatment outcomes. Our research group is developing a long-acting peptide-based hydrogel drug delivery platform, which is administered by subcutaneous or intramuscular injection. Our

goal is to formulate an in situ forming hydrogel that self-assembles in response to phosphatase enzymes present in the skin space. An ester-drug linkage covalently attaches the model drug zidovudine to the peptide. This should improve drug loading and reduce burst release

Methods: D and L- α peptides were synthesised using solid-phase synthesis. Zidovudine was modified with N-hydroxysuccinimide to form an ester linkage to peptides.¹ The mechanical properties of gels were characterised using oscillatory rheology (time, frequency, strain sweeps). The underlying structure of hydrogel fibre networks were studied using circular dichroism and small angle neutron scattering (SANS) at ILL, Grenoble. Cytotoxicity was assessed using MTS, Live/Dead and LDH assays. Biostability was studied using the broad-spectrum protease; proteinase K. In vitro drug release was assessed for 28 days in pH 7.4 PBS solution. In vivo zidovudine drug plasma concentrations was obtained across 35 days in Sprague dawley rats after subcutaneous administration of Napffk(AZT)Y(p)G-OH.

Results: Rheology study demonstrated zidovudine-conjugated peptides formed hydrogels rapidly within minutes, in response to 2U phosphatase enzymes. SANS demonstrated peptide gels closely fit model data for flexible cylinder elliptical model. The presence of entangled gel fibres also suggests there is a large component of gel stiffness/strength that can be controlled by external conditions e.g. the gelation/formulation process. Cytotoxicity assays showed peptides to be non-toxic. D-peptides demonstrated protease resistance for at least 28 days. In vitro drug release of zidovudine from (Napffk(AZT)Y(p)G-OH) gave approximately 52.9% cumulative release over 28 days and 32% less burst release in the first 72 hours compared to physically encapsulated/mixed zidovudine peptide hydrogel (47.3%). In vivo studies showed for zidovudine blood plasma concentrations to be within a clinically relevant range (IC50 :30 – 130 ng/mL) for 35 days after administration.

Conclusions: This is a potential strategy for using peptide-based hydrogels as a long-acting, water-based, injectable drug delivery platform. In the future work, we will include multiple antiretroviral drugs, and include contraceptive drugs to develop a multipurpose technology for combined HIV/AIDS and contraceptive protection.



Figure 1 2 units of alkaline phosphatase (ALP) was added into 1 ml of 2% w/v (Napffk(AZT)Y(p)G-OH) solution (a), then it rapidly formed a gel (b) as confirmed by rheology. In the rheology time sweep (c), the value of storage modulus exceeds that of loss modulus at around 35 minutes, which indicated the gelation network formed at this time.

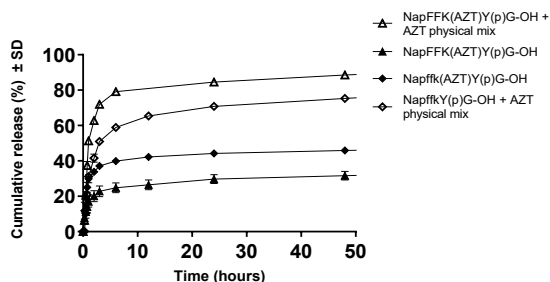


Figure 2 Physically encapsulated zidovudine D and L peptide (NapffkY(p)G-OH + AZT and NapFFKY(p)G-OH + AZT) showed great burst release in the first 48 hours (70.75% and 88.55%), which was obviously higher than drug conjugated D and L peptide at the same time (45.88% and 31.63%).

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Using iron-catalysts for the catalytic chain-transfer polymerisation (CCTP)

Cordula Hege, Poster No: P14

Catalytic chain-transfer polymerisation (CCTP) is an efficient method to polymerise for example methyl acrylates. It introduces a vinyl-functionality that can be used for post-functionalisation.

Normally cobalt catalyst are used, with the commercially available PhCoBF (bis [(difluoroboryl)diphenylglyoximate]-cobalt(II)) being the standard catalyst.

However, cobalt can be disadvantageous for biological or medical applications. Therefore, it is worthwhile to investigate alternatives.

For that, iron catalysts were explored. Iron is abundant in nature, so it is more sustainable, additionally its biocompatibility is higher.

The catalysts were generated in-situ during the reaction, which avoids extra steps otherwise needed for example to purify the catalyst and no storage is required.

As metal source iron(II)bromide was used and the ligands were dimethyl glyoxime (DMG) and diphenyl glyoxime (DPG). Different catalyst concentrations were analysed to investigate their influence on the reaction. The reactions were done in bulk and in solvent.

The level of control is influenced by the reaction conditions, as well as by the used monomers. One needs higher amounts of iron to control the reaction, than one would need for cobalt-catalysed reactions.

Still, iron catalysts were found to be a possible replacement for cobalt catalysts for CCTP. They allow to prepare reproducible, biocompatible polymers.

Poster Abstracts

Development of pH responsive platinum-containing polymeric arsenical hydrogels for biomedical applications

Alexandros Magiakos, Poster No:1

Platinum and arsenic drugs (e.g. cis-platin, As_2O_3) have been used extensively in modern medicine the last decades due to their strong anticancer and antimicrobial activity. However, the efficacy of arsenic drugs against solid tumours is low whilst intrinsic and acquired resistance are major problems associated with Pt(II) drugs. Consequently, there is an urgent need for the development of alternative complexes and delivery strategies. Recently, arsenoplatin complexes (AP1-5) containing a Pt-As bond have been shown to be more active than the parent Pt and As drugs, exhibiting dual pharmacophore properties promoted by slow breakage of the Pt-As bond after cell uptake. Nanotechnology and polymeric materials in nanoparticle or gel formulations, have emerged as effective platforms for metallo-drug delivery. Polymeric arsenicals are tuneable, reactive, responsive, and biocompatible scaffolds with distinct reactivity depending on the diverse oxidation states of As, providing efficient methods for bioconjugation as well as hydrogel and nanoparticles formation. Herein, polymeric arsenicals have been combined with Pt(II) resulting in the formation of arsenoplatinohydrogels (10% wt). The chemical interaction between Pt(II) and the arsenical scaffolds has been investigated with spectroscopic techniques (IR, ^1H -NMR, ^{195}Pt NMR and XPS) and potentiometric titration, revealing covalent interaction between Pt(II) and the -O of the pendant AsO_3H_2 groups of the polymeric arsenical scaffolds. Less acidic As^{III} scaffolds led to slower hydrogel formation (UV-Vis kinetics) and lower swelling capacity than As^{V} . The swelling and mechanical properties of the hydrogels is related to the mole fraction of As/Pt as studied with rheology and compression/swelling/self-healing tests. Elemental and morphological analysis of the hydrogels revealed a porous morphology with both As and Pt involved in the gel formation. pH responsivity was confirmed with weaker Pt-polymer interaction and better swelling/Pt drug release, in lower pHs. These bulk materials have initially been tested for antimicrobial activity showing selective toxicity against Gram negative bacteria (*E.coli*).

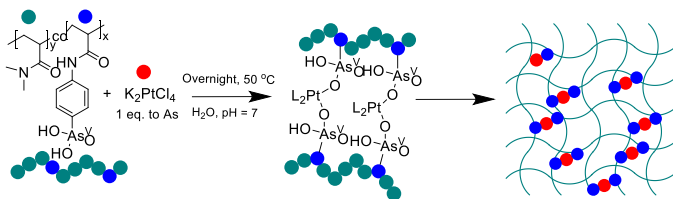


Fig.1 : Formation of the hydrogel network

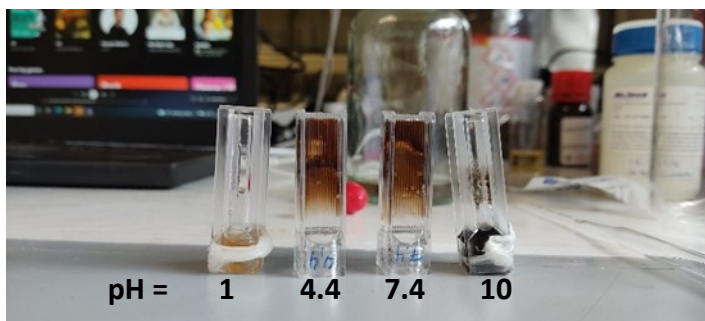


Fig.2: Hydrogels in different pHs

New Sustainable Polymers: A Greener Future for Commercial Inkjet Printing

Anisha Patel, Poster No:2

From barcodes on packaging in supermarkets to posters plastered on store windows, inkjet printing can be found almost everywhere we go. Inkjet printing is a commonly used technology that is universally used to print images and text on a range of absorbent/non-absorbent media¹. As a well-established technology, it is considered to be extremely reliable not only for use in our homes, but especially in industrial sectors due to its adaptable and robust nature² (Fig. 1).

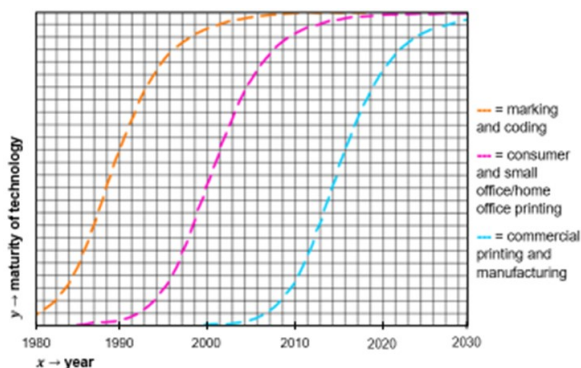


Figure 1: How the uses of inkjet printing have changed over the years. Modified from Hutchings et al.²

The evolution of ink used in conjunction with this printing technique has drastically changed over the years. The use of organic solvents has significantly decreased due to the damage they inflict upon our environment (including the release of VOC's). Large companies, such as Hewlett-Packard, are using more aqueous-based inks (with a 65% water content) that are solvent-free³. However, using aqueous-based formulations as a replacement can be problematic due to their lack of resistance to various conditions and limited use of application. Fortunately, this can be overcome by using polymeric dispersants.

Polymers in liquid formulations, formally known as PLFs, are used globally in a wide range of industries, such as food packaging and building protection. The addition of these PLFs to various products acts as a thickening/binding agent to help enhance their properties. Having an estimated global value of \$1.27 trillion, it is undeniable that we have a considerable amount of reliance upon PLFs. Approximately \$39 billion of this substantial value comes from the inks and coatings industry⁴.

Parkes et al. demonstrated how the addition of an amphiphilic block copolymer with a thermally triggerable crosslinking segment (Fig. 2) can enhance the durability and properties of industrial ink formulations. Amphiphilicity is a desirable property as it allows the polymer to be dispersed in an aqueous solution and printed on hydrophobic substrates (e.g. food packaging). The block copolymer was synthesised using reversible addition-fragmentation chain-transfer (RAFT) polymerization with

optimized conditions⁵.

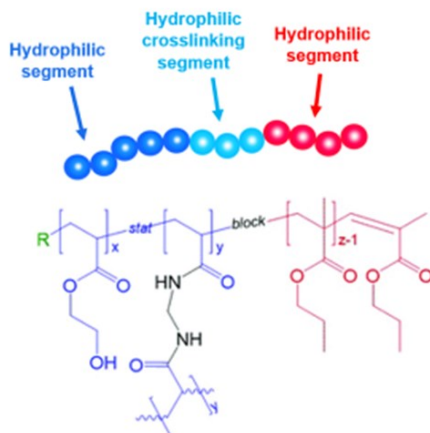


Figure 2: The structure of the amphiphilic block copolymer synthesised by Parkes et al.⁴

Currently there is a substantial drive towards more sustainable processes. Therefore in this project, monomers that are able to be derived from renewable resources are being used to synthesise a new amphiphilic block copolymer using RAFT, which can also act as a successful polymer additive in aqueous inkjet printing formulations. Additionally, the cross-linkable segment will be triggered by a more sustainable trigger process, rather than the extensive thermal treatment used by Parkes et al. These new, ‘greener’ block copolymers will be a small step in enabling more environmentally friendly approaches in this industry and help play a role in the protective maintenance of our planet.

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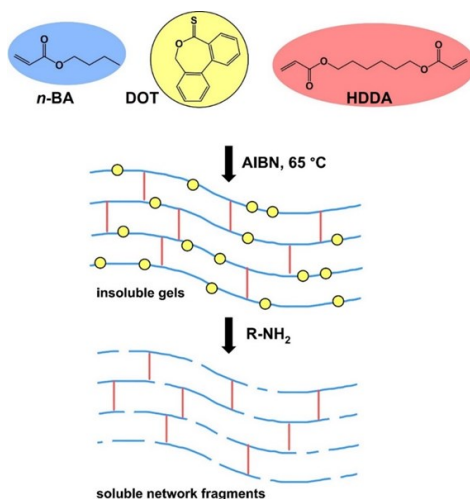
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Fully degradable polyacrylate networks from conventional radical polymerization enabled by thionolactone addition

Frances Dawson, Poster No:3

We report the preparation of degradable polymer networks by conventional free radical copolymerization of *n*-butyl acrylate with a crosslinker (1 mol%) and dibenzo [c,e]oxepane-5-thione (DOT) as a strand-cleaving comonomer. Addition of only 4 mol% of DOT imparts the synthesized networks with full degradability by aminolysis, whereas gels with less DOT (2-3 mol%) cannot be degraded. This data confirms the recently proposed reverse gel-point model and demonstrates the importance of considering copolymerization kinetics when designing fully degradable gels. Importantly, even though DOT significantly slows down the polymerization and delays gelation, it has a minimal effect on physical properties of the networks such as shear storage modulus, equilibrium swelling ratio, glass transition temperature or thermal stability.



Active learning as a tool for optimizing electrochemical atom transfer radical polymerisation

Boyu Zhao, Poster No:4

A simplified 'plug-and-play' approach to aqueous electrochemical atom transfer radical polymerization (eATRP) has been developed. Well-controlled polymerization of PEGA480 ($\overline{M}_n = 1.17\text{--}1.31$) is reported under potentiostatic (3-electrodes, undivided cell) and galvanostatic (2-electrodes, 6-steps) conditions. Combining simplified electrochemical atom transfer radical polymerization (seATRP) with machine learning to optimize polymer product is first time reported. Here, it is shown that the use of Bayesian optimization in active learning (AL) method accelerated the discovery of PEGA480 with fewer trials but promising results. Under the condition of 114:1 monomer to initiator ratio, -0.1V applying potential and 30 vol% monomer concentration, we synthesis poly (PEGA) with 1.18 dispersity and good monomer conversion. We synthesize and characterize 10 predicted polymers (10 iteration loops) from a potential space of 270 reaction conditions. In total 80% results dispersity are less than 1.3. Overall, our studies suggests that adopting AL methods into polymer laboratory practices could improve finding new polymer efficiency.

Responsive Polymeric Receptors as Diagnostic Tools

Helen Sims, Poster No:5

Bacterial diseases are responsible for millions of deaths worldwide per year, the ability to rapidly detect and identify bacterial lectins could reduce the time required for diagnosis and thus improve patient outlook. Bacterial lectins (carbohydrate binding proteins) bind to glycoconjugates on the surface of mammalian cells.¹ The monovalent interaction between lectins and their complementary glycoconjugates typically have a low binding affinity (K_d mM - M), as such lectins rely on binding to multiple glycoconjugates simultaneously.² The multiple low binding affinity interactions reinforce one another, resulting in an overall high binding affinity between the lectin and the cell surface.³ These multivalent lectin-glycoconjugate interactions can be mimicked via the use of a synthetic polymer scaffold with carbohydrate moieties upended along the polymer backbone. End group modification of the glyco-polymer scaffolds to incorporate a fluorescent re-

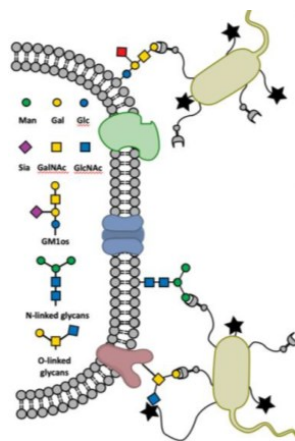
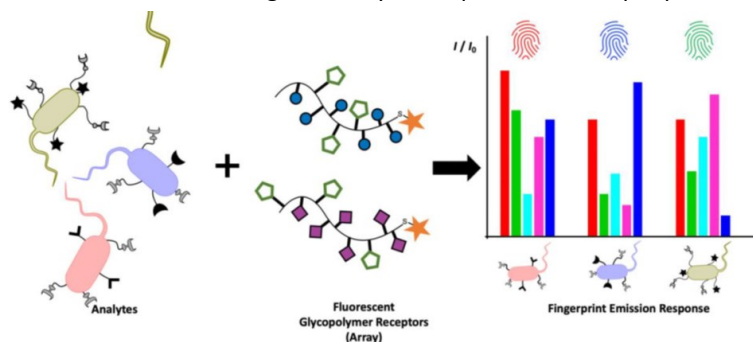


Figure 1: Schematic of cell surface glycoconjugates recognition by bacterial lectins.

porter allows for the production of fluorescent glycopolymers (FGPs). Lectin binding will result in changes to the fluorescent emission spectra of the FGP, statistical analysis of these changes is used build up an optical fingerprint for the lectin.

A library of polymer scaffolds has been synthesised via RAFT copolymerisation; all copolymers utilise a BOC-protected acylhydrazide monomer. BOC deprotection gives the reactive acylhydrazide group which provides an attachment point for carbohydrate moieties along the polymer backbone. End group modification of polymer scaffolds has been conducted via a two-step reaction. Aminolysis of the polymer scaffold produces a thiol end group which then undergoes a thiol-michael addition reaction with maleimide containing fluorophores to produce fluorescent polymer scaffolds. A library of fluorescent glyco-polymer has been synthesised, and a robust and verifiable attachment procedure has been established. Current research efforts are focused on utilising the fluorescent glycopolymers in a differential sensing array, to allow for the differentiation and identification of bacterial lectins in a complex sample.

Figure 2: Schematic of a fluorescent glycopolymer cross-reactivity sensor array which can interact with a range of analytes to produce a unique pattern response



for each analyte.

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Controlled Electropolymerisation of HEMA using Nanopipettes.

Bryn Jones, Poster No:6

Scanning electrochemical cell microscopy (SECCM) can be utilised a tool for controlled polymer synthesis on the nanoscale.^{1,2} eATRP reactions are performed in a droplet cell on SAM coated gold surfaces. The SAM layer provides the initiator for a copper mediated eATRP reaction whilst the catalyst and monomer are delivered via SECCM. The SECCM set up allows for control of the potential applied to the gold surface and gives full manipulation in 3D space, allowing control of the contact area and duration of polymer delivery. The SECCM measures the surface current during delivery and this information is correlated with droplet growth. The work investigates the extent of the achieved control via AFM surface analysis to provide a visualisation of polymer brushes and allows for measurement of their height, width, and volume of material. Interference Reflection Microscopy (IRM) and optically thin gold surfaces are employed to provide real time footage and a unique perspective on polymer brush fabrication.³

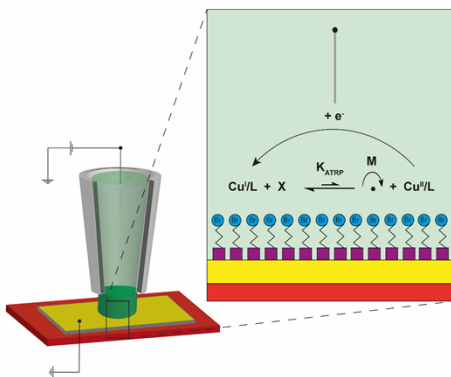


Figure 1 : Overview of nanopipette controlled surface initiated eATRP.

In this poster I will demonstrate the fine control we have established over this reaction so far and discuss the benefits of using IRM technology to monitor this process in real time.

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Development of a Universal Polymer Labelling Strategy using a Novel Photo-Affinity Labelling Probe

Jack David Fradgley, Poster No: 7

Polymers are ubiquitous commodities used extensively in everyday human life¹ with uses ranging from conspicuous plastic materials to more subtle synthetic polymers in detergent formulations. Owing to their diverse properties and behaviour, polymer chemistry is the focus of heavy ongoing research efforts in a wide variety of fields, such as the controlled drug delivery of antibiotics in biological systems and the improvement of personal and homecare products. Within these fields and others, the ability to probe and monitor polymer behaviour is highly desirable. With a view to developing an additional tool for researcher use, we set out to develop a suitable fluorescent probe which could be used to universally label a wide variety of polymers of interest in a facile manner.

