ISPAC 2023

34th International Symposium on Polymer Analysis and Characterization

24-26 April 2023, Stellenbosch, South Africa

Book of abstracts

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Welcome to ISPAC 2023 in Stellenbosch, South Africa!

ISPAC meetings have a long tradition, but this is the first time an ISPAC meeting has been held on the African continent - in Stellenbosch, a city with a remarkable history and major contributions to polymer science.

ISPAC 2023 is jointly organized by the Department of Chemistry and Polymer Science at the University of Stellenbosch and the Leibniz Institute for Polymer Research Dresden in Germany. We bring together more than 120 scientists and engineers from around the world interested in advanced polymer characterization. An exciting scientific program with distinguished experts in the field of polymer science offers also talented young researchers the opportunity to present their work. The conference starts with short courses in state-of-the-art polymer analysis and characterization targeted at the future generation of polymer scientists. They will also get in touch with experts from global companies in the Polymer Analysis meets Industry event following the conference.

The focus of this year's ISPAC is Harald Pasch's 70th anniversary. It is our great honour and pleasure to celebrate his birthday with a special all-day session. Prof. Pasch not only made an essential contribution to polymer analysis and characterization worldwide. As Chair of Analytical Polymer Science at Stellenbosch University, he literally shaped polymer science and the scientific community in Africa.

On behalf of the organizing committee, I would like to thank our supporters and award donors as well as the volunteers, the ISPAC governing board, and all participants who actively contribute to making ISPAC 2023 a stimulating and inspiring meeting. We hope that you will take the opportunity to discover the stunning town of Stellenbosch, home to the country's oldest university, and enjoy the breath-taking beauty of the Western Cape's Winelands.

Prof. Albena Lederer
Stellenbosch University, South Africa
Leibniz-Institut für Polymerforschung Dresden, Germany

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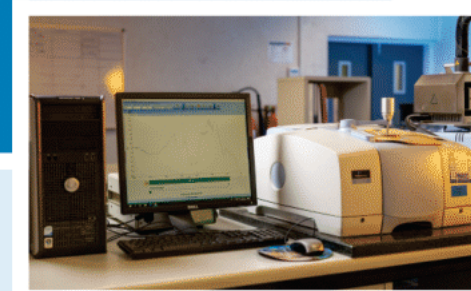
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General Information

Conference Venue
The venue of ISPAC 2023 is the Wallenberg Conference Center @STIAS, 10 Marais Road, Stellenbosch, South Africa. Conference sessions will be held in Auditorium 1 and the Library in the Manor House.

Registration
Participants can register in the foyer of the Wallenberg Conference Center @STIAS during the following period:

April 23rd (SUN)   09:30 - 10:00
April 24th (MON)   08:30 - 18:00
April 25th (TUE)   08:30 - 16:00
April 26th (WED)   09:30 - 13:00

Lunch and Break
Lunch along with coffee will be provided throughout the conference in the foyer.

Welcome reception
Welcome reception will be held on Sunday, 23 April 2023.

Conference Dinner
Conference dinner will take place at Bartinney Tasting Shed on 25 April 2023. Transport to and from conference dinner will be provided. Transport to the conference dinner will start at 17:00 from Wallenberg Conference Center @STIAS.

Short course
The short courses with be held on 23 April 2023 in Auditorium 1.

Wi-Fi
The following details can be used to connect to the conference Wi-Fi:

Name: Stias2

Password: Conference22!

Supporter Exhibition
Supporters exhibitions will take place from 24 - 26 April in the foyer.

Oral presentation

Oral sessions will take place in Auditorium 1 and Library (Manor House).

Oral presentation time is as follow:

Plenary Lectures (PL): 40 min

Keynote Lectures (KN): 30 min

Oral Lectures (OL): 20 min (including discussion)

A 30-min panel discussion will follow the morning session. Presenters have to go to the presentation auditorium 20 min prior to the start of the oral session to upload and preview their presentation.

Speaker information

Slides should be prepared in MS PowerPoint or PDF format in 16:9 or 4:3 slide size. The slides need to be loaded in the speaker prep area at Wallenberg Centre @ STIAS. Talks should be loaded on a USB flash drive and handed to the technical support preferably the day before, but no later than 3 hours before your talk. The slides can also be emailed polymerseparation@gmail.com if preferred. The speaker prep area will be open during all breaks and 30 minutes before the first lecture and after the last lecture each day.

Poster information

Poster sessions will be held in the Auditorium 2 at the STIAS venue. The posters need to be put up by the morning tea break on the day of your poster session in the correct building and according to your abstract number. Materials to hang your poster will be provided. Posters should be taken down after the poster session, or by the morning tea break on the following day at the latest.

Monday afternoon (17:50 – 19:00): Odd numbered posters

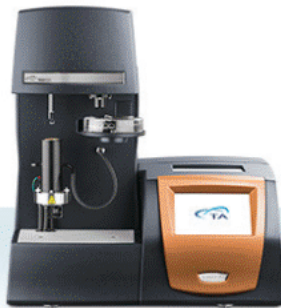**Tuesday afternoon (13:50-14:40):** Even numbered posters

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Scientific Program

	Auditorium 1	Library (Manor House)
09:00	***Opening*** Albena Lederer Chair: Julius Vansco	
09:10	***PL1 Polymers sustainability considerations*** Yeng Ming Lam	
09:50	***KN1 Neutron scattering as a powerful probe to characterize soft matter systems*** Ralf Schweins	
10:20	***KN2 Dendritic polymer integrated nanostructured membranes for water remediation*** Soraya Malinga	
10:50	***Panel Discussion***	
11:20	**Break – Exhibition opens – Posters mounting**	
	Chair: Peter Schoenmakers	Chair: André Striegel
11:50	***KN3 Tracking light gated transformations of macromolecules in solution and gas phase via mass spectrometry*** Hendrik Frisch	***KN4 Polymers for pollutant extraction and separation from water*** Luke Chimuka
12:20	***OL1 Application of mass spectrometry in polymers industry*** Chris Kgaje	***OL4 How can characterization of biofouling teach us to fabricate better interfaces?*** Julius Vancso
12:40	***OL2 Investigations on the interaction of nitrogen-based modifiers on the viscosity of alkyl magnesium polymers with mass spectrometry*** Julia Schwarz	***OL5 Bimetallic nanomaterials supported on polymeric nanofiber membranes for the removal of per-/polyfluoroalkyl substances (PFAS) from various aquatic matrices*** Mbuso Dludlu
13:00	***OL3 Mass Spectrometry as a tool for polymer reaction engineering – monitoring reactivities in multicomponent polyester-based (hybrid) resins*** Clemens Schwarzinger	***OL6 Polymeric gel supports for nanoparticle-assisted water electrolysis*** Wilhelm H. le Roux
13:20	**Lunch – Exhibition – Posters**	

	Auditorium 1	Library (Manor House)
13:20	*Product seminar: Bruker*	
13:50	*Product seminar: Postnova*	
	Chair: Lauren Ball	Chair: Harald Pacsh
14:20	**KN5 Polymers for the isolation of membrane proteins** Bert Klumperman	**KN6 Analysis of ultra-high molar mass polyacrylamides by Asymmetrical Flow Field-Flow Fractionation: Necessity of low flow rates and Dilution Control Module™ (DCM)** Frédéric Violleau
14:50	**OL7 Fabrication of a polybutylene succinate (PBS)/polybutylene adipate-co-terephthalate (PBAT)-based hybrid system reinforced with lignin and zinc nanoparticles for potential biomedical applications** Asanda Mtibe	**OL10 Facile fabrication of multifunctional metallic nanostructures: advanced analysis with novel 3D correlation Thermal Field-Flow Fractionation** Upenyu L. Muza
15:10	**OL8 Characterization of stimuli-degradable polymers for triggered drug release** Dirk Kuckling	**OL11 Size-exclusion chromatography of PEEK in mixture of acidic and chlorosolvents** Nicholas Longieras
15:30	**OL9 Multiple detection size exclusion chromatography: a powerful tool for understanding the scaling properties of enzymatically crosslinked casein nanoparticles** Joshua Johani	**OL12 Comprehensive analysis of antimalarial drug delivery systems by integrated characterisation methodologies** Zanelle Viktor
15:50	**Break – Exhibition – Posters**	
	Chair: Emmanuel Iwuoha	Chair: Clemens Schwarzinger
16:20	**OL13 Novel photoinitiators for design of hybrid smart polymers and materials** Terry Steele	**OL16 Understanding molecular complexity of biodegradable polymer: Comprehensive analysis of aliphatic polyesters** Paul Eselem Bungu
16:40	**OL14 Synthesis, characterization and application of a molecularly imprinted polymer as an adsorbent for solid-phase extraction of selected pharmaceuticals from water samples** Sinegugu Khulu	**OL17 Design and preparation of PLA/PBAT_Fe_3O_4_GO@CNC nanocomposite with excellent flame retardancy** Lesego Maubane

| 17:00 | **OL15 Structural-function characterization of therapeutic nanoreactors based on photo-crosslinked polymeric vesicles**
 Silvia Moreno | **OL18 Abiotic and biotic degradation of biobased polymers, biopolymer blends and biocomposites under different environmental conditions**
 Sudhakar Muniyasamy |

| 17:20 | *PL2 Chemically-sensitive online detection for detection of functional groups: SEC-NMR, HPLC-NMR, SEC-IR(QCL), and FT-LC*
 Manfred Wilhelm |

| 17:50 | **Poster session 1 (odd posters presented)** |

Special session in celebration of Prof. Harald Pasch's 70th birthday

	Auditorium 1	Library (Manor House)
	Chair: Albena Lederer	
09:00	*PL3 Polymer Characterization by Interaction Chromatography* Taihyun Chang	
09:40	*KN7 Determining Accurate Molar Masses by SEC/MALS Using Mixed Solvents* André Striegel	
10:10	*KN8 From Process to Polymeric Microstructure – A Journey through Experiment, Modeling & Simulation and Polymer Characterization* Markus Busch	
10:40	*Panel Discussion*	
11:10	**Break – Exhibition opens – Poster mounting**	
	Chair: John Mellor	Chair: Ralf Schweins
11:40	*KN9 Biobased and biodegradable Polymers: Analytical Challenge* Jana Falkenhagen	*KN10 Polymer Engineering for Electrochemical Sensors and Biosensors* Emmanuel Iwuoha
12:10	*OL19 Understanding Macromolecular Properties by in-depth Molecular Characterization* Peter Kilz	*OL22 Supersensitive metal free in-situ synthesized graphene oxide@cellulose nanocrystals acetone sensitive bioderived sensors* Jonathan Tersur Orasugh
12:30	*OL20 Separation and characterization of chitosan by SEC and AF4* Yonggang Liu	*OL23 A novel electrochemical sensor for the detection of zearalenone in food matrices using PEGylated Fe3O4 nanoparticles supported by multidetector AF4 and in-silico studies* Lyndon Naidoo
12:50	*OL21 SMART thermoresponsive hydrogel films and nanofibres from poly(dimethylsiloxane) grafted amphiphilic copolymers* Peter Mallon	*OL24 Fatigue damage behavior in 3D printed polylactide composites reinforced by hydroxyapatite, titan dioxide and glassy carbon* Karolina Mazur
13:10	**Lunch – Exhibition – Posters**	

Special session in celebration of Prof. Harald Pasch's 70th birthday

	Auditorium 1	**Library (Manor House)**
13:20	***Product seminar: Advanced Laboratory Solutions***	
13:40	**Poster session 2 (even posters presented)**	
	Chair: Peter Mallon	Chair: Jens-Uwe Sommer
14:40	***KN11 Polymer separation using NMR as the detector*** Wolf Hiller	***KN13 Molecular origin of shear and extensional rheology of polystyrene pom-pom model systems and validation of constitutive models*** Valerian Hirschberg
15:10	***OL25 Hydrodynamic chromatography an efficient to tool to quickly determine particle size distributions in the sub-micron range*** Wolfgang Radke	***OL28 The effect of post-consumer recyclate on the rheological extensional viscosity of polyethylene*** Dickson Motaung
15:30	***OL26 Challenges in the characterisation of polyolefin based recyclates*** Andreas Albrecht	***OL29 Morphology formation during injection molding of semi-crystalline thermoplastics*** Ines Kühnert
15:50	***KN12 45 Years of polymer HPLC – A personal account*** Harald Pasch	***OL30 The effect of mechanical recycling on the thermomechanical, chemical, and mechanical properties of poly(butylene adipate terephthalate) PBAT, poly (butylene succinate) PBS, PBAT-PBS blend, and PBAT composite.*** Nomvuyo Nomadolo
16:20	***SO27 Multidimensional separations*** Helen Pfukwa	***OL31 Characterising the properties and performance of highly filled CaCO$_3$ masterbatches*** Lucky Radebe
17:00	**Conference dinner@ Bartinney** **Depart from STIAS at 17:00**	

	Auditorium 1	Library (Manor House)
	Chair: Soraya Malinga	
09:00	*PL4 Chain walking catalysis from the theory point of view: From dendritic to bottle brush molecules* Jens-Uwe Sommer	
09:40	*KN14 Pyrrolidone based polymers in advanced polymer materials* Rueben Pfukwa	
10:10	*KN15 Challenges for automation of 2D-LC method development* Bob Pirok	
10:40	**Panel Discussion**	
11:10	**Break – Exhibition – Posters**	
	Chair: Valerian Hirschberg	Chair: Wayne Reed
11:40	*KN16 Quantitative particle analysis by a combination of optical microscopy with FTIR and Raman spectroscopy: Advanced automation enhanced by Machine learning and data management* Dieter Fischer	*KN17 Chain-walking polyethylene: Not a single type but a new family of polyethylenes* Jan Merna
12:10	*OL32 Machine learning of sequence and conformation programmed material properties* Marco Werner	*OL35 Analysis of complex polyolefins (terpolymers) using advanced separation techniques hyphenated with quantitative detection* Sampat Singh Bhati
12:30	*OL33 Time Domain NMR of sustainable polymer materials from agrowaste* Michele Mauri	*OL36 Method development for separation and characterization of chain walking polyethylene* Mawande Sigwinta
12:50	*OL34 Advancing the strength of electronic lab notebooks from organic chemistry to polymer chemistry* Dominik Voll	*OL37 Trace sample analysis by a splitless pyrolysis-GC/MS system coupled to a newly developed sampler* Michael Soll
13:10	**Lunch – Exhibition – Posters**	

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	Auditorium 1	Library (Manor House)
13:20	**Product seminar: Anton Paar**	
	Chair: Yeng Ming Lam	Chair: Hendrik Frisch
14:10	**KN18 Comprehensive two-dimensional LC of tannins using HILIC and RP-LC: How far can we go?** André de Villiers	**KN19 How polymer's nature influences the conformation of conjugates** Susanne Boye
14:40	**OL38 Nanochemical microscopy of polymer systems: Thresholds and peculiarities** Mikhail Malanin	**OL41 Stimuli-responsive homo- and copolymers in water-based solutions** Volker Abetz
15:00	**OL39 Kinetic phenomena in polymerization reactions; New findings and potential application** Wayne Reed	**OL42 Comprehensive separation and characterization of nanocarrier/drug systems based on polymers and proteins for nanomedical applications** Gerhard Heinzmann
15:20	**OL40 Revisiting Kuhn-Mark-Houwink-Sakurada: trends of the pre-exponential coefficient K of branched polymers in solution** Martin Geisler	**OL43 Molecular interaction between hydrophilic and hydrophobic polymer blocks causes order-order transition-based thermogelation** Anna-Lena Ziegler
15:40	*PL5 Novel polymer separations* Peter Schoenmakers	
16:10	**Awards/Invitation to ISPAC 2024**	
16:30	**Farewell**	

PL1

Polymers Sustainability Considerations

L.Y. Ming[1]

[1]School of Materials Science and Engineering, Nanyang Technological University (NTU)

Polymers are ubiquitous for many applications such as packaging, medical implants, electronic devices and its global production exceeds 9 billion tons at present. This class of materials has many attractive properties such as versatility in terms of shapes and mechanical/chemical properties, light weight, cost-effectiveness, etc. Most traditional polymers such as polyethylene, polypropylene, PET, PVC, and nylon, are made from petrochemicals. The environmental impact in the production of such polymers (energy consideration) and the recycling process can be difficult and expensive, and many products end up in landfills or the environment. Despite the understanding of these negative impact of these materials, it will be challenging to replace all with a sustainable option. A more reasonable approach would be how to effectively recycle and upcycle these materials. In this talk, I will share with you some work that we have been doing on recycling and upcycling of PET through enzymatic degradation and how the properties of the polymer impact the design of the platform for screening enzyme library for more effective degradation. To understand the interplay between substrate crystallinity and microstructures on the efficiency of PET degradation which can also impact other polymers degradation, I will also present the degradation behaviour of PET, PET copolymers (e.g., poly(ethylene terephthalate-co-isophthalate) or poly(ethylene terephthalate-co-butylene terephthalate)), and branched PET. Biodegradable polymers are attractive proposition considering all the challenges we faced with traditional polymers. Although biodegradable polymers are designed to break down naturally, they can still emit harmful substances during their degradation process. They may also need specific environmental conditions, such as high humidity and temperatures, to fully decompose. Furthermore, if not properly disposed of, they could still contribute to environmental pollution and littering. Polymers derived from natural resources such as cellulose, starch, protein, lignin, chitin could be a good consideration since they are generally considered as renewable and have a lower carbon footprint. I will also share some work on cellulose based materials for agriculture and biomedical applications that we have explored.

KN1

Neutron scattering as a powerful probe to characterize soft matter systems

R. Schweins[1]

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Scattering techniques are widely used in various scientific domains, to investigate the structure and dynamics of matter. Neutron scattering is complementary to both light and x-ray scattering. Due to their zero charge, neutrons can deeply penetrate into matter and are a non-destructive probe. Furthermore, they offer easy access to contrast variation by using different isotopes of atoms. Partial or complete deuteration of molecules is the most commonly used contrast variation technique in soft matter science and allows for selectively elucidating particles in a complex environment.

This contribution will briefly introduce the ILL as the world-leading flagship facility for neutron scattering. An overview of the different neutron instruments for both polymer dynamics and structural studies will be given. In addition, I will present the ILL's soft matter lab infrastructure accessible within the Partnership for Soft Condensed Matter (PSCM) that comprises many complementary lab-based techniques.

I will then focus on Small-Angle Neutron Scattering (SANS) for polymer characterization. In a recently finished PhD project, we investigated block copolymers which consist of two polyelectrolyte blocks [sodium salts of polyacrylic acid (PA) and polystyrenesulfonic acid (PSS)] in the presence of divalent cations [1, 2]. Depending on the charge ratio between anionic polymeric charges and specifically interacting counterions, supramolecular structures are formed. Contrast variation including samples with a deuterated polyacrylic acid block enabled us to confirm core-shell micellar structures. Different complexation affinities with respect to the oppositely charged cations are at the origin of these micellar structures. Furthermore, we could invert the micellar structures and trigger the micelle formation by external stimuli such as temperature, counterion concentration and pH [3].

References
[1] N. Carl, S. Prévost, R. Schweins and K. Huber, Soft Matter. **15,** 8266 (2019)
[2] N. Carl, S. Prévost, R. Schweins and K. Huber, Colloid Polym. Sci. **298**, 663–679 (2020)
[3] N. Carl, S. Prévost, R. Schweins, J.E. Houston, I. Morffin and K. Huber, Macromolecules. **52**, 8759–8770 (2019)

KN2

Dendritic polymer integrated nanostructured membranes for water remediation

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Water pollution is one of the top major problems around the world, especially in developing countries of which South Africa and most African countries make up the number in these statistics. Currently, the demand for safe drinking water has increased dramatically worldwide due to population growth, development of urban life, and industrialization. Thus, solving water problem means contributing positively towards finding solutions to one of the global challenges. Pollution of water sources limits the availability of water that can be used for human consumption. Thus, the presence of organic, inorganic, and bacterial pollutants dramatically affects the quality of human life. This presentation will dwell on the development and application of dendritic polymer integrated nanostructured membranes for drinking and wastewater treatment by applying the principles of nanoscience and nanotechnology. A highlight on how nanostructured membranes is a promising modified version of traditional polymeric membranes for water treatment due to their antibacterial properties, photocatalytic properties, biocatalytic properties, antifouling properties, enhanced permeation, and improved rejection of pollutants will be presented.

KN3

Tracking light gated transformations of macromolecules in solution and gas phase via mass spectrometry
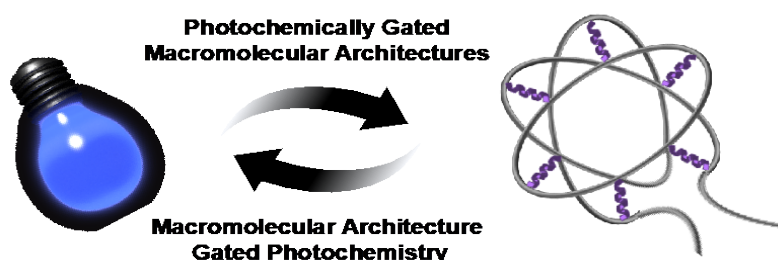
H. Frisch[,1, 2], C. Barner-Kowollik[1,2,3]

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Synthetic photochemistry has found a plethora of applications including dental materials or 3D printing. These applications utilize the spatiotemporal control of light gated reactions to manipulate macromolecules through photoreactive moieties that are usually tethered to the side chains [1] or chain ends of polymers [2]. Telechelic functionalization of macromolecular building blocks with styrylpyrene provided a unique route to control the formation, disintegration, as well as the resulting topologies of polymers. Monitoring of the wavelength gated topology control required a complex suite of analytical techniques, correlating mass spectrometry (MS) with size exclusion chromatography (SEC) and ion mobility data [2].

To incorporate functional moieties into the backbone of polymers, however, is significantly more challenging. Most chain-growth polymerization mechanisms yield polymers with all-carbon backbones, which critically limits polymer functionality and prevents degradation. A promising yet underutilized strategy to enable incorporation of functional motives rests on radical ring opening polymerizations (rROP). The complex synthesis of the required macrocyclic monomers remains a key challenge in the development of rROP: Differences between isomeric macrocycles render them either reactive or non-reactive. While conventional LC-HRMS often requires change in column material to resolve isomers, cyclic ion mobility mass spectrometry (cIM-MS) was found to enable rapid separation of mixtures of isomers only as a function of passes. Based on cIM-MS and SEC-MS it was possible to elucidate monomeric structures and ring-opening polymerization mechanisms, which enabled the incorporation of photodegradable linkages [3] and entire peptide sequences [4] into the backbone of polymers.

References
[1] D.Kodura, L.L.Rodrigues, S.L.Walden, A.S.Goldmann, H.Frisch*, C.Barner-Kowollik*, JACS, **144**, 6343 (2022).
[2] H.Frisch, K.Mundsinger, B.L.J. Poad, S.J.Blanksby, C.Barner-Kowollik, Chem. Sci., **11**, 2834 (2020).
[3] P.T.Do, B.L.J.Poad*, H.Frisch*, Angew. Chem. in press.
[4] F.Sbordone, J.Veskova, B.J.Richardson, P.T.Do, A.Micallef, H.Frisch*, under review.

OL1

Application of mass spectrometry in polymers industry

C. Kgaje[1], M. P Mothoa[1], R. D Motaung[1]

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The Analytical Services Group based at the Polymer Technology Service Centre is an enabler within Sasol Base Chemicals by providing polymer solutions through analytical testing, mechanical testing and conversion expertise. The team supports product development, plant operations and customer technical requirements.

The group is tasked to handle complex customer problems that include the identification of compounds and unknown additives in products. Typical analysis often includes the determination of the specific migration limits (SML) of various additives to ensure products comply with increasingly stringent global standards and regulations.

This paper presents the results of a detailed analysis of the composition of a polymer product comprising additives suspected of containing hazardous chemicals. Several tests revealed that the article had numerous components including flexible PVC as a main constituent with significant concentration of plasticisers. Phthalate plasticisers are regarded as endocrine disruptors especially in sensitive applications which include childcare articles, toys, medical devices and food contact [1]. Moreover, European Chemicals Agency restricted the use of several phthalates in toys and childcare articles that can be placed in the mouth [2]. It was therefore critical that further work be carried to identify and quantify the type of plasticiser used. In this regard a gas chromatograph with a time-of-flight mass spectrometer (GC-TOFMS) was used for identification and quantification. Several adipates based plasticisers were identified in the article. However, a literature review revealed that a particular plasticiser is acceptable in food contact and sensitive applications due to perceived low toxicity [3].

As a consequence of this comprehensive analysis, we were able to make several recommendations to ensure that the polymer article was safe to use in its design application and met regulatory requirements.

References
[1] Official Journal of the European Union: Directive 2005/84/EC of the European Parliament and of the Council of 14 December 2005 amending for the 22nd time Council Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations (phthalates in toys and childcare articles).
[2] European Chemicals Agency (ECHA), Evaluation of new scientific evidence concerning DINP and DIDP in relation to entry 52 of Annex XVII to REACH Regulation (EC) No 1907/2006, 2013.
[3] IARC - Summaries & Evaluations: DI(2-ETHYLHEXYL) ADIPATE, 77, International Agency for Research on Cancer, p.149. 2000

OL2

Investigations on the interaction of nitrogen-based modifiers on the viscosity of alkyl magnesium polymers with mass spectrometry

J.F. Schwarz[1], C. Schwarzinger[1]

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Alkyl magnesium compounds such as butyl ethyl magnesium or butyl octyl magnesium are used in the preparation of polyolefin catalysts. When used in high concentrations they are known to form polymeric structures which leads to highly viscous liquids that pose problems in the fabrication of the catalysts. In order to circumvent this problem, additives been tested, that interact with the polymer changes and reduce their viscosities, without having a negative effect on the following synthesis of catalysts or the final polymerization of olefins [1].

BIANs (N,N´-Bisphenyl acenaphthylene-1,2-diimines) with various substituents have been found to be effective in lowering the viscosity of alkyl magnesium solutions. In order to understand the mechanism at first SEC-MS experiments under inert conditions have been performed that showed in interaction of the BIANs with the alkyl substituents of the magnesium compounds. Depending on the type and position of the substituents two different interaction mechanisms have been found, which could also be confirmed in subsequent analyses of the quenched reaction products by HPLC-MS. Compounds such as 2,6-diisopropyl-BIAN form a stable C-alkylated species (Fig. 1), which can be reused as viscosity reducing agent while other compounds such as the unsubstituted BIAN partly decompose into aniline and acenaphtoquinone upon contact with protic solvents and only a small amount of the alkyl substituted BIAN is formed.