Here, the design and six-step synthesis of a novel photo-affinity labelling (PAL) probe is presented. The probe is comprised of a highly fluorescent naphthalimide reporter label linked through a spacer to a benzophenone warhead (Figure 1). The application of UV-Vis irradiation generates the benzophenone radical which facilitates attachment to a target of interest. For initial labelling studies, a library of polystyrene homopolymers of varying degrees of polymerisation ($DP \sim 40 - 940$, $M_n \sim 4,400 - 98,000 \text{ g mol}^{-1}$) were prepared using RAFT polymerisation. The low dispersity range of this library was confirmed using Gel Permeation Chromatography (GPC) ($\bar{D} = 1.04 - 1.22$). Current research efforts are focused on the establishment of optimal irradiation conditions to develop a reproducible and verifiable attachment protocol, and the synthesis of further, varied polymer libraries.

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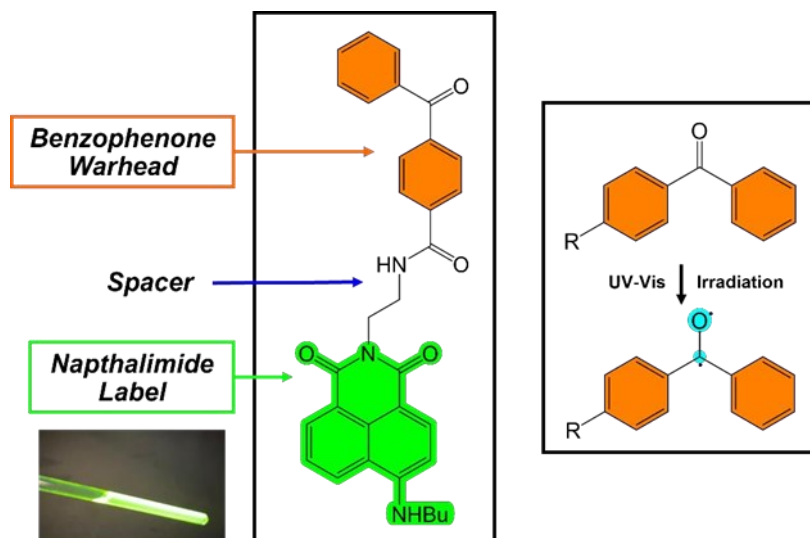


Figure 1. Schematic detailing the components comprising the novel prepared PAL probe. The bright solution-state fluorescence of the label (exc 365 nm, CDCl₃) is shown as well as the formation of the benzophenone triplet radical.

Polymer Labelling Strategy

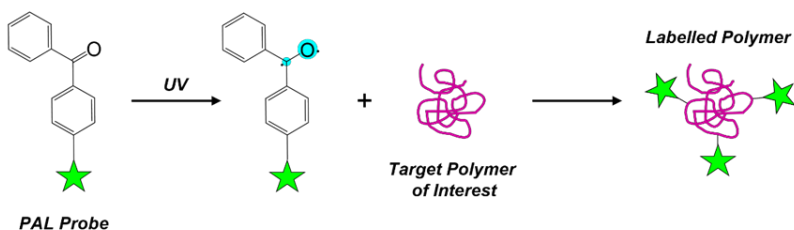


Figure 2. Schematic detailing the polymer labelling strategy using the photo-affinity labelling (PAL) probe.

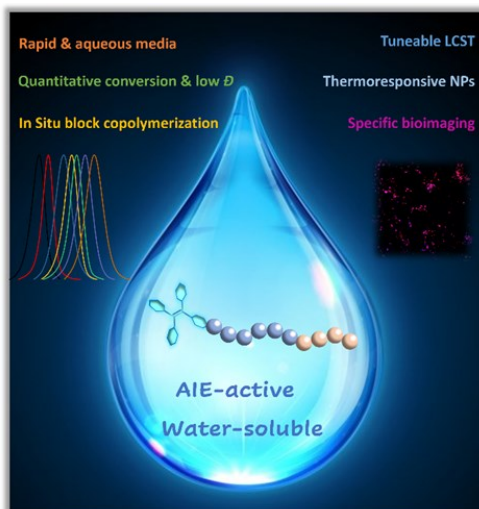
Well-defined polyacrylamides with AIE properties via rapid Cu-mediated living radical polymerizations in aqueous solution: thermoresponsive nanoparticles for bioimaging

Congkai Ma, Poster No:8

Until the concept of aggregation-induced emission (AIE) was coined by Tang and coworkers in 2001,¹ molecular aggregation had been regarded to be detrimental to luminescence due to aggregation-caused quenching (ACQ) phenomenon. The AIE effect has revolutionarily demonstrated that aggregation can allow for boosted light emission with an appropriate chemical moiety, contributing potential application in optoelectronics, stimuli-responsive materials, and the biomedical field.² However, there is a deficiency in the development of methodology for the preparation of well-controlled polymers with aggregation-induced emission (AIE) features. This directed this current work for a robust synthetic route, which would be applicable in water and the presence of functional groups. Herein, aqueous Cu-mediated living radical polymerization (LRP) has been optimized to provide facile and very rapid access to a diverse range of water-soluble AIE polymers at sub-ambient temperatures. Homo-, block and statistical copolymerization all proceeded to a near full conversion ($\geq 99\%$) within 1 or 2 h and exhibited a quite narrow dispersity, even when DP was targeted up to 1000. This excellent control associated with living polymerisation and the high-end group fidelity achieved were further demonstrated by linear first order kinetics and successful in situ block copolymerization, respectively. Fine-tuning the monomer sequences and compositions of poly(N-isopropylacrylamide) (PNIPAM) based copolymers allows for differing lower critical solution temperature (LCST) and fluorescent thermoresponsive nanoparticles, which spontaneously self-assembled to varying sizes in water as determined by a combination of techniques (DLS, SAXS and TEM). Additionally, the fluorescence intensity was demonstrated to depend on the polymer concentration, architecture of the side chains and temperature. Particularly, PNIPAM-containing polymers were resistant to reduction in thermo-induced emission. The good biocompatibility, photostability and high specificity make them promising candidates as lysosome-specific probes for application in bioimaging.

Reference

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Dark sulfur: Quantifying unpolymerized sulfur in inverse vulcanized polymers

Joe Dale, Poster No:9

The global increase in the quantity of elemental sulfur waste from the desulfurization of crude oil has led to the expansion of investigations into new sulfur based materials. Since 2013, the discovery by Chung et al. has promoted ever growing research into the field of inverse vulcanization. 1 A one-pot, solvent free synthesis wherein ring-opening of elemental sulfur at elevated temperatures, before reaction with a vinylic comonomer, yields a high sulfur content polymer product with variable and tunable properties for a wide variety of uses, such as in heavy metal capture², antimicrobial³, or Li-S battery⁴ applications. Interest is growing with regards

to the commercialisation and scale-up of this procedure. As such, questions arise in respect of polymer stability, degradation, and lifetime. Inverse vulcanized polymers are subject to aging with time, particularly in polymers synthesised using renewable crosslinkers such as limonene, pinene, or myrcene, often to the detriment of their characteristics. Herein the lifetime of inverse vulcanized polymers is investigated, with it shown that the glass transition temperature (T_g) may change over the aging period. This study subsequently prompted the discovery of unreacted sulfur, stable in an amorphous form, within the polymer matrix and not reacted into the polymer structure. It has commonly been considered that if crystalline sulfur was unobserved in these polymers by methods of powder X-ray crystallography (PXRD) or differential scanning calorimetry (DSC), then all sulfur was reacted into the polymer structure. A detailed study is presented on the quantification of free amorphous sulfur within inverse vulcanized polymers, in which free sulfur is shown to increase over a period of aging. Owing to the dynamic nature of the sulfur-sulfur bond, it is shown also that through the application of heat this aging may be reversed, with sulfur re-incorporated back into the polymer chains, by means of homolytic S-S cleavage. It goes without saying that this potential for polymer regeneration would be a key characteristic for the application of these materials in a commercial setting.

Developing a library of ionic liquid-based resins for use in printable electrochemical sensors

Siddhi Trivedi, Poster No:10

Additive manufacturing (known better as 3D printing) techniques have shown promise for developing biosensors. Stereolithography (SLA, Vat polymerisation) is an additive manufacturing technique using resins to generate printed polymer products.¹ Commercial resins used for this technique are extensively formulated using polyurethane, which can induce the growth and reproduction of bacteria under certain temperature and humidity conditions during usage and storage.² This can lead to fouling and results in degradation of the print product overtime. Growth of these micro-organisms is either prevented or inhibited by the addition of antimicrobial compounds to the formulation. Previous work has shown the ability of the monomers ethylene glycol dicyclopentenyl acrylate (EGDPA) and isobornyl acrylate (IBA) to exhibit strong antimicrobial properties.

To add biosensor activity, often a conducting component is needed. Ionic liquids are a class of low temperature (<100°C) molten salts composed exclusively of discrete anions and cations. Most ionic liquids display useful generic characteristics including low melting point, negligible vapour pressure, exceptional solvation potential as well as antimicrobial activity.³ In particular, quaternary ammonium compounds (QACs) have been previously used in many disinfectants and medical settings due to their antimicrobial properties.⁴

This current work aims to combine ionic liquids and antimicrobial monomers to build a library of materials that are able to successfully be used in resins to print biosensors with predictable properties and resistant to biofouling.

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A means to an end-group modified poly(vinyl alcohol)

Douglas Soutar, Poster No: 11

Poly(vinyl alcohol) (PVA) has untapped potential for biomedical applications, in functionalized hydrogels,¹ as a biodegradable alternative to PEG in polymer-bioconjugates, and as a cryoprotectant for biologics due to its ice recrystallization inhibition activity.²

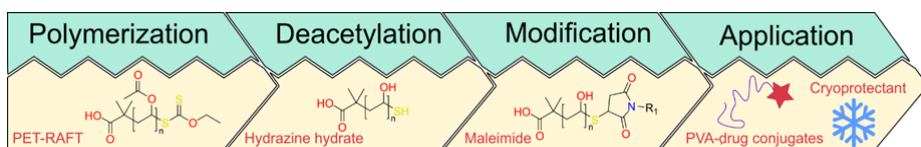
PVA is not synthesized directly, rather it is produced by hydrolysis of poly(vinyl acetate) (PVAc). Historically vinyl acetate has been difficult to polymerize with high chain-end fidelity, due to being a less-activated monomer with a reactive radical chain end.³ Recently PET-RAFT/MADIX has been applied to vinyl acetate successfully with photocatalysts including fac-[Ir(ppy)₃],⁴ and bismuth oxide,⁵ producing PVAc with low dispersity and high chain end fidelity.

Deacetylation of PVAc is typically performed by hydrolysis with methanol and a

base catalyst. However, this does not result in 100% PVA, as some acetate groups remain.⁶ Hydrazine hydrate solution can be used to completely remove the acetate groups, which is utilized in this project. During hydrolysis, the xanthate end group should also be removed, resulting in a thiol end polymer.⁷

The aim of this project has been to utilize this thiol to produce various chain-end modified PVAs. So far, reaction with maleimides has proven to be feasible with high conversion, with good evidence by DOSY ¹H NMR.

Once a range of end-group modified PVAs have been developed, their properties as ice recrystallization inhibitors will be tested, and bioconjugation strategies will be explored.



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Synthesis of low molecular weight polyimides for additive manufacturing

Bethany Husband, Poster No:12

Polyimides (PIs) are a common material employed in the manufacture of electronic circuit boards, due to their excellent thermal stability, chemical resistance and for their good dielectric properties. PI films for this application are typically prepared using conventional methods of spin coating, followed by photolithography to etch fine features. However, these manufacturing approaches can lead to a wastage of up to 90% of the material.

Additive manufacturing techniques, such as drop-on-demand inkjet printing, offer a solution to remove the inefficiency and improve the freedom of design while retaining a high throughput. However, as a high-performance engineering polymer, the physical properties of current PI formulations are incompatible with inkjet printing technology. A particular problem is the high viscosity of the polymeric ink solutions, which prevents them from being jetted without excessive dilution in harmful organic solvents. Current research has shown that only a 1 wt% solution of PI-based ink has sufficiently low enough viscosity to print using this method[1].

Here we present a synthetic route that can aid the formulations of new low viscosity inks. Poly(amic acid), the more soluble precursor to PI, was synthesised using step growth polyaddition of a diamine and a dianhydride, modified by the addition of monofunctional anhydrides used as end capping groups that limit chain extension. The viscosity of these low molecular weight PI precursors was assessed by rheological analysis and their printability was subsequently determined.

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Is Three a Crowd? Trimetallic Catalysts for Lactide Ring-Opening Polymerisation

Phoebe Lowy, Poster No: 13

Given the high societal reliance of plastics, there has been a major drive in recent years to develop sustainable alternatives to these valuable materials. Derived from biomass, poly(lactic acid) (PLA) is an attractive, biodegradable polymer with the potential to replace some petrochemical-based plastics.¹ PLA is typically prepared through the ring-opening polymerization (ROP) of lactide (LA), which requires the use of a catalyst. Salen ligand-supported aluminium complexes are recognised as efficient and versatile catalysts for LA ROP, displaying some of the best stereochemical control over the PLA microstructure reported to date.² However, the catalytic activity of Al-Salen complexes is often relatively slow compared to other systems. The use of multinuclear catalysts is emerging as a method of enhancing organometallic catalyst performance in LA ROP, where multinuclear complexes (with two or more metals held in close proximity) often outperform the mononuclear analogues in terms of reactivity, whilst maintaining good polymerization control.³ Yet this concept has been underexplored in Al-Salen catalyst development.

Here, a trinuclear Al-Salen complex has been synthesized, characterized and tested as a catalyst for LA ROP. The mononuclear Al-Salen complex was prepared for benchmarking purposes. The trinuclear complex contains three Al-Salen subunits in close proximity, and displays excellent LA ROP rates ($k_{\text{obs}} = 4.0 \times 10^{-2} \text{ min}^{-1}$), outperforming the mononuclear counterpart ($k_{\text{obs}} = 3.6 \times 10^{-3} \text{ min}^{-1}$) by a factor of 10.4. Thus, the increased catalyst activity using the trinuclear Al-salen complex is “greater than the sum of its parts”, indicating intramolecular cooperation among the three Al-Salen subunits.

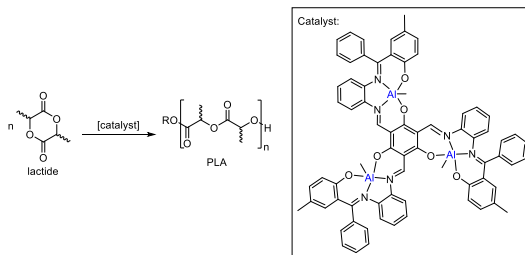


Figure 1. Trinuclear Al-Salen catalyst for the ring-opening polymerisation of lactide.

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Alternate Non-Silicone Based Lubricants Synthesized via CCTP from Naturally Derived Materials

Euan Kendall, Poster No: 14

Silicone based oils (such as dimethicones or dimethiconols) are widely used as lubricants in applications ranging from hair products to engine oil^{1,2,3} due to their excellent lubricating mechanical properties, but are produced solely from non-renewable resources.

In this work, I have set out to produce a more environmentally friendly and sustainable alternative to non-renewably sourced silicone oils using polymers synthesised via CCTP using as high a percentage of renewable feedstocks as possible.

In order to determine the effectiveness of the synthesised polymer lubricants, any polymer lubricants produced have undergone testing to determine their effectiveness relative to extant silicone-based products, as well as natural oils commonly used in cosmetic products for this purpose (e.g. coconut oil). These tests include techniques such as mechanical testing, TGA, DSC, scanning electron microscopy, and tribology.^{4,5}

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The impact of hydrophobicity, flexibility, and backbone isomerism on biological activity and mechanism of action of ionenes.

Rafał Jerzy Kopiasz, Poster No: 15

The spread of antibiotic resistance among pathogens is a serious concern for global healthcare and the economy. It has been estimated that about 700 000 people die worldwide annually due to bacterial infections caused by antibiotic-resistant strains, and this number may increase to even 10 million by 2050. To avoid a global health crisis caused by highly infective drug-resistant bacteria, a strong effort to develop novel antibacterial agents is urgently needed.¹

Membrane-lytic antimicrobials, such as antimicrobial peptides (AMPs) and polycations mimicking their physicochemical properties (SMAMPs), seem to be promising candidates. Their mechanism of action is based on many nonspecific electrostatic and hydrophobic interactions with a cell membrane, making them less prone to induce resistance development than currently used antibiotics.² Unfortunately, the nonspecific mechanism of action leads to low selectivity towards microorganisms over eukaryotic cells. Both AMPs and SMAMPs are significantly hemolytic and cytotoxic, therefore, further studies on those classes of antimicrobials are still needed.

Among already studied polycationic platforms, polymers containing quaternary ammonium salts along their mainchain (called ionenes) show interesting properties. Relatively hydrophilic ionenes are usually highly antibacterial and almost non-hemolytic,³ which was the main driving force for my research on this class of polycations.⁴⁻⁶ The aim of my studies was to enrich knowledge about the structure-activity relationship (SAR) in terms of the impact of ionenes' hydrophobicity, isomerism, and flexibility. To reach this goal, 25 new ionenes (Figure 1) were synthesized and characterized. Results of the assessment of antimicrobial and hemolytic activity along with cytotoxicity will be presented on the poster.

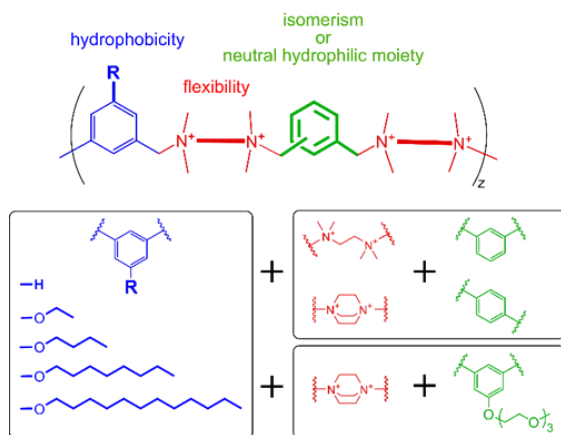


Figure 1. A library of studied ionenes.

The mechanism of the antibacterial action of ionenes is thought to be via a cell membrane disturbance. Therefore, the membrane activity of selected ionenes was investigated to understand better the impact of ionenes' hydrophobicity on their biological activity. Those studies were extended by investigating the influence of a phospholipid bilayer composition on its susceptibility toward the destructive activity of ionenes.⁴ Relevant results will be presented on the poster.

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Synthesis and evaluation of cationic antimicrobial polymers

Lena Dalal, Poster No: 16

The worldwide spread of antibiotic resistance due to the overuse of antibiotics urges the need for novel less prone to resistance antibiotics.¹ Antimicrobial peptides (AMPs) are small polypeptides that contribute to the innate immunity system. Their activity and selectivity towards microorganisms are both attributed to their amphiphilic structure.² However, AMPs instability and high production costs limited their clinical development as prospective antibiotic.³

Synthetic antimicrobial polymers (SAMPs) were introduced as promising antibiotics that mimic the amphiphilic structure of AMPs combining hydrophobic and cationic polymers in various ratios. This design is challenging as increasing the positive charge will decrease the overall hydrophobicity of the polymer and vice versa.^{3,4}

Previous work in our group focussed on the synthesis of SAMPs that mimic the common amino acids found in AMPs, e.g. arginine, lysin and leucin, to provide similar amphiphilicity structure and activity.^{5,6}

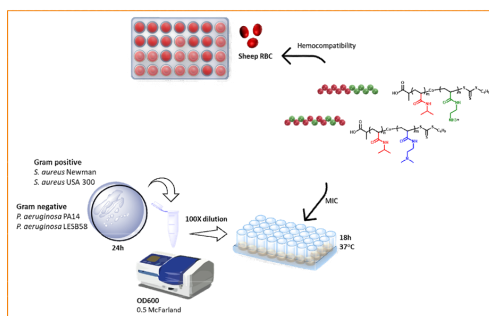
In this work, statistical and diblock polymers of the hydrophobic monomer N-isopropyl acrylamide (NIPAm) and the cationic amino ethyl acrylamide (AEAm) in 30:20, 25:25, 20:30 ratios were copolymerised by RAFT polymerisation and evaluated for activity and hemocompatibility. To assess the significance of cationic charge, AEAm was replaced with non-ionic monomer, dimethyl amino ethyl acrylamide (DMAEAm), in ratios 30, 50 and 70%.

The polymers minimum inhibitory concentration (MIC) according to the standard Clinical Laboratory Standards Institute (CLSI) broth microdilution method (M07-A9-2012) were determined against gram positive and negative bacteria *Staphylococcus aureus* (S.A) and *Pseudomonas aeruginosa* (P.A), respectively. The results showed no activity of the statistical cationic (AEAm) or the non-ionic (DMAEAm) copolymers at the highest concentration tested (512 µg/ml). Nevertheless, MICs of AEAm diblocks against S.A. decreased from 512 to 128 µg/ml as the cationic ratio increased with pNIPAM20-b-AEAM30. The same trend was observed against P.A, although the polymers were less effective by one-fold.

All the polymers showed no haemolytic activity and cationic and non-ionic diblocks did not cause agglutination at the highest concentrations tested (512 µg/ml). Hae-

magglutination was only observed in statistical polymers with no relation to the cationic content. When comparing the data, increasing the cationic percentage seems to give higher selectivity.

The results so far support the hypothesis of the importance of the cationic charge for both activity and selectivity. The cationic units needed to be compact in one side of the chain to give this effect as statistical distribution of the charge did not give similar results despite having similar cationic percentages. Further investigation is required to confirm the activity and toxicity values; however, other confirmations should be also considered to optimize the activity/selectivity overall.



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Enhancing the anticancer activity of doxorubicin via simultaneous delivery with a peroxynitrite generator using polyester based polymeric nanoparticles

Cristina Parisi, Poster No:17

Doxorubicin (DOX) is one of the most potent anti-cancer drugs for the treatment of a variety of different tumors. However, its use is hindered by the dose-dependent cardiotoxicity and the development of multidrug resistance (MDR). Different mechanisms are at the basis of MDR; the resistance to DOX is mainly exerted through its increased efflux from cancer cells as result of the overexpression of adenosine 5'-triphosphate (ATP) binding cassette (ABC) transporters [1]. Many strategies have been proposed to overcome MDR, like coadministration of DOX with compounds able to inhibit the activity of ABC transporters [2]. Peroxynitrite (ONOO⁻) is the ideal candidate for this purpose since not only it exerts a potent oxidative and cytotoxic activity, but it is also able to nitrate critical tyrosine residues of these transporters [3]. Therefore, ONOO⁻ can be exploited not only as a cytotoxic agent but also as a powerful tool to reduce the cell extrusion of drug, and thus enhancing its anticancer activity. However, due to the lack of selectivity of ONOO⁻ for bio-substrates, an accurate control of its delivery in terms of space, time and dosage represents a desirable requisite. Light allows to reach this purpose by using appropriate photoprecursors. The design and fabrication of photoactivatable ONOO⁻ generators is not an easy task; in fact, since ONOO⁻ is the result of a very fast reaction between nitric oxide (•NO) and superoxide anion (O₂•⁻), these two species need to be simultaneously generated under light input from suitable chromogenic units. Recently, it has been developed a novel molecular hybrid able to generate ONOO⁻ under activation with the highly biocompatible red light [4]. In this contribution we report the development of polymeric nanoparticles (NPs) for the simultaneous delivery of DOX and this novel generator of peroxynitrite as a tool for overcoming DOX resistance. NPs are made of amphiphilic block copolymers of polyethylene glycol (mPEG) and poly(ε-caprolactone) (PCL) properly modified in order to conjugate DOX via a pH-responsive linker and designed in order to encapsulate the novel photoactivatable ONOO⁻ generator within their hydrophobic core.

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Aqueous Electrochemical Synthesis of Polymers using ATRP on the Nano/ Macro Scale

Mahir Mohammed, Poster No: 19

My research involves using electrons to synthesise polymers. We use ATRP, a common method of polymerization with targeted molecular weight and living chain ends (chain ends are living not dead, so they can be 're-grown'). More specifically, eATRP (electrochemical ATRP) is used, with electrons to drive the synthesis. This reaction can be done in a vial, or a flask, on relatively larger scales.

Starting with large-scale polymerization and working to smaller scale, our aim is to grow polymers at a nanoscale, ultra-confined area on a surface. We have already succeeded in making surface-bound polymers using an ATRP mixture and wish to investigate using SEM, AFM, XPS.

Surface-bound polymers can be made using SECCM. A nanoscale droplet is delivered to the surface containing the mixture. Electricity is used to start the reaction. Initiators bonded to surface provide C-Br functional groups, which can be used to initiate ATRP reactions, leading to surface polymers as shown (see figure 1).

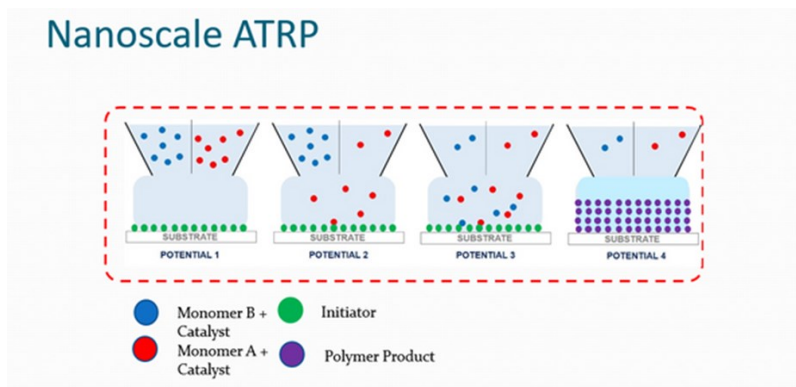


Figure 1 – showing schematically how polymers can be grown from a surface.

On the macro scale, electricity was used to generate well-controlled polymers. We are curious to see if similar conditions can be applied to the nanoscale (see figure 2). For example, can the living surface-bound polymers be re-activated for further reactions? Can monomer to initiator ratio be used to target molecular weights (eg 40 monomer molecules per one initiator molecule means a weight of 40 monomer

weight + one initiator weight)? Can length of the polymer chain determined by SEM, be related to the molecular weight targeted?

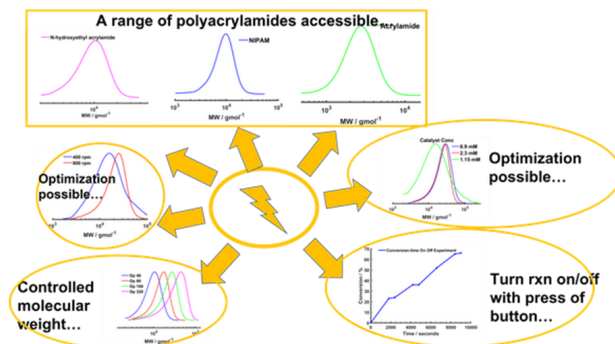


Figure 2 - summary of achievements of macroscale polymerization so far.

In summary, we wish to electrochemistry to carry out macroscale and nanoscale polymerizations. Controlled polymers on the macroscale and surface-bound polymers have already been possible. Electrosynthesis using a simple two-electrode system on the macroscale, using one set of current steps to produce controlled polymers in water has been shown. Thank you.

Tuning the Elasticity of Biodegradable Polymers using Vegetable Oils

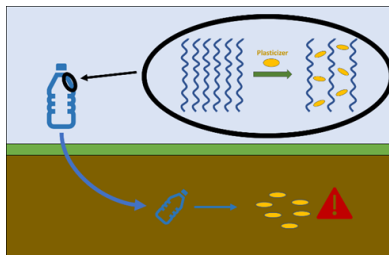
Bawan Hadad, Poster No: 20

There is an increasing demand to move away from the use of non-biodegradable polymeric materials (plastics). To do so, many biodegradable polymers have been formulated in recent years. Some have even found themselves in commercial applications, where the most widely produced in the chemical industry are polybutylene adipate terephthalate, polylactic acid and starch blends.^[1]

However, if we are to consider the sustainability of plastics made with such polymers, we must also consider the plastic additives that are also included. Some common examples of plastic additives include flame retardants, plasticizers, antioxidants, etc.

Our focus is on plasticizers. Plasticizers are added to aid in the elasticity of plastics. This helps to reduce brittleness, and aid in processability. However most common plasticizers are phthalates.^[2] It is well known that phthalates are toxic chemicals, where studies have shown that they can leach out of plastics, causing harm to the

ecosystem.^[3] This is of even more concern if they are to be used with biodegradable plastics, as these toxic additives will readily be dispersed into the environment upon degradation of the polymer network.



Our focus is to find bio-based plasticizers that are compatible with biodegradable polymers. Recently we have found vegetable oils to be a promising candidate as plasticizers for a common biodegradable polymer. They are bio-based, cheap and safe to use. By varying the content of vegetable oils, the elasticity of the plastic can be tuned for the desired application.

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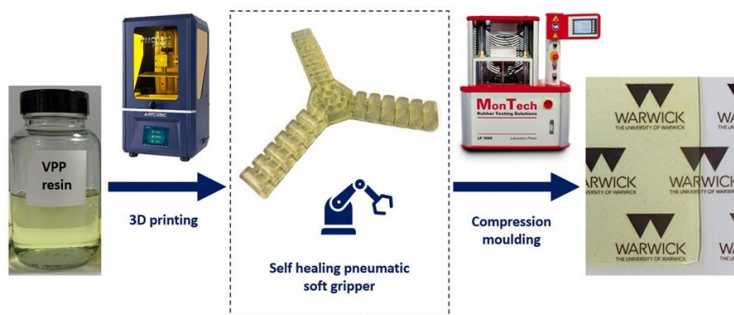
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Formulation of elastomeric 3D printing resins for vitrimer components in soft robotics

Mantas Drelingas, Poster No: 21

A



B



Figure 1 – (A) Formulation of elastomeric 3D printing vitrimer resins for soft robotics with self-healing and material reprocessing functionalities, using (B) cross-linker designed for vat photo polymerisation 3D printing with vitrimer moiety.

Soft robots and soft actuators are a type of devices which create motion using soft, deformable and compliant materials. As opposed to conventional actuators, this type of actuator was inspired by physically adaptive, agile, and multifunctional animal and human muscles. Optimised to work around people or with delicate objects, they promise to contribute to process automation safety and reliability where current actuators fall short.¹ Vat photo-polymerisation (VPP), an additive manufacturing technique allows the manufacture of intricate free-form shapes starting from a liquid resin, and therefore is highly suitable for fabrication and prototyping of soft robotics. Currently the development and commercial availability of elastomeric resins for VPP is limited, as the nature of low crosslink density elastomers and requirement of low viscosity resins makes it challenging to 3D print them.² Furthermore, the free radical polymerisation of conventional VPP resins leads to permanently crosslinked solids, which can not be recycled and contribute

to the growing problem of plastic pollution.

In this work, we designed and synthesised a functional crosslinker with vitrimer moieties, formulated two elastomeric resins suitable for VPP 3D printing using conventional consumer equipment and demonstrated their potential by fabricating a soft gripper. Two methacrylate crosslinkers containing vinylogous urethane vitrimer moiety based on poly(dimethyl siloxane) and poly(propylene glycol) backbones were synthesised using simple one-pot one-step method, making this method accessible and reproducible. Resins were formulated using monomers of low glass transition temperature, ensuring network chain mobility and crosslinked with custom made crosslinkers. Elastomers show a range of mechanical properties - elongation and tensile strength of 0.8 MPa and 500 % to 4.7 MPa and 520 %, respectively. Due to the transamination reactions occurring between free amines in the system and the vinylogous urethane vitrimer moiety, upon thermal processing in a compression moulding hot press a melt like fusion of printed material is observed, with the tensile strength retained being from 50 to 69 %, indicating the potential for thermally recycling these materials. In addition, elastomers showed an excellent healing efficiency retaining 100% of initial tensile strength after healing at 80 °C for 24 hours. Given the obtained material properties, these resins have a high potential to be used in the manufacturing of soft robotics with material reprocessing and self-healing functionalities.

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Synthesis of well-defined biodegradable polymers and study of their materials properties

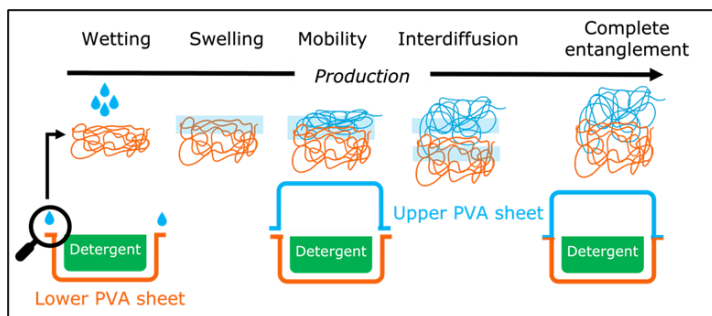
James Cresswell, Poster No: 22

Poly(vinyl alcohol) (PVA) is an important commodity polymer which is used extensively in the production of adhesives and protective films, and for biomedical applications. In contrast to other olefin-derived polymers, PVA is biodegradable through metabolism by *Pseudomonas* sp., making it an attractive material for further commercial exploitation. PVA is used to manufacture single unit dose laundry detergent capsules, providing a method of encapsulating, and segregating the components of the formulation. This application requires a strong and robust seal to be formed

between the PVA sheets to prevent leakage and product damage (Figure 1).

This work aims to investigate and improve the understanding of polymer interdiffusion at the interface of the film. PVA is prepared by the alkaline hydrolysis of poly (vinyl acetate) (PVAc), synthesised industrially via radical polymerization. Such methods offer little scope for engineering the molecular characteristics of the resultant polymers, with poor control over molecular weights and dispersity within the population.

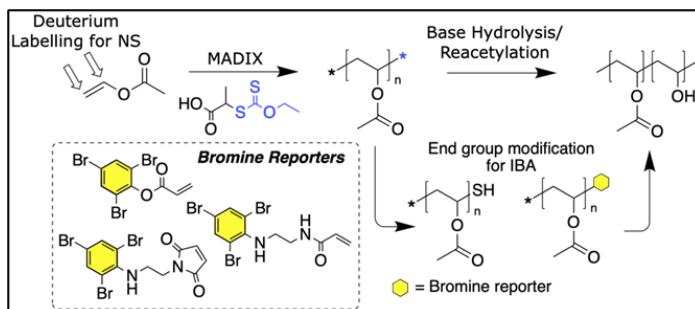
Here, PVAc was synthesised with a range of molecular weights and narrow polydispersities using a novel photocatalytic method via photoinitiated MADIX (macromolecular design by interchange of xanthate) polymerisation. Characterisation methods have been optimised to determine the degree of hydrolysis via ^1H NMR spectroscopy, as well as Tg determination of polymer films by dynamic mechanical analysis (DMA). Gel permeation chromatography (GPC) has been utilised to assess molecular weight and dispersity of materials to ensure well defined polymers are produced. Hydrolysis of PVAc to the corresponding alcohol has also been investigated, with exploration of controlled hydrolysis and full hydrolysis followed by partial reacylation. Deuterated analogues of PVAc and PVA are also targeted, incorporating deuterated pendent groups as well as backbone deuteration, providing contrast during the study of polymer interdiffusion by neutron scattering techniques (Figure 2). Preliminary work involving end group modification of xanthate



terminated PVAc is being investigated to allow attachment of a bromine containing moiety to further enable polymer migration within a film to be monitored using ion beam analysis.

Figure 1: Schematic representation of laundry capsule production, showing the sev-

eral stages of polymer entanglement required to seal the contents within the pod.



Initially the film is wet with water to swell the polymer chains, eventually to the point of chain mobility. The second PVA sheet is placed on the wet sheet, allowing interdiffusion between polymer chains, and eventually complete entanglement to form a sealed product.

Figure 2: Project overview showing partially hydrolysed poly(vinyl acetate) synthesis via PETMADIX (macromolecular design by interchange of xanthate) with potential for post polymerisation modifications and deuterium labelling.

Antibacterial Sulfur Polymers

Romy Dop, Poster No: 23

In recent years, there has been interest in employing antimicrobial surfaces to help limit microbial contamination of surfaces, especially in hospital settings where hospital-acquired infections (HAIs) are continuing to burden healthcare systems. The impact of HAIs are widespread, and are not confined to hospital settings, as they have been linked to multi-drug resistant infections such as those caused by methicillin-resistant *Staphylococcus aureus*, such resistance is amongst the most serious health threats of the century. Recently, there is growing interest in polysulfides as novel antimicrobial agents due to the antimicrobial activity of natural polysulfides found in garlic and onions.¹ In 2013, a new class of high sulfur content polymers coined 'inverse vulcanised polymers' were reported by Pyun and co-workers.² Inverse vulcanisation is a method for synthesising polymers from elemental sulfur and a small amount of vinylic comonomer, the converse of conventional vulcanisation which implements sulfur as a minor component of the reaction feedstock. Herein we demonstrate that high sulfur content polymers show an inhibitory effect against methicillin-resistant *Staphylococcus aureus* and *Pseudomonas aeruginosa*.³ In addi-

tion to this, we demonstrate that surface coatings of high sulfur content polymers can be fabricated by spray deposition of polymeric nanoparticles or polymer coated nanoparticles, such coatings have potential applications in antibacterial and/or anti-fouling surfaces.⁴

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Glycan-functionalised gold nanoparticles for the detection of cholera toxin

Melissa Ligorio, Poster No: 24

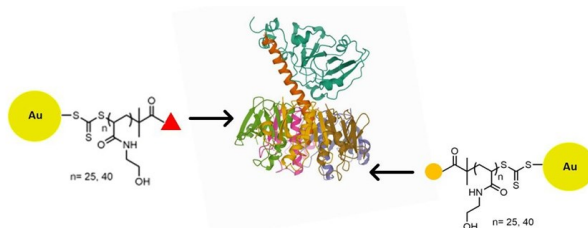
Cholera is an infectious disease that leads to severe dehydration. It is caused by the Cholera toxin, a protein secreted by the bacterium *Vibrio Cholerae*. Cholera toxin is composed of two subunits: the subunit A is the active part, responsible for the intoxication; whilst the pentameric subunit B (CTxB) is non-toxic but is responsible for the recognition of cellular receptor GM1 ganglioside on the surface of intestinal epithelium mammalian cells and therefore it initiates the cellular intake of the protein.ⁱ Each monomer of the pentameric subunit B has one galactose recognition domain which binds to the terminal galactose unit on GM1 ganglioside. In the last few years, another binding site was discovered. These are fucose recognition domain and they cooperate in the intoxication by binding fucosylated histo-blood group antigen on epithelium cells.ⁱⁱ We propose a strategy for the identification of CTxB by targeting both these distinct sites to increase the selectivity, compared to the large number of other galactose-binding lectins. Our biosensor is based on glycopolymer functionalised gold nanoparticles, which generate a colourimetric re-

The degree of polymerization was varied to balance colloidal stability (to stop aggregation in saline) whilst ensuring a rapid binding response. Using a panel of lectins, the binding responses of these hybrid polymer-inorganic biosensors is evaluated and will be discussed.

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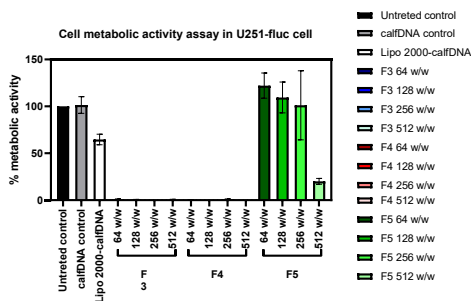
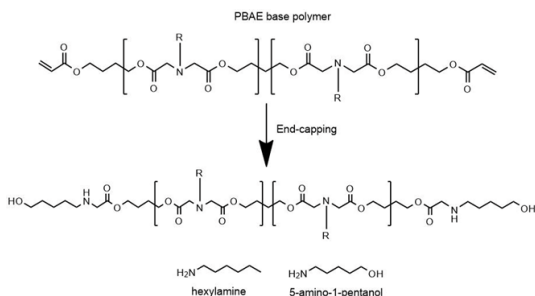
Preliminary study of the modified Poly(β -amino ester)s (PBAEs) for gene delivery in glioblastoma

Supisara Jearranaiprepame, Poster No: 25

Glioblastoma (GBM) is the most invasive and aggressive primary brain tumor with highly molecular and cellular heterogeneity and gene mutation, leading to high number of resistances to therapy and tumor recurrence. Recently, gene therapy such as small interfering RNA (siRNA) is a novel approach to silence the gene associated with progression of cancer. However, the efficiency of siRNA is limited by degradation with enzyme, renal filtration, and their off-targeting effect. One strategy to overcome the limitation is polyplex complexation with polycationic polymer. This study aims to synthesis and modify Poly(β -amino ester)s (PBAEs) polymer for improving the efficiency of gene transfection into glioblastoma cell. It is hypothesised that rising of the hydrophobicity in polymer chain probably promotes the transfection efficiency into GBM cell. Nevertheless, the cytotoxicity of polymer has been considered.