While all tested BIANs reduce the viscosity of alkyl magnesium solutions, the reusability of already alkylated derivatives gives a clear indication that the major mode of interaction must be the complex formation of magnesium with the nitrogen lone pairs, as is also supported by DFT calculations [1].
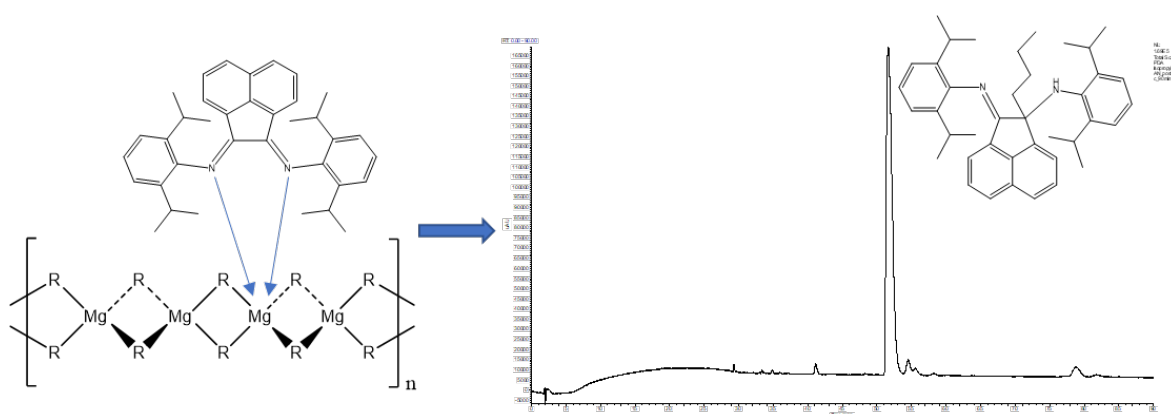
Figure 1: Interaction of 2,6-Diisopropyl-BIAN with alkyl magnesium polymer chains and HPLC-MS analysis of the formed product.

References
[1] J. F. Schwarz, T. Holtrichter-Rößmann, C. G. Liedtke, D. D. and C. Paulik, *Catalysts* **2022**, *12*(9), 973.

OL3

Mass spectrometry as a tool for polymer reaction engineering – monitoring reactivities in multicomponent polyester-based (hybrid) resins

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The polymer class of polyesters has widely been investigated for more than a century and still attracts the interest of today's scientific community due to its great versatility of suitable monomers and resulting products. The ability to adjust properties by selecting from a huge data base of available monomers is tempting. However, their reactivities are sometimes unknown and differ from each other, which has to be considered when planning the synthesis route.

A promising way to approach such tasks is mass spectrometry: on the one hand HPLC-MS can be used to track the concentration of remaining monomers during a polycondensation reaction and in some cases also gives information on small oligomers formed. On the other hand, MALDI mass spectrometry allows to determine the polymer structure itself in terms of type and number of monomers incorporated. If those techniques are used to acquire time dependent data over the course of a polycondensation reaction it is also possible to follow the incorporation of specific monomers and thus identify compositional gradients in multicomponent systems.
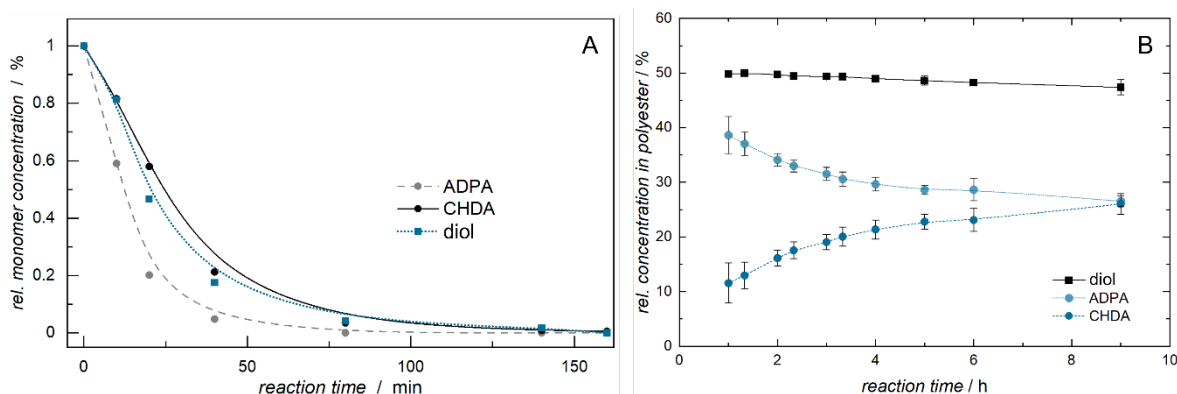
Figure: Reactivities of adipic acid (ADPA) and 1,4-cyclohexanedicarboxylic acid (CHDA) are investigated A) comparing monomer concentrations determined via HPLC-MS measurements for the first part of the reaction, and B) comparing the incorporation into the polyester via MALDI MS.

KN4

Polymers for pollutant extraction and separation from water

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In this presentation, two polymer-based systems developed in our laboratory will be presented. The first system involves an upscaled polymer inclusion membrane for possible value extraction of semi-precious minerals from acid mine drainage. The developed system was tested both in the laboratory and in the field. The developed polymer inclusion membrane system was found to be very versatile and rugged and could be deployed for up to 30 days in the field.

The second system is based on combining polymer membranes with smart polymers as passive sampler for extraction of environmental pollutants in water-based system. The developed polymer membrane in combination with smart polymers was found to be novel and was field tested.

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OL4

How can characterization of biofouling teach us to fabricate better interfaces?

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Solid materials placed in various mediums interact with their surroundings. This interaction leads to accumulation of unwanted components on their surface. In biofouling proteins, viruses and bacteria, algae, and entire organisms can become attached. Attachment depends on three parameters of the surface, including morphology, chemistry, and surface mechanical properties. If fouling is to be prevented, the related surface properties must be characterized across the length scales. Non-fouling surfaces often feature engineered molecular or polymeric layers that (as a first step in biofilm formation) prevent adsorption of proteins. Such engineered layers are often designed based on biological principles, i.e., copying composition and other molecular characteristics from nature. For example, in marine fouling, as strongly adhering components, catechol units (dopamine) are often operational. Engineered adhesive layers, if they are properly characterized and their properties are well understood, can be used also in engineering applications. Such biomimetic adhesives containing cathecols have been employed with success in the biomedical field, and in polymer composite materials, to tailor interfacial adhesion.

In this presentation following a short general introduction, three case studies will be discussed to illustrate the characterization challenge in surface fouling. First we demonstrate, how Atomic Force Microscopy (AFM) can be used across the length scales to image and monitor marine fouling, including forces of molecular attachment of proteins. Then AFM based quantitative nanomechanics, combined with a machine learning approach, will be presented to monitor death of surface attached bacteria [1]. Finally, applications of polydopamine based adhesion layers are described to tune interactions at metal fiber-polymer interfaces [2]. Interface characterization in this case is performed by single fiber pullout experiments, which will also be introduced.

The presentation will conclude with an outlook section describing some recent challenges and opportunities.

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OL5

Bimetallic nanomaterials supported on polymeric nanofiber membranes for the removal of per-/polyfluoroalkyl substances (PFAS) from various aquatic matrices

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Widespread occurrence of per-/polyfluoroalkyl substances (PFAS) has risen global concerns due to its toxic effects on the environment and to human health, which stems from its use in the food industry via food packaging, non-stick cookware and water-proof materials amongst others. Use of these products lead to the contamination of drinking water, as well as treated wastewater which is commonly used for agricultural purposes. Studies and tests have shown alarming levels of certain groups of PFAS in human and animals' blood and urine. There have been studies linking perfluorooctanoic acid (PFOA) and perfluorooctanoate sulfonate (PFOS) to certain health effects including kidney cancer, thyroid problems and high cholesterol. The United States Environmental Protection Agency (EPA) and the Food and Drug Administration (FDA) are raising awareness to environmental researchers to develop models for predicting the levels of PFAS in order to estimate how much PFAS migrates to the environment, impacting people and ecosystems, as well as running analytical detection methods to understand the occurrence of PFAS in general food. In this study, we will be investigating the occurrence and concentration of PFAS in water sources from various locations around the Western Cape Province, including dams, rivers and tap water from different areas in South Africa. The samples will be sourced every six months, over a period of thirty-six months. Analysis of PFAS compounds will be determined by ultra-high-performance liquid chromatography coupled to high-resolution mass spectrometry (UHPLC-HRMS) as well as UV-Vis. We have designed a suitable nanosystem, consisting of a recyclable polymeric membrane immobilised with suitable metal nanoparticles to be used as an extractant of PFAS from contaminated water. This will result in a considerably cheaper, safer and a simpler, more effective separation of the extractant. This technology is better than the conventional water treatment methods which require extended operating hours and higher environmental clean-up costs.

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OL6

Polymeric gel supports for nanoparticle-assisted water electrolysis

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Hydrogen is considered a sustainable solution to drive the change away from a primarily fossil fuel energy system towards a renewable energy system [1]. H_2 is attainable through water electrolysis using an electrolyser. Electrolysers are vital assets in the low-emission and sustainable production of H_2 [2]. Therefore, the development of cost-effective electrolysers for large-scale H_2 production powered by renewable sources is essential for the global future of sustainable energy. The implementation of metallic nanoparticles (NPs) in water electrolysis has had great success due to their intrinsically high surface area to volume ratio, which results in excellent catalytic activity [3]. Attachment of the electrocatalyst is achievable by means of fluorous polymeric binders referred to as 'inks', which promote adhesion to the electrode surface. However, these fluorous polymeric binders are both expensive and toxic [4], which makes upscaling of this technology very challenging, hence there is need to replace them with a self-adhesive electrocatalytic system in order to realize a cleaner and cost-effective H_2 production system. The development of self-supported poly(vinyl alcohol) and polyaniline NP hydrogel composites as electrocatalysts has great potential [5]. A linear sweep voltammogram showing the H_2 activity achieved by our PVA nanocomposites is observable in Figure 1. We anticipate that the hydrogel support system will bypass the need for the 'ink' binders, whilst simultaneously increasing the electrocatalytic activity of the NPs, towards facilitating efficient water electrolysis [3]. The application of polymers in electrochemistry is a constantly developing theme with the potential to contribute significantly towards sustainable H_2 production.
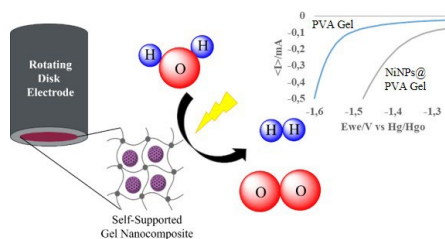
Figure 1: Graphical illustration of water electrolysis by the self-supported gel nanocomposite.

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Polymers for the isolation of membrane proteins

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Membrane proteins (MPs) play crucial roles in a wide variety of physiological processes. They are also among the most frequently used drug targets in combating a wide variety of diseases, ranging from cystic fibrosis to obesity and from migraine to asthma and miscarriage during pregnancy. Until 2009, the isolation of MPs in their fully folded and functional form was virtually impossible. Isolation was largely performed through the use of surfactants that strip the membrane lipids from the MPs and surround the hydrophobic parts of the MPs. In 2009, it was discovered that amphiphilic copolymers are able to cut MPs from the membrane with closely associated lipids retained in so-called SMALPs (styrene maleic acid lipid particles) [1]. The retention of the closely associated lipids resulted in the MPs retaining their native conformation and concomitantly, their activity.

The polymers that were used in the initial discovery of this process are poly(styrene-*co*-maleic acid) copolymers with a styrene to maleic acid ratio of circa 2 : 1. These polymers are produced via conventional radical polymerization with a relatively broad molar mass distribution. In order to optimise the copolymer composition and chain length it was deemed beneficial to use reversible deactivation radical polymerisation (RDRP) with the resulting control over molar mass distribution. The strong alternating tendency of styrene – maleic anhydride copolymerisation turns out to be a significant complicating factor in this endeavour [2].

In this contribution, an overview of the field will be provided that includes achievements of the so-called SMALP technology to date. Specific attention will be given to the development of new polymers and their effect on the isolation of MPs.
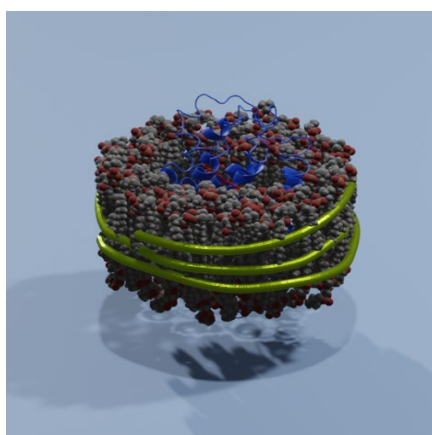

Figure: An artist's impression of rhodopsin isolated in a SMALP.

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OL7

Fabrication of a polybutylene succinate (PBS)/polybutylene adipate-co-terephthalate (PBAT)-based hybrid system reinforced with lignin and zinc nanoparticles for potential biomedical applications

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Polybutylene adipate-co-terephthalate (PBAT) was used to improve the properties of polybutylene succinate (PBS). The resultant blend consisting of PBS/PBAT (70/30) was reinforced with lignin at different loadings (5 to 15 wt.%) and zinc (ZnO) nanoparticles (1.5 wt.%). Hot melt extrusion and injection moulding were used to prepare the hybrid composites. The mechanical, thermal, physical, self-cleaning, and antimicrobial properties of the resultant hybrid composites were investigated. The transmission electron microscopy (TEM) results confirmed that ZnO was successfully prepared with average diameters of 80 nm. Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) confirmed that there were interactions between the fillers and the blend. The tensile strength and elongation at the break of the resultant materials decreased with increasing the loadings, while the tensile modulus showed the opposite trend. The melting behaviour of the blend was practically unaffected by incorporating lignin and ZnO nanoparticles. In addition, the incorporation of fillers reduced the thermal stability of the materials. Furthermore, the incorporation of ZnO nanoparticles introduced photocatalytic properties into the polymer blend, rendering it to be a functional self-cleaning material and enhancing its antimicrobial activities.

OL8

Characterization of stimuli-degradable polymers for triggered drug release

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For an effective pharmacotherapy an optimal accumulation of a drug within an affected part of the body is required. Furthermore, a controlled release of the drug at the target site is required. This can be realized by "intelligent" systems utilizing different triggers like light, pH value, or redox properties to release the drug in a controlled fashion [1–2]. Colloidal drug delivery systems based on novel switchable polymers are investigated allowing an effective drug transport into cells and tissues. Hence, on one side the intracellular pH shift in endolysosomal compartments is used to effectively degrade the polymer and release the drug. Furthermore, the increased concentration of reductive glutathione (GSH), which especially can be found in tumor cells, is used for the degradation of redox-sensitive polymers. Additionally, light switchable polymers are investigated that can release the embedded drug from the drug carrier after a short period of irradiation [3–5]. Here, we report novel polymers which are cleavable by different stimuli (light, pH value, redox agents). Degradation of these backbone- or side-chain-cleavable polymers was analyzed by UV/Vis spectroscopy and SEC as well as hyphenation of SEC with ESI-ToF-MS. Furthermore, nanoparticles were fabricated and characterized by photon correlation spectroscopy as well as scanning electron microscopy to evaluate the suitability for drug delivery application [6]. The final goal is the development of drug delivery systems being able to respond to different stimuli.

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OL9

Multiple detection size exclusion chromatography: a powerful tool for understanding the scaling properties of enzymatically crosslinked casein nanoparticles

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Nanoparticles borne of biomacromolecules have become indispensable in modern society owing to their precisely folded structures which determine their biochemical function. Taking this inspiration, caseins - milk proteins which lack any tertiary structure - can undergo intra- or intermolecular folding via enzyme-catalysed crosslinking to result in denser nanoparticles ranging from single chain nanoparticles (SCNP) to higher multimeric nanoparticles. The protein folding mechanism is done with microbial transglutaminase (mTGase), an enzyme that catalyses acyl transfer reactions between the γ-carboxamide group of glutamine and primary amines such as ε-amino groups of lysine, at ultra-low protein concentrations to avoid intermolecular cross-linking [1]. The development of well-defined casein nanoparticles to explore their technological potential is favoured by the wide availability of casein and suitable crosslinking enzymes.

While a large range of techniques exist to determine a multitude of properties of these casein nanoparticles, relating physicochemical properties of the particle to the chemical structure of the intrinsic precursors is still challenging. Here, an advanced hyphenated technique, SEC coupled to 5-fold-detection in Fig 1 (SEC-D5: UV-vis, MALS, DLS, viscosity, dRI), was recently introduced in our research group for the investigation of small SCNPs [2]. By combining molar mass separation with the determination of the corresponding hydrodynamic radius (R_h) as well as of intrinsic viscosity [η], SEC-D5 delivers systematic information on differences in the mechanisms of mTGase induced crosslinking of casein monomers and particles of different sizes.
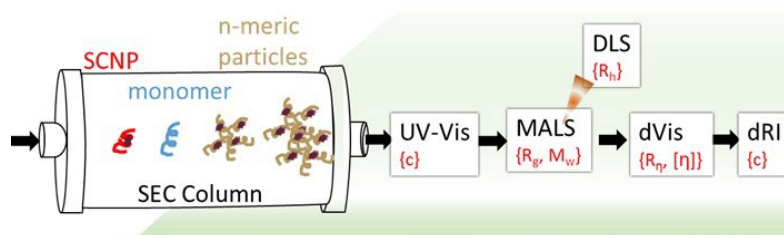

Figure 1: Measurement of the scaling properties of casein nanoparticles by SEC-D5

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OL13

Novel initiator for design of hybrid smart polymers and materials

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New designs of stimuli sensitive polymers are under development by combining monomers that have independent mechanisms of polymerization. However, these design intents suffer from requiring multiple activation stimuli that limits application and commercialization. Recent discoveries in our laboratory have found novel initiators and methods that can initiate free radical, ring-opening, carbene-based polymerization or combination thereof. Herein, the development of hybrid polymerization techniques is presented and quantified with rheometry measurements in real-time that discern multiple liquid and elastic properties, including dynamic viscosity, gelation time, shear modulus, yield stress and resin expansion/shrinkage. Structure property relationships Case studies of light activated resins (photocuring) will be presented for the first time that demonstrate flexible methods of hybrid and interpenetrating polymer design strategies. Polymeric initiation and propagation are observed in real-time, enabling tuning of mechanical properties and correlation of secondary measurements such as shrinkage, temperature, and infrared spectroscopy.

OL14

Synthesis, characterization, and application of a molecularly imprinted polymer as an adsorbent for solid-phase extraction of selected pharmaceuticals from water samples

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Most pollutant compounds exist as mixtures in the environment. In this regard, one of the 12 principles of green analytical chemistry emphasize the need for methods that allow for analysis of multiple compounds versus those that analyze a single analyte at a time. In this work, we present a molecularly imprinted polymer (MIP) synthesized for the selective and efficient extraction of selected pharmaceuticals belonging to five different classes namely: an antiretroviral (nevirapine), an antidepressant (venlafaxine), a muscle relaxant (methocarbamol), an anticonvulsant (carbamazepine) and a cardiac stimulant (etilefrine) from surface water samples. Cavity tuning experiments using the target pharmaceuticals as a single or multi-template were conducted and the venlafaxine imprinted polymer was successfully selected for the study based on its high selectivity towards targeted pharmaceuticals. Batch adsorption and kinetic studies showed that adsorption of the selected pharmaceuticals onto the particles of the polymer followed a Freundlich adsorption isotherm as well as a pseudo second order adsorption model. This indicated heterogeneity of the binding surface energies on the MIP resulting in multiple interactions through chemisorption. An analytical method for quantification of the compounds using liquid chromatography-mass spectrometry (LC-MS) was successfully developed, with detection limits ranging from 0.03 to 0.31 ng mL^{-1} and quantification limits in the 0.12 - 3.81 ng mL^{-1} range. The imprinted polymer was then evaluated as a selective adsorption sorbent for solid phase extraction (SPE) of the selected pharmaceuticals in dam water samples followed by LC-MS analysis, giving recoveries ranging from 43 - 69%.

OL15

Structural-function characterization of therapeutic nanoreactors based on photo-crosslinked polymeric vesicles

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In the field of next-generation therapeutics, smart nanoreactors should be capable of controlling therapeutic effects under different stimuli, active signalling pathways or even replace damaged cellular functions in the body that are responsible for many current diseases [1–2]. In particular, polymeric vesicles (polymersomes) have extensively used in this field due to their high stability, adaptive physicochemical properties, easy surface modification, asymmetric functionalization and tunable membrane permeability under different stimuli [3].

This contribution will focus on the design of therapeutic nanoreactors based on photo-crosslinked polymeric vesicles for different applications by varying factors such as membrane properties (tuning the polymer composition), enzymes as cargo (different size and surface charge) and cargo loading methods (in situ/post). Through the combination of advanced analytical tools, structural parameters (particle shape, enzyme location, size), physico-chemical properties (membrane permeability, stability) and biological-like functions (capture/release behavior, transport, enzyme activity) can be addressed. These key parameters were confirmed by dynamic light scattering (DLS), cryogenic-transmission electron microscopy (Cryo-TEM), zeta potential, asymmetrical flow field-flow fractionation (AF4), electron paramegnetic resonance (EPR), UV-VIS and fluorescence spectroscopy [4–6].

All these preliminary studies show a very promising synthetic platform for designing therapeutically active nanocompartments that can overcome the enzymatic lack in many current metabolic or genetic diseases with no cure.

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PL2

Chemically-sensitive online detection for detection of functional groups: SEC-NMR, HPLC-NMR, SEC-IR(QCL), And FT-LC

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The coupling of spectroscopic detectors to classical SEC and/or HPLC methods offer the promise of a spectrum at every elution slice for the monitoring of functional groups. We discuss here our development and implementation of coupled chromatographic methods in several different configurations, extending over the last decade.

With SEC-NMR, we have combined low-field 'benchtop' ^{1}H-NMR (60 MHz), an improved flow cell, and semi-preparative separation columns for detection of polymer analytes and mixtures in protonated solvents (THF and $CHCl_3$). Significant improvements in sensitivity were achieved by optimizing chromatographic parameters, flow cell geometry, NMR pulse sequence and acquisition parameters, as well as post-acquisition data processing. With this method, co-eluting polymers (e.g. PS/PMMA blends of similar hydrodynamic volume) can be easily distinguished based on their ^{1}H-NMR spectra [1].

We have additionally studied HPLC coupling with benchtop ^{1}H-NMR (80 MHz). Here, para-hydroxybenzoic acid esters (parabens) have been chosen as model compounds and are separated by means of liquid adsorption chromatography (LAC, reverse phase mode) with acetone/water as mobile phase. The analytes are then detected and identified using NMR absorption spectra (aliphatic and aromatic protons), rather than by using reference standards. We are able to measure paraben concentrations below the maximum allowed concentration in cosmetic formulations [2].

We recently developed a new chromatographic injection method called Fourier transformation liquid chromatography, FT-LC, in which analyte stock solution is continuously introduced as a sinusoidal concentration profile and detected both before and after SEC separation using two detectors. The oscillatory output signal is time delayed and corresponds to a phase-shift when evaluated by Fourier transformation. Consequently, it is possible to use the analyte phase angle for molecular weight determination after establishing a calibration curve. This method was found to improve (S/N) / $t^{0.5}$ by a factor of ca. 50, compared to conventional SEC [3].

For the ongoing development of infrared detection, we have built a spectrometer incorporating 3 mid-IR quantum-cascade-laser sources (each with tunable ranges of ca. 200 cm^{-1}), a flow-through cell, and liquid-N_2-cooled MCT detectors (SEC-IR(QCL)). As the lasers deliver ca. 10^4 more photons per wavenumber than standard thermal emitters (globar), the detection is extremely sensitive. The limit of detection on carbonyl stretching vibration at 1730 cm^{-1} of PMMA, after separation on a semi-preparative SDV column in THF, was 0.46 µg, about a factor 30 lower than reported for SEC-FTIR. We discuss here the latest improvements obtained by pulsed emission [4].

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KN6

Analysis of ultra-high molar mass polyacrylamides by Asymmetrical Flow Field-Flow Fractionation: Necessity of low flow rates and Dilution Control Module™ (DCM)

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Polyelectrolytes based on acrylamide and sodium acrylate which have high molar masses are used to oil extraction from oilfield. The physico-chemical properties of the oil are modified by the injection of this water-soluble polymers. Polymer with water has a high viscosity and can push more oil out of the pores of the oil field. Moreover, the viscosity is mainly due to the molar mass (M_w) and to the size of the polymer chains. Therefore, measuring the structure, size and mass of the polymer is important to ensure the effectiveness of polymer injection. We analyzed two type of polyacrylamide samples: Model Polymers (MP) between 1×10^5 and 10×10^5 g/mol and Industrial Polymers (IND) between 3×10^6 and 20×10^6 g/mol. As-FlFFF/MALS/RI was used to characterize precisely the polymers (Molar Mass and Polydispersity). Classical method at 1 ml/min of Detector Flow (Fd) and 2.5ml/min of Cross-Flow (Fx) was first used, Model Polymers was successfully characterized but Industrial polymer at high molar mass present a mix between steric and normal mode. A solution to avoid the steric mode is to use low flows (0.2 ml/min of Fd and 0.4 of Fx) and low injected quantities (< 2 µg). However the MALS signal is weak due to the low quantities, the Molar Mass calculation contains many uncertainties and the distribution is flat while the expected polydispersity is important. To increase the MALS signal, the Dilution Control Module™ (DCM) developed by Wyatt Technologies was used: The channel contains a second outlet to suck up a part of the eluent and allows to less dilute samples at the outlet. The channel Flow is kept at 0.2 ml/min but the Fd is set to 0.05 ml/min. The sample is concentrated by 4. The techniques allow to have better signals and to improve Mw calculation and polydispersity with low incertitude and noise.