The current work synthesis PBAEs with variety of the hydrophobic properties of polymer chain using different type of amines (5-amino-1-pentanol and hexylamine) by Michael addition reaction and end-capped with 5-amino-1-pentanol. High molecular weight PBAEs analyzed using gel permeation chromatography (GPC) were explored in polymers different percentages of 5-amino-1-pentanol amines 50, 75 and 100, respectively. The molecular weights (Mws) of the obtained polymers are closed to each other i.e. 7100, 7900, and 7200, respectively.

The high Mw polymers were then used to prepare polyplex with calf thymus DNA at different polymer:calfDNA w/w ratios (from 8:1 to 256:1) and their physiological characteristics were screened. All polyplexes possess positive charges. The particle size of polyplexes were small size (less than 250 nm) and PDI value (less than 0.2) when polymer concentration is approximately more than 128:1 in all formulations. However, the screening of polyplexes in the metabolic activity assay demonstrated contrast with our hypothesis. The polyplexes prepared from hydrophobic polymer provided high toxicity in U251-fluc cell whereas PBAE polyplex containing only 5-amino-1-pentanol gave a good metabolic activity. Nonetheless, increasing of polymer concentration trending to increase of cytotoxicity.



Polymer/ Metal Oxide Hybrid Latexes Prepared via Surfactant-Free RAFT-Mediated Polymerization

Meshari Abdullah M Alqarni, Poster No:26

Polymer/inorganic hybrid nanomaterials have gained growing interest over the last 20 years.¹ These hybrid nanomaterials can provide good combination properties between the polymer and inorganic parts such as easy processing due to the polymer component and optical properties and/or thermal resistance imparted by the inorganic component. For instance, hybrid nanomaterials based on metallic oxide nanoparticles have a wide range of potential applications, from improving the thermal conductivity of a given medium to be utilized as a contrast agent for MRI. However, these nanoparticles suffer from stabilization issues which limit their application. Polymer encapsulation of nanoparticles utilizing controlled radical polymerization (CRP) can be an excellent approach to provide stability to metal oxide nanoparticles in a dispersed medium. Macro-RAFT copolymers were used as living stabilizers for metal oxides and chain extended to form a polymeric shell by emulsion/dispersion polymerization. A poly (lauryl acrylate₂₂-co-benzyl acrylate₁₂) (LA₂₂-co-BzA₁₂) macro-RAFT was used to stabilize and encapsulate CuO by dispersion polymerization of benzyl acrylate (BzA) in diisooctyl adipate solvent. On the other hand, emulsion polymerization of a mixture of methyl methacrylate (MMA) and butyl acrylate (BA) was carried out in the presence of a poly (2-acrylamido-2-methyl propane sulfonic acid-co-butyl acrylate) (AMPS₁₀-co-BA₇) macro-RAFT, employed to stabilize Fe₃O₄ nanoparticles in water. TEM characterization of the resulting latexes confirmed the formation of encapsulated metal oxide composite latex particles (Figure 1 and 2). Monomer feed composition, chain length and [CTA]/[Initiator] ratios were found to have important effects on the overall encapsulation.

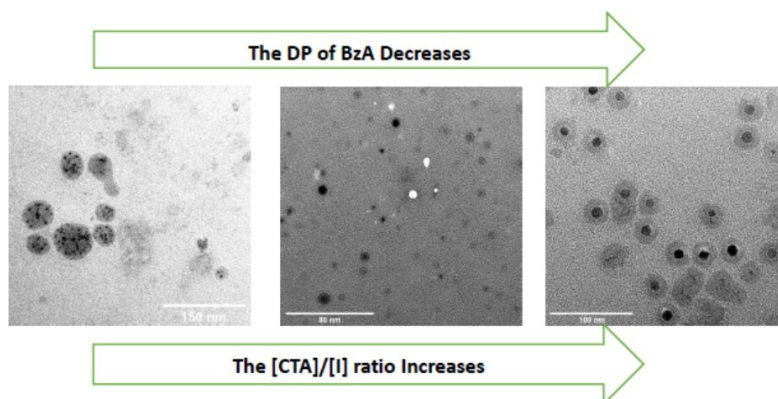


Figure 1. TEM images of CuO/polyBzA hybrid latexes in the presence of CuO clusters coated with P(LA22-co-BzA12) macro-RAFT agent

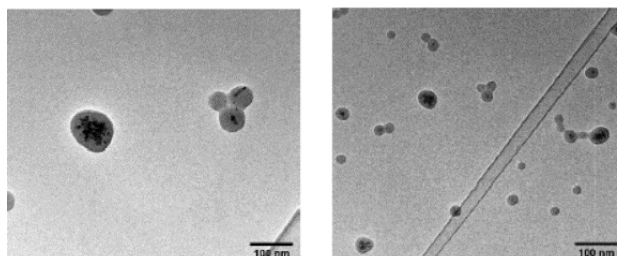


Figure 2. TEM images of Fe₃O₄ hybrid latexes obtained after emulsion polymerization of MMA/BA (90/10) (Semi-Batch) in the presence of Fe₃O₄ clusters coated with AMPS10-co-BA7) Macro-RAFT

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Linerless Pressure Sensitive Adhesives Made by Mixtures of Hard and Soft Polymer Colloids

Emily May Brogden, Poster No:27

A pressure sensitive adhesive (PSA) is a chemically non-reactive adhesive designed to stick to a surface upon contact and with light pressure.¹ One class of PSAs is made from water-based polymer dispersions and is of particular interest due to the limited volatile organic compounds released upon film formation.²

The main aims of this project are to design a collection of next generation PSAs. One project goal is to design a stick-on-demand PSA to be used in linerless labels. This new adhesive film would have no tack before activation at room temperature. However, once activated with heat, it would remain adhered to a substrate even after cooling to room temperature.

A series of binary latex mixtures comprised of hard (high T_g) latex particles and soft (low T_g) latex particles were film formed above the soft latex T_g (stage 1) and then cured above the hard latex T_g (stage 2). The hard particles form a 3D interconnected mesh network, shown via SEM and x-ray CT, where the pores are filled with the soft tacky polymer. At room temperature the hard structure isn't deformable but when heated above its T_g the mesh becomes compressible and the soft latex is squeezed out of the pores allowing adhesion to the substrate (stage 3). 34.5% hard content by volume in the adhesive film was found to produce tack when activated by heat (130 °C) but were non-tacky at 55 °C, typical conditions during transportation.

This has commercial significance due to the elimination of the need for a release coating and liner in the overall label design. This simplifies label design and reduces waste. Additionally, it would remove the silicones in the release coating from the label, which can complicate the recycling process, and may soon fall under the class of forever chemicals.

The project had a one-year (2020-2021) collaboration with UPM Rafilatac and a patent is in the filing process.

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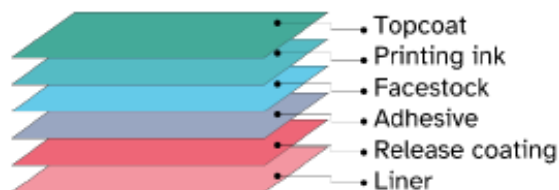


Figure 1: The general structure of an adhesive label. A new type of pressure sensitive adhesive would eliminate the need for the release coating and liner.

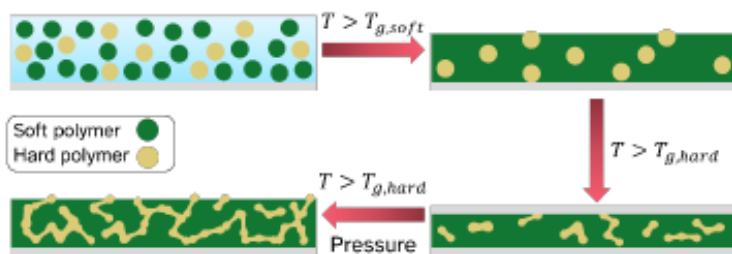


Figure 2: A graphical depiction of a 2D slice of the linerless PSA during film formation (stage 1), curing (stage 2), and activation (stage 3).

Facile & versatile covalently adaptable Diels-Alder networks for adhesive application

Jonathan Gregg, Poster No: 28

Bifunctional maleimide prepolymers and multifunctional furan crosslinkers were combined to form Covalent Adaptable Networks (CANs) that utilize thermally-reversible Diels-Alder bonds to create materials that benefit from the mechanical performance of thermosets and the reprocessability of thermoplastics. After heating above the retro Diels-Alder temperature for an hour, the network was dissociated and could be shaped or applied to a substrate. After 7 days at ambient

temperature or within hours of moderate heating, the network formed again with high conversion. The reformation of these bonds was followed via IR spectroscopy. These materials bonded and rebonded aluminium substrates multiple times with no significant loss of bond strength (figure 1).

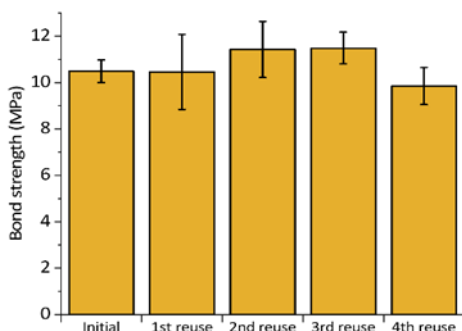


Figure 1: The effect of re-use on the bond strengths of a smart, thermally reversible crosslinked network on aluminium substrates.

Customizing the self-assembly of supramolecular peptide nanotubes via the linker group

Min Zeng, Poster No: 29

Peptides have widely used to generate synthetic materials mimicking natural nanomaterials and their fascinating properties. One path is to use the self-assembly properties of peptides to direct supramolecular assemblies into nanomaterials, although controlling such process is still challenging, especially when compared to the versatility of natural materials. Our group focuses on the use of cyclic peptide-polymer conjugates, which stack via hydrogen bonds between cyclic peptides to form nanotubes, with an outer shell functionality defined by the polymeric chains. Here, we present an innovative and facile strategy to regulate the self-assembly of these cyclic peptide nanotubes, by introducing hydrophobic interaction through a linker group positioned between the peptide and the polymeric conjugate (Figure 1). Both alkyl and aryl linkers were attached to poly(N,N'-dimethylacrylamide) (PDMA) and polyethylene glycol (PEG) before conjugation to the cyclic peptide. The hydrophobic interaction between linkers assists the self-assembly of cyclic peptide,

initially driven by hydrogen bonding, to form controllable nanotubes. We also investigated the introduction of an alkyl group with liquid crystalline (LC) mesogens, and its effect on the self-assembly into nanotubes. The interplay between hydrophilic interaction of polymer chain and hydrophobic and LC interaction of linker group, initially guided by the hydrogen bonding between cyclic peptides, are an effective strategy to control the self-assembly behaviour of these peptide nanotubes.

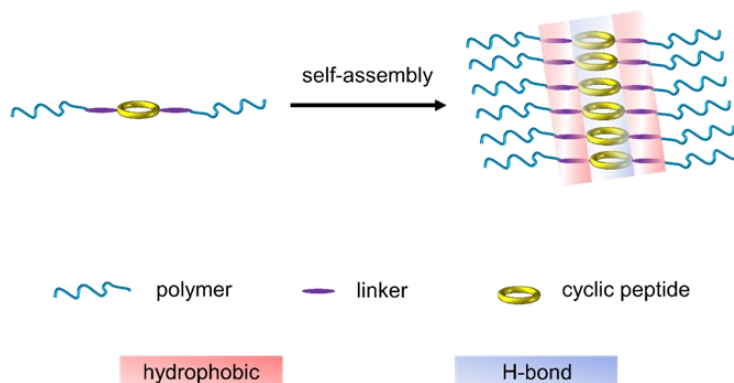


Figure 1. Scheme for the self-assembly of cyclic peptide-polymer conjugates.

Development of nanovectors for targeted delivery of p38 MAPK inhibitors to dendritic cells.

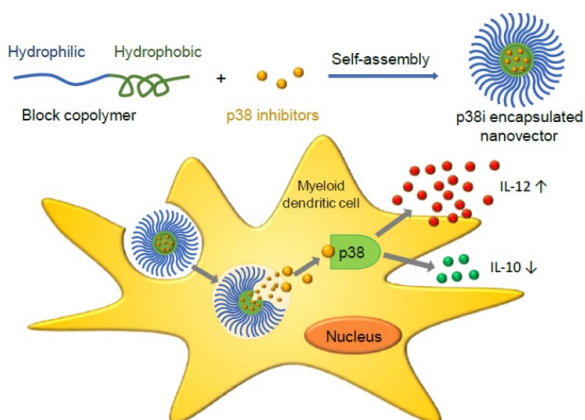
Jinge You, Poster No: 30

Dendritic cells (DCs) are antigen-presenting cells which play an important role in tumour immunity. However, the function of DCs can be suppressed due to specific conditions found in the tumour microenvironment.

Previous studies suggested that p38 inhibitors (p38i) can reverse dysfunction of tumour patient- derived dendritic cells in vitro. However, in addition to DCs, p38 is also expressed by a plethora human cells, thus treating patients with p38i may potentially lead to undesired off-target effects. Therefore, to improve drug efficacy and reduce side-effects in vivo, this work aimed at developing sugar-based nanovectors targeting lectin endocytic DC receptors for delivery of p38i to DCs.

To date, based on the chemical structure of BIRB796 p38i, we have designed and made a family of amphiphilic block copolymers including mannose, a DC targeting agent, and prepared stable nanoparticles with narrow size distribution and high drug loading efficiency, which did not show obvious cytotoxicity to human DCs. Moreover, Mannose receptor over-expressing Chinese hamster ovary (CHO) cells show obviously better uptake of nanoparticles than normal CHOs. Therefore, our polymers are potential materials for targeted delivery of p38i to dendritic cells.

In the future, biodegradable polymers will be made to improve biocapacity of our material, further cell culture experiments will be carried out to investigate internalisation of nanoparticles by DCs, DC activation ability and selectivity of nanoparticles.

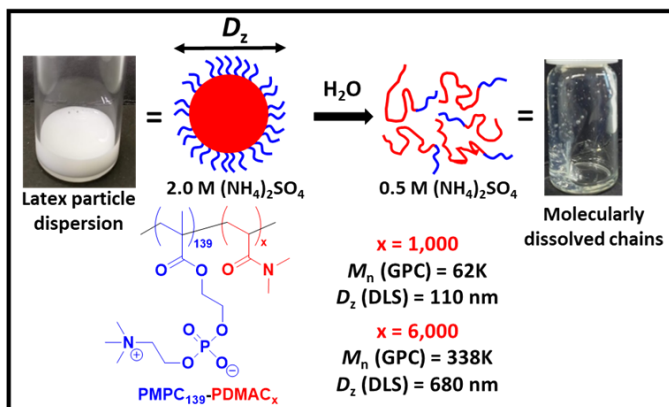


Synthesis of High Molecular Weight Water-Soluble Polymers as Low-Viscosity Latex Particles by RAFT Aqueous Dispersion Polymerisation in Highly Salty Media

Rory McBride, Poster No: 31

We report the synthesis of sterically-stabilised diblock copolymer particles at 20% w/w solids via reversible addition-fragmentation chain transfer (RAFT) aqueous dispersion polymerisation of N,N'-dimethylacrylamide (DMAC) in highly salty media (2.0 M (NH₄)₂SO₄). This is achieved by selecting a well-known zwitterionic water-soluble polymer, poly(2-(methacryloyloxy)ethyl phosphorylcholine) (PMPC), to act as the salt-tolerant soluble precursor block. A relatively high degree of polymerisa-

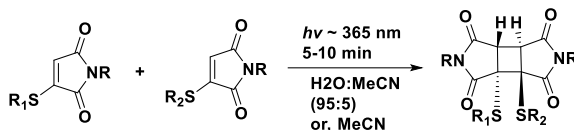
tion (DP) can be targeted for the salt-insoluble PDMAC block, which leads to formation of a turbid free-flowing dispersion by a steric stabilisation mechanism. ^1H NMR spectroscopy studies indicate that relatively high DMAC conversions ($>99\%$) can be achieved within a few hours at 30°C . Aqueous GPC analysis indicates high blocking efficiencies and unimodal molecular weight distributions, although dispersities increase monotonically as higher degrees of polymerisation (DPs) are targeted for the PDMAC block. Particle characterisation techniques include dynamic light scattering (DLS) and electrophoretic light scattering (ELS) using a state-of-the-art instrument that is capable of accurate measurements in concentrated salt solution. ^1H NMR spectroscopy studies confirm that subsequent dilution using deionised water lowers the background salt concentration and hence causes in situ molecular dissolution of the salt-intolerant PDMAC chains, which leads to a substantial thickening effect and the formation of transparent gels. Thus this new polymerisation-induced self-assembly (PISA) formulation enables high molecular weight water-soluble polymers to be prepared in a highly convenient, low-viscosity latex-like form. In principle, such aqueous PISA formulations are highly attractive: there are various commercial applications for high molecular weight water-soluble polymers while the well-known negative aspects of using a RAFT agent (i.e. its cost, colour and malodour) are minimised when targeting such high DPs.



Exploiting monothiomaleimide [2+2]-photocycloaddition in linear polymers and network formulation.

Mohammed S. M. Aljuaid, Poster No: 32

Maleimides have been reported to undergo [2+2]-photocycloaddition reaction in organic and polymer fields. The wavelength required for maleimides to follow [2+2] photocycloaddition was found to be approximately 270 nm, and the reaction completion could take up to 1 hour, while the addition of photosensitiser led to accelerating the [2+2] photocycloaddition of maleimides. Recently, it has been published that substituting the maleimide double bond with thiol group in one position, forming monothiomaleimide, led to complete conversion of the [2+2]-photodimer within only 5-10 minutes without any additives and in water/acetonitrile (95:5) mixture at concentration as low as 72 μM (Scheme 1).¹ Subsequently, these monothiomaleimides have been utilised for rebridging disulphide bonds of biomolecules in few minutes under 365 nm without observing any side products formed due to the degradation of biomolecules during the irradiation of their solution to UV light.²



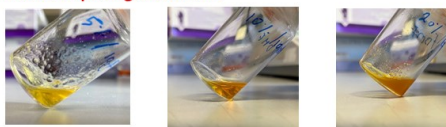
R = Linear polymers, aliphatic chains.
 R_1, R_2 = Hexyl, polymers, biomolecules.

Scheme 1. [2+2]-photocycloaddition of monothiomaleimide (Baker et al, 2012).

Herein, monothiomaleimide has been attached to linear hydrophilic polymers, and the functionalised polymers have been coupled after exposing their aqueous solution to UV light (320-390 nm). The reaction was characterised by ^1H NMR, GPC, and MALDI-ToF-MS.³ Afterwards, monothiomaleimides were attached to polyacrylamides as side chain groups. The pre-gelation polyacrylamides were characterised by ^1H NMR, GPC, FT-IR, as well as UV-Vis spectroscopy. Subsequently, these polymers were exposed to UV light (365 nm), owing photocrosslinked scaffolds due to the [2+2] photocycloaddition of monothiomaleimides (Fig. 1). These scaffolds were characterised by the mechanical and rheological tests as well as swelling behaviour.

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Before exposing to 365 nm:



After exposing to 365 nm:



Figure 1. The functionalised polyacrylamides solution before gelation (top), and after gelation by exposing them to UV light (365 nm) (bottom).

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Materials for Bioelectronic Applications

Rachel Lee, Poster No: 33

A robust hydrogel scaffold which is stable in water over several weeks and based on a naturally occurring glycosaminoglycan is presented. The scaffold is based on material naturally occurring in the body and thus provides an inherently biocompatible starting material with predetermined routes of biodegradation. The physical properties of the material were manipulated by crosslinking the polymer chains, allowing the gel to be fine-tuned to the softness of a specific tissue and to prevent rapid degradation. Here, the mechanical properties of the spinal cord are targeted. Such a scaffold can be used to improve the mechanical properties of a bioelectronic device which alone does not display compatible properties. An electronic device which can be used *in vivo* can provide information about intercellular communications, such as how the human nervous system responds to stimuli by passing a chemical signal through a series of neurons. The scaffold is being developed as an organic electrochemical transistor which could mimic this signal. The conductive polymer poly(3,4-ethylenedioxythiophene), PEDOT, forms the active layer in this device, however it is not biodegradable and is mechanically different from the spinal cord. However, the scaffold does present a natural dopant to PEDOT.

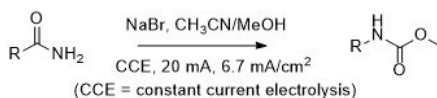
Functional polymers from sustainable electrosynthesis

Muzhao Wang, Poster No: 34

The overarching aim of this research is to develop more sustainable routes to the synthesis and functionalisation of polymers. We will explore the use of electrosynthesis to investigate a recently reported electrochemical Hoffmann reaction (eHoffmann) whereby primary amides are employed as surrogates for isocyanates, to synthesise functional polymers and functionalise polyacrylamide scaffolds with nucleophilic reagents (e.g. alcohols and amines, Fig 1.). Successful functionalisation will result in libraries of novel polyvinyl carbamate and polyvinyl urea (co)polymers, the properties of which are largely unexplored, so the final part of the project will focus on the thermal and solution properties of these polymers. The feasibility of sustainable electrochemical polymer synthesis functionalisation will be established via the following objectives:

- Reproduce Hofmann Rearrangement of benzamide and methanol, discover the conditions towards high or full conversion.
- Explore the scope of the reaction using other amide and alcohol compounds e.g. aliphatic amides, ethanol and isopropanol etc.
- Investigate the synthesis of polyureathanes using bisamides and diols as monomers.
- Determine the electrochemical stability of acrylamide (co)polymers.
- Investigate the eHofmann reaction using acylamide (co)polymers by voltammetry.
- Prepare libraries of polyvinyl carbamate and polyvinyl urea (co)polymers and explore their properties.

Previous work



This work

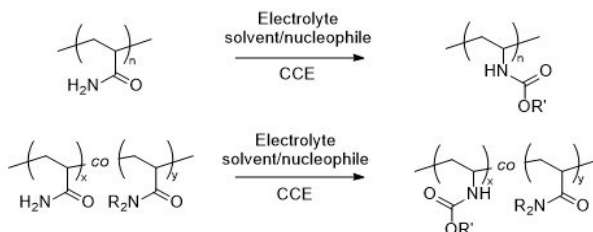


Fig 1. Reaction scheme for investigating the eHofmann

Incorporation of fillers to modify the mechanical performance of inverse vulcanised polymers

Veronica Hanna, Poster No: 35

Sulfur is a by-product of the refinement of crude oil and natural gas, produced at over 70 million of tonnes per annum, resulting in a surplus and large overground storage of elemental sulfur.¹ The process “inverse vulcanisation” as coined by Pyun et al. allows for the usage of high quantities of sulfur to synthesise inverse vulcan-

ised polymers.² Inverse vulcanised polymers have several applications such as construction materials,³ self-healing materials,⁴ IR transparent lenses,⁵ and heavy metal capture;⁶ however, they need to be further improved in their mechanical performance to widen their applications. Like with many conventional polymers, fillers can also be used to tailor the mechanical properties of inverse vulcanised polymers, for example, by increasing their tensile strength.⁷ The use of the polymer, sulfur-1,3-diisopropenylbenzene (S-DIB), as a model system for the addition of fillers (carbon black, cellulose microfibrils, and nanoclay) at 2-10 wt.% (weight percentage) and their effect on the mechanical properties of the resultant composite is reported herein.

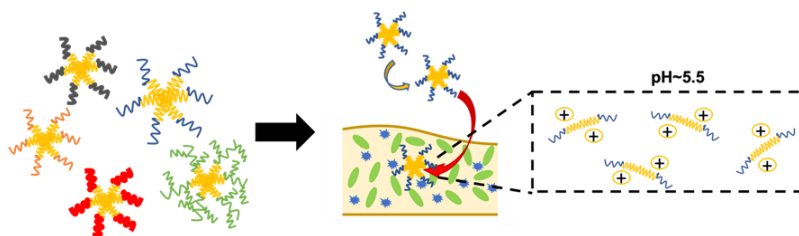
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Grafted poly(β -amino esters) as versatile scaffolds for biomedical applications

Karolina Kasza, Poster No: 36

To tackle the emerging antibiotic resistance crisis, novel antimicrobial approaches are urgently needed. Bacterial communities (biofilms) are a particular concern in this context, as they are responsible for most human infections and are inherently less susceptible to antibiotic treatments. A potential solution to overcoming the challenges associated with conventional antibiotic therapies is drug encapsulation within polymeric nanoparticles. Polymer drug carriers have been shown to enhance antimicrobial efficacy, permeation, and retention at the infection site, however all these advantages are dependent on their size, shape, charge, and functionality. In order to elucidate the optimal properties of the polymeric drug carrier we have developed a platform for the ubiquitous functionalisation of hydrophobic poly(β -amino ester)-based polymers with a range of copolymers of varying length, charge, size and hydrophilicity. This was achieved by developing a method for their copolymerization using a grafting-from approach, incorporating RAFT polymerization, by that achieving high control over the resulting copolymer molecular weights and molecular weight distributions. This versatile polymer functionalisation methodology will enable us to explore a wide chemical space of functionalities, by that establishing the optimal polymer properties needed for anti-biofilm activity. Following successful biofilm delivery the particles will then open through nitrogen protonation within the core poly(β -amino ester) chain, leading to the release of the encapsulated drug and biofilm eradication.



Synthesis of cationic polymers to exert antimicrobial activity

Natasha Reddy, Poster No: 37

We edge closer to a post-antibiotic era and the development of novel antimicrobials is urgently required. Without so the outlook is dire. The number of deaths attributed to microbial infections and healthcare procedures reliant on antimicrobials will rapidly accelerate. The failure of current antimicrobials due to the development of resistance indicates a sustainable replacement should be active against a broad-spectrum of pathogens while limiting the development of resistance. Turning to nature for inspiration has led researchers to antimicrobial peptides. These small peptides have been identified across multi-cellular organisms; they selectively target bacteria without the development of resistance due to their multimodal mechanism of action. Importantly, they have an amphiphilic structure with cationic and hydrophobic groups that are segmented on the final peptide structure. Unfortunately, the cost associated with their production, and displayed host toxicity are barriers to their widespread clinical application. Improvements in polymer chemistry have enabled the synthesis of polymer mimics of these natural peptides. These polymers are a promising platform for the development of the next generation of antimicrobials, they exert antimicrobial effects while overcoming limitations associated with the natural peptides.

In the present study a library of cationic polymers was synthesised via RAFT. This polymerisation technique allows complex polymers to be created. This enabled us to synthesise polymers mimicking both the segmented structure and the functional groups found in natural peptides. Analysis of the polymers indicated that synthesis was well controlled resulting in well-defined materials. Future work will be conducted to investigate both the antimicrobial effects and toxicity of the polymers created in this study.

Microplastic mimics produced using polymerisation induced self-assembly

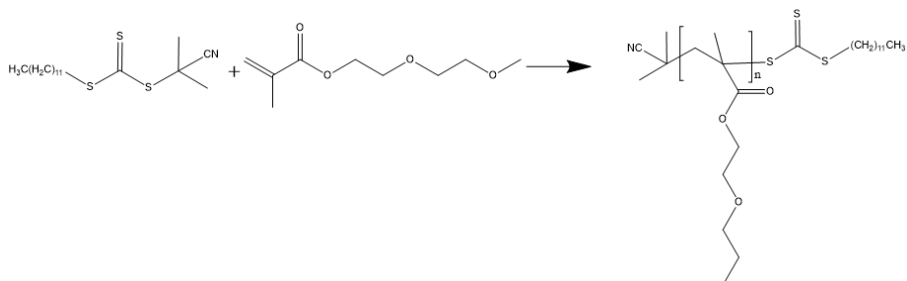
Beth Jordan, Poster No: 38

Microplastics have gained more attention recently due to the increase in awareness of the effects of plastic pollution on the global environment and on human health. The increased use of synthetic textiles in the last decades, coupled with recent emphasis on the accumulation of microplastic in the environment, has garnered interest into the effects of microplastic fibres.

The use of mimics is a popular way to study the effects of microplastics. These are polymer particles created specifically to study the effects of microplastics for different applications. Synthetic methods can be used to create particles where the morphology is controlled. However, this method currently has only been used to create spherical and 'raspberry-shaped' particles.^{3,4} Whilst representative of some types of microplastics they do not correspond to the different morphologies produced by microplastic fibres.

The aim of this project is to bridge this knowledge gap and to create microplastic mimics with 'fibre-like' morphologies produced via the synthetic method of RAFT-mediated PISA.⁵ This method produces a hydrophilic macro-CTA which acts as the outer shell of the worms and a hydrophobic core. Poly(di(ethylene glycol) methyl ether methacrylate) (PDEGMEM) has been chosen as the hydrophilic block and styrene as the core due to polystyrene being a common microplastic found in the environment. The production of the PDEGMEM macro-CTA (Scheme 1) resulted in 70% conversion in 7 hours with a \bar{M}_n of 1.25. This was then chain extended with DEGMEM to ensure the RAFT end groups remained active and therefore could be utilised further to produce the block copolymers. The next stage of this project includes creating A block copolymer of PDEGMEM-b-PMMA produced using RAFT mediated PISA. The ratio of the PDEGMEM-b-PMMA copolymer blocks will then be altered to produce non-spherical morphologies.

Future work of this project includes the use of styrene as the core to better mimic microplastics found in the environment and different macro-CTAs to change the charge of the outer shell of the worms. These microplastic fibre mimics will then be used to investigate how the effect of the shape of the microplastic affects cells.



Scheme 1. The production of the macro-CTA produced using di(ethyl glycol) methyl ether methacrylate and 2-cyano-2-propyl trithiocarbonate.

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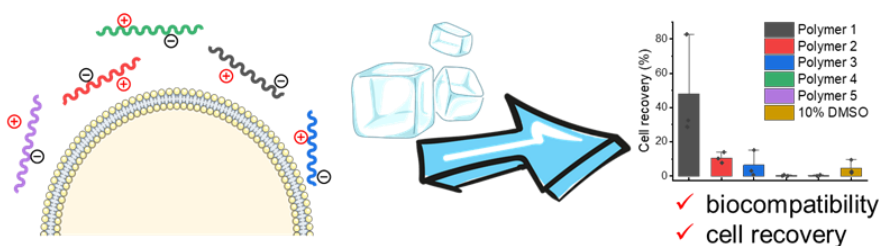
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Why are polyampholytes so good at freezing A549 cells?

Qiao Tang, Poster No: 39

Cell cryopreservation plays an essential role in cell-based therapies, cell banking and organ transportation by providing high quality of storage and transportation of frozen cells. However, it suffered from partial cell recovery rate and intrinsic cytotoxicity by conventional cryoprotectant, high percentage of DMSO1. Inspired by nature, polymers are introduced as cell cryoprotectant agent by mimicking natural antifreeze protein (AFP), which gives relatively better performance on freezing cells, including monolayer freeze2.

Polyampholyte is one type of polymer which protects monolayer cells very well from freezing damage with unclear mechanism^{3–5}. During cryopreservation process by polyampholyte, positive charges on the side chain promote its interaction with negatively charged cell membrane but also induces cytotoxicity; while at the same time, negative charges of it do the opposite way, to decrease cytotoxicity and cryoprotection efficiency. Polyampholyte with both negative charges and positive charges produces a well-balanced situation for well freezing cells at high biocompatibility. Nevertheless, how side chain structure of polyampholyte would affect cryoprotection efficiency remained poorly explored. Herein, we designed and synthesized five differently structured polyampholytes, using combinatorial of positively charged and negatively charged monomers (Scheme 1). In our work, we focused on distinguishing positive charge effect between tertiary amine and quaternary amine, and negative charge effect between carboxy and sulfo group (Figure 1a). We then use these five polyampholytes to freeze A549 monolayer and expected different cell recovery rate in the presence of comparable biocompatibility of them (Figure 1c and 1d). We aim to explore structure-efficiency relationship behind polyampholytes on monolayer freeze in the future.



Scheme 1. Illustration of polyampholytes for monolayer freeze.

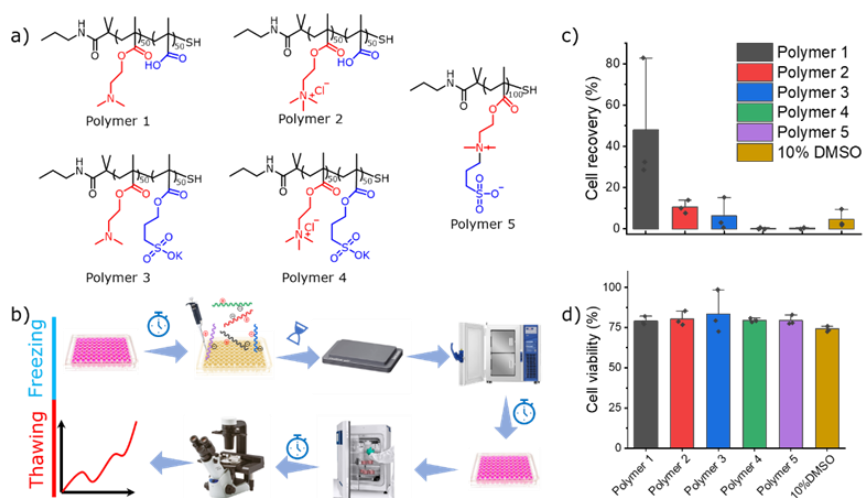


Figure 1. Chemical structure of polyampholytes and its cryopreservation efficiency on freezing A549 monolayer. a). Chemical structure of five polyampholytes. Positively charged side chain was labelled as red and negatively charged side chain was labelled as blue. b). Workflow of freezing A549 monolayer by polyampholytes. Briefly, cells were incubated with polyampholytes for 10 mins before freeze. We calculated 24-hour post thaw cell recovery rate by using cell counting under optical microscope. c). 24-hour post thaw cell recovery rate of A549 monolayer by five polyampholytes at 40 mg/mL. 10% DMSO was used as positive control. d). Cytotoxicity of five polyampholytes on A549 cells. A549 cells were incubated with each polymer at 40 mg/mL for 30 mins and then were changed with fresh media to allow additional 24-hour incubation at 37 °C. Cell viability of A549 cells were measured by resazurin assay.

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Unlocking the macrophage: Lipid-terminated glycopolymers as liposomal targeting ligands

Benjamin Fiedler, Poster No: 40

Macrophages have been identified as key drivers of auto-immune disease (e.g. rheumatoid arthritis, lupus) through the production of pro-inflammatory cytokines (e.g. TNF α). There is great potential to treat these diseases by silencing such cytokine production through siRNA therapy. However, siRNA require an appropriate drug delivery system as they; (1) are rapidly degraded in the blood by enzymes and (2) as large, charged molecules they do not readily cross the cell membrane into the cytosol where they are active.

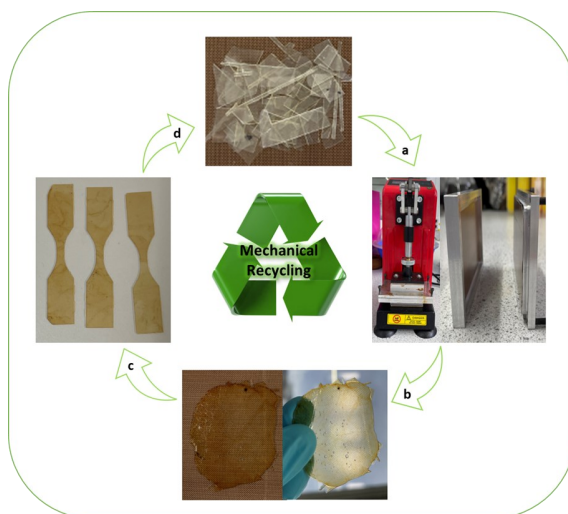
Towards these goals, we have developed a liposomal nanoparticle system capable of complexing with siRNA. These liposomes have been decorated with lipid-terminated glycopolymers which will act as targeting ligands. The use of a synthesised cholesterol-based RAFT agent has resulted in short polymers (high conversion, low \bar{M}_n) that are end functionalised with cholesterol to allow incorporation into the surface of the lipid nanoparticle. Use of a synthesised mannose-acrylamide monomer results in polymers that each display multiple mannose residues to increase the binding (and therefore uptake) of the liposomes by exploiting the multiple binding sites (multivalency) of the endocytic mannose receptor, found on the surface of macrophages.

These polymers have successfully been formulated into 100 nm cationic liposomes (alongside the lipids DOPE and DC-Cholesterol). The polymer chain length, density of these polymers, and formulation of other lipid components of these liposomes have been systematically varied. In vitro assays using a model multivalent receptor (Con-A) have found strong positive correlations between rate of binding and density/length of glycopolymer chain. Lipid content has also been optimised for binding to Con-A. Dynamic light scattering results also indicate that polymeric ligands also reduce nanoparticle aggregation through steric stabilisation.

Recyclable, high performance thermoset polymers from dynamic epoxy-amine-boronic ester hybrid networks

Lynn Anderson, Poster No: 41

A process for preparing a recyclable and dynamic epoxy thermoset via a simple one pot synthesis is presented. This method involves exploitation of b-amino diol, resultant of the synthesis of typical epoxy-amine polymers, with dynamic boronic ester bonds as a reversible crosslinking hardener to form thermosets. The described dynamic network exhibits excellent chemical resistance and mechanical properties comparable to traditional epoxy-amine equivalents. However, the dynamically formulated networks can be reprocessed under various stimulus, unlike their traditional counterparts. Reprocessability is demonstrated through both mechanical and chemical methods ascertaining versatile and practically simple recycling prospects suitable for reduction of waste upon commercial usages. Mechanical repurposing involves associative intramolecular boronic ester transesterification, reforming dioxazaborocane crosslinks upon heating above the glass transition, allowing reshaping and self-healing. Chemical recycling is realized through simple equilibrium manipulations using commercially viable, readily available diols and monoboronic esters as well as being susceptible to acid-base control. Chemical recycling has been proven by $^1\text{H-NMR}$ analyses and further supported by gel permeation chromatography (GPC).