OL10

Facile fabrication of multifunctional metallic nanostructures: advanced analysis with novel 3d correlation Thermal Field-Flow Fractionation

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Multifunctional metallic nanostructures are essential in the architecture of modern technology, notwithstanding the multiple challenges associated with their characterization. Presented herein is a novel photoreduction-based protocol for augmenting and modulating the inherent properties of acrylic polymers with imidazolium substituents (p(AAC6ImC4)Cl) through orthogonal functionalization with gold nanoparticles (Au NPs) to produce Im_Au NP nanostructures; and the novel and advanced characterization thereof via three-dimensional correlation thermal field-flow fractionation (3DCoThFFF). Coordination chemistry is applied to anchor Au^{3+} onto the nitrogen atom of the imidazolium ring, for subsequent photoreduction using UV irradiation to produce Au NPs. Thermal field-flow fractionation (ThFFF) and localized surface plasmon resonance (LSPR) of Au NPs are both dependent on size, shape and composition, thus synergistically co-opted to develop mutual correlation functions for the advanced analysis of 3D UV-Vis spectra. With 3DCoThFFF, multiple sizes, shapes, compositions and their respective distributions are synchronously correlated using time-resolved LSPR, as derived from multiple two-dimensional (2D) UV-Vis spectra per unit ThFFF-retention time. As such, higher resolutions and sensitivities are observed relative to regular ThFFF and batch UV-Vis. Moreover, 3DCoThFFF is shown to be highly competent for monitoring and evaluating the thermostability and dynamics of the metallic nanostructures, through the sequential correlation of 2D UV-Vis spectra measured under incremental ThFFF temperature gradients. Comparable sizes are measured for p(AAC6ImC4)Cl and Im_Au NP. However, distinct elution profiles and UV-Vis absorbances are recorded, thereby reaffirming the versatility of ThFFF as a robust provision for validating the successful functionalization of p(AAC6ImC4)Cl with Au to produce Im_Au NP nanostructures.

OL11
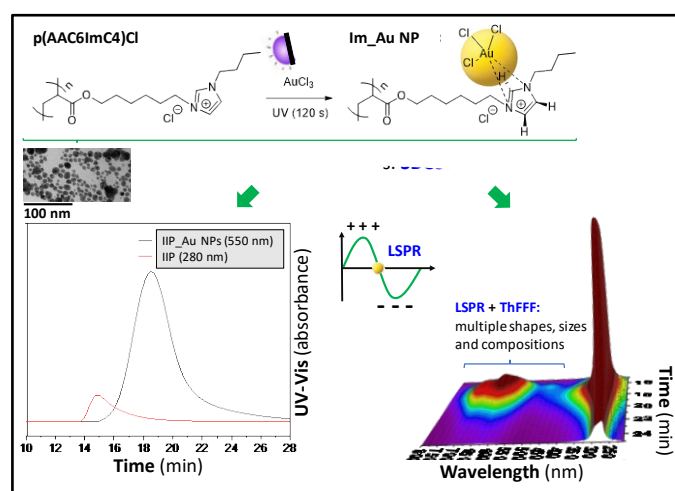
Size-exclusion chromatography of PEEK in mixture of acidic and chlorosolvents

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Polyaryletheretherketones (PAEK) and PEEK are high performance polymers with various applications in critical areas due to their outstanding chemical, thermal and mechanical properties. Aerospace, medical, scientific instrumentations are some industrial current uses.

PEEK polymers are not soluble in common laboratory solvents even in solvents such as hexafluoroisopropanol. High temperature size-exclusion chromatography at 115 °C in phenol/trichlorobenzene was set as a reference with its safety and instrumental issues. Several derivatization approaches were proposed with sulfonation (NMP as final solvent) and dithioacetalisation (chloroform as final solvent) alternatives with incomplete reaction and time pittfalls. A low temperature based on mixture of dichloracetic acid and dichloromethane was proposed but seen as corrosive and toxic with a potential degradation during analysis. The development of new low temperature SEC with high coupling capability (UV, ^{1}H NMR, FTIR) was proposed [1,2]. Such new methodology was improved by interaction chromatography of PAEK [3] but faced strong proprietary issues (non-disclosure).

Our recent investigations focused on the trial and comparison of various mixtures of acidic solvents (dichloroacetic acid and "phenols") with chlorosolvents (mainly dichloro and trichlormethane) on the low temperature size-exclusion chromatography results. From our knowledge, SEC of PEEK in such solvents have not been studied and we focused on long term repeatability/reproducibility and relative/absolute datas using MALLS detection. The corrosive and safety aspects have been reviewed.

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[3] ISPAC 2016, Singapore

OL12

Comprehensive analysis of antimalaria drug delivery systems by integrated characterisation methodologies

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The advancement of nanopharmaceuticals in research and subsequent clinical application requires suitable characterisation methods that are robust, reproducible and of high accuracy. The main aim of the work is to evaluate the application of multi-detector asymmetric-flow field-flow fractionation along with spectroscopic techniques and thermal analysis for the comprehensive characterisation of potential antimalaria drug delivery systems. Drug delivery systems are heterogeneous and complex, due to the intrinsically inherent multiple molecular distributions. Moreover, the quantitative and qualitative determination of the antimalaria drug associated with the drug delivery system contributes to its complexity.

Asymmetrical-flow field-flow fractionation coupled with multi-angle light scattering, dynamic light scattering and variable wavelength detector, is used for the characterisation of antimalarial drug-delivery nanoparticle systems, in terms of (1) particle size, (2) polydispersity, and (3) particle shape. In addition, this approach allows for the quantitative assessment of the antimalarial drug delivery system with regard to the loading and release of the antimalarial drug. Along with supporting characterisation techniques, such as Cryo-TEM, small-angle X-ray scattering, and thermal analysis, a comprehensive analytical strategy is employed for the analysis of antimalarial drug-delivery nanoparticle systems.

OL16

Understanding molecular complexity of biodegradable polymer: Comprehensive analysis of aliphatic polyesters

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Due to the growing need to preserve our environment, biodegradable and bio-compostable polymers have become increasingly relevant and are filling the gaps created by the mainly used non-degradable polymers, especially for agricultural, packaging and biomedical applications [1-3. Amongst the many existing degradable polymers, aliphatic polyesters such as polylactic acid (PLA) and poly-ε-caprolactone (PCL) have gained increasing interest in designing medical devices. Industrially, polylactic acid is produced *via* coordinative ring-opening polymerization (ROP) of the lactide (dimeric monomer) using tin (II) octanoate as catalyst and alcohol/water as initiator, as shown in Figure 1 [4,5].

Designing materials to meet a niche market requires a well-defined microstructure, including molar mass, chemical composition and distributions. With the growing interest in biodegradable polymers for biomedical applications, it is essential to characterize these materials, address their microstructural complexity, and correlate this information to the end-use properties via analytical techniques. Here, we aim to develop robust gradient interactive chromatography (GIC) methods capable of addressing various chemical composition heterogeneities (tacticity, comonomer content, functional group) of these polymers. In hyphenation with size exclusion chromatography (SEC), two-dimensional liquid chromatography (2D-LC) methods will be developed and used to map the molar mass information of the identified chemical species. The chemical structures of the separated chromatographic species will be elucidated and correlated accordingly using MALDI-TOF mass spectroscopy and nuclear magnetic resonance (NMR) spectroscopy.
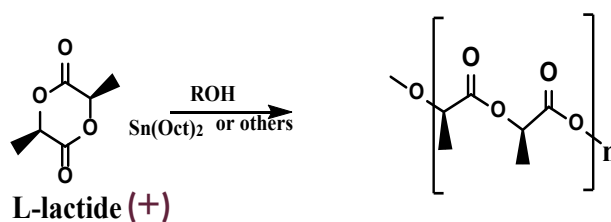
Figure 1: Industrial production of polylactic acid (PLLA) via the ROP of the dimeric lactide.

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OL17

Design and preparation of PLA/PBAT_Fe$_3$O$_4$_GO@CNC nanocomposite with excellent flame retardancy

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Petroleum-derived plastics have been used in a variety of applications due to their low production costs, ease of manufacture, and excellent physical and barrier properties. However, they have produced a large amount of waste that does not degrade or decompose over time, resulting in severe environmental pollution. As a result, new environmentally friendly alternatives such as biodegradable polymers have been sought. Poly (lactic acid) (PLA) is a commercial and important biopolymer that comes from renewable resources such as corn starch and sugar cane, is biodegradable and compostable, and is available on the market at a low cost compared to other bioplastics [1]. PLA is a polymer with properties that can be used in a variety of basic products and engineering applications, including films, EMI shields, textiles, fibers, and packaging, which all require flame retardancy. However, one of its disadvantages is that it is a delicate material. Poly (butylene adipate-co-terephthalate) (PBAT) on the other hand is an aromatic aliphatic biodegradable co-polyester (a registered trademark of BASF, known as Ecoflex®) and an ideal blending component for bioplastics. PLA-PBAT blends are promising materials because of the mechanical resistance provided by PLA and the flexibility provided by PBAT [1,2]. Furthermore, combining PLA and PBAT is a natural way to improve the properties of PLA without compromising its biodegradability(Long et al.). The utilization of green polymeric blends, their composites/hybrids as aforementioned is the drive of the research community within recent decades [3]. Materials targeted at green flame retardancy are not left out in this pursuit. In this work, we aim at utilizing graphene oxide (GO) and carbon nanocrystals (CNC) reinforced PLA:PBAT system towards preparation of efficient flame retardant materials. As per research findings, the PLA/PBAT 60/40 blend composition has been chosen because it possesses the best balance of strength and flexibility based on mechanical properties evaluation, as well as good rheological, morphological, as well as thermal properties suitable for flexible fabric preparation. Herewith we have utilized a carbon-based composite (GO@CNC) nanoparticle as reinforcement for the nanocomposite preparation leading to enhanced flame retardancy of the nanocomposite prepared. This work is expected to inspire us and other researchers to manufacture innovative materials using comparable systems and even a variety of polymeric matrices.

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OL18

Abiotic and biotic degradation of biobased polymers, biopolymer blends and biocomposites under different environmental conditions

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The polymeric materials with their extensive and short-term application have led to their accumulation in the environment, which pose a serious environmental problem due to the non-degradability in both terrestrial and in aquatic environment. Alternative plastics, such as biobased, biodegradable and compostable plastics offer more sustainable alternative to fossil-based, non-biodegradable plastics. However, there is no clear evidence on the environmental performance of biobased polymeric materials under different conditions, in terms of the role of polymer structure, additives and their (bio)degradability. The present study involved understanding the environmental degradation of biobased polymers such as polybutylene adipate terephthalate (PBAT), polybutylene succinate (PBS), polylactic acid (PLA); PBAT-PBS blends and PBAT-TPS biocomposites under different abiotic (direct sunlight, static oven temperature at 50 °C and hydrolytic) and biotic (compost, soil burial and marine water) conditions.

In this study, the mineralization (ultimate biodegradation) of these biopolymers, blends and biocomposites were assayed based on amount of carbon mineralized in biotic environments (compost, soil and marine water) for period of 180 days. During this environmental degradation conditions, hydrolysis and oxidation processes were monitored by the evaluation of the hydrolysis Index (OHi) and carbonyl Index (COi) profile by FT-IR spectroscopy. All the test materials were carried out up to the maximum extent of hydrolysis and oxidation processes. Changes in the thermal properties such as melting temperature (Tm) and degree of crystallinity were assessed by using differential scanning calorimetry (DSC), decomposition temperature (Tonset) and weight loss, were determined by using thermogravimetric analysis (TGA).

Environmental abiotic degradation results suggest that thermal and hydrolytic conditions are significantly influencing the degradation of biobased polymers as compared to sunlight exposure. The ultimate biodegradation results showed that the biopolymer blends and biocomposites have advantages of enhanced biodegradability in natural environmental conditions. The present study constitutes a useful protocol in order to collect the information necessary to understand the interaction between nature and degradation products of biobased polymeric materials, in a dynamic system, to consider as environmentally friendly materials.

P1

3D wound healing scaffolds made of nanoparticles embedded within biodegradable polymers

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Recent developments in advanced technology and nanotechnology have proven to be promising solutions in therapeutics, including wound care management [1, 2]. Advanced wound dressings in the form of hydrocolloids, films, foams, hydrogels and scaffolds have been designed and used to solve health problems underlying wound care treatment [3, 4]. These wound dressings are designed to meet ideal requirements which include the ability to maintain a balanced moist environment, adherence to the wound, allow the exchange of oxygen and prevent bacterial infection. The requirements ensure the acceleration of wound healing and reduce the complications that are associated with the process.

Herein we showcase a facile way of fabricating bioactive nanomaterials to design an advanced wound dressing in the form of 3D scaffolds. The scaffolds were made of nanocomposites containing biocompatible and biodegradable polymers decorated with metal nanoparticles with fast and broad spectrum of antimicrobial activity against gram-(positive and negative) bacteria. Additionally, these NPs are also non-toxic to mammalian cells at regulated concentrations rendering them suitable for wound healing applications. The antimicrobial activity of the scaffolds was tested against *E. coli* and *S. aureus* bacterial strains. Cell proliferation and the cytotoxicity were evaluated using human dermal fibroblasts (HDF) cells. The scaffolds were found to posses excellent antimicrobial activity against *E. coli* and *S. aureus* with minimal toxicity towards HDF cell. Eminently, the scaffolds were found to improve the rate of proliferation of HDF cells.

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P3

Advanced separation and characterization of end-chain functionalized polyolefins and block copolymers from chain walking polymerization

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The present study reports liquid chromatography at different temperatures for investigating the distribution in size, conformation, and chemical composition of end-chain functionalized and block copolymers of chain-walking polyolefins (CWPOs). For this purpose SEC with multiple detection (MALLS, QELS, Visco, RI) as well as interaction chromatography of polyolefins in solvent (SGIC) and temperature (TGIC) gradient modes has become a fast-developing technique capable of providing branching, topology, and chemical composition distributions [1]. The physical properties of CWPOs can range from rigid and mechanically strong thermoplastics that are only soluble at high temperatures to viscous rubbery elastomers that are soluble in organic solvents at room temperature. The addition of a novel type of functionalities as well as the block-copolymer size influences their properties dramatically (Fig. 1). Thus, a combination of different conditions, column types, and complementary characterization methods deliver in-depth information on the fidelity of the synthetic and the real multimodal distributions of these complex copolymers.
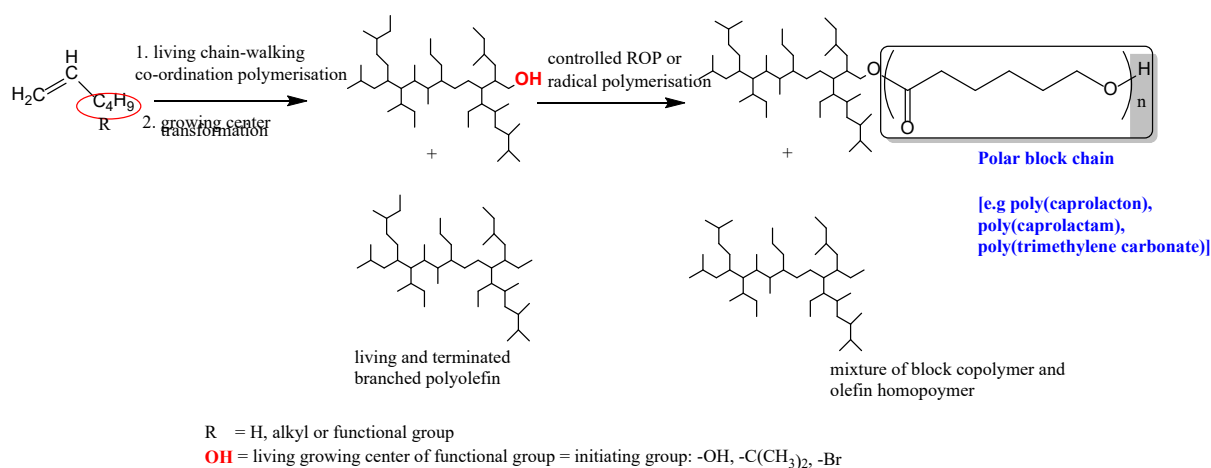
Figure 1: Preparation of block copolymers by combination of CW polymerization and ring-opening polymerisation (ROP) or controlled radical polymerization.

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P5

Preparation and characterization of specially graded, water-soluble biopolymers: From waste biomass to value-added derivatives

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In a nutshell, the centrepiece for creating a circular economy is the use of biopolymers from renewable sources rather than petroleum-derived polymers. Added to their natural abundance, polysaccharides are readily recycled by various microorganisms relative to their non-renewable petroleum-based counterparts [1]. Food processing methods often results in huge incidental biopolymer waste streams which is an ideal feedstock for valorisation that aim toward zero waste and low carbon footprints. Quite recently, a rapid global rise in the utilisation of insects to produce protein and oils from food waste has resulted in an untamed waste stream, i.e., insect skeleton and pupae rich in chitin [2]. Chitin and chitosan are heterogeneous biopolymers that could function well as is or as fractions for structure/property-specific applications [3]. Currently, the procedure of manufacturing chitin from crustacean shell waste (which has wide range of molecular weights, quality, as well as price) is water intensive and not environmentally friendly [4]. Most of the commercial applications are focused on high-volume low-cost, poorly defined biopolymer material utilised for water purification and composting. As such, this work highlights the preparation and fractionation of well-defined, quality-controlled and up scalable chitin/chitosan biopolymer supply from sustainable sources that have remarkable aqueous solubility attributes together with reproducible bioactivity properties.

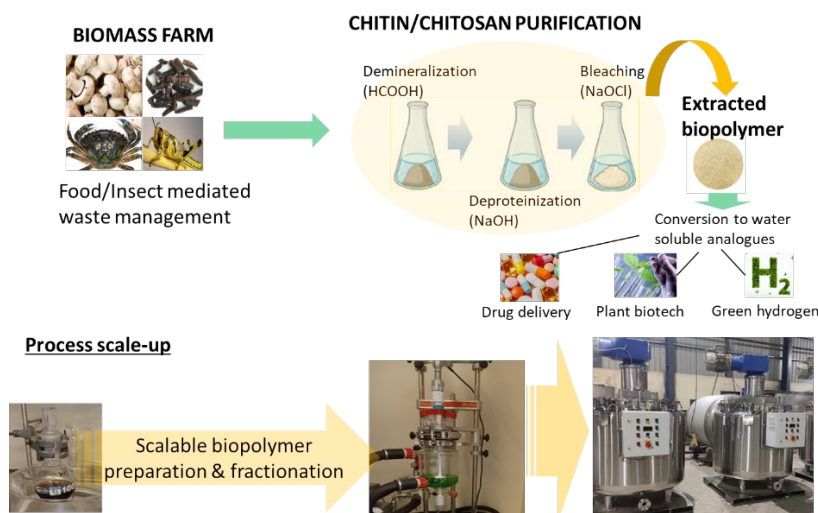Figure: Scalable preparation and fractionation of well-defined chitin/chitosan from waste biomass.

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P7

Microwave-assisted synthesis of phenanthrenequinone-based triazine covalent organic frameworks (COFs) via Friedel-Crafts reaction for use treating brackish water

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Water scarcity is becoming an ever-growing problem in society. This is all due to the rapid increase in human population, harsh changes in the weather climate. New approaches for treating and recycling brine water into freshwater instead of discharging are needed, significantly large reduction in energy usage and decreasing harmful impact to the environment must be achieved in brine recovery. This study aims to introduced green technology into the reclamation of brine water by use of covalent organic frameworks (COFs) materials which will be used as part of a novel traizine-based COFs material which can be used as a nanomembrane for desalination of brine water from water treatment plants at Umgeni Water. Current technological approaches used are inefficient and unsuitable in 3rd world, developing countries including the republic of South Africa. This work focuses on a microwave-assisted synthesis involving Friedel Crafts reaction between monomers to yield a product of a triazine-based covalent organic frameworks (COFs) membranes. To confirm the products high resolution transmission electron microscopy (HRTEM), carbon NMR (^{13}C NMR) with peaks at chemical shifts of 131, 143 and 172 ppm respectively. Fourier-transform infrared spectroscopy (FTIR) was employed and showed N-H stretches at a region of 3396 to 3050 cm^{-1}. The COFs that were successfully synthesised were going to be incorporated on a polymeric substrate to fabricate a nanofiltration membrane and applied for nanofiltration or ultrafiltration purposes.

P9

A novel electrochemical sensor for the detection of zearalenone in food matrices using PEGylated Fe_3O_4 nanoparticles supported by multidetector AF4 and *in-silico* studies

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Zearalenone (ZEN) is a carcinogenic non-steroidal estrogenic mycotoxin produced by the *Fusarium* fungi species widely found in mouldy maize, wheat, and rice, as well as other cereal and dairy products [1].

In this work, an electrochemical biosensor was developed using PEGylated Fe_3O_4 NPs and cMWCNTs for the detection of ZEN in commercial food samples. Multidetector Asymmetrical-Flow Field-Flow Fractionation (MD-AF4) was employed to determine the particle shape, size characterization and distribution of the synthesized PEG-Fe_3O_4 NPs. The surface interactions between the layer-by-layer fabricated electrodes and ZEN were investigated by a combination of Monte Carlo (MC) and molecular dynamics (MD) simulations. Finally, by identifying redox reactive sites using density functional theory (DFT) calculations, the sensing mechanism for ZEN by GCE/PEG-Fe_3O_4 NPs/cMWCNTs was proposed.

The methodology employed in this study can be extended to complement toxicity studies in the food, pharmaceutical and agricultural industries in South Africa.

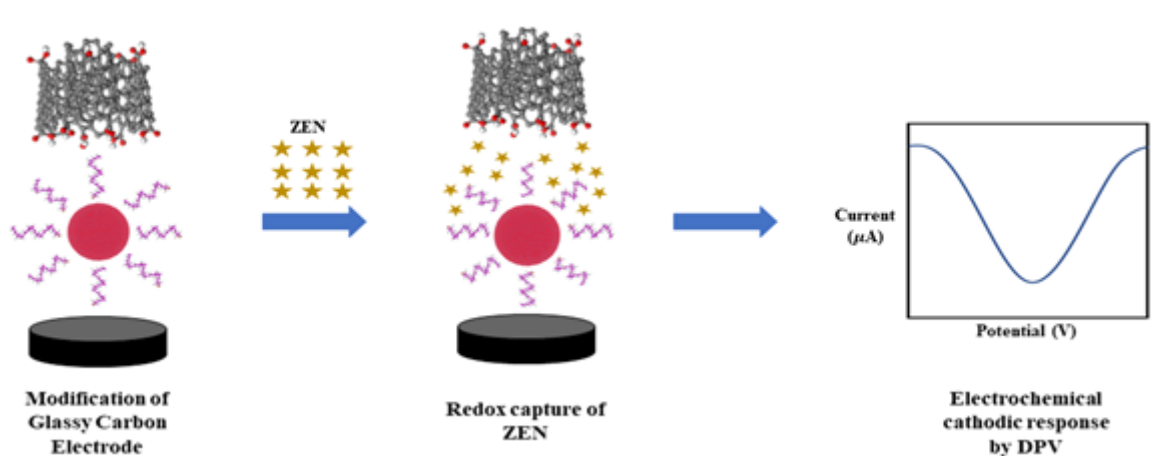Figure 1: Schematic diagrammatic representation of GCE/PEG-Fe_3O_4 NP/cMWCNTs electrode for ZEN detection.

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P11

Nano-encapsulated Melia azedarach extract within chitosan polymeric nanoparticles as preferred alternatives to synthetic pesticides

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Increased surface temperatures observed across Africa have triggered the outburst of vegetable pests that feed on essential crops as a result of climate changes [1]. Such developments negatively impact crop production and are likely to exacerbate food insecurity, especially in the fast-growing population. Fruit extract of Melia azederach tree have been argued to contain extracts that discourage feeding, retard development, and cause mortality in the larval stage of the most destructive pest. However, these plant extracts are composed of volatile components, and rapidly evaporate [2]. It is desirable to formulate them in a cover protecting the extracts against environmental conditions. Chitosan is believed to be an ideal biopolymer for plant extracts nanoencapsulation due to its biodegradability, availability, safety, and biocompatibility. It is composed of D-glucosamine and N-acetyl-D-glucosamine with reactive amino & hydroxyl groups. Thus, due to its positively charged surface, chitosan is able to stabilise the plant constituents through electrostatic interaction [3]. In the current study, nanoencapsulation systems from chitosan nanoparticles (CSNPs) and tripolyphosphate were used to improve the stability and controlled release of the encapsulated Melia Azederach extracts. FTIR & UV-Visible spectroscopy were used to monitor the formation of the nanoparticles and dynamic light scattering detected that the sizes of CSNPs increased to (95 ± 1 – 238 ± 12 nm) range with positive surface charges (18 ± 1 – 26 ± 1 mV) due to addition of melia azedarach extracts at different concentrations. Electron microscopic (SEM and TEM) analysis confirmed spherical morphology and dispersity of the nanoparticles. The encapsulation efficiencies, release behaviour, Thermogravimetric and Brunauer-Emmett-Teller surface area analysis will be presented. These promising eco-friendly CSNPs show characteristics and potential for exploration as sustainable alternatives to environmentally hazardous chemical pesticides.

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P13

Investigation of micro and nano plastic translocation, fate and bioaccumulation in mice using spectroscopic and microscopic techniques

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Recent studies have shown humans to be susceptible to great exposure measures of environmental micro and nano-plastics [1], with an estimated rise in environmental concentrations of nano-plastics [2]. Only recently, has the impact of these plastic fragments drew concern towards human health due to the potential daily exposure by varying exposure routes, with possibility of eliciting toxicological activities [3]. Furthermore, the aspects of these microscopic plastic particles in relation to effects, fate and behavior in the human body remains a great mystery. In this study, the fate or translocation of micro and nano sized polystyrene (PS) plastic particles was investigated using mice model organisms through a histopathological experimental approach using spectroscopic and microscopic techniques.

Mice were exposed to test particles once every week by oral gavage, for 4 weeks at 4 mg/kg doses, 1 mg/ml concentration and a maximum volume of 100 µL. Mice were euthanized by CO_2 inhalation, and death was confirmed by cervical dislocation. Fetuses of pregnant dams were removed during necropsy and decapitated with sharp scissors. Tissues were then extracted, affixed into histological slides, and analyzed. Under Raman spectroscopy, development of new peaks was observed under treated samples, characteristic of polystyrene (Fig. 1A) under the 700 cm^{-1} to 900 cm^{-1} region (C-S, C-O-C, O-O) (Fig. 1B). To verify their presence, the same set of samples were observed under fluorescent microscope. The observations revealed a presence of fluorescing particles sized within our particle ranges (Fig.1C).
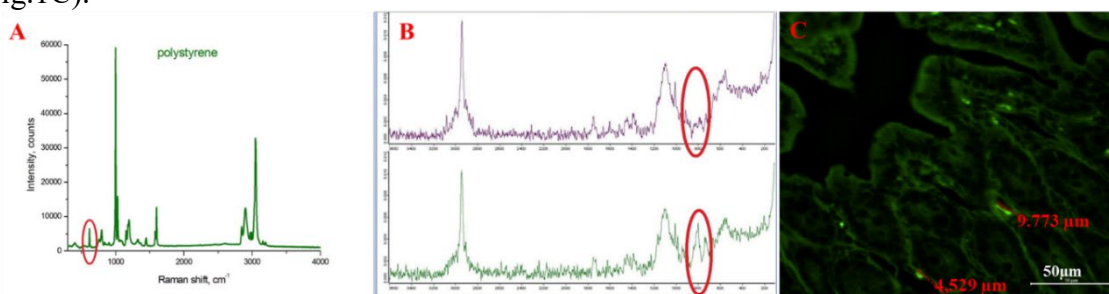
Figure 1: A) Raman spectrum of pristine Polystyrene B) Raman spectra of gut tissue with estimated polystyrene (Observed new peak), C) Fluorescing particles observed under a fluorescent microscope sized approximately 5µm and 10 µm.

The potential to study the fate and translocation of plastic particles using spectroscopy and microscopy exists but setbacks still exist regarding identification.

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P15

PLA-*b*-SMA as an amphiphilic diblock copolymer for encapsulation of lipophilic cargo

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The physicochemical properties of active pharmaceutical ingredients (APIs) can limit the efficiency of drugs administered in bulk forms such as injectable formulations, capsules, suspensions, tablets, etc[1]. These limitations include solubility, bioavailability and a reduction in the APIs half-life and selectivity [1]. The therapeutic efficiency of APIs can be improved via encapsulation in polymeric nanoparticles (PNPs) constituting block copolymers with a hydrophobic and hydrophilic block. Encapsulation of lipophilic components in the PNP core is facilitated by the hydrophobic block, while the hydrophilic block forms the corona, helping to stabilize PNPs against aggregation in solution. Poly(lactic acid)-*b*-poly(styrene-*alt*-maleic acid) (PLA-*b*-SMA) is an attractive block copolymer for the synthesis of PNPs, as the hydrophobic PLA block is biodegradable and the hydrophilic SMA block provides opportunity for post-polymerisation functionalisation and helps prevent PNP aggregation. This study investigates the synthesis of the novel PLA-*b*-SMA block copolymer via sequential ring-opening polymerisation (ROP) and reversible addition-fragmentation chain transfer (RAFT) polymerisation. Monodisperse PLA-*b*-SMA nanospheres and nanocapsules are synthesized via nanoprecipitation and range in hydrodynamic diameter between 60 and 220 nm. Fluorescent PLA-*b*-SMA nanocapsules (NCs) are produced via encapsulation of the lipophilic dye DiI, and the uptake of these NCs assessed in a preliminary cell uptake study.
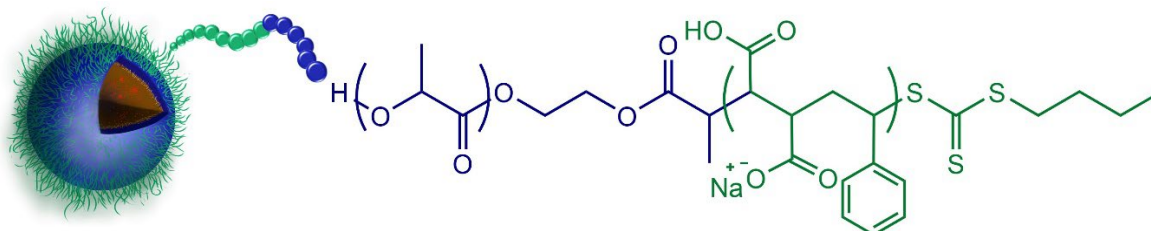
Figure 1: Fluorescent PLA-*b*-SMA NC (DiI in red, PLA in blue and SMA in green).

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P17

Water electrolysis assisted through polymeric gel nanocomposites

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There is an increasing need to sustainably produce H_2, a clean energy source, due to the rate of fossil fuel depletion [1]. Electrolysers are important technology for generating clean H_2, through water electrolysis [2], however due to the expensive nature of the catalysts required; only 4% of global H_2 production is through electrolysis [3]. As a result, the development of economical electrolysers is necessary for H_2 production on an industrial scale, in order to realise a sustainable energy future. Inexpensive transition metal nanoparticles (NPs) such as Ni, Mo, Fe etc., have shown excellent catalytic activity in alkaline water electrolysis [4]. The biggest challenge currently is bridging the gap between lab and industrial scale, as upscaling is challenging due to the need to use expensive and toxic fluorous polymeric binders, to help the NPs 'stick' to the electrodes [5]. A potential solution is to develop self-adhering electrocatalytic systems, which have the potential to bypass the need for conventional binders, while synergistically promoting the NP's electrocatalytic activity [4]. In this regard, polyaniline/poly(vinyl alcohol) composite hydrogels have shown potential for application in water electrolysis [6]. Figure 1 presents a linear sweep voltammogram showing H_2 evolution achieved by our PVA nanocomposites as well as highlighting the improved catalytic activity achieved upon nanoparticle incorporation into the PVA hydrogel material. We believe that the drive towards sustainable H_2 production can greatly benefit from the combination of polymeric materials in electrocatalytic application.
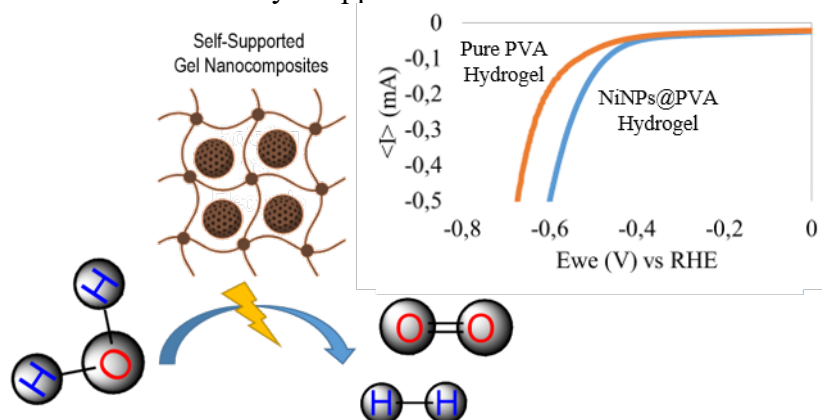
Figure 1: Graphical illustration of water electrolysis by the self-supported gel nanocomposite.

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P19

Ion specific effect on the viscous flow and deformation behaviour of stress-responsive cellulose nanofibril-based hydrogels

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Understanding flow behaviour of water-based formulations is fundamental for careful design and subsequent production of functional cosmetic products. For example, an efficient shampoo necessitates high shear viscosity and stability during storage, however, the same product should possess the ability to flow during application on hair. The performance of personal care products can be significantly enhanced by the use of polymers [1], herein, we study the rheological properties of cellulose-based soft gels.

Plant-derived cellulose nanofibrils were isolated through a combination of mild chemical treatment and low energy ultrasound-assisted mechanical disintegration. The average nanofibril diameter, as determined from high resolution TEM images, was *ca.* 10 nm, which translates to high aspect ratio [2]. To formulate the gels, the isolated nanofibrils were dispersed in distilled water at concentrations below 0.5 wt.% and the resulting nanodispersion had zeta potential values in excess of -60 mV, indicative of excellent colloidal stability [3]. Thereafter, gelation was induced through the addition of different Hofmeister salts.

In the presence of ionic strength, a marked improvement in shear viscosity, yield stress and elastic modulus was observed. The gel stiffness showed a strong dependence on ionic radius and valency, as well as ionic strength. The formulated gels displayed pseudo-plastic flow as a function of applied shear rate. In the absence of ionic strength, the elasticity of the gels showed strong frequency dependence, signalling weak gel structure. However, in the presence of Hofmeister salts, this phenomenon was completely eradicated, even at high frequencies and short timescales, suggesting the formation of a more stable gel network. In addition, the gels exhibited excellent thixotropic behaviour, wherein an almost immediate structural recovery of the gel network was evident upon the cessation of applied shear stress. In conclusion, the study has demonstrated the tenability of gel mechanics through the use of various Hofmeister ions. In light of this, the materials described herein have the potential to be employed as additives and rheology modifiers in cosmetics and personal care applications. Moreover, the use of nanocellulose is an attractive prospect given its renewable, non-toxic and biocompatible nature.

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P21

Synthesis of magnetic polymers via coordination polymerization of styrene by Ni and Cu nanoparticles immobilized on iron oxide supports

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Magnetic polymers have been widely utilized in the absorption of various toxins from water [1]. These magnetic polymers require complicated and expensive synthesis methods and are thus not suitable for mass production [2]. A recent study by Le Roux et. al. proved that Ni nanoparticles (NPs) are active in polymerization of various monomers [3]. This study proposes a new synthesis method to produce magnetic polymers by utilizing affordable active metals on iron oxide surface to facilitate coordination polymerization [4].

For this study we immobilized Cu and Ni NPs on superparamagnetic iron oxide NPs (SPIONs) through simple impregnation methods. Both these active metals evaluated are affordable and have shown promise as polymerization catalysts [3,5]. These NPs are then used as catalysts in the polymerization of styrene to produce magnetic polystyrene nanocomposites. Polymer formation was confirmed by FT-IR and the molecular weight determined by gel permeation chromatography (GPC). The obtained polymeric materials were evaluated as adsorbents for oil spills, after which the polymer was easily separated by a magnet and then recycled after desorption of the oil.
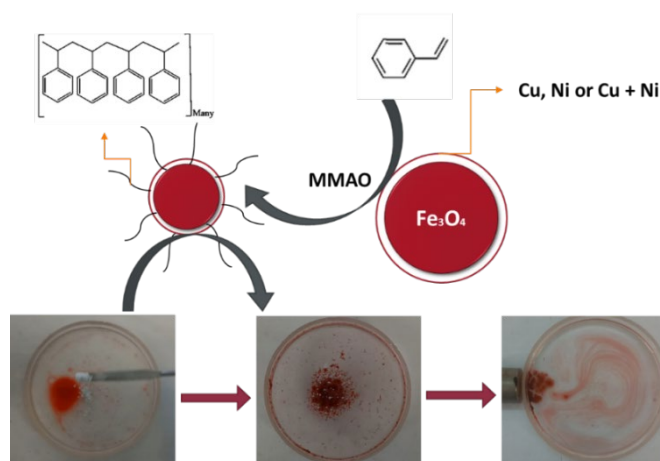
Figure: Synthesis of magnetic polymers via coordination polymerization of styrene to produce oil absorbing material. [4]

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P23

Nanochemical microscopy of polymer systems: Thresholds and peculiarities

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To reveal a structure of polymeric materials the Fourier Transform Infrared (FTIR) spectroscopy is a well-known and reliable choice. Using FTIR one can characterize chemical composition, crystallinity, orientation, intermolecular interactions and lateral distribution of components in polymeric systems in most of cases unambiguously. At the same time, so-called diffraction limit restricts FTIR strongly, especially in the case of FTIR microscopy in the range of several micrometers. Since 2005 a powerful combination of atomic force microscopy and IR spectroscopy (AFM-IR) was established and developed for last 17 years [1], what solved the diffraction limit obstacle, providing nowadays the measurement opportunity with lateral resolution down to tens of nanometers (Fig. 1). Despite the excellent qualitative coincidence between AFM-IR and FTIR spectra, there are some practical peculiarities and thresholds in sample preparation, measurement and contemporary technique limitations what are worth to be shown. The aim of this work was to highlight such difficulties working with polymers as well as in understanding of AFM-IR result to avoid data misinterpretation in practice. As research objects amide-ether copolymer, aliphatic-aromatic polyamide and poly(olefine-urethane) blends were chosen, because of the good spectroscopic contrast of the different components. Prior to the measurements, the samples were microtomed at different thicknesses (from 300 nm to several micrometers). The AFM-IR system NanoIR2 (Anasys-Bruker) coupled with OPO-laser was used to acquire AFM-IR spectra as well as samples' imagings. The thresholds in sample preparation, qualitative and quantitative differences and peculiarities between conventional FTIR and AFM-IR spectra as well as influence of IR-source onto the result and spectra interpretation are going to be discussed.
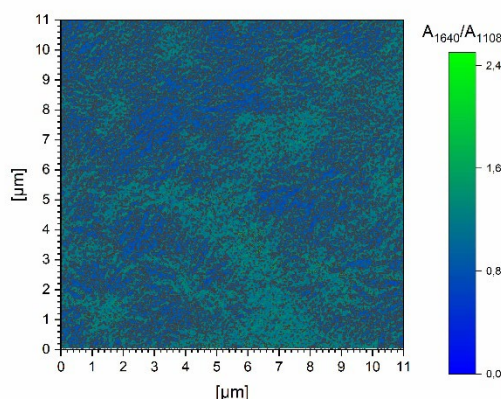

Figure 1: AFM-IR image of polyamide-poly(ethylene oxide) block-copolymer

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P25

Fabrication of novel dendrimer functionalized SiO$_2$@Fe$_3$O$_4$ nanoparticles for water treatment

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Severe water crisis in South Africa necessitates conservation of the limited supply that is available. The existence of heavy metals effluent in environmental water bodies is becoming a growing concern to environmentalists and civilians due to negative health effects. To make water free of pollutants, recyclable, and to fulfil the rising demand for fresh water, numerous methods have been established for water and wastewater treatment [1]. Adsorption has gained greater recognition among these approaches because it is straightforward and affordable [2]. Polyamidoamine (PAMAM) dendrimer-based materials have been developed for use in wastewater treatment owing to the ongoing quest for innovative and efficient materials [3]. Dendrimers are radially symmetric, nano-sized molecules with homogeneous, mono-dispersed and well-defined structures consisting of the tree-like branches, characterized by huge number of reactive end groups [4]. Dendrimers are comparatively inexpensive, environmentally friendly, very effective, and easy to functionalize over other substrates [4].

In this study, a series of poly(amidoamine) (PAMAM) dendrimer functionalized nanoparticles were synthesized and used for the adsorption of lead metal ions. The PAMAM dendrimer functionalized composites were prepared by grafting the poly(amidoamine) dendrimer on the surface of silica coated Fe$_3$O$_4$ magnetic nanoparticles. Co-precipitation was utilized for the Fe$_3$O$_4$ synthesis. The structural, surface, and magnetic characteristics of the nanosized adsorbent were investigated by Fourier Transform Infrared Spectroscopy, Elemental analysis, Scanning Electron Microscopy, powder X-ray diffraction, and Thermogravimetric analysis. Parameters such as contact time, concentration of adsorbent, pH and metal concentration have been optimized. Therefore, equilibrium isotherms and adsorption kinetics were determined. Atomic absorption spectroscopy was used to estimate how much metal was removed. Findings of the present work highlights the potential for using dendrimer-functionalized nanoparticles as an effective and recyclable adsorbent for the removal of heavy metal ions in water and wastewater treatment.

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P27

Development of bio-based hydrogels derived from Brachystegia woodiana Harms

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Hydrogels have gained popularity due to their ability to absorb large quantities of water and retain them. Hydrogels from nature have been reported to be environmentally friendly reflecting these properties: non-toxic, bio-compostable and bio-compatible. This study focuses on the development of hydrogels from Branchystegia woodiana Harms gum 'Mupangara'. The hydrogels were prepared by placing the tree gum in NaOH, water and acetone solution under reflux for 120 minutes at 80 °C. The solution was cast into a petri dish and allowed to cool, after cooling the solution was stirred with glutaraldehyde so as to crosslink the hydrogel. The hydrogels were characterized by FTIR and XRF analysis. The FTIR analysis showed the presence of the following critical functional groups: -NH, -COOH and aromatic rings, the XRF analysis showed presence of the following inorganic elements: SiO_2, Fe, Ni, CaO and MgO. The inorganic elements will reinforce the hydrogel hence improving the mechanical properties of the hydrogel. Other tests done were swelling degree and gel fraction analysis. The swelling degree of the hydrogels in NaOH, water and acetone were as follows: 2.73, 2.05 and 1.89 respectively. The gel fractions of the hydrogels were as follows: 0.84, 0.77 and 0.71 respectively.

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P29

Synthesis and application of polymer coated TiO_2/Fe_3O_4 photocatalyst in water treatment

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Increased water pollution across the world, has drawn considerable attention for the need of environmentally friendly and clean chemical technologies to remove the contaminants [1]. For the last decades, conventional methods have been applied for the purification of water but due to industrialization these methods fall short [2]. Advanced oxidation processes and their reliable application in degradation of many contaminants have been reported as a potential method to reduce and/or alleviate this problem [3]. Adsorption by magnetic particles, which is effective in treating dye pollutants is one of the methods that have recently attracted the attention of many researchers due to its effectiveness, low cost and its convenience [4].

The current study is centred on the synthesis of polymer coated Fe_3O_4/TiO_2 photocatalyst. Magnetically separable Fe_3O_4/TiO_2 composite were synthesized by the deposition of uniform anatase TiO_2 NPs on Fe_3O_4 by using titanium butoxide (TBOT) as titanium source. Then, the TiO_2 layer was coated with polymers to reduce band gap of the nanoparticles in order to reduce charge recombination and utilize visible light in the photocatalytic degradation of organic compounds. Integration of magnetic nanoparticles was suggested to avoid the post separation difficulties associated with the powder form of the TiO_2 catalyst, increase of the surface area and adsorption properties. The as synthesized catalysts were characterized using Infra-red Spectroscopy, Thermogravimetric analysis, Scanning Electron Microscope and Energy Dispersive Spectroscopy. The photocatalytic activity of the catalyst was tested using methylene blue (MB) as a model pollutant and was based on the decolourization of the dye as it was degraded. UV-Vis. analysis was used to determine the changes in concentration of the MB. Furthermore, the photocatalytic performances of the magnetic catalysts were assessed in comparison with that commercial titanium dioxide for MB degradation using photochemical reactor under ultraviolet light and visible light.

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P31

Characterization of antimalarial drug delivery systems by X-ray scattering and electron microscopy

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For the optimal development of lipid-based antimalarial drug delivery systems, and to ensure the necessary particle properties are achieved, in-depth characterization is required. Properties of the lipid-based nanoparticle formulation does not only depend on the different components of the system, but also on how these components interact. Analytical techniques, such as small and wide-angle X-ray scattering (SAXS, WAXS) and transmission electron microscopy (TEM) were employed as a comprehensive analytical strategy for the characterization of the antimalarial drug delivery nanoparticle system. By combining these analytical approaches, complementary information can be obtained for the lipid-based nanoparticles with regards to their crystalline structure, the shape, and the size.

An evaluation of the SAXS curves of the lipid-based nanoparticles in water, indicated a tablet-like shape of the particles with a less dense core. A tablet diameter in the range of 30 nm to 35 nm; and a thickness of approximately 15 nm were modelled from the SAXS data. For a nanoparticle constituted only of carnauba wax, a scattering length density close to water was modelled for the tablet core. Crystallinity of the carnauba wax was confirmed in the WAXS range. The outer dimensions obtained by SAXS are in line with the particle size determined by TEM.

The results show that combining these analytical methods is a valuable tool for the in-depth characterization of lipid-based nanoparticles.

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Probing solvent-dependent local polymer's segment flexibility using ThFFF

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Sophisticated polymer characterization normally involves the determination of conformation characteristics by measuring dilute solution properties in order to probe relevant characteristic length scales of the polymer chains. To enable a rather realistically modelling of the polymer's intrinsic flexibility or its coiling behavior in solution, respectively, the influence of a polymer's local chemistry is to be respected [1]. To access polymer chain characteristics on the local segment-like scale, so far elaborate and rarely available scattering experiments such as small-angle neutron scattering (SANS) are applied.

Based on a revisited approach to predict thermal diffusion coefficients [2] we demonstrate a method for probing the segmental size of polymer chains with varying topology based on temperature-dependently computed solvent interaction parameters and experimental thermal diffusion data, which are among other methods rather easily accessible by thermal field flow fractionation (ThFFF) [3].

The previously indicated link between thermal diffusion properties and local segment stiffness [4] is applied here for the first time for an exemplary polymer model system of differently branched polyethylenes synthesized earlier by Pd-chelate catalyzed chain walking polymerization [5]. This polymer system allows characterization experiments at ambient conditions in a broad range of solvents with different polarity.

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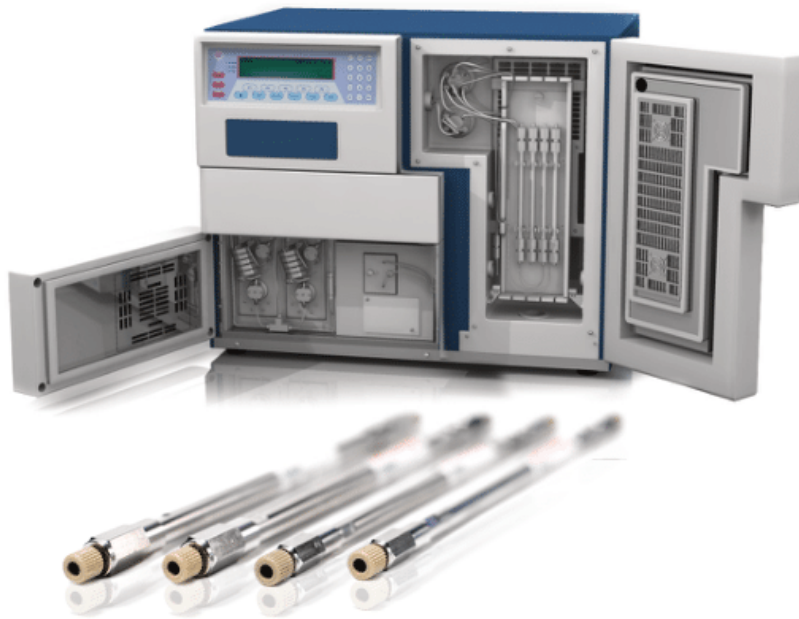
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PL3

Polymer characterization by interaction chromatography

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Size exclusion chromatography (SEC) is the most widely employed chromatographic separation technique for characterization of synthetic polymers. SEC separates polymer molecules according to their chain size utilizing size dependent pore-accessibility of polymer molecules. Since the polymer chain size depends on not only molecular weight (MW) but also other molecular characteristics such as composition, chain architecture and microstructure, SEC cannot separate, for instance, nonlinear homo-polymers according to MW or copolymers according to their composition.

In contrast to SEC, interaction chromatography (IC) fractionates polymers according to the interaction strength between the polymer molecules and the sorbent. As a result, IC separation is sensitive to chemical nature and MW of polymers unlike the size sensitive SEC. Furthermore, one can access to the chromatographic critical condition by adjusting the solute interaction strength with the sorbent until the exclusion and interaction contributions to the solute retention are exactly compensated. At the critical condition, polymers of different MW co-elute. Therefore, liquid chromatography (LC) at the critical condition (LCCC) is a unique tool for LC separation of polymers since the peak dispersion of polymers due to their MW distribution can be suppressed for effective analyses of other molecular characteristics. Recently, polymer separations using two-dimensional LC by various combinations of SEC, IC or LCCC is increasingly used for the characterization of polymers with multivariate distributions.

For effective IC separations, solute interaction strength needs to be controlled judiciously during the elution. For this purpose, either solvent gradient or temperature gradient elution is often used. In this presentation, principles and applications of IC and LCCC separation methods of synthetic polymers will be briefly reviewed with an emphasis on the temperature gradient elution method.

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KN7

Determining accurate molar masses by SEC/MALS using mixed solvents

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Accurate determination of polymer molar mass (M) averages and distributions via size-based separation methods employing mixed solvents remains one of the great macromolecular characterization challenges. This is chiefly due to the tendency for preferential solvation in mixed solvents, whereby the region in the immediate vicinity of the polymer is enriched in one solvent over the other, as compared to the solvent ratio away from the polymer. As such, when employing on-line differential detectors such as static light scattering photometers, differential refractometers, etc., the solvent baseline is no longer representative of the solvent contribution to the detector peak or to each slice thereof. This, in turn, leads to errors in calculated M. Here, we examine two approached developed in out lab to overcome this problem, namely the use of an isorefractive solvent pair and the use of a "near-isovirial" solvent pair; the first approach confronts the problem, the second one circumvents it. Each approach presents its own set of unique challenges. These latter will be discussed to the extent time permits, but emphasis will be on results of the experiments using well-characterized, narrow-dispersity standards across a large M range. A counterexample shows the extent to which preferential solvation can occur in solution and its quantitative implications for calculated M averages and distributions.

KN8

From process to polymeric microstructure – A journey through experiment, modeling & simulation and polymer characterization

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The high-pressure polymerization technology of LDPE is on the one hand a mature process, but on the other hand it has never lost its scientific challenges due to its complex polymerization mechanism and enormous production scales of more than 400 kt / line & year in combination with extreme safety requirements due to process conditions up to 3000 bar and 300 °C. On the one hand, the costs and risks at these scales and parameters make full-scale experiments based on trial and error increasingly unattractive. On the other hand, the extreme scale-up factor from laboratory to large scale is the challenge of today.
 Based on independent laboratory-scale kinetic experiments, detailed analysis of the polymer microstructure and technical knowledge, simulation models can be built that describe the control of the polymer microstructure by process conditions. Transferring the microstructure into rheological models bridges the gap to application properties. It is important to validate such concepts on well-defined experiments, which will be demonstrated using well-defined mini-plant experiments. Scalability will be demonstrated by applying the identical concept to the production scale state of the art reactor technology. In doing so, it will be unveiled what needs to be accounted for being successful in this process. The decomposition of peroxides used as initiators is altered by the changing viscosity of the reaction medium and in addition the interactions of species within the technical peroxide cocktails used. Even effects of the intrinsically fast mixing feed back to the product properties. A detailed characterization of the polymer being formed is an indispensable task to understand such complex interactions.
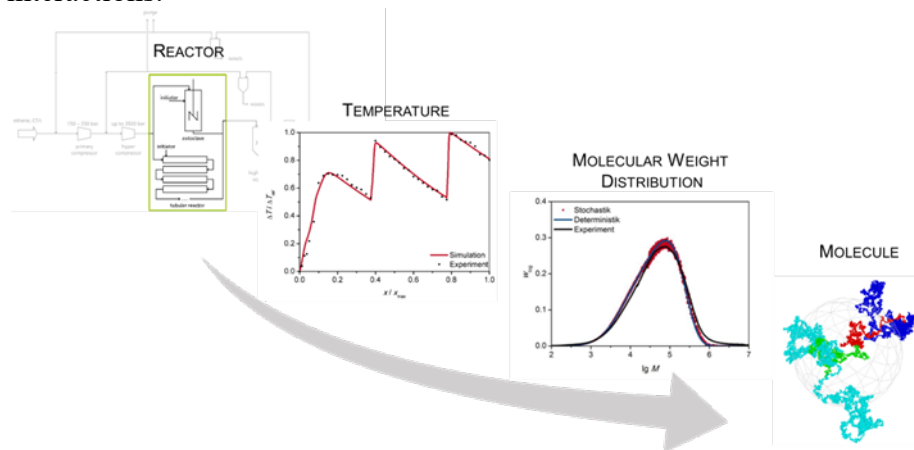
Figure 1: From process to structure, how process conditions control polymeric micro-structure.