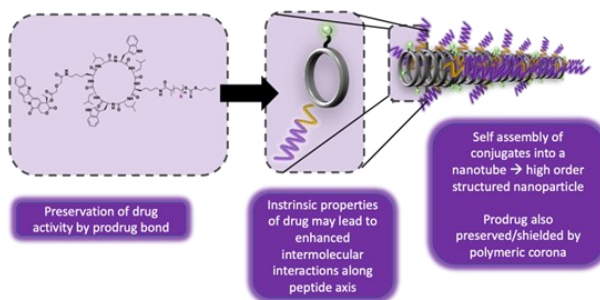


Cyclic Peptide – Polymer Conjugates for Drug Delivery Applications

Sophie Hill, Poster No: 42

Many nanoparticle designs often mimic the structures we observe in nature and operate on the principle of a 'bottom up' modular synthesis whereby the properties of the individual components can be translated to the non-covalent macromolecular architecture. By careful selection of building blocks, a set of detailed instructions for the layer - by - layer spontaneous assembly can be written. Typically, many anti-cancer drugs have hydrophobic, aromatic or hydrogen bond donor/acceptor features capable of intermolecular interactions that result in random aggregation and poor solubility. However, these same hindrances can be exploited by small modifications (with peptides, charges, fatty acids, polymers, targeting moieties etc.) to produce amphiphiles which self-assemble into a useful delivery vector, i.e. drug – peptide conjugates. In parallel, since the polymer – prodrug model reviewed by Ringsdorf in 1975, conjugation of drugs to polymers for therapeutic application has now advanced from needing simple coils for shielding and solubility, to highly complex and functional polymeric nanoparticles guided by drug – drug interactions. Thus, we here have an opportunity to use drug molecules as a guiding component of supramolecular polymeric systems. Cyclic peptide – polymer conjugate nanotubes offer an interesting new opportunity to utilize nanomaterials with high aspect ratio as drug delivery vehicles. Attachment of various hydrophilic polymers to control aggregation and improve water solubility means a high degree of versatility in manipulating these structures is possible. The supramolecular self-assembly of conjugates into nanotubes results in a prolonged circulation time in vitro and in vivo, giving rise to higher cellular uptake at target tumor sites, whilst also permitting eventual clearance from the body. Moreover, covalent conjugation of hydrophobic anti-cancer drugs onto the nanotube at various possible sites via cleavable linkers will allow tunable release for improved efficacy when compared to encapsulation-based systems. In this project, both the structural architecture and drug loading/release mechanism can be systematically modified to generate a blueprint for the most efficient drug delivery treatment using these materials. We elected to optimise the existing design by incorporation of topoisomerase I inhibitor, camptothecin, via two distinct prodrug linker chemistries, and modification of RAFT (Reversible Addition- Fragmentation Chain- Transfer) polymer properties, finding that both factors are highly influential on the drug hydrolysis profile in a biological

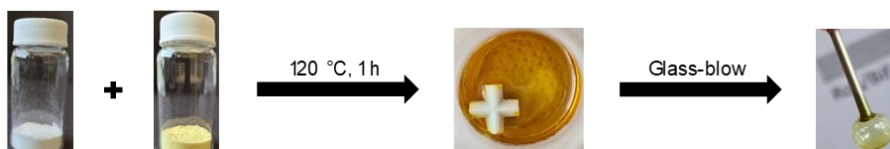
medium. Following this the synthetic protocol, self-assembly properties and in vitro performance of the nanotubes are thoroughly investigated.



Small Molecule Organic Glasses as Replacements for Polymers in Colloidal Delivery Systems

Josh Ryan, Poster No: 43

Legislative change and shifting consumer behaviour is driving a need for innovation within the colloid formulation sector. Polymeric materials are commonly used as storage and delivery matrices. However, these are often non-degradable and pollute our environment, especially since most global waste-water streams are not closed-loop. We believe that molecular glasses made from mixtures of small organic molecules provide an attractive alternative preserving, or even improving upon, desirable physical properties of polymers (barrier, moldability, fragility).



Synthesis and characterization of quaternised poly(amidoamine) qpABOL in a combination of PGA for highly efficient delivery of saRNA

Nazgol Karimi Dastgerdi, Poster No: 44

Gene delivery requires an efficient vehicle to transfer the genes to the target. Naked genes cannot cross cell membranes as a result of their size, charge, hydrophilicity, and degradability. Cationic polymers have been developed for gene delivery. The high positive charge density of Cationic polymers can condense the negatively charged gene by electrostatic interaction and form polyplexes and protect the genes from degradation.

Reducible cationic polymers can be cleaved by their disulfide bonds and release the gene intracellularly and improve transfection efficacy. One such example are cationic poly(amidoamines) (pAMAM) synthesized by aza-Michael polyaddition between disulfide containing bisacrylamides and primary amines.

The high positive charge of the cationic polymer is the main strength for gene entrapment and endosomal escape, but it can also cause cellular toxicity due to interactions with the negative lipid membrane. We hypothesised that by incorporating a third component (other than the nucleic acid and cationic polymer) such as second polyanion, we may be able reduce the toxicity of such delivery systems. To this end we investigated the impact of incorporating poly(γ glutamic acid) (PGA), a naturally occurring polyanion.

For our polycation, we synthesised a new quaternised pAMAM qpABOL to improve encapsulation via charge attraction with nucleic acids (Figure 1A). Formulations were then prepared with different ratios of the quaternised pAMAM, qpABOL, and non quaternised pAMAM, pABOL and complexed with a luciferase encoding self-amplifying messenger RNA and negatively charged (Figure 1B.) We identified that by decreasing the ratio of the qpABOL the size was increased and the zeta potential was decreased. The gel electrophoresis shows that using a more amount of the qpABOL leads to a more saRNA encapsulation. In conclusion, using quaternized pABOL could be an effective cationic polymer for preparation of the qpABOL/PGA/saRNA ternary complex. qpABOL in comparison with pABOL can reduce the ternary complex size and improve the saRNA entrapment efficacy.

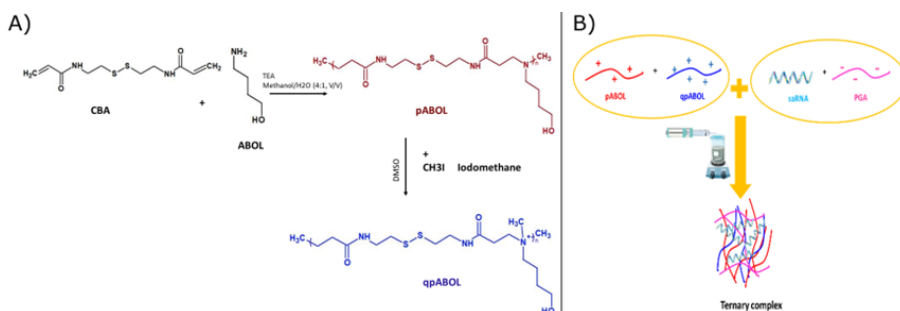


Figure 1. Schematic scheme for A) pABOL and qpABOL synthesis, B) ternary complex preparation

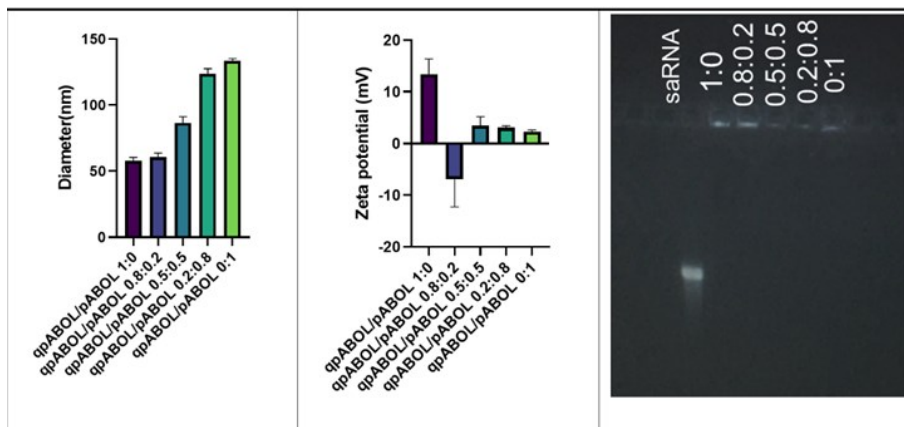


Figure 2. The ternary complexes with the N/C/P ratio of 50:1:1 were prepared. Different ratio of qpABOL to pABOL as cationic polymer were used (1:0, 0.8:0.2, 0.5:0.5, 0.2:0.8 and 0:1). A)size, B)zeta potential and C)agarose gel electrophoresis of these ternary complexes were measured.

Synthesis and Modifications of Polybutadiene Under Continuous Flow With Real-Time NMR Analysis, Online Monitoring and Self Optimisation using AI.

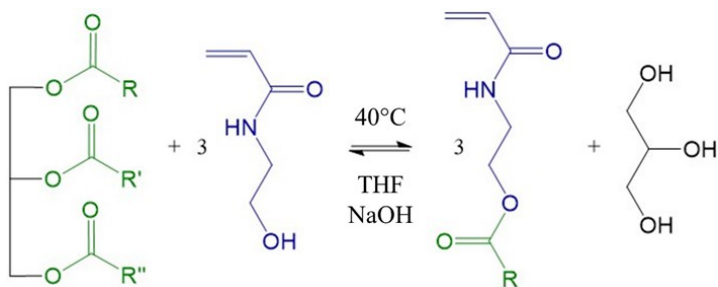
William Pointer, Poster No: 45

The synthesis of polyisoprene and polybutadiene via anionic polymerisation with selective termination is of particular interest for potential utilisation as dispersants and surfactants. This work will describe the synthesis of polydienes with tuneable stereochemistry, at predictable molecular masses with a variety of head-groups via selective termination and chain functionalisation with and without hydrogenation. Polymerisation, modification and hydrogenation will be described in flow as well inclusion of real time analysis with Flow NMR and self-optimisation of flow conditions with digital decision making.

Synthesis of vinyl monomers from commercial olive oil via transesterification with N-hydroxyethyl acrylamide

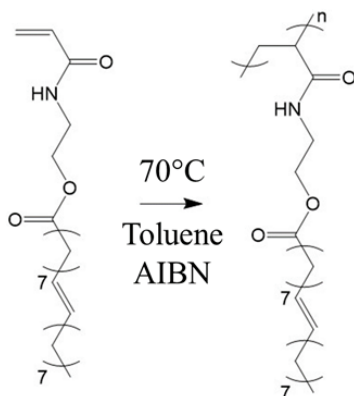
Oliver Harris, Poster No: 46

Plant oils are an abundant renewable resource that have been demonstrated in the literature^{1 2} to be a suitable feedstock for polymers with interesting properties (low T_g , hydrophobicity, functionalisation of unsaturations in pendant groups). The aim of this project is to synthesise plant oil based monomers (POBMs) and investigate the properties and applications of the resulting polymers³. A one-step transesterification reaction of commercial olive oil with N-hydroxyethyl acrylamide (40° C, 3h, NaOH catalyst, THF cosolvent) (see Scheme 1)¹ was performed to obtain a high purity monomer (>95%) suitable for radical polymerisation.



Scheme 1: Transesterification of commercial olive oil with N-hydroxyethyl acrylamide

A free radical polymerisation was conducted in toluene using 2,2'-azobis(2-methylpropionitrile) as an initiator with 25% w/w olive oil monomer at 70°C for 3h (see Scheme 2)¹. A conversion of 87% was achieved and ¹H NMR spectroscopy confirmed that unsaturations in the fatty chain were not significantly affected by the polymerisation. A range of monomers with different molecular weights or different degrees of unsaturation can be synthesised based on the choice of oil feedstock which could allow for simple tuning of the polymer's properties. Copolymerisation of POBMs with higher T_g or hydrophilic blocks will be performed to produce materials that may be of interest in applications such as adhesives, bulk thermoplastic elastomers and as rheology modifiers.



Scheme 2: Free radical polymerisation of olive oil monomer

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Investigation of novel addition fragmentation monomers to improve the properties of 3D-printer resins

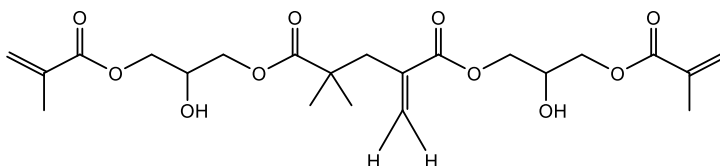
Zhongyuan Wan, Poster No: 47

Photopolymerization-based 3D printing techniques include stereolithography (SLA), digital light processing and continuous liquid interface production. SLA is based on UV laser and resin and is a very suitable method to fabricate accurate and complex structures.

Addition fragmentation monomers have a dimethacrylate structure. When is mixed, in different concentrations, with stereolithography resins it could potentially improve the properties of the 3D printed products. The dimethacrylate AFM that participates readily in network formation by copolymerizing with multifunctional meth-

acrylates or acrylates will be useful for this application. As the addition fragmentation monomer (AFM) has methacrylate functional groups on each end, each monomer is ready to integrate into the network structure, which contains methacrylate groups.

These novel AF (AFM-1) crosslinkers are added to polymer resin systems (both commercial and specially formulated for this project) for 3D printing. Moreover, 3D-printed objects were evaluated and the effect of unstable bonds introduced by adding crushing monomers on the physical properties of the photocured resin were studied.



This process of forming and breaking covalent bonds via a RAFT process during photo printing and subsequent photo curing while the overall network is being generated can go on repeatedly, promoting the approach to a thermodynamic sink reducing shrinkage and thus hopefully reducing stress during polymerization through the continual reshuffling of covalent bonds, inevitably leading to a stress relief and improved mechanical performance.

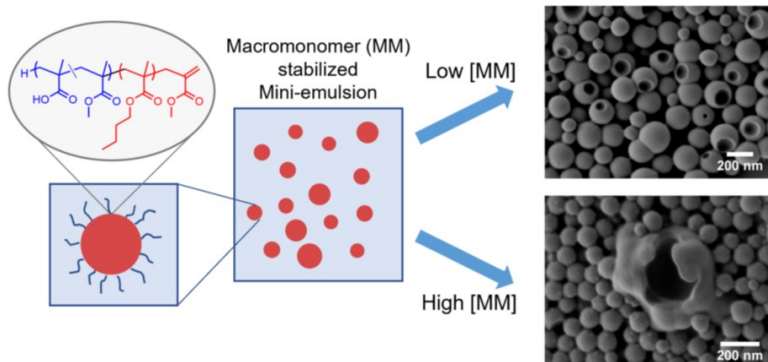
This project focuses on the synthesis of a new family of functional monomers and copolymers. Those products can be used as crosslinkers as they contain addition fragmentation (AF) sites and if mixed with resins in stereolithography. they can lead to dynamic covalent bonds during the manufacture. The new AF molecules can be combined with both commercial and in house resins and used with a photopolymerization process, with the aim of improving the physical and chemical properties of the final products. As the use of addition fragmentation monomers (AFM) increases, we will develop copolymers which will make us to produce new materials with specific properties and controllable sizes for different applications.

ω -Unsaturated methacrylate macromonomers as reactive polymeric stabilizers in mini-emulsion polymerization

Joshua D. Davies, Poster No: 48

Polymer latexes of poly(benzyl methacrylate) P(BzMA) were synthesized by mini-emulsion polymerization, using hexadecane as the hydrophobe and ω -unsaturated methacrylate- based macromonomers as a reactive stabilizer. The amphiphilic macromonomers were synthesized by catalytic chain transfer emulsion polymerization (CCTP) and subsequent chain extension via sulfur-free reversible addition–fragmentation chain transfer (SF-RAFT). Their critical micelle concentration (CMC) was determined by dynamic light scattering (DLS), and micelle size was measured using DLS and small angle X-ray scattering (SAXS). The surface activity of the stabilizers was measured by pendant drop tensiometry and compared to modelled behaviour. For the mini-emulsion polymerizations, macromonomer stabilizers were added at a range of concentrations, with respect to the dispersed phase. Using less than 5 wt% stabilizer, SEM micrographs showed many of the particles were bowl-shaped. This morphology was studied in depth and we propose that monomer transport occurs between particles during polymerization towards the smaller particles as a direct result of compartmentalization. At concentrations of 5 wt% and higher, bimodal droplet and particle distributions were observed by DLS and SEM. We propose shear- dependent depletion flocculation as the explanation. Lastly, the effectiveness of the reactive stabilizers was tested in terms of latex stability and molecular weight control. Resistance to coagulation during freeze–thaw cycles and prolonged dialysis were tested. Examination of P(BzMA) reaction kinetics and molecular weight indicated that the incorporation of macromonomer is gradual and less than quantitative at the end of the polymerization process, in agreement with the mechanistic understanding.

ω -Unsaturated methacrylate macromonomers as reactive polymeric stabilizers in mini- emulsion polymerization, J. R. Booth, J. D. Davies and S. A. F. Bon, Polym. Chem., 2022, 13, 1335–1349.



Responsive Nanotubes from Asymmetric Cyclic Peptide-Polymer Conjugates

Zihe Cheng, Poster No: 49

Tubular nanomaterials are omnipresent in nature, with application varying from structural to biological. Nature has evolved a variety of designs, from helical structures such as the natural antibiotic gramicidin A to proteins assembled like barrel stave structure as in the cholera toxin. Inspired by these self-assembly strategies, our project is exploring the use of self-assembling cyclic peptides (CPs), which supramolecular stacking leads to nanotubes of defined inner diameter and guided functionality. CPs stack into supramolecular cyclic peptide nanotubes (SCPNs), driven by antiparallel β -sheet hydrogen bonding. Conjugating polymers of controlled size and functionality onto cyclic peptides enable the construction of nanotubes with well-defined functionalities and properties. Our group previously reported Janus cyclic peptide-polymer nanotubes with dual functionality through the attachment of two different phase-separating polymers onto the cyclic peptide cores, which provided a new strategy in the synthesis of transmembrane channel mimics [1]. We have also harnessed these structures to develop novel structures called tubisomes[2], based on asymmetric cyclic peptide polymer conjugates, based on one hydrophobic and one hydrophilic polymer conjugates per peptide. These conjugates assembled in hierarchical structures, forming single CP nanotubes first, which then self-assemble into tubisomes via hydrophobic interactions.

Herein, we focus our study on responsive asymmetric cyclic peptide-polymer conjugates by the attachment of a series of responsive polymers such as tertiary amine-based (meth)acrylates and acrylamide monomers on one side of the CP, and a hydrophilic polymer on the other side of the CP. We have designed a family of responsive asymmetric cyclic peptide-polymer conjugates and established their applications as transmembrane channels, gene delivery and drug delivery.

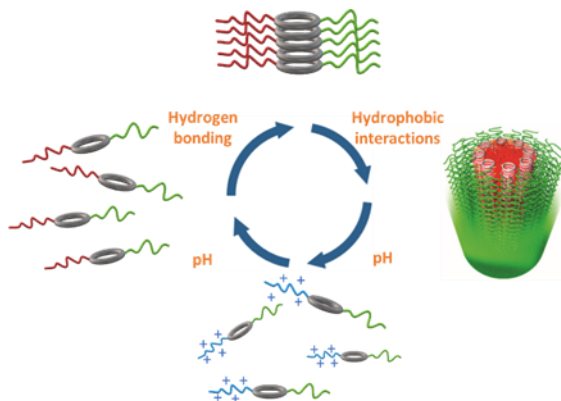


Figure 1. Schematic mechanism of pH-responsive asymmetric cyclic peptide polymer conjugates.

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Microwave-assisted Degradation of Polymers with Supercritical Carbon Dioxide for Plastic Recycling

Bradley Hopkins, Poster No: 50

Microwave radiation is able to heat a material to very high temperatures in a short timeframe. This makes it a very efficient technology for pyrolysis, capable of processing large amounts of material quickly.¹ However, polymers are poor microwave absorbers, due to their high molecular weight and varying degrees of crystallinity. This results in very inefficient heating.²

Supercritical carbon dioxide is a benign solvent that possesses the unique ability to

soften polymers and increase the free volume between individual chains. This makes it possible to modify the matrix of the polymer with relative ease, with supercritical carbon dioxide being an established solvent for both the impregnation of polymers with guest species 3, as well as the extraction of additives.⁴

Current work is focussed on using supercritical carbon dioxide to impregnate polyethylene terephthalate and bisphenol-A polycarbonate with small, polar molecules, as these are strong microwave absorbers. Dielectric measurements are then carried out to determine if the impregnated polymer has a stronger interaction with microwave radiation, compared to the unmodified polymer. This project has strong sustainable credentials as it aims to develop a route to degrade plastics at a very rapid rate, resulting from their modification in a non-toxic solvent where isolation of products from the medium can be achieved by simply de-pressuring the reactor.

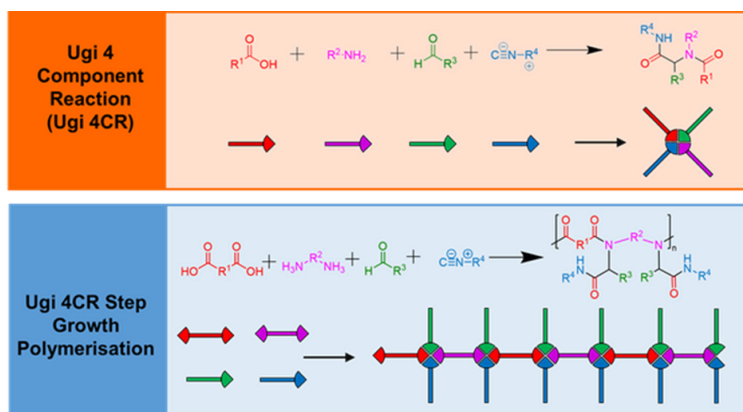
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Tuneable N-Substituted Polyamides with High Biomass Content via Ugi 4 Component Polymerisation

Daniel MacKinnon, Poster No: 51

The Ugi 4-component reaction (Ugi 4CR) is an efficient tool which benefits from high atom efficiency, compatibility with green solvents such as methanol, simple purification, and a water side-product. By using two bifunctional starting materials for Ugi-4CR, N-substituted polyamides can be prepared via a step-growth process. As polyamides play important roles in applications including films, coatings, and adhesives, the preparation of N-substituted functional polyamides from largely sustainable monomers is investigated. Herein, the combination of renewable diamine, diacid, and aldehydes with commercially available isocyanides yield polyamides with tuneable side chain functionalities and ~80% renewable biomass content. Rela-

tively high yields (up to 96%) are recorded for polymers of moderate molecular weights (M_w up to 8100 g mol⁻¹). The prepared polyamides possess backbones which exhibit excellent thermal stability ($T_{deg}=440 \pm 10$ °C), while functional side chains result in additional lower-temperature degradations (215-285 °C). Variation in side-groups enables shifting of the glass transition temperature (T_g) across the range 9 °C-38 °C and variation in hydrophobicity resulting in water contact angles ranging from 47 o-105 o. This work presents a reliable approach to prepare sustainable polymers with diverse side chain functionalities in a short reaction time and without need for a catalyst or complicated purification steps.