But it is not only the product properties that are determined by the polymer microstructure. It also controls the system viscosity of the reaction medium, which in turn affects the safety of the process. Since ethene has no upper limit for decomposition, dissipation of the considerable heat of reaction is critical. System viscosity is a critical parameter for this purpose. If time permits, the safety aspects of the process and their implications will also be addressed.

KN9

# Biobased and biodegradable polymers: Analytical challenges

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The variability and heterogeneity in their structural composition is significant for nearly all synthetic and natural polymers. Beside molar mass also functionality type distribution, copolymer composition distribution and architectural features are responsible for changing the material properties.

A wide range of analytical techniques are available to get insight into these parameters. However, in most cases it is essential to combine different sophisticated techniques to get closer to actual structures and to avoid statistical averages.

Different liquid chromatographic separation modes and their coupling in a two-dimensional way (SEC, LCCC, HILIC, 2D-LC) in combination with suitable detection techniques (e.g. UV, RI, LS, IR, MALDI/ESI-MS) as well as techniques like BET, DCS, SEM/TEM were applied to make structural features visible.

A few aspects are discussed for structural different **polylactides** from various synthesis routes and their behavior in LC-MS.
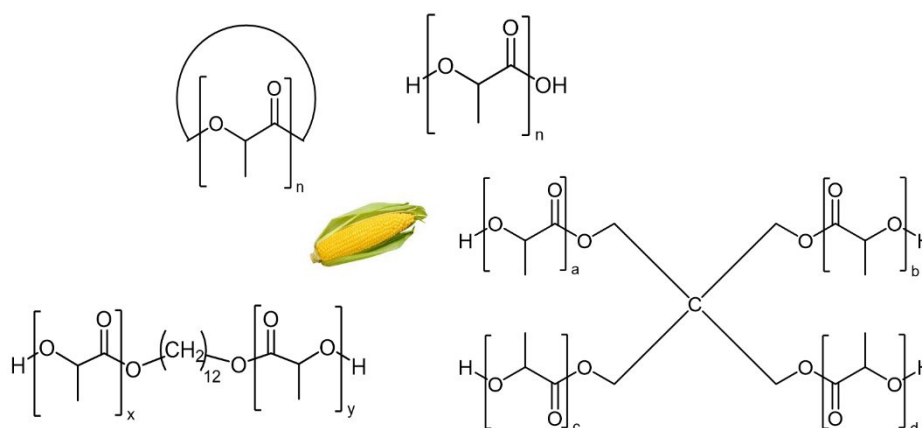
Moreover, some analytical results for **technical lignins** valorized by mechanochemical treatment or modified by functional polymers are presented.

- degraded lignins
- functionalized green adsorption phases
- composites

OL19

Understanding macromolecular properties by in-depth molecular characterization

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Comprehensive characterization of macromolecules by 2-dimensional chromatography has matured and grown substantially in acceptance during the 30 years since pioneers envisioned its benefits for the better understanding of polymer properties [1] - [3]. Since then, the scope of 2D applications has widened significantly: from polymers in its infant state, it expanded to food, cosmetics, home care, protein applications and more recently to the comprehensive characterization of antibodies.

The hyphenation with information-rich detection (mainly spectroscopic and spectrometric) opened additional insights into the species separated with highest efficiency [4]. The hyphenation of 2D separations with mass spectrometry detection offers benefits with regard high sensitivity and specificity. MS also allows to identify separated species which are otherwise much more difficult and/or labor intensive if the synthesis of reference compounds might be required. However, such setups require knowledge in chromatography method development and expertise in the operation of MS detectors as well as the interpretation of mass spectra.

This presentation with summarize the state-of-the-art and exemplify the operation of 2D separations in different application fields.

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OL20

Separation and characterization of chitosan by SEC and AF4

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Conformation of chitosan in acidic aqueous solution is strongly influenced by solution pH and ionic strength, as well as its degree of deacetylation and degree of polymerization. Here I will present our recent studies on the separation and characterization of chitosan by size exclusion chromatography (SEC) and asymmetric flow field-flow fractionation (AF4) [1-4]. SEC of chitosan is limited to acetate buffers of ionic strength higher than 100 mM to avoid the polymer adsorption on the columns. For high molar mass chitosan, a sufficiently low flow rate must be used to avoid the chromatographic mode transition to slalom chromatography, which originates from the coil-stretch transition of polymer chains in elongational flow through the packed columns. The conformation and persistence length of chitosan in acetate buffers down to millimolar ionic strength can be studied by AF4, thereby overcoming the problem of polymer adsorption in SEC. Characterization of *N*-methylated chitosan derivatives and chitosan-based nanogels will also be discussed. The developed SEC and AF4 methods are applicable to many other natural and synthetic polyelectrolytes.

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OL21

SMART thermoresponsive hydrogel films and nanofibres from poly(dimethylsiloxane) grafted amphiphilic copolymers

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Hydrogels are an interesting class of materials due to their high biocompatibility. This has made them attractive for a range of biomedical applications. In order for a hydrophilic polymer to be a hydrogel, it needs to be crosslinked in some way so that it will not undergo complete dissolution in water. This has mostly been accomplished by chemical crosslinking processes, however, a number of physical crosslinking processes, in which the macromolecules are held together by non- covalent interactions, have also been reported. In this study, we focus on developing novel thermoresponsive hydrogel polymers by crosslinking via hydrophobic interactions that arise from the introduction of a hydrophobic side chains to a form an amphiphilic graft copolymer. In these cases, the monomers that make up the main chain of the graft copolymer undergo a thermal transition in solution causing a rapid deswelling of the hydrogel at a specific temperature due to the critical lower solution temperature (LCST) of the main chain components. The water insoluble graft segments bundle together and are then able to act as linkages between the polymer chains when swollen in water. This not only provides a simpler method of crosslinking, since no further chemical treatment is required, but can also potentially be used to improve the properties of the material by selecting the appropriate type and amount of the hydrophobic comonomer. This also allows for easy processing from solution in a common solvent to produced electrospun nanofibre hydrogels from solution. Two novel thermoresponsive graft copolymer systems are discussed. Both are based on producing the PDMS graft copolymers by way of free radical copolymerization using the 'grafting through' macromonomer technique. The first system is based on poly(N-isopropyl acrylamide)-graft-poly(dimethylsiloxane) and the second is a terpolymer based on oligo(ethylene glycol) methyl ether methacrylate (OEGMA), ethylene glycol methyl ether methacrylate (EGMA) and poly(dimethyl siloxane) (PDMS) to produce poly(OEGMA-co-EGMA)-g-PDMS. It is shown that the presence of the hydrophobic PDMS grafts was effective in producing a physically crosslinked hydrogel network. The dimensional stability of the films and nanofibres on swelling in water improved with an increased PDMS content, but the dimensional stability is also highly dependent on the length (molar mass) of the PDMS graft side chains. Rheological data of the hydrogels is presented which gives further insight into the dimensional stability of the physically crosslinked hydrogels. The effect of the copolymer composition on the LCSTs of both the fibres and films are discussed. In the case of the terpolymer the LCSTs can be tuned to between 40 °C and 60 °C. Significant difference between the LCST and swelling behaviour of the films and nanofibres are observed and these are ascribed to differences in the induced morphology of the nanofibres as a result of the electrospinning process.

KN10

Polymer engineering for electrochemical sensors and biosensors

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Polymer-modified electrodes [1] have attracted much attention in the last three decades, due to the ease and affordability of polymer thin film preparation, as well as, its excellent stability and high sensitivity/reactivity in the pristine, composite or co-polymer forms. Electrodes and sensor chips are normally functionalised with polymer films in order to activate their electronics and interfacial electrochemistry for the desired applications. Through the modification of (a carbon, metal or conducting glass) electrode surface with a polymer film, the biocompatibility of an electrode or sensor chip could be engineered for molecular wiring that involves the linking of the polymer and the biomolecule or the polymer and other electro-sensitive species or probes [2,3]. Surface modification of electrodes with polymer films may be used to control the dynamics and specifications of an electrode reactions and the associated electrochemical properties, including the electrode kinetics, electroconductivity and the nature of possible electrocatalysis. Polymeric materials for sensors and bioelectronic applications may be preformed polymers or those produced *in situ*, e.g. by gamma irradiation, electro polymerization or electrodeposition. Among the types of polymeric materials developed at the SensorLab over the years for sensor applications are conductive polymers, redox polymers, electropolymerized nonconductive polymers, insulating overoxidized polymers, preformed non-conductive polymers, ion-exchange polymers, molecularly imprinted polymers, composite carbonaceous polymers, composite metallopolymers, dendritic co-polymers and metallo-dendritic co-polymers [4]. Their applications in biosensors (e.g. aptasensor, enzyme-based biosensor, genosensor, immunosensor and receptorsensor), electrocatalytic sensors and molecularly imprinted polymer sensors for diagnostics and environmental analyses, will be discussed [4]. The principles, mechanisms and procedures for the integration of electrochemical signal transduction techniques, such as AC voltammetry, DC voltammetry, electrochemiluminescence (ECL) and electrochemical impedance spectroscopy (EIS), with the plastic electronics of polymeric materials for sensor development, will also be presented [4-5].

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OL22

Supersensitive metal free in-situ synthesized graphene oxide@cellulose nanocrystals acetone sensitive bioderived sensors

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A series of graphene oxide@cellulose nanocrystal (GO@CNC) nanoparticles (NPs) were synthesized in this study using a room temperature-based simple modified hummers process. The morphological structures, as well as chemical characteristics of these materials were characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD), among others. The results show that the as-prepared nanoparticles are made up of crystallite grains with an average size of around 7.82, 14.69, 10.77, 7.82, and 12.51 nm for GO, CNC, GO1@CNC1, GO2@CNC3, and GO3@CNC3 respectively, and -OH & -COOH functionalities on the NPs' surfaces. GO@CNC NPs exhibit significantly better sensing characteristics toward acetone when compared to virgin GO nanoplatelets; specifically, the optimal sensor based on GO3@CNC3 NPs showed the highest response (60.88 at 5 ppm), which was higher than that of the virgin GO sensor at 200 °C operating temperature and including those reported. Furthermore, the sensors have high sensitivity towards acetone in sub-ppm concentrations as well as a detection limit of 5 ppm, making it a viable candidate for diabetes breath testing.

OL23

A novel electrochemical sensor for the detection of zearalenone in food matrices using PEGylated Fe_3O_4 nanoparticles supported by multidetector AF4 and *in-silico* studies

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Zearalenone (ZEN) is a carcinogenic non-steroidal estrogenic mycotoxin produced by the *Fusarium* fungi species widely found in mouldy maize, wheat, and rice, as well as other cereal and dairy products [1].

In this work, an electrochemical biosensor was developed using PEGylated Fe_3O_4 NPs and cMWCNTs for the detection of ZEN in commercial food samples. Multidetector Asymmetrical-Flow Field-Flow Fractionation (MD-AF4) was employed to determine the particle shape, size characterization and distribution of the synthesized PEG-Fe_3O_4 NPs. The surface interactions between the layer-by-layer fabricated electrodes and ZEN were investigated by a combination of Monte Carlo (MC) and molecular dynamics (MD) simulations. Finally, by identifying redox reactive sites using density functional theory (DFT) calculations, the sensing mechanism for ZEN by GCE/PEG-Fe_3O_4 NPs/cMWCNTs was proposed.

The methodology employed in this study can be extended to complement toxicity studies in the food, pharmaceutical and agricultural industries in South Africa.

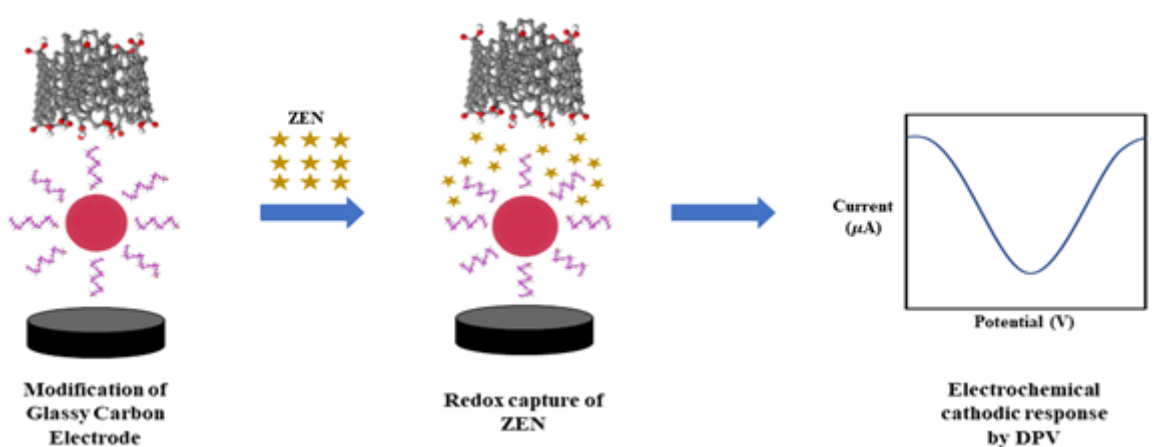Figure 1: Schematic diagrammatic representation of GCE/PEG-Fe_3O_4 NP/cMWCNTs electrode for ZEN detection.

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OL24

Fatigue damage behavior in 3D printed polylactide composites reinforced by hydroxyapatite, titan dioxide and glassy carbon

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3D printing is a rapidly growing waste-free production technique that allows minimizing the production time of a single unique product at high temperatures. Although this method is a versatile production technique, at the same time it is not sufficiently optimized and described. One of the materials used in this technique are polymers. Polymer materials used for medical and construction applications are subjected to cyclical loads, which lead to a reduction in their properties. It is worth noting that in the case of polymeric materials, even loads below the yield point can fatigue the material, causing microcracks and ultimately failure. Understanding fatigue behavior and failure mechanisms are essential to evaluate the emergence of materials in a variety of applications to determine the durability and long-term reliability [1].

In the presented study composites based on polylactide (PLA) modified with hydroxyapatite (HaP), titan dioxide (TiO2) and glassy carbon (GC) were produced by three dimensional technique. The content of each filler was 10 wt%. The produced standard dumbbell samples were subjected to extensive characterization mainly physical, thermal, mechanical and dynamic tests. In order to reference the mechanical\dynamic tests, the fracture morphology was determined using SEM images. The fatigue tests were carried out at constant minimum and maximum stress for a specified number of cycles (5000 cycles), and then the maximum stress was increased to continue the fatigue test for the next 5000 cycles. During testing, the amplitude was changed every 5000 cycles by increasing the maximum stress level by 5% of the material's tensile strength (σ_M), starting from 30% σ_M for each material.
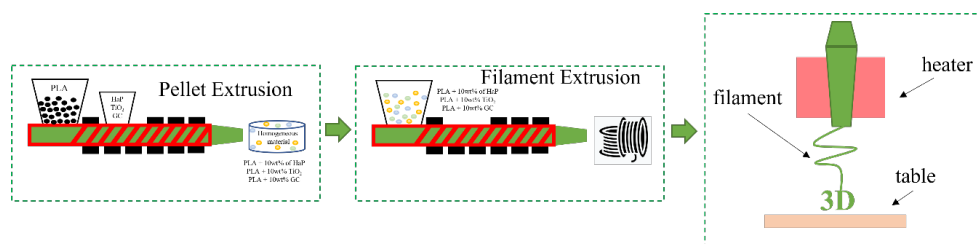
The test results showed that the addition of fillers had a positive effect on the mechanical properties. Tensile strength values improved by 20% for PLA/TiO2 or remained constant for HaP and GC. The positive effect of additives on the stiffness of the tested materials was noticed, where the highest properties were achieved by GC composites – an increase of 12% compared to unmodified PLA. Similar relationships were obtained during three-point flexural test, where the highest values were obtained for PLA/TiO2 – an increase of 12% and 20% for flexural strength and flexural modulus, respectively.

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KN11

Polymer separation using NMR as the detector

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Polymer separation is mainly performed for the analysis of the macromolecules regarding their molar mass distribution, chemical composition, and chemical heterogeneity. In this respect, liquid chromatography is one of the most important separation methods. The most common used method is size exclusion chromatography (SEC) for the determination of molar mass distributions. However, liquid adsorption chromatography (LAC) and particularly liquid adsorption chromatography at critical condition (LCCC) are also important methods for separating polymers according to the chemical properties such as microstructural distribution, end groups, chain lengths and chemical compositions.

The lecture will be focused on a number of different applications where the chromatographic separations are online coupled with nuclear magnetic resonance (NMR). It will be shown, for instance, how LAC-NMR is used to analyse polyethylene oxide mixtures [1] and separate poly(methyl methacrylate) regarding tacticity [2]. LCCC-NMR will be used to separate and analyse block copolymers [3] as well as separating polyisoprene isomers [4]. In case of diblock copolymers, the behaviour of both blocks will be studied under critical conditions. Furthermore, two-dimensional chromatography will be online coupled to NMR in order to separate and analyse the polymers both regarding their end groups and chain lengths [5], respectively. It will also be shown how field flow fractionation (FFF) can be coupled to NMR for the molar mass determination of block copolymers in comparison to SEC-NMR [6].

Recent developments of NMR diffusion ordered spectroscopy for the determination of molar mass distributions of block copolymers will be shown and compared to the dual detector analysis of SEC [7].

Further applications of polymer separations with NMR as the detector will also be presented.

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OL25

Hydrodynamic chromatography an efficient to tool to quickly determine particle size distributions in the sub-micron range

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Hydrodynamic chromatography (HDC) is a size-based separation method allowing determining particle size distributions in the 20-1000 nm range. Thus, HDC extends the separation range of size exclusion chromatography to larger moieties. The principle of hydrodynamic chromatography is based on the distribution of the particles in the flow streams of parabolic flow profiles occurring in narrow capillaries. Small particles can sample all streamlines, while larger particles can access the streamlines close to the center of the capillary, which are of higher velocity. Thus, larger particles experience a higher average velocity than smaller ones, and are therefore eluted before smaller ones, similar to the separation order in size exclusion chromatography.
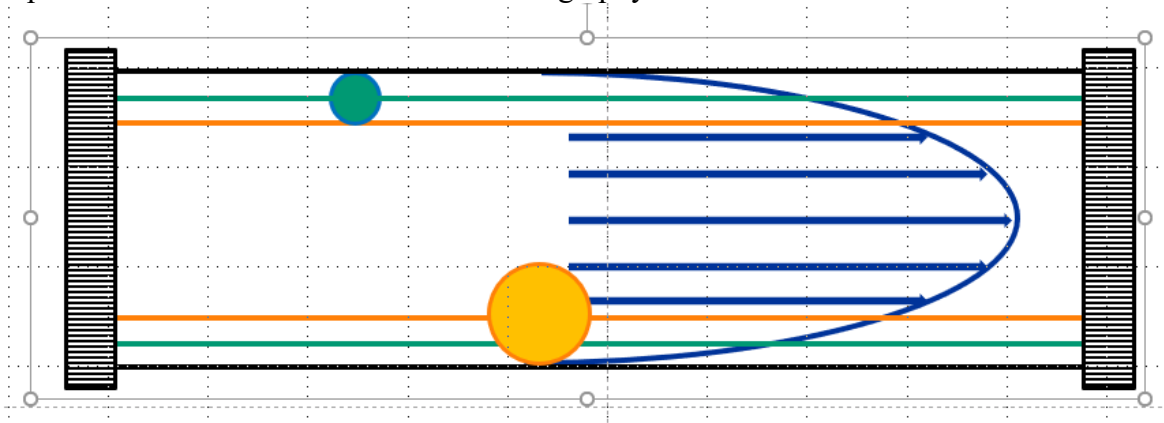
Figure 1: Schematic representation of HDC separation mechanism.

However, a single capillary might easily block, if too large particles are applied. Therefore, it is of advantage to perform HDC in packed columns, where the interparticle volume serves as a bundle of capillaries. Therefore, by simple installing an appropriate HDC column into a conventional GPC/SEC device, information on particle sizes and their distribution can be obtained after relating retention time to particle size using commercially available particle standards. However, HDC is a low-resolution technique. Significant enhancement of resolution enhancement is achieved, however, by using more sophisticated instrument control in combination of efficient deconvolution software. The contribution will present selected applications.

OL26

Challenges in the characterisation of polyolefin based recyclates

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The characterisation of the chemical heterogeneity of virgin polyolefins is well established. The chemical composition of polyolefins is commonly characterised by infra-red (IR) or ^{13}C nuclear magnetic resonance (NMR) spectroscopy and the molar mass distribution (MMD) by gel permeation chromatography (GPC). However, with these analytical approaches, the determination of the chemical composition distribution (CCD) or the chemical heterogeneity of these fractions is still not possible.

While the CCD of the crystalline fraction can be determined by crystallisation-based techniques like Temperature Rising Elution Fractionation (TREF) [1] or techniques based on various differentiation scanning calorimetry (DSC) [2] methods, the CCD of the amorphous fraction or the whole composition can be determined by Interaction Chromatography (IC) techniques based on adsorption-desorption mechanism [3,4]

In polyolefin recyclates the composition containing mixtures of various polyolefin types like homo-PP, crystalline and amorphous ethylene-copolymers (EPR), HDPE and LLDPE, as well as other polymer types and in combination with inorganic fillers have the consequence that the analytical approach needs to be modified.

In the presentation, an analytical approach is presented for determination of the chemical heterogeneity of PO recyclates using a multistep approach. Spectroscopic techniques like IR, extraction techniques are utilized for the characterisation and investigation of the non-PO composition. Combination with DSC and fractionation techniques like GPC, TREF, CFC techniques, PO composition of the recyclates can be determined.

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KN12

45 Years of Polymer HPLC – A personal account

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Until the end of the 70's of the last century the major tool for fractionating complex polymers regarding molecular composition was gel permeation chromatography (more accurately size exclusion chromatography, SEC) that, based on entropic interactions between the macromolecules and the stationary phase of a SEC system, separates the sample according to hydrodynamic size. As the hydrodynamic size is directly related to molar mass, SEC was the primary method for molar mass analysis of polymers [1]. Information on chemical composition as a function of molar mass could be obtained by coupling SEC with information-rich detectors. A milestone in fractionating polymers with regard to chemical composition was achieved when Teramachi et al. showed that random copolymers could be separated according to copolymer composition using solvent gradient HPLC [2]. Another important step towards selective fractionation was taken by Belenkii et al. who presented a new HPLC method – liquid chromatography at the critical point of adsorption – as an efficient way to separate functional polymers with regard to their functionality type distribution [3]. These techniques are based on influencing the enthalpic interactions between the macromolecules and the stationary phase by changing the composition of the mobile phase. Another milestone was the discovery by Chang et al. that temperature gradients could also be used for the selective separation of complex polymers with regard to composition [4]. The combination of different LC methods in comprehensive two-dimensional HPLC setups was pioneered by Kilz and others [5,6]. As per today, a toolbox of HPLC methods is in place that enables the fractionation of complex polymers according to all molecular parameters including tacticity and branching. The first publication on the interaction of polyolefins with stationary phases for HPLC at high temperatures appeared in 2003 [7]. After the successful application of temperature rising elution fractionation and the introduction of crystallization fractionation for the analysis of polyolefins with regard to chemical composition this was a major step towards methods for chemical composition analysis that are not based on crystallizability of the polyolefin. The first application of this new approach to the separation of ethylene-methyl methacrylate block copolymers was presented in 2005 [8]. The development of the first commercial HT-HPLC instrument [9] and the discovery of graphitic materials as efficient stationary phases for HTHPLC [10] were further important milestones in the development of advanced separation techniques for complex polyolefins. The ultimate goal of comprehensively analyzing complex polyolefins by composition and molar mass was achieved by high temperature two-dimensional chromatography, which is based on the online coupling of HT-HPLC and HT-SEC [11]. As the author had the privilege to take part in a number of developments in polymer HPLC over the last three decades, an overview on the different techniques and some major applications is presented.

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KN13

Molecular origin of shear and extensional rheology of polystyrene pom-pom model systems and validation of constitutive models

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Understanding the structure-property relationship is a key interest in polymer science and the requirement to reverse the design arrow to engineer new polymeric materials on the molecular level. The target is to predict rheological shear and elongational melt properties from the topology. Beside star and comb topologies, the so-called pom-pom topology is of huge interest, connecting two stars with a linear chain. Well-defined pom-pom shaped model systems of Polystyrene (PS) were synthesized by anionic polymerization of a polyisoprene-*b*-polystyrene-*b*-polyisoprene (ISI) triblock copolymer with short PI blocks (<10 mol%), followed by epoxidation of the PI blocks and grafting-onto of living PS [1]. This synthetic route enables complete control over molecular parameters and allows high arm numbers. The influence of the arm number, the molecular weight of the backbone, and the arms on the shear and elongational melt rheological properties are investigated experimentally and theoretically modeled with the constitutive pom-pom model. The experimental results reveal a huge impact of the molecular properties. For example, the zero-shear viscosity can be de- or increased and in elongational rheology, the strain hardening factor (SHF) can be increased above SHF >> 100 [2]. Additionally, as it can be seen in figure 1, fundamental topology-based rheological predictions of the pom-pom constitutive model under shear and elongational flow could be validated, allowing to design polymers with well-controlled properties. Especially nonlinear elongational behavior and strain hardening can be fully predicted from the linear viscoelastic response and the topological parameters.
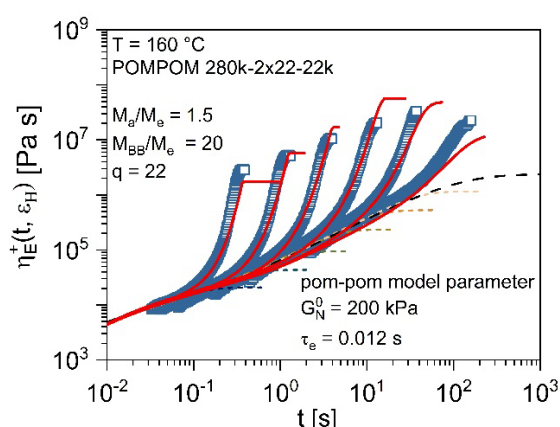
Figure 1: The extensional stress growth coefficient (open blue symbols) as a function of the measurement time, showing high strain hardening. Modeling with the pom-pom model (bold red line) reveals great prediction, using the topological parameters of the PS pom-pom model system.

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OL28

The effect of post-consumer recyclate on the rheological extensional viscosity of polyethylene

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Polyethylene, a thermoplastic polymer with a variable crystalline structure has found many applications ranging from packaging to construction. The polyethylene market is enormous, matured and is predicted to show rapid growth in the future. It is this versatility which results in an increase in the level of pollution, affecting every kind of environment including terrestrial and aquatic systems. From this perspective, recycling post-consumer waste has become a necessary pathway to circular economy. The addition of post-consumer recyclates helps to eliminate the need to extract more fossil fuels and in this way, they can contribute to the sustainability efforts.

The effect of subtle crystallinity and structural differences such as short or long chain branching distribution between polyethylene samples using extensional viscosity has been studied in our rheology laboratory. It was observed that in contrast to linear low density polyethylene (LLDPE), low density polyethylene (LDPE) samples displayed strain hardening behaviour. Strain hardening is usually associated with polymers with high molecular weight and a high degree of long chain branching. The results presented herein and previously from our group suggested that strain hardening is caused by the significant deviation from linear viscoelastic behaviour at high strains which is attributable to polymer backbone stretch that is subsequently followed by melt rupture at much higher deformation. This extensional behaviour between LDPE and LLDPE is consistent with literature findings [1].

It is noted that considerable research has been done on the effect of blending post-consumer recyclate polyethylene (PCRPE) and LDPE on physical properties [2] however, there exists a gap in understanding the extensional rheology of such blends. To contribute to the subject, our group is currently studying the effect of adding different concentrations of PCRPE into virgin LDPE. This work is focused on the determination of melt strength using high shear capillary rheometery as well as evaluating extensional viscosity with respect to strain hardening. The results give qualitative information on how PCRPE and LDPE blends will perform during film extrusion. Rheological measurements (melt strength and extensional viscosity) from the authors' work will be given in this presentation, together with compounding and extrusion process used.

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OL29

# Morphology formation during injection molding of semi-crystalline thermoplastics

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The influence of the internal structure of semi-crystalline thermoplastics on material properties is directly related to the processing method and the adjusted process parameters. In particular, the cooling rates and thermo-mechanical stresses on the melt during injection molding often lead to orientation, changed degrees of crystallization and the formation of different crystalline phases along the flow path. In addition, the process setup as well as the size and geometry of the samples are also of relevance. By scaling down from macro to micro samples, the sensitivity of the morphology evolution to changes in processing parameters becomes stronger. Visualization and analysis of the anisotropic morphology distribution resulting from the process and its correlation with the mechanical properties requires the use of different methods.

In this study a comprehensive comparison for different semi-crystalline polymers namely polyoxymethylene (POM), polypropylene (PP) and polylactic acid (PLA) will be presented. The different crystallization kinetics and the rheologic behavior of the materials lead to the formation of clearly defined morphological zones (Figure 1a). Accurate preparation methods and the testing of thin sections allows the selective characterization of these zones (Figure 1b). Furthermore, possibilities for simulative prediction of the morphological structure formation will be presented.

The results thus make a decisive contribution to the question of the impact of the process-related structure on the mechanical properties of a molded part, and the extent to which these properties can be optimized.
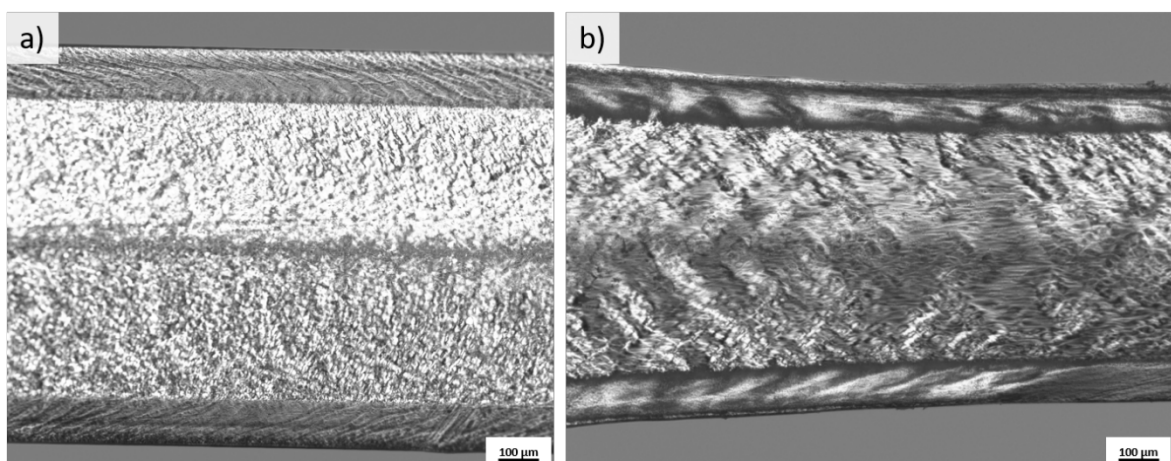
Figure 1: Process induced morphological zones of iPP in the undeformed (a) and deformed (b) state.

OL30

The effect of mechanical recycling on the thermomechanical, chemical, and mechanical properties of poly (butylene adipate terephthalate) PBAT, poly (butylene succinate) PBS, PBAT-PBS blend, and PBAT composite

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The production of biobased biodegradable polymers is constantly expanding to achieve the sustainability of renewable resources and a path away from plastic waste generated by petroleum-based polymers. However, little to no knowledge is disseminated on the mechanical recyclability of biodegradable and biobased polymers [1,2]. Therefore, this work focused on evaluating the effect of mechanical recycling on the mechanical, chemical, and thermal properties of poly (butylene adipate terephthalate) PBAT, poly (butylene succinate) PBS, polylactic acid, (PLA), biopolymer blend (PBAT-PBS), and PBAT reinforced with soymeal thermoplastic starch biocomposite (PBAT-SM). The blend and composite were prepared via a twin-screw extrusion process at 160 °C, and the mechanical recyclability was performed by subjecting the test samples to 8 extrusion cycles. The characterization techniques used for measurements included a tensile tester, impact analyser, melt flow index (MFI), differential scanning calorimetry (DSC), thermogravimetry (TGA), dynamic mechanical analysis (DMA), and Fourier transform infrared spectroscopy (FTIR) at each extrusion cycles. Mechanical recyclability results showed that PBAT and PBAT-SM composite were melt-processable up to 8 cycles and were comparable to LDPE recyclability performance. Tensile strength, impact, and melt flow index (MFI) further confirmed that the thermomechanical stress applied on neat PBAT, and PBAT-SM composite materials did not significantly affect their mechanical properties. While the mechanical properties of PBS and PBAT-PBS blend began to decline after the 2nd heat cycle. Deductions from the study imply that after the service life of PBAT and PBAT-SM biopolymers can be extended and are eligible to compete with petroleum-based plastic in terms of economical sustainability.

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OL31

Characterising the properties and performance of highly filled CaCO₃ masterbatches

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Calcium carbonate is used as an extender in blown polyethylene film and in the extrusion of polypropylene tapes. In both cases cost reduction is a factor but in the latter case the filler also reduces the tendency of the tape to fibrillate. The incorporation of the CaCO₃ is achieved via highly-filled calcium carbonate masterbatches. The masterbatch formulation includes, beyond the coated filler, waxes and lubricants. Their purpose is to control the melt viscosity and to assist with the dispersion of the individual filler particles in the final extruded film or tape.

The effects of filler content, filler particle size and surface coating, as well as the natures of the wax and metal stearate lubricants on the properties of calcium carbonate-filled linear low-density polyethylene compounds were investigated [1]. The effect of shear rate on the apparent melt viscosity followed an empirically modified Carreau-Yasuda model which included the effect of filler content. It features the zero-shear viscosity and the flow consistency index as adjustable parameters. These characterize the viscosity trends at low- and high shear rates respectively. In the absence of additives, the melt viscosity at 60 wt-% filler exceeded that of the neat polymer by a factor of three. Adding 3 wt-% wax and 1.0 wt-% zinc stearate returned the melt viscosity to levels just above that of the neat polymer. Calcium stearate and magnesium stearate were less effective at reducing the apparent melt viscosity but a blend of the latter with zinc stearate performed particularly well.

A novel method for the visualization and quantification of the state of dispersion of calcium carbonate particles in thin blown polymer films was described [2]. Particle imaging was achieved by elemental mapping using energy dispersive spectroscopy. This generated outlines of particles and agglomerates located close to the film surface. ImageJ software facilitated the extraction of the corresponding Feret diameters. Finally, the Bootstrap technique was used to estimate confidence intervals for the kurtosis of the Feret particle size distribution. Kurtosis is a statistic that describes the shape of a distribution's tails in relation to its overall shape. It therefore provides a measure that characterizes the degree of particle agglomeration. The proposed procedure was applied to analyse high-density polyethylene films prepared using different calcium carbonate masterbatches in which formulation parameters were varied.

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P2

Determination of microplastics in aerosol particle samples: Challenges in combining Raman spectroscopy and Pyr-GC/MS

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Microplastics (MP) are a ubiquitous pollutant in the environment and have been reported in urban, rural and isolated areas across the earth. While aquatic and soil samples are broadly characterised, the analysis of aerosol samples is still an emerging field. Monitoring the abundance of MP in air samples raises the possibility to assess their human intake. The inhalation exposure to nano- and microplastic particles is in particular interesting, since the fraction of particulate matter with aerodynamic diameter smaller than 10 μm (PM10) is suspected to have the biggest effect on human health [1]. MP are analyzed using mass balanced or particle related methods. Mass related methods provide the information of precise quantity. They are only applicable if a limit of detection is reached and no information on particle shape or size is gained. These particle characteristics can be derived from particle related methods combining microscopy with spectroscopy. They show the disadvantage of size limitations due to wavelength of the employed light and prolonged measurement times.

To allow the detailed characterisation of MP in PM10, we are combining both method types by using Raman Microscopy (μRaman) and pyrolysis Gas Chromatography-Mass Spectronomy (pyr-GC/MS). This combination raises the possibility to compare the results of both method types but raises challenges in the sample transfer. The election of filter material during sampling is crucial. Membrane filters like microquartz filters show a high retention of PM, but impede the subsequent analysis with microscopic methods for particles are caught in fibrous material. A sample work-up is tested out for the resuspension of particles taken with a High-Volume-Sampler on microquartz filters for the subsequent filtration on a flat silicon wafer filter.

In comparison, air samples taken by liquid deposition sampling are analysed after filtration on silicon wafer filters. For both sampling methods, particles need to be resuspended from silicon wafers after μRaman. A method is introduced for resuspending the particles and transferring them to pyr-GC/MS. The results of μRaman are compared to pyr-GC/MS by employing a mass estimation. Particle dimensions used for mass estimation are taken from automated particle recognition software GEPARD [2]. We will show that the combination of both methods can be a significant contribution to the analysis of MP in the atmosphere.

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P6

Responsivity analysis of smart nanoparticles using Asymmetric Flow Field-Flow Fractionation

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Future research on advanced nanoparticles (NPs) for drug delivery systems (DDSs) will be based on smart and biodegradable polymers. Amphiphilic block copolymers can self-assemble into NPs, specifically polymersomes, which are versatile carriers due to the possibility to tune their properties at the molecular level and their potential to encapsulate a range of bioactive compounds [1]. Smart polymersomes, in particular, exhibit a variety of characteristics that are essential for DDSs as they are stimuli-responsive and can modify their structure or morphology in response to a given stimulus. More complex structures have been developed to respond to the presence of multiple stimuli such as dual-responsive polymersomes (pH and temperature) which exhibit morphological changes depending on the characteristic pH value and lower critical solution temperature (LCST) of the corresponding polymers [2]. A detailed understanding of self-assembly, responsive behaviour, and the influence of structural features are required to develop smart polymersomes for a given application. The separation and characterization of such complex self-assemblies prove to be a challenge due to their polydisperse nature and the possible decomposition under strong shear forces. Asymmetric flow field flow fractionation (AF4) is an emerging technology for the detailed separation and characterization of complex, fragile self-assemblies [3]. Coupled with a number of highly sensitive detectors, AF4 can deliver essential information about the molar mass, shape and conformation properties. Consequently, multi-detector AF4 may be used to characterize smart NPs and investigate their responsivity.

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P8

Designing an antibacterial polymer material for 3D printed consumer and medical devices

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Additive manufacturing is an ideal method for preparing materials with complex geometries [1], as shown by literature examples with applications in the medical industry in prosthetics, tissue engineering and surgical tools [2]. Common engineering polymers provide good mechanical properties but lack the antibacterial properties needed for the medical field. There is a need, therefore, for polymer materials suitable for additive manufacturing, with antibacterial properties. To achieve this, we developed a method of blending two polymers, i.e. an engineering polymer (polyamide-11) and a quaternary amine functional polymer, (antimicrobial polymer), giving rise to a new polymer blend with properties from both individual polymers. Varying blend ratios were investigated, and blend compatibility was evaluated by determining the Flory-Huggins parameters via differential scanning. A proof-of-concept device, i.e., a surgical forceps, was then printed and post printing parameters evaluated.

Figure 1: Proof of 3D printed concept - Forceps

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P10

Compositional analysis of *Aloe vera* extracts

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Aloe vera is a plant that is a member of the Liliaceae family and is known for its health and cosmetic benefits like skin hydration, anti-inflammatory and wound healing properties [1]. These benefits have been attributed to the polysaccharides that are found within the leaf gel [2]. One of the main polysaccharides present in the gel is Acemannan, which is found in the parenchyma plant cells in the leaf gel [1,3]. This polysaccharide is mainly composed of partially acetylated mannose units along with glucose with small amounts of galactose, with a molecular weight of about 40-50 kDa [4]. The molecular structure can be described as a single chain of β-(1→4) mannose with β-(1→4) glucose which is inserted into a backbone along with α-(1→6) galactose units found as side chains [4]. Inconsistencies in the leaf composition has previously been attributed to seasonal differation [5]. The extraction and processing of *Aloe* gel are also variables that can affect the difference in the composition observed [6]. Acemannan is seen as unstable and can degrade by factors like high temperature, bacterial contamination, enzymes, or pH changes [4]. Different drying methods also lead to deacetylation of the mannose units [4]. The aim of this study was to obtain *Aloe vera* extracts and to characterise them by determining a good solvent that will dissolve the extracts in order to study their molar masses along with compositional studies by spectroscopic methods. A dried sample supplied by the Changchun institute of Applied Chemistry, who were also the collaborators in this project, was initially used as a reference due to its ability to easily dissolve. The solubility trends of the polysaccharides of processed gel samples were studied in different solvents by dynamic light scattering (DLS) to determine the best solvent. ATR-FTIR (Attenuated Total Reflectance Fourier Transform Infrared) and NMR (Nuclear Magnetic Resonance) spectroscopy were used to study the composition and structure of the polysaccharide fractions. The separation techniques size exclusion chromatography (SEC) and Asymmetrical flow field flow fractionation (AF4) were used to study the molar mass of the extracts, as well as to collect SEC fractions that were also characterised.

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P12

Data-driven polymer analysis in microplastic pollution research: Prospects and use cases for machine learning based workflows

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The detection and characterization of microplastics in environmental samples is a crucial challenge in environmental research. The vast volume of data produced and handled in this context has initiated the development of tools and methods to facilitate the process. Gepard is an open-source software that provides advanced microscopy control and data analysis for detection and characterization of microplastic particles [1]. The software is designed for particle-based Raman and FTIR microscopy, and provides a fully integrated workflow from meta-data management and instrument control to spectroscopic evaluation, reporting, and data archiving.

In this poster, we demonstrate machine learning-based workflows which are or can be implemented in Gepard, such as image segmentation, optical particle recognition, and spectra de-noising using deep learning methods. The neural net model developed by Brandt et al. [2] radically improves the quality of noisy FTIR and Raman spectra, opening the way for subsequent evaluation.

Spectroscopic classification of polymer materials is a further step towards microplastic quantification that benefits from higher degree of automatisation. Gepard provides an API for different modules conducting the step of polymer type assignment. Here, we demonstrate the performance of a random forest prototype for polymer classification, comparing auto-assigned polymer classes with classification confirmed by human expertise.

We also introduce the use of cross-validated geo-spatial modelling for environmental predictions of microplastics distribution. Finally, we highlight the connectivity of Gepard to custom SQL databases for transparent archiving, publishing, and analysis of produced measurement data and metadata, in line with FAIR data science principles.

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P14

Insight into the molecular behaviour of alkali lignin

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There is an increasing drive towards sustainable feedstocks such as lignin to develop valuable products. Lignin contains an abundance of aromatic structures making it desirable for bio-based chemical applications. For these applications the chemical and physical properties needs to be well understood. However, the complex heterogenous structure of lignin presents challenges such as [1] poor solubility, [2] self-fluorescence and [3] aggregation which increases the difficulty of accurate molar mass determination [1]. Molar mass is a molecular parameter, providing information about the properties of alkali lignin. This study focused on the development of advanced analytical techniques, such as size exclusion chromatography (SEC) coupled to refractive index (RI) and multi-angle laser light scattering (MALLS) detectors to determine the molar mass of alkali lignin. First, alkali lignin was fractionated according to hydrodynamic volume using preparative SEC followed by the analysis of the fractions using analytical SEC to determine whether the elution was size-based and the molar mass of each fraction. However, the self-fluorescence of alkali lignin led to the over estimation of the molar masses determined. To provide insight into the fluorescence behaviour and structural properties, fluorescence spectroscopy and Fourier transform infrared (FTIR) spectroscopy were studied. To circumvent the influence of the self-fluorescence of lignin on the molar mass, matrix-assisted laser desorption ionization – time of flight (MALDI – ToF) mass spectrometry (MS) was utilized as a complementary technique for molar mass analysis.

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P16

The effect of hydrogen bonding on foldamer self-assembly

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Foldamers are chain molecules (oligomer or polymers) that fold into a conformationally ordered state when in solution. These polymers have been shown to have applications in host-guest chemistry [1,2], catalysis [3], and show great promise as responsive gel polymers. In previous literature [4,5], a large *para*-aryl triazole foldamer system with an internal diameter of 30 Å was developed and studied by Klumperman and co-workers. The foldamer's superhelical structures were shown to be unstable, where the structures would collapse (forming spherical objects made of secondary structure helixes) at high fractions of the selective solvent (water) in the non-selective solvent (dimethylformamide). This was hypothesized to have occurred because of the polymer being poorly solubilized.
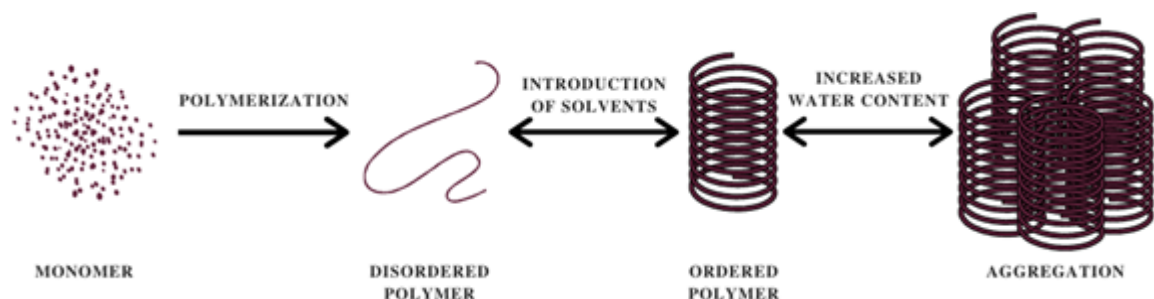
Figure 1: A simplistic scheme of the mode of action of foldamer formation and solvent responsive folding.

A library of polymers with varying amounts of hydrogen bonding moieties incorporated within the monomeric units was therefore modelled, synthesized, and successfully characterized. The properties of the library were then investigated *via* various analytical techniques (molecular weight of the polymers could not be determined). It was determined that the polymers with hydrogen bonding moieties would not fold, instead, the polymers would form a conglomerated mass of polymer chains. This may be a result of two factors; firstly, although the hydrogen bonding was expected to increase the stabilization of the helical structure, the amount of hydrogen bonding groups incorporated within the polymers could be too large and result in inhibition of the polymers' ability to fold. Secondly, the polymers may have not folded as the molecular weights of the polymers could have been below the threshold for forming a stabilized helical turn, which would inhibit folding. To confirm which hypothesis is the most accurate, new analytical techniques would need to be developed to determine whether the molecular weight is the issue, or, if the newly incorporated hydrogen bonding moieties are inhibiting the folding.

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P18

Side reaction in the copolymerization of maleic anhydride and *n*-butyl vinyl ether

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Chain transfer (CT) to polymer, either via intra or intermolecular processes, Figure 1, resulting in mid chain radical (MCR) formation is a well-known phenomenon in radical polymerization, particularly in the synthesis of polyacrylates [1]. Herein, we report some of the findings from our investigation into the occurrence of CT side reactions during the conventional radical copolymerization of maleic anhydride (MAnh) with *n*-butyl vinyl ether (*n*-BVE). Evidence of CT followed by β-scission was obtained via ^{1}H NMR spectroscopy which showed the appearance of vinylic signals in the region 5.7 ppm to 6.9 ppm. Further investigations via APT NMR experiments, examining the carbon multiplicities, also revealed branch formation. This work, for the first time, presents evidence of unsaturated product formation due to H abstraction and subsequent β-scission during radical copolymerization of MAnh and *n*-BVE.
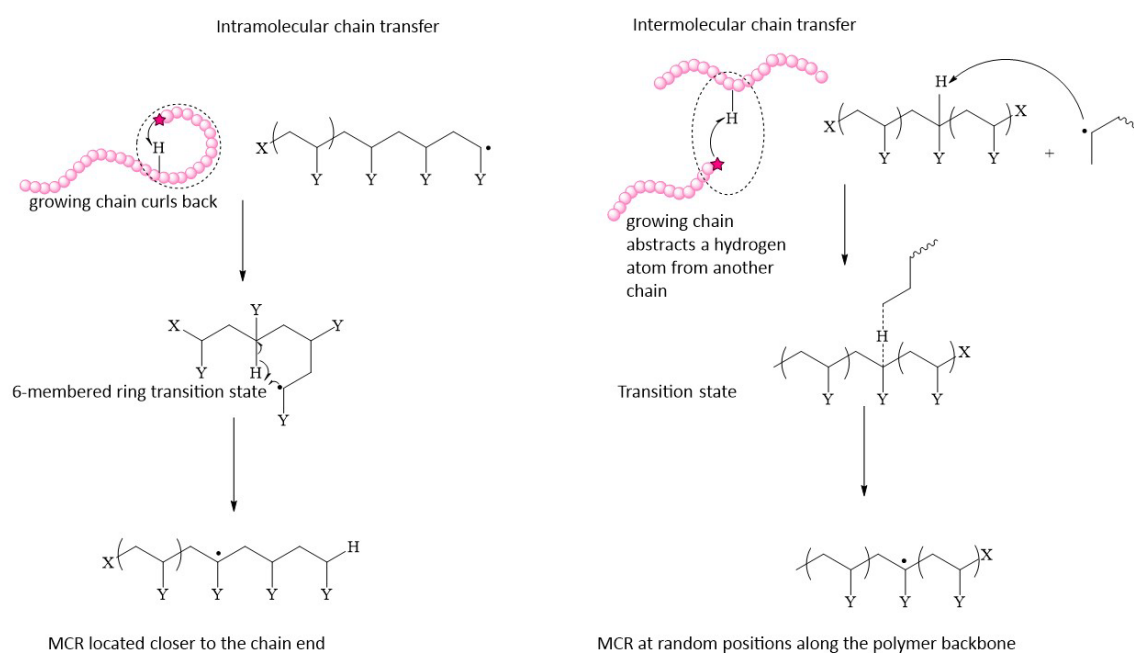
Figure 1: An illustration of intermolecular and intramolecular chain transfer

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P20

Surface modification of commercially available thermoplastics for biological applications

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The immobilization of bioactive compounds onto functionalized surfaces has been utilized extensively in biosensors, microarrays, and enzyme reactors [1]. Synthetic polymers, especially commercial thermoplastic films, are ideal for bio-functionalization due to their excellent mechanical properties, durability, and low cost [1,2]. However, the inert nature of these non-polar commercial polymers necessitates surface modification prior to the immobilization of bioactive compounds [1,2]. In this study, a UV-induced surface modification technique was investigated to functionalize commercial thermoplastic films for subsequent biological applications [2]. This UV-induced surface modification method exploits the photo-sensitive nature of dimethylformamide (DMF) and it can be applied in two ways: (i) using DMF in conjunction with vinylic monomers to introduce specific functionalities to the surface or (ii) using DMF to produce an amine-terminated surface [1, 2]. Commercial polyethylene (PE), polypropylene (PP), and poly(ethylene terephthalate)(PET) films were considered for functionalization. Attenuated total reflectance Fourier transform (ATR-FTIR) spectra and Orange II staining results determined that PET films were the most susceptible to surface modification via the UV-induced modification method, compared to PE and PP films. Thus, commercial PET films were selected as the base polymer to be functionalized with different bioactive compounds, for two separate biological applications. The first application exploited the ability of the UV-induced method to introduce specific functionalities on the surface to produce a pH indicator. The second application exploited the ability of the UV-induced method to produce an amine-terminated surface to develop a bio-scaffold film for potential microalgae cultivation. Scanning electron microscopy (SEM) and ATR-FTIR data confirmed the surface modification and subsequent immobilization. The performance of each developed application was also evaluated used metrics such as colour response, red cabbage extract stability, and retention of biological activity. In conclusion, our study illustrated the utility of the UV-induced surface modification method for functionalizing inert thermoplastic films, which could then be immobilized with bioactive compounds for various applications.

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P22

Analysis of "Bio"- Plastic Bags using evolved gas analysis and Pyrolysis-GC/MS

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Environmental pollution by plastics has attracted much concern globally. As an alternative to petroleum-based plastics in the context of sustainability, "bioplastics" have recently been utilized as environmentally friendly plastics. Here, we define two types of bioplastics, one is bio-based (and not biodegradable) plastics and the other is biodegradable (and bio-based) plastics which are naturally degraded and completely broken down by micro-organisms at ideal conditions. Biodegradable plastics may contain additives which accelerate the degradation under light, oxygen, and heat. However, there could be the risk of the toxic residues and the production of small plastic fragments (micro-bioplastics) during the degradation. Thus, it is important to analyze both main constituents and additives of bioplastics. In this work, analysis of bioplastic bags was carried out by vertical micro-furnace pyrolyzer coupled to GC/MS using EGA-MS, single-shot, double-shot, and heart-cut measurement methods. Four different plastics bags used as samples were commercially obtained: conventional plastic bag (STD), bio-based plastic bag (BP-A), polyethylene plastic bag with 30 % biomass resin (BP-B) and a biodegradable plastic bag (GP). From EGA thermograms, optimum pyrolysis and thermodesorption temperatures were defined for the different samples. The pyrograms of plastic bag STD and BP-A show a similar pattern characteristic to polyethylene (PE), showing that the main component is PE. The bio-based plastic BP-B shows characteristic peaks ascribed to the pyrolyzates of polypropylene and polysaccharides in addition to peaks ascribed to PE, suggesting the existence of the plant-derived components, maybe Rice Resin. GP shows quite different pyrogram patterns compared to other plastic bags and pyrolyzates of PBSA, PLA and PBAT could be identified. In all four plastics bags various additives could be identified and quantified. As described above, identification of main constituents and identification and quantification of additives of bioplastic bags could be easily done by Py-GC/MS.