Poly(2-Oxazoline) Terpolymers with Tuneable Thermal Properties and Solution Behaviour in Non-aqueous Media

Zivani Varanaraja, Poster No: 52

Poly(2-oxazoline)s (POx) are an emerging class of polymers due to their high versatility and hence have proven to be beneficial in numerous applications. The living Cationic Ring-Opening Polymerization (CROP) of 2-oxazolines was first reported in 1966 and since then, there has been a plethora of research concerning POx. Their extensive study and interest are largely because this polymer class has a great synthetic flexibility and exhibit good biocompatibility, resulting in the synthesis of extremely functional material, particularly advantageous in biomedical applications. Although the thermoresponsive behaviour of POx have been studied in aqueous media, there are only limited literature on polymers with temperature sensitivity and solubility in non-aqueous media. Herein, a library of 21 tuneable POx has been synthesised and their thermal properties and solution behaviour in aqueous and

non-aqueous media have been investigated via thermal analyses (TGA and DSC) and turbidity measurements. The focus of this study is on the CROP of Fatty Acid Oxazoline (FaOx), 2-Phenyl-2-Oxazoline (PhOx) and 2-Ethyl-2-Oxazoline (EtOx). The CROP of EtOx has been researched considerably but there are only comparatively few studies on the CROP of PhOx and even fewer on FaOx. The copolymerisation of FaOx and PhOx and the terpolymerisation of the three monomers is herein reported for the first time, presenting an opportunity to utilize their interesting solution behaviour and thermal properties.

The Synthesis and Continuous Manufacture of Novel, High Performing Polymeric Lubricants for the Next Generation of Electric Transportation

Xiao Yuan Wang, Poster No: 53

Polyurea thickened greases have gained increasing interest, particularly in the lubrication of electric motor bearings, due to its inherent oxidative stability, high operating temperature and good mechanical stability. However, they can be difficult to manufacture due to the health and safety concerns of the starting materials (isocyanates). Additionally, both the grease thickener chemistry and morphology play an important role in the final grease properties. Previous attempts at defining the structure of a grease have largely involved removal of the oil component via organic solvents, which modifies the true structure. The alternative is to use cryogenic techniques; however, this is held back by challenging sample preparation. In this study, we explore the use of the less toxic polymeric isocyanates for the synthesis of polyurea. We also develop a method for in depth chemical and structural analysis of polyurea grease. Commercially manufactured polyurea grease will be investigated, with the potential to extend into the analysis of polyurea grease synthesised via less hazardous chemistries. Emphasis is placed on characterising the grease thickener without distorting the original microstructure, to relate the thickener chemistry and morphology to the final grease performance.

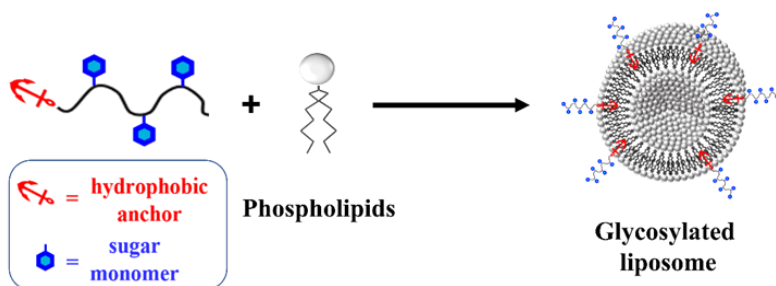
Glycosylated Liposomes for Cell-Targeted Delivery of Active Compounds

Roberto Terracciano, Poster No: 54

Receptor-mediated targeting is a promising approach to obtain selective delivery of active compounds (drug, antibiotics, nucleic acids, etc.). One particular method exploits the mechanisms of sugar recognition by lectins on specific cell types. Lectins are carbohydrate-binding proteins which are able to selectively recognise specific

sugar-ligands, decipher sugar-encoded instructions, and convert them into downstream biological processes. On the other hand, liposomes are lipid-based vesicles extensively developed over the last 30 years in order to encapsulate active agents for improving their therapeutic indices and making them available for human use. Sugar ligands and liposomes can therefore be combined to formulate potential carriers which, by exploiting the sugar-recognition mechanism, can assist in active targeting, thus enhancing the pharmacological effect and reducing the side-effects during therapy.

This work focussed on the use of glycosylated liposomal systems as promising vectors for active targeting.



The application of ion-pairs in the synthesis of sequence-controlled polymers

Toby Watts, Poster No: 55

Sequence controlled polymers are macromolecules in which monomer units of different chemical nature are arranged in an ordered fashion.¹ An ion pair is a species formed by the association of oppositely charged ions in electrolyte solutions.² This project aims to determine whether ion pairs with polymerizable functions would form strictly alternating copolymers as opposed to statistical copolymers. In order to control the sequence of a polymer using an ion pair you need to control the degree of association between the ions in the ion pair. Ion association can be directly correlated with the permittivity of solvents, e.g. a solvent with a high dielectric constant will result in an ion pair with a low ion association. Ideally ion pairs in low permittivity solvents will be closely associated and this in turn should lead to more alternating character.

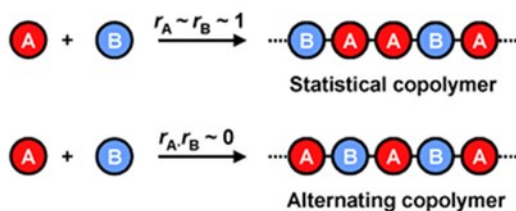


Figure 1 – Formation of a statistical and alternating copolymer.

We chose the two monomers for the ion pair because one was commercially available (3-sulfopropyl methacrylate potassium salt) and the other was easily synthesised (triethyl vinylbenzyl ammonium chloride). These two monomers were then used in a random copolymerisation (figure 2a) and to form an ion pair which was polymerised (figure 2b). So far, we have looked at using a number of different solvents to control the association constant of the ionic species and confirmed this by measuring relative diffusion coefficients by DOSY NMR. It was expected that the free radical polymerisation of ion-pair comonomers in less polar solvents (e.g. dioxane) would result in higher alternating character than in more polar solvents (e.g. water) as a consequence of the changes in the association constant. To confirm this change in the sequences the copolymers were analysed by ^1H and ^{13}C NMR, GPC and DSC.

To confirm this change in the sequences, the copolymers were analysed by ^1H and ^{13}C NMR, GPC and DSC.

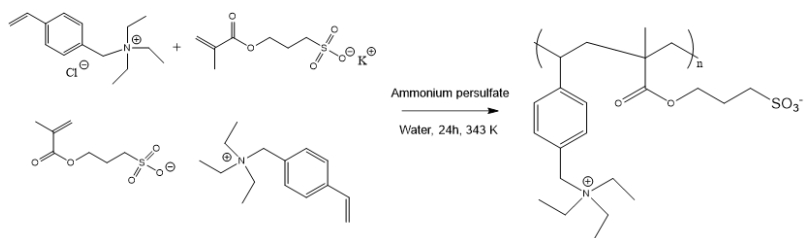


Figure 2 – Synthetic route for the copolymerisation.

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Development of smart polydiacetylene nanosystems for in vitro and in vivo tracking

Benedetta Brugnoli, Poster No: 56

Polydiacetylenes (PDAs) are conjugated polymers that can form highly ordered structures with unique chromatic features. PDAs are typically obtained by polymerisation of diacetylene (DA) monomers using ultraviolet (UV) light irradiation without the need of any initiators, which generates a polymeric backbone with alternating C=C and C≡C bonds (ene-yne), giving a blue non-fluorescent PDAs. Several stimuli, such as pH, temperature and ligand-receptor interaction, can induce a red-shift and weakly fluorescent colorimetric transition that makes PDAs a very interesting system in the field of sensors and drug delivery systems [1].

PDAs systems are usually prepared using amphiphilic commercial monomers like 10,12 - pentacosadiynoic acid (PCDA) and 10,12 - tricosadiynoic acid (TCDA), with the addition in the final formulation of phospholipids [2] and/or water-soluble polymers [3], that can influence PDAs system sensitivity, stability and drug-released properties.

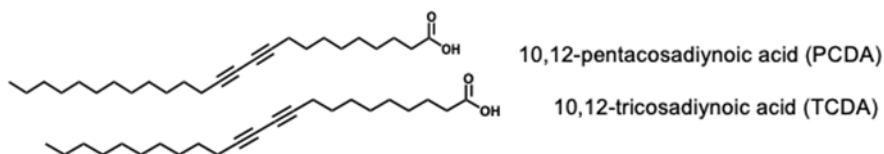


Figure 1 Monomeric structure of 10,12-pentacosadiynoic acid (PCDA) and 10,12-tricosadiynoic acid

In the present project, we selected poly(glycerol adipate) (PGA) as a novel greener polymeric alternative to develop PDAs nanosystems. The addition of PGA will confer to the final formulations biodegradability and biocompatibility [4]. Furthermore, PGA can self-assemble into nanoparticles (NPs) in aqueous media using nanoprecipitation method, which is highly compatible with traditional process for the formation of PDAs [5]. Due to PGA low toxicity and possibility to produce active polymeric prodrugs by drug coupling to the PGA backbone, PDA/PGA nanosystems can be considered a potential platform intrinsically biodegradable which may facilitate in vivo and in vitro tracking of delivery systems [6].

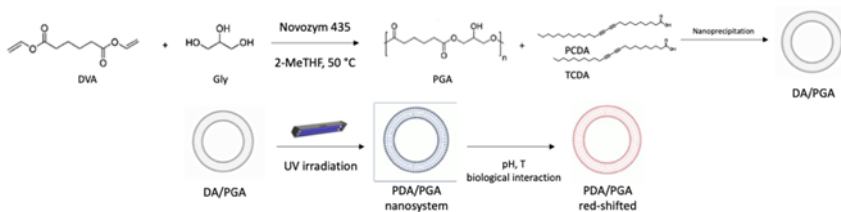


Figure 2 Schematic representation of PDA/PGA nanosystems.

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Step-growth glycopolymers with a defined tacticity for selective biological recognition

Jonas Becker, Poster No: 57

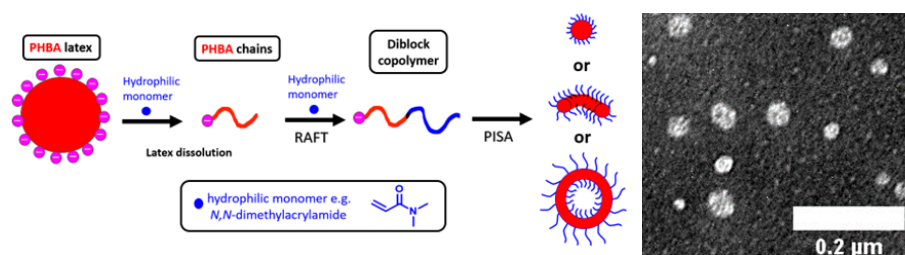
Glycosylated polymers are a versatile tool to mimic natural glycans and present a variety of potential biomedical applications. By exploiting multivalent binding between glycomaterials and carbohydrate-binding proteins, glycopolymers can emulate cellular recognition processes. Since biological activity of synthetic macromolecules is governed by structural complexity, new generations of glycomaterials require a distinct architecture to precisely modulate these interactions. Biopolymers

use chirality as a feature to gain a high degree of complexity for a variety of functions in cells. Herein, a glycopolymer backbone with a defined chirality is employed to study the influence of glycopolymer tacticity on the interactions with human lectins. Furthermore, a strategy is proposed to link these polymers onto nanoparticles for the delivery of a payload by encapsulation.

Synthesis and Characterisation of Thermoresponsive Poly(4-hydroxybutyl acrylate) Latexes: Precursors for Reverse Sequence Polymerisation-Induced Self-Assembly in Aqueous Media

Hubert Buksa, Poster No: 58

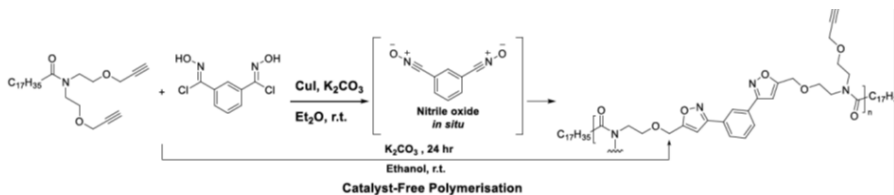
Polymerisation-induced self-assembly (PISA) is a well-known method of producing well-defined diblock copolymer nano-objects. Traditionally, aqueous PISA formulations involve chain extension of a water-soluble precursor block, which acts as a steric stabiliser for the resulting diblock copolymer nano-objects. Herein we challenge the paradigm that the hydrophilic block must be prepared first. Instead, the hydrophobic polymer is prepared first in the form of a charge-stabilised latex, followed by chain extension with the desired hydrophilic monomer. More specifically, poly(4-hydroxybutyl acrylate) (PHBA) latex particles are prepared by reversible addition-fragmentation chain transfer (RAFT) dispersion polymerisation using either a cationic or an anionic RAFT agent. Such latexes were prepared at 10-40% w/w solids while targeting a degree of polymerisation (DP) of 100-400. Targeting PHBA DPs above 250 invariably gave colloidal unstable latexes. However, targeting shorter DPs led to colloidal stable PHBA latexes owing to the location of the charged RAFT end-group at the particle surface. The best results were obtained using 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT). This RAFT agent afforded PHBA latexes of 438 nm diameter at 40 % w/w solids within 70 min at 70 °C. GPC analysis indicated that an M_n of 30,400 g mol⁻¹ and an M_w/M_n of 1.19 was obtained when targeting a PHBA DP of 150.



Synthesis of Poly(isoxazoles) from Renewable Biomass

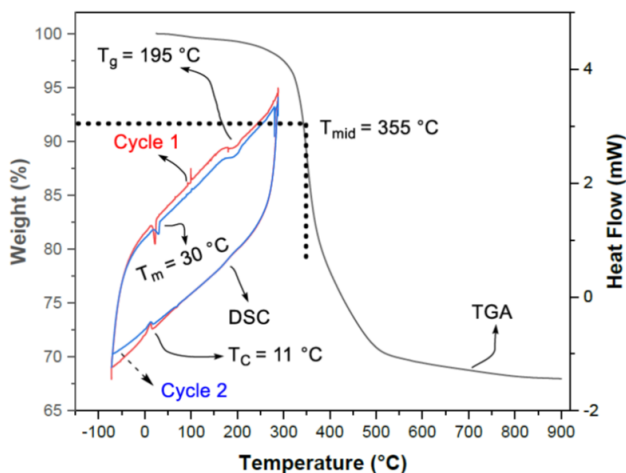
Abdulrahman Alhathir, Poster No: 59

Click chemistry has been a reliable, selective, and simple synthetic method for incorporating heteroatoms in polymer chemistry and material science. Poly(isoxazoles) can be prepared by the polycycloaddition of two clickable monomers, such as nitrile oxides and alkynes. However, the synthesis of poly(isoxazoles) from renewable materials (such as vegetable oils) has not been well studied. To this end, novel model compounds of renewable poly(isoxazoles) with various different structures were successively synthesised using nitrile oxide click chemistry. After that, renewable poly(isoxazole) was prepared under various optimised reaction conditions using nitrile-oxide click polymerisation.



To prepare the required monomers for poly(isoxazole) synthesis, commercially available stearic acid ($C_{17}H_{35}CO_2H$) was used as a building block for monomer and polymer synthesis. The amidation of stearic acid with amino alcohols led to the formation of the desired fatty amides (stearamide). Further chemical modification of fatty amides with a polymerisable group (alkynes) resulted in a novel alkyne model and the dialkyne monomer. In a two-step reaction from commercially available aldehydes, nitrile oxides were generated in situ by HCl elimination of oximoyl chloride compounds. The 1,3-cycloaddition reactions between nitrile oxides generated in situ and the renewable alkyne or diyne monomers were performed under thermal and catalytic conditions. In general, according to the optimisation studies, the optimal condition for the synthesis of isoxazole compounds was by using copper(I) as a catalyst which resulted in a good yield of the corresponding isoxazoles. On the other hand, click step-growth polymerisation was carried out under copper and catalyst-free poly(isoxazoles) synthesis. The highest molecular weight polymers were obtained using free-catalyst polymerisation with environmentally-friendly solvents such as ethanol.

The obtained isoxazole compounds were subjected to the reductive ring cleavage to provide a series of novel β -aminoenone models of renewable polyamines. Reducing reagents such as $\text{Mo}(\text{CO})_6$ and Raney-Ni have shown a high ability to cleave and convert isoxazoles into the analogue β -aminoketones in good to excellent yields. A novel model of β -hydroxyketone of polyols was synthesised by in situ acidic hydrolysis of the prepared β -aminoketones. A range of techniques (such as IR, 2D NMR, MS spectroscopy, MALDI-TOF, GPC, TGA, and DSC) was used to comprehensively analyse and characterise each monomer and polymer.



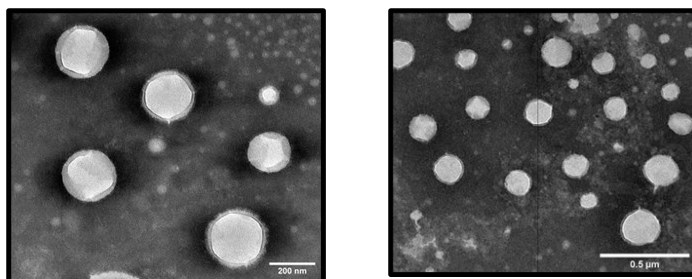
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Direct endcapping of Poly(2-ethyl-2-oxazoline) Homopolymers and their Self-assembly

James Lefley, Poster No: 60

From targeted drug delivery - to nanoreactors for catalysis - to biomimetic protocells. These are just some of the innovative and exciting applications for polymersomes that have been described in recent years. The greatest challenge of designing such complex self-assembled structures is choosing the most appropriate synthetic route. Typically, polymersomes are prepared from finely tuned block copolymers. Where the length, and composition, of each block have been pre-calculated and tightly controlled. However, these syntheses can be challenging and often complicated. Usually sacrificing speed and efficiency of preparation for lengthy, multi-step reactions. Given the future potential of polymersomes as gene and drug delivery vectors, there will be a demand for upscaling and mass synthesis of these polymers on an industrial level. Hence the need for a scalable, simplistic and refined route to prepare these nanoparticles without compromising on function or fidelity. Herein, we report the facile one-pot synthesis and preparation of poly(2-ethyl-2-oxazoline) polymersomes via direct endcapping in aqueous solution. Endcapped poly(2-ethyl-2-oxazoline) polymersomes were prepared via direct injection and film rehydration methods and analysed by DLS and TEM for their potential candidacy as mass produced vectors for a variety of applications.



TEM images of polymersomes prepared from P(EtOx)5-S-C12H25 (left) and P(EtOx)10-S-C12H25 (right).

PET/PEG Copolymer Electrolytes for use in All-Solid-State Li-ion Batteries

Charles Tkaczyk, Poster No: 61

Increased drive to develop electric vehicles (EV) in recent years has led to lithium-ion (Li-ion) batteries receiving substantial interest. Traditionally, Li-ion batteries use a liquid electrolyte to facilitate the movement of ions. Commonly used solvents including diethyl carbonate (DEC) and dimethyl carbonate (MEC), are highly flammable, and therefore pose a significant safety concern.