P24

The development of SASOL's polypropylene grade for 3D printing

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Additive manufacturing, also known as 3D printing, is the building of three-dimensional (3D) objects by adding layer on layer of material to form 3D objects without tooling, moulds or cutting implements, from a 3D Computer Aided Design (CAD) modelling software. The term additive manufacturing is used to differentiate the process from traditional subtractive manufacturing which involves removing layers from a solid object to build a 3D part using tools, moulds or cutting implements [1].

The "ink" used can be materials such as polymers, metals, concrete and on a smaller scale, human tissue. Polymers are the largest group of 3D printing materials due to their low cost, versatility and wide range of mechanical and chemical properties, compared to materials such as metals. Commonly used polymers in 3D printing include polycarbonate (PC), acrylonitrile butadiene styrene (ABS), poly-ether-ester-ketone (PEEK), polyetherimide (ULTEM) and Nylon [2]. Polyethylene (PE) and polypropylene (PP), the highest produced commodity polymers by volume are not commonly used due their semi-crystallinity which is a disadvantage in 3D printing because it causes dimensional shrinkage leading to warping during the slow cooling rates typical in the printing processes. This project was carried out to develop a 3D printing "ink" using Sasol's homo-polypropylene (HPP) grade which is a low-cost polymer with very good tensile properties in moulded parts. However, the printed parts also require good impact strength which was achieved by the inclusion of thermoplastic elastomers. An acceptable balance of properties was obtained with good compatibility of the components as shown in the figures below.

a   b
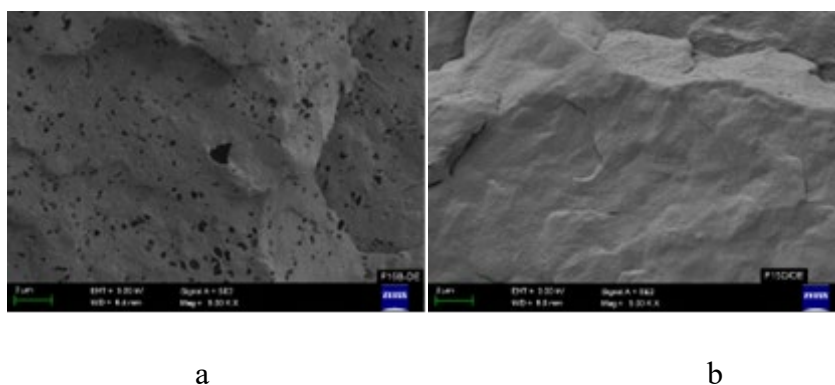
Figure 1: SEM micrographs of showing incompatible (a) and compatible (b) phases

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P26

Synthesis, spectroscopic and electrochemical characterization cobalt phthalocyanine and nickel phthalocyanine nanoparticles – A comparative study

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This study focuses on the synthesis, spectroscopic and electrochemical characterization of cobalt phthalocyanine and nickel phthalocyanine nanoparticles. Both CoPc and NiPc nanoparticles were synthesized using a similar method, which involved a high-temperature reaction of the respective metal salts with phthalonitrile in the presence of a catalyst. The resulting nanoparticles were characterized by various techniques, including UV-Vis spectroscopy, Fourier transform infrared spectroscopy (FTIR), Energy dispersive X-Ray (EDX), Scanning electron microscopy (SEM), and X-ray diffraction (XRD). The UV-Visible spectra showed characteristic absorption bands of phthalocyanines in the visible region for both CoPc and NiPc. FTIR analysis showed slight differences in the vibrational frequencies of the phthalocyanine ligands between CoPc and NiPc. The XRD patterns showed similar crystalline structures for both compounds, with the NiPc complex exhibiting slightly higher crystallinity than CoPc. The cyclic voltammetry results revealed that both CoPc and NiPc exhibited dissimilar electrochemical properties, with a reversible redox process attributed to the phthalocyanine macrocycle. The electrochemical Impedance properties of the synthesized nanomaterials also revealed that both CoPc and NiPc exhibited a little different capacitive properties and electron transport capability. The stability and reproducibility of the nanomaterials were also investigated. Overall, this study provides insight into the similarities and differences in the synthesis and characterization of CoPc and NiPc, highlighting the potentials of these compounds in developing new materials for applications in catalysis, electronic devices, and biomedical applications.

P28

A study anti-amyloidogenic activity of glycolyzed dendrimers and pseudodendrimers

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Dendritic and Pseudo-dendritic [1] structures have a novel type of density distribution and high number of functional groups, making them quite attractive for medical or biological applications. In the present work, three generations of dendritic and pseudo-dendritic structures have been obtained from hyperbranched aliphatic polyester core by modification of a protected AB*2 monomer. The chosen sequence of repeated protection and deprotection steps gave the corresponding dendrimers and pseudo-dendrimers with OH-terminal units. Further modification of all the three generations of dendrimers and pseudo-dendrimers with α-D-Mannose-pentaacetate were performed using copper catalysed "click" reaction, forming glyco-dendrimers and glyco-pseudodendrimers. ^{1}H NMR was used to confirm the degree of branching and the extent of modification in all three generations. The molar mass of each generation was measured by size-exclusion chromatography coupled to static light scattering. Furthermore, the interaction of glyco-pseudodendrimers with amyloid Aβ 40-a β-sheet rich protein, is investigated using these methods - AF4, ThT assay, CD spectroscopy and AF4. A comparative study of their behaviour is performed that gives a concise review of their physio-chemical properties and their possible use in various areas of research [2–4]. Further studies of these dendritic and pseudo-dendritic structures with the amyloid protein residues gives a chance for pioneering investigations in a biological system.
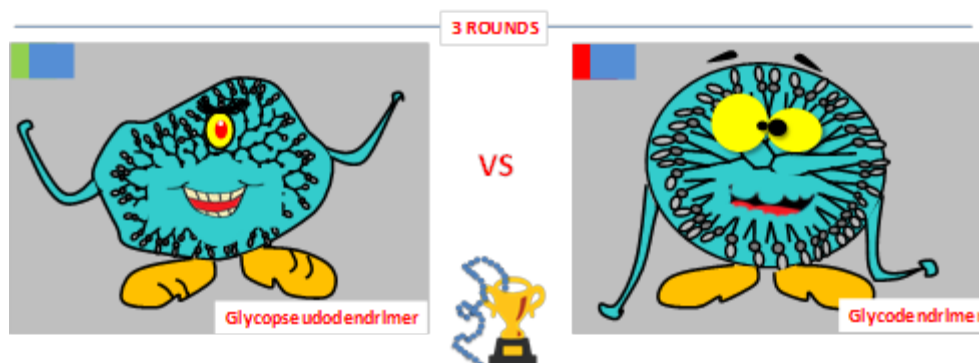
Figure: Dendrimers have been used in biomedicine field since a long time. Recently, their cousins the pseudo dendrimers joined the field. Let's seen who wins this match. This fight is for amyloid proteins-one of the culprits of Alzheimer's disease. May the best win.

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P30

Influence of hydrogen bond donor on zinc chloride in the separation of binary mixtures: Activity coefficients at infinite dilution

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Deep eutectic solvents (DESs) are ionic liquid analogues that consist of Lewis or Brønsted acids and bases [1]. These systems are characterized by a substantial decrease in melting points as compared to those of neat constituents. DESs have been identified as potentially cost-effective and environmentally friendly replacements for traditional volatile organic solvents. In designing separation techniques, the activity coefficients at infinite dilution of solutes in the deep eutectic solvents (DESs) are crucial. The gas-liquid chromatography technique (GLC) was used to determine activity coefficients at infinite dilution for 34 polar and non-polar organic solutes: solutes include alkanes, alkenes, alcohols, ketones, thiophene, heterocyclics, cycloalkanes, acetonitrile, tetrahydrofuran, cycloalkenes, aromatic hydrocarbon and water in two zinc chloride based DESs [zinc chloride + acetic acid] (1:4) and [zinc chloride + phosphoric acid] (1:2.5) at temperatures (313.15, 323.15, 333.15, 343.15, 353.15) K. Partial molar excess enthalpies at infinite dilution were calculated from the temperature dependence of activity coefficients at infinite dilution. The selectivity and capacity values for separation of benzene/ethanol, cyclohexane/ethanol, n-octane/acetonitrile, ethylbenzene/butanol, n-heptane/butanol at T = 323.15 K were calculated and compared to literature values for DESs, ionic liquids (ILs), and sulfolane to assess the suitability of the DESs for possible use as an entrainers. The potential of DES to replace traditional solvents was observed for [zinc chloride + phosphoric acid] (1:2.5) because it had a high separation parameter (capacity and selectivity) for all chosen systems involving close boiling point mixtures.

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P32

The synthesis of a potential antiplasmodial drug and the study of its uptake into a biodegradable polymer drug delivery system

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Resistance to currently available anti-malarial drugs is responsible for the increase in malaria-related mortality, prevalent in sub-Saharan Africa. Artemisinin-based combination therapy (ACT) is one of the leading treatments in the fight against malaria [1]. Some therapeutic agents are linked to toxicity due to poor intrinsic characteristics such as low water solubility and stability. Poor water solubility can hinder the delivery of highly efficacious therapeutic compounds. Targeted delivery and controlled release approaches to drug delivery are eliciting extensive research [2]. Nanoparticles have been widely researched due to their potential to improve the stability and solubility of encapsulated or conjugated drugs, promote the transport across membranes and prolong circulation times within the body to increase safety and efficacy [3,4]. Novel metallocene complexes containing ferrocene were synthesised and characterised using various techniques with the potential for anti-malarial activity due to the presence of the artesunate moiety attached. The polymer drug delivery system that was synthesised are micelle nano-drug carriers composed of poly(ethylene glycol) (PEG) and poly(lactic acid) (PLA) to form the amphiphilic block copolymer PEG-*b*-PLA. Due to the nature of the block copolymer, under aqueous conditions self-assembly will occur where the hydrophobic block will form the core and the hydrophilic block will form the corona of the micelle. The process of self-assembly was monitored and the micelles were analysed using various techniques.

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P34

High-resolution tracking of multiple distributions in metallic nanostructures: Advanced analysis with novel 3D correlation Thermal Field-Flow Fractionation

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Multifunctional metallic nanostructures are essential in the architecture of modern technology; however, the characterization thereof remains challenging due to their hybrid nature. In this study we present a novel photoreduction-based proto-col for augmenting and modulating the inherent properties of imidazolium ionic polymers (IIP) s through orthogonal functionalization with gold nanoparticles (Au NPs) to produce IIP_Au NP nanostructures; and the novel and advanced characterization via three-dimensional correlation thermal field-flow fractionation (3DCoThFFF). Coordination chemistry is applied to anchor Au^{3+} onto the nitrogen atom of the imidazolium ring, for subsequent photoreduction to Au NPs using UV irradiation. The thermal field-flow fractionation (ThFFF) and localized surface plasmon resonance (LSPR) of Au NPs are both dependent on size, shape and composition, thus synergistically coopted herein to develop mutual correlation functions for the advanced analysis of 3D spectral data. With 3DCoThFFF, multiple sizes, shapes, compositions and their respective distributions are synchronously correlated using time-resolved LSPR, as derived from multiple two-dimensional UV-Vis spectra per unit ThFFF-retention time. As such, higher resolutions and sensitivities are observed relative to regular ThFFF and batch UV-Vis. Moreso, 3DCoThFFF is shown to be highly competent for monitoring and evaluating the thermostability and dynamics of the metallic nanostructures, through the sequential correlation of UV-Vis spectra measured under incremental ThFFF temperature gradients. Comparable sizes are measured for IIP and IIP_Au NP, however, distinct elution profiles and UV-Vis absorbances are recorded, thereby reaffirming the versatility of ThFFF as a robust provision for validating the successful functionalization of IIP with Au to produce IIP_Au NP.
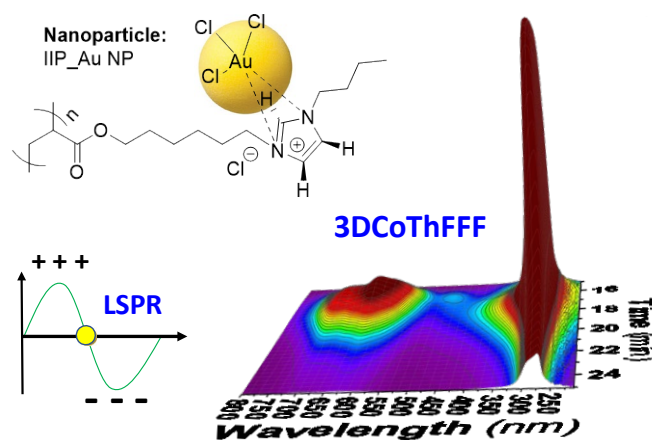

Figure: Anchored Au^{3+} on imidazolium ring structure; 3DCoThFFF spectrum

PL4

Chain walking catalysis from the theory point of view: From dendritic to bottle brush molecules

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Walking catalysts give rise to new molecular structures which can be controlled in various ways by external parameters such as temperature, pressure, and time of reaction. At the same time walking catalysis is a fascinating topic for statistical physics: The catalyst performs a random walk on the molecule, each time it reaches a reactive site there is a probability to extend its own territory. We have applied scaling theory and computer simulations to better understand the generic features of macromolecules emerging from such a polymerization process. Under the condition that the catalyst can form branched units we can show that the ultimate limit of the reaction process are bottle-brush molecules with dendtitic side chains. We have identified the walking rate which is the ratio of the average number of walking steps taking place between two successive reaction events as the key quantity which characterizes the extension of the dendritic parts (blobs) and the crossover to the bottle-brush regime. Using computer simulations the theoretical predictions can be confirmed and detailed information about various model parameters can be obtained [1]. The theoretical results are in agreement with experiments on polyolefins obtained from chain-walking catalysis using a Paladium catalyst [2].
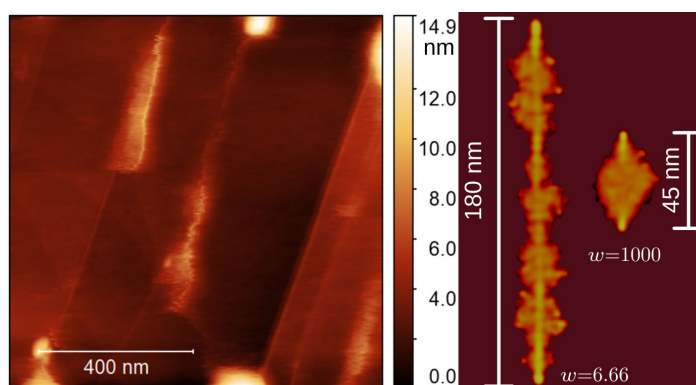
Figure 1: Left: AFM picture of individual molecules obtained by walking catalysis, Right corresponding picture obtained from computer simulations, from Ref.[2].

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KN14

Pyrrolidone based polymers in advanced polymer materials

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Pyrrolidone functional polymers have many important applications due to the properties of the pyrrolidone ring, i.e. biocompatibility, amphiphilicity, hydrogen bonding and metal coordination capacity. The preeminent example is poly(N-vinylpyrrolidone) (PVP), a water soluble and biocompatible polymer with many biomedical and industrial uses. Another family of pyrrolidone functional polymers based on 3-methylene-2-pyrrolidone (3M2P), in which the vinyl group is directly attached to the pyrrolidone ring, retains the same favourable aqueous solubility and biocompatibility as PVP. PVP and P3M2P are readily synthesized via radical polymerization methods, including reversible deactivation radical polymerization (RDRP) techniques, producing well-defined polymers with predictable end-groups and molar masses, and low molar mass dispersity. Herein we will show our recent work on PVP and P(3M2P) based polymer materials. The polymers are easily end-functionalised and incorporated into block copolymers for subsequent self-assembly into nanostructured materials for biomedical applications.

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KN15

Challenges for automation of 2D-LC method development of polymer separations

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Two-dimensional liquid chromatography (2D-LC) technology is continuing to gain interest. However, relative to 1D-LC, the number of potential users remains lagging behind for 2D separations. A prime obstacle for large-scale usage is the considerable investment needed for method development and data processing. Automation in any step of the method development reduces the required investment.

To address this challenge, we recently developed a closed-loop and interpretive algorithm for automated LC method development for complex samples of unknown composition [1]. The algorithm was designed to automate the method development process and featured a modular design to allow coupling with other tools published by other groups. Our algorithm directly and iteratively programs the LC with new method parameters obtained from previous raw experimental data until convergence of a specified objective function is reached. The algorithm can accommodate different optimization strategies using peak tracking and retention modeling, as well as machine learning.

The Dutch Science Council TTW-VENI project Unleashing the Potential of Separation Technology for Achieving Innovation in Research and Society project aims to capitalize on this progress and extend it to 2D-LC. The goal is to develop a chemometric method development tool that can be used by public and private organizations. With the proof-of-concept demonstrated for LC-MS, our attention thus shifted to 2D-LC, selectivity screening and method validation. Another key aim is the applicability to polymer separations. This presentation will discuss the scientific state-of-the-art and challenges related to achieving these goals in particular related to polymer separations.

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KN16

Quantitative particle analysis by a combination of optical microscopy with FTIR and Raman spectroscopy: Advanced automation enhanced by Machine learning and data management

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Microplastic (MP) analysis is a complex, multi-step process that includes sampling, sample treatment, measurement and data analysis. For each step, a multitude of protocols has been developed, but mandatory standards do not yet exist. Thus, comparability of results is an issue, even if the same methods are used. Result alterations can occur at each point in the process, and to ensure precision and accuracy, it is necessary to evaluate the contribution of each step. Here, we investigate the measurement and the data analysis. For the measurement, we focus on a combination of optical particle detection and FTIR and Raman microspectroscopy. For the data analysis, a common method in spectroscopy is an automated database search that uses comparison algorithms such as the Pearson correlation coefficient to determine the best match. Hence, the results often require a manual follow-up control, which is time-consuming and prone to human bias. We present first results for a model-based machine learning approach that reduces the need for additional expert evaluation, which reduces human bias.

To illustrate the result variations that occurred when measuring a sample with different settings, we employed the software tools ParticleScout (WITec), which is commercially available, and GEPARD, which is an open source program developed at the IPF Dresden [1,2]. Both tools allow a highly automated analysis. We used samples from riverine surface water, aquatic reference samples and round robin samples. For each sample, we compared the results obtained by varying the software and the settings of the microscops used.

ParticleScout as the proprietary software of the Raman microscope manufacturer WITec fully utilizes the instrument's capabilities, which results in optimized analysis speed, precision and ease of use. GEPARD is free of charge, and any user can adapt it to their specific demands. Furthermore, it provides a unique result evaluation module for correcting particle over-fragmentation. For the analysis of the spectra, we introduced a machine learning-based approach [3]. We compared the results obtained with the model to those of an automated database search with and without follow-up control by an experienced spectroscopist with FTIR and Raman. The machine learning-based approach showed potential to reduce the number of misidentified particles in comparison to a commonly used database search. Therefore, it offers a possibility to lower the need of manual post-processing and thus, of human bias in data analysis.

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OL32

Machine learning of sequence and conformation programmed material properties

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We investigate machine learning methods for exploring hidden physical patterns and variables in simulation data sets that determine their self-organization and interaction with heterogenous environments. For instance, the interaction of sequenced copolymers with lipid membranes is controlled by the polymer's hydrophobicity and its adsorption strength at the bilayer-solvent interface. It was shown that a neural network architecture we call transencoder [1] allows to extract these essential physical variables via learning the relation between amphiphilic sequence and the free energy landscape of the copolymer near the membrane from a large data set. We demonstrate that the patterns learned for highly coarse-grained simulation data were transferable to a more detailed model using a transfer learning approach that required only a small number (~20) of detailed data examples as compared to the sequence space.
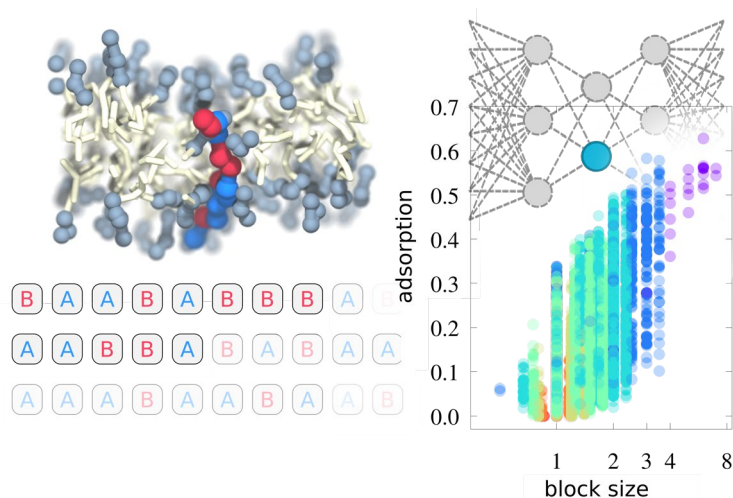
<u>Figure</u>: Identifying essential physical parameters such as the adsorption strength of a polymer interacting with lipid membranes [1].

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OL33

# Time Domain NMR of sustainable polymer materials from agrowaste

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Waste from agriculture and food processing contains a wealth of macromolecules such as cellulose, lignin, pectin, and can reprocessed into materials for packaging, pollution removal, apparel, and more. Treated samples from different sources differ not only in chemistry but also in terms of polymer ramification and for the presence of fibers, particles, and other morphological features descending from the specific phytotomy. The widening industrial applications need characterizing the intrinsic variability of agrowaste and the properties endowed by each processing step to the recycled material.

Time Domain NMR (TD-NMR), the analysis of Free Induction Decay displayed by a material after a given pulse sequence, provides several useful tools [1] for tackling such complex systems. In TD-NMR the chemical composition is left aside in favour of measuring the molecular mobility: specific sequences can then measure the mobility of soft phases, the amount of crystalline and glassy fractions, their spatial distribution.

Here we characterize several bioderived films, exemplified in figure 1. Such films are normally produced by drying, grinding, and activating vegetable waste that is then mixed with green polymer film-formers, crosslinkers, and dyes [2]. We used MSE refocusing block to evaluate the presence of water and its plasticizing effect, spin diffusion sequences to evaluate the domain size associated to residual fiber or particle structures, and advanced Multiple Quantum techniques to verify crosslinking in rubbery phases.
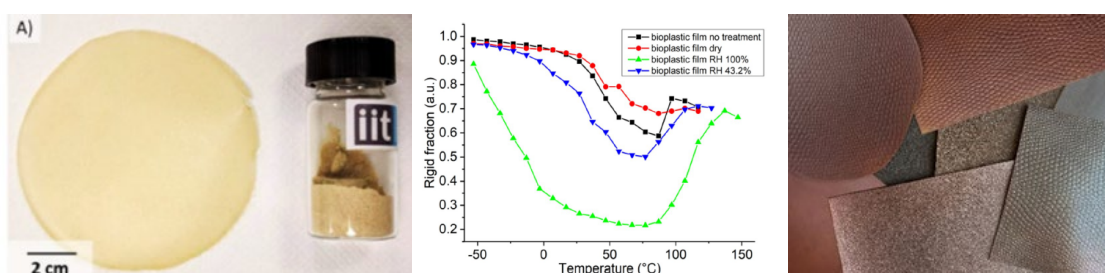
Figure 1: Left: an example of biofilm obtained from powdered carrot pomace, followed by an evaluation of the plasticizing effect of humidity on the same. On the right, leather-like materials from similar process.

TD-NMR results could be related with mechanical properties and could also elucidate the impact and mechanism of action of varying the processing conditions, as well as evaluate the effect of aging and weathering. This approach demonstrated general applicability since it can be extended to other multiphase systems such as methylcellulose thermogels or pastes for the cosmetics sector that are rheologically tuned using green microparticles.

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OL34

Advancing the strength of electronic lab notebooks from organic chemistry to polymer chemistry

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Electronic Lab Notebooks (ELNs) are a key prerequisite for the comprehensive documentation of research processes, the digital storage of research data, and their reuse. ELNs can be used to plan, record, store and – in combination with repositories - disclose experiments or research data. In the long run, the benefit of ELNs is the option to store and manage experimental data in a standardized way and to enrich the data with (ideally automatically generated) information such as metadata, identifiers and descriptors. For scientists, ELNs offer advantages such as faster research processes and a faster access to information. The Chemotion ELN is open source and offers special features for chemical syntheses and includes diverse functions that allow the use of it also in other disciplines.[1] As an example, the latest adaptions and integration methodologies for macromolecular chemistry will be presented, demonstrating the power and versatility of this specific ELN. Specific information for the exhaustive characterization of macromolecules can now be included by expanding existing information from organic chemistry resulting in a "Polymer Details" feature. Combined with an ongoing integration of polymer-specific analytical devices and evaluation tools – such as size exclusion chromatography (SEC) – the foundation is set for an integrated application of the Chemotion ELN. Further, Chemotion ELN can be used in combination with the open access repository Chemotion, enabling the direct disclosure of research data to the public transfer of information from the ELN to the repository. The interoperable systems ELN and repository guarantee on the one hand an easy process for the disclosure of information and on the other hand the availability of comprehensive research data including primary data and descriptions following the FAIR principles: findable, accessible, interoperable, reusable.
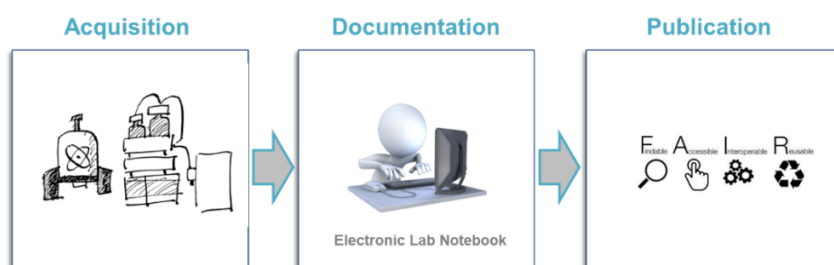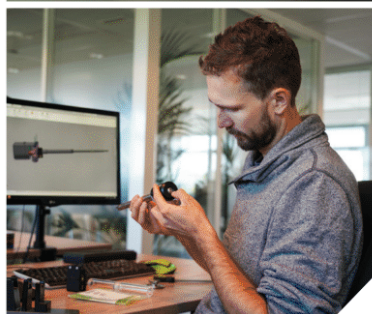

Figure: From acquisition of research data over evaluation and unified documentation to its publication (Image-Source: Johannes Liermann, preparation of DFG-defense, Gif-Source: https://gifer.com/en/PsKr).