One potential solution to this is the use of a solid-state electrolyte (SSE). There are two classes of materials currently being investigated for this role: inorganic ceramics materials and polymer-based films. Although inorganic SSEs can achieve ionic conductivities similar to those of liquid electrolytes, (e.g., 16.1 mS cm^{-1} for lithium argyrodite sulfide as reported by Yu et.al¹) their high cost and brittleness makes them challenging to implement. Polymer materials on the other hand show a higher degree of flexibility and tend to be significantly cheaper than their inorganic counterparts. The possibility of utilising ion-conducting polymers in this emerging energy sector acted as the driving force for DuPont Teijin Films to sponsor this PhD project.

One of the most heavily investigated polymer ion carriers is polyethylene glycol (PEG). However, pure PEG only obtains practical ionic conductivities at elevated temperatures, which poses an issue of practicality due to PEG's low melting point. In order to improve on PEG's poor mechanical and thermal stability, our research aims to synthesise a range of PET/PEG copolymers (Figure 1) via melt-polycondensation and characterise their performance as ion carriers before evaluating their viability as SSEs. To date we have synthesised a range of copolymer compositions with the length of PEG being used varied. The effect of branching is also investigated as it can significantly reduce the extent of crystallinity, and thus increase the ionic conductivity across the matrix.² We confirm incorporation of PEG into the polymer using standard ¹H NMR spectroscopy and characterise the crystallinity of the resulting copolymer via DSC. Preliminary results indicate that increasing the copolymer fraction of PET results in lower PEG T_g and T_m values. As the PEG fraction is decreased the number of conductive regions across the polymer matrix is also decreased. Hence to obtain a sample exhibiting the highest ionic conductivity, a balance between PEG efficiency and quantity is needed. We will present our latest findings relating to our PET/PEG copolymers and comment on the feasibility of using such systems as electrolytes in the future.

findings relating to our PET/PEG copolymers and comment on the feasibility of using such systems as electrolytes in the future.

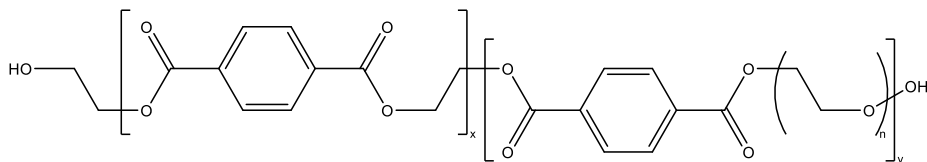


Figure 1: Molecular structure of a PET/PEG copolymer where x is the hard PET segment and y is the soft PEG segment.

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Platelet-Inspired Nanoparticles for Targeted Drug

Delivery to the Atherosclerotic Plaque

Yangshuo Hu, Poster No: 62

Atherosclerosis is a chronic inflammatory disease that underpins most coronary heart diseases. An occlusive lipid plaque develops in the arteries increasing the risk of fatal ischaemic events. Systemic drug treatments are associated with off-target side effects, calling for the development of more specific drug delivery to the atherosclerotic site. Inspiration is drawn from platelets' natural ability to marginate and adhere to injured vasculature, via adhesion to collagen and von Willebrand Factor under pathologically elevated shear stress. I hypothesize that a polymeric nanoparticle drug carrier, deformable under shear stress to enhance adhesion to von Willebrand factor, would enable targeted drug delivery to the atherosclerotic site. An *in vitro* microfluidic model that mimics the geometry and shear stress environment *in vivo* is developed to evaluate nanoparticle designs. To create polymeric shear-deformable nanoparticles with adhesion to von Willebrand factor, a gelatin-based

layer-by-layer assembly approach will be taken. The nanoparticle platform will then be optimized for atherosclerosis drug delivery, leading to validation in a clinically relevant animal model.

Novel polymers from anhydrosugars: synthesis, catalysis and applications of polysaccharide mimics

Ella Clark, Poster No: 63

The preparation of bio-derived polyesters is of great interest due to the widespread concern surrounding the extensive use of fossil fuel-derived plastics and their potential in new technologies. Ring-opening copolymerisation (ROCOP) can produce multiple polymer types, architectures and functionalities by simple variation of monomers and initiators.¹

The living nature of ROCOP allows for formation of block copolymers through sequential monomer addition, as well as control of molar masses via a chain transfer agent.² Epoxide copolymerisation is a well-established field in terms of catalyst development and understanding, and monomer scope, but for many other potential monomers, such as oxetanes, development is in the early stages.³

Our group has reported the ROCOP of an oxetane co-monomer (d-Ox), derived from D-xylose, with cyclic anhydrides.⁴ This poster will detail the investigation of new and existing catalysts for the ROCOP of d-Ox. Two existing catalysts were found to outperform the existing Cr(III) Salen catalyst; an Al(III) aminotris(phenolate) complex was found to produce high molecular weight copolymers at improved rates compared to the Cr system and an Al(III) porphyrin complex catalysed the copolymerisation of d-Ox at a far greater rate, although lacked control over the alternating sequence.

With a more efficient catalyst system in hand, isothiocyanates (ITCs) were identified as new comonomers in the ROCOP of d-Ox. The high reactivity of ITCs gave access to sugar derived polythioimidocarbonates, facilitated crosslinking and allowed for microstructure variation.

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Disulfide cross-linked Linear methacrylamide based micelles as Redox-responsive drug nanocarriers for Triple Negative Breast tumor-targeted therapy: Histopathological evaluation

Fatemeh Mehradnia, Poster No: 64

Background: The therapeutic efficacy of anticancer nanocarriers is highly dependent on their size, shape, targeting ability, and stimuli-responsiveness [Su & Hu, 2018]. Stimuli-responsive nanocarriers that show enhanced blood circulation time and triggered drug release at target sites in response to a specific stimulus are promising candidates as efficient cancer nanomedicine [Mi, 2020].

Method: The in vivo therapeutic efficacy of Doxorubicin (Dox) loaded redox responsive micellar nanoparticles (MNPs) based on linear 2-hydroxypropyl methacrylamide (HPMA) was studied via histopathological evaluations. The animals from different experimental group, control, free Dox and Dox-MNPs were sacrificed 46 days post-treatment, and the harvested tissues including tumor, heart and liver were fixed in 10% formalin. Paraffin-embedded tissue blocks were sectioned by microtome to obtain 10- μ m thick tissue sections and then stained with haematoxylin and eosin (H&E) for histopathological examination.

Results: The H&E-stained tissue sections were examined histologically. The heart and liver sections in the control and Dox-MNPs groups had a normal architecture however some degeneration and disorganization of the liver cells was observed in Dox-MNPs sections. The normal structure of the liver was somewhat lost in Free-Dox section. Tumor sections in Dox-MNPs group showed extensive apoptosis and necrosis associated with moderate to marked inflammatory cell infiltrate together seen with scattered apoptotic bodies, which was not the case in control and Free Dox group. Dox encapsulation in micelles improves its tumor accumulation and sim-

ultaneously decreases its accumulation in the healthy tissues and enriched drug into the tumors which consequently results in enhanced apoptosis and therapeutic efficacy and less toxic side effects.

Conclusion: These redox responsive crosslinked HPMA-based micellar nanoparticles with acceptable therapeutic efficacy and apoptosis induction in cancerous cells and reduced cardiotoxicity and liver toxicity proved to be promising nanomedicine for breast cancer chemotherapy.

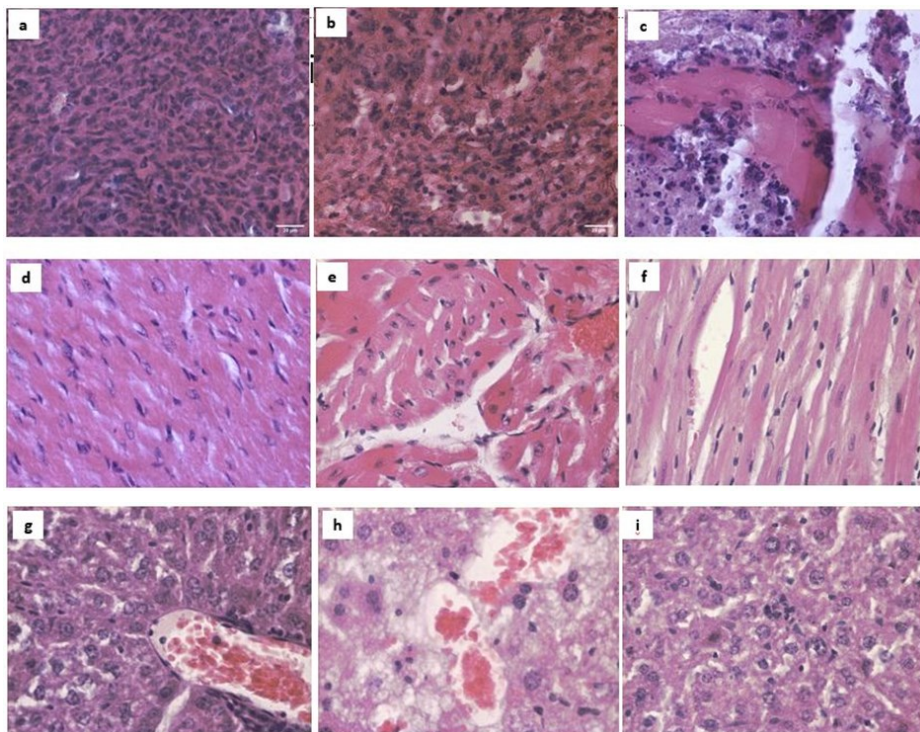


Fig1. H&E images of TNBC tumor, heart and liver tissues 46 days post treatment. Tumor in a) control, b) Free Dox, c) Dox-MNPs groups; Heart in d) control, e) Free Dox, f) Dox-MNPs groups; Liver in g) control, h) Free Dox, i) Dox-MNPs groups. (40x magnification)

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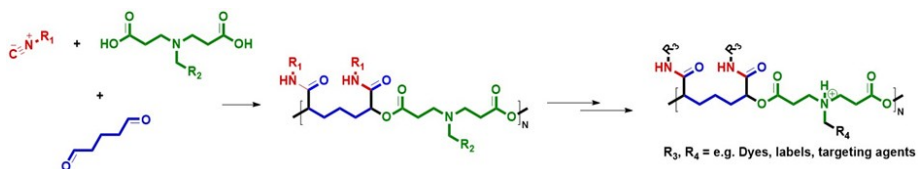
Tracking Intracellular Transport of Self-Reporting Nanomaterials

Lewis O'Shaughnessy, Poster No: 65

Oligonucleotide therapies have the potential to selectively treat a range of life-limiting disorders by selectively modulating expression of disease associated pathways.^{1,2} They operate by binding intracellular mRNA to block translation, thus functioning exclusively in the cytosol. Their hydrophilicity and negative charge however limit their translocation across cell membranes, requiring them to be packaged in delivery vectors.³ Cationic polymers show potential as delivery vectors, but existing strategies do not possess the requisite synthetic tuneability to meet their therapeutic needs such as organ- and cell-specific targeting.^{3,4}

This work seeks to overcome this constraint by exploiting the Passerini 3-component reaction (P3CR) to synthesise polymers with far greater functionality than possessed by conventional polycation vectors. By employing dicarboxylic acid and dialdehyde monomers, the P3CR can be used as a polymerisation reaction that simultaneously introduces two functional groups and an ionisable amine into a polymer chain within a single step (see Scheme 1).^{5,6} Choice of orthogonal reactivities for the resultant side chains allows for easy incorporation of desired groups. We aim to utilise this to attach a range of functionalities from dyes and labelling moieties to biologically relevant groups like targeting motifs and endosomal buffering agents. This facilitates rapid iterative design and modification of custom-built polymers for targeted oligonucleotide delivery, optimised to meet a range of therapeutic needs.

By utilising the robust and high yielding P3CR we will synthesise an exceptionally versatile polymer template that leads us to bespoke, multifunctional materials with the potential to revolutionise oligonucleotide delivery.



Scheme 1: Project Outlines

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Acetals for Adaptable, Degradable and Reprocessable Thermosets

Joshua Hayles, Poster No: 66

Thermoset networks are important in a range of industries such as dental care, composites and coatings, providing excellent mechanical strength and durability. However, cross-linking causes them to become insoluble and therefore makes their reuse, separation from high value components and recycling challenging. Existing recycling techniques can be broadly encompassed into two categories; mechanical recycling, where networks are broken down into fibres or fillers for reuse and thermal processing, where networks are typically used as fuel. However, chemical recycling of materials into useful chemicals is a desirable alternative. Furthermore covalently adaptable networks have emerged as promising candidates for reprocessa-

reagents.

Firstly a pH responsive methacrylate cross-linker was synthesised from 2-hydroethyl methacrylate and tri(ethylene glycol) divinyl ether. Under acidic conditions the cross-linker readily hydrolysed to the commodity chemicals tri(ethylene glycol) and acetaldehyde. Cross-linked methacrylate networks were subsequently synthesised, containing the aforementioned cross-linker, via redox initiated free radical polymerisation. Networks containing the labile acetal moiety were shown to degrade and solubilise on exposure to mild solutions of sulfonic acid derivatives. The polymeric product of may be collected and reprocessed to give cross-linked networks similar in structure to the virgin material.

Furthermore, the acetal groups impart the networks with adaptable properties transacetalisation reactions between cross-linkers. We demonstrated this by repeated re-joining of mechanically separated lap shear substrates, the bond strength was ~60 % that of the original material.

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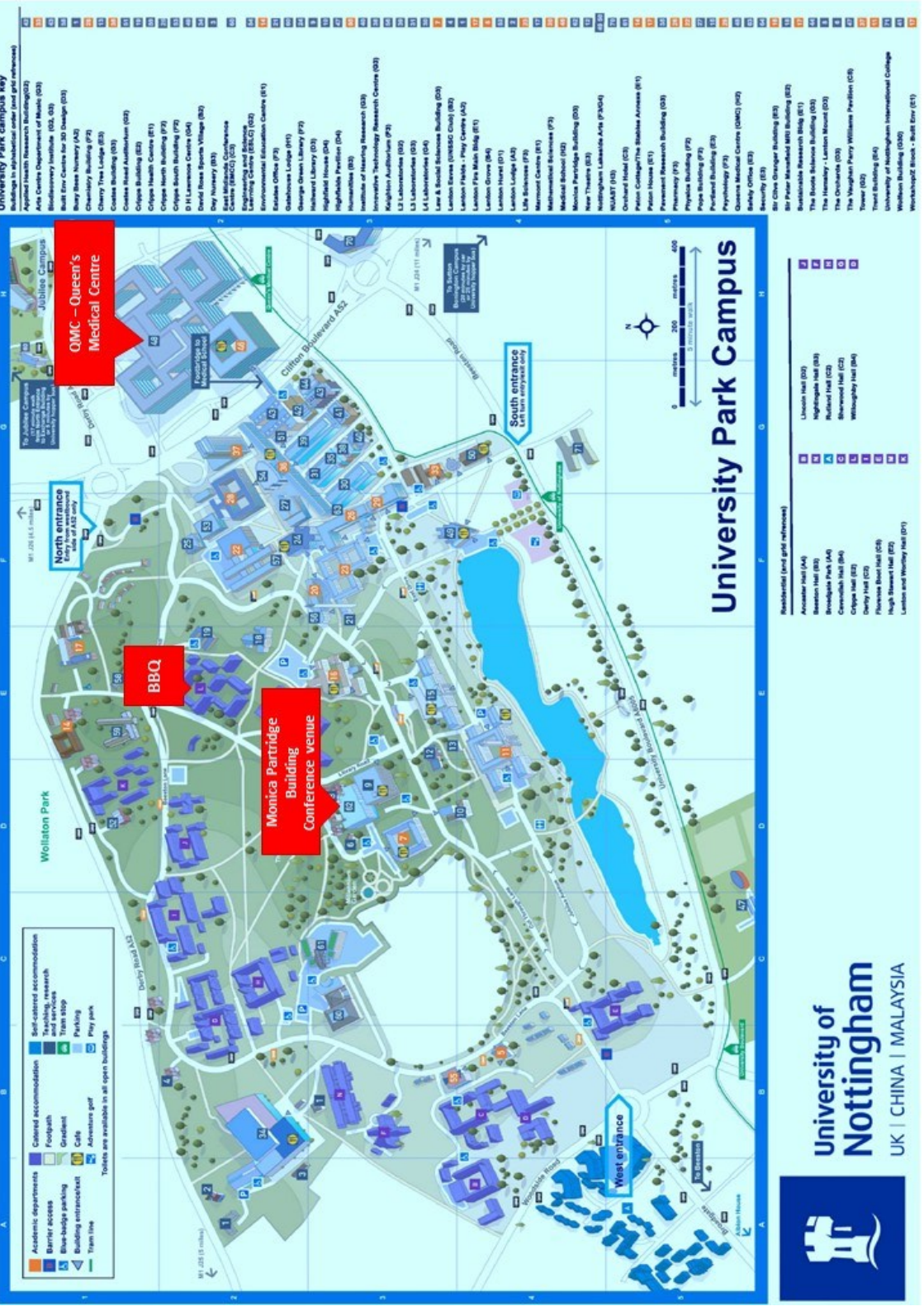
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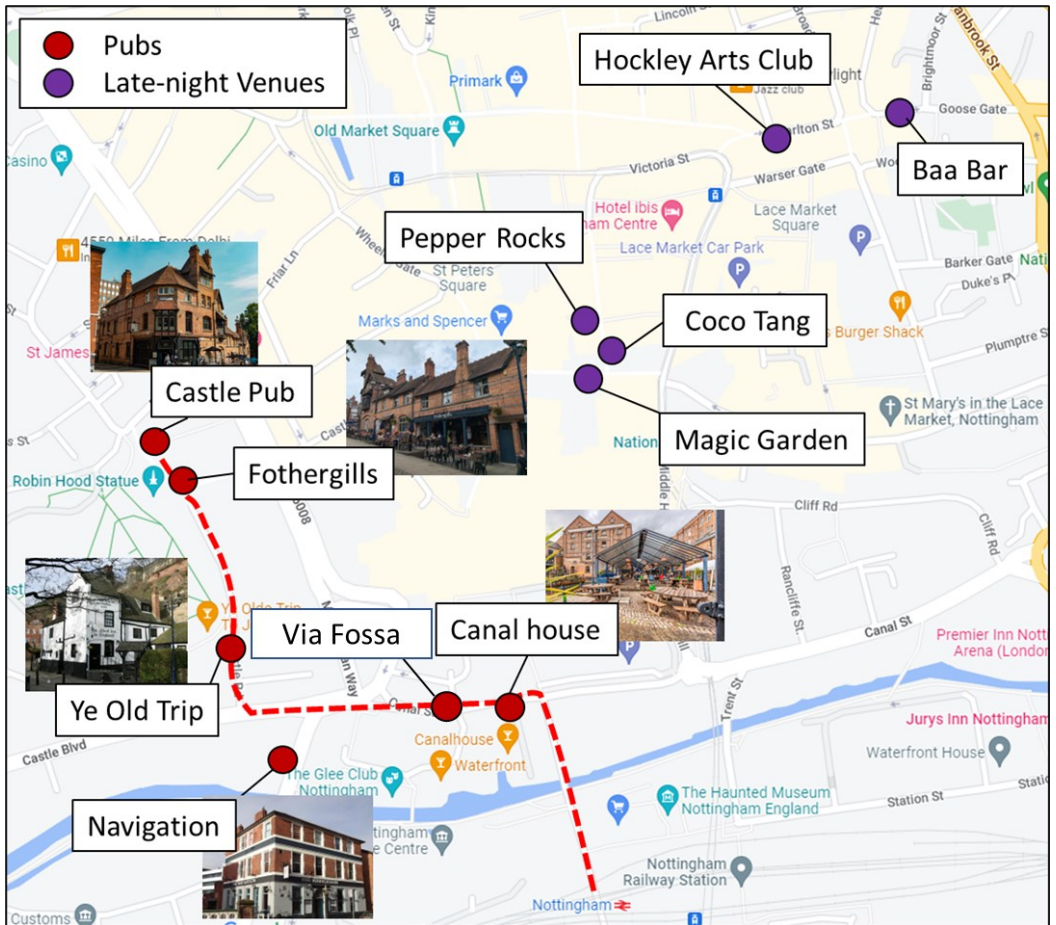
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