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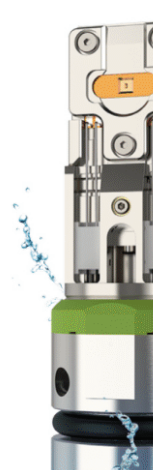
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KN17

Chain-walking polyethylene: Not a single type but a new family of polyethylenes

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The contribution will introduce novel class of chain-walking polyolefins which have unique branched structure. Their microstructure can be modified in broad range by the choice of catalysts and reaction conditions. That results in possibility to prepare completely amorphous or semi-crystalline polyolefins of various branching degree and topology. In this paper, an overview of methods capable to describe short-chain, long-chain and topology will be described. The catalytic polymerization using alpha-diimine complexes of nickel or palladium (Brookhart catalysts) is living. That allows to modify basic homopolymers to introduce end-chain or in-chain functionality by various synthetic strategies. Such functionalized polyolefins were used to form block and grafted amphiphilic copolymers. The fidelity of the structures was verified using NMR, SEC and interaction chromatography techniques.

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OL35

Analysis of complex polyolefins (terpolymers) using advanced separation techniques hyphenated with quantitative detection

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Polyolefins are by volume commercially the most relevant polymers. A readily available feedstock and differentiations in their microstructure have made it possible to adapt polyolefin to many application areas. Important molecular metrics present in olefin copolymers are the molar mass distribution (MMD) and the corresponding average values, comonomer type, and chemical composition distribution (CCD) with the corresponding average and the tacticity distribution (TD) [1].

Advanced characterization tools i.e., high temperature gel permeation chromatography (HT-GPC) with infrared detection, high temperature high performance liquid chromatography (HT-HPLC), and their hyphenation in the form of high temperature two-dimensional liquid chromatography (HT 2D-LC) with infrared detection have made it possible to analyse macromolecular heterogeneities of complex polyolefins. HT-GPC using infrared detection helps in understanding overall MMD and distribution of methyl- and carbonyl groups along the MMD. Use of porous graphitic carbon (PGC) as a stationary phase in HT-HPLC makes it possible to characterize the CCD of these complex polyolefins [2]. Finally, their hyphenation in the form of HT 2D-LC helps in understanding the MMD x CCD correlation [3].

In this work, ter-polymers of ethylene, vinyl acetate and a third comonomer are characterized by using HT-GPC and HT 2D-LC for their MMD x CCD.

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OL36

Method development for separation and characterization of chain walking polyethylene

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Functionalized polyolefins possess properties that are of interest for various novel nanomaterial applications [1]. The late-transition metal catalysts (based on Ni and Pd) have been successfully employed to synthesize polyethylene with incorporation of polar functionalities in a one pot procedure following the chain-walking mechanism [2]. More interestingly, the chain walking mechanism of the catalysts results in macromolecule with a novel architecture but extraordinary complex molecular topology. Furthermore, palladium catalyst particularly produces polyolefin that is characterized by its highly amorphous nature due to high branch incorporation (up to 100 branches/1000 carbon) with branch-on-branch structures [3–5]. Additionally, it is known that the branching topology and the overall molecular architecture of chain walking polyethylene are significantly influenced by the reaction conditions, notably ethylene pressure and temperature [5,6]. Herein we report the analytical protocol for a comprehensive study of the influence of synthesis conditions on the molecular structure of ethene-methyl acrylate random copolymers that is synthesized using Pd-catalyst. Preparative fractionation in combination with advanced analytical techniques including quadruple detector high temperature size exclusion chromatography (HT-SEC-4d), high temperature solvent interaction chromatography (HT-SGC), atomic force microscopy (AFM), nuclear magnetic resonance spectroscopy (NMR) unable in-depth understanding of the composition and structural distribution of these macromolecules.

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OL37

Trace sample analysis by a splitless pyrolysis-GC/MS system coupled to a newly developed sampler

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In pyrolysis (Py-)GC/MS, a polymer sample of ca. 0.1 mg is usually measured by the split injection method. In contrast, when analyzing a trace sample in a microgram range, the splitless injection method is used as a possible method to improve the detection sensitivity. To do this, however, it is necessary to set the carrier gas flow rate to ca. 1 mL/min in both the pyrolyzer and the GC separation column, and it takes several tens of seconds for the pyrolyzates formed by the flash pyrolysis to be swept to the GC separation column. The slow carrier gas flow rate in the pyrolyzer causes secondary reactions of pyrolyzates, which results in large changes in the peak intensity ratios of the pyrolyzates.

The aim of this study was to develop a new sampler, by which the carrier gas flow rate in the pyrolyzer for splitless Py-GC/MS method can be controlled to more than 10 mL/min in order to suppress the secondary reactions and improve the detection sensitivity.

A pyrolyzer (EGA/PY-3030D, Frontier Laboratories Ltd.) was installed to the GC injector of a GC/MS system coupled to a newly developed sampler (MFS-2015E, Frontier Laboratories Ltd.) through a splitter placed between the pre-column and the separation column, as shown in Fig. 1. The developed sampler consists of a suction pump to exhaust the carrier gas out of the system during sample introduction. First, the septum purge and split vent are closed before introduction of a sample, and then the suction pump is operated to exhaust most of the carrier gas out of the system through the pre-column, splitter, and the sampler controller. Pyrolyzates formed by flash pyrolysis are swept to the pre-column kept at room temperature. Condensable compounds are trapped in the pre-column before GC run. Then, the suction pump is stopped, and after the inlet pressure becomes stabilized, the split vent is opened, and the temperature programming of GC oven is started. Thin polystyrene (PS) films (0.01 ng to 5000 ng) were used as samples.

The calibration curves of PS obtained by the conventional split method and the developed splitless method are shown together with extracted ion chromatograms (EICs, m/z 91) of the styrene trimer (SSS) used for calibration at 10 ng of PS. The signal to noise ratio (S/N) was about 50 times higher for the splitless method, compared to the split method. The limit of quantification (S/N=10) was 1 ng for the splitless method, and the excellent reproducibility was obtained with the RSD value (n=5) of 4.8 %. Trace HDPE detection and reproducibility is shown as additional example for significantly increased sensitivity.

In conclusion, the developed sampler allowed to operate splitless Py-GC/MS effectively for the analysis of trace amounts polymers like PS and PE as examples.

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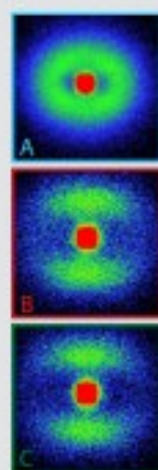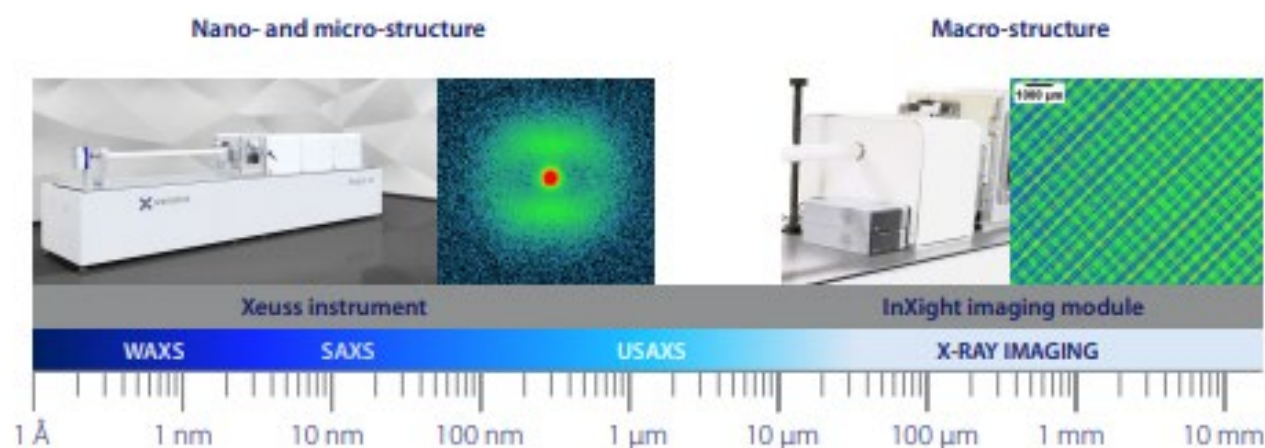
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Polymer film under strain. Left: X-ray transmission image
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KN18

Comprehensive two-dimensional LC of tannins using HILIC and RP-LC: How far can we go?

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The combination of HILIC and RP-LC separations in comprehensive two-dimensional LC (LC×LC) is attractive due to the high degree of orthogonality of these separation modes, despite the challenges associated with their hyphenation. For the improved separation of natural tannins, on-line HILIC×RP-LC in particular has found extensive application. However, the extreme complexity of such samples means that their complete characterization, even when hyphenating LC×LC with advanced mass spectrometric detection, remains elusive.

In this contribution, we evaluate the current performance limits of on-line LC×LC-MS where HILIC and RP-LC are combined for tannin analysis. A comparison of the kinetic performance limits of on-line HILIC×RP-LC and RP-LC×HILIC will be presented and discussed in terms of the requirements for tannin analysis. Experimental data for a range of phenolic tannin extracts will be used to support the theoretical predictions, and demonstrate the performance of these methods for these samples.

Particular emphasis will be placed on the separation of condensed tannins, since the very large number of isomeric species present in these samples present an especially severe challenge. We will show how even with state-of-the-art LC×LC-MS methods, the performance is insufficient for the characterization of oligomeric condensed tannins. Finally, means of improving LC×LC separation performance using multiple heart-cutting instrumentation and stop-flow operation, as well as the incorporation of ion mobility spectrometry to further improve compound identification will be explored. Preliminary data for rea-life samples will be used to critically assess the potential of these approaches and highlight further work that should be performed to enable more detailed characterization of complex tannin samples.
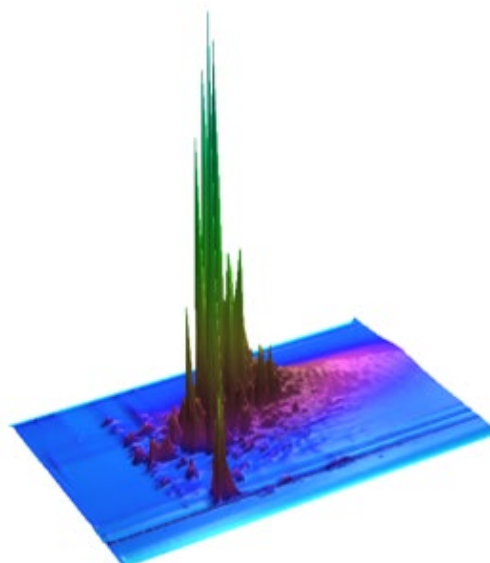

Figure: On-line HILIC×RP-LC analysis of a condensed tannin extract.

OL38

Nanochemical microscopy of polymer systems:
Thresholds and peculiarities

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To reveal a structure of polymeric materials the Fourier Transform Infrared (FTIR) spectroscopy is a well-known and reliable choice. Using FTIR one can characterize chemical composition, crystallinity, orientation, intermolecular interactions and lateral distribution of components in polymeric systems in most of cases unambiguously. At the same time, so-called diffraction limit restricts FTIR strongly, especially in the case of FTIR microscopy in the range of several micrometers. Since 2005 a powerful combination of atomic force microscopy and IR spectroscopy (AFM-IR) was established and developed for last 17 years [1], what solved the diffraction limit obstacle, providing nowadays the measurement opportunity with lateral resolution down to tens of nanometers (Fig. 1). Despite the excellent qualitative coincidence between AFM-IR and FTIR spectra, there are some practical peculiarities and thresholds in sample preparation, measurement and contemporary technique limitations what are worth to be shown. The aim of this work was to highlight such difficulties working with polymers as well as in understanding of AFM-IR result to avoid data misinterpretation in practice. As research objects amide-ether copolymer, aliphatic-aromatic polyamide and poly(olefine-urethane) blends were chosen, because of the good spectroscopic contrast of the different components. Prior to the measurements, the samples were microtomed at different thicknesses (from 300 nm to several micrometers). The AFM-IR system NanoIR2 (Anasys-Bruker) coupled with OPO-laser was used to acquire AFM-IR spectra as well as samples' imagings. The thresholds in sample preparation, qualitative and quantitative differences and peculiarities between conventional FTIR and AFM-IR spectra as well as influence of IR-source onto the result and spectra interpretation are going to be discussed.
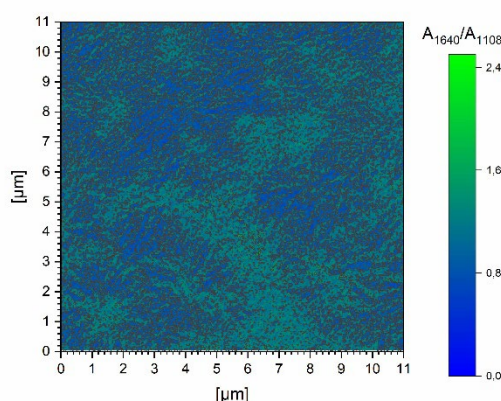

<u>Figure 1</u>: AFM-IR image of polyamide-poly(ethylene oxide) block-copolymer

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OL39

Kinetic phenomena in polymerization reactions; New findings and potential application

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Free radical transfer effects during both free radical (FRP) and RAFT polymerization reactions can lead to intriguing phenomena. In the case of acrylic and styrenic copolymerization the lower energy of the styrene group effectively captures the acrylic free radical, inhibiting the propagation of acrylic polymer chains, while leading to an increased rate of styrene polymerization. If a tiny trace of O_2 is introduced during acrylic or styrenic FRP and RAFT homopolymerization a sharp O_2 concentration threshold is found, $[O_2]_t$, at which all monomer conversion abruptly stops. All O_2 above $[O_2]_t$ is automatically eliminated in the case of acrylamide (Am) aqueous FRP, and the reaction spontaneously re-starts. The effect is attributed to a catalytic transfer cycle of free radical from Am* to O_2 and back to Am. In acrylamide RAFT and styrene sulfonate FRP the same sharp threshold is found but O_2 is not automatically eliminated quickly enough to spontaneously restart the reactions. Purging with N_2, however, drives $[O_2]$ below $[O_2]_t$ and the reactions re-start and resume the exact conversion and molar mass trajectories they were on prior to introducing O_2. Below $[O_2]_t$ the O_2 acts as a chain termination agent, producing shorter chains, similar to a chain transfer agent. Since the O_2 can be added and purged at will, there is a possibility of using tightly controlled low flow of O_2 into a reactor as a reversible chain-shortening agent.
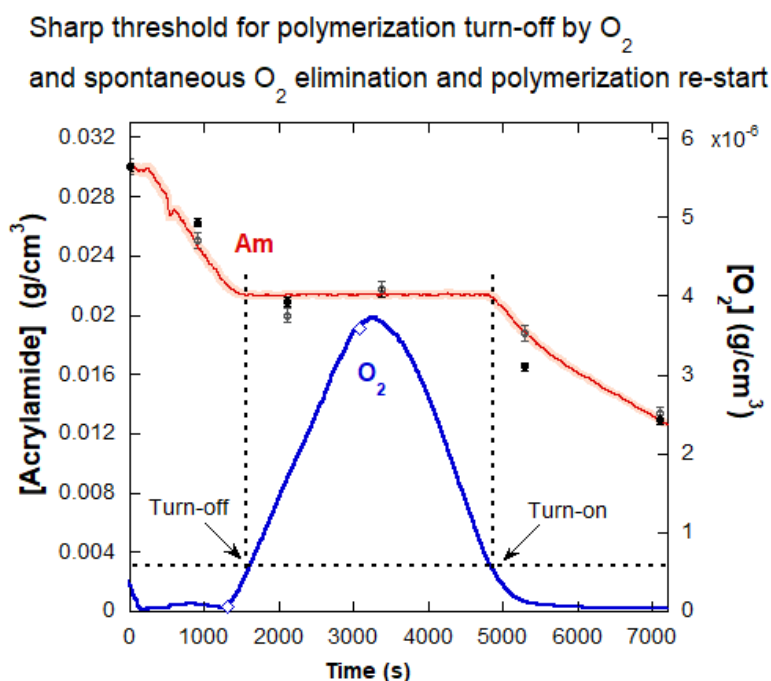
Figure: O_2 flows into an Acrylamide free radical polymerization. The polymerization abruptly halts at a threshold $[O_2]_t$, as O_2 flows in. After flow stops O_2 is catalytically eliminated by Acrylamide and the reaction spontaneously re-starts.

OL40

Revisiting Kuhn-Mark-Houwink-Sakurada: Trends of the pre-exponential coefficient *K* of branched polymers in solution

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Polymer characterization based on viscometry and molar mass determination is widely established since it provides information about polymer's conformation or topology in a wider sense by the well-known Kuhn-Mark-Houwink-Sakurada (KMHS) relationship:

$$[\eta] = K\, M^{\alpha}$$

This empirically found relation describes the proportionality of the polymer's molar mass and its corresponding intrinsic viscosity with the KMHS pre-exponential factor K and the scaling exponent α [1]. Whereas the information given in α displays straight forward the conformation and overall branching of a polymer, the information represented by the prefactor K is however not as obvious. Previous studies suggested an information on the polymer's flexibility on the local scale in an order of just a few chain segments [2].

It is empirically observed that the prefactor as $\log(K)$ decreases with increasing side chain length of globally linear short chain branched polymers [3]. However, it rather remains constant for differently branched, but solely long chain branched polymers [4]. Though, due to superimposition of short and long-chain branching, trends remained unclear so far. Previously developed theories such as the Burchard-Stockmayer-Fixman (BSF) approach stated a dependency of K under theta conditions to the polymer's solvent interaction only, regardless of its branching characteristics. However, this hypothesis cannot be hold true anymore since the universal constant from the Flory-Fox-theory being used in BSF and complementary theories were shown to increase for highly branched polymer structures [5].

In this generic survey study, we elaborate which information we can possibly gain from the KMHS prefactor K with regard to polymer's topology or branching composition, and in particular for cases of randomly superimposed short and long chain branching. Insight to that, we tackle the up-to-date discussed hypothesis, if unperturbed dimensions and thus, K_{θ} can be also defined for (highly) branched polymer systems [6].

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PL5

Novel polymer-separations

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Molecular weight (MW) is not the only property which distribution strongly affects the properties of synthetic polymers, but a molecular-weight distribution (MWD) is always present. Any other distributions exist alongside the MWD and the different distributions are easily confounded. Therefore, new methods have been aimed at either measuring several confounded distributions simultaneously, or suppressing the effects of all but one distribution on the separation, so as to obtain a single, accurate distribution.

Comprehensive two-dimensional liquid chromatography (LC×LC) can be used to fully characterize two co-existing distributions, such as the MWD and the chemical-composition distribution (CCD) or the MWD and the functionality-type distribution. One aspect of LC×LC that has seen much progress is in the "modulation", i.e. the interfacing between the two separation dimensions. Active modulation can be used to achieve better separations, avoid breakthrough, and to sudy different distributions or other aspects of the sample in the two dimensions. The latter approach can benefit from altering the sample in a "reaction modulation". For example, nanoparticles can be separated according to size, the resulting fractions can be dissolved, and the constituting polymers and particle load can be examined.

The influence of the molecular weight on retention in gradient-elution LC can be suppressed by running very fast gradients, but the range of these is usually limited by instrumental factors. Becausse the effective slope is determined by the ratio of the column volume and the gradient volume the slope can also be increased by increasing the former. The length of the column is also restricted in practice. Recycling LC (LCPLC) offers an elegant solution to greatly increase the effective length of the column and slope of the gradient, so that MW effects can be completely suppressed and accurate CCDs can be obtained.

Several novel techniques will be discussed in this lecture and applications of these will be presented.

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# How polymer's nature influences the conformation of conjugates

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In biotechnical and biomedical applications, biomolecule-polymer hybrids are an increasingly important component. Modification with polymer chains can prolong body circulation time, increase stability and improve solubility of biomolecules. Sophisticated analysis of physico–chemical properties, in particular, molar masses, sizes, composition and their dispersities are critical parameters that determine the functionality and conformation of these hybrid systems. The main challenge is that hybrid systems exhibit broad complexity and heterogeneity. This is either already given by nature or caused by specific hybridization with e.g. proteins or self-assembly.

Commonly used characterization techniques include size exclusion chromatography (SEC), dynamic light scattering (DLS), spectroscopy, etc. However, there are fundamental limitations associated with all these techniques that can result in wrong description of the prepared materials [1].

Here, we demonstrate the potential of asymmetrical flow field-flow fractionation (AF4) coupled to a fourfold detection system (dynamic and static light scattering, refractive index and UV-Vis) for the accurate determination of sizes, absolute molar masses, dispersities and conformational properties of a broad variety of biomolecule-polymer hybrids (Figure 1). A library of different conjugates varying in monomer type, polymer grafting density, charge, chain length a biomolecule type was analysed [2-4].
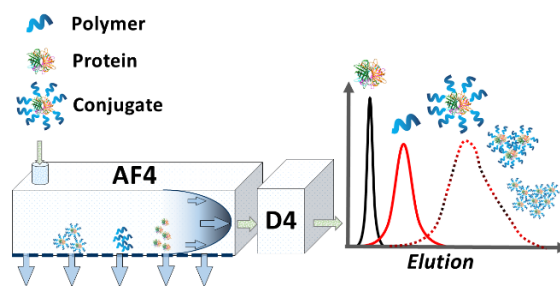
Figure 1: Scheme of asymmetrical flow field-flow fractionation with fourfold detection system (AF4-D4) for the conformation analysis of protein-polymer conjugates. Adapted from [3] licensed under CC BY 3.0.

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OL41

Stimuli-responsive homo- and copolymers in water-based solutions

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Different stimuli-responsive homo- and copolymers showing a lower critical solution temperature (LCST) or an upper critical solution temperature (UCST) in water-based solutions will be presented. These polymers were synthesized by atom transfer radical polymerization (ATRP) [1], thermally initiated or light-inititated reversible addition–fragmentation chain transfer (RAFT) polymerization [2-9], or by combining RAFT polymerization with living anionic polymerization [4]. The structural properties in water-based solutions containing different additives, such as organic compounds or inorganic salts, were investigated as a function of temperature. Depending on the additives the cloud points increased or decreased. Multiple phase transitions and cononsolvency effects were observed in some cases and will be discussed.

While the bulk structures of microphase separated block copolymers were characterized by scanning force microscopy and small angle X-ray scattering, the solution properties were studied by dynamic light scattering as a function of temperature and cryo-transmission electron microscopy.

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OL42

Comprehensive separation and characterization of nanocarrier/drug systems based on polymers and proteins for nanomedical applications

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In the new research area of Nanomedicine, typically a Nanocarrier is used in combination with a drug. The most popular combination of Nanocarrier and drug at the moment is the combination of a lipid nanoparticle (LNP) together with mRNA. This combination is used in many of the current vaccines against the Corona Virus.

Apart from LNP, other materials are under investigation, that can be used as Nanocarriers, e. g. extracellular vesicles (EV), virus-like particles (VLP) and polymersomes. It is important to know if both the drug and the Nanocarrier are monodisperse and not aggregated, because aggregation might lower the efficiency of the drug. And it is interesting, how much drug is loaded on the Nanocarrier. When Liposomes or Micelles are used as Nanocarrier, the encapsulation efficiency is an important parameter. All these parameters can be determined using a Field-Flow Fractionation (FFF) system coupled to Multi-Angle Static Light Scattering (MALS), UV-Detection and Refractive Index Detection (Figure 1).

By separating the drug and the Nanocarrier from each other with the FFF system, the polydispersity and degree of aggregation of both species can be determined. The MALS detector will deliver absolute molar mass of the drug and size of the Nanocarrier, and by using the UV and RI detectors, the loading of the Nanocarrier and the encapsulation efficiency can be calculated.

For all these different materials and drug-Nanocarrier systems, FFF coupled to MALS, RI and UV is a powerful technology, that can be used for separation and advanced characterization. In this presentation, the separation and characterization of several Nanocarrier/Drug systems are presented using FFF coupled with MALS, UV and RI.
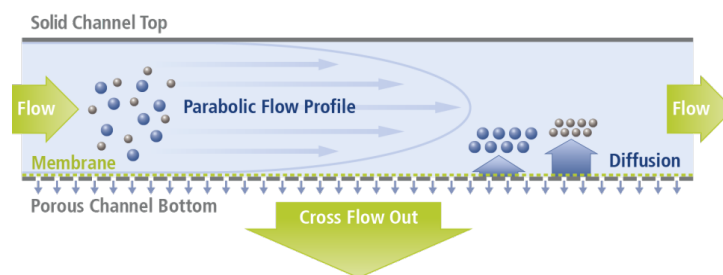

Figure 1: Principle of Asymmetrical Flow Field-Flow Fractionation (AF4)

OL43

Molecular interaction between hydrophilic and hydrophobic polymer blocks causes order-order transition-based thermogelation

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Poly(2-oxazoline)s (POx) and poly(2-oxazine)s (POzi) represent two versatile polymer classes with great potential for applications especially in the biomedical field. Noteworthy, in recent years, the aqueous solutions of several POx- and POzi-based amphiphilic block copolymers have been reported to possess thermogelling properties [1-4]. Such thermoresponsive hydrogels based on biocompatible polymers are of particular interest as they can be used as stimuli-responsive biomaterials for cell culture platforms, wound dressings and drug depots [5] and have gained increasing interest as bioinks in the research field of biofabrication [6].

Recently, we described an ABA-type triblock copolymer comprised of hydrophilic poly(2-methyl-2-oxazoline) (pMeOx) A blocks and an aromatic hydrophobic poly(2-phenyl-2-oxazine) (pPheOzi) B block, which exhibits a reversible cooling-induced sol-gel transition (inverse thermogelation) [4]. In the gel state, shear thinning behaviour and rapid shear recovery was verified, making the thermogel applicable to extrusion-based 3D bioprinting. More importantly, however, it was demonstrated, that the sol-gel transition of this POx/POzi-based thermogel is associated with an unusual order-order transition in polymer self-assembly from spherical to worm-like micelles.

Here, using a variety of state-of-the-art analytic tools complemented by molecular modelling, we reveal that the order-order transition and thus the thermogelation of the system results from a previously undescribed interaction pattern between the hydrophilic units and the hydrophobic aromatic 2-phenyl-2-oxazine moieties [7]. Therefore, the use of PheOzi as the hydrophobic monomer is essential for the order-order transition – and thus the thermogelation – to occur, whereas small changes in the structure of the hydrophilic A blocks can be used to tune the interaction potential and consequently the specific gel characteristics. In the future, this insight will serve as the basis for adjusting hydrogel's properties precisely for the specific application.

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